

The Story of

METALS

Discovery, Recovery and Uses

Volume 2



Fathi Habashi

Laval University
Quebec City, Canada

The Book

The Story of Metals in two volumes covers the history, metallurgy, and uses of metals, fully illustrated in coloured pictures. It starts with a description of the metallic character then goes on to the ancient metals, the metalloids of the alchemists, metals from South America, metals from the East, metals of the 18th, 19th, and 20th centuries.



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THE STORY OF METALS

Discovery, Recovery and Uses

Volume 2



A Roman coin showing the god Janush from which the month of January is named, has two faces: one looking to the past and the other looking to the future

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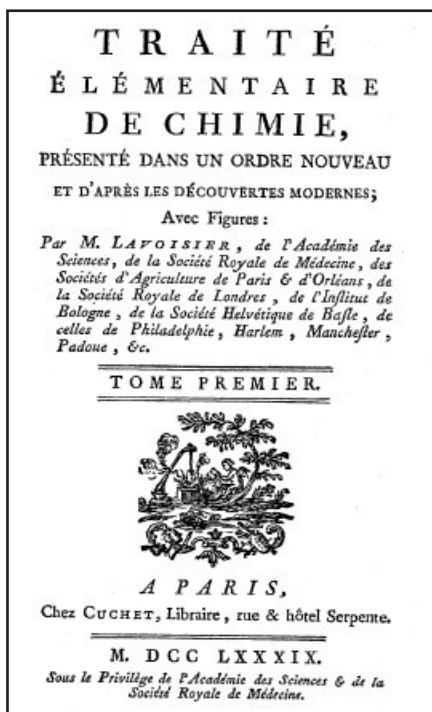
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Part 7 - Eighteenth Century Metals



Lavoisier's chemistry book 1789

7.1 Introduction

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NEW METAL DISCOVERY

The eighteenth century is characterized by the great intensity of travellers collecting samples of minerals, the establishment of mineral collection museums, and the analysis of these by chemists. Mineralogists and chemists were actively analyzing and arranging minerals for display and study which resulted in the discovery of many metals (Figure 7.1.1) (Table 7.1.1).

Li	Be															B					
Na	Mg	Al													Si						
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se						
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te						
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po						
Fr	Ra	Ac																			

*	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
**	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

Ancient metals
Medieval metals
Eighteenth century metals

Figure 7.1.1 - Metals in the eighteenth century

Table 7.1.1 - Metals discovered in the eighteenth century

Year	Metal	Discoverer	Remarks
1735	Cobalt	Brandt	Discovered in Sweden
1741	Platinum	Wood	Metal from South America
1745	Boron	Bergman	Metal from the East. Isolated in 1808 by Gay-Lussac, Thénard, and Davy
1746	Zinc	Marggraff	Metal from the East
1751	Nickel	Cronstedt	Discovered in Sweden
1753	Bismuth	Geoffrey	Metalloid of the alchemists
1774	Manganese	Ghan	Discovered in Sweden
1781	Molybdenum	Hjelm	Discovered in Sweden
1782	Tellurium	Müller von Reichenstein	Isolated by Müller von Reichenstein but not named. Named in 1798 by Klaproth
1783	Tungsten	Elhujar brothers	Discovered in Spain
1789	Uranium	Klaproth	Klaproth believed that he prepared uranium metal when he reduced U ₃ O ₈ with carbon. In fact he obtained only a lower oxide (UO ₂). The metal was isolated by Peligot in 1841 by the reduction of UCl ₄ with potassium
1789	Zirconium	Klaproth	Isolated by Berzelius in 1824 by the reduction of the fluoride with sodium
1791	Titanium	Gregor	Isolated by Berzelius in 1824 (impure metal), Nilson and Pettersson in 1887 (95 % pure), and by Hunter in 1910 (99.9 % pure).
1794	Yttrium	Gadolin	Discovered in Sweden
1797	Beryllium	Vauquelin	Isolated by Wöhler and Bussy in 1828 by the reduction of the fluoride with sodium.
1797	Chromium	Vauquelin	Isolated by Wöhler in 1859 by reducing molten chromium chloride with zinc

MINERAL COLLECTIONS

The beauty of minerals attracted scientists to study them. Collection of minerals became a fascinating hobby not only for scientists but also for monarchs (Figure 7.1.2).



Figure 7.1.2 - Emperor Franz I (1708–1765) of Austria studies minerals and fossils with his scientists at the Museum of Natural History in Vienna

The newly founded Mining Institute in Saint Petersburg by Catherine the Great (1729-1796) (Figure 7.1.3) in 1773 had an impressive collection of minerals housed in the Mineral Museum (Figures 7.1.4 and 7.1.5). Private collections were also established.



Figure 7.1.3 - Catherine the Great (1729-1796)



Figure 7.1.4 - Mineral Museum

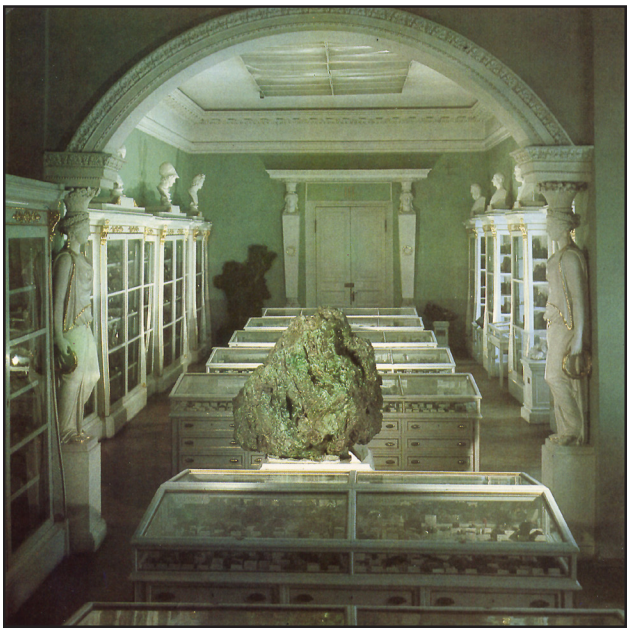


Figure 7.1.5 - Mineral Museum

Wealthy people also found it a fashionable attraction. Joseph Franz Maximilian Lobkowitz (1772-1816) Duke of Roudnice (Figure 7.1.6) who is remembered as the greatest of Beethoven's patrons to whom Beethoven dedicated many works, had a huge mineralogical collection. Alexandra Pavlovna (1783–1801) (Figure 7.1.7) daughter of Tsar Paul I of Russia and sister of Emperors Alexander I and Nicholas I who became Archduchess of Austria upon her marriage to Archduke Joseph of Austria, Governor of Hungary had also a fascinating collection that was arranged by the famous mineralogist of that time Ignaz von Born (1742-1791). Museums for natural history were founded in most European capitals.



Figure 7.1.6 - Joseph Franz Maximilian Lobkowitz (1772-1816)



Figure 7.1.7 - Grand Duchess Alexandra Pavlovna (1783 –1801)

Prince Gregory Gregorevich Gagarin (1810-1893) (Figure 7.1.8) was of an aristocratic Russian family. The extensive mineral collection of his family is now preserved in the Vernadsky State Geological Museum in Moscow.



Figure 7.1.8 - Prince Gregory Gregorevich Gagarin (1810-1893)

Terra Mineralia

The Mineralogical Museum in the Freudenstein Castle (Figure 7.1.9) in Freiberg, Germany contains an outstanding collection of about 3,500 precious stones, minerals, meteorites, and rock samples from around the world. The collection has been donated in 2008 by Erika Pohl-Ströher, a Swiss lady who was born in 1919 in Saxony.



Figure 7.1.9 - Terra Mineralia in Freudenstein Castle

Arranging of minerals

Axel von Cronstedt (1722-1765) (Figure 7.1.10) was the first to arrange minerals according to their chemical constitution (Figure 7.1.11). Before him minerals were arranged according to their color or different properties.



Figure 7.1.10 - Axel von Cronstedt (1722-1765)

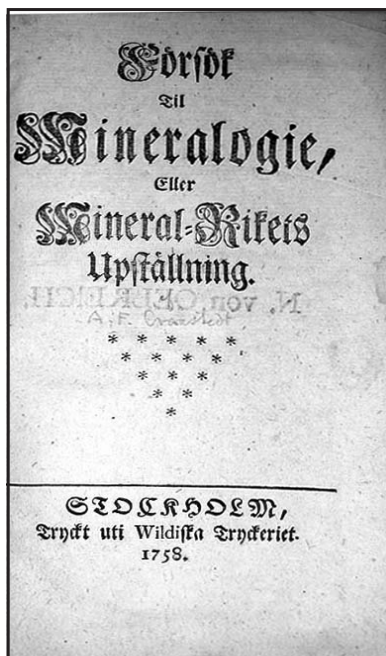


Figure 7.1.11 - Front page of Cronsted book on mineralogy

THE BLOWPIPE

The chemist of today is often unaware of the importance of that most simple instrument, the blowpipe, which was so essential for chemical analysis in the eighteenth and nineteenth centuries. With the help of the blowpipe the qualitative composition of most minerals was ascertained. The blowpipe (Figure 7.1.12), essentially a narrow tube with which air can be blown into the flame had been in use by goldsmiths of ancient Egypt and by the seventeenth century was widely used in the glass industry.

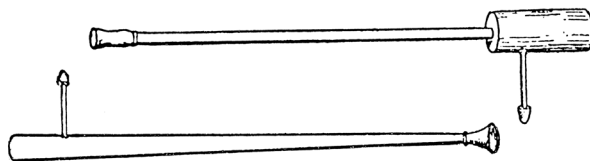


Figure 7.1.12 - The blowpipe

The German chemist Johann Kunckel (1630-1703) (Figure 7.1.13) described this instrument in his book *Ars vitraria experimentalis oder vollkommene Glasmacherkunst* published in 1679. Towards the end of his career, Kunckel was offered a post as Minister of Mines by Charles XI of Sweden, and was later raised to the nobility. Another German chemist Johann Cramer (1710-1777) recommended the use of the blowpipe to melt small quantities of substances.



Figure 7.1.13 - Johann Kunckel (1630-1703)

The Swedish metallurgists and mining analysts carried on the development of the use of the blowpipe. For example Anton Swab (1703-1768) director of the Royal Mining Office used it in 1738 for the examination

of antimony, and Sven Rinman (1720-1792) member of the Royal Mining Council reported its use in the examination of tin ores containing iron and cobalt. However, most of the earlier work on the analysis of minerals using a blowpipe is due to Cronstedt. He used sodium carbonate, borax, and sodium ammonium phosphate as fusion mixtures.

In his work *Försök till mineralogiens eller Mineral Rikets upsällning* published in 1758 he made frequent reference to results obtained with a blowpipe. When Guztaf Engeström (1738-1813) translated this book into English, he added a chapter dealing with practical instructions on the use of the blowpipe and this was later published in Swedish. Wilhelm August Lampadius (1772-1842) in his *Handbuch zu chemischen Analyse der Mineralkörper* mentioned that oxygen was first used in blowpipe procedures by Antoine Laurent Lavoisier in 1782 to melt platinum.

The Swedish chemist Tobern Bergman (1735-1784) who was the greatest analyst of the eighteenth century, made many references to the use of the blowpipe, and in 1779 published a book which contained all the existing knowledge on the use of this tool. In his book *De tubo feruminatorio*, he enumerates the many advantages of the method, namely that it does not require any specialized apparatus, very little sample is required, and the operation is extremely rapid. Bergman described the method of obtaining a suitable flame, i.e., a candle or a burner fed with vegetable oil, and also the substances suitable for fusing agents. Finally he systematically recorded the reactions of the various groups of minerals with the blowpipe. The technique of blowpipe analysis was further refined by Bergman's assistant Jöns Gottlieb Gahn (1745-1818) who discovered manganese in 1774 by its means.

Berzelius wrote a book on blowpipe examinations in 1820, under the title *Afhandling om Blassrörets användande i kemien och mineralogien*, which was soon translated into most European languages. Another book on the blowpipe was published in Leipzig in 1835 by Carl Friedrich Plattner (1800-1858) professor of metallurgy at the Freiberg Mining Academy entitled *Die Probierkunst mit dem Löthrohre*, i.e., "The Art of Assaying with the Blowpipe".

Since the last half of the nineteenth century, the blowpipe has gradually fallen into disuse, partly due to the improvement of wet methods of analysis, but mainly due to the emergence of emission spectroscopy, which is far more accurate and depends less on the skill of the operator.

NEW REAGENTS

The discovery of new reagents contributed to the isolation of metals, particularly the refractory metals, in pure form.

Hydrogen

Hydrogen discovered by Henry Cavendish (1731-1810) (Figure 7.1.14) in 1766 was responsible for the isolation of pure metallic tungsten by the Swedish chemist Jons Jakob Berzelius (1779-1848) around 1783.



Figure 7.1.14 - Henry Cavendish
(1731-1810)



Figure 7.1.15 - Karl Wilhelm
Scheele (1742-1786)

Chlorine

Chlorine discovered by the Swedish chemist Karl Wilhelm Scheele (1742-1786) (Figure 7.1.15) in 1774 was used to convert oxides to chlorides from which metals could be obtained by reduction when the oxides resisted reduction to metals. For example, niobium, zirconium, vanadium were first prepared by reduction of chlorides when it was not possible to reduce the oxides.

Hydrofluoric acid

Hydrofluoric acid discovered by Scheele in 1771 when he reacted fluorite with sulfuric acid, was used to prepare fluorides and reduce them to metals when the oxides resisted reduction. Titanium fluoride was prepared in this way.

FALL OF THE PHLOGISTON THEORY

In the seventeenth century, attempts were made to understand the nature of fire and the smelting process. It was once believed that when coal was burnt, phlogiston which in Greek means flame, was released and a calx, that is, ash remained. If an ore or an oxide was heated with coal it takes up the escaping phlogiston in the fire to form the metal, that is



It was the French chemist Antoine Laurent Lavoisier (1743-1794) (Figure 7.1.16) who in 1772 finally directed the fatal blow to the theory, when a few years earlier oxygen was discovered, and he interpreted the phenomenon of combustion as an oxidation process.

Another revolutionary step in the technique of smelting took place, when hydrogen was used for the first time to prepare metallic tungsten by the gaseous reduction of its oxide around 1783. It should be pointed out, however, that although hydrogen is a more powerful reducing agent than hot

carbon, yet it failed to liberate the alkali metals, the alkaline earth metals, and aluminum from their oxides.



Figure 7.1.16 - Antoine Laurent Lavoisier (1743-1794)

Foundation of Schools of Mines

The need for schools to train students in the fields of geology, mining, metal extraction and metallurgy was then realized and this was accomplished by establishing schools in many European cities as well as in the New World where important mining activities were taking place in the Spanish colonies. The professors at these schools created the basic literature for the next generations and also contributed to the discovery of metals.

7.2 Cobalt¹

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INTRODUCTION

Cobalt is always associated with nickel in its ores. There is only one important mineral in which cobalt is the principal metal, occurring as an arsenide, CoAs_3 , known as skutterudite (figure 7.2.1) named after the town Skutterud in Norway where it was first discovered.



Figure 7.2.1 - Museum sample of skutterudite

Metallic nickel occurs in nature as an alloy with iron known as ferronickel. The mineral awaruaite, FeNi_3 (named after Awarua Bay, New Zealand, where it was first discovered), and josephinite, FeNi_2 (named after Josephine County, Oregon, where it was first discovered) in microscopic amounts in the beginning of the twentieth century. Both minerals contain

¹ Based on F. Habashi, "History of Cobalt," pp. 157–165 in *Hydrometallurgy of Nickel and Cobalt*, edited by J. J. Budac et al., Canadian Institute of Mining, Metallurgy, and Petroleum, Montreal 2009

cobalt, usually in the ratio $\text{Ni}/\text{Co} = 10/1$. Nickel also occurs as microscopic lamella in association with serpentine, and as microscopic particles associated with the minerals pentlandite, $(\text{Fe},\text{Ni})\text{S}$, and hazelwoodite, NiS , in serpentine rocks. Cobalt also occurs associated with nickel in meteorites.

DISCOVERY OF COBALT

Analysis of blue-colored glass from Persia dating from the fourteenth century indicated that it contained cobalt. Cobalt ores known as “Zaffer”, were certainly known in the Orient as glass coloring pigments. This knowledge seems to have been transmitted to Europe by Dutch and Portuguese traders from the East Indies. Artisans in Delft and Lisbon are skilled today in producing ceramic articles with “cobalt blue” (Figure 7.2.2). The French glassmaker Bernard Palissy (1510-1589) (Figure 7.2.3) and other contemporary writers were familiar with this material.



Figure 7.2.2 - Examples of cobalt blue



Figure 7.2.3 – The French glassmaker Bernard Palissy (1510-1589)

Near the end of the fifteenth century, a troublesome and supposedly worthless mineral was found in large quantity in the mines of Erzgebirge (Ore Mountains) on the borders of Saxony and Bohemia. The miners disliked it because of the labor of removing it from the exploited silver ore and also because of its arsenic content which injured their health. They thought that “Kobolds” were responsible for its presence. The Kobolds, according to ancient German superstition, were delighted in destroying the work of the miners causing them troubles. In mining towns the people used to pray in the churches for deliverance from the power of these malicious spirits.

A new metal was discovered in 1730 by the Swedish chemist Georg Brandt (1694-1768) in an ore that resembled a copper ore in some of its properties but did not yield copper. This testified to the belief of German miners of the day that the false ore was bewitched. They called the ore Kobold after an earth spirit which they believed had bewitched the copper ore. He prepared a dark blue pigment from an ore found in the Skila copper works (Riddarhytta). After strongly roasting the ore he was able to obtain a regulus of the new metal which he called “Cobalt”. An analysis of the mineral done in 1810 by W. von Hisinger revealed it to be a cobalt sulfide. The mineral is now known as linnaeite, in honor of the Swedish naturalist Linnaeus.

Brandt was born in Riddarhytta, Vestmanland, where his father, a former apothecary, operated a copper smelter, an iron works, and some mines. He sent his son to study medicine and chemistry at Leyden in the Netherlands under Herman Boerhaave. Before his return home in 1727 Georg Brandt stopped in the Harz where he visited some metallurgical plants. He was then put in charge of the chemical laboratory at the Bureau of Mines in Stockholm. He then moved to the Royal Mint where he discovered cobalt and in 1730 became its assay master. He was later appointed professor of chemistry at the University of Uppsala.

COBALT IN CONGO

In 1914 cobalt-containing copper ores were discovered at the Katanga Mine in Congo of the Union Minière. The Société Générale de Belgique was the main organization running the Congo for the Government. Under the Société Générale was the Comité Spécial du Katanga that was specialized in running the mines discovered. A part of this Comité, the Union Minière du Haut Katanga was the metal-producing organization. Extraction of cobalt began in 1924 and two years later Katanga became the world's leading producer, a position which she has maintained ever since; between 1940 and 1960 she produced more than 50 % of the world's cobalt (Figure 7.2.3). Three types of ores were processed:

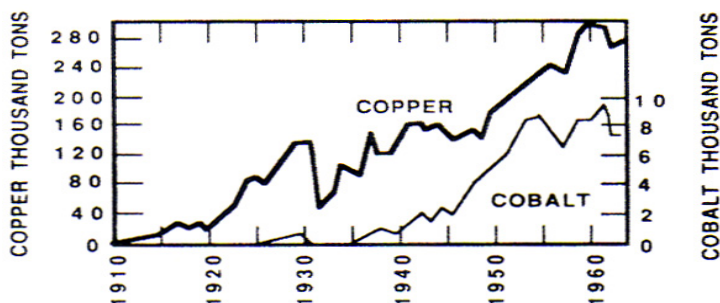


Figure 7.2.3 – Production of copper and cobalt in Belgian Congo.

- Copper oxide ore containing minor amounts of cobalt (5 % Cu and 0.2 % Co). This is concentrated by flotation to 26 % Cu and 1 % Co, leached by acid, and the solution electrolysed selectively for the recovery of both metals (Jadotville plant north west of Lumumbashi).
- Cobalt–copper oxide ore containing approximately equal quantities of the two metals (2.3 % Cu and 2.0 % Co). This is concentrated by flotation to 10 % Cu and 8 % Co, then reduced in an electric furnace to produce two alloys:
 - A heavy red alloy: 89 % Cu and 4.5 % Co. This is refined to copper at the local smelter.
 - A light white alloy: 42 % Co, 15 % Cu, and 34 % Fe. This is sent to Olen where it is dissolved in acid and cobalt separated by precipitation as carbonate.
- Mixed ores containing both cobalt and copper oxides and cobalt and copper sulfides. These are separated by flotation to get two products:
 - A sulfide concentrate: 46 % Cu, 0.4–2.5 % Co. This is roasted and leached.
 - An oxide concentrate: 20 % Cu and 1.7 % Co. This is treated by leaching as well as by reduction in electric furnace.

Figure 7.2.4 shows the mineral wealth of Congo. Thus, Katanga became an important metallurgical centre where all modern extractive metallurgical processes were applied locally, and the Olen refinery (Figure 7.2.5) became one of the most diversified nonferrous metallurgical operations in Europe.

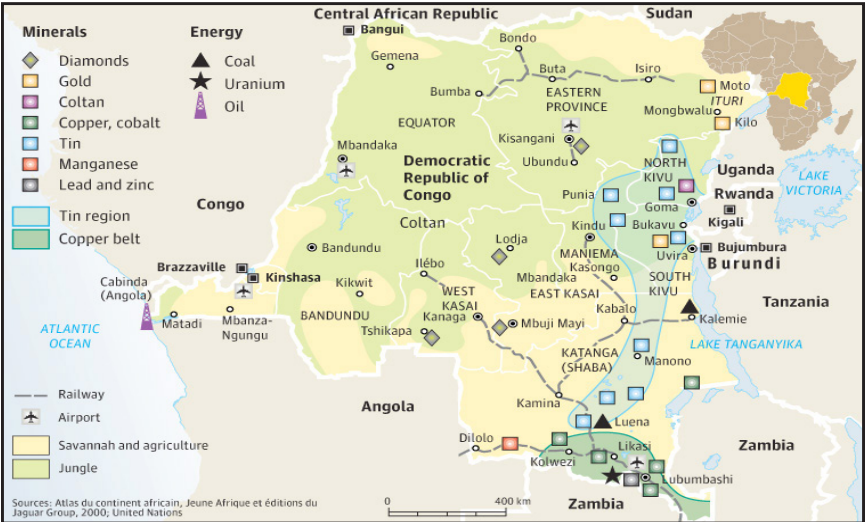


Figure 7.2.4 – Mineral map of the Democratic Republic of Congo showing the location of Lubumbashi near the border with Zambia



Figure 7.2.5 – General view of Olen Works, Belgium

COBALT IN CANADA

Cobalt, Ontario (Figure 7.2.10) is a small town where a major complex cobalt arsenide ore containing about 10% of native silver was discovered in the area in the summer of 1903, during the construction of the Temiskaming & Northern Ontario Railway. Prospectors and miners came from all over the world to search for silver, stake claims, and extract riches of silver. At that time cobalt had little commercial value and the technology was not available for its recovery from arsenides.



Figure 7.2.10 - Location of Cobalt, Ontario

Within a few years the area was one of the largest silver producing areas in the world. The town was incorporated in 1906. By 1908 about 9% of the world's silver was produced. In 1911, there were more than 100 mines in operation and by 1918 about 10,000 tons of silver were shipped. By the late 1920's, the boom was over and the town began to decline.

In World War II era cobalt became a valuable metal and a number of operations opened to process the tailings for the cobalt but most of these closed by the 1970s (Figure 7.2.11). Cobalt Mining Museum has the world's largest display of silver. In the region is Haileybury Heritage Museum and Haileybury School of Mines which was established to train mining engineers.

RECENT ADVANCES

Cobalt in small amounts is essential to many living organisms, including humans. Trace amounts of cobalt (about 0.30 mg/kg) in soils markedly improves the health of grazing animals. Cobalt is a central component of the vitamin cobalamin, or vitamin B₁₂. ⁶⁰Co is a high-energy gamma ray emitter was discovered in 1938 by Glenn Seaborg and his co-workers. Acute high-dose exposures to the gamma emissions can cause severe burns and death. Extended exposures increase the risk of morbidity or mortality from cancer.

Cobalt from Pyrite Cinder

Noting the success of Duisburger Kupferhütte Company in Germany for the recovery of nonferrous metals from pyrite cinder, producers of sulfuric acid from pyrite in Europe, Japan, and USA became interested to market their iron oxide produced to the steel industry by upgrading their pyrite cinder. As a result, processes were developed to deal with this problem.

Kowa-Seiko Process

This is a Japanese process developed at Kitakyushu in which the cinder is mixed with calcium chloride, pelletized, then heated in a rotary kiln at 1100°C to volatilize nonferrous metal chlorides. These are scrubbed in water from the exit gases and the solution treated for metal recovery. The process was also used in Portugal and in other countries.

Bethlehem Steel process

At the plant at Sparrows Point in Maryland, cobalt from the cinder was recovered by a process based on a careful temperature control during the roasting of pyrite. If the temperature is kept at 550°C, cobalt in the pyrite will be converted to sulfate and therefore can be leached directly from the cinder with water. The hot pyrite cinder was quenched with water to give a slurry containing 6–8 % solids. When the solids are filtered off, the solution contains 20–25 g/L Co; it is processed further for metal recovery. In the cinder, the Fe:Co ratio is 50:1; in solution it is 1:1. This plant supplied

the only domestic source of cobalt in USA.

Outokumpu process

In Finland at the Outokumpu plant in Pori a similar process is in operation in 1979; the sulfated pyrite cinder contains 0.8–0.9 % Co and other nonferrous metals. It is leached with water to get a solution at pH 1.5 analyzing 20 g/L Co, 6–8 Ni, 7–8 Cu, 10–12 Zn, and trace amounts of iron, which is treated for metal recovery.

Precipitation from aqueous solutions

In the 1950s Sherritt-Gordon Mines in Fort Saskatchewan developed a process to recover metallic cobalt from ammoniacal solutions by precipitation by hydrogen under pressure at about 200°C. The metal precipitates in form of tiny hexagonal crystals which reflects the atomic structure of the metal (Figure 7.2.6).

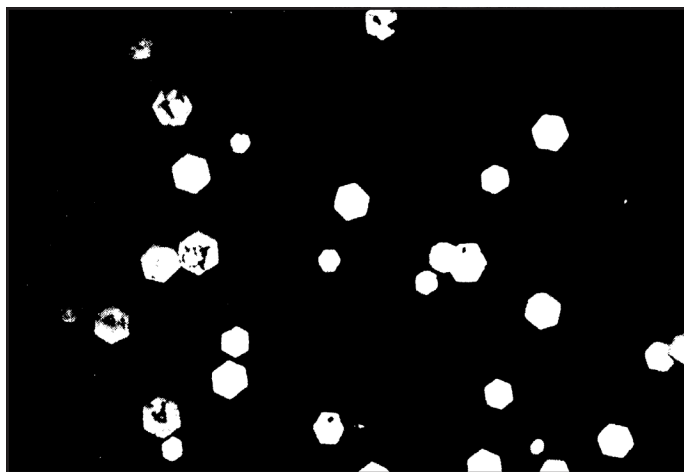
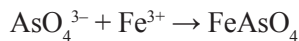


Figure 7.2.6 – Tiny cobalt hexagonal crystals precipitated from ammoniacal solution by hydrogen under pressure

Calera Process

The Calera process [Figure 7.2.7] operated in the 1950s for few years at

Garfield Refinery near Salt Lake City for the recovery of cobalt from a sulfarsenide ore [Table 7.2.1]. It was shut down because of corrosion and erosion problems. It has the advantage of eliminating the danger of having arsenic in solution; instead, it is removed as an insoluble residue. Leaching was carried out at 200°C, and under oxygen pressure of about 1200 kPa. Cobalt and copper were converted into soluble sulfates while iron and arsenic salts were oxidized and combined to form insoluble iron arsenate:



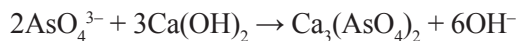
The leaching reaction is slow unless dilute acid is present. Acid was obtained in the process from the oxidation of pyrite present in the ore. The slurry was filtered to recover cobalt and copper from the solution. Copper was precipitated by cobalt powder while cobalt was precipitated by hydrogen under pressure in the presence of ammonia. The solution was then evaporated to crystallize ammonium sulfate.

Sill Process

The Sill Process was invented by Harley Sill and is based on the alkaline oxidation of cobalt arsenide ore to solubilize both arsenic and sulfur to arsenate and sulfate respectively, while the metal values remain undissolved (Figure 7.2.8).



The residue was then processed by conventional methods to yield cobalt (or nickel) free from arsenic. Treatment was carried out at 115°C, 840 kPa oxygen pressure. Arsenic can be removed from the leach solution by precipitation with lime to give calcium arsenate, or with H_2S to give arsenic sulfide. When lime is used, sodium hydroxide is regenerated:



Analysis of an ore treated by this process is given in Table 7.2.2.

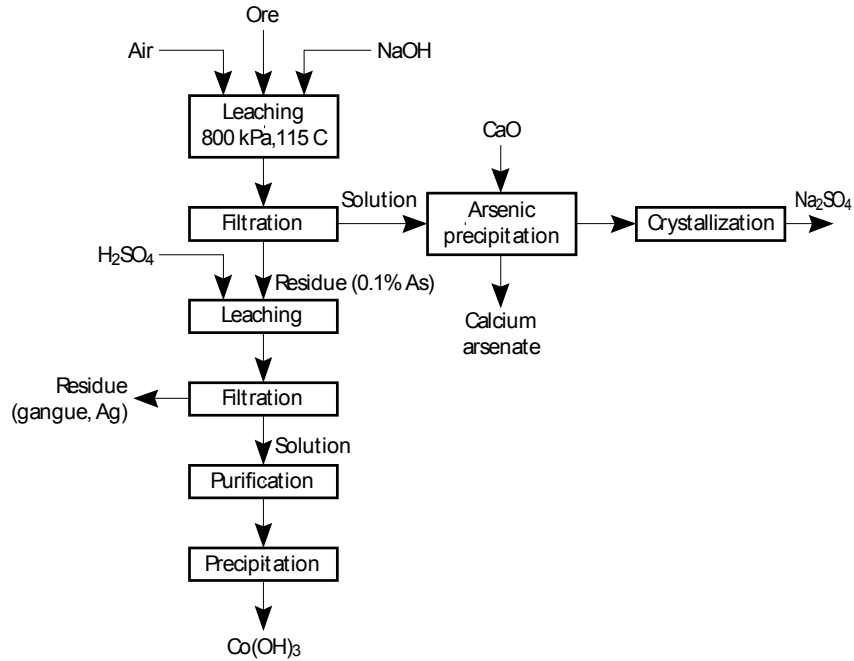


Figure 7.2.8 - Leaching of arsenide ore with sodium hydroxide.

Table 7.2.2 - Analysis of ore processed by sodium hydroxide leaching.

	%
As	45
S	20
Fe	19
Co	12
Ni	3
Cu	1
Ag	100–150 oz/ton

APPLICATIONS OF COBALT

The temperature stability of cobalt alloys make them suitable for turbine blades within gas turbines and jet aircraft engines. These alloys are also corrosion and wear-resistant. Some high speed steels also use cobalt to increase heat and wear-resistance. The special alloys of aluminum, nickel

and cobalt, known as Alnico, and of samarium and cobalt (samarium-cobalt magnet) are used in permanent magnets, which can be used for recording media. Cemented carbides (also called hard metals) and diamond tools. Lithium cobalt oxide, (LiCoO_2), is widely used in lithium ion battery electrodes. Several cobalt compounds are used in several chemical reactions as catalyst. Cobalt and its compounds; especially cobalt carboxylates, known as cobalt soaps; are good oxidation catalysts. They are used in paints, varnishes, and ink as drying agents in which the oxidation of certain compounds leads to the drying. Figure 7.2.9 shows world cobalt production. The sharp drop in production in the period 1985 -1995 is due to the civil war in Congo and the shut down of metallurgical plants in Katanga.



Figure 7.2.9 – Production of cobalt

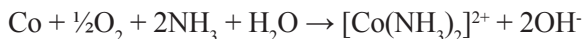


Figure 7.2.11 - A Canadian stamp honouring cobalt and silver

THE METAL

The relative abundance of cobalt is 2.3×10^{-3} , it has a density 8.9, melts at 1495°C , and boils at 2927°C . It exists in two allotropic modifications: a close-packed hexagonal ϵ -form stable below ca. 400°C and a face-centered cubic α -form stable at high temperature. The transformation temperature is 421.5°C .

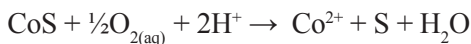
The main oxidation states of cobalt are Co^{2+} and Co^{3+} . In acid solution and in the absence of complexing agents, Co^{2+} is the stable oxidation state. Cobalt is often removed from solution as its sulfide. It dissolves in ammoniacal solutions in presence of oxygen forming ammine complex:



Cobalt sulfide undergoes oxidation in neutral medium at ambient conditions to CoSO_4 :



In acidic medium, however, elemental sulfur forms:



EPILOGUE

An ore from the mines of Erzgebirge on the borders of Saxony and Bohemia resembled a copper ore in many of its properties but did not yield copper. German miners of the day believed that the ore was bewitched and called it Kobold after an earth spirit which they thought that it had bewitched the copper ore. When the Swedish chemist Georg Brandt (1694-1768) analyzed a sample of this ore in 1730 he reported that the ore contained a new metal which he called cobalt. Analysis of blue-colored glass from Persia dating from the fourteenth century indicated that it contained cobalt. Cobalt ores known as “Zaffer” were known in the Orient as glass coloring pigments. This knowledge seems to have been transmitted

to Europe by Dutch and Portuguese traders from the East Indies. The circumstances of the discovery of the metal, the situation of Sweden at that time, and the most important contemporary scientists are outlined.

7.3 Nickel¹

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HISTORICAL

Kupfernickel

Axel Fredrik Cronstedt (1722-1765) (Figure 7.3.1) faced a situation similar to that of his teacher Georg Brandt (1694-1768) the discoverer of cobalt, when studying a sulfo-arsenide mineral from Sweden that resembled copper ore but did not yield copper. The miners named this ore Kupfernickel, i.e., Old Nick's copper in reference to the devil.

¹Based on F. Habashi, "History of Nickel," pp. 77-97 in *Pyrometallurgy of Nickel and Cobalt*, edited by J. Liu et al., Canadian Institute of Mining, Metallurgy, and Petroleum, Montreal 2009.



Figure 7.3.1 - Axel Fredrik Cronstedt (1722-1765) discoverer of nickel

On the other hand, this false copper ore was not a cobalt ore either and did not impart a blue color to glass as cobalt ore did. In 1751, he obtained green crystals from this ore which when heated with charcoal yielded a white metal that certainly was not copper. It resembled iron and cobalt, though it was different from both. He noted that the metal was attracted by a magnet - - the first time anything but iron had been found subject to magnetic attraction since the days of Greek philosophers. In 1754 Cronstedt named the new metal “nickel”.

It was not until 1804 that the metal was produced and its essential properties described. The mineral from which the metal was first extracted is now called nicolite, a nickel arsenide, NiAs . A nickel smelter was constructed in Sweden in 1838, soon after the Swedish chemist Jons Jakob Berzelius (1779-1848) discovered nickel in ore from the Klefva copper mines in the south of Sweden. These Swedish mines were worked for nickel for about 50 years.

Cronstedt was born in Stroepsta, Södermanland in Sweden as the son of a high ranking army officer. He was trained in mathematics and the physical sciences. He then studied mining and mineralogy under the Georg Brandt and was appointed as metallurgist in the Swedish Bureau of Mines in Stockholm. Cronstedt reformed mineralogy by initiating a classification of minerals not only according to their appearance, but also according

to their chemical structure. In 1758, he published this new system in a book entitled in translation “Essay on Mineralogy or a Classification of Minerals”. Cronstedt died at the young age of 43. The mineral cronstedtite was named in his honor. He was a member of the Swedish Academy of Science and was bestowed the title of baron.

White copper

For centuries before Cronstedt’s discovery, however, the Chinese had been making “pai thung” or “white copper”, an alloy which resembled silver in appearance but did not contain silver, by reduction of certain ores (Figure 7.3.2). This material appeared in Europe in small quantities in the late 1700s. Since it cost only one quarter the price of silver, the alloy had obvious commercial potential as a silver substitute. Later analysis indicated that the alloy was composed of 40% Cu, 32% Ni, 25% Zn, and 3% Fe.

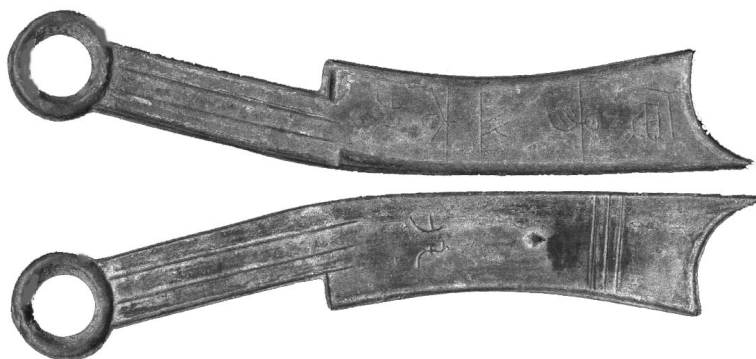


Figure 7.3.2 - Chinese “pai thung” or “white copper

German Silver

Ernest August Geitner (1783-1852) (Figure 7.3.3), born in Gera, Germany studied medicine and chemistry and practiced medicine for a while then in 1810 erected a factory for fabricating the copper pigment known as New Green. In 1815 he erected a second factory in Schneeberg to manufacture chromic acid salts. He made use of nickel-cobalt speiss which was discarded as a waste to produce cobalt and nickel. In 1823 he prepared an

alloy containing 20% Ni, 55% Cu, and 25% Zn which he called Argentan or New Silver which received great demand because of its similar appearance to silver. It became known outside Germany as German silver. By the 1830s, German Silver was produced commercially in both Germany and England in significant amounts. In addition to its silver color, this alloy was easy to cast and fabricate, was resistant to tarnishing, and was economical to produce. Geitner published *Briefe Über Chemie* in 2 volumes (Leipzig 1808).



Figure 7.3.3 - Ernest August Geitner (1783-1852)

Nickel in the periodic table

When Dmitry Ivanovich Mendeleev (1834-1907) discovered the periodicity of the elements when arranged with the increasing atomic weights in 1869, the atomic weights were not yet exactly known. The atomic weight of nickel was 59 while that of cobalt was 60 and therefore he put nickel before cobalt in his Periodic Table. Later, however, when Henry Moseley (1887-1915) discovered in 1913 that the atomic number (Figure 7.3.4) and not the atomic weight is the basis of the periodicity, he reversed the positions of nickel and cobalt because nickel has 28 protons in the nucleus while cobalt has only 27.

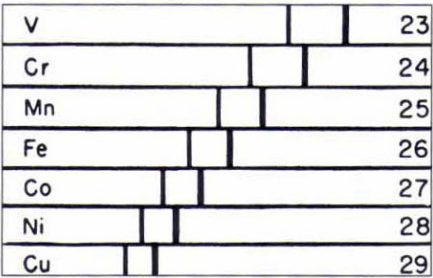


Figure 7.3.4 -X-ray spectra produced on a photographic plate by a series of metals from vanadium through copper. This shows the relative position of cobalt and nickel, which is not in accordance with their atomic weights

The apparent paradox was explained later when the neutron was discovered by James Chadwick (1891-1974) in 1932, and the realization that atoms are composed of different isotopes (Tables 7.3.1 and 7.3.2). Hence, the atomic weight of an element is the average weight of its different isotopes.

Table 7.3.1 - Naturally occurring stable isotopes of cobalt

Isotope	Abundance %
Co 57	0.2
Co 59	99.8
	100.0

Table 7.3.2 - Naturally occurring stable isotopes of nickel

Isotope	Abundance %
Ni 58	66.4
Ni 60	26.7
Ni 61	1.6
Ni 62	3.7
Ni 64	1.6
	100.0

OCCURRENCE OF NICKEL

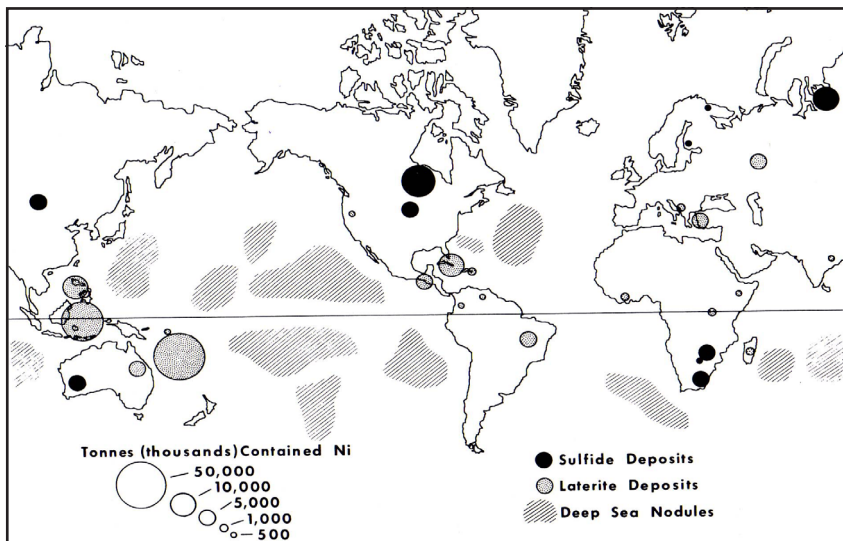


Figure 7.3.5 – Map showing the main nickel deposits

Major deposits

The major nickel deposits are shown in Figure 7.3.5. They are of four types:

- Sulfides which can be enriched by flotation yielding a high-grade concentrate, e.g., Sudbury and Norilsk. Pentlandite, $(\text{Ni,Fe})_9\text{S}_8$, is the major nickel sulfide mineral. It occurs associated with other sulfide minerals as follows:

- Pyrrhotite, e.g., as in Thompson, Manitoba
- Pyrrhotite and chalcopyrite, e.g., as in Sudbury, Ontario and Norilsk, Russia
- Pyrrhotite, pyrite, and chalcopyrite, e.g. as in Lynn Lake, Manitoba

- Oxides composed of Fe_2O_3 containing about 1% Ni known as laterites which cannot be beneficiated by physical methods, e.g., Cuba and Indonesia.
- Hydrated magnesium silicate containing nickel in isomorphous substitution with magnesium in the mineral garnierite, $(\text{Ni,Mg})\text{SiO}_3 \cdot n\text{H}_2\text{O}$, as in New Caledonia
- Oxides composed of MnO_2 containing about 1% copper, 1% nickel, and 10 to 15% iron. These deposits occur on the bottom of oceans in form of black nodules about 10 cm in diameter present at a concentration of about 12 kg/m^2 . These deposits were discovered by H.M.S. Challenger in 1870s during her expedition around the world. It was only in 1960s that Kennecott and Newport Shipbuilding Company became interested in studying these deposits and devising methods for their exploitation.

Native Nickel

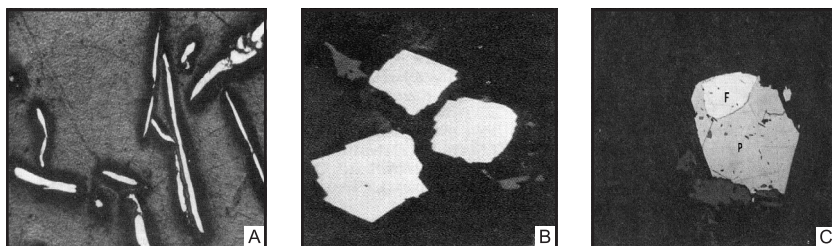


Figure 7.3.6 - Photomicrograph of polished sections: (A) Lamella of ferronickel in asbestos deposit 0.05–0.5 mm in size (magnification 70 $\times$); (B) Microscopic crystals of ferronickel (magnification 560 $\times$); (C) Microscopic particles of ferronickel (F) cemented with pentlandite (P) from serpentine rock (magnification 210 $\times$)

The mineral awaruaite, FeNi_3 (named after Awarua Bay, New Zealand, where it was first discovered), and josephinite, FeNi_2 (named after Josephine County, Oregon, where it was first discovered) in microscopic amounts in the beginning of the twentieth century. Both minerals contain

cobalt, usually in the ratio $\text{Ni/Co} = 10/1$. Nickel also occurs as microscopic lamella in association with serpentine, and as microscopic particles associated with the minerals pentlandite, $(\text{Fe,Ni})\text{S}$, and hazelwoodite, NiS , in serpentine rocks Figure 7.3.6.

Nickel in Meteorites

Metallic nickel also occurs in iron meteorites to the extent of 6-18%. In 1799, the French chemist Joseph-Louis Proust (1754-1826) who held a teaching position in Madrid obtained a fragment of an Argentinian meteorite that caused great controversy because it was shiny and ductile like silver but did not contain silver.

Proust was the first to declare that this meteorite consisted of 90% iron and 10% nickel. He also pointed out that if metallurgists could unite iron and nickel in a certain proportion, they could get an alloy that would not rust. In 1819, Michael Faraday (1791-1867) just did that, but he did not pursue the matter, being occupied with his research into electromagnetic induction. He left records of his work and a large number of specimens, which were analyzed in 1931 by Robert Hadfield. Hadfield pointed out that had Faraday continued his investigations, the Steel Age would probably have started 50 years earlier.

Nickel in New Caledonia

When Jules Garnier (1839-1904) (Figure 7.3.7) graduated from the School of Mines of Saint Etienne, France in 1860 he was sent to the French colony of New Caledonia (Figure 7.3.8). As a Chief Mining Engineer, he made a study of the mineral resources of the island. There he discovered in 1863 a new nickel mineral at Noumea at the southern tip of the island which was named garnierite after him; it is a hydrous magnesium silicate containing



Figure 7.3.7 - Jules Garnier (1839-1904)

nickel. The deposits are exploited at the Doniambo smelter. In 1870 he served in the army during the Prussian – French War. He is honored in France by a postage stamp issued in the French colony (Figure 7.3.9).

Mining of the nickel deposit started in 1875 and in the following year the first blast furnaces were erected at Pointe Chaleix near Noumea. However, because of a native rebellion the plant was shut down. In 1880, the Société Le Nickel was founded in France and a large smelter was erected in 1889 at Thio, on the other coast of the island. Earlier plants were at the same time closed. The matte produced was shipped to Le Havre in France for refining. This French island became the world's main producer of nickel, which position it retained until displaced by Canada in 1905.



Figure 7.3.8 – Location map of New Caledonia



Figure 7.3.9 - Jules Garnier stamp

Nickel in USA

In 1870s Joseph Wharton (1826-1909) (Figure 7.3.10) produced nickel salts from Gap mine at Lancaster in Pennsylvania from an ore containing 1.5% Ni apparently by leaching the matte with HCl. Operations were discontinued in 1891.



Figure 7.3.10 - Joseph Wharton (1826-1909)

Nickel in Norway

In 1870, Norway had 40 nickel mines and seven smelters in operation and produced 75 % of the world's nickel at the turn of the century. One of the major mines was the Flat mine at Evje at the southern tip of the country near Kristiansand (Figure 7.3.11) which remained in operation until 1946. Kristiansand was an established trade and industrial centre with close links to markets outside of Norway.

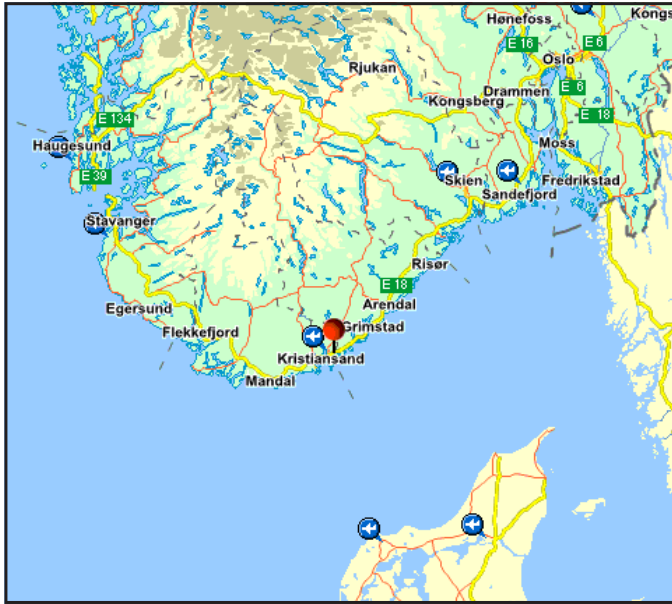


Figure 7.3.11- Kristiansand in Norway

In 1910, a small group of businessmen and engineers formed Kristiansand Nikkelraffinerings Verk (Figure 7.3.12), which was purchased in 1929 by the Canadian mining company Falconbridge Nickel Mines, after the discovery of major nickel deposits in Sudbury, Canada where the need arose for a refinery to produce pure nickel from the matte.

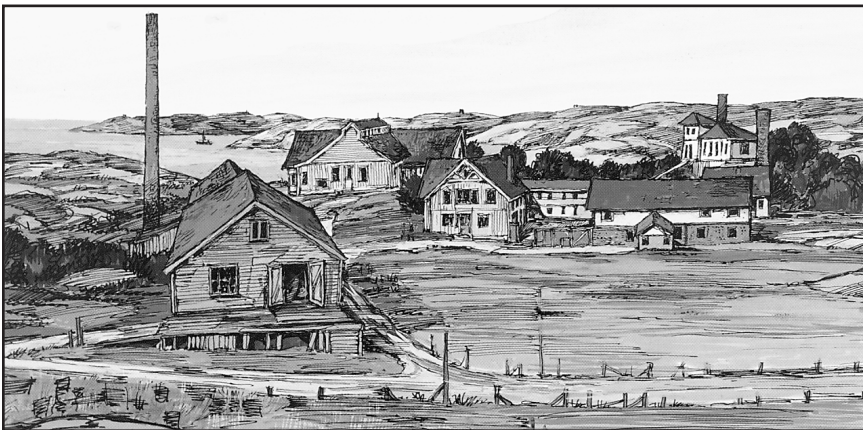


Figure 7.3.12 - The farm in Kolsdalen purchased in 1910 to become Falconbridge's nickel refinery with an annual capacity of 200 tonnes

Nickel in Canada

In 1883 a rich copper discovery was made accidentally near the locality that became later known as Sudbury in Ontario (Figure 7.3.13) during the construction of the Canadian Pacific Railroad. The Canadian Copper Company was then formed and an agreement was made to send the ore to Orford in the Province of Québec for smelting at the Orford Copper and Sulphur Company. The matte produced in 1886 was sent to Swansea for refining. However, it was found that on smelting, the ore produced a pale yellow metal and not the red metal. On analysis, the product was found to be an alloy of copper with nickel.

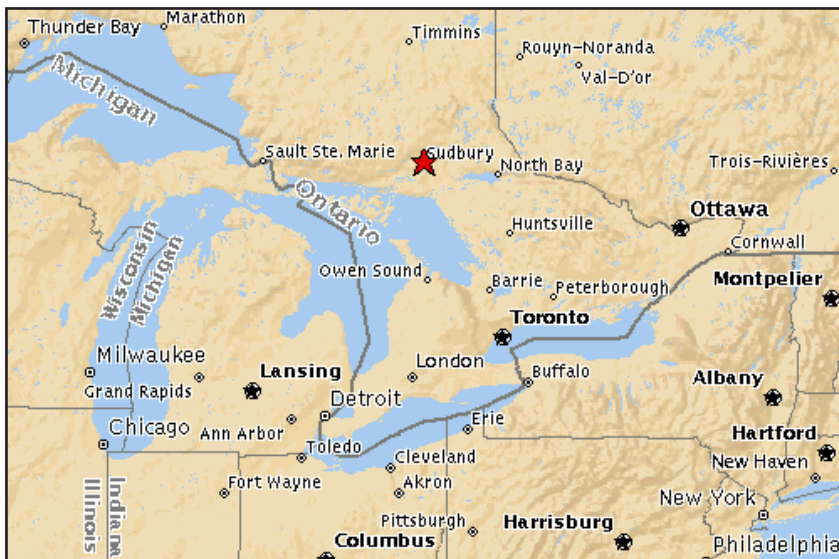


Figure 7.3.13 – Location map of Sudbury

The company thus was facing two problems: no method was available at that time for making the separation of copper from nickel, and the uses of nickel were restricted. Nickel was mainly used in making German silver, coinage, and electroplating and the only nickel produced at that time came from the garnierite ore in New Caledonia. However, its price was six times that of copper. Both problems were eventually solved with great success and nickel production shifted from French to Canadian hands.

EMERGING TECHNOLOGY

Orford Process

The separation of nickel from copper remained a problem until the discovery of the Orford Process in 1890. In this process molten sodium sulfide selectively dissolved nickel sulfide from a Ni_3S_2 - Cu_2S mixture. Sodium sulfide was obtained by reduction of sodium sulfate -- a waste product of a nitric acid plant in Orford. The plant was treating the sodium nitrate from Chile by sulfuric acid, to make explosives. When the matte was produced in presence of sodium sulfate and coal and allowed to cool two layers separated: The upper layer contained most of the copper while the lower layer contained most of the nickel (Figure 7.3.14).

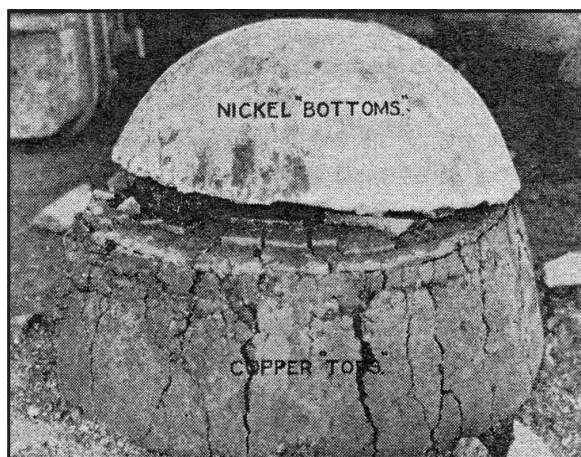
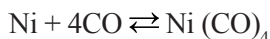


Figure 7.3.14 – Separation of nickel from copper by the tops and bottoms process [Orford process]

This resulted in what became known as the tops and bottoms Process. In 1902 the two companies (Canadian Copper and Orford Copper) merged into what became known as the International Nickel Company. The name changed later to the International Nickel Company of Canada, became known as INCO, and now Xtrata. The Orford process continued to be used until 1948 when it was replaced by the controlled cooling process followed by comminution and flotation.

Carbonyl process

In the late 1880's, Ludwing Mond (1839-1909) (Figure 7.3.15) a German chemist who had established a chemical factory (Brunner, Mond & Co.) in the Midlands in England noticed that a valve made of nickel was attacked by carbon monoxide. On closer examination it was concluded that nickel reacted with CO to form a gas, nickel carbonyl, which could be decomposed at a higher temperature to deposit nickel:



The ease with which these reactions took place suggested to Mond that this was a possible method for refining nickel. Together with the Austrian chemist Carl Langer (1860-1935) they built a plant in 1900 at Clydach not far from Swansea to treat a matte from the Sudbury ore. This continued until 1929 when the Mond Nickel Company merged with the International Nickel Company of Canada.

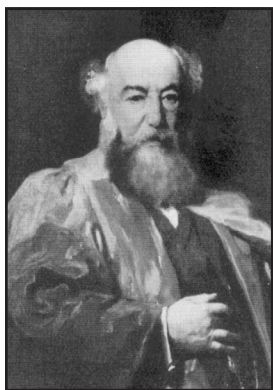


Figure 7.3.15 - Ludwing Mond
(1839-1909)



Figure 7.3.16 - Robert Stanley
(1876-1951)

Monel metal

In 1904, Robert Stanley (1876-1951) (Figure 7.3.16) a young engineer at Orford Copper Company in Bayonne, New Jersey thought of directly producing the “nickel silver” from the nickel-copper sulfide matte produced in his plant. He roasted the mixed sulfides, then successfully reduced the

oxides with charcoal to an alloy of nickel and copper analyzing 68% to 72% Ni and the balance copper with traces of iron, sulfur, and carbon. The alloy was inexpensive to produce and was marketed under the trademark Monel (one “l”) in honour of the then president of International Nickel Company, Ambrose Monell (1873-1921). Stanley became President of the International Nickel Company in 1937.

Hybinette Cell

The electrowinning of nickel takes place according to:

Cathodic reaction: $\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$

Anodic reaction: $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2\text{e}^-$

Overall reaction: $\text{Ni}^{2+} + \text{H}_2\text{O} \rightarrow \text{Ni} + 2\text{H}^+ + \frac{1}{2}\text{O}_2$

Since the anolyte is acidic and the catholyte is nearly neutral, a diaphragm is introduced to separate one from the other. The cell is known as Hybinette cell after its inventor (Figures 7.3.17 and 7.3.18).

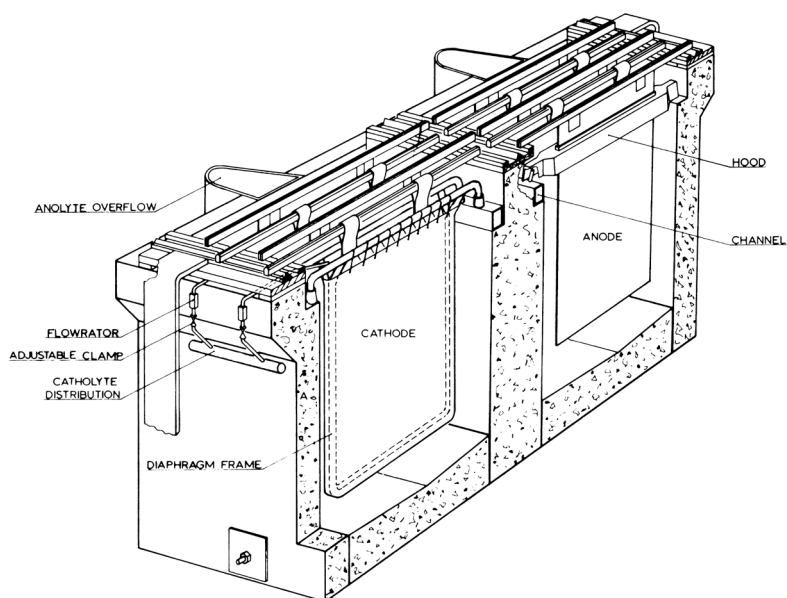


Figure 7.3.17 – The Hybinette cell

The same cell is also used in the electrorefining of nickel. To avoid contamination of the refined nickel the impure anolyte solution is taken through a purification process. The purified solution is then returned to the cathode compartment of the cell, which is separated from the anode by a porous diaphragm in the form of a box enclosing the cathode. The purified solution is fed into the cathode compartment at a rate sufficient to maintain the rate of nickel deposition. The diaphragm cloth is tightly woven so that a hydrostatic head of solution builds up relative to the rest of the electrolyte. This hydrostatic head forces nickel-depleted electrolyte through the diaphragm, from the cathode compartment into the anolyte, at a rate sufficient to prevent the entrance of either anolyte itself, or impurity ions, by diffusion into the cathode compartment (Figure 7.3.19).



Figure 7.3.18 –
Viktor Hybinette
(1867-1937)

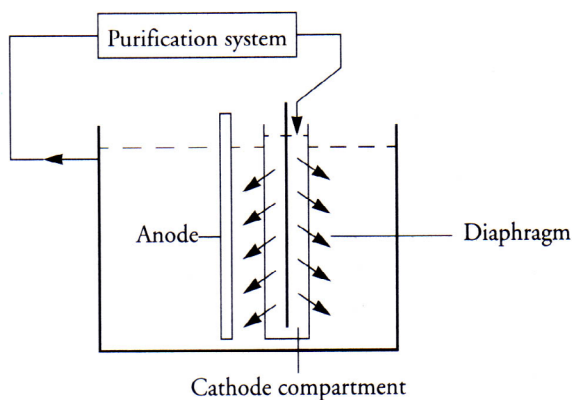
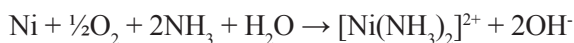


Figure 7.3.19 – Principle of the purification scheme

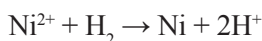
Hybinette was a Norwegian metallurgist who developed in 1929 the electrolytic process, now known by his name, for the refining of nickel at Kristiansand Refinery based on a diaphragm cell with continuous circulation of the electrolyte: The process revolutionized the nickel industry and was adopted world wide.

THE METAL

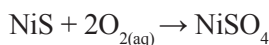
Nickel melts at 1455°C, boils at 2730°C, and has a density of 8.9. It is a hard silver white metal, which forms cubic crystals. Its relative abundance is 8×10^{-3} . The metal exhibits magnetic properties below 345°C. It dissolves in ammoniacal solutions in presence of oxygen forming ammine complex:



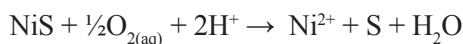
Nickel powder is precipitated from nickel sulfate solution by hydrogen at high temperature and pressure:



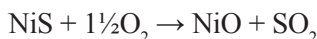
Nickel sulfide undergoes oxidation in neutral medium at ambient conditions to NiSO_4 :



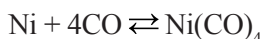
In acidic medium, however, elemental sulfur forms:



Nickel sulfide is oxidized at high temperature to NiO and sulfur dioxide:



Carbon monoxide reacts with nickel powder at 60°C to form the volatile nickel tetracarbonyl, $\text{Ni}(\text{CO})_4$. This reaction is reversible, with the carbonyl compound decomposing to carbon monoxide and nickel at higher temperatures (180°C):



This reaction is the basis for the refining of nickel. No other metal forms

similar carbonyl compounds under such mild conditions at atmospheric pressure. Nickel carbonyl is highly toxic.

NICKEL IN COINAGE

One of the early uses of nickel was in coinage. The use of 75-25 type cupro-nickel for coinage dates from 1860, when it was adopted by Belgium after an exhaustive enquiry. The alloy combined the merit of ease of melting and fabrication. The melting point of the alloy is approximately 1200°C. The example of Belgium was followed five years later by the United-States for a 3-cent coin. In the following year the 5-cent coin, the so-called “nickel”, was introduced, minted in the same alloy. The demand for the 5-cent piece increased rapidly due to the introduction of slot machines and to the use of the 5-cent coin in buses and subways, also for a drink of beer, a five-cent cigar and many other popular commodities then available for a “nickel”. Finally, in 1881, the Swiss authorities settled on pure nickel, which at that time was twice as expensive as cupronickel. Although it was the intrinsic value of pure nickel which originally led to its adoption for coinage, the choice was fortunate, and the serviceability of the nickel piece has proved so satisfactory that specimens of even the earliest issues are still in circulation.

When nickel is used as an addition element in coinage materials its properties are conferred on the alloy to a degree roughly corresponding with the amount of nickel added. Thus, the normal 75-25 cupro-nickel, consisting of three parts copper and one part nickel, has an essentially white appearance, although copper is its major constituent.

The Canadian 5-cent coin was first issued in pure nickel in 1922, and the “beaver” design was adopted in 1937 (Figure 7.3.20). Nickel has been used continuously for this coin through to the present day, with the exception of periods during World War II and the Korean War, when, in order to release nickel for strategic uses, brass or plated steel was temporarily substituted. From 1960 to 2001 the coin was made by hydrometallurgical route.



Figure 7.3.20 - Canadian 5-cent coin was first issued in pure nickel in 1922

In 1929 the Royal Mint in London was commissioned by the Government of Romania to make coins to replace paper notes, as part of a program of monetary stabilisation. The Romanian currency law stipulated that the coins should contain either aluminum or nickel, and, in order to avoid possible confusion with white cupro-nickel coins already in circulation, the Royal Mint decided to use a yellow alloy containing 79% copper, 20% zinc and 1% nickel. This material subsequently came to be known as “nickel brass”, and although the addition of nickel was fortuitous, the improvement in corrosion and wear-resistance conferred by that element was soon appreciated.

Nickel-brass coins have since been used in the currencies of other countries. Pure nickel coins have been introduced chiefly in replacement of pieces previously minted in silver alloys. Since 1945 the largest single use of pure nickel coinage has been for the replacement of the silver rupee, half rupee, and quarter rupee throughout India.

In 1951 when nickel was 200 years old, Canada was producing 90% of the world's nickel. On this occasion a 5-cent nickel coin was issued showing a nickel smelter (Figure 7.3.21) and a monument was constructed in Sudbury showing a 5-cent nickel coin to mark the importance of the region for nickel production (Figure 7.3.22).



Figure 7.3.21 - A five-cent nickel coin issued showing a nickel smelter



Figure 7.3.22 – Nickel monument in Sudbury

The Canadian Dollar

The Canadian dollar in circulation today (Figure 7.3.23) is minted at Sherritt Gordon Mines. It is made of nickel blanks on which a copper-tin alloy, 50m thick, is electrodeposited to give it the gold color. It is known as Aureate Nickel and has the analysis 91.5% Ni, 7.5% Cu, and 1% Sn. Because of its nickel content it is magnetic. Nickel is produced as a powder by hydrometallurgical route (precipitation by hydrogen under pressure). The powder is compacted into strips from which the blanks are punched. The total cost of the dollar was 10.1 cents in 1985. This coin replaced the \$1 dollar bills in circulation.



Figure 7.3.23 - Canadian dollar in circulation today

NICKEL IN ALLOY STEEL

The demand for nickel increased abruptly in 1870-1880 when its use in alloy steels was demonstrated. An important use emerged in 1885 when the superiority of armor plate from French nickel-steel was demonstrated and the US government decided to adopt it. During World War I, the world had consumed all the nickel that could be supplied. Tests showed that a steel containing 3% Ni developed remarkable projectile-breaking qualities complete with tremendous toughness.

Invar

In 1896 Charles Edward Guillaume (1861-1938), Swiss meteorologist and physicist (Figure 7.3.24) found that steels containing about 40% Ni have a very low coefficient of expansion and hence are useful for surveyors tapes, clock pendulums, and metal-in-glass seals. Such alloys known as Invar a shortened word for invariant. Guillaume was born at Fleurier in Switzerland, educated at Neuchâtel, became director of the Bureau of International Weights and Measures in Sevres, France, was awarded the Nobel prize for physics in 1920 for his for his invention, the only prize ever given for a metallurgist.



Figure 7.3.24 - Nobel prize winner Charles Edward Guillaume on a Swedish stamp



Figure 7.3.25 - Harry Brearley (1871-1948)

Stainless Steel

Rust-resistant steels were introduced in 1912 by Harry Brearley (1871-1948) (Figure 7.3.25) in Sheffield, England while working on a military project to develop an erosion-resistant steel for rifle barrels. He used nickel and chromium as alloying ingredients in concentrations up to 8 and 18%, respectively. He etched samples with nitric acid before examining the steel's grain structure under the microscope. He was surprised to find that this new steel strongly resisted chemical attack. Researchers before him have already investigated corrosion resistant alloys but it was Brearley who created the industry.

Brearley was born in Sheffield and started work at the age of twelve in the same Crucible Steel Workshop as his father. By the age of twenty, he was apprenticed as a laboratory assistant. He left Sheffield for Russia to manage Firth's Steel plant in Riga but returned to Sheffield in 1907 to manage the Brown Firth Research Laboratory. He left Firth in 1915 to become works manager at Brown Bayley's Steel Works in Sheffield, where he continued with the development and production of stainless steel. He was awarded the Iron and Steel Institute's Bessemer Gold Medal in 1920 and became a director of Brown Bayley in 1925. Brearley's chrome steel formed the basis for the wide range of stainless and special steels which are now widely used.

THE GROWTH OF THE INDUSTRY

Nickel in Russia

In 1935 the Council of Peoples' Commissars of the USSR passed a resolution to build the Norilsk Combine for the exploitation of the nickel-copper deposits (Figure 7.3.26). That was the beginning of the country's biggest mining and metallurgical complex, nearly 2000 km to the north of Krasnoyarsk the capital of Siberia. In 1939 the first copper-nickel matte was produced. Norilsk plant is also a large producer of platinum group metals.



Figure 7.3.26 – Map showing the location of Norilsk in Siberia

On the Kola Peninsula (Figure 7.3.27) there are two enterprises also that produce copper and nickel: Pechenganickel and Severonickel. The Pechenganickel mining and metallurgical plant was built by Inco in 1940 in Petsamo in Finland's territory that went to the Soviet Union after the Second World War and became known as Pechenga. The Severonickel combine was created in 1935, and operates in nearby Murmansk in the Kola Peninsula. In 1989 these works as well as the Gipronickel Research Institute in St Petersburg were consolidated in one enterprise.

Nickel in Finland

During the period between the Winter War of 1939 between the Soviet Union and Finland, and the German invasion of the Soviet Union in 1941, there were disputes between Finland and the Soviet Union over mining rights in Petsamo. German troops from Norway occupied the Petsamo region in 1941, securing the nickel supply for the war effort. The war ended in 1944, with Finland's capitulation and ceding Petsamo to the Soviet Union. In more recent years, several small nickel deposits have been mined in other parts of Finland and a refinery was established in Harjavalta.



Figure 7.3.27 – Map showing the location of the nickel works at Pechenga [formerly Petsamo] and nearby Murmansk in the Kola Peninsula, and the Finnish nickel refinery at Harjavalta in the south of Finland.

Nickel in Cuba

The deposits in Cuba are in form of laterites and are mainly in the Holguin Province which is a part of the former Oriente Province (Figure 7.3.28). These deposits are of two types:

- Limonitic at Moa. These are iron oxide containing nickel and minor amounts of magnesium silicates.
- Serpentine at Nicaro. These are mainly nickeliferous hydrated magnesium silicates. They cannot be acid leached because acid consumption would be excessive; hence these ores are treated by Caron process [see later].

Treatment of the Limonitic Ore

In early 1950s researchers of Freeport Sulphur in USA found that when samples from the Moa ore owned by the company was treated with sulfuric acid at 230 - 260°C, only minor amounts of iron and aluminum dissolve, while 95-96% of nickel and cobalt in the ore were leached within one or two hours. Consequently, Vice President Maurice Dufour, contacted the large consulting firm Chemical Construction Corporation (a subsidiary of American Cyanamid) known as Chemico to develop the high-pressure acid leach process for the Moa ore. He also asked Chemico and Arthur D. Little to devise a scheme to recover nickel and cobalt values from the solution.



Figure 7.3.28 – Map of Cuba showing the location of the laterite deposits

While Arthur D. Little recommended a solvent extraction method, Chemico proposed a novel hydrogen sulfide precipitation scheme. Although

nickel and cobalt are not precipitated by hydrogen sulfide from an acidic solution at ambient conditions, precipitation does take place at 90-120°C and at 4-6 atmosphere pressure. It was further found that when this sulfide concentrate was oxidized with compressed air at about 120°C and 5000 kPa, the metallic values dissolved as sulfates. Freeport Sulphur chose Chemico's technology. By 1954, a pressure acid leaching pilot plant was successfully operated by Freeport at Hoskin's Mound, Texas. Work was begun on construction of an integrated demonstration plant at Braithwaite, Louisiana as desired by the US Government.

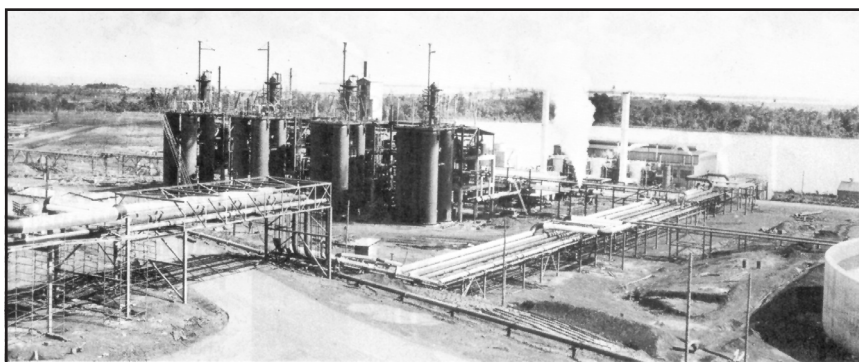


Figure 7.3.29 - High pressure acid leaching plant at Moa

Freeport Sulphur had decided to locate the leaching and sulfide precipitation refinery at Moa (Figure 7.3.29) and the metal production part in Braithwaite known also as Port Nickel. The high-grade sulfide concentrate was to be transported from Moa to Port Nickel as water slurry in storage tanks fitted in the transport ships. The tank agitators could be stopped during the voyage and re-started at the destination before pumping of the slurry to the refinery storage tanks.

The sulfide precipitation reactors at Moa began producing nickel-cobalt concentrate for shipment to the Port Nickel Refinery in late 1959. At Port Nickel the sulfide concentrate was oxidized with compressed air to form a concentrated sulfate solution. Nickel and cobalt were then separated by selective hydrogen reduction. However, due to change in the political situation in Cuba, Freeport Sulphur decided to shut down the plants in March,

1960. Freeport's engineers left Cuba and later sanctions were imposed on Cuba by the US Government and the Cuban Government confiscated the Moa plant.

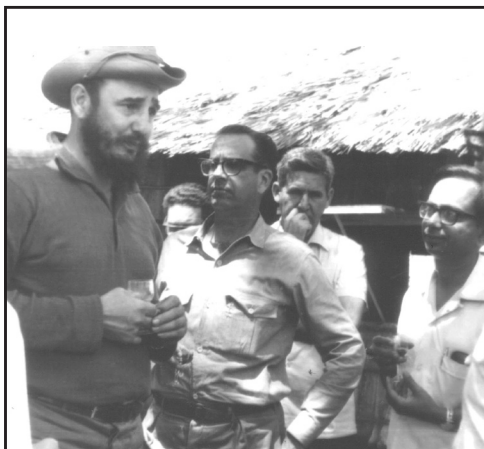


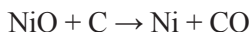
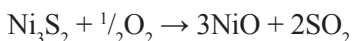
Figure 7.3.30 - Fidel Castro discussing with Indian engineers at Moa

In late 1964, Che Guevara, the then Industries Minister of Cuba, decided to start the Moa plant using the help of an Indian consulting firm that had some of her engineers previously participated in the US project. This was achieved and the plant went again successfully into operation. Figure 7.3.30 shows Fidel Castro discussing with Indian engineers at Moa. No metallic nickel is produced in Cuba to this date. Today there are 20 autoclaves for conducting the leaching operation.

Flash Smelting

When high grade sulfide ores were exhausted and it was necessary to use low grade material which can be enriched by flotation, the finely divided concentrate can no longer be charged to a shaft furnace to produce a matte. The concentrate was usually smelted in a reverberatory furnace which was highly polluting and required heating by burning a fuel. As a result the flash smelting furnace (Figure 7.3.31) was invented in the 1940s to solve this problem. After removing iron sulfide by slagging, metallic nickel was then produced from the white metal in two steps: oxidation to

form an oxide followed by reduction of the oxide to metal:



While the first step is exothermic, the second is endothermic.

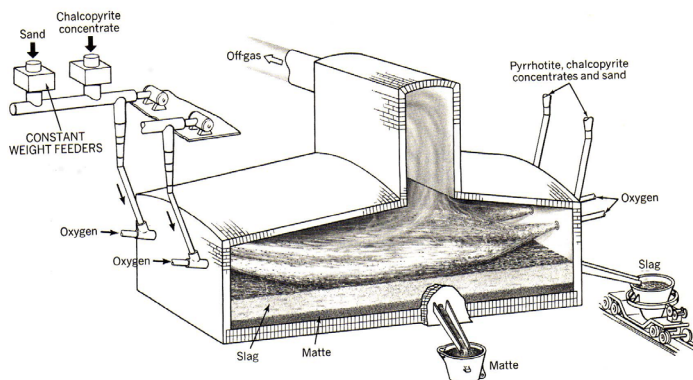
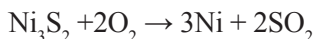


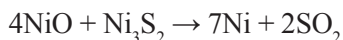
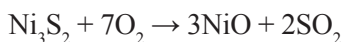
Figure 7.3.31 – INCO flash smelting furnace

Converting of nickel sulfide

It has been known long ago that the conversion of nickel sulfide to metal according to:



is thermodynamically feasible and in addition is an exothermic reaction. Such reaction eliminates the use of a reducing agent and is a one step process thus should be economically attractive. However, it was not possible to conduct it in practice. The conversion reaction can be expressed by the equations:



The difficulties are encountered were:

- Nickel oxide is insoluble in the sulfide phase and has a high melting point. As a result it separates as a finely dispersed phase that increases the viscosity of the bath and reduces the rate of mixing, thus the converting reaction stops. A great part of NiO is also slagged.
- Metallic nickel is completely soluble in the sulfide phase, thus its formation does not aid in shifting the equilibrium to the right.
- Metallic nickel has a relatively high melting point thus to keep the bath molten and easily agitated a temperature of more than 1600°C is needed.

To solve these problems means have to be provided to mix the nickel oxide intimately in the sulfide phase to prevent its slagging, and to have as high a temperature as possible in the bath to keep metallic nickel in the molten state. This was successfully achieved in the 1960s by using a rotating converter provided with an oxygen lance known as Top Blown Rotary Converter or TBRC (Figure 7.3.32). Nickel produced by this method is refined by carbonyl process.

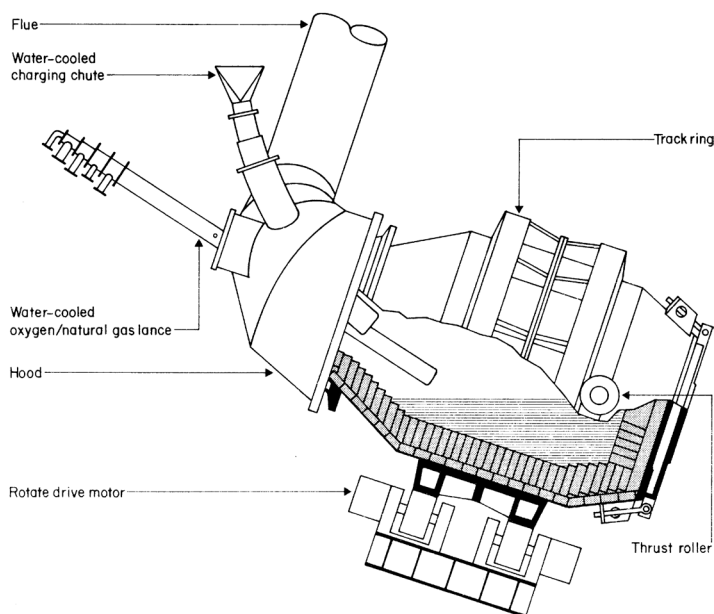


Figure 7.3.32 - Top Blown Rotary Converter

Ammonia leaching of nickel sulfide

In 1949, executives from Sherritt Gordon Mines in Canada in conjunction with the Chemical Construction Corporation, met to discuss the establishment of a small pilot plant in Canada to research the ammonia leach process for a nickel ore from a mine owned by Sherritt in Lynn Lake, a remote location in Manitoba, lacking local supplies of fuel and power in addition to the relatively low ore reserves. Hence constructing a smelter there was not economically viable. Samples of ore were sent to Frank Forward (1902-1972) (Figure 7.3.33), professor of metallurgy at the University of British Columbia. Forward had considerable success in his attempts to apply the ammonia leaching process to the treatment of samples of concentrate. Following this initial success, Sherritt funded additional test work which was carried out by Val Kudryk, a graduate student, under Forward's direction. This prompted the establishment of a pilot plant at the Mines Branch in Ottawa, to continue to do test work on nickel-copper concentrate.

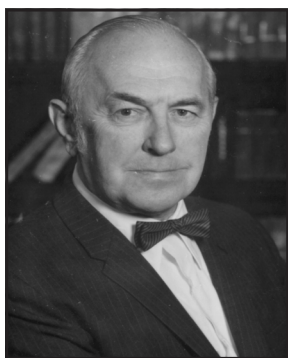


Figure 7.3.33 - Frank Forward
(1902-1972)

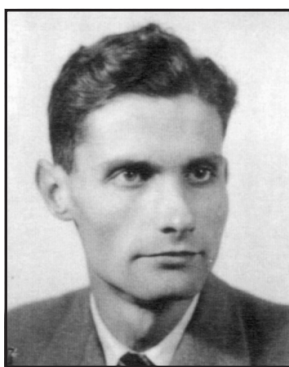


Figure 7.3.34 - Felix A. Schaufelberger
(1921- 2009)

Pressure precipitation by hydrogen

In 1946, the Chemical Construction Corporation (Chemico) in New York City had some problems in the removal of carbon monoxide impurity from synthesis gas, a mixture of hydrogen and nitrogen. Chemico was a

subsidiary of American Cyanamid Company, which was in the business of building ammonia and nitric acid plants.

This problem was given to Felix A. Schaufelberger (1921- 2009) (Figure 7.3.34) a young graduate from the Federal Institute of Technology in Zurich, Switzerland who had joined Cyanamid's Stamford Research Laboratories in Connecticut a year before. Towards the end of 1948, Schaufelberger succeeded in precipitating pure copper from sulfate solution by reduction with hydrogen in quantitative yield, liberating sulfuric acid for recycling in the leaching circuit. He had also prepared the first samples of nickel and of cobalt metal powder with his co-worker Tuhin K. Roy from India. This technology was adopted by Sherritt for the new plant in Fort Saskatchewan.

Vladimir N. Mackiw (1923-2001) (Figure 7.3.35) was born in Stanislawiw, Western Ukraine, obtained his diploma and MSc. in 1946 in chemistry from the Universities of Breslau (now Wroclaw in Poland) and Erlangen in Germany, respectively. He completed his postgraduate studies at the University of Louvain in Belgium, in 1948. That year he immigrated to Canada. Later he joined the research group at the Mines Branch and played a key role in developing the process.



Figure 7.3.35 - Vladimir N. Mackiw
(1923-2001)



Figure 7.3.36 - Louis S. Renzoni
(1915-1994)

Anodic dissolution of nickel sulfide

Louis S. Renzoni (1915–1994) (Figure 7.3.36) was born in Copper Cliff, Ontario, obtained a B.Sc. from Queen's University in 1935 and D.Sc. in 1969, was with International Nickel Company where he and his co-workers developed in 1964 the anodic dissolution process for nickel sulfide that was applied at the Thompson Refinery in Manitoba (Figure 7.3.37). The basic reactions for the process are:

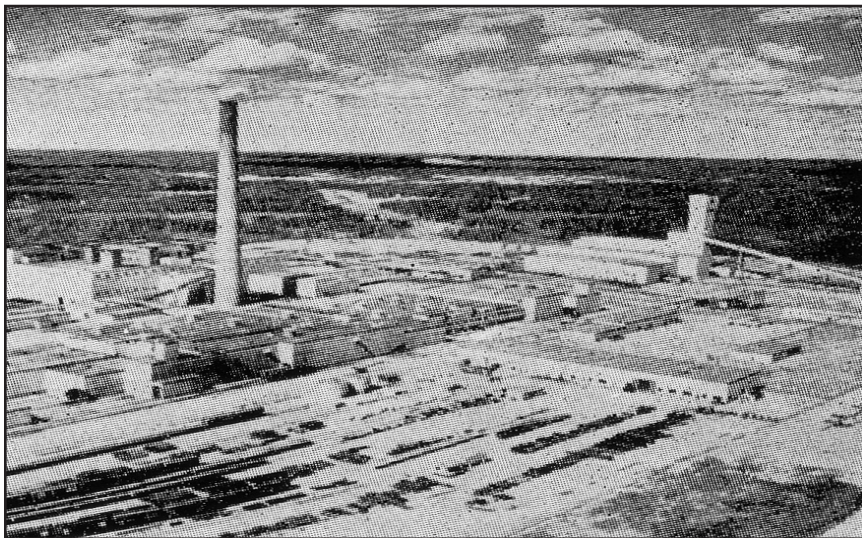


Figure 7.3.37 - Thompson Refinery in Manitoba

Nickel in Australia

Australian nickel was first discovered in laterites at Greenvale, Queensland, in 1957 and was treated by the Caron process at Yabulu refinery 225 km to the east coast. However, it was the discovery of nickel sulfide mineralisation at Kambalda in 1966 that led to the nickel boom of the late '60's and early '70's. Laterite deposits were discovered later in Western Australia at Murrin Murrin, Cawse, and Bulong near Kalgoorlie while Greenvale operations closed in 1992 when the mine was exhausted (Figures 7.3.38 and 7.3.39).

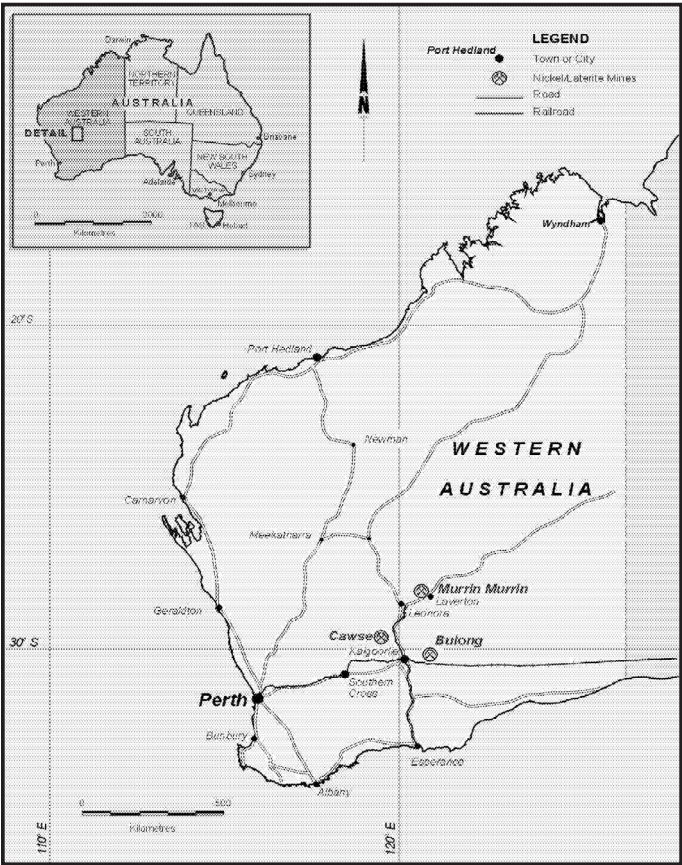


Figure 7.3.38 – Location of the three laterite nickel operations in Western Australia around Kalgoorlie

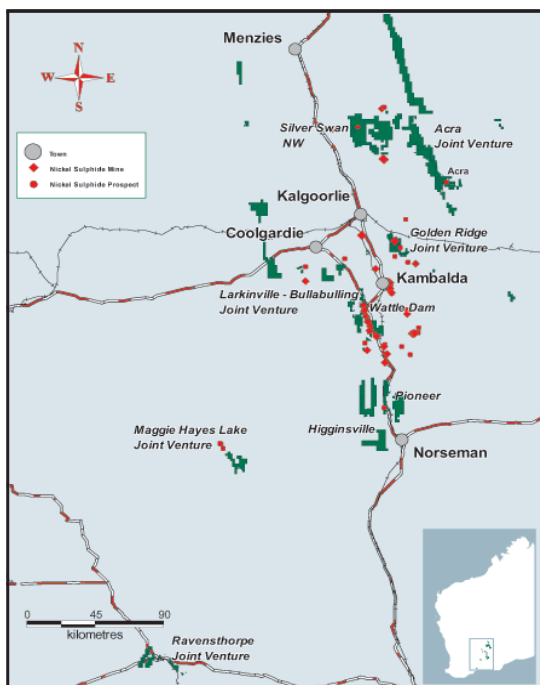


Figure 7.3.39 – Map showing Kambalda operations 50 km south of Kalgoorlie

Nickel in Southeast Asia

Vast nickel laterite deposits were known to occur in Celebes Island in Central Indonesia [also known as Sulawesi] and at Nonoc Island near Manila in the Philippines at the beginning of the 20th century. Martinus Hendrik Caron (1883 - 1958) (Figure 7.3.40), a Dutch native born in Indonesia, became professor of metallurgy at Delft University from 1928 till 1951 and advisor to Billiton Company. He devised in 1924 the ammonia leaching process for treating nickel laterites in Indonesia that contain appreciable acid-consuming gangue minerals.



Figure 7.3.40 -
Martinus Hendrik Caron
(1883 - 1958)

The process was adopted during World War II by US metallurgists to exploit the Cuban deposits. It was also applied by INCO in the early 1960s to treat a low-grade pentlandite ore after roasting followed by reduction of NiO to metallic nickel, but the process was shut down. Later it was applied to treat the Greenvale laterite at Yabulu in Queensland, Australia in 1970, in the Philippines, and other places.

Ferronickel

For a brief period in the nineteenth century New Caledonia nickel ores were smelted in blast furnaces to produce ferronickel. However, when attempts at refining the crude product failed to yield a nickel metal of acceptable purity, the operation was abandoned. The rotary kiln-electric furnace smelting process is now used almost universally for the production of ferronickel from oxide ores. The first commercial scale electric furnace to produce ferronickel was the 10.5 MVA units installed by SLN at its Doniambo smelter in 1958 (Figure 7.3.41). The refining of ferronickel resembles that of steel in that the principal impurities are sulfur carbon, silicon, phosphorus, and oxygen. Ferronickel is not usually treated to remove cobalt, copper, or arsenic, which may be present in significant amounts.

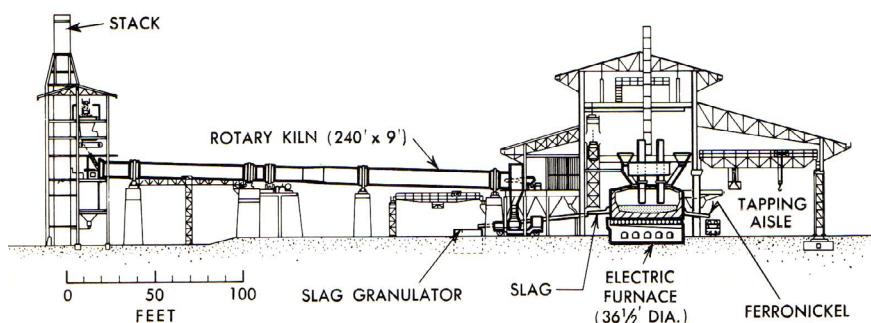


Figure 7.3.41 – Ferronickel plant in New Caledonia

Nickel in the Canadian North

With the recent discovery of the Voisey Bay sulfide deposits in the Canadian North (Figure 7.3.42) it was decided in 2005 to use a pressure leaching process similar to that used for zinc and copper sulfides shown in Figures 7.3.43 and 7.3.44 to produce elemental sulfur instead of SO_2 .



Figure 7.3.42 – Location map of the nickel deposits in the Canadian North at Voisey Bay and the hydrometallurgical plant Argentina in Newfoundland

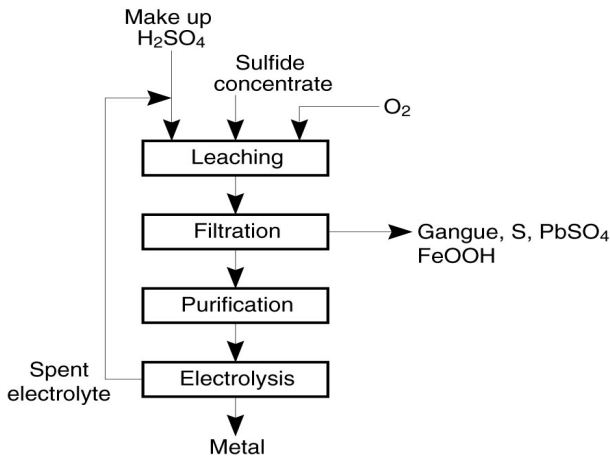


Figure 7.3.43 – Pressure leaching process for treating the Voisey Bay concentrate

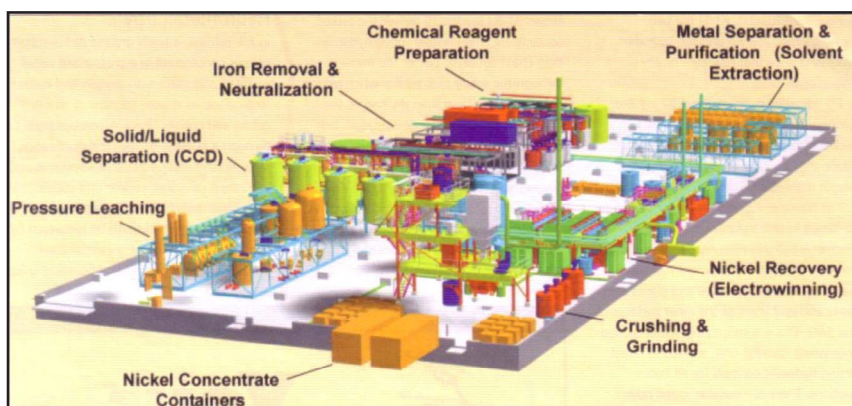


Figure 7.3.44 – Nickel sulfide pressure leaching plant under construction at Argentina in Newfoundland

SUMMARY

Although nickel was discovered in 1751 by the Swedish chemist Axel Fredrik Cronstedt, it was already known centuries earlier by the Chinese in form of an alloy known as pai thung or “white copper”. The alloy became known in Europe in the late 18th century through traders. It resembled silver in appearance but was much cheaper than silver. This encouraged researchers in Europe to investigate this alloy. In 1821, the presence of nickel in pai thung was confirmed and was imitated by a German chemist in form of an alloy that became known as German Silver. Once the metal was isolated in pure form it found numerous applications. Further, a large number of processes were developed later to recover and refine the metal from a variety of ores. Figure 7.3.45 shows a Canadian stamp commemorating the discovery of nickel in Sudbury in 1883.



Figure 7.3.45 - A Canadian stamp commemorating the discovery of nickel in Sudbury in 1883

Nearly 60% of the nickel produced today worldwide is by smelting the sulfide concentrates and 40% from laterites. Since copper, cobalt, and the platinum metals are usually associated with the sulfide concentrates, different fractions are obtained and these are treated by different processes to recover these metals. For example:

- Conversion of the purified sulfide to metal followed by electrolytic refining
- Anodic dissolution of the purified sulfide
- Thermal oxidation of the sulfide then reduction of the oxide to metal followed by electrolytic refining
- Aqueous oxidation of the sulfide followed by electrowinning
- Other processes, for example, the carbonyl process and precipitation by hydrogen under pressure.

It is interesting to note that the newest process for treating nickel sulfide concentrates to be adopted at the Canadian North is a hydrometallurgical process. Figure 7.3.46 gives a summary of the major processes for treating the low-grade and high-grade nickel sulfide concentrates.

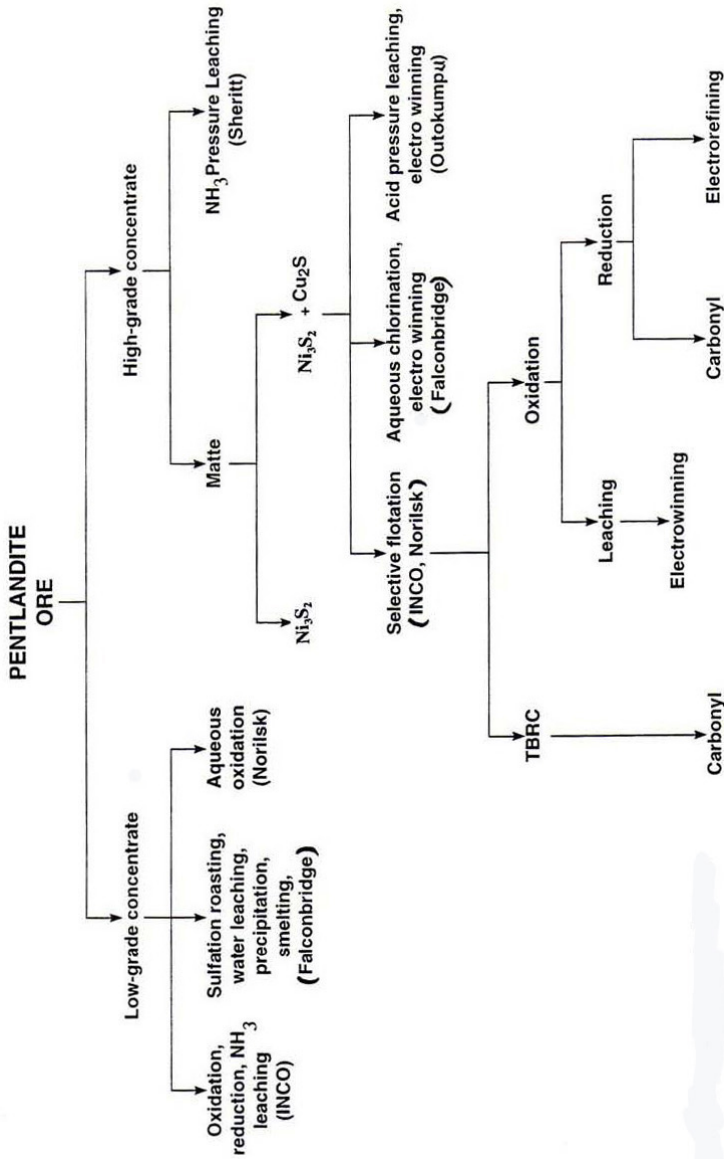


Figure 7.3.46 - A summary of processes for treating the low-grade and high-grade nickel sulfide concentrates

7.4 Manganese

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INTRODUCTION

Pyrolusite, MnO_2 , (Figure 7.4.1) known in Germany as Braunstein, has been used for centuries by glass makers to eliminate green or yellow color from glass. When added in large amounts, it gave glass a violet color. The name pyrolusite, first used in 1826 is derived from two Greek words meaning *fire* and *to wash* because of its use to free glass through its oxidizing effect of the colors due to iron.



Figure 7.4.1 - Museum sample of pyrolusite

In 1740, the Berlin glass and porcelain technologist J.H. Pott prepared “chameleon mineral” (potassium permanganate, KMnO_4) and other compounds from it. The mineral was also known as “manganese” or “black magnesia”. However, the Swedish chemist Torbern Bergman (1735-1784) described it as the calx of a new metal. However, he failed to prepare this

new metal and turned the problem over to his friend Carl W. Scheele. In 1774 Scheele presented the result of his work to the Stockholm Academy of Sciences in the form of a paper entitled “Concerning Manganese and Its Properties”. In this paper, he announced the existence of the gaseous element chlorine and paved the way for the discovery of oxygen. He also confirmed that the mineral known as “manganese” was the calx of a metal different from any then known.

DISCOVERY

In 1774, Johan Gottlieb Gahn (1745-1818) (Figure 7.4.2) lined a crucible with moist charcoal dust, placed in the center a mixture of the pulverised pyrolusite and oil, and covered it with more of the charcoal dust. After luting another crucible to this, he heated them intensely for an hour. Upon opening the crucible, he found in it a button of metallic manganese (*regulum magnesiae*), weighing about a third as much as the ore from which he had isolated.



Figure 7.4.2 - Johan Gottlieb Gahn (1745-1818)

Gahn was born at Voxna, an iron-mining town in South Helsingland in Sweden. His father died at an early age and he was obliged to earn his living by working in the mines. He studied mineralogy under Bergman and became expert in the use of the blowpipe. After his isolation of metallic manganese he was made assessor at the College of Mines in Falun in 1784. In 1819, he served as deputy to the Diet and was known politically as a liberal.

Gahn was also a successful business executive. He owned and managed mines, smelters, and a sulfuric acid plant. It was in this acid plant the Berzelius discovered selenium.

THE METAL AND ITS COMPOUNDS

Manganese is a silver-grey metal, resembling iron. It is hard and brittle, and its primary uses in a metallic form are as an alloying, desulfurizing, and deoxidizing agent for steel, cast iron, and nonferrous metals. It is a transition metal hence it is less reactive than the typical metals and more reactive than the less-typical metals. Manganese is an essential trace nutrient in all forms of life.

Relative abundance in the Earth's crust, %	0.10
Density at room temperature, $\text{g}\cdot\text{cm}^{-3}$	7.21
Density at melting point, $\text{g}\cdot\text{cm}^{-3}$	5.95
Atomic radius, pm	127
Melting point, $^{\circ}\text{C}$	1246
Boiling point, $^{\circ}\text{C}$	2061

Manganese exists in four allotropic forms: α , β , γ , and δ :

a-Mn	b-Mn	g-Mn	d-Mn
Complex cubic	Complex cubic	Face centered cubic	Body centered cubic
a D b 727 $^{\circ}\text{C}$	b D g 1095 $^{\circ}\text{C}$	g D d 1104 $^{\circ}\text{C}$	d D liquid 1244 $^{\circ}\text{C}$

Manganese dissolves in acids with liberation of hydrogen and formation of Mn (II) salts. Hot concentrated sulfuric acid dissolves manganese with evolution of SO_2 , and nitric acid with evolution of hydrogen, nitrogen, and dinitrogen monoxide. At normal temperatures, pure manganese is not attacked by oxygen but high temperature it reacts violently with oxygen, sulfur, and phosphorus. It is therefore a powerful agent for deoxidizing and desulfurizing metals, whereby it is converted to a divalent oxide or sulfide.

Manganese exists in the following oxidation states: +7, +6, +5, +4, +3, +2, +1, -1, -2, -3. The oxides: acidic, basic or amphoteric depending on the

oxidation state. Manganese compounds where manganese is in oxidation state +7, which are restricted to the unstable oxide Mn_2O_7 and compounds of the intensely purple permanganate anion MnO_4^- , are powerful oxidizing agents (Figure 7.4.3).



Figure 7.4.3 - Potassium permanganate crystals and solution



Figure 7.4.4 - Rhodonite



Figure 7.4.5 - Rhodochrosite

Compounds with oxidation states +5 (blue) and +6 (green) are strong oxidizing agents. The most stable oxidation state for manganese is +2, which has a pale pink color, and many manganese (II) compounds are known, such as manganese (II) sulfate, MnSO_4 , and manganese (II) chloride, MnCl_2 . Manganese (IV) oxide, MnO_2 , is amphoteric. Manganese silicate, $(\text{Mn,Fe,Mg,Ca})\text{SiO}_3$, occurs in nature as the mineral rhodonite - - meaning rosy in Greek (Figure 7.4.4) and rhodochrosite (manganese(II) carbonate) (Figure 7.4.5).

TECHNOLOGY

Classification of manganese ores

These are classified as follows (Table 7.4.1):

- *Metallurgical.* Ore with a high manganese content (minimum 40 % Mn) are suitable for the manufacture of ferromanganese and special manganese alloys.
- *Battery.* This is a high grade ore at least 75 % MnO_2 suitable for the manufacture of batteries.
- *Chemical.* This is also a high grade ore at least 80 % MnO_2 suitable for use as an oxidizing agent in chemical processes or in the production of potassium permanganate and other manganese chemicals.

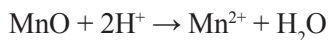
Table 7.4.1 - Classification of manganese ores

Grade	Specifications	Use
Metallurgical	> 40 % Mn	Manufacture of ferromanganese and special manganese alloys
Battery	> 75 % MnO_2	Manufacture of batteries
Chemical	> 80 % MnO_2	As oxidizing agent in chemical processes, potassium permanganate, and other manganese chemicals

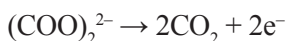
Recovery from ores

Pyrolusite is the most important manganese mineral. Manganese ores are used for making ferromanganese, pure MnO_2 for batteries, or to a minor extent metallic manganese.

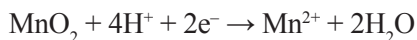
Manganese dioxide is insoluble in dilute H_2SO_4 , but when reduced to MnO , it readily dissolves to give a solution of MnSO_4 :



Since manganese is recovered from this solution by electrolysis, the spent electrolyte can be used for leaching. Manganese dioxide can be solubilized, however, in dilute H_2SO_4 in presence of a reducing agent such as ferrous sulfate, sulfur dioxide, coal, or oxalic acid which reacts by oxidation–reduction steps as follows:



while MnO_2 reacts according to:



Ferromanganese

Ferromanganese was first produced on an industrial scale in 1841 by Pourcel in France for use in crucible steels and by 1850 spiegeleisen, an iron alloy containing 20% manganese, had been produced commercially in Prussia. The Bessemer process was made practical by Mushet who advised the addition of spiegeleisen to de-oxidize steel in 1856-57. The use of ferromanganese as an additive to steel to counteract the harmful efforts of sulfur and phosphorus was patented by Siemens in 1866. Ferromanganese was first produced in an electric furnace in 1890.

Alloy steels containing manganese

In 1888, Hadfield developed wear-resistant steel containing manganese as an alloying agent.

Metallic manganese

Metallic manganese is prepared industrially by leaching manganese ores with sulfuric acid and electrowinning. Metallic manganese is used as alloying element with aluminum and copper.

Manganese nodules

Oceans contain manganese, copper, nickel, and cobalt in the form of black nodules about 10 cm diameter, deposited on the ocean floor (Figure 7.4.6). These nodules are mainly manganese dioxide containing about 1% copper, 1% nickel, and 10 to 15% iron. The nodules are present at a concentration of about 12 kg/m². Studies are under way to exploit this source.

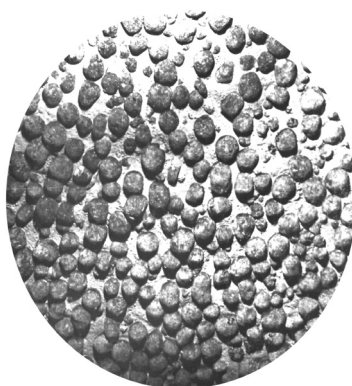
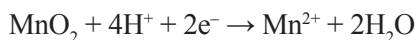
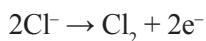


Figure 7.4.6 - Manganese nodules, about 10 cm in size on ocean floor

Generation of chlorine

Manganese dioxide dissolves in hydrochloric acid liberating chlorine:



7.5 Molybdenum

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INTRODUCTION

The black mineral molybdenite (Figure 7.5.1) was usually confused with graphite (Figure 7.5.2). The distinction was made in 1778 by Carl Wilhelm Scheele in Sweden when both minerals were reacted with nitric acid: molybdenite yielded a white residue of molybdic acid, while graphite did not. In 1781 Scheele sent the white powder to his friend chemist Peter Jacob Hjelm (1746-1813) who reduced the oxide with carbon and obtained the first sample of metallic molybdenum. Hjelm was educated at Uppsala University and in 1782 he became master of assaying for the Royal Mint, Stockholm, and in 1794 he was appointed director of chemical laboratories at the Swedish Bureau of Mines.



Figure 7.5.1 - Museum sample of molybdenite on quartz



Figure 7.5.2 - Peter Jacob Hjelm (1746-1813)

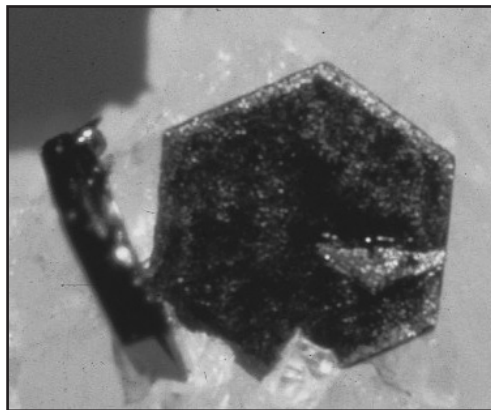


Figure 7.5.3 - Graphite crystal

Recent research has indicated the similarity in properties and structure between graphite and molybdenite. Both have a layered structure (Figure 7.5.3) and that is why both are used as lubricants,

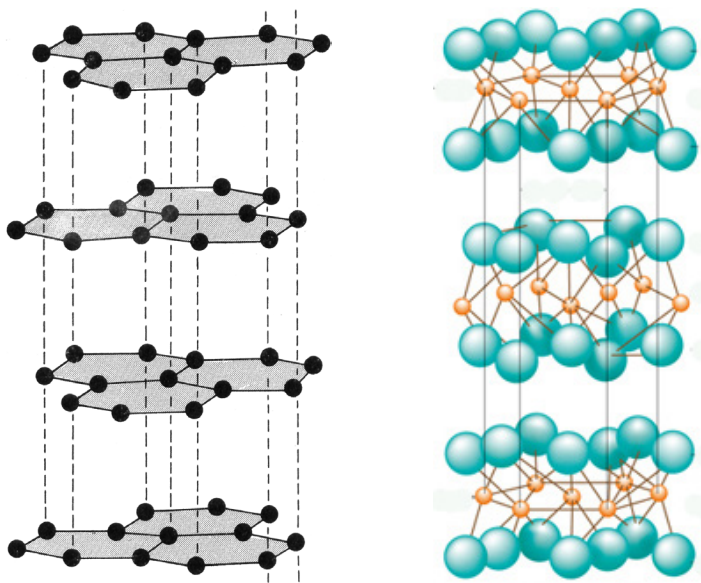


Figure 7.5.4 - Layered structure of graphite [left] and molybdenite [right]

The main source of molybdenite throughout the nineteenth century was the Knaben mine in Norway. World War I demand for molybdenum

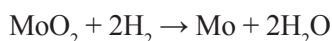
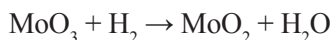
stimulated development of the Climax Mine in Colorado, which was put on stream in 1918 by the Climax Molybdenum Company. By that time the froth flotation process had replaced hand sorting for concentrating ores.

In 1933 a process for the selective flotation of molybdenite from copper porphyry ores was developed by the Anaconda Company at its Cananea plant in Mexico. The Kennecott Copper Company soon followed at its Utah mines. The technology was later extended to Chile at Kennecott's El Teniente and Anaconda's Chuquibambilla. Thus began the age of molybdenum production as a by-product of copper. During World War II, the United States supplied about 90% of the world molybdenum demand. Climax Molybdenum Company continued to be the largest Western World producer into the 1980s, doubling its capacity when it opened the Henderson mine in Colorado in 1976.

While molybdenite in quartz veins does not contain rhenium that associated with porphyry copper contains about 700 ppm rhenium and is the major source of this metal.

RECOVERY

Molybdenum is recovered from molybdenite by roasting then leaching (Figure 7.5.5). The metal is produced by the reduction of high purity MoO_3 with hydrogen. MoO_3 is volatile at high temperature. Therefore, reduction is conducted in two stages: the first at 600°C to obtain a nonvolatile oxide which is then crushed, ground and then further reduced to the metal at 1000°C :



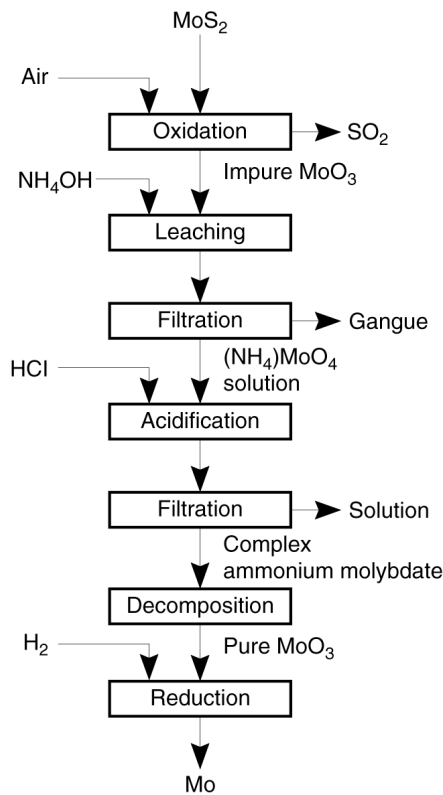


Figure 7.5.5 - Recovery of molybdenum

THE METAL AND ITS COMPOUNDS

Molybdenum is a lustrous silver-white solid with typically metallic properties.

Relative abundance in Earth's crust, %	2.3 x 10-4
Density at 20°C, g/cm3	10.22
Crystal structure	Body centered cubic
Atomic radius, pm	139
Melting point, °C	2617
Boiling point, °C	4612

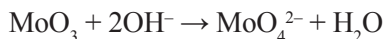
The metal retains its luster almost indefinitely in air. On prolonged heating in air below 600°C, it becomes covered with its trioxide; at 600°C the oxide sublimates and rapid oxidation occurs. Molybdenum burns in oxygen at 500–600°C. Dilute acids and concentrated hydrochloric acid have very little effect on the metal. Moderately concentrated nitric acid dissolves it but concentrated nitric acid soon passivates the surface and reaction ceases. It is practically unaffected by alkaline solutions and very nearly so by fused alkali-metal hydroxides. However fused oxidizing salts such as sodium peroxide, sodium or potassium nitrate or perchlorate dissolve the metal rapidly.

As a transition metal molybdenum may have a valency of +2, +3, +4, +5, or +6. It also forms many complexes and colored compounds. Its aqueous chemistry is complicated. It is dominated by oxo-species which are prone to dimerize or polymerize. Typical compounds of molybdenum(VI) are: the trioxide, MoO_3 , sodium molybdate, Na_2MoO_4 , ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 2\text{H}_2\text{O}$. Well characterized oxides are molybdenum trioxide, MoO_3 , and molybdenum dioxide, MoO_2 . Molybdenum blues, so called because of their blue color, are mixed oxide hydroxides of molybdenum (VI) and molybdenum (V). They are amorphous solids that are soluble in water and alcohols. A typical species is $(\text{Mo}_3^{6+}\text{Mo}_3^{5+}\text{O}_{18}\text{H})^-$.

Molybdate ion, MoO_4^{2-} , is stable above pH 7. When the pH is gradually decreased, insoluble poly-ions are formed:

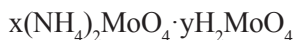
Anion	MoO_4^{2-}	→	$\text{Mo}_3\text{O}_{11}^{4-}$	→	$\text{H}_3\text{Mo}_6\text{O}_{21}^{3-}$
pH	14–6.5		6.5–4.5		4.5–1.5

Molybdenite, MoS_2 , the major source of molybdenum, is usually oxidized to MoO_3 , and the oxide is dissolved in excess ammonium hydroxide to form molybdate ion:



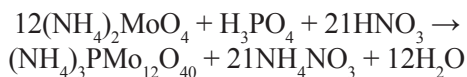
The solution obtained is subjected to a purification step which involves

acidification to precipitate a series of hexaammonium molybdates which may be considered to be composed of:



where $x = 1.5, 2$, and 2.5 when $y = 4.5, 4$, and 3.5 , respectively. This is a commercial product which can be thermally decomposed to pure oxide then reduced to metal.

Ammonium molybdate is used to determine traces of phosphorus in solution by colorimetric analysis using the yellow color produced or in gravimetric analysis to precipitate phosphorus as a voluminous yellow precipitate of ammonium phosphomolybdate:



Molybdenite, MoS_2 , is the major molybdenum mineral but molybdenum trisulfide, MoS_3 , is precipitated when hydrogen sulfide is passed through an acidified molybdate solution. It is like the sulfides of tin, arsenic, and antimony, dissolves in yellow ammonium sulfide giving a tetrathio salt, MoS_4^{2-} . When heated in nitrogen at ca. 350°C molybdenum trisulfide decomposes to amorphous molybdenum disulfide. Heated in air, it begins to oxidize to molybdenum trioxide at 200°C .

Molybdenum is an essential trace element for enzymes which fix nitrogen in leguminous crops. Molybdenum compounds in general are of a low order of toxicity.

USES

The first major use of molybdenum came during World War I when it was added to steel to increase its toughness and strength at high temperature for use as tank armor and in aircraft engines. After the war new peace

time uses of molybdenum, largely in the automotive industry, were developed. Demand for molybdenum steadily grew as new chemical and metallurgical applications continued to be developed.

It is a refractory metal used in lamp and lighting industries, in electronic and semiconductor industries, in high-temperature and vacuum furnace construction, in glass and ceramic industries, and in nuclear technology. Molybdenum-containing catalysts are used for a broad range of reactions. Molybdenum disulfide is an important solid lubricant, being used to reduce wear, friction, and sustain lubrication under boundary sliding conditions.

7.6 Tellurium

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DISCOVERY

An uncommon mineral known as *aurum problematicum* (Figure 7.6.1) from a gold mine in Transylvania in the Austrian Empire [today a part of Romania] was examined by Anton von Rupprecht, professor of chemistry at the Mining Academy in Schemnitz [today Banská Štiavnica in Slovakia]. He concluded that it was native antimony.

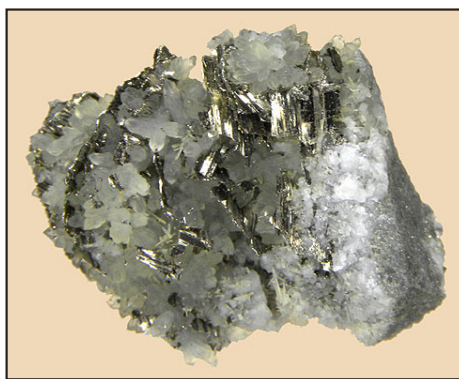


Figure 7.6.1 - Museum sample of aurum problematicum
(gold telluride)

In 1782, the Austrian chemist Franz Joseph Müller von Reichenstein (1740-1825) (Figure 7.6.2) isolated a metallic substance from this mineral and concluded that it was bismuth. Upon careful examination of the regulus, however, he decided in 1783 that although the mineral bore some resemblance to bismuth, it must contain a new metal, different from all others

and that gold was an essential constituent of it. Seeking confirmation of his work, he sent a specimen to the famous Swedish chemistry professor Torbern Bergman; but, with such a small sample, the latter could do no more than prove that it was not bismuth.



Figure 7.6.2 - Franz Joseph Müller von Reichenstein (1740-1825) on an Austrian postage stamp issued in 1990 on the occasion of his 250th anniversary



Figure 7.6.3 - Paul Kitaibel (1757-1817) on an Austrian postage stamp issued in 1992 on the occasion of 175th anniversary of death of Kitaibel

In 1790 the Hungarian scientist Paul Kitaibel (1757-1817) (Figure 7.6.3) at the Hungarian University at Pest was asked to determine the silver content in a new mineral in an ore from Deutsch-Pilsen which was described by Ignaz von Born as *argentiferous molybdenite*. Kitaibel concluded that it contained a new metal beside silver. When his report was read in Vienna by the mine captain Karl Haidinger (1756-1797), he was informed that *aurum problematicum* may have contained also the same new metal found by Müller. When Kitaibel investigated the matter further, he found that indeed the same new metal was also present there.

NAMING OF THE NEW METAL

In 1794 Müller von Reichenstein presented Martin Heinrich Klaproth (1743-1817) (Figure 7.6.4) the leading analytical chemist in Germany with his supply of *aurum problematicum* and the results of his studies. Klaproth

reported in 1798 to the Prussian Academy of Sciences in Berlin the existence of a new metal which he named tellurium and that the discoverer of this metal was Müller von Reichenstein without any mention of Kitaibel.



Figure 7.6.4 - Martin Heinrich Klaproth (1743-1817)
the leading analytical chemist in Germany

Klaproth studied the sample of gold ore sent to him and isolated tellurium from it by the following method. After digesting the pulverized ore with aqua regia, he filtered off the residue and made the solution alkaline with caustic potash. The white precipitate that appeared dissolved in excess alkali, leaving only a brown, flocculent deposit containing gold and hydrous ferric oxide. Klaproth removed this precipitate by filtration and added hydrochloric acid to the filtrate until it was neutral. A copious precipitate appeared. After washing and drying, he stirred it up with oil and introduced the oil paste into a glass retort, which he gradually heated to redness. When he cooled the apparatus, he found metallic globules of tellurium in the receiver and retort.

In summary, tellurium was discovered independently by the Austrian chemist Franz Joseph Müller von Reichenstein and the Hungarian scientist Paul Kitaibel between 1782 and 1790, and named by the German chemist Martin Heinrich Klaproth in 1798. Tellus is a Latin word meaning «Earth».

TECHNOLOGY

Calaverite, AuTe_2 , and sylvanite, AgAuTe , are two rare minerals containing tellurium. They are a nuisance when present in gold ores and must be decomposed by roasting before cyanidation for gold recovery. Calaverite is named from Calaveras County in California where it was originally found in the Stanislaus mine. Sylvanite is derived from Transylvania where it was first found. The main occurrence of tellurium, however, is in copper sulfide ores.

Although present in parts per million ranges, it is concentrated in the anodic slimes during electrolytic refining and is recovered as a by-product. The old method used was by baking with concentrated H_2SO_4 followed by leaching with water to remove soluble sulfates then numerous steps till electrowinning from sodium tellurate solution. Since 1970s, the process generally used is aqueous oxidation in autoclaves.

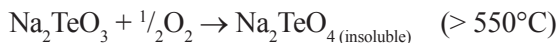


Figure 7.6.5 - Tellurium

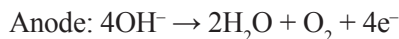
Tellurium is a metalloid found in close association with sulfur and selenium, has the appearance of a metal but lacks all properties of metals (Figure 7.6.5). It is recovered from the anodic slimes obtained during the electrolytic refining of copper and nickel during processing of their sulfide ores. On melting, the specific volume increases by ca. 5 %. Tellurium vapor is yellow-gold and consists mainly of Te_2 molecules.

Relative abundance in Earth's crust	$1.8 \times 10^{-7}\%$
Density, g/cm^3	6.2
Melting point, $^{\circ}\text{C}$	449.5
Boiling point, $^{\circ}\text{C}$	988
Crystal structure	Hexagonal

Tellurium burns in air to form tellurium dioxide, TeO_2 . Tellurium dioxide can also be obtained by treating tellurium powder with nitric acid, followed by heating the nitrate. Tellurium dioxide dissolves in water to form tellurous acid, H_2TeO_3 . Sodium tellurite can be oxidized to tellurate:



Tellurium is obtained by electrolysis of a tellurite solution:



Tellurium obtained by electrolysis may be further refined by vacuum distillation and zone refining to yield the higher-purity grades 99.99–99.9999 %. Hydrogen telluride, H_2Te , is a colorless, highly toxic gas which decomposes above 0°C .

USES

Tellurium is used in cadmium telluride, CdTe , solar panels (Figure 7.6.6) which are lower in cost than silicon solar cells.



Figure 7.6.6 - Cadmium telluride solar cells

BIOGRAPHICAL NOTES

Franz Joseph Müller, was born in (Sibiu, Nagyszeben or Heramnnstadt) in the Transylvannian Alps. After studying law and philosophy in Vienna, he attended the School of Mines at Schemnitz (Selmezbánya, or Baňská Štiavnica), where he became interested in mining, mineralogy, and chemistry. At the age of 28 he became a surveyor in Hungary, and two years later he served on a committee which managed the mines and smelters in the Banat. In 1775 he went to the Tyrol as mine captain and acting superintendent, and later became chief inspector of all the mines, smelters, and salt works in Transylvannia. He died in Vienna at the age of 85.

Paul Kitaibel was born at Nagy Márton (Mattersdorf), and attended the University of Buda. In 1793, after a scientific tour of Croatia, he returned to Pest to join the staff of the School of Pharmacy. After managing the botanical garden for a time, he became professor of botany and chemistry. He published a number of books and articles on the flora and mineral waters of Hungary. He died at Budapest.

7.7 Tungsten

Discovery	547	The metal and its compounds	551
Recovery from ores	549	Uses	553

DISCOVERY

The mineral wolframite (Figure 7.7.1) was known in the tin mines of Saxony and Bohemia. It was first described in 1574 by Lazarus Ercker, and thought to be a tin mineral. Wolfram is the wolf that preyed on tin. In 1757, a new heavy mineral with density 6 (scheelite) was described by the Swedish chemist Axel Fredrik von Cronstedt (1722-1765) (Figure 7.7.2) who named it “tungsten” (Swedish for heavy stone) and considered it to be a calcium-containing iron mineral. In 1761 Johan Gottlob Lehman (1719-1767) (Figure 7.7.3) the director of the Imperial Mineralogical Museum in Saint Petersburg in Russia thoroughly investigated the mineral and obtained tungstic acid.



Figure 7.7.1 - Museum sample of wolframite known also as scheelite



Figure 7.7.2 - Axel Fredrik von Cronstedt (1722-1765)



Figure 7.7.3 - Johan Gottlob Lehman (1719-1767)



Figure 7.7.4 - Juan José and Fausto Elhuyar

In 1781 Scheele analyzed the mineral and announced that it contained calcium with a hitherto unknown acid. He described digesting the mineral with K_2CO_3 and precipitating the unknown acid with nitric acid. In 1783, the metal was produced by Juan José Elhuyar (1745-1796) and his brother Fausto De Elhuyar (1755-1833) (Figure 7.7.4) from wolframite by reduction of the oxide with carbon. They named it wolfram. In 1821, K.C. von Leonhard proposed the name scheelite for the mineral $CaWO_4$.

Elhuyar brothers played an important role in the Spanish Empire. They came from Logroño in the Basque region of northern Spain from a well to do family. They travelled extensively in Europe, and went on missions to the Spanish colonies. They were sent to Paris for their education, where they heard lectures at the Royal Botanical Garden and the University of Paris. On their return from Paris in 1778, they were sent on a scholarship to the Mining Academy in Freiberg, Germany, to study chemistry and mineralogy under Werner and Gellert. They finished their studies in December 1781.

Fausto went to the Patriotic Seminary of Vergara in northern Spain to take up teaching duties; Juan José joined him later. Juan José went to Uppsala to work for half a year in Torbern Bergman's famous laboratory. In 1783, the brothers worked together on the analysis of a specimen of wolframite from a tin mine in Zinnwald, Germany, and separated from it an insoluble yellow powder which they called wolframic acid. They later showed it to be identical with tungstic acid, which the Swedish chemist Carl Scheele

separated from the mineral known at that time as tungsten, this mineral is known today as scheelite.

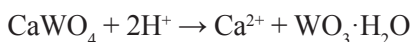
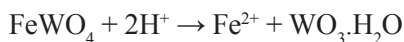
The possibility of obtaining a new metal by reducing tungstic acid had already been suggested by Bergman and Scheele. The Elhuyar brothers heated an intimate mixture of tungstic acid with powdered charcoal in a sealed crucible. After cooling, they found a dark brown metallic button, which crumbled easily in their fingers, and when they examined the powder with a lens they saw metallic globules of tungsten.

In 1786, Fausto was sent to Schemnitz, Freiberg, and Vienna to study the new method of amalgamation developed by Ignaz von Born. There he married a German lady. In 1788, he was sent to New Spain to be Director General of Mines, stayed there for more than thirty years until the outbreak of the War of Independence (in 1811), when he returned to Spain in 1812. There he was made Director General of Mines and planned the School of Mines of Madrid. He wrote in 1818 a treatise on *The Influence of Mining in New Spain*.

Juan José D'Elhuyar in 1784 was sent to New Granada (present day Colombia) to direct the exploitation of silver mines. He married in 1788, and his son José Luciano accompanied Bolivar in the liberation of Venezuela. Juan José also helped writing the publication of "The Rights of Man" and was put under house arrest.

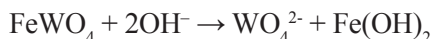
RECOVERY FROM ORES

Wolframite and scheelite are the most important sources of tungsten. Both material can be decomposed by either acids or alkaline solutions. Acid digestion is usually conducted with concentrated HCl in excess:

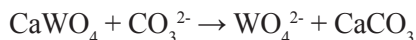


Sulfuric acid cannot be used because of the formation of insoluble calcium sulfate. The digested mass is washed to remove impurities and the residue is then dissolved in hot NH_4OH . Ammonium wolframate is crystallized from the solution by evaporation.

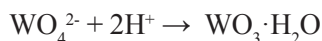
Leaching of wolframite with concentrated NaOH at high temperature in an autoclave yields a solution of sodium wolframate, while iron and manganese are precipitated as hydroxides:



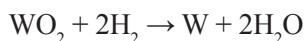
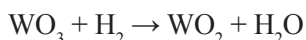
Scheelite is decomposed by sodium carbonate solution at 225°C :



The formation of CaCO_3 films on the mineral particles retards the reaction. This factor can be eliminated, however, by using rotating autoclaves containing steel balls. The solution of sodium wolframate is purified by precipitation with acid:



Reduction of tungsten oxide is conducted in two stages: the first at 510°C to obtain a nonvolatile oxide which is then crushed, ground and then further reduced to the metal at 800°C :



Because of its high melting point, the metal obtained are in the form of powders which are then sintered in another operation to massive metal if desired.

One of the most important uses of tungsten is in the manufacture of incandescent lamps. When tungsten wire is heated for many hours it undergoes re-crystallization and as a result it becomes brittle. To avoid this unwanted effect, additives such as ThO_2 are added in about 1 % of the weight of WO_3 before its reduction.

THE METAL AND ITS COMPOUNDS

Tungsten has a silvery white luster, has the highest melting point of all metals and also has one of the highest densities (Table 7.7.1). When combined with carbon, it becomes one of the hardest man-made materials. For use at high temperatures, tungsten parts must be coated, used in a vacuum, or be surrounded by a protective atmosphere because an oxide film forms which is volatile above 540°C; for example, in incandescent lamp filaments, electron tube electrodes, and various types of heating elements. Silicide coating and cladding with platinum gold alloys are effective oxidation-resisting coatings.

Table 7.7.1- Data on tungsten

Relative abundance, %	1×10^{-4}
Density, g/cm ³	19.3
Crystal form	Body-centered cubic
Atomic radius, nm	0.139
<i>Melting point</i> , °C	3410
Boiling point, °C	5900

Tungsten is resistant to many severe environments. It resists nitric, sulfuric, and hydrofluoric acids at room temperatures. It is only subject to slight attack by hot alkaline solutions such as potassium, sodium, and ammonium hydroxides. Tungsten also has good resistance to several liquid metals including sodium, mercury, gallium, and magnesium; to molten oxide ceramics such as alumina, magnesia, zirconia, and thoria. It is often used for crucibles to melt these materials in an inert atmosphere.

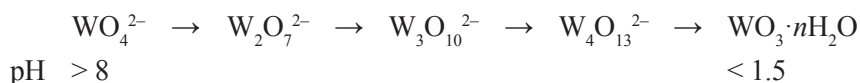
Pure metallic tungsten is brittle at room temperature, and is therefore not suitable for cold forming. At elevated temperatures (ca. 100–500°C) it is transformed into the ductile state. Other applications are in high-speed steels, high-temperature steels, and tool steels.

Tungsten is stable in air up to 350°C, but begins to oxidize above 400°C. A thin film of blue tungsten oxides forms on the surface, and this at first prevents further attack. As the temperature increases, cracks develop

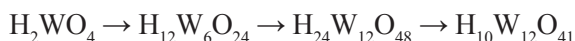
in the oxide film, and these favor oxidative attack. Above 800°C, rapid oxidation takes place with formation of WO_3 , which sublimates. Tungsten is stable to mineral acids in the cold, and is only slightly attacked at higher temperatures. It is stable in cold and hot hydrofluoric acid. Mixtures of hydrofluoric and nitric acids dissolve tungsten readily. Alkaline solutions do not attack tungsten, which is also stable to molten alkalis. In the presence of oxidizing agents (Na_2O_2 or NaNO_3), rapid dissolution takes place.

Tungsten occurs in all oxidation states from 2+ to 6+ inclusive, the most important being 6+. This chemistry is extremely complex as the tungstate anion exists in monomeric form only in strongly alkaline solutions. In mildly alkaline solution, they polymerize. Below pH 1, sparingly soluble tungsten oxide hydrate (tungstic acid) precipitates.

Tungstate ion, WO_4^{2-} , is stable at $\text{pH} > 8$. When the pH is gradually decreased by adding an acid, numerous poly-ions form:



Before the precipitation of the hydrated oxides, however, tungstic acid and hexatungstic acid are supposed to form first by polymerization and splitting of water:



since stable crystals of sodium para-tungstate, $\text{Na}_{10}\text{W}_{12}\text{O}_{41} \cdot 28\text{H}_2\text{O}$, have been isolated (industrial product). In practice, wolframite concentrates, FeWO_4 , are leached with alkali to form the soluble tungstate ion which is filtered then acidified to form hydrated tungsten oxide:



Scheelite concentrates, CaWO_4 , are digested with acid to form $\text{WO}_3 \cdot n\text{H}_2\text{O}$ which is filtered, washed, and purified by dissolution in alkali then precipitation by acid

USES

The developments that led to the industrial use of tungsten began in 1890 with the production of tungsten carbide in the electric furnace by the French chemist Henri Moissan (1852-1907) (Figure 7.7.5). They may be summarized as follows:



Figure 7.7.5 - Henri Moissan (1852-1907) and his electric furnace

1900 - The Bethlehem Steel Company announced the first high-speed, high-temperature steel at the Paris Exhibition.

1903 - The first tungsten filaments for incandescent lamps were produced in Hungary.

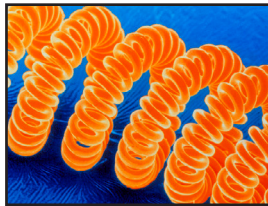


Figure 7.7.6 - Tungsten filaments

1909 - W.D. Coolidge described the production of ductile tungsten wire by powder metallurgy. This represents the first industrial use of powder metallurgy.

1922 - Osram Research patented the production of tungsten carbide-cobalt hard metals.

1926 - Krupp introduced the first hard metal cutting tool at the Leipzig Exhibition.

The increasing use of hard metals in the machining of steel and in the mining industry led to a great increase in the demand for tungsten. As a result of the increased use of tungsten materials in the armaments industry the metal has become of strategic importance.

7.8 Uranium¹

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INTRODUCTION

Joachimsthal (Figure 7.8.1) is located on the southern slopes of the Erzgebirge² Mountains at an altitude of 650 m, in an area exceptionally rich in ore deposits (Figure 7.8.2). The town was founded by Count Stephan Schlick³ (Figure 7.8.3) in 1516 when few years earlier silver was discovered. The town was named after its patron Saint Joachim, Mary's father (Figure 7.8.4). The name was chosen to harmonize with the then existing settlements in Saxony on the other side of the mountains known as Annaberg (1491) and Marienberg both from Jesus family. Further settlements in the neighbourhood, Freiberg (1168) and Schneeberg (1446) are also known by their silver discoveries.

¹Based on articles by F.Habashi in *Bull. Can. Inst. Min. & Met.* 94 (1046), 83–89 (2001), *ibid.* 94 (1047), 97–105 (2001), and *ibid.* 94 (1048), 133–134 (2001).

²Joachimsthal (Joachim's Valley) is Jachymov in Czech and the Erzgebirge (Ore Mountains) is Krušné Hory. The German names are used here in the text when the Kingdom of the Lands of Czech consisting of Bohemia, Moravia, and Silesia were part of the Austrian Empire while the Czech names after World War I when the Republic of Czechoslovakia was founded.

³In Czech : Štěpán Šlik



Figure 7.8.1 - A view of Joachimsthal (now known as Jachymov) and the Erzgebirge (Ore Mountains) in the background



Figure 7.8.2 - Location map of the Ore Mountains [Erzgebirge] showing Joachimsthal and Freiberg



Figure 7.8.3 - Count Stephan Schlick (1487-1526) founder of Joachimsthal

Ordinug des freyen und loblichē verckwercks in Sandt Joachims thal.



Figure 7.8.4 - Saint Joachim with his wife Anna, daughter Mary and the child Jesus holding the town's coat of arms, a 1525 woodcut now at Karlovy Vary (Karlsbad) Museum

Within few years, it became known that the German miners in the town suffered from a mysterious and un-healable sickness that became known to the physicians of that time as the « miners' sickness ». It was also too often that the miners came across a heavy lustrous black mineral which was for them a bad luck because it did not contain silver. For this reason they called it « Pechblende » which is German for « the bad luck mineral ». Because it was black, it became known in English as « pitchblende » (Figure 7.8.5). Soon, the miners' sickness was attributed to this black mineral. Figure 7.8.6 shows a doctor and a nurse attending to a sick miner in the town's hospital; from the window one can see mining activity. Figure 7.8.7 shows the town's apothecary from a woodcut dated 1568, while Figure 7.8.8 shows the Town Hall of Joachimsthal.



Figure 7.8.5 - The black mineral the miners called « Pechblende » which is German for « the bad luck mineral »

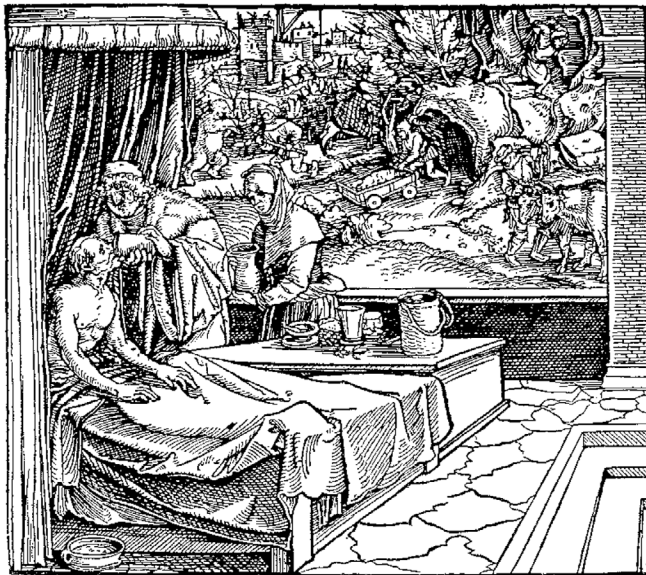


Figure 7.8.6 - A doctor and a nurse attending to a sick miner in Joachimsthal hospital. One can see the mining activity from the windows.
A woodcut dated 1518



Figure 7.8.7 - Joachimsthal apothecary. A woodcut dated 1568



Figure 7.8.8 -The Town Hall of Joachimsthal founded in the 16th century

The town recognized remarkable prosperity, the population increased gradually, becoming the second largest town in Bohemia after Prague with population mostly German miners (Table.7.8.1). In 1520, King Ludwig of Bohemia (1505-1526) elevated the town to a « Free Royal Town ». Ludwig died few years later at the young age of 21 in the Mohasz battle against the Turks. He was the last member of Jagiello dynasty and the rule went over to Ferdinand I of Habsburg who married Ludwig's sister Anna.

Table 7.8.1 – Population of Joachimsthal

Year	Population
1520	4 963
1525	13 411
1 533	18 000
1 601	2 177

In 1533 silver production amounted to 14 tonnes. However, during the religious war of 1546-1547 and the decreased silver production to 1.5 tonnes due to the lack of pumps needed for deeper mining made it difficult to compete with silver from the new American colonies, which was arriving in increasing quantities on the European market, the town knew its depression and the population decreased drastically. It has been estimated that Joachimsthal mines produced a total of 307 tonnes of silver during its life time.

In 1534, King Ferdinand I (1503-1564) visited the town to supervise the construction of a new mint. Few years later, however, in 1538 a fire destroyed the building. Georgius Agricola (1494-1555) the famous medical doctor at Chemnitz on the German side of the Ore Mountains visited Joachimsthal in 1550 to examine the ailing Count Hieronymus Schlick (1494-1551), brother of Stephan Schlick. He stayed there a month during which he consulted with the evangelical preacher and director of the Latin School, Johann Mathesius (1504-1565) author of *Sarepta*, which contained description of Jáchymov mines and the life of miners, regarding his manuscript *De Re Metallica*. Agricola was not new to the town - - he had already practiced medicine from 1527 to 1531 and wrote his book

« Bermannus » there. It is known also that he met there the artist Basilius Weffringer, a native of the town, and engaged him to make the illustrations for *De Re Metallica*. In 1651 the Royal Mint was moved to Prague and in 1716 a School of Mines was founded.

DISCOVERY OF URANIUM

With decreased silver production, Joachimsthal was about to become a ghost town when Martin Klaproth (1743-1817) (Figure 7.8.9) a pharmacist in Berlin who became later professor of chemistry at the Royal Mining Academy in Berlin, discovered that the black mineral from Joachimsthal can be used to give glass a brilliant yellow color with green fluorescence when added to the molten batch. He was also convinced that this mineral must have contained a new metal. This discovery coincided with the discovery in 1781 of a new planet in the solar system by his compatriot William Herschel who had immigrated to England in 1757 and called the planet Uranus. Hence Klaproth named the new metal « uranium » to honour his compatriot. In 1789 he was able to isolate a black heavy solid from the ore which he thought it to be the new metal.



Figure 7.8.9 - Martin Klaproth
(1743-1817)

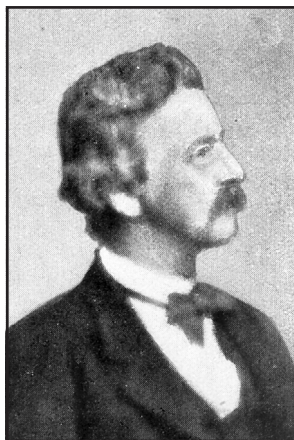


Figure 7.8.10 - Adolf Paterna
(1819-1894)

Uranium pigment

In 1815 the Austrian chemist, Adolf Patera (1819-1894) (Figure 7.8.10) was developing an analytical method for determining uranium in ores at the Imperial Geological Institution in Vienna and investigating the possibility of the commercial application of Klaproth's discovery. He devised a procedure for preparing « uranium yellow» known at that time as « Uranoxyd-natron » which is the yellow cake of sodium uranate.

The process involved roasting the ore containing about 40% uranium with sodium carbonate to volatilize arsenic and sulfur, leaching the calcine with water to remove soluble impurities then leaching the residue with sulfuric acid to solubilize the uranium which is then precipitated by adding sodium hydroxide. Any silver present was recovered from the sulfuric acid leach residue. Consequently, a plant was built in 1854 (Figure 7.8.11) next to the silver smelting operations to process this black uranium mineral for pigment manufacture which was kept a guarded secret and a monopoly of Bohemian glass manufacturers. A typical glass products containing uranium pigment is shown in Figure 7.8.12.

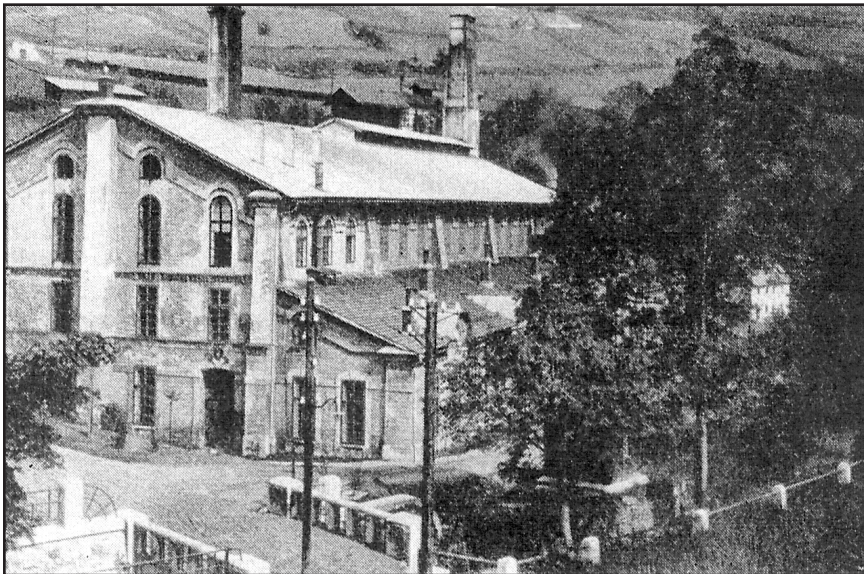


Figure 7.8.11 - Uranium pigment plant in Joachimsthal that became later radium recovery factory. It was demolished in 1941



Figure 7.8.12 - Glass containing uranium pigment

Autunite

About 1837 a yellow uranium phosphate deposit was discovered in Autun in France which was first called uranite d'Autun and later became known as autunite. A sample of the mineral was sent to the French chemist Eugène Peligot (1811-1890) (Figure 7.8.13) who analyzed it and was able to isolate metallic uranium in 1841 indicating that Klaproth's isolated substance was only an oxide of uranium and not the metal itself as he claimed. Peligot who was teaching a course on glass making at the École Centrale des Arts et Metiers in Paris, also recommended the use of the mineral for coloring glass.



Figure 7.8.13 - Eugène Peligot (1811-1890)

Other uses of uranium

In 1859 it became known that photographic paper containing uranyl nitrate gives a sepia tint to prints. Other tints were obtained when uranyl nitrate was mixed with other salts. For example, a green tint when ferrous chloride was added, etc. Hence, a market for uranium salts was opened.

Closing of the mines

Few years later, however, the silver operation became unprofitable and the government of the then existing Austrian Empire decided to close all the mines at the end of the nineteenth century. In 1873, the town suffered greatly from a fire.

DISCOVERY OF RADIOACTIVITY

Joachimsthal was about to become a ghost town again when new discoveries came to its rescue. One year after the discovery of X-rays by Roentgen in 1895, came the discovery of radioactivity by Antoine Henri Becquerel (1852-1908) (Figure 7.8.14) in 1896 when he was trying to find a relation between phosphorescence of uranium salts and the possibility of emission of X-rays. Indeed, he found that uranyl potassium sulfate

crystals did fog photographic plates although they were wrapped in black paper. This was followed by the search of Marie and Pierre Curie for the element causing the intense radioactivity of the mineral.

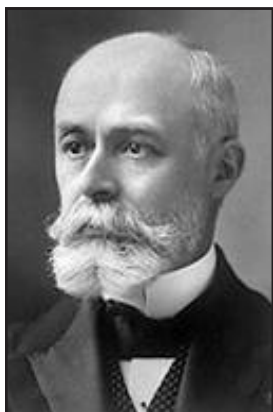


Figure 7.8.14 - Antoine Henri Becquerel (1852-1908)



Figure 7.8.15 - Marie Curie (1867-1934)

Discovery of polonium and radium

The Austrian government permitted that 100 kg of the waste material from the Joachimsthal uranium-based pigment factory to be dispatched to Paris for the Curies. Marie Curie (1867-1934) (Figure 7.8.15) succeeded in the isolation of polonium in 1898 followed by radium in December of the same year. Between 1898 and 1902 the Curies then purchased 11 tonnes of the residue from the Austrian government to process them for the production of radium and for further research.

As soon as the Curies announced that radium salts emit light in the dark (Figure 7.8.16), two distinguished physicists at McGill University in Montreal, Ernest Rutherford and Frederick Soddy immediately took up investigation of this new element. Within few years the area was thoroughly explored and important conclusions regarding the origin of radium and polonium, the radioactive decay, the structure of the atom, isotopes, etc., were formulated.

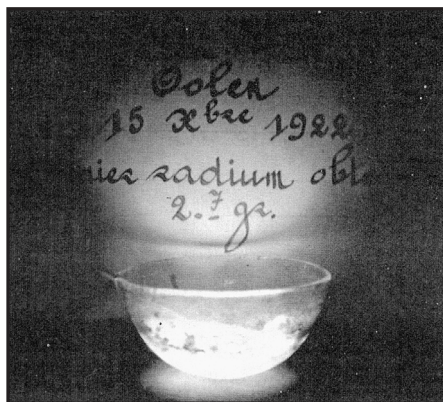


Figure 7.8.16 - Radium salts emit light in the dark

France

The Radium Institute was founded in Paris in 1909, but inaugurated in 1914, to replace the shed (Figure 7.8.17) where Madame Curie discovered polonium and radium. Marie Curie was appointed its first director and was succeeded by Debierne after her death in 1934.

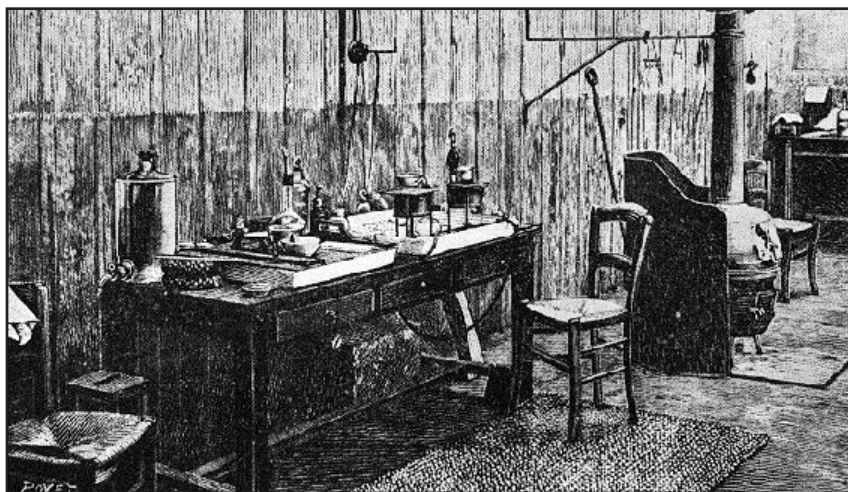


Figure 7.8.17 - The shed used by Madame Curie in her treatment of residues from pitchblende

RENEWAL OF THE URANIUM INDUSTRY

During World War II the extraction of uranium became a key part of the industry as nations sought to take military advantage of the newly discovered fission reaction. Many pioneers of the radium industry turned their attention to nuclear fission and its military applications. After the war, attention remained focused on uranium but radium production went on in Canada until 1954 and in Belgium until 1960.

A key role in US uranium industry was played by Edgar Sengier (1879-1963) (Figure 7.8.18) the managing director of Union Minière du Haut Katanga in the Belgian firm's New York Office. When Belgium was occupied by the Nazi troupes in 1940 the administration of Union Minière moved from Brussels to New York. A year earlier, in 1939, Sengier had been alerted by French and British scientists about the strategic importance of uranium. As a result, he had ordered 1250 tons of rich ore shipped to the United States. Some 2000 steel drums full of it, worth more than \$2 million at that time, were stored in a Staten Island warehouse. Sengier had tried several times to interest the State Department in his ore but without success.



Figure 7.8.18 - Edgar Sengier (1879-1963)

It was only on September 18, 1942 when a high ranking US officer from the Manhattan Project visited Sengier after receiving a tip that the Belgian company might own some of the scarce ore that had first caused the physicist Leo Szilard turn to Albert Einstein for help three years before to write his letter to President Franklin D. Roosevelt alerting him for the possibility of a uranium bomb.

An agreement was immediately drawn and the first difficulty facing the US atomic project was overcome. On September 24, 1942 the order was given to Oak Ridge National Laboratory to construct the first uranium separation plant in the United States. Sengier was decorated in 1946 by President Harry Truman with the Medal of Merit accorded for the first time to a foreigner. In 1949 when a new uranium mineral was discovered in Katanga, it was named sengierite in his honour by Paul F. Kerr of Columbia University.

Canada

In 1940 Eldorado Gold Mines was quietly taken over by the government as a war industry. The Port Hope refinery began to produce uranium from old plant tailings and from concentrate brought in from the Belgian Congo. By 1944, plans were completed for the establishment of the National Research Council facility at Chalk River, Ontario, the first step in the series of events that led to the formation of Atomic Energy of Canada and the development of CANDU reactor. In anticipation of an increased demand for uranium when World War II ended, the ban on private prospecting for it was lifted in 1947 and the boom was on.

In the mean time researchers from the Radioactivity Division of the Mines Branch, Department of Mines and Technical Surveys in Ottawa, from the Port Radium operations, and from the Uranium Extraction Section at Port Hope, tackled the problem of uranium recovery from the gravity plant tailing. A pilot plant to prove out the process started up at Port Radium in 1950 and the commercial plant began operations in 1952. In 1959, twenty three mines were supplying 12,000 tonnes of uranium annually.

A major development, however, was the finding of large uraninite deposits near Beaverlodge on the north shore of Lake Athabaska in Northern Saskatchewan (Figure 7.8.19). These discoveries, made by Eldorado, now a Crown Corporation, posed a problem because of the high calcite content of the ore, and the consequent excessive acid consumption. Researchers from Sherritt Gordon Mines, the University of British Columbia, from Port Hope, and from the Radioactivity Division of the Mines Branch developed the pressure carbonate leach with caustic precipitation of yellow cake. A mill was constructed, and the town of Uranium City was built to house the workers. The plant ran for nearly thirty years, closing down in June 1982.

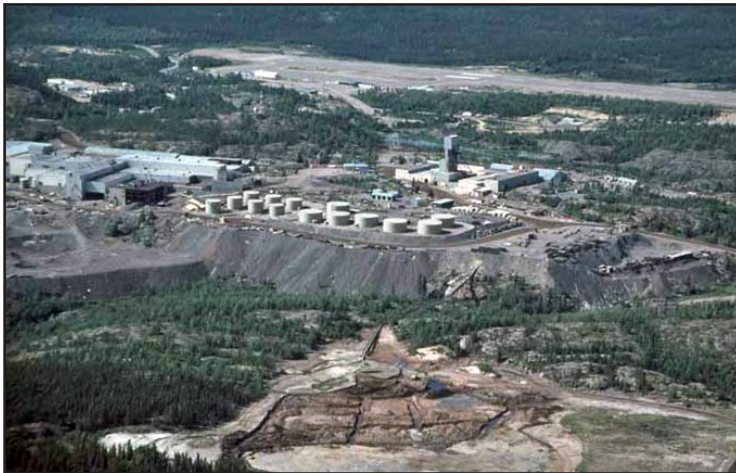


Figure 7.8.19 - Uraninite deposits near Beaverlodge on the north shore of Lake Athabaska in Northern Saskatchewan

In 1953, geologists of Gunnar Gold Mines discovered another uranium ore body near Lake Athabaska and a mill went on-stream (Figure 7.8.20). In 1954, the Lorado discovery was made near Uranium City.

Uranium prospecting in Ontario began about 1948 after the wide-spread introduction of the Geiger counter as a prospecting tool. One of the early finds in the Bancroft area that became productive was the Faraday Mine discovered in 1949. In 1952 the property was taken over by Newkirk

Mining Corporation and Faraday Uranium Mines Limited (changed name later to Federal Resources Corporation) was formed. Production began in 1957 and continued until 1964. In 1952 a uranium deposit in Cardiff Township was discovered and the property was acquired by a Toronto syndicate and Centre Lake Uranium Mines was formed; it later became Bicroft Uranium Mines Limited. The mine went into production in 1956 and closed in 1963. There were two other uranium producers in the Bancroft area: Canadian Dyno Mines Limited, from a discovery in 1953 came into production in 1958 and closed in 1960 and Grey-hawk Uranium Mines Limited in Faraday Township opened its mine in 1957 and closed in 1959.

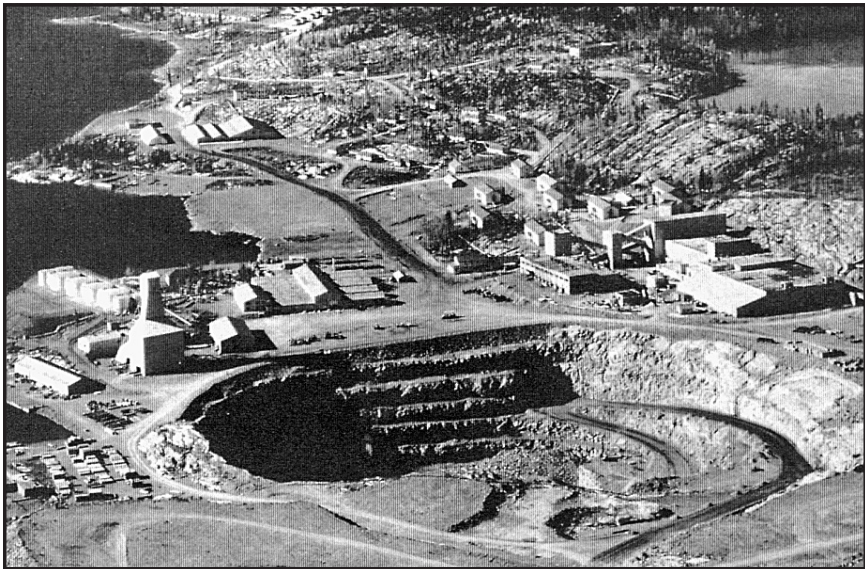


Figure 7.8.20 - Gunnar Gold Mine

The discovery of uranium in the Blind River area was made in 1948 but no development resulted due to the low tenor. However, in 1952 the area was re-examined and Peach Uranium Syndicate was formed to explore the claims, diamond drilling was done in 1953, and production began in 1955. The mine was closed in 1960, but the mill continued to operate on copper ore from the Pater Mine. In 1953 a major discovery of many ura-

nium ore bodies in the Elliot Lake area was made, and twelve mines came into production in 1955 to 1957. The deposit became one of the world's largest uranium operations. However, by 1971 only two mines were still in production: the Denison and New Quirke Mines. Today all are closed.

USA

In 1940, Glenn T. Seaborg and his coworkers discovered the first artificially-prepared isotope of plutonium and in 1942 isolated the metal from Canadian pitchblende and Colorado carnotite in which traces ($\text{U}:\text{Pu} = 1:10\text{-}12$) are formed continuously by neutron capture. During 1942-1945 the US Army Corps of Engineers ran the Uravan plant in Colorado. In 1948 the Uravan mill was renovated to produce uranium for US weapons program, and at the time received feed from more than 200 mines in the area. A uranium plant processing 7000 tonnes/day of ore was constructed by Kerr-McGee near Grants, New Mexico became the largest uranium operation in USA (Figure 7.8.21).



Figure 7.8.21 - Grants Uranium Mine, New Mexico

The Atomic Energy Act of 1954 required Government ownership of all fissionable materials but provided for the encouragement of private de-

velopment within certain boundaries of peaceful uses of nuclear energy. Procurement of domestic uranium concentrates was arranged through contracts with privately owned mills. As many as 1000 mines were in production in any one year providing about 5.9 million tonnes of ore to 20 mills. The yellow cakes were shipped to the Atomic Energy Commission refinery at Weldon Spring, Missouri which was operated by Mallinckrodt Chemical Works and produced UO_3 , UF_4 , and high purity natural uranium metal. Since uranium also occurs in Florida phosphates, units were added to the existing fertilizer plants to extract uranium.

Production of reactor fuel cores were fabricated at Fernald, Ohio operated by National Lead Company of Ohio. UO_3 was processed to UF_6 at Puducah, Kentucky which was used there as feed to a gaseous diffusion plants at Oak Ridge, Tennessee and Portsmouth, Ohio for further enrichment. The Puducah and Oak Ridge plants were operated by Union Carbide Corporation, and the Portsmouth by Goodyear Atomic Corporation.

Plutonium was produced in nine graphite-moderated reactors at Hanford, Washington which had been operated by General Electric Company. Battelle Memorial Institute in Columbus, Ohio operated the laboratories. Five heavy-water production reactors at Savannah River Company in South Carolina operated by E.I. du Pont de Nemours & Company, also produced plutonium.

South Africa

Uranium in South Africa was discovered in 1923 as grains of uraninite in the Witwatersrand gold ore. The first full-scale uranium leaching plant was commissioned in 1952, and production increased rapidly. In 1980, South Africa produced 6147 tons of uranium oxide from 18 plants. However, in the early 1990's, due to the drop in uranium price because of cancelled reactor projects, South Africa's production fell to less than 2000 tons/year and only three plants remained in operation.

Since most of South Africa's uranium was as a by-product of gold mining,

the uranium producers have been able to respond to changes in demand in a flexible manner. The speed at which the country entered the uranium industry was due to the fact that the uranium processing facilities could be added at the tailings of existing gold plants. South Africa was the first world's user of an ion exchange resins in mineral processing. The next major advance came with the development of the solvent extraction process for treating the eluate from the ion exchange process. This resulted in a higher-purity product that was suitable as starting material for the production of nuclear-grade uranium metal. This process was more economical than the original ion-exchange and precipitation route.

A minor amount of uranium was also recovered as a by-product of the copper mining operation at Palabora since 1971. The ore contained only 0.004% uranium oxide.

Czechoslovakia

When World War II ended, the prisons and military hospitals were dissolved, and the German inhabitants expelled from Joachimsthal. In 1947, Edward Beneš, then the president of the republic visited the city. But, the Cold War started, and an agreement between the Czechoslovak Government and the former Soviet Union listed uranium ore as a strategic material. Immediately, the number of miners in the three existing mines increased in the next few years from 300 to 10 000. By the middle 1950's it became 40 000 of which about the third were political prisoners. The town was closed, hotels and schools transformed into offices for security agents, and many hundreds of Russian experts came with their families. Ore production increased from 0.9 tonnes contained uranium in 1845 to 780 tonnes in 1955. The total amount of uranium contained in the ore shipped to the former Soviet Union from 1945 to 1962 is estimated at 8000 tonnes.

By 1960's, however, it was realized that the ore body had been exhausted and gradually the town was opened. The demand for radium also declined greatly when larger and cheaper cobalt 60 sources became available

from nuclear reactors. Patients started to arrive for the spa. In 1966, a distinguished visitor and Nobel Prize winner Otto Hahn (1879-1968) was invited to the town on the occasion of its 450th anniversary. The focus of the uranium industry, however, shifted from Joachimsthal now known as Jachymov to Příbram in the mid 1950's when uranium was discovered there.

Příbram

Few kilometers south of Jachymov is another mining town Příbram that came into existence in 1311 (Figure 7.8.22-7.8.23). In 1579 the town was granted the rights of a Free Royal Town by emperor Rudolph II of Hapsburg in recognition of the large amounts of silver and lead produced. The town took the side of the Hussites in their religious war and later during the thirty years war (1618-1648), it was plundered and fell into ruins. The outcome of the war brought about forced re-catholicization of Bohemia. In 1647, however, it became renowned as a center for pilgrimage and this was a major source of income when the Jesuits took over the administration of the chapel of the Svata Hora shrine (Holy Mountain) dedicated to Virgin Mary (Figure 7.8.24).



Figure 7.8.22 - Czech Republic showing Příbram south of Prague



Figure 7.8.23 - A view of Pribram



Figure 7.8.24 - Chapel of the Svata Hora shrine (Holy Mountain)
dedicated to Virgin Mary

At the end of the eighteenth century, mining of silver turned out to become a successful venture and in 1849 a Mining Academy was founded. In 1892, the town was the scene of the worst mining disaster in the world in which 319 miners died. In 1948, uranium was discovered and the district came under the influence of the former Soviet Union. Convicts and political prisoners were supervised by armed guards as they operated the mines. After the war, the Mining Academy which was closed during the Nazi occupation, re-opened and moved to the coal mining district at Ostrava in Moravia.

Mining Museum

The Mining Museum in Příbram is the largest mining museum in the Czech Republic (Figure 7.8.25). It is situated in the area of three historical mines and the exhibits were built in the original mine working and administrative buildings to show visitors the rich mining past of the region, the economic, social and cultural development from the Middle Ages up to the twentieth century.

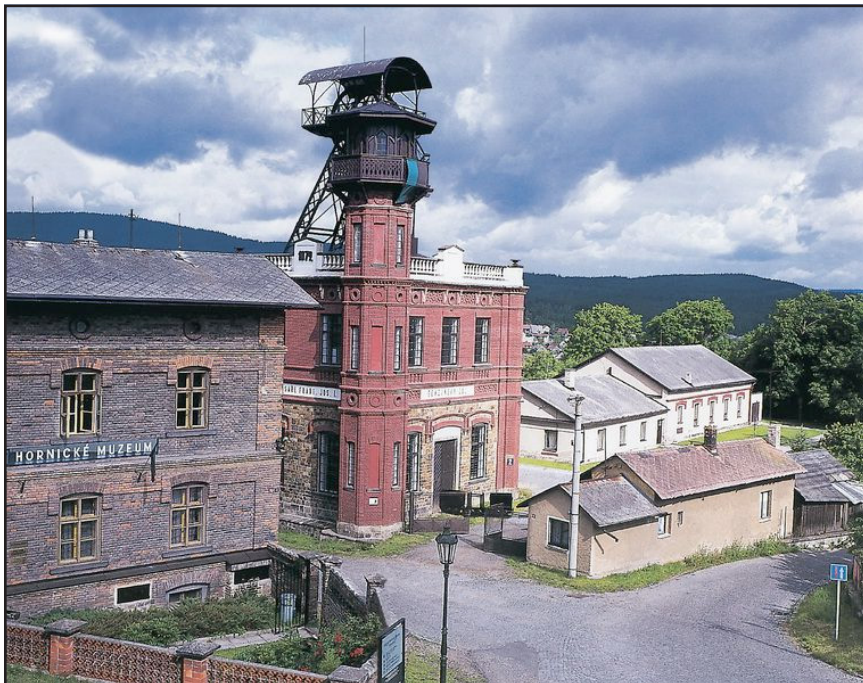


Figure 7.8.25 - Mining Museum in Příbram

The exploitation of the historical silver district and the extraction of uranium deposit after 1948 are well documented. The exhibits include the oldest documents about the beginning of the mining activity, the bronze objects from the period of the Celtic colonization, the oldest written document confirming the existence of Příbram (from 1216), the first written document concerning local smelting works and mines (from 1311), samples of medieval and present-day miner's working tools, miner's uniforms (Figure 7.8.26), measuring and rescue equipment, samples of silver, lead and uranium ores, and information about the Mining College that once stood there and the mine catastrophe of 1892.



Figure 7.8.26 - Miner's uniforms

In a near-by engine room there is a unique steam engine dating from 1889. The museum also recalls the infamous part of the history of uranium mining, when political prisoners were forced inhumanely to work in the mines after the revolution in February 1948. Visitors can also visit an original miner's cottage with an exhibition documenting the life of a miner's family at the turn of the nineteenth century.

There is also an exhibition of local folk toy and puppet-making, and another dedicated to the achievement of the world's premier in reaching the vertical depth of 1000 m in the Vojtech pit in 1875. From the yard of the Anna shaft it is possible to go underground by little mining train to the 260 m long Prokop Gallery dating from 1832, which leads to the Prokop pit.

Former German Democratic Republic

A joint German-Soviet company was founded to exploit the uranium deposits that stretched from Dresden in Saxony to Ronneburg in Thuringia in the former German Democratic Republic (Figure 7.8.27). So as not to arouse any suspicion, the company was named Wismut, i.e., bismuth, after another metal. The Soviets needed large quantities of uranium to build enough nuclear weapons to keep up in the arms race.

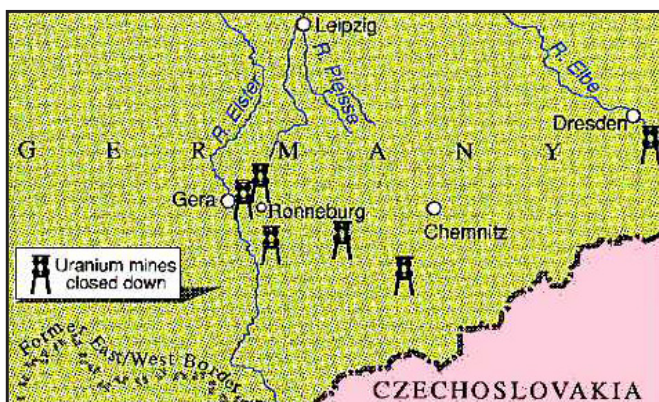


Figure 7.8.27 - The location called Wismut in the former German Democratic Republic where uranium was extracted

A giant industry rose up, shrouded in secrecy. It is estimated that 220,000 tonnes of uranium were shipped to Russia from this region in form of uranium oxide. At one time, 130,000 miners were employed in five mines and two processing plants. The company was a state within a state with its own police force, its own hospitals, stores, sports facilities, car license plates, and residential areas. The former East German state security apparatus, Stasi, had a special spy force there.

After the fall of the Berlin Wall in 1989, Wismut fell apart. The Soviet Union withdrew and work came to a halt. Between 1946 and 1990 a total of 7163 uranium miners who had been employed with Wismut died from lung cancer. For 5237 of these, the occupational exposure was recognized as the cause of the disease. At present, still approximately 200 lung cancers of former Wismut miners per year are recognized as occupationally caused.

Today the company has only 4,700 employees and only one task: to remedy the environmental damage that it inflicted in the region for 45 years. Wismut became an environmental rehabilitation company. Its job was to remove over 174 million tonnes of radioactive waste, dry out the mud lakes and re-cultivate the ground of a surface area of about 650 hectares. The costs are enormous; in one year the German federal government has channeled 750 million marks into the region to rehabilitate the area and return the villages to their original state.

Gabon

In 1972, research workers of the French Commissariat à l'Énergie Atomique made an astonishing discovery: fission chain reactions had been triggered spontaneously in the very remote past within a uranium deposit in Gabon and parts of the deposit had behaved like a modern nuclear reactor for hundreds of thousands of years. Subsequent investigations showed that the reaction sites had remained in a remarkable state of preservation, so that detailed study was possible.

The discovery began with the observation of a very slight isotopic anomaly in a natural uranium sample during a routine analysis in the laboratory: 0.7171% as against 0.7202 ± 0.0010 . Between December 1970 and May 1972, the ore which originated from Oklo was deficient in U^{235} by a total amounting 200 kg of U^{235} . In one sample the U^{235} content was as low as 0.29%. Fission products discovered in the ore pointed clearly to the origin of the anomaly. Parts of the reaction sites were studied in detail through boreholes and sampling.

Of the two principal isotopes of uranium, which are naturally radioactive, U^{235} has a shorter half-life than U^{238} (7.1×10^8 years as against 4.51×10^9 years). Consequently, the concentration of U^{235} in natural uranium is decreasing constantly with time; in the very remote past it was much higher than it is now (3.65% two billion years ago as against 0.72% now). It was therefore suggested some time ago that fission chain reactions might have been triggered spontaneously within uranium deposits in the very

remote past, given the existence of certain conditions: high concentrations of uranium, the absence of strongly neutron-absorbing elements, and the presence of water.

TRANS-URANIUM ELEMENTS

After the discovery of the trans-uranium metals (Table 7.8.2) and elucidating their electronic structure which resembled that of the lanthanides, Glenn T. Seaborg (1912-1999) (figure 7.8.28) proposed a second series of inner transition metals similar to the lanthanides that became known as “actinides”. Thus, uranium was removed from Group VI to become a member of this new group as shown in Figure 7.8.29

Table 7.8.2 - The trans-uranium elements

Element	Symbol	Atomic number	Atomic weight	Occurrence or preparation
Actinium	Ac	89	227	Relative abundance 3×10^{-14}
Thorium	Th	90	232.038	Relative abundance 1.1×10^{-3}
Protactinium	Pa	91	231	Relative abundance 8×10^{-11}
Uranium	U	92	238.03	Relative abundance 4×10^{-4}
Neptunium	Np	93	237	Bombarding ^{238}U by neutrons
Plutonium	Pu	94	242	Bombarding ^{238}U by deuterons
Americium	Am	95	243	Bombarding ^{239}Pu by neutrons
Curium	Cm	96	247	Bombarding ^{239}Pu by α -particles
Berkelium	Bk	97	247	Bombarding ^{241}Am by α -particles
Californium	Cf	98	249	Bombarding ^{242}Cm by α -particles
Einsteinium	Es	99	254	Product of nuclear explosion
Fermium	Fm	100	253	Product of nuclear explosion
Mendelevium	Md	101	256	Bombarding ^{253}Es by α -particles
Nobelium	No	102	254	Bombarding ^{243}Am by ^{15}N or ^{238}U with α -particles
Lawrencium	Lw	103	257	Bombarding ^{252}Cf by ^{10}B or ^{11}B and of ^{243}Am with ^{18}O



Figure 7.8.28 - Glenn T. Seaborg (1912-1999)

																H	He		
Li	Be													B	C	N	O	F	Ne
Na	Mg	Al												Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	Ga	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba	*La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
Fr	Ra	**Ac																	

*

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
----	----	----	----	----	----	----	----	----	----	----	----	----	----

**

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw
----	----	---	----	----	----	----	----	----	----	----	----	----	----

Figure 7.8.29 - Uranium as a member of actinides in the Periodic Table of 1945 and the discovery of technetium, rhenium, and the radioactive elements francium, and astatine

RECOVERY FROM ORES

Uranium ores

Although uranium forms numerous oxides (Table 7.8.3), only two are the most important: UO_2 and U_3O_8 because they constitute the bulk of uranium ores. Uranium trioxide, UO_3 , is soluble without the need of an oxidizing agent. Uranium in this oxide is in the hexavalent state; it does not however occur in nature in the free state, but in association with vanadium and potassium in the mineral carnotite.

Table 7.8.3 - Uranium oxides

Oxide	Valency	Natural form	Solubility in dilute H_2SO_4 in absence of oxygen
UO_2	4	uraninite	insoluble
U_2O_5	4	does not occur in nature	partially soluble
U_3O_8	4,6	pitchblende	partially soluble
UO_3	6	occurs only in combination with vanadium oxide as the mineral carnotite	soluble

Uraninite, UO_2 , is insoluble in dilute H_2SO_4 , and uranium in this oxide occurs in the tetravalent state. Pitchblend, U_3O_8 , is partially soluble in dilute H_2SO_4 ; uranium in this oxide occurs in both the hexavalent and tetravalent states and may be represented as $\text{UO}_2 \cdot 2\text{UO}_3$. This accounts for the fact when dissolved in dilute H_2SO_4 in absence of air, mixtures of uranium(IV) and uranium(VI) are obtained:



The reaction, however, seems to be more complex because the composition UO_2 is never reached; in practice a maximum dissolution of about 58 % is reached as shown in Figure 7.8.30 and not 66.67 % as expected according to the above equation. It seems that the intermediate oxide U_2O_5 is formed and the product is a mixture of UO_2 and U_2O_5 :



The formula $\text{UO}_2 \cdot 2\text{UO}_3$ should not be taken as indicating the presence of two types of uranium in U_3O_8 . X-ray analysis shows that all uranium atoms in U_3O_8 occupy equivalent positions; there is probably a resonance between two (or more) valence states, e.g., U^{4+} and U^{6+} .

As mined, pitchblende contains about 1 % U_3O_8 , but it can be easily concentrated by gravity methods to 50 % U_3O_8 . The main occurrences

are in Joachimsthal (Czechoslovakia), Shinkolobwe (Zaire), Elliot Lake (Ontario), and Athabasca Lake (N.W. Canada). Thucholite is a uranium mineral containing thorium, carbon, hydrogen, and oxygen that occurs mainly in South African gold ores. These ores average 0.02–0.1 % U_3O_8 and are processed first for the recovery of gold. Davidite is another uranium mineral containing iron, cerium, titanium, vanadium, chromium, and zirconium that occurs mainly at Broken Hill, Australia. It is a refractory mineral difficult to dissolve. At Palabora in South Africa, uranium is associated with copper sulfides; it is recovered from the flotation tailings by gravity methods as a concentrate containing 2.5–5 % U_3O_8 mainly as the mineral urano-thorianite.

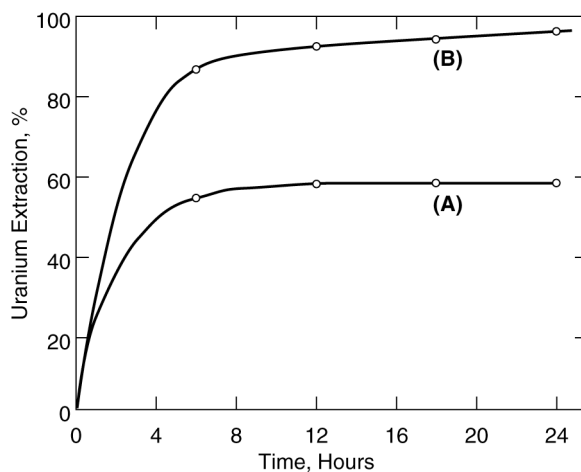


Figure 7.8.30 - Solubility of a pitchblende ore sample containing 0.22 % U_3O_8 in dilute H_2SO_4 . (A) In absence, and (B) in presence of oxidizing agents

In Australia, a uranium deposit containing 0.06 % U_3O_8 and 2.1 % Cu as sulfide is under exploitation at Olympic Dam. A copper sulfide concentrate is obtained by flotation leaving a residue containing the bulk of uranium and 0.3 % Cu. Both copper and uranium are leached from the residue by acid in presence of Fe^{3+} ion. On the other hand Northern Saskatchewan in Canada became the world center for uranium industry: large deposits are under exploitation at Key Lake (1.5 % U_3O_8), Cigar Lake (13.6 % U_3O_8), and McArthur River (18.7 % U_3O_8).

By-product of copper ores

Porphyry copper ores can also be a source of uranium although the uranium content may be only 2-5 ppm. When leached and copper is precipitated from solution and recovered and the filtrate is recycled to the leaching step, uranium is gradually enriched in the solution. A plant was operated successfully at the Bingham Canyon operation in Utah to recover uranium using ion exchange columns (Figure 7.8.31).

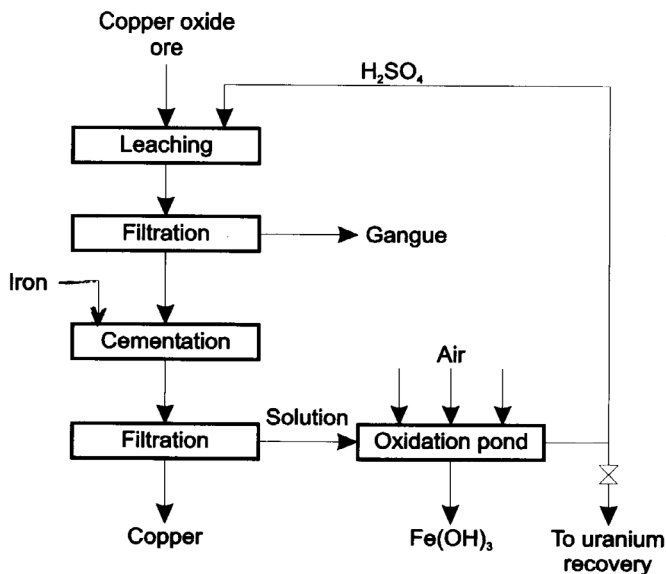
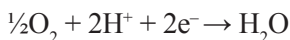


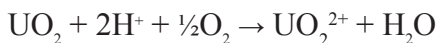
Figure 7.8.31- Recovery of uranium from porphyry copper ores

Acid leaching

- *Sulfuric acid.* Sulfuric acid, either dilute for easily soluble uranium minerals, or concentrated for the refractory minerals, is the most commonly used acid. Leaching may be represented by the following equations:

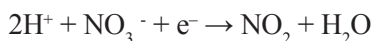


Overall reaction:

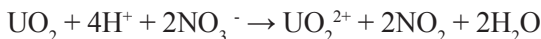


- Negatively charged sulfate complexes are formed, e.g., $[\text{UO}_2(\text{SO}_4)_3]^{4-}$. Oxygen or other oxidizing agents such as MnO_2 , NaClO_3 , or NaNO_3 are commonly used. Uranium is recovered from solution by ion exchange or solvent extraction.

- *Nitric acid*. At Palabora, South Africa, the uranium concentrate is leached by concentrated nitric acid at 75°C :



Overall reaction:

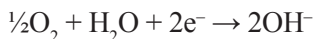
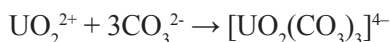


or

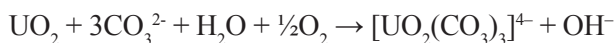


Alkali carbonate process

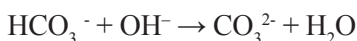
The reactions that take place in this case are:



Overall reaction:



Since OH^- ion is formed during leaching and there is a possibility that insoluble uranates may be formed, sodium bicarbonate is usually added to the solutions to prevent such side reactions:



Ammonium carbonate leaching under pressure has the advantage of having less attack on silicate minerals and on alumina and uranium can be precipitated by stripping with steam to decompose the uranium complex; the evolved NH_3 and CO_2 are absorbed and recycled. It is used together with hydrogen peroxide for in situ leaching of underground uranium ores, e.g., in Texas.

Treatment of carnotite⁴

Carnotite, $\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5$, is readily soluble in acids in the absence of oxidizing agents. Leaching of carnotite ores, however, is usually done after a preliminary salt roasting to convert vanadium minerals into a water-soluble sodium vanadate which can be recovered ahead of the acid leaching.

Leach residues

Residues from uranium extraction plants using either H_2SO_4 or Na_2CO_3 contain all the radium originally present in the ore. These residues are at present stock piled because radium is not in demand. Radium decays into the radioactive gas radon. The diffusion of this gas in the environment, the scattering of radioactive dust particles by wind, and erosion of the piles of residues by water, represent a serious pollution problem. A typical disposal pond contains 0.6 mg radium per ton of solids. Abandoned plant sites are particularly hazardous because tailings dams may either erode or rupture and release tailings to streams. Therefore, controlled storage of uranium mill residues must be maintained after the life of the plant to safeguard the environment from radioactive pollution.

Considering the 1622-year half life of radium 226, storage must be controlled for many thousands of years to enable abatement of the radiation hazard by natural decay of radium and its products.

A practical solution is to fill the open pit mine with water and deposit the tailings and residues at the bottom, thus the water above will act as a protective layer against radiation (Figure 7.8.32).

⁴ See Vanadium

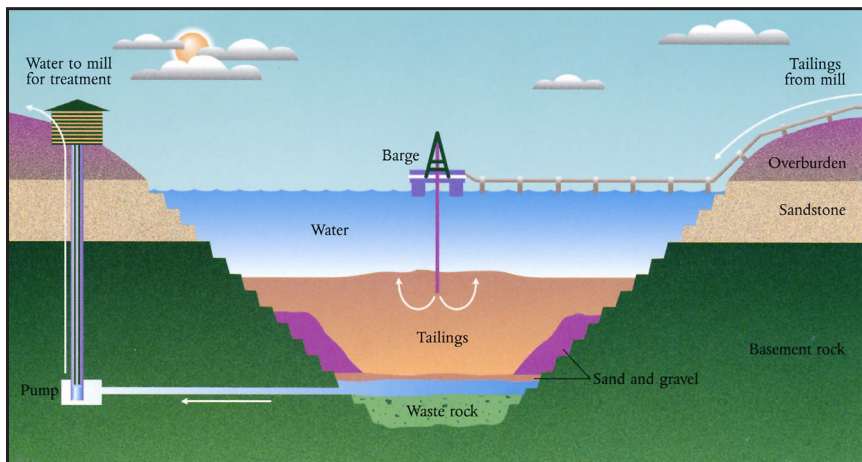


Figure 7.8.32 - Tailings and residues from uranium treatment plant being stockpiled under water in an unused open pit mine

Uranium from phosphate rock

The search for uranium deposits continued and in 1908 the British physicist John William Strutt [Lord Rayleigh] (1842-1919) (Figure 7.8.33) noted that phosphate rock was radioactive due to the presence of uranium. Since large tonnage of this rock is used annually to produce fertilizers, this represented an important potential source of uranium.



Figure 7.8.33 - John William Strutt [Lord Rayleigh] (1842-1919)

Phosphate rock is the major source of phosphorus in nature. It exists mainly in the form of hydroxy - and fluoroapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, respectively or a mixture of both and is used mainly for the production of fertilizers and elemental phosphorus. There are two main types of phosphate rock:

- *Sedimentary* These supply 85% of the phosphate rock for the industry, contains 100-200 ppm of uranium, 2-20 ppm thorium and about 0.5% lanthanides. Florida and North Africa phosphates are typical of this category.
- *Igneous* These supply the remaining 15%, contain < 10 ppm uranium but contain appreciable amount of thorium and lanthanides. Kola phosphate which is mined in Russia is typical of this category.

Uranium is present mainly in the tetravalent state in isomorphous substitution with calcium ion; the ionic radius of U^{4+} which is $0.97\text{\AA}$ being very near to that of Ca^{2+} which is $0.99\text{\AA}$ (Figure 7.8.34). In most cases uranium exists in radioactive equilibrium with its decay products (Figure 7.8.35).

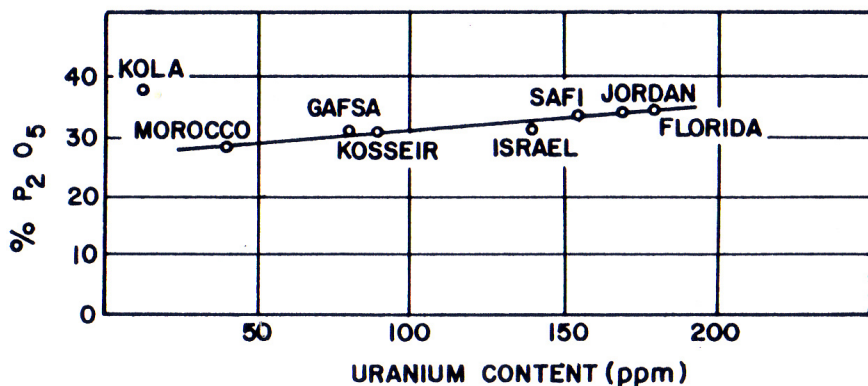


Figure 7.8.34 - Illustration of the isomorphous substitution of uranium with calcium in phosphate rock of different origin

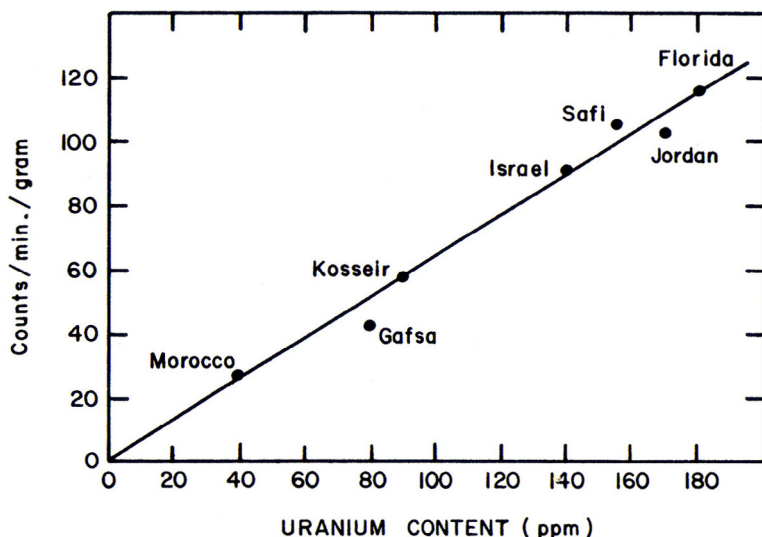


Figure 7.8.35 - Illustration of the radioactive equilibrium of uranium with its decay products in phosphate rock

The presence of uranium in phosphates was known since 1908 but it became important only during the 1940's because of the need for uranium in the USA in connection with the Manhattan Project to produce an atomic bomb. No local uranium deposits were known at that time. The recovery of uranium as a by-product was economically feasible. Processes were therefore developed and applied to extract uranium from phosphoric acid produced by H_2SO_4 acidulation of phosphate rock. Eight plants for the recovery of uranium from phosphoric acid have been built and operated in the US since 1976.

Parallel to this activity, intensive exploration for uranium was under way which resulted in the discovery of rich uranium ores. This rendered the recovery from phosphate uneconomical, and many plants were shut down. In the early 1970's, however, the phosphate fertilizer industry became again interested in uranium as a result of development in the nuclear energy industry and shortages in uranium supplies. Consequently many fertilizer plants became again engaged in the recovery of uranium from the technical acid.

Recovery

Uranium was recovered from phosphoric acid by precipitation methods but mainly by extraction with organic solvents without interfering with the manufacture of fertilizers (Figure 7.8.36). At least three extraction processes were used commercially (Table 7.8.4):

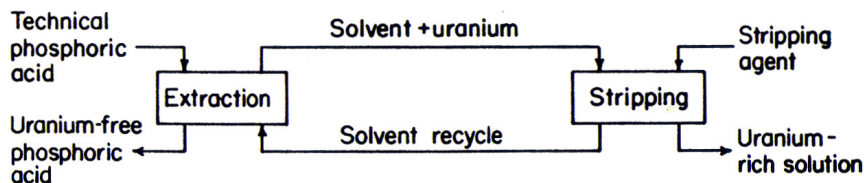


Figure 7.8.36 - Typical solvent extraction process for uranium from phosphoric acid

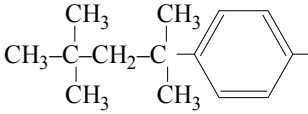
OPPA process

This was the first solvent used industrially in the 1950's by the International Minerals & Chemical Corporation in Bartlow, Florida, prepared by dissolving P_2O_5 in octyl alcohol in absence of moisture and below $15^\circ C$. It is a complex mixture of organic phosphorus compounds, and its effectiveness as an extractant is due to a synergic effect between its components. It extracts uranium in the tetravalent state; therefore, a reducing agent, usually metallic iron is added to the acid to reduce its uranium content. It is unstable and hydrolyzes slowly to octyl orthophosphoric acid which is a much less effective solvent. The hydrolysis is accelerated by strong acids and by increased temperature. Uranium is stripped from the solvent by concentrated hydrofluoric acid yielding UF_4 .

Other extractants

Table 7.8.4 shows other extractants used.

Table 7.8.4 - Extraction of uranium from phosphoric acid

OPPA process Octyl pyrophosphoric acid	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{RO}-\text{P}-\text{O}-\text{P}-\text{OR} \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$ where R is $\text{CH}_3 \cdot (\text{CH}_2)_6 \cdot \text{CH}_2 -$
D2EHPA process A mixture of di(2-ethylhexyl) phosphoric acid used and trioctyl phosphine oxide, $\{\text{H}_3\text{C}(\text{CH}_2)_7\}_3\text{-P=O}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{P}-\text{OR} \\ \\ \text{OH} \end{array}$ where R is $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \underset{\text{C}_2\text{H}_5}{\text{CH}} \cdot \text{CH}_2 -$
OPhPA process The extractant is a mixture of mono and di-octylphenyl phosphoric acids and tributyl phosphate, $(\text{C}_4\text{H}_9\text{O})_3\text{-P=O}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{P}-\text{OR} \\ \\ \text{OH} \end{array}$ + $\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{P}-\text{OR} \\ \\ \text{OR} \end{array}$ Where R is 

THE METAL AND ITS COMPOUNDS

Uranium consists of three isotopes whose concentrations in different resources are exactly the same: ^{238}U , 99.2762 %; ^{235}U , 0.7182 %; ^{234}U , 0.0056 % except from at the Oklo mine in Gabon the proportion of ^{235}U is 0.7078 %. This was attributed to the occurrence of a fission process 1.8×10^9 years ago. Uranium occurs in three modifications:

α -Uranium, < 669°C, orthorhombic
 β -Uranium, 669–776°C, tetragonal
 γ -Uranium, 776–1135°C, body-centered cubic.

Relative abundance in Earth's crust, %	4×10^{-4}
Density, g/cm ³	19.13
Melting point, °C	1125 - 1132
Boiling point, °C	4234

Radioactivity of uranium

Uranium is a radioactive element that is transformed into the stable element lead via many intermediate stages involving the emission of α - and β - radiation with a very long half life (Figure 7.8.37). Pure uranium compounds are only slightly radioactive, because all the decay products with short half-lives such as radon, polonium, etc., which contribute to the activity of uranium ores have been removed during the recovery and refining steps.

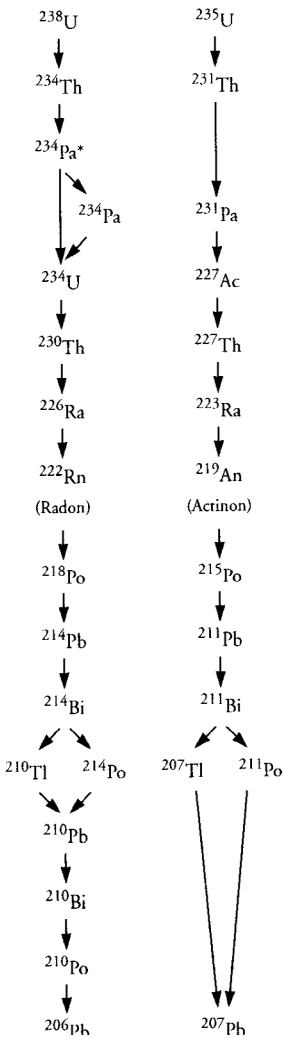
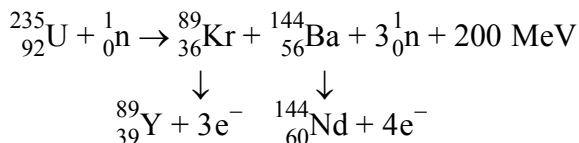


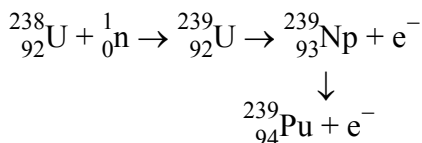
Figure 7.8.37 - Decay chain of uranium isotopes.
Half life of ²³⁸U is 4.5×10^9
and of ²³⁵U is 7.13×10^8

Uranium fission

Uranium 235 undergoes fission when bombarded by thermal neutrons; it breaks apart into two smaller elements and at the same time emitting several neutrons and a large amount of energy:



Uranium 238 absorbs neutrons forming uranium 239 which is a beta emitter with a short half-life; its daughter neptunium 239 also emits an electron to form plutonium 239.



Uranium compounds

Powdered uranium reacts vigorously with water and with dilute acids. Strong solutions of alkali attack the metal to form uranates.

Anionic complexes of uranium are present in both acid and alkaline uranium solutions. Strongly basic ion exchangers are generally used to extract these complexes.

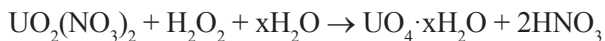
The most important end product is UO_2 which is the only nuclear fuel used in power station reactors, although uranium carbide, UC, is sometimes used in sodium-cooled fast breeder reactors because of its higher density and superior thermal conductivity. Uranium metal is used as the fuel in materials testing reactors. U–Zr alloys are used as nuclear fuel in marine reactors.

The freshly exposed surface of massive uranium metal has a silvery luster, but it is oxidized relatively rapidly in air. Within a few hours, the metal becomes covered with a thin oxide layer of iridescent colors and eventually turns black.

Uranium combines readily with hydrogen at 225°C to form UH_3 , which decomposes again at 436°C. This behavior is utilized in the manufacture of the powdered metal from its compact form.

Uranium peroxide

The hydrate $\text{UO}_4 \cdot x\text{H}_2\text{O}$ is precipitated from aqueous uranyl nitrate solutions at room temperature by H_2O_2 :

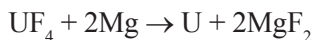


Uranium fluorides

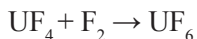


Figure 7.8.38 - Reactor containing a mixture of UF_4 and magnesium ready to enter the furnace for reduction to uranium metal

Uranium reacts vigorously with halogens and hydrogen halides. The reaction with HF gas proceeds only to the UF_4 stage; reaction with aqueous HF leads to hydrated UF_4 . Calcium, magnesium, and sodium are suitable agents for the reduction of UF_4 to uranium metal, e.g. (Figure 7.8.38),



Three industrial processes are currently used for enrichment of uranium: the diffusion process, the ultracentrifuge process, and the jet nozzle process. They employ gaseous UF_6 which is prepared by reaction of UF_4 with fluorine:



The first UF_6 diffusion plant at Oak Ridge, Tennessee, of the 1940s is shown in Figure 7.8.39.

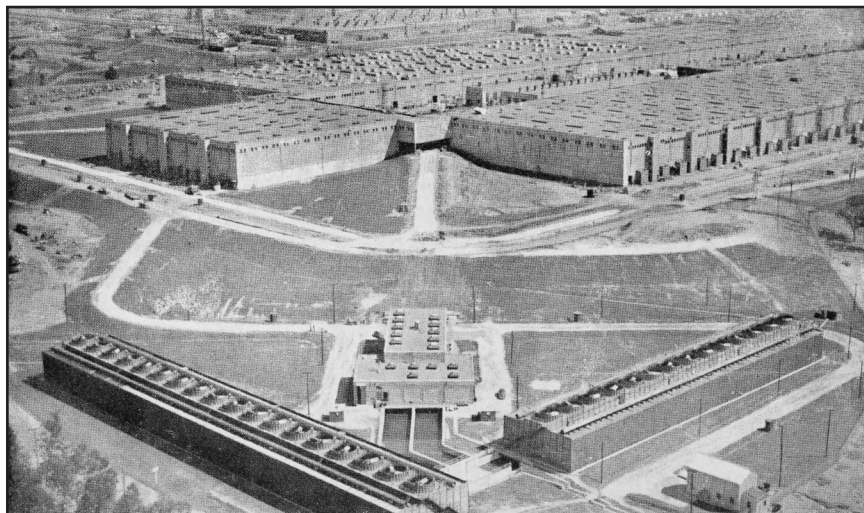


Figure 7.8.39 - UF_6 diffusion plant at Oak Ridge, Tennessee, 1940s

URANIUM AS A STRATEGIC METAL

In 1994 it was revealed by US Energy Secretary that the total US production of highly enriched weapons-grade uranium was 994 tonnes of which about 259 tonnes were stockpiled (Figure 7.8.40). Most of the remaining 735 tonnes were contained in the weapons themselves. Weapons-grade uranium is uranium containing at least 20% uranium 235 with the remainder uranium 238, but most of that produced for weapons is at least 90% uranium 235. Naturally-occurring uranium contains only 0.7% of the isotope uranium 235. A nuclear bomb can be made from about 25 kg of weapon-grade uranium.

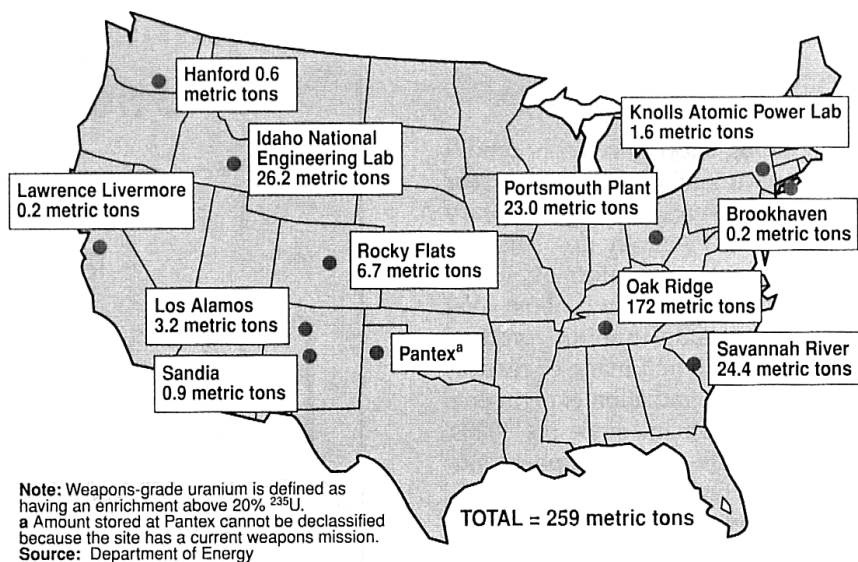


Figure 7.8.40 - Stockpiled highly enriched weapons-grade uranium

The US Department of Energy and the Department of Defense are now in the process of deciding how much of the weapons-grade stockpile is surplus and what to do with it. Eventually, it may be mixed with uranium 238 and used for commercial nuclear power plants. The US warheads were disclosed in the same report to have been 22,229 in 1961 of which 17,187 were dismantled between 1980 and 1994. Also, the exact total

number of US nuclear weapons tests was revealed to be 1,054 of these 67 atmospheric bomb tests were conducted between 1946 and 1962 in the Marshall Islands in the Pacific.

According to another 1994 report by the Russian Minister of Atomic Energy, Russia had produced 1250 tonnes of highly enriched uranium of which 550 tonnes would be diluted with uranium 238 to 4.4% uranium 235. Realizing that the isotope enrichment process is one of the most tedious, slow, and expensive operations, one can only regret the wasted effort in conducting such operations. In addition, it has been reported recently that about 100 tonnes of plutonium originating from the dismantlement of American and Russian missiles is being considered for use for peaceful purposes which is not a simple matter. Figure 7.8.41 shows depleted uranium in gaseous hexafluoride stock piled in USA.



Figure 7.8.41 - Depleted uranium gaseous hexafluoride stock piled in USA

EPILOGUE

The word “dollar” is derived from “Thaler” the large silver coin minted at the rich silver mines of Joachimsthal in Bohemia during the sixteenth century. At the World Exhibition of 1967 in Montréal a replica of an old

coin from Joachimsthal was on sale (Figure 7.8.42). On one side was shown the Bohemian lion, the year 1520, and the name of King Ludwig. On the other side was shown Saint Joachim and the names of Stephan von Schlik and his brother the Count von Bassan, and the year 1967.



Figure 7.8.42 - Replica of the Thaler the large silver coin minted at the rich silver mines of Joachimsthal

When the silver mines were nearly exhausted and Joachimsthal was about to become a ghost town, uranium was discovered there in 1781 and a pigment industry started for coloring glass. This, however, came to an end when the silver mines were closed at the end of the nineteenth century.

The discovery of the phenomenon of radioactivity of uranium in 1896 followed by the discovery of radium in uranium ores two years later, created two new industries when the radiation from radium became known as a means for cancer treatment. The spa industry which was centralized in Bohemia, and the radium production industry which was centralized in Belgium when rich uranium ores were discovered in the Belgian Congo, and in Canada when rich ores were also discovered in the northern territories.

During World War II, as a result of the discovery of uranium fission, there was a great demand for the metal for military purpose. As a result of the

availability of cobalt 60, the demand for radium diminished. Hence, the uranium industry rose again and that for radium was shut down.

The discovery of the trans-uranium elements forced the transfer of uranium from its position in Group VI in the Periodic Table to a new group similar to the lanthanides, that became known as the actinides.

When the uranium industry started after World War II, the ore grade was in general 0.2-0.3% U_3O_8 . In the early 1980's the discovery of an ore with 2.5% U_3O_8 at Key Lake in Canada was considered a break through in ore grades. In the 1990's, however, deposits were discovered with 15% U_3O_8 at MacArthur River mine and 22% U_3O_8 at Cigar Lake project. Such rich deposits rendered Canada the largest uranium producer, supplying over 20% of the world requirement.

Today there are about 400 nuclear reactors in 30 countries supplying energy and Canada is a major supplier of uranium for these reactors. But the problems associated with the disposal of enriched uranium and plutonium from nuclear arsenal and stockpile are now a major concern not only to nuclear engineers but also to the uranium industry in general.

7.9 Zirconium¹

Discovery and isolation	600	Sources	604
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The metal	604		

DISCOVERY AND ISOLATION

On analyzing the gem mineral known as jargon (Figure 7.9.1) from Ceylon (now known as Sri Lanka) Martin Heinrich Klaproth (1743-1817) (Figure 7.9.2) in 1789 found it contained an oxide which he could not identify and which he later called “Zirconerde”, i.e., zircon earth.



Figure 7.9.1 - Museum samples of zircon

In 1824 Berzelius prepared the first zirconium metal, an impure black powder by heating potassium hexafluorozirconate and potassium in a closed pot (the metal still contained hafnium). Through the attempt of many research workers, zirconium of higher and higher purity was obtained. The name origin is Persian, Zargun = gold colored, the name zirconia was given to an earth separated from a gemstone.

¹See also Hafnium, Twentieth Century Metals



Figure 7.9.2 - Martin Heinrich Klaproth (1743-1817)

Purification

In 1914, D. Lely, Jr., and L. Hamburger of Philips Metal-Incandescent Lamp Works in Eindhoven, Holland, obtained the metal with highest purity. Their method consisted in heating a mixture of the tetrachloride and sodium in a bomb. Van Arkel (1893-1976) (Figure 7.9.3) and De Boer (1899-1983) (Figure 7.9.4) developed the iodide process which produced the first massive zirconium metal that could be cold worked and which exhibited good ductility at room temperature.



Figure 7.9.3 - Anton Edward van Arkel (1893 - 1976)



Figure 7.9.4 - Jan Hendrik de Boer (1899-1983)

Wilhelm Kroll (1889-1973) (Figure 7.9.5) carried out the first inert-atmosphere magnesium reduction of zirconium tetrachloride in his Luxembourg laboratory in 1938. In 1944 the US Bureau of Mines in Albany, Oregon started a project to make ductile zirconium economically, Kroll who escaped Nazi Europe and immigrated to US, was assigned to take over direction of the project. By 1947, a pilot plant was producing 30 kg of zirconium sponge per week.



Figure 7.9.5 - Wilhelm Kroll (1889-1973) in his laboratory

In 1916, mining engineer K.C. Li founded a trading company for the refinement and export of tungsten and antimony ores from his native China. Li called his new company *Wah Chang*, meaning “great development”. In 1956, he established a manufacturing plant in Albany, Oregon, to supply zirconium for the US Navy (Figure 7.9.6). Wah Chang expanded its refractory and reactive metals production to include niobium, tantalum, zirconium, hafnium, vanadium, and titanium. In 1967 it was acquired by Teledyne, Incorporated.

THE METAL

The ionic radius of zirconium and hafnium are almost identical because of the lanthanide contraction. Both elements exhibit a valence of four (Table 7.9.1). Therefore, the chemistry of zirconium is similar to that of hafnium. Although zirconium [and hafnium] has two electrons in the outermost shell and it would have been expected that to have valency of 2, yet its valency is 4.

Table 7.9.1 - Properties of zirconium and hafnium

	Zirconium	Hafnium
Atomic number	40	72
Atomic weight	91.22	178.49
Density, g/cm ³	6.5	13.31
Relative abundance in Earth's crust, %	2.2×10^{-2}	4.5×10^{-4}
Atomic radius, pm	206	208
Ionic radius, nm	7.5	
Melting point, °C	1852	2227
Boiling point, °C	3859	4602
Crystal structure	Hexagonal	Hexagonal

Sources

The chief mineral is zircon, ZrSiO_4 , which always contains about 1% hafnium - - another refractory metal with a high melting point. Zircon sand is obtained during the processing of alluvial heavy mineral sands to recover the titanium minerals rutile and ilmenite. Commercial deposits are found in China, Malaysia, Thailand, India, Sri Lanka, Australia, South Africa, Madagascar, and the United States.

High quality zircon contains 64% ZrO_2 , 34% SiO_2 , 1.2% HfO_2 , with the balance including aluminum, iron, phosphorus, rare earths, titanium, uranium, and thorium.

Uses

In the 1940's researchers at Massachusetts Institute of Technology and at Oak Ridge National Laboratory were evaluating the physical and atomic properties of metals as potential uranium fuel cladding materials for nuclear power reactors. In 1948 hafnium-free zirconium was selected as most promising. A satisfactory hafnium separation process was then developed and by the end of 1950, 3000 kg of hafnium-free zirconium metal strip had been produced, and the zirconium metal producing industry was launched as an integral part of the beginning nuclear power industry. Zirconium is a refractory metal with a high melting point.

The corrosion resistance in nitric acid is excellent at all concentrations up to 90 % and temperatures up to 200°C. Zirconium is rapidly attacked by hydrofluoric acid, even at concentrations below 0.1%. The corrosion resistance in sodium hydroxide and potassium hydroxide is excellent at all concentrations, up to the boiling temperature. Zirconium is resistant to molten sodium hydroxide up to 1000°C. It is also resistant to most organic compounds at all concentrations and temperatures.

Zirconia linings for metallurgical furnaces are very permanent, and because of their low heat conductivity, may be made very thin. Zirconia refractories, such as crucibles, are very resistant to the action of heat, slag, and most acids, and may safely be plunged into water while red-hot.

7.10 Titanium¹

Discovery	607	Pigment from slag.....	623
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Pigment from ilmenite.....	621		

DISCOVERY

Titanium, one of the most abundant elements in the Earth's crust [relative abundance 0.44%] discovered in 1790, was produced on an industrial scale only in 1948:

- 1790 Titanium was discovered by the British amateur mineralogist William Gregor (1761-1817) in the iron-bearing black sands in Manaccan, Cornwall, England. The element was initially called manaccanite.
- 1795 The German chemist Martin Klaproth (1743-1817) (Figure 7.10.1) investigated the mineral rutile (Figure 7.10.3) and found that it was the oxide of a new element which he called titanium from Greek mythology the Titans (Figure 7.10.3). It was subsequently established that it was the same element discovered earlier by Gregor.

¹Based on

- F. Habashi, "Two Hundred Years Titanium. The Processing of Titanium Ores for Pigment and Metal Production," *Arab Min. J.* 11(1,2), 74–84 (1993). Arabic Summary *ibid.* 20–21

- F. Habashi, "Titanium in Kazakhstan," *Bull. Can. Inst. Min. & Met.* 95 (1061), 88–89 (2002)

- F. Habashi, "Chemical Beneficiation of Ilmenite," pp. 184–192 in *The Third International Congress Nonferrous Metals* 2011, edited by G. L. Pashkov and P. V. Polyakov, published by Siberian Branch of the Russian Academy of Sciences, Krasnoyarsk, Russia 2011



Figure 7.10.1 - Martin Klaproth
(1743-1817)



Figure 7.10.2 - Museum sample of
rutile



Figure 7.10.3 - A representation of one of the Titans in Greek mythology

- 1887 Lars Nilson (1840-1890) (Figure 7.10.4) and Sven Pettersson (1848-1941) (Figure 7.10.5) in Stockholm isolated the impure metal.



Figure 7.10.4 - Lars Nilson
(1840-1890)



Figure 7.10.5 - Sven Pettersson
(1848-1941)

- 1910 Matthew A. Hunter (1878-1961) (Figure 7.10.6) in USA succeeded in preparing 99.5% pure titanium metal by reducing TiCl_4 with sodium in a steel bomb.
- 1922 Anton Edward van Arkel (1893-1976) in the Netherlands produced pure ductile titanium in the laboratory by the iodide process.



Figure 7.10.6 - Matthew A. Hunter
(1878-1961)

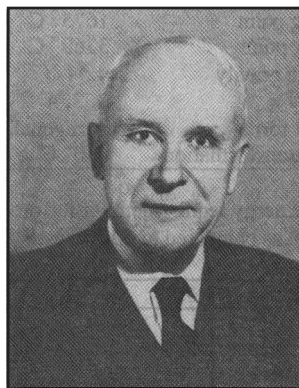


Figure 7.10.7 - Wilhelm Kroll
(1889-1973)

- 1938 Wilhelm Kroll (1889-1973) (Figure 7.10.7) in Luxemburg produced pure titanium by reducing TiCl_4 with magnesium in an inert

atmosphere. He fled his home town in 1940 to the United States when Nazi troops were advancing in Europe.

- 1942 The US Bureau of Mines under Kroll's direction operated a pilot plant in Boulder City, Nevada based on his process.
- 1948 E.I. du Pont de Nemours & Co. produced the first commercial titanium (10 tons/year).

1952 Imperial Chemical Industries in England produced titanium on a commercial scale (5 tonnes/year) by the Hunter Process.

- 1954 Osaka Titanium Company in Japan produced titanium on a commercial scale (12 tons/year) by the Kroll Process. At about the same time, titanium production also started in the former USSR.
- 2010 Total world titanium sponge production more than 200,000 tonnes/ year [USA production withheld].

THE METAL

Titanium is a refractory and a light metal: it melts at 1675°C and has a specific gravity of 4.54. Its crystal form is hexagonal but undergoes transformation to cubic at 880°C. The metal is produced only in USA, the former USSR, Japan, and England. Titanium production is energy-intensive as compared to other metals (Table 7.10.1).

Long before the availability of the metal, however, its oxide in the pure form was known and appreciated as a high quality white pigment. At present, TiO₂ pigment accounts for over 90% of all white pigments used. Its main application is in the paint, plastics, paper, and ceramic industries. Over 90% of titanium minerals are used to manufacture pigment and the remainder for making the metal. World TiO₂ pigment production in 2012 was 6.5 million tonnes.

Table 7.10.1 - Energy requirement for the production of titanium as compared to other metals

	Kwh/Kg
Steel ingot	2.6
Refined copper	11.7
Ferrochrome	13.5
Aluminum ingot	25.6
Magnesium ingot	37.5
Titanium sponge	43.0

OCCURRENCE

Ilmenite, FeTiO_3 , is the major titanium mineral. It represents 90 % of the world titanium ore reserves while rutile and anatase, TiO_2 , and minor amounts of perovskite, CaTiO_3 account for the remaining 10 % (Table 7.10.2). Table 7.10.3 shows crystallographic data for TiO_2 modifications and Table 7.10.4 gives typical analysis of ilmenite ores. Ilmenite occurs either as massive deposits, e.g., in the Province of Quebec (Figure 7.10.8), or as black sand at the mouth of rivers, e.g., in India, Japan, Brazil, and Egypt (Figure 7.10.9).

Table 7.10.2 - The main titanium minerals

Mineral	Formula
Rutile, anatase, brookite	TiO_2
Ilmenite	FeTiO_3
Leucoxene	$\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$
Perovskite	CaTiO_3
Sphene (titanite)	CaTiSiO_5
Titanomagnetite	$\text{Fe(Ti)Fe}_2\text{O}_4$

Table 7.10.3 - Crystallographic data for TiO_2 modifications.

Phase	Crystal system	Lattice constants, nm			Density, g/cm^3
		a	b	c	
Rutile	tetragonal	0.4594		0.2958	4.21
Anatase	tetragonal	0.3785		0.9514	4.06
Brookite	rhombic	0.9184	0.5447	0.5145	4.13



Figure 7.10.8 - A chunk of massive ilmenite from Quebec



Figure 7.10.9 - Typical beach sand containing ilmenite

Table 7.10.4 - Typical analysis of ilmenite ores

	Quebec %	Norway %	USA %	Malaysia %	Australia %	India %
TiO ₂	34.3	43.5	44.6	51.9	52.9	59.9
FeO	27.5	32.6	36.7	30.8	9.3	---
Fe ₂ O ₃	25.2	13.8	8.2	11.9	25.2	---
SiO ₂	4.3	4.0	4.0	0.4	—	0.7
Al ₂ O ₃	3.5	1.3	3.2	1.5	0.25	1.6
P ₂ O ₅	0.015	0.03	0.04	0.2	—	0.18
MgO	3.1	3.9	2.6	0.08	0.54	0.95
CaO	0.9	0.6	0.8	0.1	—	< 0.1
Nb ₂ O ₅	—	0.01	0.01	0.22	—	0.17
MnO	0.16	0.4	0.32	0.8	1.77	0.48
Cr ₂ O ₃	0.1	0.015	0.015	0.015	0.14	0.13
V ₂ O ₅	0.27	0.23	0.12	0.03	0.16	0.25
S	0.3	—	—	—	—	---

BENEFICIATION

Black sand is beneficiated by gravity, magnetic, and electrostatic methods to yield a number of valuable products (Figure 7.10.10).

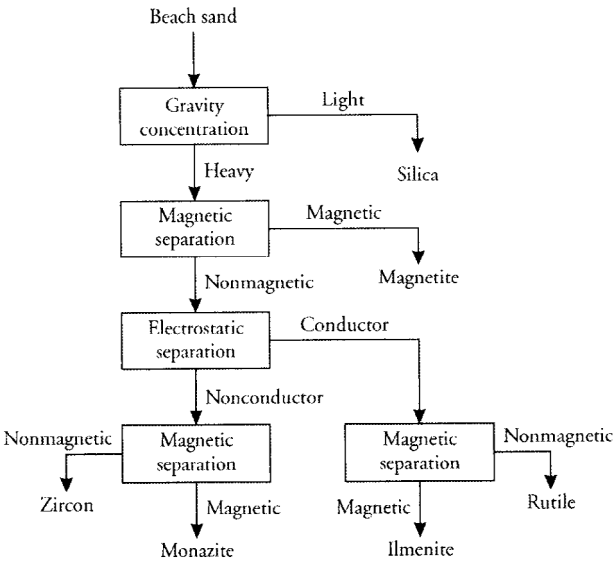


Figure 7.10.10 - Separation of titanium minerals and other valuable minerals from black sands by physical methods

Ilmenite from Quebec is crushed and ground then beneficiated by gravity methods to a concentrate containing 36.8% TiO_2 , 41.8% Fe (total) and a small amount of sulfur.

TREATMENT OF RUTILE

Rutile and anatase are the preferable source for titanium because of their higher titanium content than ilmenite. They are treated directly by chlorination to produce TiCl_4 which after purification can be reduced to produce the metal or oxidized to produce the pigment (Figure 7.10.11).

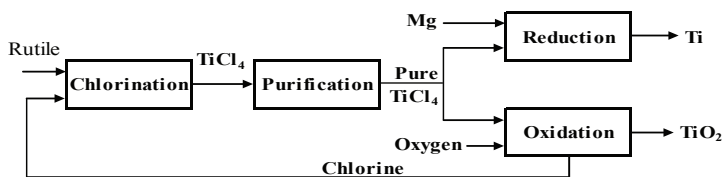


Figure 7.10.11 - Production of titanium or TiO_2 pigment from rutile

ELIMINATION OF IRON FROM ILMENITE

Because of the scarcity of rutile and anatase, ilmenite is used. Ilmenite concentrate can be used directly to make pigment or prepare titanium metal, but it is usually preferred to process it to an intermediate product low in iron to minimize reagents consumption and waste disposal problems. Two methods are used industrially for this purpose (Figure 7.10.12).

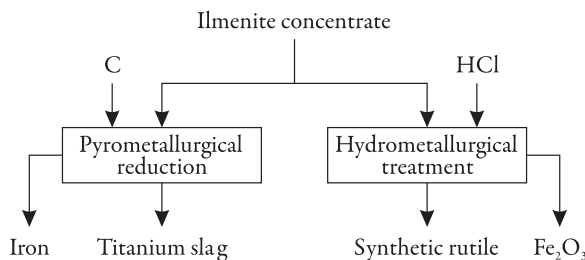


Figure 7.10.12 - Methods for eliminating iron from ilmenite

Pyrometallurgical method

The pyrometallurgical method (Figure 7.10.13) applies for high grade ore only. The ore is mixed with a certain amount of anthracite [a high quality coal] which is just enough to reduce the iron oxide component of the ore then charged in an electric furnace at 1650°C where iron oxide is reduced to metal while titanium is separated as a slag. Titanium slag is mainly iron titanium with magnesium as a main impurity, $(\text{Fe,Mg})\text{Ti}_4\text{O}_{10}$, and a small amount of calcium and aluminum silicates.

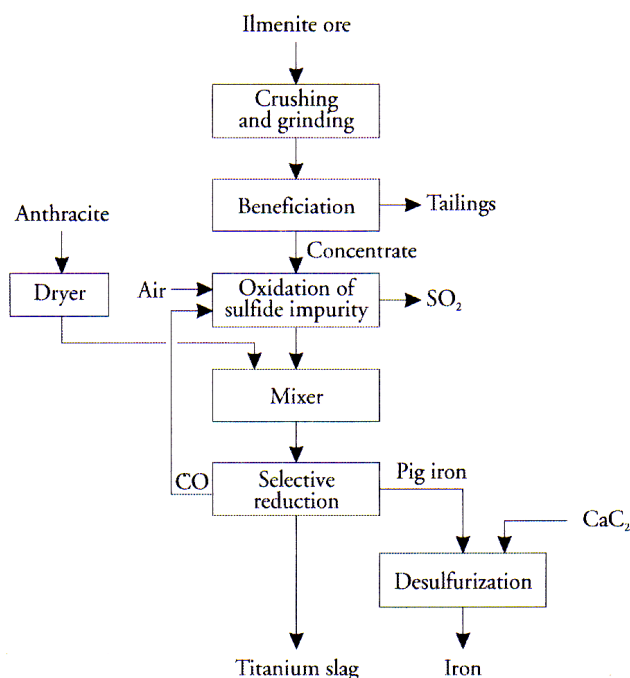
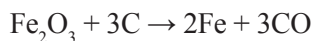


Figure 7.10.13 - Pyrometallurgical method for treating ilmenite

This method is used by the QIT Fer et Titane at its plant in Sorel near Montreal (Figure 7.10.14) and at Richards Bay in South Africa. It is also used in the Soviet Union at Zaporozhye (Ukraine) and in Japan. The reaction taking place during reduction is the following:



Any iron oxide in the ore is also reduced:



No fluxes are added so that the titanium content in the slag is not reduced.



Figure 7.10.14 - QIT Fer et Titane plant at Sorel, Quebec. Electric furnaces are in the building to the left; facing the building are piles of anthracite and ilmenite and mineral beneficiation plant. The river at the top of the photograph is Saint Lawrence River

The reduction of the iron oxides is not taken to completion so that some iron oxide is left in the slag to decrease its melting point (Melting point of TiO_2 1840°C and ilmenite 1435°C). A small amount of Ti(IV) is, however, reduced to Ti(III). The total titanium content of the slag expressed as TiO_2 varies between 72 and 98 % (Table 7.10.5).

Table 7.10.5 - Analysis of typical titanium slags

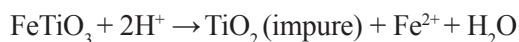
	QIT-Sorel, Quebec	Richards Bays, S. Africa	Ozaka Titanium, Japan
Total TiO ₂ *	72.5	84.5	97.9
TiO ₂	58.8	53.1	58.6
Ti ₂ O ₃	12.4	28.2	35.3
FeO	10.6	12.8	2.2
Fe ₂ O ₃	0	0	0
Fe (metallic)	0.6	0.4	0
MgO	5.9	1.0	1.5
CaO	0.6	0.5	0.03
Cr ₂ O ₃	0.3	0.2	—
V ₂ O ₅	0.4	0.2	0.2
Al ₂ O ₃	5.0	1.0	0.5
SiO ₂	4.2	1.5	1.0
MnO ₂	0.2	1.7	0.6
P ₂ O ₅	0.03	0.03	0.04
C	0.02	0.01	0.2
S	0.06	0.05	0.02
Total	99.1	100.7	100.2

*Total TiO₂ includes the Ti₂O₃ content calculated as TiO₂

At QIT in Sorel the ore is not a high grade ore and as a result the slag is treated further by pressure leaching to remove as much as possible of soluble impurities and to increase its titanium content.

Hydrometallurgical method

For high-grade ilmenite, leaching is conducted by 20% HCl at 120°C and under 200 kPa pressure (Figures 7.10.15-7.10.16). This method involves leaching of iron oxide and obtaining a residue rich in titanium (90-95% TiO₂) known as “synthetic rutile”.



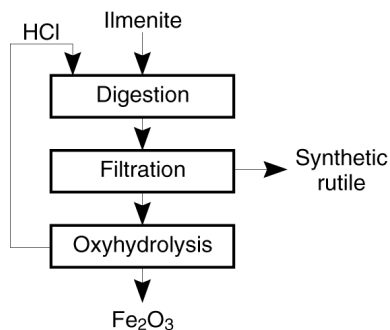


Figure 7.10.15 - Hydrometallurgical method for treating high-grade ilmenite

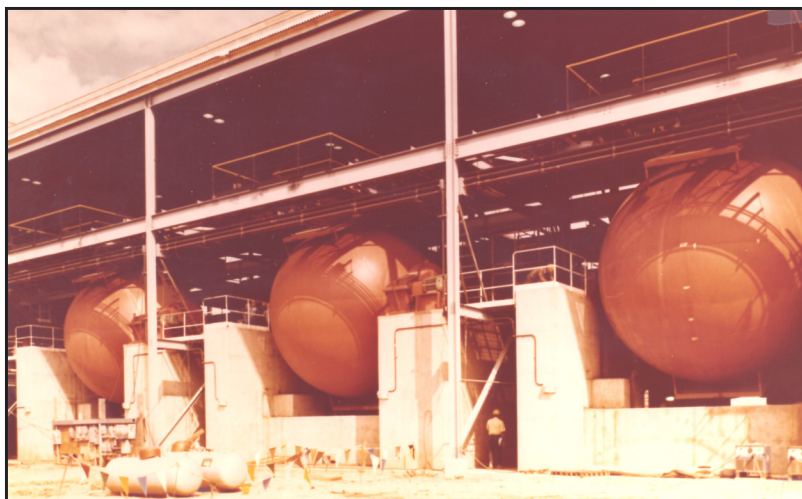
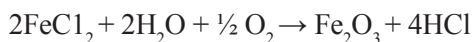


Figure 7.10.16 -. Spherical rotating pressure reactors used for the manufacture of synthetic rutile from ilmenite

After filtering off the ferrous chloride solution, the residue is known as synthetic rutile and contains about 95% TiO₂. Hydrochloric acid is preferred to sulfuric acid, although it is more expensive, because it can be regenerated from the spent solution by an oxyhydrolysis step (Figure 7.10.17):



For low-grade ore because of the high percentage of gangue, leaching is conducted at 80°C and a longer time. After filtering off the gangue the solution is then hydrolyzed to get synthetic rutile (Figure 7.10.18).

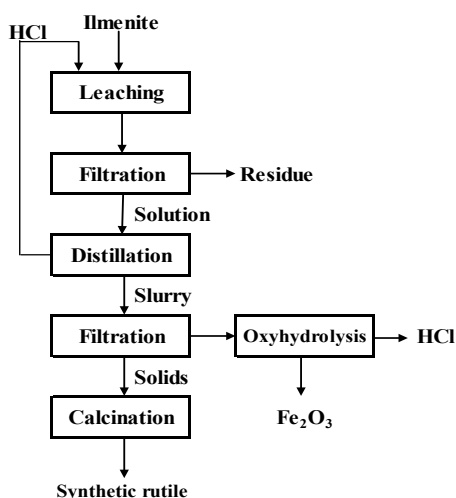


Figure 7.10.17 - Hydrometallurgical method for treating low-grade ilmenite

Fluidized bed oxyhydrolysis

In a fluidized bed reactor the ferrous chloride solution is introduced onto a large bed of hot ferric oxide where heating is provided by the hot fluidizing combustion gases (Figure 7.10.19). As the combustion gas flows through the well agitated bed of oxide it quickly reaches thermal equilibrium with the bed. The solution is fed on top of the bed of oxides. The liquid feed wets the outer layer of the hot oxide particles and is quickly evaporated to form an onion-like layer of new solid oxide on top of the existing oxide, thereby producing dense homogeneous particles.

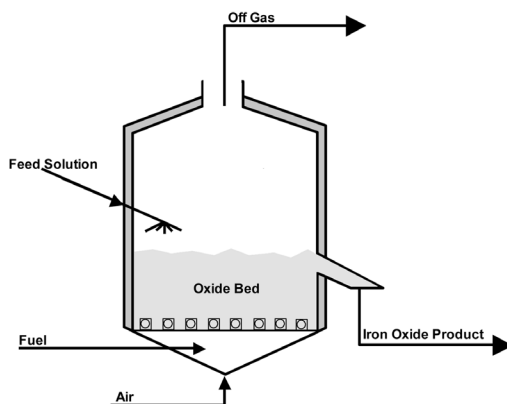


Figure 7.10.18 - Fluidized bed reactor for oxyhydrolysis of ferrous chloride

Spray roaster oxyhydrolysis

In this type of oxyhydrolysis roaster, the ferrous chloride solution is sprayed into an empty cylindrical vessel, while the required energy is supplied by the up flow of hot gases generated in the bottom burners (Figures 7.10.19-7.10.20). Spray roasters have large diameters to keep the gas velocities low. If the gas velocity is high, too many particles are elutriated with the off-gas, and the product quality and the efficiency of the roaster drop. The off-gas and oxides leave the roaster counter-currently at about 400°C to 500°C. The residence time of the sprayed particles in the high-temperature reaction zone is very short; therefore, very small liquid droplets, which can be quickly heated, should be created by atomization. The fast heat-up results in the formation of a solid oxide crust on the surface of each droplet. As the bulk of the droplet heats, the water content vaporizes and breaks through the oxide shell. Therefore, the spray roasted oxide is composed of very fine “fluffy”, hollow spheres.

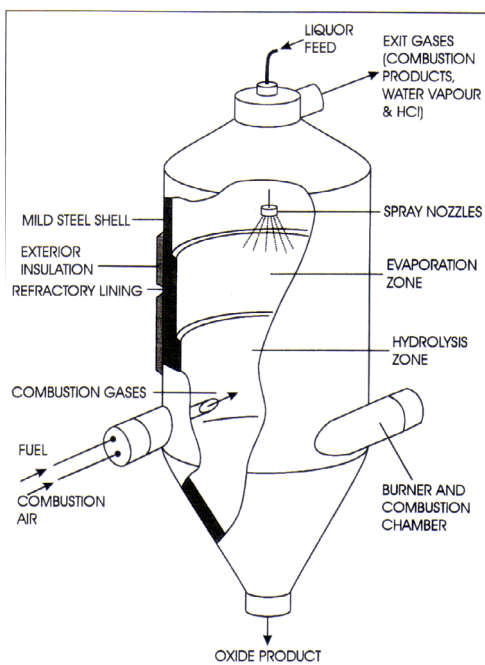


Figure 7.10.19 - Regeneration of HCl from ferrous chloride solution by oxyhydrolysis in spray roaster

The slag and synthetic rutile are lower in iron content than ilmenite can then be processed to TiO_2 pigment or titanium metal, as a substitute for rutile (Figure 7.10.20).

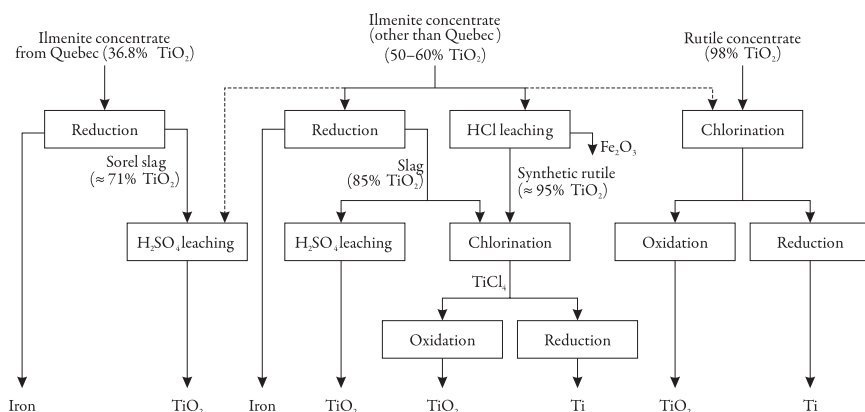


Figure 7.10.20 - Processing routes for ilmenite and rutile.
Dotted lines represent special cases

PIGMENT PRODUCTION

Nearly 90% of titanium ores are used in pigment manufacture and only 10% in metal production. Titanium pigment produced from rutile is limited because of the scarcity of rutile. The pigment is usually produced from ilmenite, titanium slag, or synthetic rutile.

Pigment from ilmenite

This process is the oldest and was developed in 1908. In this case the ore is transformed with concentrated H_2SO_4 at $110\text{--}120^\circ\text{C}$ into titanyl sulfate and ferrous sulfate:



The reaction is conducted in large concrete tanks lined with acid resisting brick, heated by direct injection of high pressure steam (Figure 7.10.21) or in pug mill (Figure 7.10.22). When the temperature of reaction is reached,

steam is stopped and the heat generated by the reaction is enough to take reaction to completion. This usually takes 8-10 hours during which the reaction mixture is solidified.

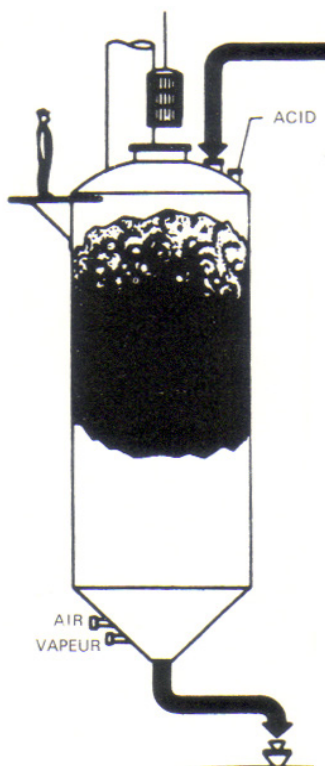


Figure 7.10.21 - Concrete tanks lined with acid resisting brick for treating ilmenite with concentrated sulfuric acid

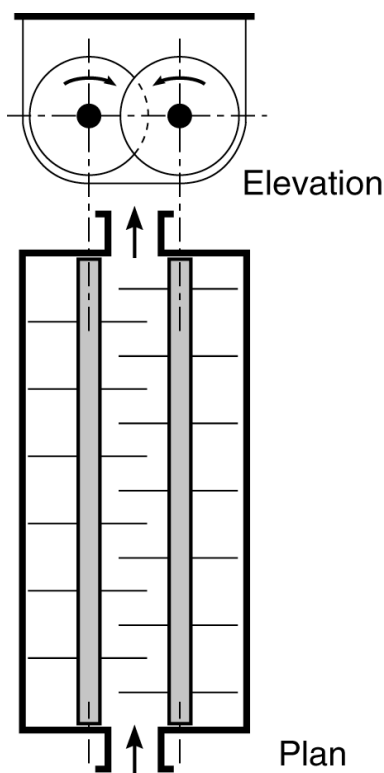


Figure 7.10.22 - Pug mill for treating ilmenite with concentrated sulfuric acid

The solid mass is then dissolved in water; scrap iron is added to reduce any ferric ion. After filtration, the solution containing 120-130 g/L TiO_2 and 250-300 g/L FeSO_4 is then concentrated under vacuum at 10°C to crystallize ferrous sulfate which is then centrifuged. Titanium oxide is then precipitated from solution by dilution and seeding resulting in the formation of dilute H_2SO_4 for disposal (Figure 7.10.23).

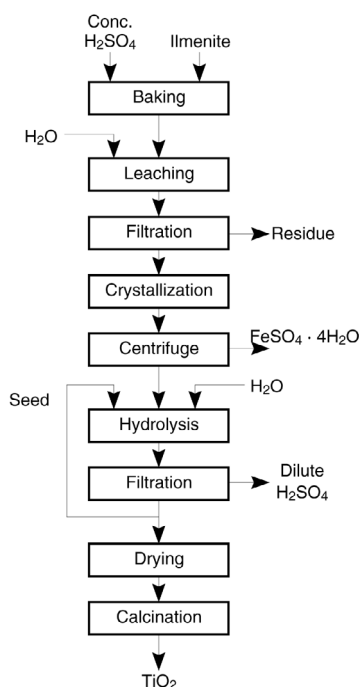


Figure 7.10.23 - The early method for treating ilmenite for TiO_2 production

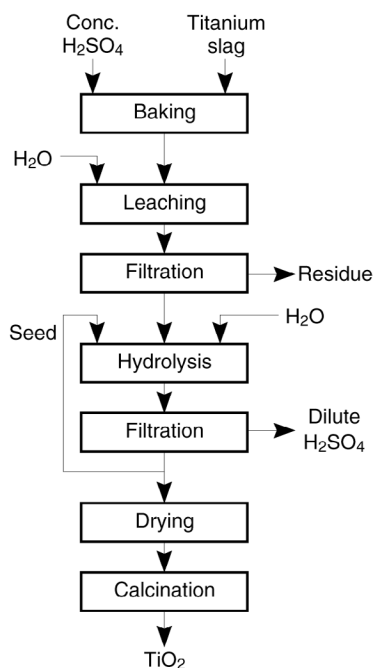


Figure 7.10.24 - Leaching of titanium slag for production of TiO_2 pigment

Pigment from slag

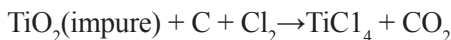
This process was developed in the 1950s when slag production was invented. Titanium slag is treated in the same way as ilmenite with the exception that no separation of ferrous sulfate is necessary because the bulk of iron is already separated by reduction in an electric furnace in an earlier step (Figure 7.10.24):



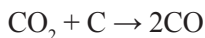
Pigment from synthetic rutile

Synthetic rutile is insoluble in H_2SO_4 and therefore the chlorination route is used.

Titanium tetrachloride is produced by the chlorination of impure TiO_2 in presence of carbon:



some CO will form at high temperature by the reaction



This reaction is undesirable since more carbon is consumed and the total volume of gases produced per mole of metal chloride will increase (Figure 7.10.25). Since the metal chloride is volatilized during this process, then its concentration in the exit gases will decrease with increasing temperature of chlorination.

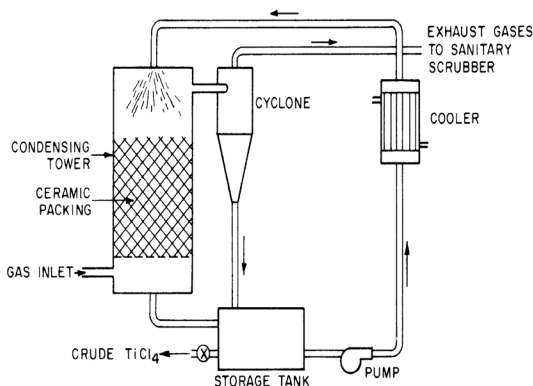


Figure 7.10.25 - Condensing unit for TiCl_4

Fluidized beds and occasionally rotary kilns are commonly used for the chlorination reaction. The volatilized chlorides are collected in condensers. Figure 7.10.26 shows a condenser for collecting the solid chlorides of iron, manganese, and chromium while Figure xx shows a condenser for collecting liquid TiCl_4 . In this case condensation is achieved by spraying the gases with cooled TiCl_4 in a packed tower. A flowsheet of the process is given in Figure 7.10.27. Purification of a liquid TiCl_4 (b.p. 136.4) is achieved by distillation in a fractionating column.

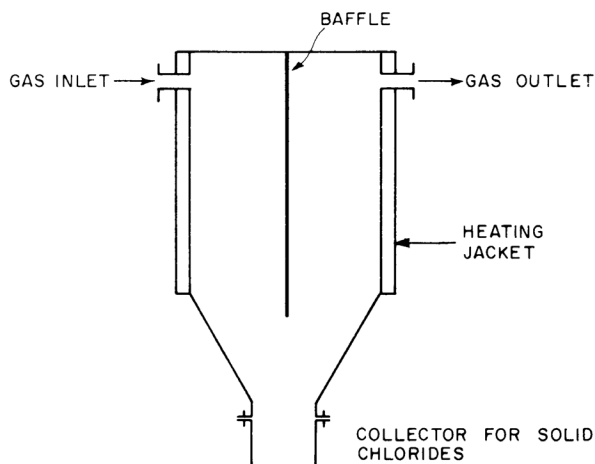
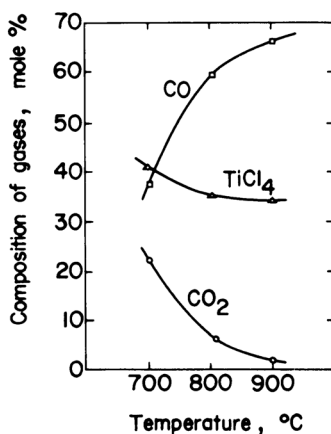


Figure 7.10.26 - Condenser for solid chlorides

Figure 7.10.27 - Volume and composition of exit gases in the chlorination of TiO_2 in presence of carbon

The exhaust gases from chlorination cannot be emitted directly into the atmosphere because of the presence of residual chlorine which is poisonous; the gases must first be scrubbed with NaOH solution to remove chlorine.

The Sorelslag produced in Quebec is not suitable for chlorination because of its high impurity level - about 16.6% as compared to about 6% in other slags. These impurities will not only consume unnecessary amount of

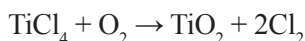
chlorine but also will create a disposal problem. Furthermore, some of these impurities, e.g., calcium and magnesium will interfere with the chlorination process itself which is conducted at 800°C, by forming a molten phase (CaCl_2 m.p 770°C, MgCl_2 m.p 708°C). For these reasons Sorelslag is used only for making pigment by the sulfuric 'acid process, in spite of its acid disposal problem.

The main problems encountered in chlorination are in condensing and collecting the reaction products. These difficulties originate from the following sources:

Carry-over of fine dust that contaminates the reaction product. This can be eliminated to a large extent by careful preparation of charge and close regulation of gas flow.

- Plugging of condenser lines due to the condensation of crystalline chloride. This can be avoided by heating the lines to a certain temperature.
- Corrosion of the condensing system with chlorine and HCl.
- Leakage of air and moisture into the system, especially near the reaction zone, causes oxidation or hydrolysis of the chlorides and the formation of HCl. These effects can be minimized by thorough drying of the charge and by maintaining the system under a slight positive pressure.

Pure TiCl_4 is vaporized and heated with oxygen to form TiO_2 powder which is separated from the exit gases by a system of filters. During this reaction chlorine is formed:



It is collected and recycled in the chlorination step.

PRODUCTION OF METALLIC TITANIUM

Metallic titanium is produced by the reduction of pure TiCl_4 by metallic magnesium or sodium. Reduction by magnesium accounts for 80 % of world production. The metal produced is in form of a sponge which is then purified and then melted.

Reduction by magnesium

When magnesium is used, the reaction can be represented by:

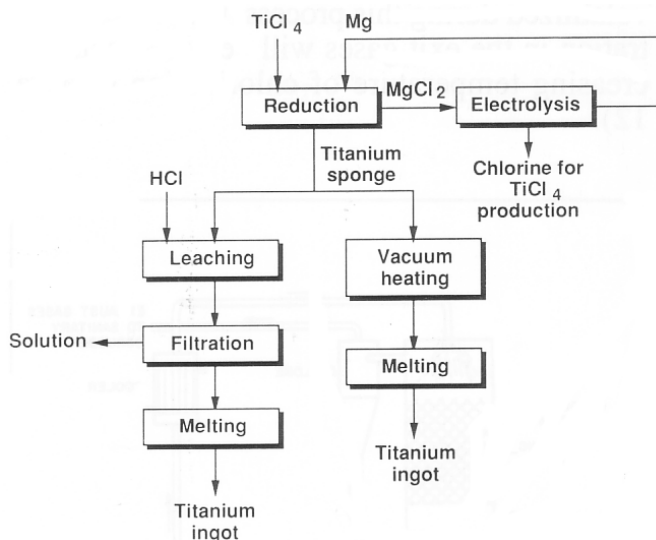
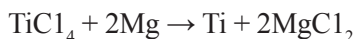


Figure 7.10.28 - Production of titanium from TiCl_4

Titanium tetrachloride which is liquid at room temperature is injected into an evacuated air-tight heated reactor containing the reducing metal in the molten state. Titanium tetrachloride immediately evaporates and the vapors interact with the molten metal to deposit titanium crystals on the walls of the reactor at the liquid interface. These crystals form the nuclei for the further deposition of the metal in the form of a sponge.

Liquid slag (MgCl_2) obtained in the reaction sinks to the bottom below the molten metal because of differences in the specific gravities. Enough TiCl_4 is admitted into the reactor so that the molten metal is completely consumed. The bulk of slag is then forced out of the reactor from the discharge pipe by means of argon. Figure 7.10.29 show typical reactor used for the reduction of TiCl_4 ,

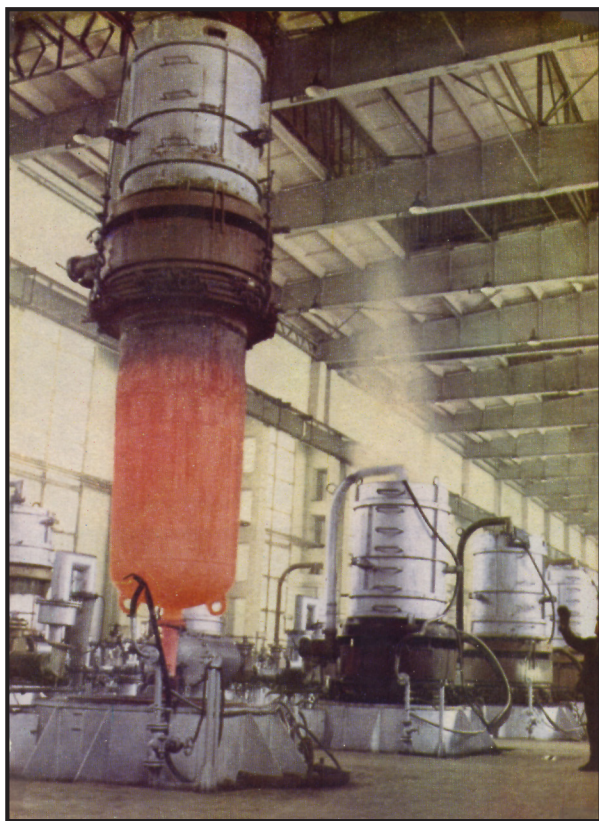


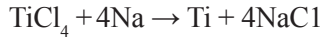
Figure 7.10.29 - Reactors for reduction of TiCl_4 at Ust-Kamenogorsk plant in Kazakhstan

Electrolysis of MgCl_2

Magnesium chloride formed in the reduction step is treated in an electro-winning plant in the fused state to produce the magnesium necessary for reduction and the chlorine necessary for the formation of TiCl_4 .

Reduction by sodium

When sodium is used as a reducing agent, the reaction can be represented by:



Although the stoichiometric amount of sodium is twice that of magnesium, the overall cost of sodium is less than that of magnesium per kilogram of titanium. However, sodium has higher vapor pressure than that of magnesium which necessitates the use of a pressure reactor. Also, the volume of the reducing vessel and slag per kilogram titanium are larger than when magnesium is used.

Processing of titanium sponge

Titanium sponge (Figure 7.10.30) obtained by reduction of TiCl_4 is then purified in two ways:

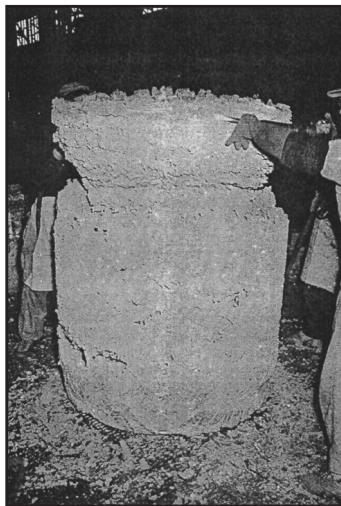


Figure 7.10.30 - Titanium sponge produced at Ozaka titanium company in Japan

Vacuum heating

In this case the temperature of the furnace is then increased to about 1200°C and the reactor is again evacuated to volatilize the remaining slag and any reducing metal that may be adhering to the sponge. When this is achieved, the reactor is removed from the furnace, allowed to cool, opened, and the lumps of sponge removed.

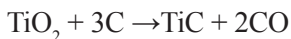
Acid leaching

In this case the reactor is removed from the furnace, allowed to cool, opened, and the lumps of sponge are crushed then leached with dilute HCl to remove any remaining magnesium or MgCl_2 .

The crushed and purified sponge is then consolidated into ingots by melting using an electric arc or any other methods.

OTHER INDUSTRIAL PRODUCTS

Titanium enters in the manufacture of numerous alloys. It is also used in the production of titanium carbide which is a hard refractory substance with some metallic properties (metallic luster, electrical conductivity). It is used as a component of hard titanium tungsten tool steels. These alloys contain 10-40 % TiC, 50-85 % WC, while the remainder is cobalt. Titanium carbide is also used as a component of scale-resistant refractory alloys which are used for the production of gas-turbine parts for jet engines. It is prepared by heating a mixture of TiO_2 and carbon at about 2000°C.

**Welding rod coating**

Improved electric welding rods are produced by the use of coatings containing titanium oxide, which stabilize the electric arc and reduce the viscosity of the slag formed during welding.

Titanium cladding

Titanium cladding makes construction of autoclaves economically and technically viable. Titanium is required in all parts of the system to resist the hot sulfuric acid. In high-pressure areas the equipment is fabricated from steel plate integrally clad to titanium. The explosion welding process uses the energy of an explosion to create a weld between metals. The process is most commonly used to clad steel with a thin layer of corrosion-resistant alloy metal. When two plates are being clad, the mating surfaces of both metals are ground flat to achieve a smooth finish and prepare the surfaces for the explosion. The plates are then ready to be assembled into the pack, which locks the plates into position. A small gap is left between the base metal and cladding metal. Next, explosive powder of exact formulation is evenly spread on top of the cladding plate. The explosion is detonated from one edge of the cladding plate and moves across the top of the pack at a uniform speed, which results in a high-pressure collision of the metals. The newly formed clad is flattened out by a press (Figure 7.10.31).

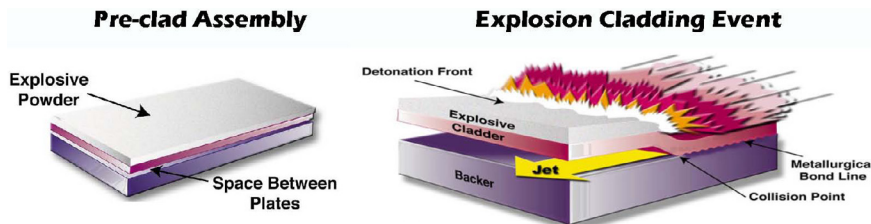


Figure 7.10.31 - Explosive cladding



Figure 7.10.32 - Autoclave manufactured from titanium-clad steel

7.11 Yttrium¹

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DISCOVERY

In 1787, Carl Axel Arrhenius found a new mineral near Stockholm in Sweden (Figures 7.11.1) and named it ytterbite, after the village Ytterby. Johan Gadolin (1760-1852) discovered yttrium's oxide in Arrhenius' sample in 1789, and Anders Gustaf Ekeberg named the new oxide yttria. Elemental yttrium was first isolated in 1828 by Friedrich Wöhler when he was teaching chemistry at the Polytechnic School in Berlin.

The location was recognized in 1989 by the ASM International [American Society of Metals] as a Historic Site (Figures 7.11.2-7.11.4). Other rare earths that trace their discovery to the same quarry are:

- Scandium, named after Scandinavia, discovered in 1879 by Lars Fredrik Nilson (1840-1899)
- Holmium, named after Stockholm, discovered in 1879 Per Teodor Cleve (1840-1905)
- Thulium, named after Thule, in a Scandinavian mythology, discovered in 1879 Per Teodor Cleve (1840-1905)
- Gadolinium, after the chemist Johan Gadolin, discovered in 1880 by Jean Charles Marignac (1817-1894)

¹See also Rare Earths [Metals of the Nineteenth Century]

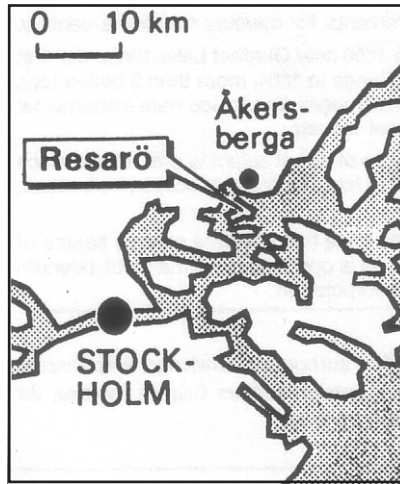


Figure 7.11.1 - Location of Ytterby



Figure 7.11.2 - Yttriumvägen in Ytterby quarry near Stockholm where Carl Axel Arrhenius found the mineral that later was named gadolinite in honour of the chemist Johan Gadolin



Figure 7.11.3 - Terbium Road and the direction to the mine in Ytterby



Figure 7.11.4 - ASM International plaque

THE METAL

Yttrium is a transition metal. It occurs in nature in association with the lanthanides. Although it has 2 electrons in the outermost shell yttrium is exclusively trivalent. It is stable in air in bulk form, due to the formation of a protective oxide, Y_2O_3 , film on its surface. When finely divided, however, it ignites in air when heated. Like its members of the group it forms only colorless compounds. Yttrium forms a water-insoluble fluoride, hydroxide, and oxalate, but its bromide, chloride, iodide, nitrate and sulfate are all soluble in water.

Only the isotope Y 89 exists. The most important use of yttrium is in making phosphors, such as the red ones used in television set cathode ray tube displays. It is also used in the production of electronic filters, lasers and superconductors; various medical applications.

7.12 Beryllium

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INTRODUCTION

The mines in the Red Sea hills which were mentioned by the Roman writers Strabo and Pliny the Elder were probably the only source of beryl in ancient times. The green precious stones called smaragdus (Figure 7.12.1) included at least two varieties: beryl and emerald, which were known from ancient times. Beryl was analyzed by the German chemist Klaproth and he found it to be aluminum silicate, while emerald was analyzed by the French chemist Vauquelin as well as by the Swedish chemist Berzelius and found it to be a calcium aluminum silicate.



Figure 7.12.1 - A museum sample of beryl

When, however, the French mineralogist Abbé René Just Haüy (1743-1822) (Figure 7.12.2) discovered the remarkable similarity in crystalline structure, hardness, and density of a beryl from France and an emerald from Peru, he asked Vauquelin in 1798 to analyze these samples. On performing the analysis, Vauquelin found that the two minerals were indeed identical and he noticed this time that the hydroxides precipitated from acid solutions of these minerals differed from that known for aluminum hydroxide. For example, they dissolved in ammonium carbonate, and their salts had a sweet taste.



Figure 7.12.2 - Abbé René Just Haüy (1743-1822)

Vauquelin, therefore, suspected the presence of a new earth that was common in both minerals and was overlooked in earlier analyses. He called the new earth “glucina” meaning sweet because of the sweet taste of its salts. Klaproth later suggested that the name should be changed to beryllia which is the name accepted today. Beryl and emerald are now known to be a beryllium aluminum silicate, $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ (Figure 7.12.3).

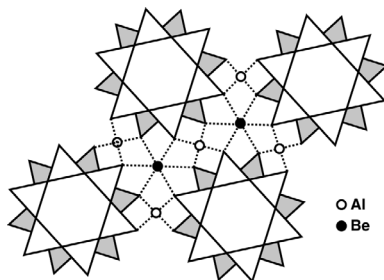


Figure 7.12.3 - Structure of beryl showing the hexagonal silicate rings

PREPARATION OF THE METAL

The metal was prepared in 1828 in minute amounts by Friedrich Wöhler (1800-1882) (Figure 7.12.4) and independently by Antoine Bussy (1794-1882) (Figure 7.12.5) by the action of potassium on beryllium chloride. The French chemist Paul Lebeau (1868-1959) prepared the pure metal in 1898 by electrolysis of a fused beryllium fluoride-potassium fluoride mixture as a part of his doctoral thesis. In 1932 Alfred Stock and Hans Goldschmidt in Germany devised the first commercial process, in which a mixture of the fluorides of beryllium and barium are electrolyzed.



Figure 7.12.4 - Friedrich Wöhler
(1800-1882)

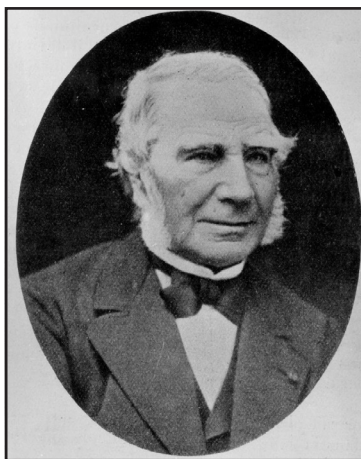


Figure 7.12.5 - Antoine Bussy
(1794-1882)

Bussy was born in Marseilles, finished education at École Polytechnique in 1813, became lecturer at the School of Pharmacy in Paris in 1821, then professor in 1836, and director of the school from 1844 to 1873. He was nominated member of the Academy of Sciences in 1850 and was founder of the Scientific Union of Pharmacists of France. He authored *Traité des moyens de reconnaître les falsifications des drogues* in 1829.

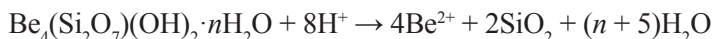
OCCURRENCE

Beside ores containing beryl which is an anhydrous silicate, a new ore was discovered in Spor Mountain Utah in containing the mineral bertrandite - a beryllium hydrated silicate containing about 1% BeO associated with clay.

EXTRACTION FROM ORES

Bertrandite

The ore is leached easily with sulfuric acid:



Beryl

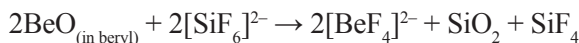
Beryl is a highly refractory mineral that is not attacked by concentrated acids.

Melting and quenching

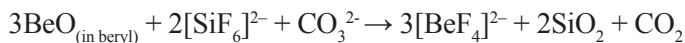
When beryl is melted (m.p. 1627°C) and the molten mass is rapidly quenched in water, an amorphous glassy product is obtained from which beryllium can be leached by dilute acids leaving a porous siliceous matrix. Melting is conducted in an electric arc furnace. The quenched material is leached with dilute H_2SO_4 to extract both beryllium and aluminum leaving behind silica which is removed by filtration.

Fluorination

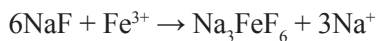
In this process beryl is melted with Na_2SiF_6 at 850°C to convert beryllium into the water-soluble Na_2BeF_4 while aluminum is converted to insoluble Na_3AlF_6 . Silicon is partly volatilized as SiF_4 and partly liberated as SiO_2 :



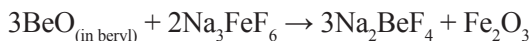
The process was invented by the French chemist Hippolyte Copaux, professor at the École supérieure de physique et de chimie industrielles de la ville de Paris. It was improved later by adding Na_2CO_3 to the reaction mixture to prevent the formation of SiF_4 , and thus economize the consumption of Na_2SiF_6 :



Ferric sulfate solution at pH 4 is then added to precipitate sodium ferric fluoride:



Sodium ferric fluoride obtained is added to the beryl substituting about 60 % of the Na_2SiF_6 requirement:



A schematic flowsheet is shown in Figure 7.12.7.

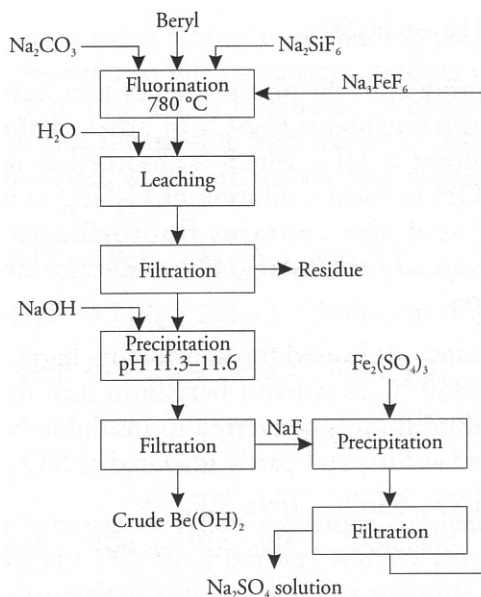
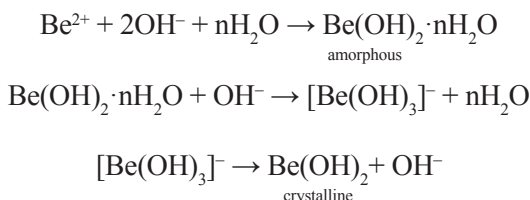


Figure 7.12.7 - Flowsheet for the treatment of beryl by fluorosilicate process

Preparation of the metal

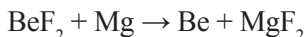
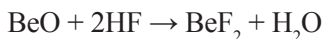
Raw material is BeO which in turn is obtained by calcination of $\text{Be}(\text{OH})_2$. To get the crystalline hydroxide, precipitation should be carried out from alkaline medium. This is achieved by dissolving the hydroxide in excess alkali then boiling the beryllate solution to precipitate the crystalline hydroxide as follows:



Separation of beryllium from aluminum, the major impurity in beryllium ores, is achieved by adding ethylene diamine tetraacetic acid (EDTA) together with NaOH to form beryllium and aluminum hydroxides which redissolve on adding excess NaOH. On boiling the solution, only $\beta\text{-Be}(\text{OH})_2$ is precipitated, while aluminum is not, due to the presence of EDTA.

Two methods are available for obtaining the metal:

- **Metallothermic reduction.** Raw material is BeF_2 obtained by fluorination of BeO. Beryllium fluoride is then reduced by magnesium in graphite-lined furnaces at 1300°C :



- **Electrowinning.** Raw material is BeCl_2 prepared by the chlorination of BeO. Beryllium is made by batch electrolysis of fused salt, starting with 25% BeCl_2 and 75% NaCl in a chrome–iron pot with a perforated inner liner which acts as cathode to a graphite anode. Figure 7.12.8 shows the system $\text{BeCl}_2\text{--NaCl}$. Cell voltage is 6–9 volts. Temperature of the bath

is about 400°C. The metal is deposited in the liner in the form of bright crystalline flakes is removed, drained above the cell and then dumped into water. Purity greater than 99.4% may be obtained.

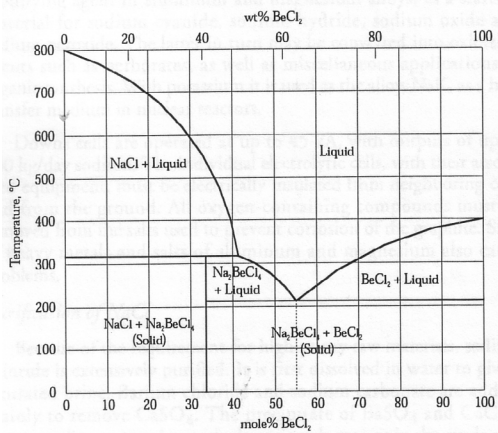


Figure 7.12.8 - Phase diagram of the system $\text{BeCl}_2\text{--NaCl}$.

Beryllium alloys

Beryllium alloys are made in arc furnaces by reduction of oxides by carbon in the presence of molten alloying metals. A beryllium–copper eutectic can be made by using a copper cathode. Beryllium alloys containing copper and nickel are made from BeO in arc furnaces.

THE METAL AND ITS COMPOUNDS

Relative abundance	$6 \times 10^{-4} \%$
Atomic radius	112.50 pm
Crystal structure	Hexagonal closest packed
Transition at 1254°C	Body-centered cubic
Melting point	1287°C
Boiling point	2472°C
Density	1.85

and the remaining 10 % is used as a refractory oxide. In the metallic form it is used as a moderator to slow down fast neutrons in nuclear reactors because of its low atomic weight and low neutron cross section. As an alloy with copper, it is particularly important in springs because such alloys possess high elasticity and great endurance.

Relatively long-wave gamma rays cause beryllium to emit neutrons, on account of a (γ, n) reaction, hence it can be used as a source of neutrons.

7.13 Chromium

Discovery.....	648	The metal and its compounds	652
Occurrence and recovery	649		

DISCOVERY

Chromium was discovered in 1797 by the French chemist Louis Nicolas Vauquelin (1763-1829) (Figure 7.13.1) in the mineral crocoite, PbCrO_4 (Figure 7.13.2). He called it chromium from Greek chroma which means color, because the metal has many colored salts. The mineral crocoite was discovered at Berezovsk Mines near Ekaterinburg in the Urals in 1766 and named crocoise by F. S. Beudant in 1832, from the Greek κρόκος (krokos), saffron, in allusion to its color, a name first altered to crocoisite and afterwards to crocoite. In 1798 Vauquelin isolated the metal by reducing its oxide with carbon.



Figure 7.13.1 - Louis Nicolas Vauquelin (1763-1829)



Figure 7.13.2 - A museum sample of the mineral crocoite, PbCrO_4

OCCURRENCE AND RECOVERY

Chromite, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, is the only commercial source of chromium. In nature it is a mixture described by the formula $(\text{Fe}^{2+}, \text{Mg})\text{O} \cdot (\text{Cr}, \text{Al}, \text{Fe}^{3+})_2\text{O}_3$. Most of the mineral came from the Ural Mountains up to 1827 when large deposits were found in Turkey in 1860. It is found in Bushveld Igneous Complex in Transvaal in South Africa, the Great Dyke in Zimbabwe, the Stillwater Complex in Montana, USA, in Albania, and the Philippines.

- Finely ground chrome ore is roasted with Na_2CO_3 under oxidizing conditions at 1100°C then leached with water. The solution containing hexavalent chromium can be reduced with SO_2 and used for electrowinning, or $\text{Na}_2\text{Cr}_2\text{O}_7$ can be crystallized from it and converted to CrO_3 for use in electrolysis or to Cr_2O_3 for use in metallothermics:

$$4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$$
- The ore is leached with sulfuric acid, iron and aluminum are separated as ammonium alum. Separation of chromium is based on the formation of violet alum $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ [or $\text{NH}_4\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] (Figures 7.13.3-7.13.4). An alum is a double salt of ammonium and chromium sulfates.

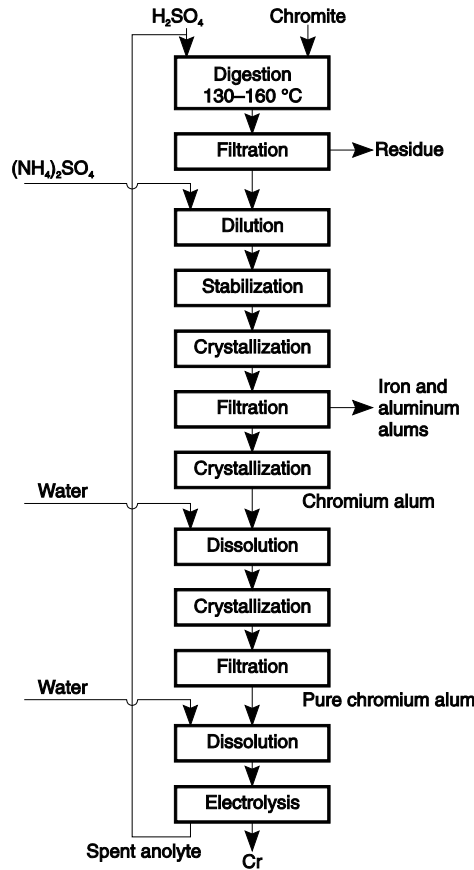


Figure 7.13.3 - Production of chromium by aqueous electrolysis

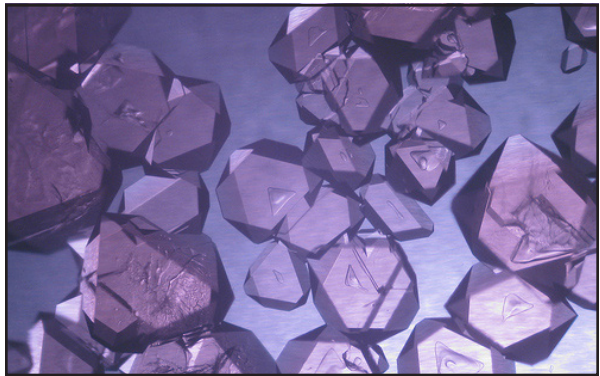
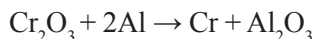


Figure 7.13.4 - Violet chromium alum

- Ferrochromium is first produced then ground and dissolved in sulfuric acid. Iron is removed by crystallization as iron(II) ammonium sulfate, $[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2]$. A diaphragm is necessary to prevent migration of Cr(VI) into the cathode compartment where its reduction by Cr(II) would lead to loss of current efficiency. Flow is maintained into the anode compartment from the cathode compartment by a higher level of solution in the latter. The pH of the catholyte must be controlled. At too low a value, H_2 evolution increases; at too high a value, precipitation of $\text{Cr}(\text{OH})_3$ occurs. Chromium is plated onto stainless steel cathodes until it attains a thickness of ca. 3 mm. The plate is stripped from the cathode and dissolved oxygen is removed by heating at 420°C .
- The metal can be obtained from Cr(VI) solutions by electrolysis, but the process is less efficient and is used primarily for plating.
- In 1898, Hans Goldschmidt (1861-1923) (Figure 7.13.5) produced chromium by the reduction of Cr_2O_3 with aluminum powder:



The reaction is highly exothermic and two molten phases are produced.

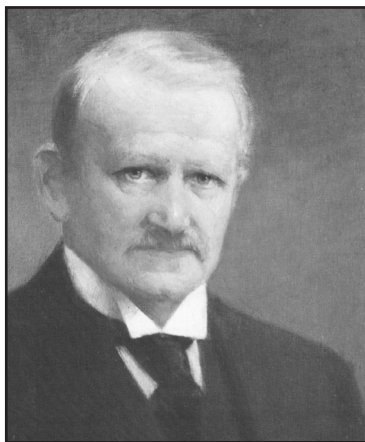


Figure 7.13.5 - Hans Goldschmidt (1861-1923)

THE METAL AND ITS COMPOUNDS

At room temperature chromium is resistant to ordinary corrosive agents, which explains its use as an electroplated protective coating. It dissolves in nonoxidizing mineral acids, such as hydrochloric and sulfuric acids, but not in cold aqua regia or nitric acid, which passivate the metal. Stainless steels account for most of chromium consumption.

Chromium chemicals are used in the manufacture pigments for use in paints, leather tanning, and others. Chromite is used in the refractory industry.



Figure 7.13.6 -
Nichrome wire

Nichrome contains 80% Ni and 20% Cr used as a resistance wire due to its resistance to oxidation and stability at high temperatures; melting point 1,400°C (Figure 7.13.6). Typically, it is wound in coils and when current is passed through it produces heat.

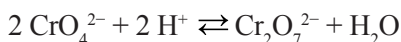
Chromite ores are classified into three grades (Table 7.13.1):

- *Metallurgical.* Ore with a high chromium content (minimum 68 % chromium) and the chromium/iron ratio must not be less than 2.8/1, will be suitable for the manufacture of ferrochrome alloy or chromium metal.
- *Refractory.* Ore with a high aluminum oxide (the sum Cr_2O_3 and Al_2O_3 is more than 59 %) would be suitable for the manufacture of refractories.
- *Chemical.* Low-grade chromites, that is those with high iron content, are mainly used for the manufacture of dichromates needed for the electroplating and tanning industry.

Table 7.13.1- Classification of chromite ores

Grade	Specifications	Use
Metallurgical	68 % Cr minimum Cr/Fe ratio < 2.8/1	Production of ferrochrome alloy or chromium metal
Refractory	$\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3 \geq 58 \%$	Manufacture of refractories
Chemical	Low-grade ores	Manufacture of dichromates for electroplating and tanning industry

Anhydrous chromium (III) chloride is violet and $\text{CrCl}_2 \cdot 6\text{H}_2\text{O}$ is green (Figure Figure 7.13.7). Chromium (VI) in potassium chromate is yellow and the dichromate is orange (Figure Figure 7.13.8). In aqueous solution, chromate and dichromate anions exist in a chemical equilibrium.



The chromate ion is the predominant species in alkaline solutions, and dichromate can become the predominant ion in acidic solutions. All hexavalent chromium compounds are toxic.

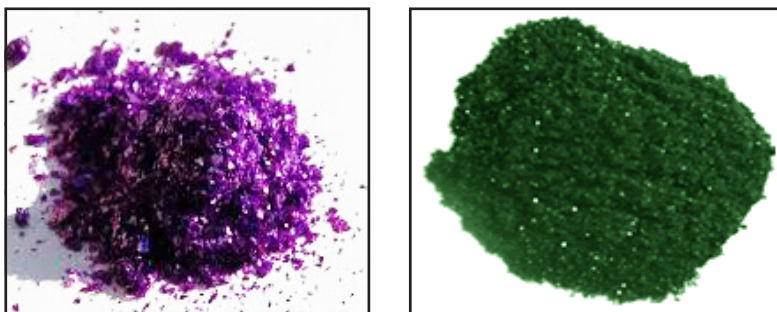
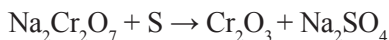
Figure 7.13.7 - Chromium III chlorides: anhydrous [left], $6\text{H}_2\text{O}$ [right]

Figure 7.13.8 - Potassium chromate (yellow) and dichromate (orange)

Chromium oxide, Cr_2O_3 , is a green pigment (Figure Figure 7.13.9). Its industrial production involves heating of solid sodium dichromate with sulfur:



The reaction is exothermic and after cooling the product is leached with water to remove sodium sulfate.



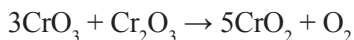
Figure 7.13.9 - Chromium oxide, Cr_2O_3 , green pigment



Figure 7.13.10 - Chromium (VI) trioxide, CrO_3

Chromium trioxide, CrO_3 , forms dark red crystals (Figure 7.13.10) which deliquesce in air, melts at 198°C and starts to decompose, giving off oxygen and brownish red vapours with a pungent smell forming chromium(III) oxide, Cr_2O_3 . Chromium(VI) oxide dissolves in water to form chromic acid:

Chromium(III) hydroxide prepared by precipitation with alkali from chromium(III) salt solutions have a composition corresponding to $\text{Cr}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$, or $\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3$. It is bright bluish green powder. Upon heating, dehydration occurs in steps. Chromium dioxide, CrO_2 , is a black magnetic solid its Curie temperature is 120°C , behaves as a metallic conductor. When heated above 350°C it decomposes into chromium(III) oxide and oxygen. It is prepared by decomposition of chromyl chloride, CrO_2Cl_2 , or by decomposing chromium trioxide under hydrothermal conditions:



Chromium dioxide crystals could be evenly dispersed in a magnetic coat-

ing and that led to low noise in audio tapes. Chromyl chloride, CrO_2Cl_2 , is an opaque dark red liquid (Figure Figure 7.13.11).

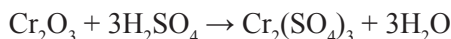


Figure 7.13.11 - Chromyl chloride, CrO_2Cl_2



Figure 7.13.12 - Chromium(III) sulfate, $\text{Cr}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$,

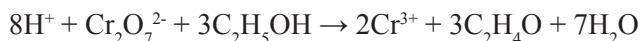
Chromium(III) sulfate (Figure 7.13.12), $\text{Cr}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$, is used in tanning of leather. It is formed by the reaction of chromium(III) oxide and sulfuric acid:



The anhydrous form is produced from chromate salts by reduction with sulfur dioxide.

Breath analysis test

The for the detection of ethanol involves the oxidation of alcohol in the breath of a person who has consumed alcohol, by acidic potassium dichromate and observing the change in the colour of the chromium ion Cr(VI) from orange to Cr(III) which is blue green colour:



Part 8 - Metals of the Nineteenth Century

8.1 Introduction

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NEW METAL DISCOVERY

Most of the metals were discovered in the nineteenth century because of great advancement in methods of chemical analysis and the discovery of new phenomena (Figure 8.1.1) (Table 8.1.1). The discoveries in that century started by the voltaic cell and ended by the discovery of radioactivity.

[illegible]

Ancient metals
Medieval metals
Eighteenth century metals
Nineteenth century metals

Figure 8.1.1 - Metals of the nineteenth century

Table 8.1.1 - Metals discovered and isolated in the nineteenth century

Year	Metal	Discoverer	Remarks
1801	Niobium Hatchett	Hatchett	Isolated by Blomstrand in 1864 by reduction of NbCl_5 with H^2 and by Moissan in 1901 by carbon reduction of Nb205 in an electric furnace
1802	Tantalum	Ekeberg	Discovered in Sweden
1803	Iridium Osmium	Tennnat	Discovered in England
	Palladium Rhodium	Wollaston	Discovered in England
1807	Potassium Sodium	Davy	Discovered in England
1808	Boron	Gay-Lussac, Thenard, Davy	Discovered in France and England
	Barium	Davy	Discovered in England
	Calcium	Davy	Discovered in England
	Magnesium	Davy	Discovered in England
	Strontium	Davy	Discovered in England
1814	Cerium	Berzelius	Isolated by Hillebrand and Norton in 1895
1817	Lithium	Arfwedson	Isolated by Davy in minute amounts, but in pure form by Arfwedson
	Cadmium	Stromeyer	Discovered in Germany
	Selenium	Berzelius	Discovered in Sweden
1823	Silicon	Berzelius	Discovered in Sweden
1827	Aluminum	Wöhler	Discovered in Germany
1828	Thorium	Berzelius	Discovered in Sweden
1830	Vanadium	Sofstrom	Isolated by Roscoe in 1869 by H_2 reduction of VCl_2 . Prepared by Marden and Rich in 1927 [purity 99.9%] by reduction of the oxide with Ca
1839	Lanthanum	Mosander	Discovered in Sweden
1843	Erbium	Mosander	Discovered in Sweden
	Terbium	Mosander	Discovered in Sweden
1844	Ruthenium	Klaus	Discovered in Russia
1860	Cesium	Bunsen and Kirchhoff	Discovered in Prussia
1861	Rubidium	Bunsen and Kirchhoff	Discovered in Prussia
	Thallium	Crookes	Discovered in England

1863	Indium	Reich and Richter	
1875	Gallium	de Boisbaudran	Discovered in France
1878	Ytterbium	Marignac	Discovered in France
1879	Samarium	de Boisbaudran	Discovered in France
	Scandium	Nilson	Discovered in Sweden
	Holmium	Cleve	Discovered in Sweden
	Thulium	Cleve	Discovered in Sweden
1880	Gadolinium	Marignac	Discovered in France
1885	Praseodymium	Auer von Welsbach	Discovered in Austria
	Neodymium	Auer von Welsbach	Discovered in Austria
1886	Dysprosium	de Boisbaudran	Discovered in France
	Germanium	Winkler	Discovered in Prussia
1896	Europium	Demarçay	Discovered in France
1898	Polonium	Curie	Isolated by Mme. Curie and Debierne in 1910
	Radium	Curie	Isolated by Mme. Curie and Debierne in 1910
1899	Actinium	Debierne	Isolated by Giesel in 1902

THE BEGINNING OF THE CENTURY



Figure 8.1.2 - Alessandro Volta (1745-1827)

The nineteenth century began with the discovery of electric current by Alessandro Volta (1745-1827) (Figure 8.1.2). The construction of voltaic cells was a great tool for chemists to use electricity to decompose compounds. Humphry Davy (1778-1829) (Figure 8.1.3) was instrumental in isolating sodium and potassium at the Royal Institution using the enormous 600-plate voltaic batteries. The alkali metals were used later by chemists to liberate other metals from their compounds like aluminum.



Figure 8.1.3 - Davy using Volta cells to isolate sodium and potassium

THE MIDDLE OF THE CENTURY

Flame tests

It was Robert Bunsen (1811-1899) (Figure 8.1.4) at the University of Heidelberg, who paved the way for the great discoveries in the nineteenth century with his invention of the burner in 1852 that carries his name and is found today in most chemical laboratories (Figure 8.1.5). This burner permitted higher temperature in the laboratory. Before this burner the flame of a candle or from alcohol was used. The Bunsen burner flame permitted performing the flame tests and later spectroscopic analysis.

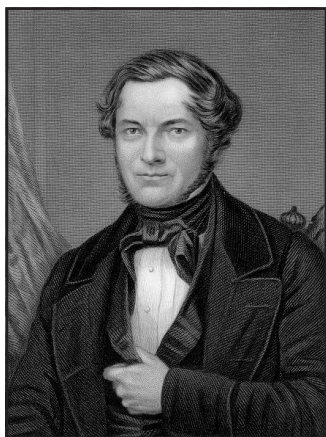


Figure 8.1.4 - Robert Bunsen
(1811-1899)

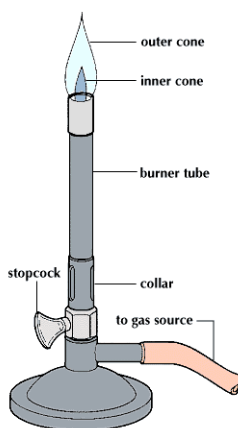


Figure 8.1.5 - Bunsen
burner

Bunsen showed that several distinct zones exist in the flame, each of which can be utilized for producing particular reaction:

- A comparatively cold zone at the base of the flame, which serves for the volatilization of salts in order to obtain flame colorations.
- A reducing flame at the top of the dark zone.
- The upper oxidizing flame at the extreme tip of the flame.

A flame test was an analytic procedure used to detect the presence of certain elements, based on the color of flames. The test involves introducing a sample to a hot, non-luminous flame, and observing the color of the flame that results. Samples are usually held on a platinum wire cleaned with acid to remove traces of previous samples. The compound is usually made into a paste with concentrated hydrochloric acid, as metal halides, being volatile, give better results. Examples of coloured flames are shown in Figure 8.1.6.

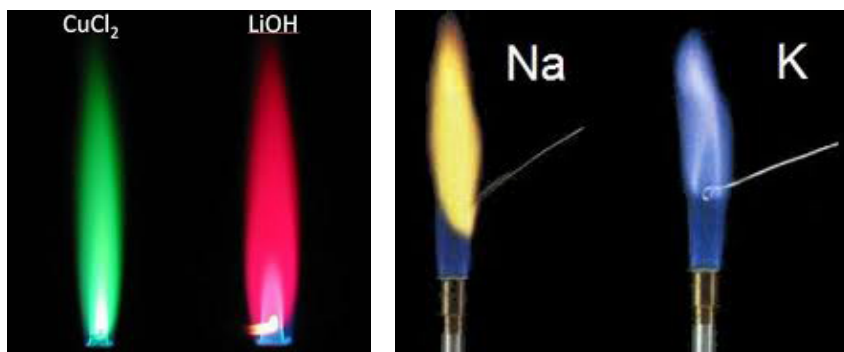


Figure 8.1.6 - Examples of coloured flames

The spectroscope

In collaboration with his colleague the physics professor Gustav Kirchhoff (1824-1887) (Figure 8.1.7) Bunsen refined the technique of studying the flame coloration by introducing a set of lenses and prisms which led

to the invention of the spectroscope in 1859 (Figures 8.1.8-8.1.11). In 1866 Bunsen published his book *Flammenreaktionen*, i.e., *Flame Reactions*, a second edition appeared in 1886.



Figure 8.1.7 - Gustav Kirchhoff (1824-1887)



Figure 8.1.9 - The house where spectroscopic analysis was discovered in Heidelberg

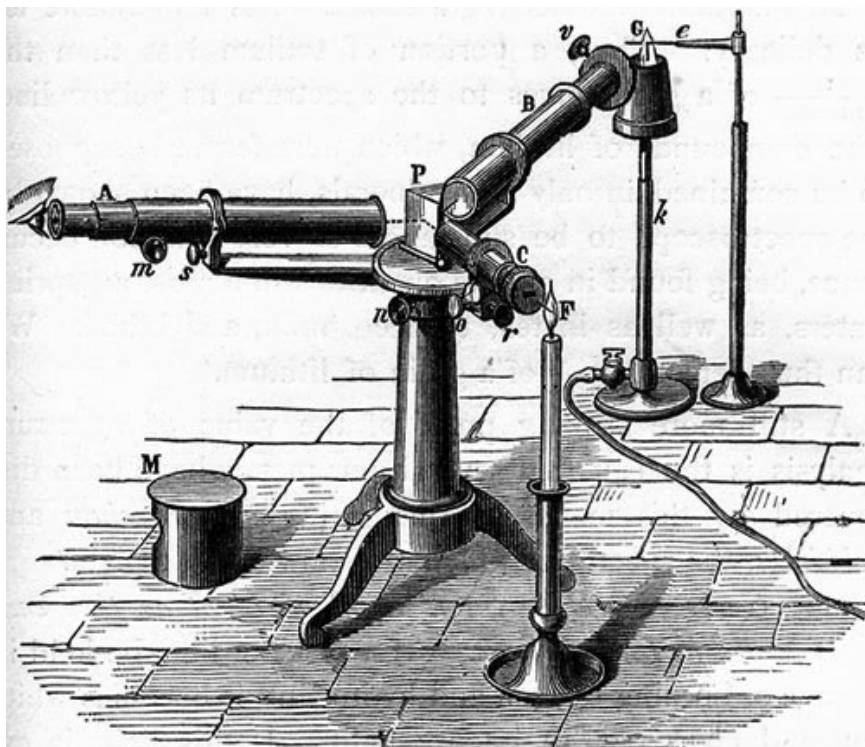


Figure 8.1.8 - A first spectroscope

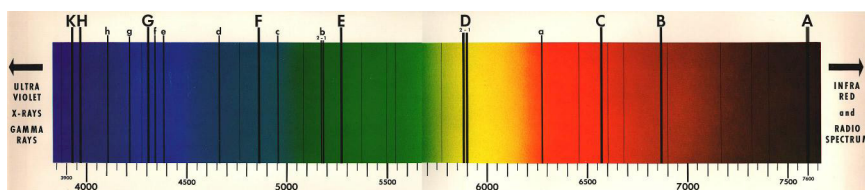


Figure 8.1.10 - Spectrum of the Sun

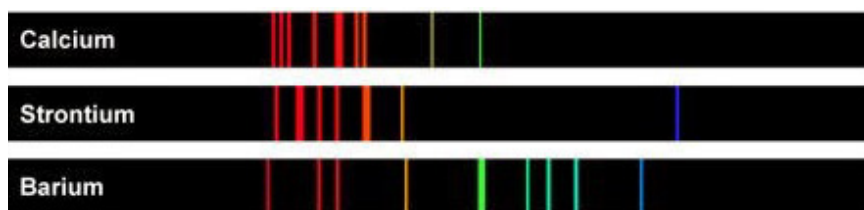


Figure 8.1.11- Spectra of calcium, strontium, and barium

The method proved to be so successful that immediately after putting it into use, the discoverers were able to find two new elements rubidium and cesium. Students visited Bunsen from all over Europe to learn this technique and chemists brought samples there to be analyzed. This method of analysis was found to be a useful tool in the discovery of new elements.

Thallium was discovered by William Crookes in England (1861), indium by Ferdinand Reich and Hieronymus Richter in Freiberg (1863), helium in the sun by the French astronomer Pierre Jules Janssen (1868), then gallium by Paul-Emile Lecoq de Boibaudran in France (1875). The Swiss chemist of French origin Jean Charles de Marignac (1812-1894), who went to the École Polytechnique and the École des Mines in Paris, was the first to apply spectroscopic analysis to rare earths minerals.

Discovery of helium

A great achievement of spectroscopic analysis was the discovery of helium on the sun before it was found on the earth. Pierre-Jules-César Janssen (1824-1907) (Figure 8.1.12) a French astronomer, noticed a yellow line in the sun's spectrum while studying a total solar eclipse in 1868. Sir Norman Lockyer, an English astronomer, realized that this line could not be produced by any element known at the time. It was hypothesized that

a new element on the sun was responsible for this yellow emission. This unknown element was named helium by Lockyer from the Latin helios meaning Sun.

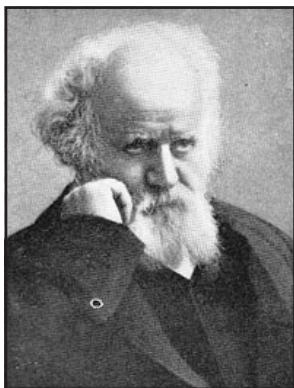


Figure 8.1.12 - Pierre-Jules-César Janssen (1824-1907)

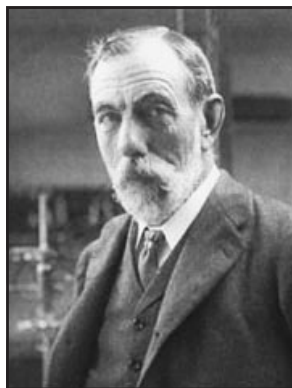


Figure 8.1.13 - William Ramsay (1852-1916)

To find helium on earth Sir William Ramsay (1852-1916) (Figure 8.1.13), a Scottish chemist, conducted in 1895 an experiment with the mineral cleveite containing uranium. He dissolved the mineral in mineral acids and collected the gases that were produced. He then sent a sample of these gases to two scientists, Lockyer and Sir William Crookes, who were able to identify the helium within it. Two Swedish chemists, Nils Langlet and Per Theodor Cleve, independently found helium in cleveite at about the same time as Ramsay.

It was Ernest Rutherford (1871-1937) who proved that helium is produced by alpha decay (Figure 8.1.14). An alpha particle can become a helium atom once it captures two electrons from its surroundings. This newly formed helium can eventually work its way to the atmosphere through cracks in the crust. Helium is commercially recovered from natural gas deposits, mostly from Texas, Oklahoma and Kansas.

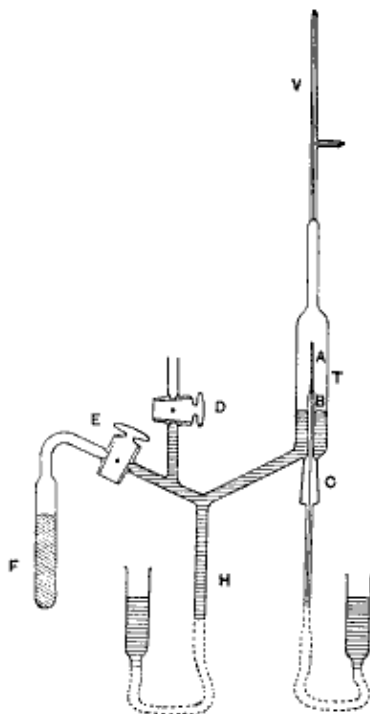


Figure 8.1.14 - Apparatus used by Rutherford and his workers to collect alpha particles formed from radioactive decay of radium and by means of spectroscopic analysis it proved to be helium

Foundation of the atomic theory

John Dalton (1766-1844) (Figure 8.1.15) the English teacher of mathematics and physics at New College in Manchester showed in his book *New System of Chemical Philosophy* published in 1810 how his atomic theory can be used to explain the laws which govern chemical combination. He assigned a weight to each atom.

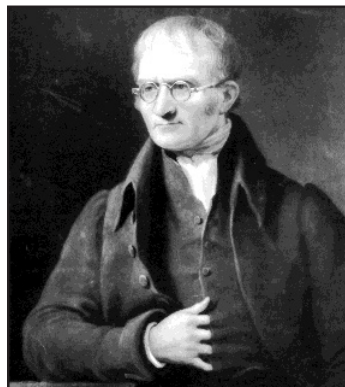


Figure 8.1.15 - John Dalton (1766-1844)

The Periodic Table

In 1869 Mendeleev (1834-1907) (Figure 8.1.16) arranged elements according to their atomic weights and published his Periodic Table as a means to organize the 62 elements then known. He also predicted the future discovery of some elements that were not yet known to chemists. Although helium was discovered spectroscopically in the spectrum of the Sun one year before Mendeleev published his Table, it was not included in the Table apparently because the discovery was still doubtful (Figure 8.1.17).

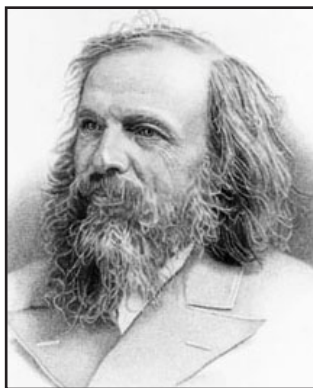


Figure 8.1.16 - Mendeleev (1834-1907)

																H			
Li	Be													B	C	N	O	F	
Na	Mg	Al												Si	P	S	Cl		
K	Ca		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			As	Se	Br			
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I			
Cs	Ba	*La		Ta	W		Os	Ir	Pt	Au	Hg	Tl	Pb	Bi					
			Th		U														
*	Ce											Er							

Figure 8.1.17 - Mendeleev's Periodic Table of 1869 in modern form. Shaded areas were predicted elements, empty spaces were unknown

In the period 1868-1897, three of the predicted elements were discovered namely gallium, scandium, and germanium. More rare earths also became known that created a problem for locating them in the Periodic Table. This was solved by the Czech chemist Bohuslav Brunauer (1855-1935)

who proposed that all the rare earths be located in the same square with lanthanum (Figure 8.1.18).

																H	He														
Li	Be											B	C	N	O	F															
Na	Mg	Al												Si	P	S	Cl														
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	Ga	As	Se	Br															
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I															
Cs	Ba	*La		Ta	W		Os	Ir	Pt	Au	Hg	Tl	Pb	Bi																	
			Th		U																										
* <table><tr><td>Ce</td><td>Pr</td><td>Nd</td><td></td><td>Sm</td><td>Eu</td><td>Gd</td><td>Tb</td><td>Dy</td><td>Ho</td><td>Er</td><td>Tm</td><td>Yb</td><td></td></tr></table>																		Ce	Pr	Nd		Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	
Ce	Pr	Nd		Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb																			

Figure 8.1.18 - The Periodic Table after the fulfilment of some of Mendeleev's prediction

THE END OF THE CENTURY

X-rays and radioactivity

In 1895 x-rays were discovered by Wilhelm Conrad Roentgen (1845-1923) (Figure 8.1.19) followed by the discovery of radioactivity in 1898 by Antoine Henri Becquerel (1852-1908) (Figure 8.1.20) which was responsible for the discovery of polonium and radium shortly afterwards by Marie Curie (1867-1934) (Figure 8.1.21).

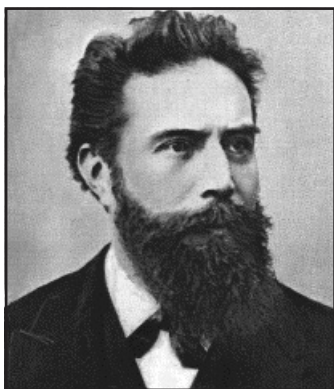


Figure 8.1.19 - Wilhelm Conrad
Roentgen (1845-1923)

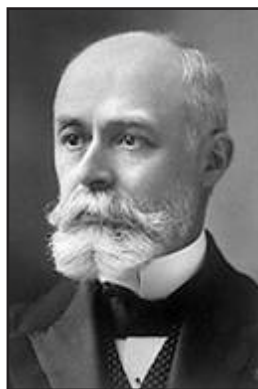


Figure 8.1.20 - Antoine Henri Becquerel (1852-1908)

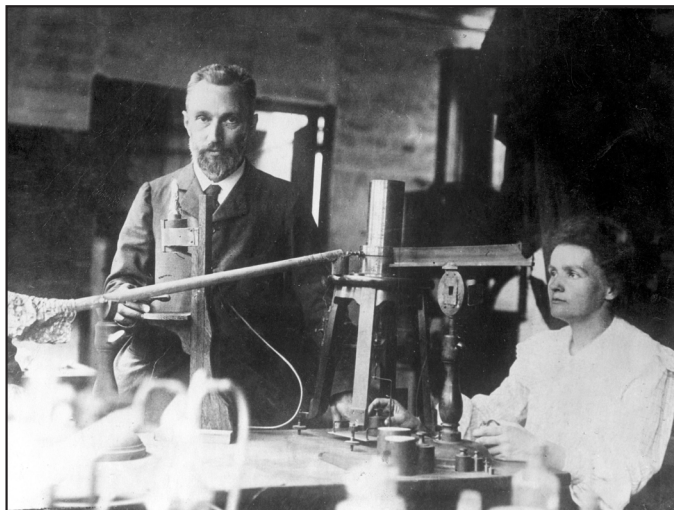


Figure 8.1.21 - Pierre Curie (1859-1906) and Marie Curie (1867-1934) making a measurement of a radioactive substance

The beginning of radiochemistry

The researches of Marie Curie and her husband Pierre Curie (1859-1906) turned from physics to chemistry. To isolate a postulated new element Marie Curie had to follow the scheme of analysis devised by Fresenius in 1841: dissolving the sample in nitric acid, passing H_2S in solution, etc., and measuring the radioactivity of the precipitate.

Radiochemistry was one of the most difficult tasks in chemistry. The measuring devices were primitive, scientists were dealing with un-weighable amounts, it was not known at the time that a radioactive element is generated by the decay of another, that an element may exist in different isotopes, that a substance may gradually lose its activity during the experiment or it may disappear completely because of its short half life, that radioactive gases may form during the decay, etc. Half lives varied from a fraction of a second to millions of years and became the criterion to identify a new radioactive substance. Confusion and controversies were evident. Moreover, health issues from radioactive substances were not known at that time.

8.2¹ Niobium and Tantalum

Introduction	671	Recovery	679
Discovery and isolation	672	Production	680
Occurrence and extraction	676	Uses	680
Niobium	676	Tantalum	680
Pyrochlore	676	Uses	681
Columbite	678		

INTRODUCTION

The close similarity between niobium and tantalum and their occurrence together in minerals caused confusion among chemists for more than half a century. Starting from 1801 when the announcement of discovery of a new metal till finally the two were separated and identified in 1866. Tantalum is less abundant than niobium and both having the same ionic radius due to the lanthanide contraction (Table 8.2.1).

Table 8.2.1 - Comparison between niobium and tantalum

	Niobium	Tantalum
Atomic number	41	73
Atomic weight	92.91	180.95
Density, g/cm³	8.57	16.6
Relative abundance, %	2.4 x10 ⁻³	2.1 x10 ⁻⁴
Crystal structure	Body-centered cubic	Body-centered cubic
Atomic radius, Å	1.43	1.43
Melting point, °C	4927	2996
Boiling point, °C	2468	5425

¹See also F. Habashi, “A History of Niobium”, Metall 61(1–2), 54–57 (2007)

DISCOVERY AND ISOLATION

In 1801 in London, the English chemist Charles Hatchett (1765-1847) (Figure 8.2.1) announced the discovery of a new earth which implied the discovery of a new metal. He called it columbium because he found it in a specimen of a heavy black mineral called columbite from New England in the North American colony, in honor of Christopher Columbus. The mineral was supplied to the British Museum by the Governor of Connecticut, John Winthrop, who was a manufacturing chemist, physician, and mineral collector.

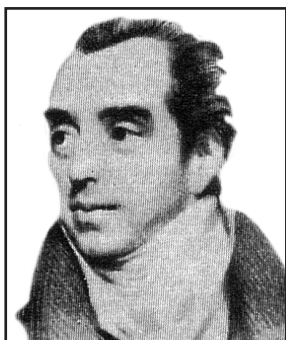


Figure 8.2.1 - Charles Hatchett
(1765-1847)



Figure 8.2.2 - Anders Gustaf Ekeberg
(1767-1813)

A year later in 1802, the Swedish chemist Anders Gustaf Ekeberg (1767-1813) (Figure 8.2.2) in Uppsala analyzed a specimen of a mineral from Kimito in Finland and another from Ytterby quarry in Sweden and found that both contain a hitherto unknown metal which he called tantalum because it had been a tantalizing task to trace it down.

In 1809, another English chemist William H. Wollaston (1766-1828) (Figure 8.2.3) analyzed the same mineral studied by Hatchett and came to the conclusion that Hatchett's columbium must be the same as Ekeberg's tantalum. This erroneous opinion was held by the greatest chemists in Europe for forty years until proved wrong by Heinrich Rose (1795-1864) (Figure 8.2.4) in Germany who in 1844 analyzed a large number of minerals from America and Europe and came to the conclusion that what was

thought to be an oxide of tantalum is in fact the oxide of new metal which he called niobium.



Figure 8.2.3 - William H. Wollaston
(1766-1828)

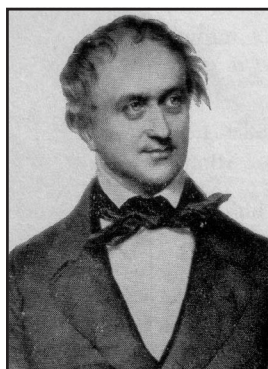


Figure 8.2.4 - Heinrich Rose
(1795-1864)

It was the Swiss chemist Jean-Charles Marignac (1817-1894) (Figure 8.2.5) in 1866 who was able to make the separation of niobium oxide from tantalum oxide by utilizing differences in solubilities of their complex fluorides and have resolved the confusion regarding the two metals (Figure 8.2.6). He was then able to isolate tantalum after repeated crystallization of double fluorides followed by reduction. Today, solvent extraction methods are used to separate niobium from tantalum, for example, using Hexone.

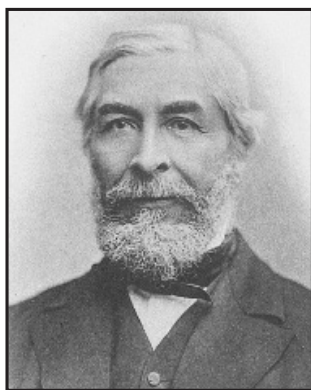


Figure 8.2.5 - Jean-Charles Marignac
(1817-1894)

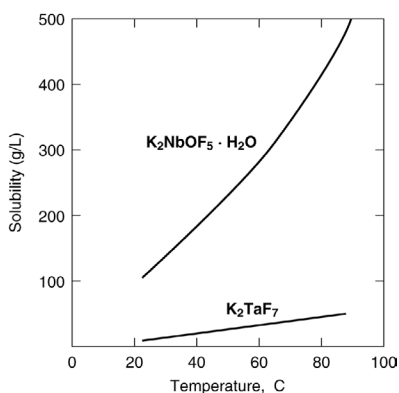


Figure 8.2.6 - Solubilities of complex fluorides of niobium and tantalum

Niobium was isolated in 1864 by the Swedish chemist Christian Wilhelm Blomstrand (1826-1897) (Figure 8.2.7) by reduction of NbCl_5 in hydrogen but the metal still contained tantalum. The first pure samples of both niobium and tantalum were not made until 1907 when the German chemist Werner von Bolton (1868-1912) (Figure 8.2.8) at Siemens - Halske laboratories in Berlin reduced K_2NbOF_5 and K_2TaOF_5 with aluminum powder. It had taken over 100 years to go from the discovery to the isolation of niobium.

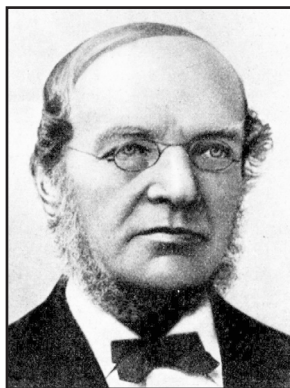


Figure 8.2.7 - Christian Wilhelm Blomstrand (1826-1897)



Figure 8.2.8 - Werner von Bolton (1868-1912)

In the United States the metal discovered by Hatchett used to be known as columbium, but in Europe the name niobium given by Rose is used. The *International Union of Pure and Applied Chemistry* recommended in 1949 the use of the name niobium. In mythology Niobe was the daughter of Tantalus (Figure 8.2.9). Tantalum was named from Greek mythology after King Tantalus son of Zeus (Figure 8.2.10). The English verb to tantalize recalls the unsuccessful attempts of Tantalus that was so near and desirable. The discoverer found difficulty in dissolving the earth of that metal.



Figure 8.2.9 - One of the representations of Niobe



Figure 8.2.10 - One of the representations of Tantalus

OCCURRENCE AND EXTRACTION

Niobium and tantalum always occur together, in varying proportions, in the columbite-tantalite minerals of formula $(\text{Fe,Mn})\text{M}_2\text{O}_6$ ($\text{M} = \text{Nb,Ta}$), and in pyrochlore.

Alkali fusion followed by digestion with acids is used to dissolve out impurities in the minerals leaving Nb and Ta un-dissolved. The problem is then to separate the two similar elements. M.C. Marignac developed a method in 1866, which remained in use for a century. He treated the mixture with dilute hydrofluoric acid: tantalum forms the less soluble K_2TaF_7 , and can be separated from the more soluble $\text{K}_3\text{NbOF}_5 \cdot 3\text{H}_2\text{O}$.

The modern process uses solvent extraction to separate the metals. Tantalum is extracted from dilute HF solution by methylethylketone (MEK) and increasing the acidity allows niobium to be extracted separately. Addition of water strips out the metals from MEK solution. Both metals are then converted to their pentoxides, M_2O_5 , which are reduced with either sodium or carbon to the metals. The carbon reduction is done at over 2000°C in vacuum and the product is vacuum refined by electron beam melting. An alternative process uses the electrolysis of molten fluorides.

NIOBIUM

Pyrochlore

The most important niobium mineral is pyrochlore, $(\text{Ca,Na})_{2-m}\text{Nb}_2\text{O}_6(\text{O,OH,F})_{1-n} \cdot x\text{H}_2\text{O}$, discovered in 1826 (Figure 8.2.11). The lattice positions of Na and Ca can also be occupied by Ba, Sr, rare earths, Th, and U. The latter two elements are responsible for the radioactivity of some pyrochlore concentrates. The name comes from the Greek $\pi\upsilon\rho$, fire, and $\chi\lambda\omega\rho\acute{o}\varsigma$, green in allusion to the fact that the mineral usually turns green on ignition.



Figure 8.2.11 - Museum sample of pyrochlore

Two types of niobium ore deposits are known. The Brazilian deposits at Araxá and Catalão both in Minas Gerais State (Figure 8.2.12), the niobium content of the carbonate minerals has been considerably enriched by weathering. The ore contains about 3% Nb_2O_5 , 46% Fe_2O_3 , 17-18% BaO as barite, and 1.5% P as apatite. The world's largest deposit is located in Araxá and is owned by Companhia Brasileira de Metalurgia e Mineração. The reserves are about 460 million tons. The mining of weathered ore, running between 2.5 and 3.0% Nb_2O_5 , is conducted by simple open pit mining without the need for drilling and explosives.



Figure 8.2.12 - Location of Araxá

The other pyrochlore mine in Brazil is owned and operated by Anglo American Brasil Mineração Catalão and contains 18 million tonnes at 1.34% niobium oxide.

The Canadian deposit in Quebec Province at Saint Honoré (Figure 8.2.13) and Oka near Montreal. The calciopyrochlore is interstratified in dolomite. The ore contains 0.5-0.7% Nb_2O_5 .



Figure 8.2.13 - Location of Saint Honoré north of Chicoutimi, Quebec

The pyrochlore mineral is processed by primarily physical processing technology to give a concentrate ranging from 55 to about 60% niobium oxide. These three companies produce about 85% of the world's demand for niobium products, with most of that output being in the form of ferro-niobium with a nominal 60% niobium oxide content, for making high-strength, low-alloy steel. Metallic niobium is produced at Araxá.

Columbite

The second most important niobium mineral is columbite, $(\text{Fe}, \text{Mn})(\text{Nb}, \text{Ta})_2\text{O}_6$, in which niobium is always present with tantalum. These ores are referred to as columbites if the Nb_2O_5 content is greater than that of Ta_2O_5 , otherwise as tantalites. Columbites and tantalites contain at least 60% combined pentoxides. These minerals occur as primary deposits in granites and pegmatites, or in alluvial secondary deposits. It was in these minerals that both niobium and tantalum were discovered. An important potential reserve lies in a belt stretching from China to Indonesia via Thailand and Malaysia, and consists of cassiterite, SnO_2 , that contains some tantalum and niobium. During tin smelting, the tantalum and niobium become concentrated in the slag.

Recovery

Two separate processing schemes are utilized for niobium production. Those companies that mine pyrochlore convert the niobium oxide units into HSLA ferro-niobium through the aluminothermic reduction process or by reduction in an electric arc furnace. CBMM has installed capacity for the production of a high purity oxide that can be used to produce vacuum grade ferro- and nickel-niobium as well as niobium metal ingots via electron beam refining.

The use of columbite and tantalum-bearing ores, such as tantalite, as feedstocks results in the necessity to process these materials chemically as described in the tantalum section. The purified niobium-containing process stream is generally converted to niobium hydroxide by the introduction of ammonia, followed by washing, filtration, and calcining to the oxide. Purities exceeding 99.99% can be achieved.

Niobium oxide (Nb_2O_5) is generally the starting chemical for the production of other compounds, such as niobium chloride (NbCl_5), niobium carbide (NbC), or lithium niobate (LiNbO_3). Niobium metal is produced by the aluminothermic reduction of the oxide followed by electron beam refining. Niobium powders can be produced by the reduction of potassium niobium heptafluoride (K_2NbF_7) with sodium, or by the reduction of niobium oxide with magnesium.

The various metallurgical products are generally produced from electron beam or vacuum arc melted niobium ingot. Double and triple melt ingots achieve a very high level of purification. Ingots are used to produce niobium alloys such as niobium-1% zirconium, niobium-titanium, C-103, Inconels, and others.

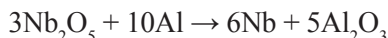
Several capacitor manufacturers are developing capacitors using niobium metal powder or niobium oxide, and these models are gradually being brought to the market.

Uses

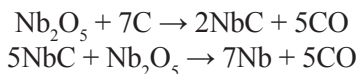
The major use of niobium is as an alloying element for steel. Because of its lower density and low thermal neutron cross section compared to other refractory metals, niobium is useful in atomic reactors. At ordinary temperatures niobium will resist attack by all mineral acids, with the exception of hydrofluoric, and it is not affected by mixed acids such as aqua regia. In 1999 the world mine production of niobium was 18,500 tons with Brazil (16,000 tons) and Canada (2,300 tons) being the major sources. World mine production of tantalum is much smaller at 473 tons in 1999, Australia (350 tons), Brazil (60 tons) and Canada (60 tons) being the major sources.

The metal and its compounds

The metal is produced by reduction of its oxide with aluminum:



An alternative route involves carbothermic reduction in two stages - the first stage by heating under vacuum at 1800°C:



Niobium pentoxide, Nb_2O_5 , is a colorless powder that can only be dissolved by fusion with NaOH or in hydrofluoric acid. It is prepared by hydrolyzing niobium pentachloride or by precipitation from hydrofluoric acid solutions with alkali-metal hydroxides.

Niobium pentachloride, NbCl_5 , is produced exclusively by chlorination of ferroniobium, niobium metal, or niobium scrap. It forms hygroscopic yellow crystals that react with water to form NbOCl_3 or $\text{Nb}_2\text{O}_5 \cdot x \text{H}_2\text{O}$. Pure niobium pentachloride is used for large scale production of niobium pentoxide and niobium metal.

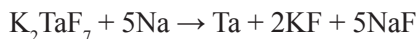
Niobium oxychloride, NbOCl_3 , is a colorless, crystalline compound that

sublimes at 400°C and partly decomposes into niobium pentoxide and niobium pentachloride on further heating.

TANTALUM

Tantalum is closely related to niobium with which they are associated in their ores that are mainly complex oxides, $(\text{Nb,Ta})_2\text{O}_5$.

Tantalum and niobium are closely associated because of the lanthanide contraction. Like niobium, tantalum has principal oxidation states +2 and +5. Below 100°C, the metal is extremely resistant to corrosion by most organic and inorganic acids, with the exception of hydrofluoric acid. This is due to a dense adherent film of tantalum oxide, a characteristic which is utilized in the manufacture of electrolytic capacitors. Metallic tantalum is produced almost exclusively by reduction of potassium heptafluorotantalate with sodium:



Tantalum pentoxide, Ta_2O_5 , occurs in two thermodynamically stable modifications. The transition temperature from the orthorhombic modification to the tetragonal a modification is ca. 1360°C. Tantalum pentafluoride, TaF_5 , is produced by passing fluorine over metallic tantalum, or from tantalum chloride by adding anhydrous hydrogen fluoride. Both tantalum pentafluoride and niobium pentafluoride are used in the petrochemical industry as catalysts.

Potassium tantalum fluoride, K_2TaF_7 , is an industrially important intermediate in the production of tantalum metal. It crystallizes in colorless, rhombic needles when K^+ ions are added to solutions of tantalum in hydrofluoric acid from the extraction process. Its solubility in hydrofluoric acid solution decreases from 60 g/100 ml at the boiling point to < 0.5 g/100 ml at room temperature. As the corresponding stable niobium salt K_2NbOF_5 is significantly more soluble, tantalum can also be separated from niobium

by fractional crystallization (Marignac process).

Tantalum pentachloride, TaCl_5 , forms colorless, hygroscopic, needle-shaped crystals produced on an industrial scale by chlorination of metallic tantalum, ferrotantalum, or tantalum metal scrap. It is soluble in absolute alcohol, with formation of the corresponding alkoxide. Ultrafine tantalum oxide powder can be produced by hydrolysis of this alkoxide. Tantalum pentachloride and tantalum alkoxides are suitable for use in the chemical vapour deposition of tantalum metal or tantalum oxide.

USES

The metal powder is used in the production of electronic components, mainly capacitors and some high-power resistors. Tantalum electrolytic capacitors exploit the tendency of tantalum to form a protective oxide surface layer. Because the dielectric layer can be very thin a high capacitance can be achieved in a small volume. Used for portable telephones, computers, and automotive electronics. Tantalum is also used to produce a variety of alloys that have high melting points. It can be drawn into fine wires or filaments. It is widely used in making surgical instruments and implants. Tantalum is an ideal metal for chemical reaction vessels and pipes for corrosive liquids.

8.3 Discoveries by Humphry Davy

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INTRODUCTION

Humphry Davy (1778-1829) (Figure 8.3.1) discovered sodium, potassium, calcium, magnesium, strontium, and barium. He was born in Penzance, Cornwall in the southwestern corner of England (Figure 8.3.2), apprenticed at 16 to an apothecary-surgeon, Davy taught himself chemistry by studying the English translation of Lavoisier's *Elements of Chemistry*. At 20, he found employment at the Pneumatic Institute at Clifton near Bristol, founded to investigate the use of « factitious airs » (gases) to treat diseases. Here Davy performed analyses of the oxides of nitrogen. His investigations of the physiological effect of nitrous oxide attracted widespread popular and scientific attention.



Figure 8.3.1 - Humphry Davy
(1778-1829)

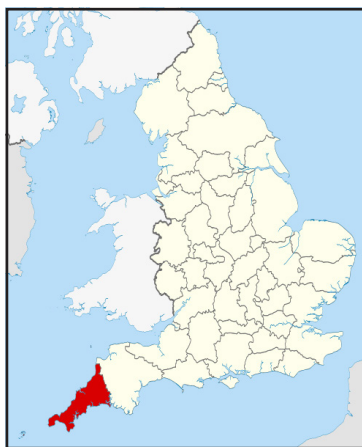


Figure 8.3.2 - Cornwall

In 1801, Davy was appointed assistant lecturer in chemistry and director of the laboratory of the Royal Institution. In 1812, Davy married a wealthy widow. Few months later, he published his *Elements of Chemical Philosophy*. He then went to a tour of Europe, which lasted 2 ½ years. While in Italy, Davy showed that diamond is pure carbon. He made use of the great burning glass of the Academia del Cimento in Florence to burn the diamond in oxygen and show that it had the same composition as charcoal. On his return from the Continent he was asked by the authorities to study mine safety. In 1816 he invented the miner's safety lamp. In 1820, Davy was elected president of the Royal Society at the age of 41. He resigned, however, that position in 1827 because of his weak health he died at the young age of 51.

The connection between agriculture and chemistry, was extremely important in the early founding years of the Royal Institution, and indeed was one of the reasons that Davy was appointed professor of chemistry there. Davy had been attempting to find chemical means of improving agriculture for the landowners who ran the Royal Institution at that time. He lectured on agricultural chemistry for ten years which resulted in his publication of *Elements of Agricultural Chemistry* in 1813.

Davy and Volta's discovery

Volta's discovery of the chemical source of generating electric current was immediately exploited in London at the Royal Institution (Figure 8.3.3). A very large battery was constructed to decompose the caustic alkalis. He obtained the metal from potash, he named it potassium. Davy then attempt and named to decompose caustic soda by a similar method. Few days later, he announced the discovery of sodium. He later isolated calcium strontium, and barium.

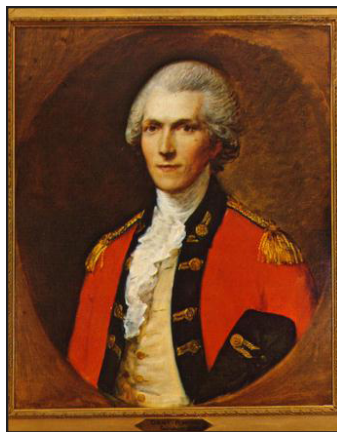


Figure 8.3.4 - Count Rumford

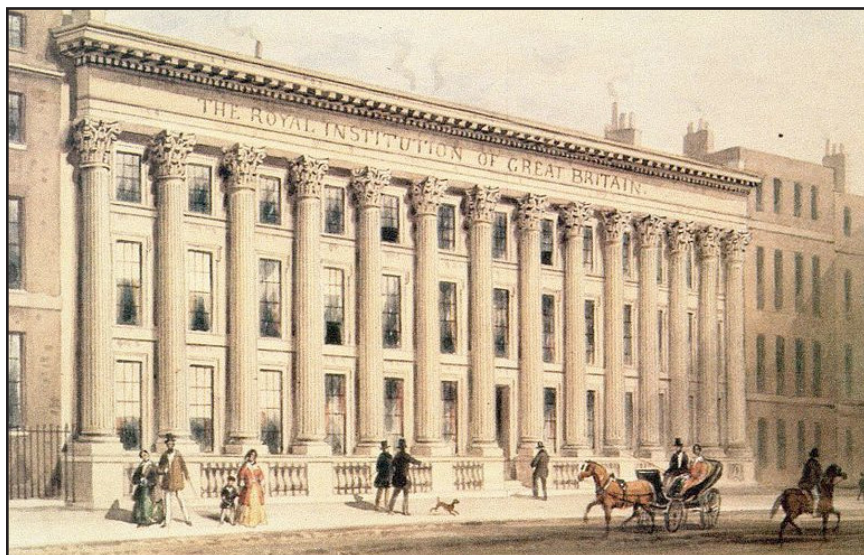


Figure 8.3.3 - Royal Institution, 21 Abermale street in London

The Royal Institution of Great Britain was founded in 1799 to apply science « to the common purposes of life ». It was proposed by American-born Benjamin Thompson (1753-1814), better known as Count Rumford (Figure 8.3.4) who was philanthropic, a brilliant social reformer, a superb organizer, and an exceptionally innovative scientist. At that time, Britain was rapidly industrializing, and from 1803 to 1815 was involved in the Napoleonic Wars against France. British trade was badly affected by the Napoleonic blockade of Britain, and science was seen by landowners as being one way of increasing agricultural production.

Boron

Davy succeeded in decomposing borax by potassium and liberating a new element which he called « boracium »; it is now called boron.

In 1801, while experimenting with the new science of electricity, Davy discovered that an arc could be created with a high-voltage electric circuit by bringing the two terminals near each other. This arc, which cast a bright light and generated considerable heat, could be struck and maintained at

will, and its length and intensity could be varied within limits determined by the circuit voltage and by the type of terminals.

Davy's isolation of the alkali and alkaline earth metals had important consequence to metallurgy. Once these metals became available they were used to liberate other metals from their compounds, e.g., sodium liberated titanium from TiCl_4 , magnesium from UF_4 , etc.

Arc welding

In 1801, while experimenting with the new science of electricity, Davy discovered that an arc could be created with a high-voltage electric circuit by bringing the two terminals near each other. This arc, which cast a bright light and generated considerable heat, could be struck and maintained at will, and its length and intensity could be varied within limits determined by the circuit voltage and by the type of terminals. Davy demonstrated the arc at the Royal Institution in 1808, where his discovery aroused great interest. However, for many years it remained a scientific curiosity as no one found a practical use for it.

Probably the first attempt to use the intense heat of the carbon arc for welding was made in 1881, when Auguste De Meritens used a carbon electrode to arc-weld lead storage-battery plates. In this experiment, he connected the work to the positive pole of a current source, and attached a carbon rod to the negative pole in such a manner that the distance between the rod and plate could be controlled. Some of the heat was lost to the surrounding air, but enough reached the plate to fuse the lead and join the parts. In 1889, a Russian, N.G. Slavianoff, announced a process in which the carbon rod was replaced by a metal rod. After an arc was struck, the rod gradually melted and added fused metal to the weld. The process represented a giant step forward, because the metal electrode not only supplied the fusing heat, but also added filler metal necessary for the joint. Despite this advance, commercial applications in the following years grew slowly because satisfactory metal electrodes were not available. It was not until 1912, when a heavily covered electrode that industry had an elec-

trode capable of producing weld metal with good mechanical properties. These early covered electrodes were slow in gaining acceptance because of their cost.

Corrosion research

At the request of the British Admiralty, Davy in 1824 was the first to propose the principle of cathodic protection when he initiated the use of zinc to control the corrosion of ship's hulls. At that time ships were made of wood and covered by sheets of copper.

Davy legacy

Davy is honoured by statue in his home town (Figure 8.3.5) and a medal (Figure 8.3.6) by the Royal Society in London.



Figure 8.3.5 - Davy statue in his home town



Figure 8.3.6 - Davy medal

8.4 Discoveries by Davy:

Sodium and Potassium¹

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INTRODUCTION

Salt (sodium chloride) (Figures 8.4.1-8.4.2) was one of the earliest materials produced by man. Ancient Chinese documents showed illustrations of evaporating sea water to get salt. Rock salt deposits were also discovered and reached by wells. Natron (sodium carbonate) deposits were found in ancient Egypt and the material was used in mummification.

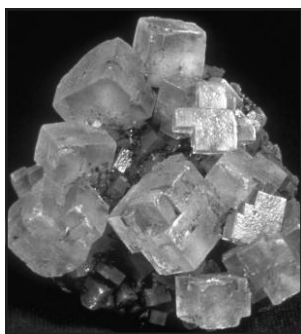


Figure 8.4.1 - Crystals of sodium chloride

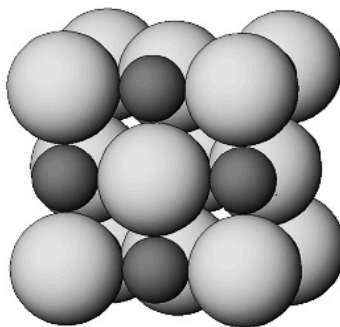


Figure 8.4.2 - Structure of NaCl
[dark spheres are Na⁺, others are Cl⁻]

¹ For other alkali metals see: Lithium, Rubidium, Cesium and Francium

Ancient writers did not distinguish between mineral alkali (sodium carbonate) and vegetable alkali (potassium carbonate). Both are white solids. Mineral alkali was found in nature as deposits while vegetable alkali was obtained by leaching wood ashes with water. The Greek scientist Dioscorides knew that a soluble substance can be leached out of wood ashes with water. Later writers crystallized the pot ashes and used it to make glass by melting it with sand. Glass was also produced by melting natron with sand. Wood ash was an important commodity and was traded between different countries. The production of soap by boiling oils and fats with wood ashes was described by the Roman writer Pliny the Elder.

Salt mines at Hallstatt in Austria and at Wieliczka in Poland are probably the oldest mine in the world, were worked in circa 1000 BC (Figure 8.4.3). The extent to which salt was used as an article of commerce is shown by the appearance of the salt roads in China, Africa, and Europe, and the foundation of towns such as Salzburg, Salzach, Hall, Hallein, and Heilbronn (Celtic *hal* = salt). Also salt was used as currency, hence the word “salary” and as source of tax revenue.



Figure 8.4.3 - Wieliczka salt mine near Krakow in Poland, now a museum

Saltpeter and gunpowder

Saltpeter or nitre (potassium nitrate) is “salt of stone” was obtained from soil contaminated with urine of animals, by extraction with water and evaporating the solution. It was used as a component of gunpowder. Description of its production was given by Biringuccio and Agricola. Francis Drake visited the coasts of Peru in 1578 and reported on the Chilean nitrate deposits which were used by the Indians as fertilizer. Saltpeter was also prepared by the German chemist Johann Glauber (1604-1668) by throwing putrefied matter of both vegetable and animal origin into pits and adding wood ashes (potassium carbonate). He obtained in due time a “saltpeter earth” from which he extracted a solution that yielded crystals of saltpeter on evaporation.

Gunpowder, also known as black powder, is a mixture of sulfur, charcoal, and saltpetre capable of detonation when heated. It is believed that the Chinese used this material in the seventh century in fireworks. In the 13th century, gunpowder was beginning to spread from China to the rest of the world, starting with the Islamic world. Black powder, known as “baroud” was used by the Arabs against the Crusaders in Palestine in 1249. In 1242 the English Friar Roger Bacon (1214-1294) published black powder formula while in 1380 the German Franciscan monk Berthold Schwartz (?) developed black powder and its use in guns.

Every country was desperate for gunpowder, which probably accounts for the continuing use of swords, and bows, long after firearms had made them technically obsolete. Eventually a saltpetre industry grew up, based on artificial nitre beds. For 300 years, the composition of black powder has been approximately 75 % saltpetre (potassium nitrate), 15 % charcoal, and 10 % sulfur. In 1453 the Ottoman Turks used black powder and enormous guns in their siege of Constantinople. Fireworks were mentioned in 1540 by Biringuccio in his *Pirotechnia*.

In 1627 black powder was used for the first time for rock blasting instead of “fire-setting” for loosening rock in the Hungarian mines of the Austrian Empire. By 1670 the use of black powder spread to tin mines of

Cornwall in England by German miners. Lavoisier (1743-1794) was in charge of the black powder factory in Paris and when he was executed during the French Revolution, his student Eleuthère Irénée du Pont de Nemours (1771-1834), emigrated to America and established in 1802 near Wilmington, Delaware a plant to produce black powder. Saltpetre lost its importance when the ammonia synthesis industry was developed during World War I and nitric acid was made by the oxidation of ammonia. This also resulted in the ruining of the industry in Chile based on the naturally occurring-nitrate.

Alum

Alum, another white solid (hydrated potassium aluminum sulfate) found abundantly in nature was known to the ancients and used as a mordant to enhance the color of dyed textiles.

NATURE OF THE ALKALIES

It seems that the first distinction between sodium and potassium salts was made by the German physician Johannes Bohn (1640-1718) in Leipzig in 1683 when he prepared aqua regia by distilling a mixture of salt (sodium chloride) and aqua fortis (nitric acid) and noticed that the cubic crystals which remained² (sodium nitrate) was different from saltpeter prepared by Glauber (potassium nitrate) from “saltpeter earth”. The distinction was an important step in the proof that soda and potash are two different alkalies. This observation was confirmed by the French chemist Henri Louis Duhamel du Monceau (1700-1782) in 1737.

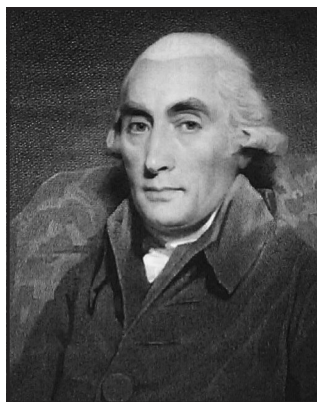


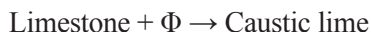
Figure 8.4.4 - Joseph Black (1728-1799)

² $3\text{NaCl} + 4\text{HNO}_3 \rightarrow \text{Cl}_2 + \text{NOCl} + 3\text{NaNO}_3 + 2\text{H}_2\text{O}$
Aqua regia

The true nature of the alkalies was, however, largely elucidated by the Scottish scientist Joseph Black (1728-1799) (Figure 8.4.4) in 1752. He classified alkalies as follows:

- Mild vegetable alkali obtained by lixiviation of wood ashes (K_2CO_3). By treatment with caustic lime, known also as « quick lime », this gave caustic vegetable alkali (KOH).
- Mild marine alkali obtained by lixiviation of ashes of seashore plants (Na_2CO_3). With caustic lime this gave caustic marine alkali (NaOH).

The transformation of the mild to caustic alkali was explained in terms of the theory of phlogiston that was dominating during this period. Limestone on calcination absorbs phlogiston, Φ , from the fire and this phlogiston was regarded as the “principle of causticity”:



The process of caustification of mild alkali by caustic lime was, therefore, regarded as a transfer of phlogiston from the lime to the alkali. At that time caustic alkalies were regarded as elements.

The alkalies gave characteristic reactions of alkalinity:

- They have a soapy feel and a corrosive action on the skin.
- They restore the colors of various dyes which are changed by acids, like litmus.
- They neutralize the acids to form salts.

Since 1860 potash salts have replaced wood as a raw material for the manufacture of potassium carbonate. The term potash today refers to potassium carbonate as well as all potassium salts that are used as fertilizers; the potassium content is given as K_2O . The glass industry is the most important of K_2CO_3 .

ISOLATION OF THE METALS

The chemical nature of these common alkalies remained unknown until the beginning of the nineteenth century when Humphry Davy (1778-1829) succeeded in decomposing both of them with the electric current from a voltaic cell. At first when he attempted to decompose the caustic alkalies using saturated solutions he simply electrolyzed water. In 1807, however, he used molten material. He then noticed intense light at the negative pole and a column of flame rising from the point of contact. The small metallic globules appearing at the cathode burst into flame when contacted water. He concluded that the new metal liberated hydrogen from the water, and that the flame was caused by the burning of this gas. Because he had obtained the metal from potash, he called it potassium. In Latin it is kalium, from the Arabic Al Qualia, i.e., the pot ash.

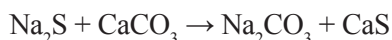
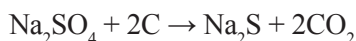
After successfully isolating potassium from potash, Davy then turned his attention to caustic soda. Within few days he isolated another new metal which he called sodium. In Latin it is natrium from the Arabic natron. Davy's isolation of the two alkali metals soon led to the discovery of the alkaline earth metals by a similar electrochemical method. After the preparation of sodium on large scale, it was used to liberate other metals from compounds that resisted all previous methods of attack, for example, the production of aluminum from alumina earth.

THE ALKALI INDUSTRY

Sodium carbonate

During the eighteenth century the limited demand for sodium carbonate for the manufacture of soap and glass was supplied from the trona deposits in Egypt (Wadi Al-Natron) and from the ash of sea weed. Potash was obtained by leaching the wood ashes. When the demand for this material increased, the necessity to produce it on a large scale became evident, so in 1782, the French Academy offered a prize for a satisfactory solution.

Interested in this prize, Nicholas Leblanc (1742-1806) (Figure 8.4.6) suggested a process in 1791 based on reacting sodium chloride with H_2SO_4 , then reducing the resultant sodium sulfate by carbon to form sodium sulfide, which was then reacted with CaCO_3 to form Na_2CO_3 and CaS . Sodium carbonate was recovered from the reaction mass called “black ash” by leaching with water:



The process was very successful, but because of his connections with the Duke of Orleans who financed his project and who was guillotined in 1793, his plant was confiscated and his financial failure caused him to commit suicide. He was, however, honored later and his statue stands today in the court of the Conservatoire National des Arts et Métiers in Paris. His process dominated the world chemical industry until it was superseded by the Solvay process about a century later.



Figure 8.4.6 - Nicholas Leblanc (1742-1806)

In Leblanc process, hydrogen chloride was generated and was emitted to the atmosphere since there was no use for it. Naturally, this caused excessive damage to the environment. As a result, a legislation to control the obnoxious emissions came into effect in England in 1864 and 1874 that became known as the Alkali Acts.

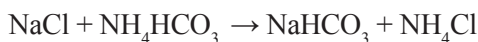
Solvay process

The ammonia-soda process was invented by the Belgian chemist Ernest Solvay (1838-1922) (Figure 8.4.7) in 1863, the son of a salt refiner. While working at the Brussels Gas Works, he was looking for uses for the ammonia produced as by-product. The Gas Works made coke from coal in order to produce the city gas necessary for heating in houses and for street illumination.



Figure 8.4.7 - Ernest Solvay (1838-1922)

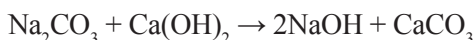
The ammonia-soda process was based on the fact that when ammonium bicarbonate was added to a saturated solution of sodium chloride, the ammonium salt dissolves and sodium bicarbonate separates as a solid. This is then filtered, dried, and calcined to yield sodium carbonate. Ammonium bicarbonate was prepared by adding NH_3 gas to a saturated NaCl solution then saturated with CO_2 .



Ammonium chloride is then decomposed to recover NH_3 which is then re-acted with carbonic acid to form NH_4HCO_3 . In 1872 Solvay gave a license for England to Ludwig Mond (1839-1909) who, founded what is now I.C.I.

Sodium hydroxide

Sodium hydroxide was produced from sodium carbonate by reaction with Ca(OH)_2 , filtering off CaCO_3 formed, then concentrating the solution:



The reaction was slow, the product was impure and dilute, concentration by evaporation was necessary which was an added cost. In the early 1890s Hamilton Young Castner (1859-1899) (Figure 8.4.8), a Columbia University graduate invented a new method of making sodium hydroxide by the electrolysis of brine using a mercury cathode.



Figure 8.4.8 -
Hamilton Young Castner
(1859-1899)

The process had been anticipated by Carl Kellner (1851-1905), a chemical engineer in Salzburg, Austria. Rather than litigate, the two chemists cooperated and, in 1896, set up the Castner-Kellner Alkali Company at Niagara Falls and, in 1897, another plant in Runcorn, Cheshire, England, where there was a cheap and abundant supply of salt. In 1899, it was already producing 20 tons of caustic soda a day and 40 tons of bleaching powder a day as a by-product. However due to the difficulties in handling mercury and the low energy efficiency, there were attempts to replace it.

Hooker cell was introduced in 1929 in which sodium chloride solution was electrolyzed using perforated iron cathode separated from the graphite anodes by means of a diaphragm. A co-product of both processes was chlorine which must be collected, liquified, and stored.

Sodium hydroxide is one of the most important chemicals. It has been used since 1892 for leaching bauxite in autoclaves to produce high purity Al_2O_3 needed for the aluminum industry. The process was invented by the Austrian chemist Karl Joseph Bayer (1847-1904) when he was working in Russia. About 100 million tonnes of bauxite are treated annually by this process.

OTHER ALKALI TOPICS

Alkali cyanides

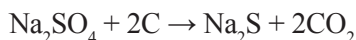
Sodium or potassium cyanides are used to leach gold and silver from their ores. They are manufactured from methane and ammonia in the presence of oxygen and a platinum catalyst:



Gaseous hydrogen cyanide may be dissolved, e.g., in aqueous sodium hydroxide solution to produce sodium cyanide; cyanides are toxic while cyanate, CNO^- , are not.

Sodium sulfide

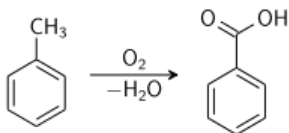
Sodium sulfide, Na_2S , more commonly the hydrate, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, are colorless water-soluble salts that give strongly alkaline solutions. When exposed to moist air they emit hydrogen sulfide. Industrially Na_2S is produced by carbothermic reduction of sodium sulfate:



Sodium sulfide is primarily used in pulp and paper industry in the Kraft process. Lignin and hemicellulose degrade to give fragments that are soluble in the strongly basic liquid.

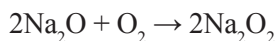
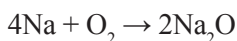
Sodium benzoate

Sodium benzoate is a food preservative prepared from benzoic acid and NaOH. Benzoic acid is a colorless crystalline solid produced commercially by partial oxidation of toluene with oxygen in presence of cobalt or manganese naphthenates catalysts:



Sodium Peroxide

Sodium peroxide was prepared by Castner in 1891 by reacting metallic sodium with dry air heated at 300°C and free from CO_2 :



Sodium sulfate

Sodium sulfate was already known since 1658 when it was prepared by Glauber by heating salt (sodium chloride) with green vitriol (ferrous sulfate). He distilled off “spirit of salt” which became known as muriatic acid (hydrochloric acid). The residue in the retort was Glauber’s salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). It was used as a laxative.

Plant nutrition

While it is a matter of indifference whether a solution of potassium or sodium hydroxide is used in the laboratory, a difference was found with

respect to plants. The German biologist Hermann Hellriegel (1831-1895) discovered around 1883 at the Experimental Station in Brandenburg that under otherwise identical conditions, plant can grow in solutions or soils quite free from sodium salts, but are unable to develop in the absence of salts of potassium. The cultivation of sugar beet in particular requires much potash hence the importance of potash as a plant nutrient and the need to mix it with fertilizers.

Potash deposits

There have been salt works at Stassfurt for a long period (Figure 8.4.9). In 1843, an immense deposit was located which became a German government monopoly. The Dutch chemist Jacobus Henricus van't Hoff (1852-1911) has done extensive studies on the physical chemistry of Stassfurt deposits during his stay in Berlin. After World War II, the deposits belonged to the German Democratic Republic. Potash deposits were later discovered in many other places, e.g., Northern Urals, Searles Lake in California, in Canada, etc.

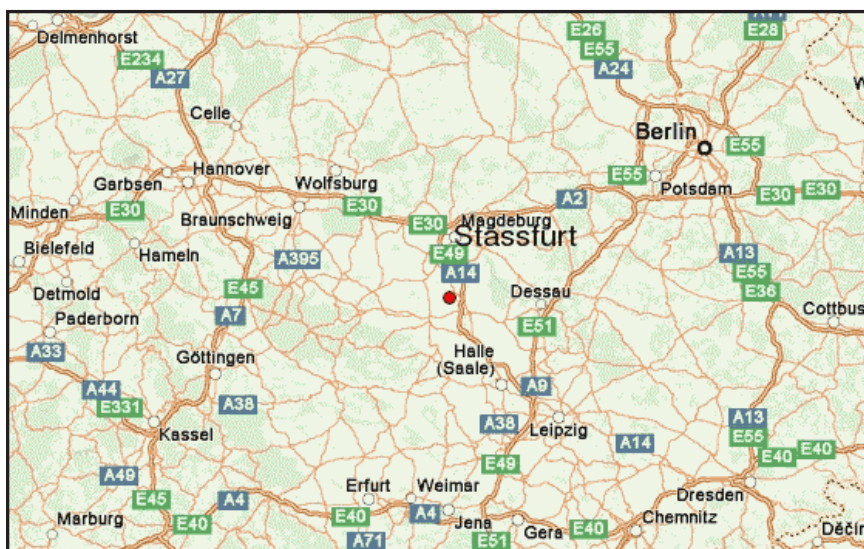


Figure 8.4.9 - Location of Stassfurt in Germany

Radioactive potassium

Potash ores, a mixture of KCl , K_2CO_3 , and other minerals, are radioactive due to the isotope ^{40}K , which occurs to the extent of 0.01 % in the element. Potassium 40 disintegrates according to the scheme:



Solubilities of NaCl and KCl

In a solution of a binary mixture of NaCl and KCl the concentration of one component is plotted on the horizontal axis and that of the other on the vertical axis. Each salt decreases the solubility of the other (Figure 8.4.10). The solubility diagram is represented by two curves AB and BC. The solubility of NaCl decreases with increased concentration of KCl (curve AB) and at the same time the solubility of KCl decreases with increased concentration of NaCl (curve BC). The point B represents a solution saturated with respect to both salts and the area ABCO represents a homogeneous solution.

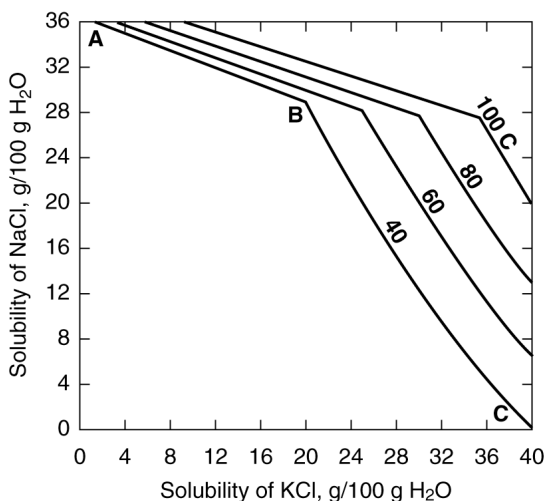


Figure 8.4.10 - Solubilities in the system KCl–NaCl

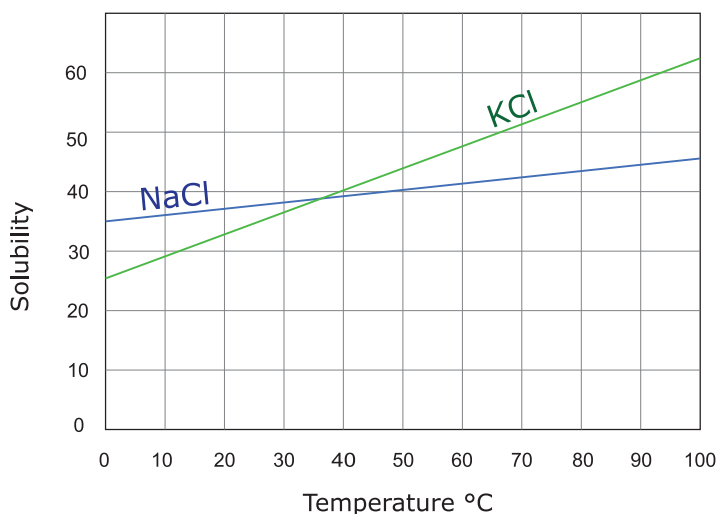


Figure 8.4.11 - Solubility of NaCl and KCl expresses in g/gH₂O

On crystallizing a binary mixture of NaCl and KCl, a heterogeneous mixture of crystals composed of the two original salts is obtained. The solids obtained will be a mixture of NaCl and KCl as can be identified by the individual X-ray diffraction pattern of each salt, i.e., each salt has preserved its identity during dissolution and crystallization. This is because the ionic radii of Na⁺ and K⁺ are different and therefore no chance of one ion taking place of the other in the crystal lattice.

It is possible to separate KCl from NaCl because of differences in solubilities with respect to temperature. Thus by cooling a hot solution saturated with both salts; KCl crystallizes out while NaCl remains in solution because the solubility of KCl decreases greatly with decreased temperature but that of NaCl remains practically the same.

ALKALI METALS AS REDUCING AGENTS

Table 8.4.1 gives the most important properties of sodium and potassium. The metals are soft and can be cut by a knife (Figure 8.4.12).

Table 8.4.1

	Sodium	Potassium
Atomic weight	22.997	39.096
Mass of isotopes	23	39, (40), 41
Atomic number	11	19
Melting point, °C	97.5	62.3
Boiling point, °C	880	760
Density, g./ml. At 20°C.	0.971	0.87
Ionic radius, Angström	0.95	1.33
Flame colors	Yellow	Red

The Swedish chemist Jöns Jakob Berzelius (1779-1848) was the first to use metallic sodium as a reducing agent. In 1824, he isolated zirconium and titanium by reacting their chlorides with metallic sodium. The method was developed on industrial scale in 1850s by the French chemist Henri Sainte-Claire Deville (1818-1881) who produced the first aluminum ingot by heating $\text{AlCl}_3 - \text{NaCl}$ with sodium.

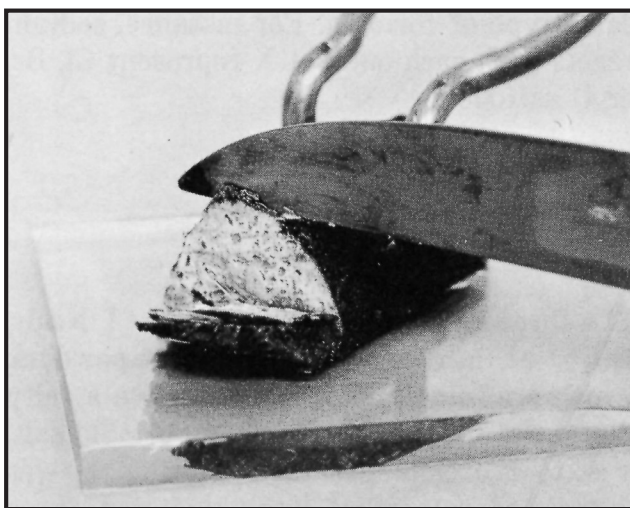


Figure 8.4.12 - Potassium can be cut by a knife

Production of metallic sodium

Metallic sodium was first prepared on industrial scale in connection with its use as a reducing agent for aluminum chloride by Sainte-Claire Deville process. The method used was heating at 1100°C a mixture of anhydrous sodium carbonate, lime, and coal in a retort. Sodium vapor was collected in a condenser. An annual production of 5-6 t was achieved per year. But, the process was very inefficient. Hamilton Young Castner invented a new process in 1886 based on reducing molten NaOH with a mixture of coal and iron at 1000°C . About 150t/year were produced by this method. The process was, however, expensive and was not successful industrially.

Few years later, in 1889, Castner patented another method based on the electrolysis of fused NaOH (Figure 8.4.13). The current efficiency, however, was less than 50% because half of the sodium produced was lost by reaction with water:

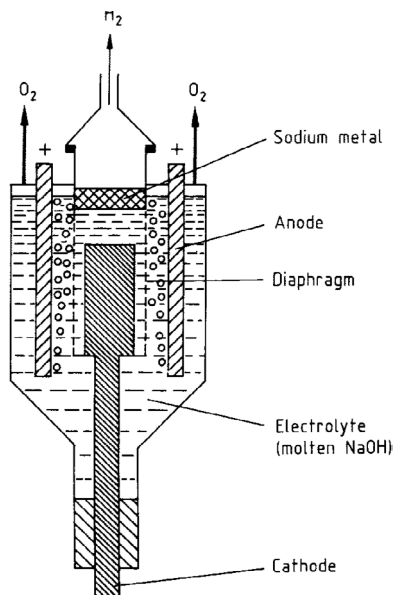
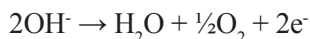
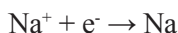


Figure 8.4.13 - Castner cell for the production of sodium from fused NaOH

The cell was composed of a cylindrical nickel anode surrounding the copper cathode concentrically. The cost of the metal produced by this method was still high.

It was Downs who in 1924 invented a new cell using molten NaCl instead of molten NaOH (Figure 8.4.13). It consisted of a lined steel vessel in which graphite anodes pass through the floor, and the two electrical conductors are connected by the cylindrical iron cathode. The diaphragm prevents sodium droplets formed at the cathode from reacting with the chlorine bubbles formed at the anode.

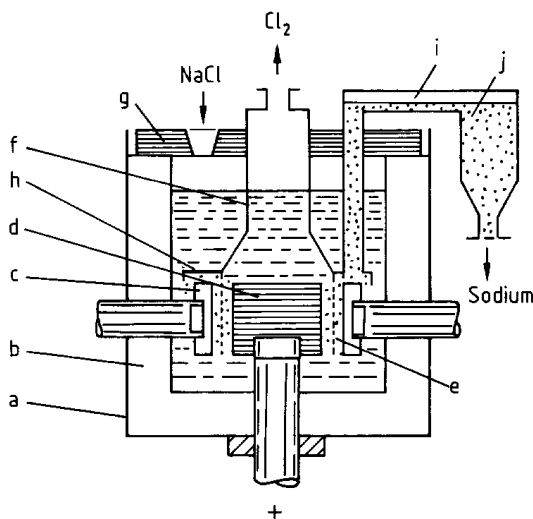
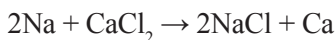


Figure 8.4.14 - Downs cell for electrolysis of molten NaCl

The Downs process used a mixture of 60% CaCl_2 and 40% NaCl at an operating temperature of 560°C to 585°C . This composition represents a compromise between the melting point of the salt mixture and the calcium content in the sodium. The eutectic mixture, which contains 66.8% CaCl_2 and 33.2% NaCl, melts at about 505°C . Although increasing the CaCl_2 content reduces the melting point of the binary mixture, it also increases the concentration of calcium in the product due to the reaction:



Production of metallic potassium

Degussa in Germany operated an electrolytic process developed in the 1920s with an electrolyte of 60% KOH, 19% K_2CO_3 , and 15% KCl. Later, use was made of a salt mixture of KCl and KF with a few percent K_2CO_3 (mp 600°C). However, the Doron's cell was not successful and since 1950s potassium has been produced by the reduction of KCl by sodium.

Sodium – potassium alloys

Sodium and sodium-potassium alloy NaK were first used on a large scale as heat transfer media by the nuclear energy industry in 1940s. Power stations may contain several thousand tonnes of the metals. An alloy containing 44% K and 56% Na has a melting point of 19°C .

Amalgams

Sodium and potassium form a number of intermetallic compounds with mercury called amalgams.

8.5 Discoveries by Davy:

Calcium, Strontium, and Barium¹

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INTRODUCTION

Though most eighteenth century chemists thought that lime and baryta² were elements, Lavoisier believed them to be oxides of metals having more affinity for oxygen than for carbon. Hence these oxides could not be reduced to the metallic state by carbon. In his first attempts to produce the alkaline earths, Davy passed an electric current through the moist earth which was protected from the air by a layer of naphtha. There was slight decomposition, but any metal that may have been formed combined immediately with the iron cathode.

Davy then tried again by mixing the non-conducting dry earth (lime, strontia³, or baryta) with excess potash, fused it, then covered the alkaline mixture with naphtha and passed an electric current through it. He soon

¹ See also Magnesium

² From « barys » in Greek meaning heavy. Named so because the naturally occurring sulfate is heavy (although the metal itself is light).

³ Named after Strontian, a location in Argyleshire, Scotland where the mineral was found in large amounts in a lead mine.

saw metallic globules rising and bursting into flame. When the flame died out, there remained nothing except potash and the alkaline earth with which he had started.

On Berzlius' suggestion, Davy mixed the moist earth with mercuric oxide, placed the mixture on a platinum plate connected to the positive pole of his powerful battery. He then made a small cavity in the center of the mixture, poured a globule of mercury into it, then dipped a platinum wire connected to the negative pole. By this method he obtained enough of calcium amalgam which he distilled to get an impure silvery-white calcium. In 1808, Davy isolated the metal strontium from its oxide by the same method he used for calcium and barium. The quantity of magnesium he prepared in the same way was too small and it was not until 1831 that it was first prepared in a coherent form by the French chemist Antoine Bussy (1794-1882).

CALCIUM

Occurrence

Calcium is the fifth most abundant element in the earth's crust. Some important, naturally occurring minerals are the carbonate: calcite (Figure 8.5.1), limestone, dolomite $[(\text{Ca},\text{Mg})\text{CO}_3]$ (Figure 8.5.2), the sulfate: gypsum (Figures 8.5.3-8.5.4), alabaster is translucent gypsum (Figure 8.5.5), phosphates: apatite (Figure 8.5.6) and silicates like wollastonite.

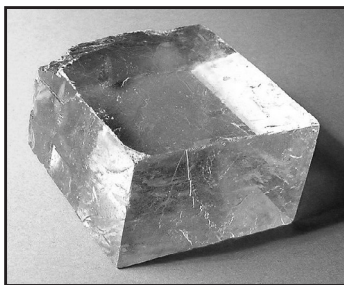


Figure 8.5.1 - A museum sample of calcite $[\text{CaCO}_3]$

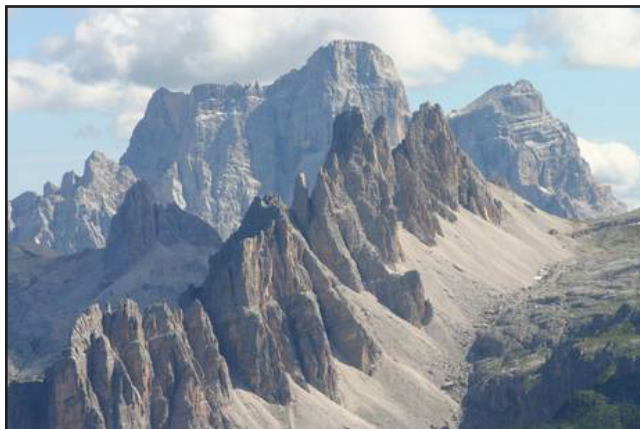


Figure 8.5.2 - Dolomite Mountains in South Tyrol, Italy



Figure 8.5.3 - A museum sample of gypsum [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$]



Figure 8.5.4 - Gypsum in desert



Figure 8.5.5 - Ancient Egyptian statues made of alabaster [translucent gypsum]



Figure 8.5.6 - A museum sample of apatite, $\text{Ca}_{10}(\text{PO}_4)_5(\text{OH}, \text{F}, \text{Cl})_2$

Giant Crystal Cave is connected to the Naica Mine 300 m below the surface in Naica, Chihuahua, Mexico contains the largest natural crystals ever found. The crystal of gypsum found is 12 m in length, 4 m in diameter, and 55 tons in weight (Figure 8.5.7). The cave is extremely hot with air temperatures reaching up to 58°C .



Figure 8.5.7- Gypsum crystals in Giant Crystal Cave
in the Naica Mine in north of Mexico

In New Mexico, USA the White Sands National Park is composed of gypsum (Figure 8.5.8).



Figure 8.5.8 - White Sands National Park, New Mexico

Aragonite

Aragonite is calcium carbonate formed by biological and physical processes, including precipitation from marine and freshwater environments. It was named in 1797 after Aragon in Spain where a cave was discovered nearby. Aragonite forms orthorhombic crystals, whereas calcite forms trigonal crystals. Pearls (Figure 8.5.9) and corals are mainly aragonite produced within the soft tissue of a living mollusks. The iridescent surface of pearl is a layer of aragonite secreted by mollusks.



Figure 8.5.9 - Pearls

Stalactites and stalagmites

Stalactites and stalagmites (Figure 8.5.10) are a type of formation that hangs from the ceiling of caves and the accumulation of material deposited on the floor from ceiling drippings. The words are derived from the Greek *stalasso* “to drip” and *stalagmitês* “dropping”.

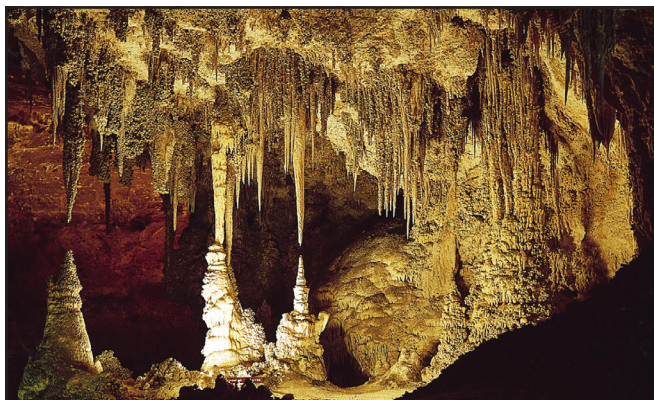


Figure 8.5.10 - Stalactites and stalagmites in a calcium carbonate cave

Limestone is dissolved by water that contains carbon dioxide, forming a calcium bicarbonate solution. This solution travels through the rock until it will drip down. When the solution comes into contact with air, particles of calcium carbonate are deposited. The drops that fall from the tip of a stalactite deposit more calcite on the floor below, eventually resulting in a cone-shaped stalagmite. Given enough time, these formations can meet to create *columns* of calcium carbonate.

Quicklime

In 1755 Joseph Black proved that the loss of weight of limestone on heating was due to the escape of “fixed air” (CO_2). Lime was usually produced in a vertical kiln (Figure 8.5.11). The process was operated batch-wise; at the end of heating the charge, the kiln was allowed to cool and the product raked out. Naturally, this was a wasteful process due to the consumption of large amounts of fuel. This was replaced later by the rotary kiln and then the fluidized bed.

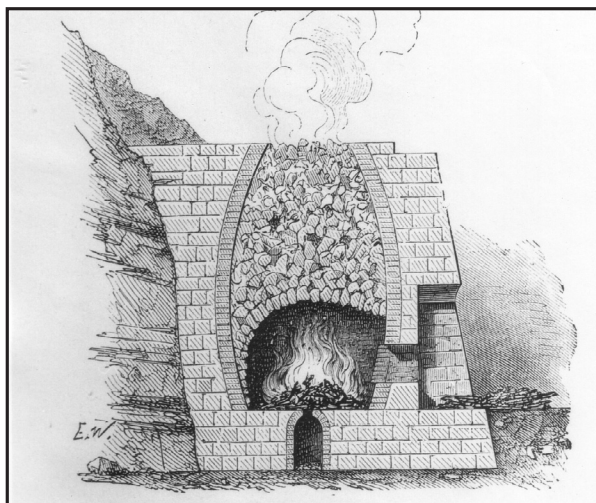
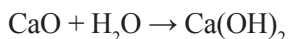


Figure 8.5.11 - Lime kiln

When heated intensely, e.g., with oxyhydrogen blowpipe it becomes incandescent and emits a brilliant white light. This property was formerly made use of in “limelight”. It reacted with water violently forming slaked lime:



which is used for building purposes. Mortar is a thick paste made by mixing slaked lime with sand and water. It sets on exposure to the air by loss of water after which it gradually hardens by slowly absorbing CO_2 with formation of calcium carbonate.

Marble

Marble (Figure 8.5.12) is a metamorphic rock composed of re-crystallized carbonate minerals, most commonly calcite or dolomite. The resulting marble rock is typically composed of an interlocking mosaic of carbonate crystals. Marble is commonly used for sculpture and as a building material. Many famous buildings are made of white marble, e.g., Hagia Sophia in Constantinople, Taj Mahal in Agra in India, Tower of Pisa in Italy. Also, many famous statues are made of marble.



Figure 8.5.12 - Marble blocks ready for shipment

Marmara islands in the Sea of Marmara is famous for their white marble. The islands were colonized by the Greeks in the 3rd millennium BC. The word “marble” derives from the Greek (*mármaros*), “crystalline rock”.

Plaster of Paris

The term plaster of Paris was first used in the 1700s due to large quarry deposits of gypsum located in Montmartre, a district of Paris, which was a leading center of plaster at the time. The plaster was produced by heating gypsum to about 150°C



When the dry plaster powder is mixed with water, it re-forms into gypsum in about 10 minutes and is complete in about 45 minutes.

Plaster of Paris is tough when dry but still soft enough to be sanded and carved. It is used for frescoes. Many of the greatest mural paintings in

Europe, like Michelangelo's Sistine Chapel ceiling are executed in fresco, meaning they are painted on a thin layer of wet plaster. Plaster is widely used as a support for broken bones; a bandage impregnated with plaster is moistened and then wrapped around the damaged limb, setting into a close-fitting yet easily removed tube.

The metal

Calcium is produced by the thermal reduction of lime with aluminum in a retort under vacuum at 1200°C; the vapors of calcium are then collected in a condenser. The metal is unstable in moist air, rapidly forming a hydration coating. It can be stored in dry air at room temperature. It reacts spontaneously with water to form Ca(OH)_2 and hydrogen gas; when finely divided, it will ignite in air. Being a typical metal, all its compounds are colorless and exhibit only one valence state, +2, in all of its reactions.

Calcium is a typical metal, i.e., it has the tendency to lose its outermost electrons and in doing so it achieves the inert gases electronic structure (table 8.5.1). Also its two outermost electrons are lost in one step. It is a ductile metal and can be formed by casting, extrusion, rolling, etc.

Table 8.5.1 - Physical properties

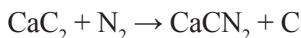
Relative abundance, %	3.63
Density at 20°C	1.55
Melting point, °C	838
Boiling point, °C	1440
Heat of fusion, J/g	217.7
Heat of vaporization, J/g	4187
Thermal expansion (0–400°C), K ⁻¹	22.3×10^{-6}
Electrical resistivity at 0°C, W cm	3.91×10^{-6}
Thermal conductivity at 20°C, W cm ⁻¹ K ⁻¹	1.26

Calcium undergoes phase transformation at 448°C from face centered cubic to body centered cubic.

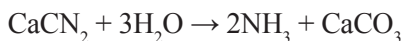
Uses

The metal is used as a reducing agent while CaO produced from limestone by calcination is used as a flux in iron and steel production, in gas desulfurization processes, and other metallurgical operations. Calcium hydroxide obtained by dissolving CaO in water is used as a pH control reagent in hydrometallurgy. Both gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and anhydrite, CaSO_4 , are used as materials of construction. Limestone is a major component of cement.

Naturally occurring calcium phosphate is treated for the production of fertilizers. Calcium carbide is produced by reacting quicklime with coke in furnaces which are heated electrically to 2000°C . It is used to produce acetylene by reaction with water. Calcium cyanamide is synthesized from calcium carbide and nitrogen at $900\text{--}1000^\circ\text{C}$:



It is used as a fertilizer since ammonia is generated when it comes in contact with water:



STRONTIUM

Strontium is present in the earth's crust at an average concentration of 0.04 %. Only the minerals strontianite (SrCO_3) and celestite (SrSO_4) are of economic importance.

Discovery and isolation

Strontium mineral was discovered by Adair Crawford (1748-1795) (Figure 8.5.13) in 1790. Strontium carbonate which was originally thought to be barium carbonate, was associated with a lead mine located in Strontian, Scotland (Figure 8.5.14). In 1791 Thomas Charles Hope (1766-1844) (Fig-

ure 8.5.15) confirmed the discovery, distinguishing strontium carbonate from calcium and barium carbonates and named the new metal strontium after Strontia.



Figure 8.5.13 - Adair Crawford
(1748-1795)



Figure 8.5.14 - Location of Strontia
in Scotland

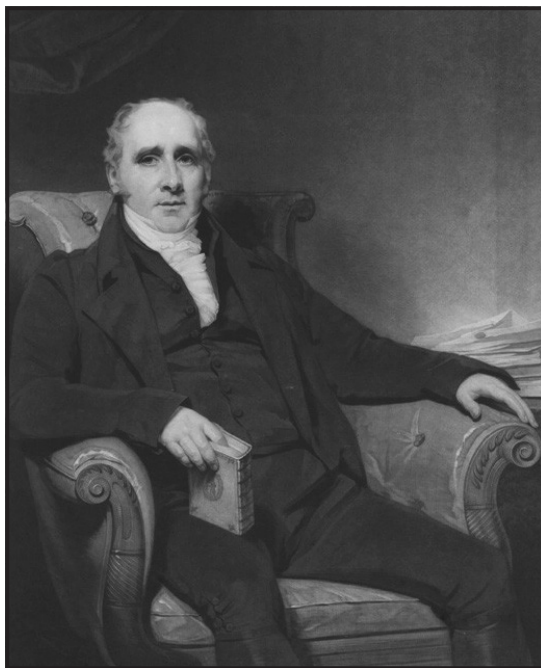
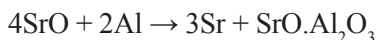


Figure 8.5.15 - Thomas Charles Hope (1766-1844)

Thomas Charles Hope was a Scottish physician and chemist, served as president of the Royal College of Physicians of Edinburgh and was assistant to Joseph Black. Charles Darwin was one of his students. He showed that water reaches its maximum density at 4°C

In 1808 Davy produced strontium metal from strontium carbonate by reducing the oxide and electrolyzing a mixture thereof with mercuric oxide to produce a strontium amalgam.

Commercial production is by reduction of the oxide with aluminum under vacuum:

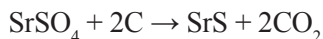


The strontium evolves as a gas and is transported through the production retort to a cooler end where precipitation occurs. Due to its reactive nature strontium must be handled with care. Strontium is a strong reducing agent and forms explosive hydrogen gas when in contact with water.

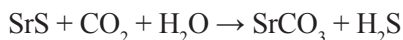
Properties

Strontium metal is silvery white and lustrous, but it readily forms a surface coating when exposed to air and water. Its density is 2.63, melting point 768°C, and boiling point 1381°C. It displays three crystal forms: below 215°C it is face-centered cubic, between 215 and 605°C it is hexagonal, and above 605°C it is body centered cubic.

Celestite is reduced by carbon at 1200°C to the sulfide:



The sulfide is extracted with hot water from which the carbonate is prepared:



Celestite can also be converted directly to strontium carbonate by hot sodium carbonate solution.

BARIUM

Occurrence

Barium content in the earth's crust is estimated to be 250 g/t. Its major minerals are barium sulfate (barite, heavy spar) (Figure 8.5.16) and barium carbonate witherite (Figure 8.5.17) named after W. Withering who discovered the mineral in Cumberland, Great Britain, in 1783.



Figure 8.5.16 - A museum sample of barite, BaSO_4



Figure 8.5.17 - A museum sample of witherite, BaCO_3

Discovery and isolation

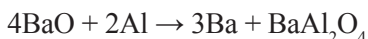
The first mention of barium compounds dates from the year 1602 when the Italian alchemist Vincenzo Casciarolo (1571-1624) in Bologna, realized that Bologna stone [barite] when heated in the presence of organic substances, phosphoresces in the dark. Much later, after 1774, C. W. Scheele discovered barium oxide and described its properties. He noted that a precipitate formed when sulfuric acid was added to barium oxide dissolved in water and in 1779 he distinguished barite from lime.

Davy first prepared barium metal by electrolyzing mixtures of barium oxide and mercuric oxide and subsequently evaporating the mercury. He

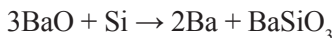
proposed the name barium Greek for heavy. The reduction of BaO with aluminum was described in 1878, and a large amount of barium of high purity was obtained by aluminothermic reduction of the oxide.

The metal

On industrial scale the metal is produced in a vacuum by reduction of its oxide with aluminum:



Silicon powder is also used 1200°C in a vacuum:



Barium has a body-centered cubic crystal structure. It is a soft silvery-white metal, density 3.74, melting point 726.2°C, boiling point 1637°C at 101.3 kPa, and good electrical conductivity. In all of its compounds it has an oxidation state of 2⁺. Although the mineral barite has a high specific gravity the metal is very light.

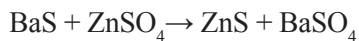
Barium is more reactive than magnesium, calcium, or strontium. On heating, it readily combines with the halogens in strongly exothermic reactions. The metal must be protected from oxidation by storage under paraffin oil or an inert gas. Barium reacts vigorously with water, liberating hydrogen, to form barium hydroxide. It reacts with nitrogen at about 250°C to form Ba₃N₂, with carbon to form the carbide BaC₂, and with hydrogen to form the hydride BaH₂. The metal reacts similarly with alcohols to form the alkoxides and hydrogen.

Blanc fixe

The industrially-precipitated BaSO₄ is called blanc fixe. It is mainly used as a filler and extender, in some fields also as a white pigment. It is colorless rhombic crystals of refractive index 1.64, hardness 3–3.5 on Mohs scale, and density 4.48 g/cm³. Barium sulfate is almost insoluble in water, the solubility being 2.5 × 10⁻⁴ %. Special grades are used as a medium

opaque to X-rays for medical purposes (stomach X-rays).

Lithopone, discovered in 1870s by DuPont, is a white pigment produced by co-precipitation of barium sulfate and zinc sulfide:



Application

About 90 % of the world output of barite is ground and used to increase the density of drilling mud to allow faster discharge of cuttings. The rest is reduced with carbon to yield water-soluble barium sulfide to be used as a raw material for other barium compounds.

8.6

Discoveries by Davy:

magnesium¹

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INTRODUCTION

The history of magnesium goes back to 1618 when a farmer from Epsom, a suburb of London (Figure 8.6.1), attempted to give water from a well to his cows but they refused to drink. He found out that the water was bitter. Gradually, the region became a spa that attracted visitors. The salt that was crystallized from this water became known as Epsom salt (magnesium sulfate) and was used as a purging medicine all over Europe.

Around 1700 a product came into commerce from Rome known as magnesia alba, i.e., white magnesia, which had also a bitter taste and was separated from the mother liquor during the crystallization of salt from sea water. In 1755, the Scottish chemist Joseph Black (1728-1799) (Figure 8.6.2) clearly distinguished magnesia from lime, showing that the first formed a soluble sulfate while the latter produced an insoluble sulfate thus acknowledging that magnesia alba is the salt of a new metal.

¹ Based on F. Habashi, “A History of Magnesium,” pp. 31–42 in *Magnesium Technology in the Global Age*, edited by M. O. Pekguleryuz and L. W. F. Mackenzie, published by Canadian Institute of Mining, Metallurgy, and Petroleum, Montreal 2006

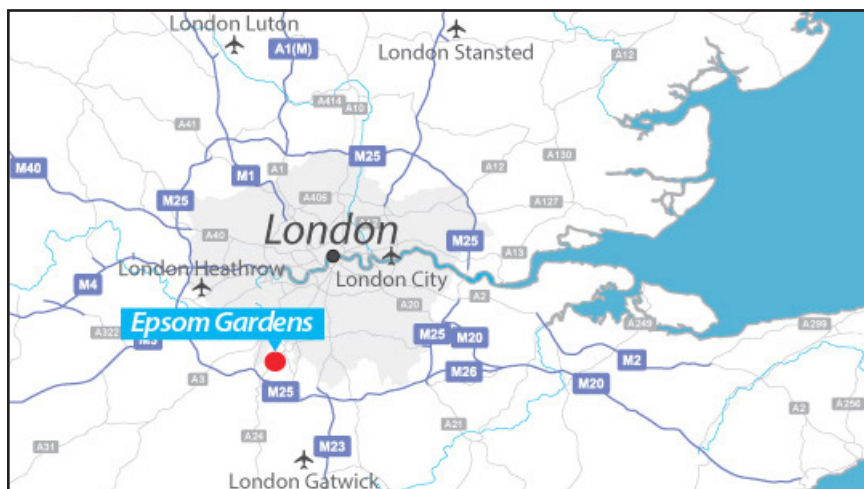
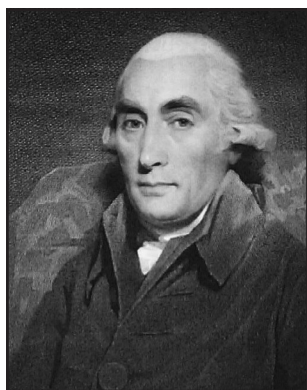
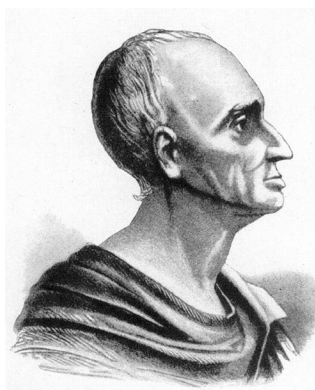


Figure 8.6.1 - Location of Epsom

Figure 8.6.2 - Joseph Black
(1728-1799)Figure 8.6.3 - Andreas Marggraf
(1709-1782)

In 1760 the German chemist Andreas Marggraf (1709-1782) (Figure 8.6.3) analyzed some serpentine found in abundance in the Saxon mountains and found that when he decomposed the mineral with sulfuric acid, a silicic residue remained while the solution contained a peculiar alkaline earth, which was neither lime nor alumina. When he evaporated the solution, it formed no alum but displayed crystals identical with those from natural Epsom salt.

When Humphry Davy (1778-1829) (Figure 8.6.4) in England in 1808 isolated a minute amount of the metal from magnesia alba he called it “magnium” instead of “magnesium” to avoid confusion with manganese. Nevertheless the name “magnesium” persisted and Antoine Bussy (1794-1882) (Figure 8.6.5) in France prepared the metal in 1831 in a coherent form by heating a mixture of magnesium chloride with potassium vapor.



Figure 8.6.4 - Humphry Davy
(1778-1829)

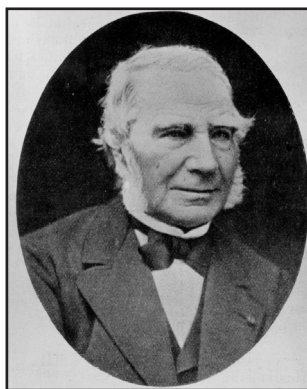


Figure 8.6.5 - Antoine Bussy
(1794-1882)

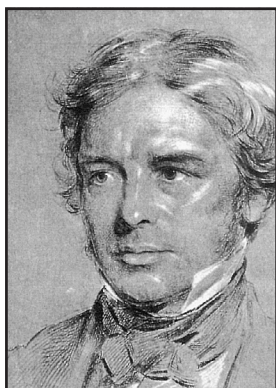


Figure 8.6.6 - Michael Faraday
(1791-1867)

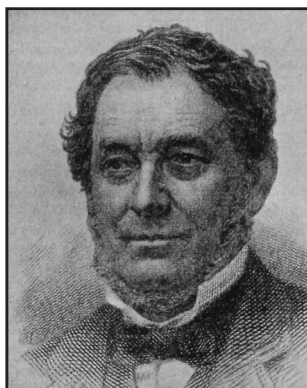


Figure 8.6.7 - Robert Bunsen
(1811-1899)

In 1833 Michael Faraday (1791-1867) (Figure 8.6.6) electrolyzed dehydrated liquid magnesium chloride to form liquid magnesium and chlorine gas. In 1852, Robert Bunsen (1811-1899) (Figure 8.6.7) in Heidelberg, Germany confirmed Faraday's work by preparing metallic magnesium by

the electrolysis of fused anhydrous MgCl_2 in a porcelain crucible fitted with graphite electrodes. The cathode was cut so as to form pockets inside which the metal was captured (Figure 8.6.8). Unless this precaution was taken, the metal being lighter than the fused salt rose to the surface and burned.

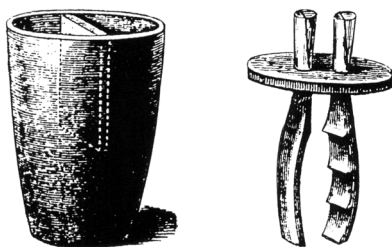


Figure 8.6.8 - Bunsen's crucible and cathode for electrolysis of molten MgCl_2

MAGNESIUM IN NATURE

Magnesium is the eighth most abundant element in the earth's crust (average magnesium content, 2.1%). The main sources for magnesium are shown in Table 8.6.1. In addition, there are magnesium-rich brines such as in the Great Salt Lake in Utah while sea water contains 1.4 g/L. Magnesium-rich brines are obtained as by-products from potash production or from surface or underground brine deposits.

Table 8.6.1- Main magnesium minerals

Mineral	Formula	Origin of name
Dolomite	$\text{CaCO}_3 \cdot \text{MgCO}_3$	In honor of the French mineralogist Dieudonné de Dolomieu (1750-1801)
Magnesite	MgCO_3	In allusion to its chemical composition
Brucite	$\text{Mg}(\text{OH})_2$	In honor of the American mineralogist Archibald Bruce (1777-1818)
Carnallite	$\text{MgCl}_2 \cdot \text{KCl} \cdot x\text{H}_2\text{O}$	In honor of the German geologist Rudolf von Carnall (1804-1874)
Kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	Named after the German physician Dietrich Georg Kieser (1779-1862)
Bischofite	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	Named in honor of the German geologist Karl Gustav Bischof (1792-1870)
Kainite	$\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$	From Greek kainos = new
Langbeinite	$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4$	In honor of the German chemist A. Langbein

Magnesium is a major component of asbestos and talc which are principally serpentine, a hydrated magnesium silicate containing about 40% MgO. Magnesium enters in the composition of chlorophyll hence its great importance (Figure 8.6.9). In 1906 Richard Willstätter (1872-1942) prepared pure chlorophyll which yielded on incineration an ash composed mainly of magnesia thus proving that magnesium is widely spread in nature. He was awarded the Nobel Prize for chemistry in 1915 for his work on plant pigments.

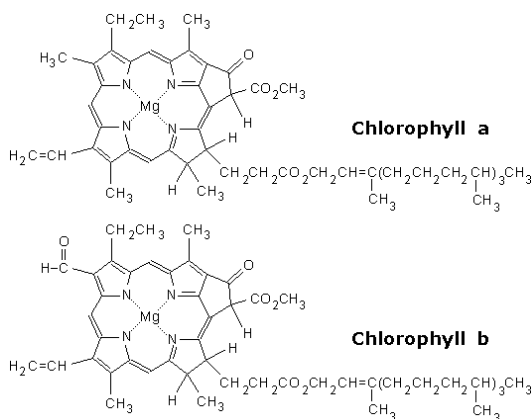


Figure 8.6.9 - Structure of chlorophyll

Brine pumped from underground containing magnesium is sent to basins which are interconnected by channels equipped with sluices. As the water in the basins evaporates, CaSO_4 , NaCl , MgSO_4 , KCl , and carnallite separate out in that order. When a given salt has crystallized, it is harvested mechanically while the brine is transferred to the following basin. The brine which is now considerably enriched in magnesium chloride is freed from impurities before sending it to the magnesium chloride plant.

The sabkha is brine in contact with a complex salt deposit of chlorides of sodium, potassium, and magnesium as well as some sulfates, contaminated with sand and clay. It is an Arabic word meaning “fertilizer”. Such material found associated with sand and clay is so used because also of its nitrate and potassium contents - - two essential nutrient elements for plant. The brine is usually pumped to the surface while the salt deposit is solubilized by injecting water underground, then bringing it to the surface in the same way.

INDUSTRIAL PRODUCTION

Magnesium is produced commercially by electrolysis of magnesium chloride melts and by metallothermic reduction of magnesium oxide with silicon.

Electrolysis of molten salt

The first industrial production of the metal began in 1886 in Germany by the Aluminium-Magnesium Fabrik in Hemelingen near Bremen by electrolysis of molten carnallite from Stassfurt deposits. The quantities were small but sufficient for the limited need in the world at that time. Few years later another operation started by Chemische Fabrik Griesheim Elektron in Bitterfeld near Leipzig. In 1915, Dow Chemical Company started producing magnesium in Midland, Michigan from naturally occurring subterranean brine. The German chemical companies were amalgamated in 1916 and became known as IG Farbenindustrie in 1925. In the 1930s production increased owing to the introduction of the light, corrosion-resistant magnesium alloy Electron, containing aluminum, manganese, and zinc.

Metallothermic reduction

The use of magnesium in the aircraft industry in World War II resulted in greater demand and large-scale production methods had to be found. This was achieved by the metallothermic reduction of MgO . In 1940 Lloyd M. Pidgeon (1903-1999) (Figure 8.6.10) a researcher at the Canadian National Research Council pioneered the first industrial metallothermic magnesium extraction plant in Canada; it was based on reducing calcined dolomite with ferrosilicon under vacuum.



Figure 8.6.10 - Lloyd M. Pidgeon (1903-1999)

Magnesium from the sea

In 1941, the Dow Chemical Company produced at Freeport, Texas an ingot of magnesium which was the first metal ever to be taken from sea water. During World War I the first Dow plants in Texas to extract magnesium from sea water came online. After the Japanese attack on Pearl Harbour, the US Government asked Dow to step up its magnesium production, so a second plant was constructed nearby Velasco.

Production options

As a result of the research of the pioneers in this field, two routes are presently used to produce magnesium metal: the electrolytic and the thermal. The electrolytic route accounts for about 70% of the magnesium produced world wide. The electrolytic process is based on MgCl_2 while the thermal route is based on MgO . Magnesium chloride can be obtained by:

- Solar evaporation of brine
- Calcination of magnesite followed by chlorination
- Dissolution of magnesite in HCl followed by crystallization of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
- Dissolution of asbestos tailings in HCl followed by crystallization of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. The largest and most modern electrolytic process using magnesium chloride obtained by leaching asbestos tailings with HCl started operation end of the year 2000 in the Province of Quebec in Canada and is known as the Magnola process, but was shut down few years later due to economic and technical problems.

Magnesium oxide can be obtained by

- Calcination of magnesite

- Dehydroxylation of $\text{Mg}(\text{OH})_2$ obtained by precipitation of magnesium ion in solution

The decision on using one method or the other is economic and is based on the availability of the raw material. Magnesium chloride as a source for magnesium production is generally adopted when evaporation of the brine by solar energy can be made use of to produce the feed material for the cells.

In cold climates where solar ponds are not possible, vacuum evaporators may be used to crystallize the feed material from brines. But, this is a costly venture and that is why precipitation methods are used to get magnesium hydroxide from which MgO can be obtained by calcination. Precipitation method is also used when the concentration of magnesium in the brine is low, such as the case for sea water. All extraction processes are followed by refining and casting.

THE ELECTROLYTIC PROCESS

The extraction of magnesium by electrolysis consists of two steps: preparation of magnesium chloride and electrolysis.

Preparation of magnesium chloride

The feed to the electrolytic process can be either anhydrous magnesium chloride, anhydrous carnallite, or hydrous magnesium chloride ($\text{Mg}\cdot\text{Cl}_2\cdot\frac{1}{2}\text{H}_2\text{O}$). Electrolysis of molten carnallite is used only in the former Soviet Union and recently in Israel by Russian immigrants. In Russia, the carnallite deposits are the largest in the world. Crystalline carnallite deposits occur in large amounts in nature, e.g., in Stassfurt, Germany and in Upper Kama in Russia. However, these are not suitable as such for production of magnesium because of the impurities they contain. These must be beneficiated by physical methods including leaching with water and crystallization. The product is then referred to as *artificial carnallite*.

The preparation of anhydrous magnesium chloride is more difficult than that of carnallite because of its ease of hydrolysis during dehydration requiring extensive precautions. On the other hand, carnallite is less sensitive to hydrolysis during drying but the energy requirement during its electrolysis is higher than in the case of magnesium chloride, and further the potassium chloride that accumulates in the cell during electrolysis has to be bled from time to time which causes losses of magnesium. Anhydrous magnesium chloride is also prepared from magnesium oxide obtained by calcination of magnesite or dehydroxylation of precipitated magnesium hydroxide by chlorination.

The brine is concentrated in solar evaporation ponds to crystallize potassium chloride, sodium chloride, and some carnallite. The resulting crude brine is then de-sulfated with calcium chloride solution obtained in a later step then other impurities removed. It is then spray-dried to get a crude magnesium chloride powder containing some water and some magnesium oxide. This is melted in an electrically heated, brick-lined furnace and treated with carbon and chlorine to lower the content of magnesium oxide, water, and other impurities. Off-gases from this operation are scrubbed with calcium hydroxide slurry to form the calcium chloride solution used in the de-sulfation stage. The molten magnesium chloride is then transported to the electrolytic cells.

On the other hand, on dehydration of carnallite, minimum side reactions take place thus the process is not as complex as the previous one. But since carnallite is a complex chloride, potassium chloride containing small amounts of magnesium chloride must be bled from the cell. This molten salt bleed is cooled, granulated, and used as a fertilizer. While 15-16 tonnes of carnallite are needed to produce one tonne of magnesium, only 4-5 tonnes of magnesium chloride are needed. The yield of magnesium from a cell fed by magnesium chloride is 84-85% and it is 79-80% when fed by carnallite. Material handling and size of equipment should therefore be considered when deciding on the route to be adopted.

Electrolysis of MgCl_2

The cell concept first developed by IG Farben Industrie in Germany in the 1930s is now in operation in the former Soviet Union, China, and the United States. Figure 8.6.11 illustrates the electrode configuration and the circulation of the electrolyte.

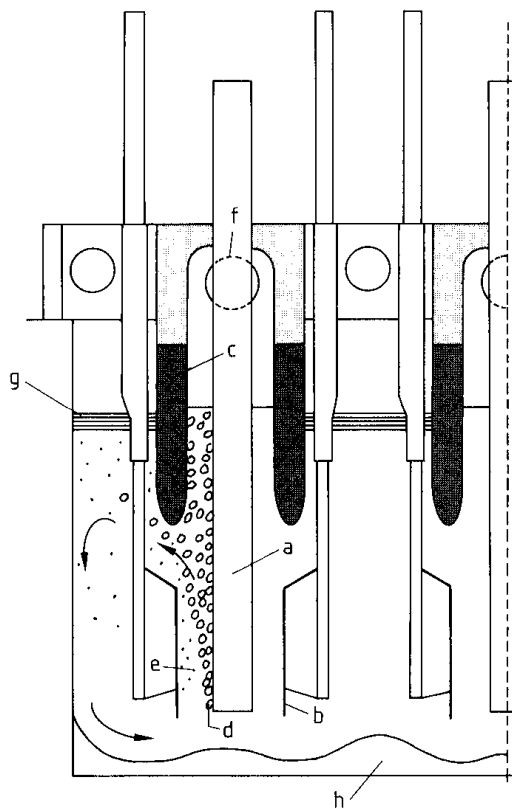


Figure 8.6.11 - Electrolytic cell used in 1930s by IG Farben in Germany.
a) Graphite anode, b) Steel cathode, c) Partition, d) Chlorine bubbles, e) Magnesium globules, f) Chlorine outlet, g) Magnesium, h) Sludge.

Electrolysis of hydrous cell feed ($\text{MgCl}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$) in the Dow cell (Figure 8.6.12) developed in 1940 requires graphite anodes which can be lowered into the cells to compensate for consumed graphite.

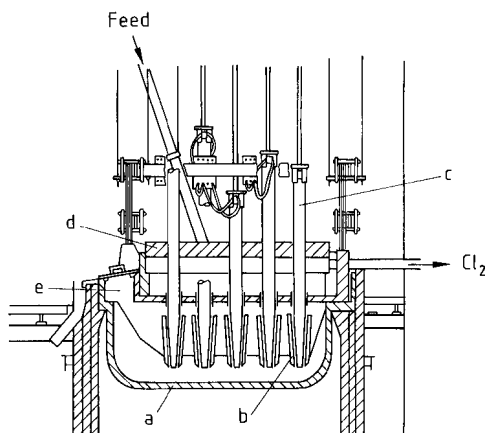


Figure 8.6.12 - Dow cell (1940). A) Steel mantle, b) Steel cathode, c) Graphite anode, d) Refractory cover, e) Magnesium collection compartment

The Alcan Multipolar Cell developed in the 1950s is claimed to be the most efficient electrolytic cell for magnesium production and is presently the most widely used technology for the production of magnesium from MgCl_2 melt (Figure 8.6.13). It has been used by Sumitomo Sitix in Japan, formerly known as Osaka Titanium, since 1980, by TIMET in USA, and more recently by Magnola in Quebec and Australian Magnesium Corporation. It is referred to as “diaphragmless” because the diaphragms of the original IG Farben cell were eliminated. This simplification leads to a more efficient utilization of the working space, a more robust construction, and easier operation at high amperages.

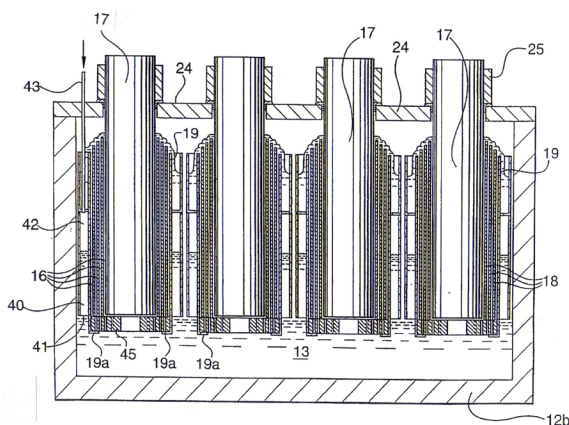


Figure 8.6.13 - Alcan multipolar cell developed in the 1950s

Purified molten magnesium is then transferred to a holding furnace where the surface of the metal is protected against oxidation by a cushion of helium or argon. Billets are cast in multistand continuous or semi-continuous direct-chill casting machines. Standard purity level is 99.8%.

Byproducts

Natural brines yield not only magnesium but also numerous by-products:

Chlorine

For each tonne of magnesium produced by the electrolytic process 2.9 tonnes of chlorine are produced. In addition, large amounts of hydrogen chloride are generated in the cathodic compartment due to the partial hydrolysis of the melt, and a small amount of electrolyte dust is entrained in the gas. The gas contains also a trace amount of organic chlorine compounds (dioxins). The typical composition of the cell gas is given in table 8.6.2. The hot gas is cooled in the off-gas hood and in the duct system from the cell to the chlorine handling system which consists of (Figure 8.6.14):

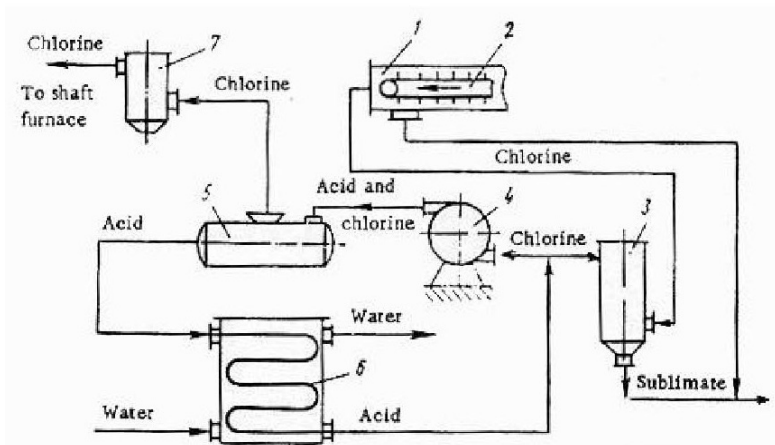


Figure 8.6.14 - Chlorine plant.

- 1) Chlorine duct, 2) Conveyor, 3) Filter, 4) Compressor,
- 5) Acid separator, 6) Cooler, 7) Drop separator

- A primary gas cleaning stage used to remove entrained dust by contacting the gases in counter-current process water in an unpacked tower.
- A drying step where the wet chlorine is scrubbed in counter-current with sulfuric acid which absorbs the moisture content.

About half of this chlorine is used in the magnesium chloride purification step (one fourth if carnallite is used) and the other half should be marketed. In the event of operating problems in the cells, the gas can be diverted directly to the caustic scrubbers.

Table 8.6.2 – Average composition of gases removed from electrolytic cells

	vol %
Chlorine	85-90
HCl	2-3
CO + CO ₂	1-2
Oxygen	3-4
Nitrogen	12-15

- Chlorine gas is a highly reactive chemical; it is liquefied and transported in special tank cars. There are no practical or economic means to store this product. If no market is available, means must be found to utilize it.
- *Alkali chlorides* Brines from underground contain appreciable amounts of potassium and sodium chlorides that crystallize prior to the crystallization of magnesium chloride or carnallite. Both are important raw materials for the chemical industry. Potassium chloride is used as a fertilizer.
- *Other by-products* Bromine, boron, and lithium compounds are usually found in the brines and may be extracted prior to the crystallization of magnesium chloride or carnallite.

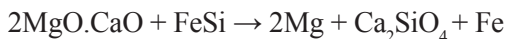
METALLOTHERMIC REDUCTION

The thermal route accounts for the remaining 30% of magnesium production and is based on the reduction of magnesium oxide by silicon. This route is generally adopted in two cases:

- When high quality magnesite is available
- When evaporation of the brine by solar energy cannot be used due to cold climate.

Therefore, precipitation methods are used to get magnesium hydroxide from which magnesium oxide can be obtained by calcination instead of using expensive vacuum evaporators to crystallize magnesium chloride.

Since elemental silicon is expensive, ferrosilicon (an alloy of silicon and iron produced in an electric furnace) is used instead because it is cheaper. Magnesium forms as vapour and is condensed as a solid metal that is collected and melted batchwise in steel crucibles. Calcined dolomite is heated under vacuum with ferrosilicon at about 1100°C so that the following reaction takes place:



Reduction is conducted batch-wise in cylindrical retorts 250 mm in diameter and 7 m long made of chrome-nickel steel and heated in a furnace (Figures 8.6.15 - 8.5.17). Magnesium is the only volatile product of the reaction, thus it can be easily condensed at the cold end of the tube. Sodium and potassium volatilize also if present in the raw material.

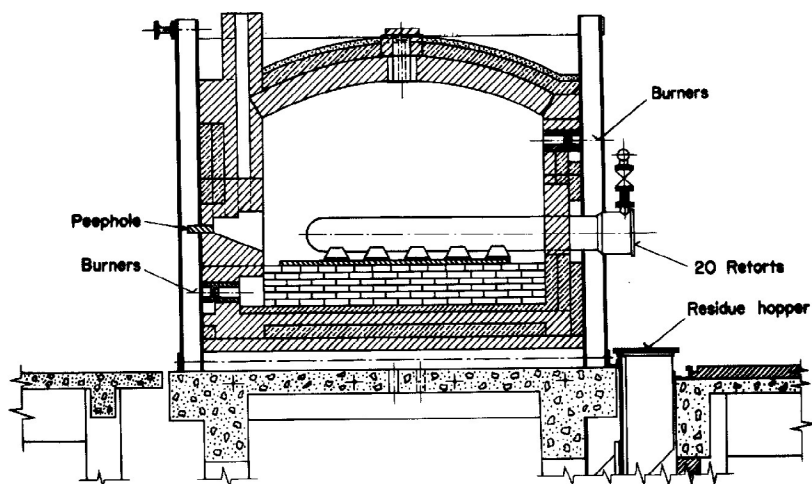


Figure 8.6.15 - Retort furnace for the production of magnesium, 1940s

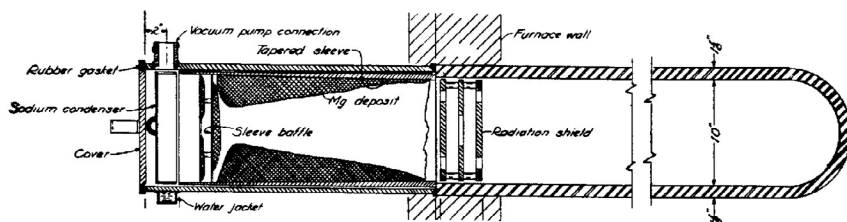


Figure 8.6.16 -Retort for the production of magnesium, 1940s



Figure 8.6.17 – An operator collecting the magnesium from the condenser, 1940s

The Magnetherm Process was developed in France in 1970s by the Société française d'électrométallurgie in Marignac (Figure 8.6.18). It incorporated two improvements over the Pidgeon Process:

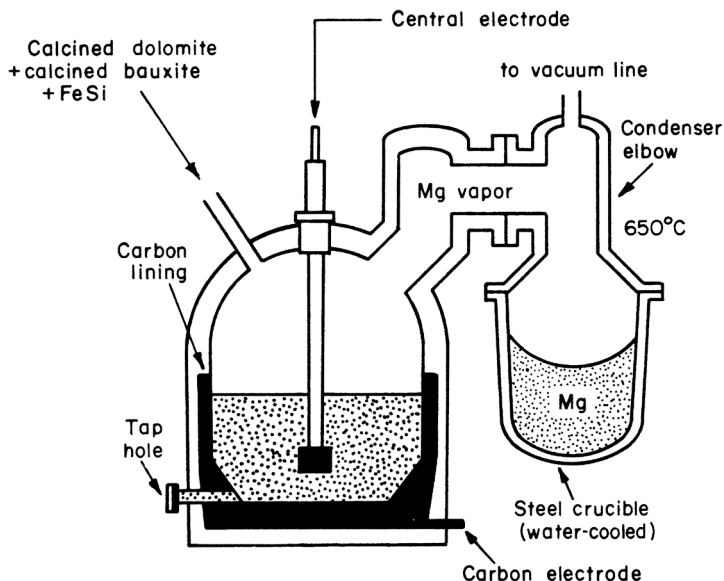


Figure 8.6.18 - Magnetherm process, 1970s

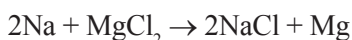
- Calcined bauxite is added to the reaction mixture to lower the melting temperature of the slag and allows the reactor contents to be kept liquid at an operating temperature of 1600°C
- Direct electric heating is used which is more efficient than indirect heating.

A carbon lining serves as one electrode for electric heating. Another electrode projects vertically downward from the reactor roof. The metal vapors diffuse to the condenser which is maintained at 650°C and condenses as liquid in the water-cooled steel crucible where it solidifies.

REFINING AND CASTING

Refining

Molten magnesium from the electrolytic cell contains some chlorides from the electrolyte, some magnesium oxide and magnesium nitride as a result of reaction with air. Removal of these impurities is achieved in an electrically heated furnace (Figure 8.6.19) containing a molten salt at 420-580°C whose density is lighter than that of magnesium. Thus, it will form a protective coating on the surface of the metal as well as reacting with the impurities to form a sludge which settles at the bottom. A typical molten salt for refining may have the composition shown in Table 8.6.3. Any alkali or alkaline metal present in magnesium will react with MgCl_2 in the electrolyte displacing the magnesium, for example, for sodium:



Any MgO present will react with MgCl_2 forming oxychloride which also settles to the bottom.

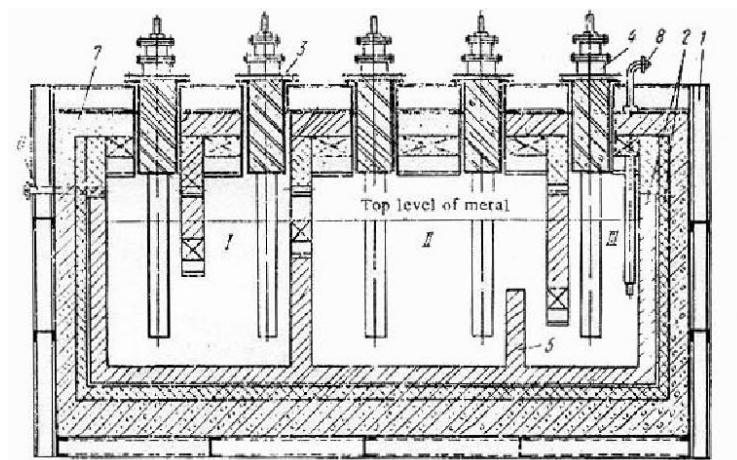


Figure 8.6.19 - Refining furnace.

- 1) Furnace jacket, 2) Lining, 3) Thermal installation tubes, 4) Heating elements, 5) Threshold, 6) Charging tube, 7) Thermal insulation, 8) Intake tube, I, II, III) Chambers.

Table 8.6.3 – Typical analysis of molten salt used for refining magnesium

	%
MgCl ₂	36-43
KCl	31-37
NaCl	7-8
CaCl ₂	4-17
BaCl ₂	7-15

The molten salt must be so chosen to have a melting point below that of magnesium, has a high surface tension, beside having a lower density than magnesium at 700-800°C. The process is conducted continuously with air-tight hatches in the ceiling of the furnace provided for introducing the molten magnesium and for withdrawing the sludge. The high surface tension requirement is to allow the nonmetallic particles to be wetted while magnesium is not, thus facilitating their settling at the bottom of the furnace.

Hydrogen may be present in magnesium as a result of reaction with humidity. One hundred grams magnesium at 760°C dissolves 41 mL H₂. During casting, the release of hydrogen due to decreased solubility causes undesirable porosity in the solidified metal. To avoid this problem, hydrogen is removed by exposing the molten metal in a crucible under vacuum for few minutes - a process is known as de-gassing. Also, bubbling chlorine gas in the melt displaces the hydrogen, and any excess reacts with magnesium to form magnesium chloride. Purified molten magnesium is then transferred to a holding furnace where the surface of the metal is protected against oxidation by a cushion of helium or argon.

Casting

The refined magnesium from the refining furnace is sent to the casting conveyor by means of an electromagnetic pump (Figure 8.6.20) mounted between the furnace and the conveyor. The intake tube connected to one end of the pump is dipped into the metal through a hole in the furnace roof. The discharge tube runs from the other end of the channel and ends above the pans of the conveyor.

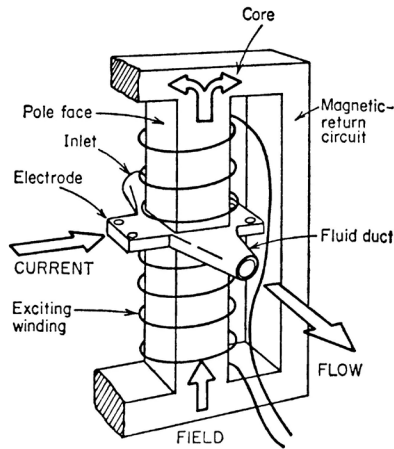


Figure 8.6.20 - An electromagnetic pump

The discharge of the pump is readily adjusted by varying the voltage applied to it. This is done by feeding the pump with current supplied by an auto-transformer with a continuous voltage regulation. The direction of operation of the pump may be reversed, in order to rapidly expel the metal from the pump channel back into the furnace after the pouring has been terminated or if the conveyor has broken down. The technique of semi-continuous vertical ingot casting may also be employed. The magnesium ingot is cooled by spraying with water.

Protective treatment of magnesium

A number of methods are employed to minimize the corrosion of magnesium ingots, magnesium bars, and magnesium alloys during transport and storage, and corrosion of objects made of magnesium alloys during their service life. The methods depend on whether the object is intended for immediate use or for prolonged storage.

Ingots intended for immediate use should receive protective treatment immediately after casting otherwise corrosion nuclei are formed on the surface, from which corrosion will spread out. Ingots which are to be stored for long periods of time are first washed in hot alkaline water, then

in water, then in hot water containing 2 g/L potassium dichromate, finally dried and coated with protective grease before wrapping in waxed paper and packing in aluminum drums or wooden boxes.

Finished and semi-finished products made of magnesium and magnesium alloys are first sand blasted, boiled in 2% solution of chromic acid, then washed before being protected by application of anodized oxide films and of non-metallic coatings.

THE METAL AND ITS COMPOUNDS

Magnesium is a silvery white light metal. It is a typical metal in that when it loses its outermost electrons it attains the electronic structure of the inert gases hence it is a reactive metal.

Relative abundance	2.09%
Density (solid), g/cm ³ At 20°C At 600°C	1.738 1.622
Crystal structure	Hexagonal
Melting point	650°C
Boiling point	1107°C

Magnesium burns in air with an intense white flame forming a mixture of oxide and nitride (Figure 8.6.21). It is readily dissolved by most organic and inorganic acids but resistant to alkali hydroxide solutions, hydrofluoric acid, fluorine, and fluorine compounds due to the formation of protective hydroxide and fluoride films.

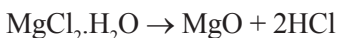


Figure 8.6.21 - Burning magnesium in air

MAGNESIA

Magnesium oxide is a highly desirable refractory for the steel industry. It was produced on large scale after Sidney Gilchrist Thomas (1850-1885) (Figure 8.6.22) in 1875 solved the problem of Bessemer steel production in England and suggested the use of a basic refractory instead of silica sand. Naturally occurring magnesium carbonate (magnesite, MgCO_3) is mainly calcined to give sintered magnesia for the production of magnesia bricks.

It can be produced in two ways: from magnesium chloride monohydrate by heating in special furnaces:



or by calcining magnesite at high temperature:



By-product HCl is absorbed in water and can be marketed as a pickling acid for the steel industry, for treating phosphate rock to make fertilizers, or other uses in the chemical industry.



Figure 8.6.22 - Sidney Gilchrist Thomas (1850-1885)

USES

The largest single use of magnesium is as an alloying element in aluminum alloys. Other uses include its use as a reducing agent in the production of titanium, zirconium, uranium, beryllium, and hafnium. Organomagnesium compounds are also known, the most important of these being the Grignard reagents which play an important role in synthetic organic chemistry.

8.7

Discoveries by Berzelius:¹

cerium, selenium, silicon, and thorium

Berzelius	743	Selenium	750
Discoveries	744	Silicon	752
Writings	745	Silicon and ferrosilicon	753
Legacy	746	Uses	755
Cerium	747	Silicates.....	756
Cerium metal	748	Thorium	759
Uses	749		

BERZELIUS

Jöns Jacob Berzelius (1779-1848) (Figure 8.7.1) studied medicine at the University of Uppsala and wrote a dissertation in 1802 on galvanotherapy inspired by Volta's invention of the galvanic pile two years earlier. In 1807, he was appointed professor of medicine and pharmacy (later chemistry and pharmacy) in Stockholm, and in 1819 he was appointed secretary of the Academy of Science. There he obtained a laboratory, a library, and an apartment in the Academy building.



Figure 8.7.1 - Jöns Jacob Berzelius (1779-1848)

¹ See also

·Rare Earths

·Vanadium

Discoveries

Berzelius discovered cerium (1803), selenium (1817), silicon (1823), and thorium (1829). Together with his student Johan August Arfwedson (1792-1841) he discovered lithium and played an important role in the discovery of vanadium. His students discovered a number of metals:

- Heinrich Rose discovered niobium in 1820
- Carl Gustaf Mosander discovered lanthanum, didymium [which was resolved later into praseodymium, neodymium, samarium, and europium by others], erbium, and terbium in the period 1824-1831

Prominent Berzelius' students and coworkers are shown in Table 8.7.1.

Table 8.7.1 - Prominent Berzelius' students and coworkers

Period	Student or Co-Worker	Nationality	Later Occupation
1812-20	Nils Gabriel Sefström (1787-1845)	Swedish	Director of the Falun Mine 1820-22, first director of the School of Mines at Falun (1822-39). Discovered vanadium.
1815-16	Christian Gottlob Gmelin (1792-1860)	German	Professor in Tübingen.
1817-18	Johan August Arfwedson (1792-1841)	Swedish	Discovered lithium.
1820-21	Eilhard Mitscherlich (1794-1863)	German	Professor in Berlin, discoverer of isomorphism.
	Heinrich Rose (1795-1864)	German	Professor in Berlin, discovered niobium.
	Gustav Rose (1798-1873)	German	Professor in Berlin.
	Gustav Magnus (1802-1870)	German	Studied selenium and tellurium.
1823-24	Friedrich Wöhler (1800-1882)	German	Professor in Göttingen, synthesized urea, introduced the concept of isomerism.
1824-31	Carl Gustaf Mosander (1797-1858)	Swedish	Professor of Chemistry at Karolinska Institutet (1832-58). Discovered lanthanum, didymium, erbium, and terbium.
	Carl Axel Arrhenius (1757-1824)	Swedish	Lieutenant Colonel in the Swedish Army, discovered the mineral gadolinite.

Writings

Berzelius' work in chemistry was remarkable. He was the first to determine accurately the atomic weight of the elements. He systematized the chemical language by introducing the chemical symbols for the elements and compounds that we use today. He invented the concepts of catalysis and isomerism. He wrote an important textbook of chemistry in Swedish which was translated into German and then revised and updated into five editions from Swedish manuscripts. Beside these, unauthorized editions appeared in Stuttgart (1832-33) in three volumes (1,505 pages) and in Quedlinburg (1833-43) in four volumes (2,327 pages). Translations into other languages were also published.

Berzelius founded and edited a chemical journal and published a summary of progress in chemistry each year in the form of Annual Reports which were translated in German. His scientific correspondence with chemists of the time, published after his death in numerous volumes, filled thousands of pages. He also kept a diary of his travels which was published in a 430-page volume.

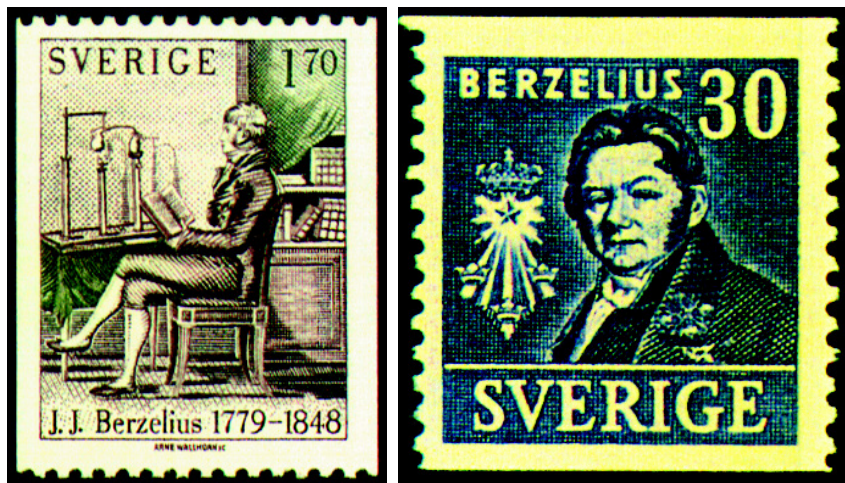


Figure 8.7.2 - Berzelius stamps in Sweden

Legacy

Berzelius' laboratory equipment, specimens, and other personal effects are kept in a Museum maintained by the Academy in Stockholm (Figure 8.7.4). A statue for him were erected in Stockholm (Figure 8.7.5) in addition to postage stamps (Figures 8.7.2-8.7.3) and medals in his honour.



Figure 8.7.3 - Berzelius medal



Figure 8.7.4 - Berzelius Museum



Figure 8.7.5 - Berzelius statue in Stockholm

CERIUM

Cerium was discovered in 1814 in a heavy brown mineral in the iron mine of Bastnas and named after the asteroid Ceres, which had been discovered in 1800–1801. The mineral is mainly a cerium silicate and it was given the name cerite (Figure 8.7.6). Analysis of a sample gave 35% Ce_2O_3 and 30% La_2O_3 . Its chemical composition as known today is:



Cerium is the most abundant rare-earth element and exceeds in abundance such well-known elements as tin, cobalt, and lead.

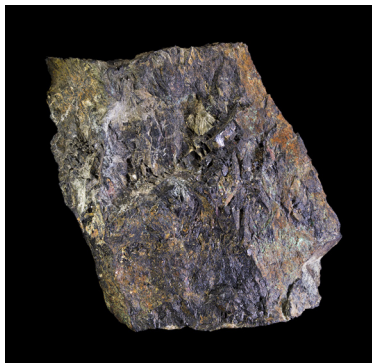


Figure 8.7.6 - Museum sample of cerite

Cerium metal

The metal was first isolated in 1872 by William Francis Hillebrand (1835-1925) (Figure 8.7.8) in collaboration with Thomas Norton when they were in Germany. They used Bunsen's fused salt electrolytic method for obtaining the metal. Hillebrand studied at Cornell University and then in Germany at the University of Heidelberg under Robert Bunsen where he received his Ph.D. in 1875.

Hillebrand studied organic chemistry with Wilhelm Rudolph Fittig at the University of Strasbourg, but changed to geochemistry and metallurgy at the Freiberg Mining Academy in Germany. After returning home to the United States in 1878, he opened an assay office in Leadville, Colorado, in 1879, and then worked as a chemist at the United States Geological Survey in 1880. That year he was sent to Denver to establish a chemical laboratory for the Rocky Mountain Division of the Survey. For five years he remained in charge of this laboratory, and then was transferred to the chief laboratory in Washington. He moved to the National Bureau of Standards in 1909 to become chief chemist.

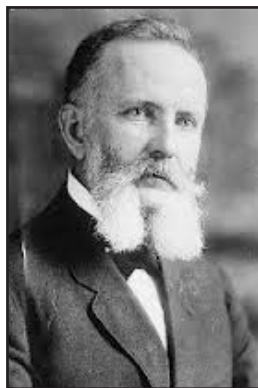


Figure 8.7.8 - William Francis Hillebrand (1835-1925)

He was professor of chemistry and physics at the National College of Pharmacy in Washington, DC from 1892 to 1910 now part of George Washington University, President of the American Chemical Society in 1906, and in 1908 he founded and became editor of *Industrial and Engineering Chemistry*. He was the author of several books on chemical subjects.

Relative abundance %	2.5×10^{-3}
Density, g/cm ³	6.770
Crystal structure	Face centered cubic
Melting point, °C	798
Boiling point, °C	3433

Cerium has not only the normal rare-earth +3 oxidation state, but also the exceptional +4 state which simplifies its separation from the other rare-earth elements.

Uses

Cerium is separated from other rare-earth elements by oxidation of solutions resulting from attack of bastnäesite or monazite. The most important uses of cerium [or mischmetall] is its ability to react with oxygen, hydrogen, nitrogen, sulfur, arsenic, bismuth, and antimony, thus reducing the effects of these elements on the properties of the metals.

Mischmetall is a mixture of cerium, lanthanum, neodymium, and praseodymium with cerium as the major constituent. It is the lowest priced rare-earth metal because no expensive chemical separation is needed to produce it being produced by fused-salt electrolysis of rare-earth chlorides. Mischmetall dissolves in dilute mineral acids with evolution of hydrogen.

Mischmetall or cerium-containing master alloys are added to cast iron to improve ductility, toughness, and the microstructure. Cerium allows graphite to form nodules, causing nucleation in spheroidal and vermicular cast iron, and neutralizes the harmful effect of the tramp elements.

Addition of mischmetall to copper alloys improves tensile strength and deep-drawing properties.

Lighter flint alloy consists basically of mischmetall and iron. Some other metals are added in small amounts to modify the pyrophoric properties and to improve processing. The frictional pyrophoric properties of cerium-iron are based on a combination of microstructure and mechanical and chemical properties of the alloy. The principal uses for cerium compounds are as polishing agents and as a component in glass.

SELENIUM

Selenium was discovered in 1817 in the gas cleaning mud from a sulfuric acid plant in which Berzelius was a partner. He named the new element after Selene the goddess of the Moon (Figure 8.7.9). The acid was manufactured from pyrite from the Falun Mine in Sweden by the chamber process.

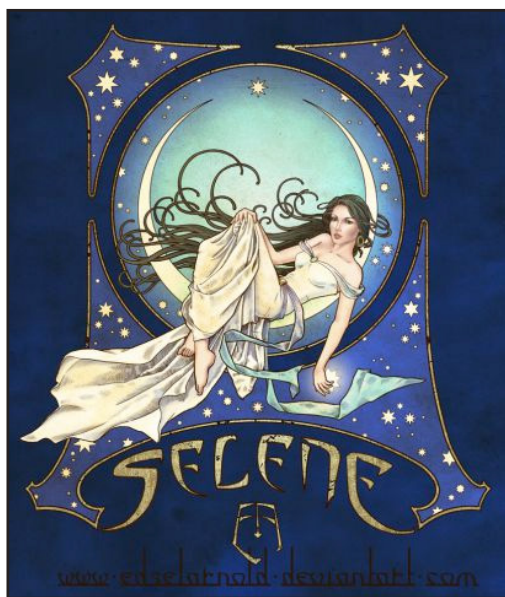


Figure 8.7.9 - A representation of Selene the goddess of the Moon

At present selenium is a by-product of the extraction of copper and nickel from their sulfide ores. It is concentrated in the anodic slimes of electrorefining of these metals from which it is obtained. It is known in two varieties: grey and red (Figure 8.7.10).



Figure 8.7.10 - Grey and red selenium

Red amorphous selenium is produced by reducing selenous acid with sulfur dioxide, by crystallization from solution, or by quenching of selenium vapor or molten selenium. It consists of Se_8 rings (Figure 8.7.11) similar to elemental sulfur, soluble in carbon disulfide giving red solutions from which selenium can be crystallized. Red selenium is an electrical non-conductor. On heating to $> 100^\circ\text{C}$, is transformed into the stable, grey, hexagonal metal-like form in an exothermic reaction. In the vapor phase, red selenium exists mainly as Se_8 rings. At higher temperature these decompose into smaller units, eventually forming Se_2 molecules.

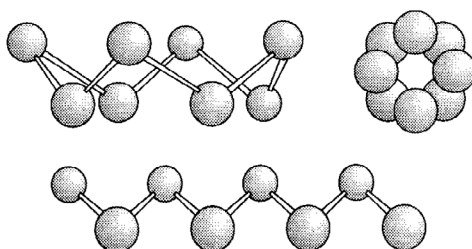


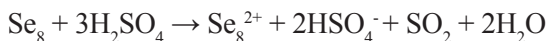
Figure 8.7.11 - Structure of red selenium [top] and grey selenium [bottom]

The grey, hexagonal crystals have metallic appearance, and is composed of helical chains which melts at 220°C . It is a semiconductor whose electrical conductivity increases by a factor >1000 under the influence of light

(photoconductivity). The electrical conductivity is strongly dependent on purity. Thus, the conductivity of selenium, including the poorly conducting amorphous form, can be increased considerably by traces (a few parts per million) of halide ions or by alloying elements such as tellurium or arsenic. Because the electrical properties are sensitive to the presence of crystal defects, the purity of selenium, which can be deliberately controlled by doping or alloying with other elements, plays an important role in its use in electrical and electronic applications.

Relative abundance in Earth's crust	$9 \times 10^{-6}\%$
Density of grey Se at 25 °C, g/cm ³	4.2
Melting point of grey Se	220°C
Boiling point (101.3 kPa; 760 mm Hg)	684.7°C

In its compounds, selenium exhibits the oxidation states -2, +4, and +6. Selenium burns in air to form selenium dioxide, which has the smell of rotten radishes. Selenium is oxidized by nitric acid to selenous acid. Hot, concentrated sulfuric acid dissolves selenium, giving a green color and forming polymeric selenium cations, for example:



With chlorine, vigorous oxidation to selenium tetrachloride occurs. Selenium reacts with electropositive elements (e.g., many metals) to form selenides and is therefore strongly corrosive, especially at high temperature. With hydrogen, the toxic gas hydrogen selenide, H_2Se , is formed.

SILICON

The ancient Egyptians made glass by fusing together quartz and natron in clay crucibles. Pliny the Elder was familiar with quartz and its use in glass-making, and gave a description of rock crystal. Although Humphry Davy (1778-1829) in England was certain that silica (Figure 8.7.12) is not an element, he was unable to decompose it with his powerful voltaic pile, and was also unsuccessful in his attempts to isolate silicon by passing potassium vapor over red-hot silica.



Figure 8.7.12 - Quartz



Figure 8.7.13 - Silica

When Berzelius heated a mixture of silica, iron, and carbon to a high temperature he obtained iron alloy. When he decomposed this with hydrochloric acid, silicon was precipitated,

Silicon and ferrosilicon

Silicon is a metalloid having the diamond structure (Figure 8.7.14). It has the appearance of a metal but lacks all properties of metals.

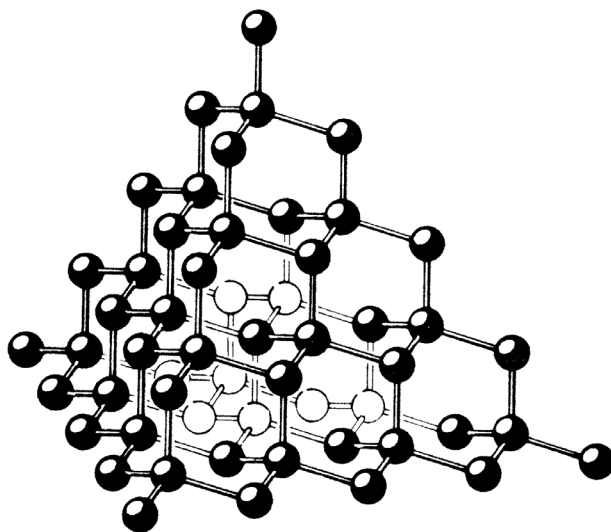
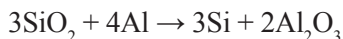
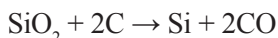


Figure 8.7.14 - Structure of silicon

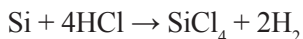
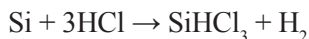
Relative abundance, %	27.72
Density, g/cm ³	
At room temperature	2.329
At melting point	2.51
Volume increase at transition from liquid to solid, %	+ 9.1
Melting point, °C	1414
Boiling point, °C	3231

Commercial production of ferrosilicon, which had proved to be an excellent de-oxidant in steel production, began in the early 1900s. Ferrosilicon is produced in an electric furnace. Metallurgical grade silicon (98% Si) has been produced by reduction of silicon dioxide in electric furnace using graphite electrodes. The purity of the product depended on the purity of the raw materials, the purity of graphite, and the furnace lining. For ferrosilicon production Söderberg electrodes are used.

Silicon is produced by reduction of silica with carbon or aluminum:



For semiconductor devices impure silica is refined by first converting it into a compound such as SiHCl_3 , SiCl_4 , SiH_2Cl_2 , or SiH_4 :



After purification, the silicon compound is transformed back into elemental, high-purity silicon by chemical vapour deposition. Bulk silicon is resistant to acid, including HF or HNO_3 , but not to a mixture of the two. In this mixture, HF first etches away the SiO_2 layer from the silicon surface, then HNO_3 oxidizes silicon again, the new SiO_2 layer is removed by HF, and so on. Silicon reacts violently with dilute alkaline solutions to generate hydrogen. Heating in an oxygen-containing atmosphere forms an SiO_2 layer that inhibits further oxidation. At room temperature, silicon and fluorine produce SiF_4 .

Uses

For applications in electronics, metallurgical grade silicon must be refined to a much higher purity by first converting it into a compound such as trichloro silane, SiHCl_3 , by reaction with HCl gas. After purification, the silicon compound is transformed back to the elemental, high-purity silicon by chemical vapor deposition. Trichloro-silane was first prepared by Friedrich Wöhler in 1857, the same method used today.

More than 95% of all electronic devices are made from single-crystal silicon. In addition, single-crystal silicon is used at present for about 40% of all photovoltaic solar cells and for all micro-mechanical devices. The method commonly used is the crystal pulling method. In this method, a silicon melt is held in a crucible and a single-crystal seed of the proper orientation is dipped into the melt and slowly withdrawn vertically. With suitable pulling speed and crystal and crucible rotation rate, a single crystal of the desired shape can be grown (Figure 8.7.15 and 8.7.16).

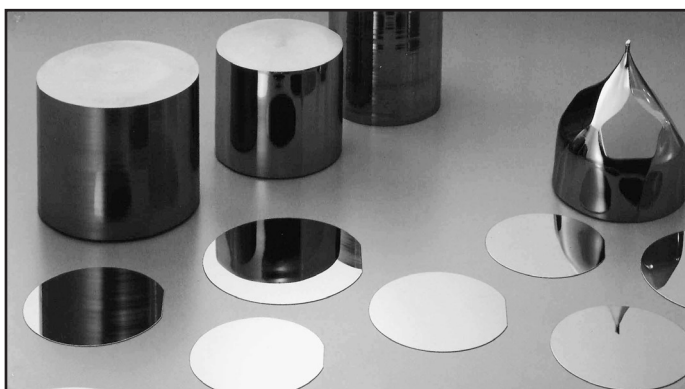


Figure 8.7.15 - Silicon wafers



Figure 8.7.16 -
Single crystal
of silicon

Silicates

Granite, the most abundant rocks in nature (95% of the Earth's crust) is a mixture of feldspar, mica, and quartz. Silica, SiO_2 , is the major constituent of rock-forming minerals. The basic building block of the silicates is the SiO_4^{4-} tetrahedron (Figure 8.7.17). The variety in the structures of the silicates is due to the various possible combinations of these tetrahedral, both with each other and also with other ions (Figure 8.7.18).

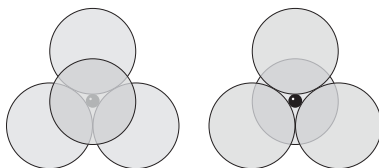


Figure 8.7.17 - The SiO_4 tetrahedron, the basic building unit of silicates.
Left: plan, right: side view

The simplest structure is the single isolated tetrahedra as in olivines. The simplest binding is the double isolated tetrahedra which results from the sharing of a corner with another neighboring SiO_4^{4-} tetrahedron to form the disilicate ion. Rings, chains, and sheets result from sharing of more corners. The chains carry a total negative charge and are bound together by positive calcium and magnesium ions placed between them.

In the sheet structure, layers of $\text{Al}(\text{OH})_3$ or $\text{Mg}(\text{OH})_2$ may be built in and are bounded to the sheets by the weak van der Waals' forces and this explains the softness of such minerals such as kaolinite (Figure 8.7.19) and mica which easily cleave into thin layers.

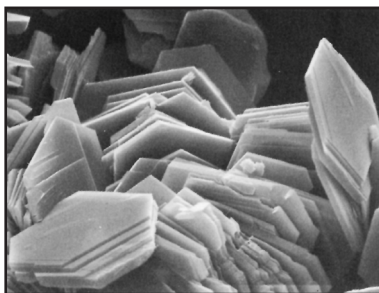


Figure 8.7.19 - Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, a representative clay mineral

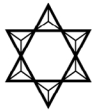
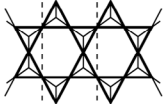
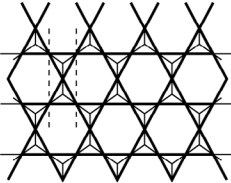
Arrangement of SiO ₄ tetrahedra	Number of oxygen ions of a tetrahedra participating in the link	Structural unit	Formula	Ratio Si : O
Single isolated tetrahedra	0		[SiO ₄] ⁴⁻	1:4
Double isolated tetrahedra	1		[Si ₂ O ₇] ⁶⁻	2:7
Rings (3 membered)	2		[Si ₃ O ₁₈] ⁶⁻	1:3
Rings (6 membered)	2		[Si ₆ O ₁₈] ¹²⁻	1:3
Chains	2		[Si ₂ O ₆] ⁴⁻	1:3
Double chains	2 1/2		[Si ₄ O ₁₁] ⁶⁻	4:11
Sheets	3		[Si ₂ O ₅] ²⁻	2:5
Framework	4	 The top O atom is shared with a top layer	[SiO ₂] ⁰	1:2

Figure 8.7.18 - Schematic representation of silicates.
Repetitive unit is shown between dotted lines

Chrysotile, the main asbestos mineral, is composed of a silicate sheet wrapped like a scroll to form fibrils (Figure 8.7.20). An asbestos fiber is thousands of fibrils attached together with their axes parallel to each other.

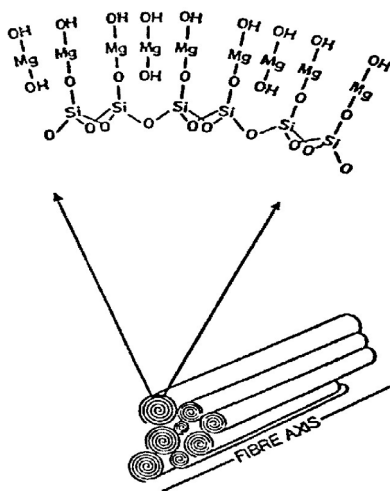


Figure 8.7.20 - Structure of chrysotile asbestos

In the framework structure, all four oxygen ions in the tetrahedron are shared resulting in a three-dimensional structure. Silica, SiO_2 , is the simplest of these structures. The great hardness, the difficult cleavage, and the high boiling point are manifestations of the great energy content of this bond. Any fracture requires that many of these chemical bonds be broken. Feldspars result from the substitution of Al^{3+} ions for some of Si^{4+} ions in the silica structure. The addition of alkali ions in the holes between the tetrahedra compensates for the charge deficit which arises. Network silicates are one of the most abundant minerals; they account for over 50% of the Earth's crust. That is why they are the most common gangue minerals found associated with ore deposits.

Zeolites are framework silicate minerals, have an open structure through which corridors run which are sufficiently large to permit ions to move in and out (Figure 8.7.21). They may also contain water molecules in these corridors. When a crystal of one of these minerals, such as chabazite, $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}$ is heated, the water molecules are driven out. The crystal does not collapse but retains its original size and shape, the spaces within the framework formerly occupied by water molecules remaining unoccupied.

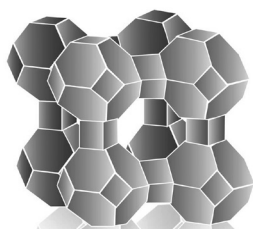


Figure 8.7.21 - Zeolite

Quartz may be colored due to impurities. For example, amethyst (Figure 8.7.22) and citrine (Figure 8.7.23) due to ferric ion.



Figure 8.7.22 - Amethyst



Figure 8.7.23 - Citrine

Quartz crystals have piezoelectric properties; they develop an electric potential upon the application of mechanical stress. An early use of this property of quartz crystals was in phonograph pickups. One of the most common piezoelectric uses of quartz today is as a crystal oscillator in the quartz clock.

THORIUM

In 1815, Berzelius was studying a new mineral found in the Falun district of Sweden. From his analysis, he concluded that he had found a new element. He named the element thorium, in honour of the Scandinavian god Thor (Figure 8.7.24). At the time, Berzelius did not know that thorium was radioactive. That was discovered later, in 1898, by Polish-French physicist Marie Curie (1867-1934) and English chemist Gerhard C. Schmidt (1864-1949).

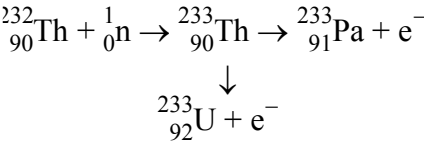


Figure 8.7.24 - A representation of the Scandinavian god Thor

Thorium is a silvery-white, ductile metal, with low strength properties and chemical. Relative abundance in Earth's crust is $1.1 \times 10^{-3} \%$, density 11.72 g/cm^3 , melting point 1750°C , and boiling point 4702°C . The most widely occurring and important mineral of thorium is monazite, a phosphate of rare earths and thorium.

Thorium is stable at room temperature but transformed to the β -phase at 1360°C . In moist air, it oxidizes slowly at its surface even at room temperature. It can be melted only in an inert-gas atmosphere or in a vacuum. The thorium ion forms anionic complexes with a large number of ions in acidic or neutral solution, e.g., CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, SO_4^{2-} , HSO_4^- , citrate, and tartrate. Thorium is nearly always tetravalent. It cannot be deposited electrolytically from aqueous solutions.

Thorium is radioactive with a half life of 2.2×10^{10} years (Figure 8.7.25). It absorbs neutrons and is transformed to uranium 233:



Uranium 233 undergoes fission; and can be used to operate a breeder reactor in presence of a thorium blanket according to the scheme:

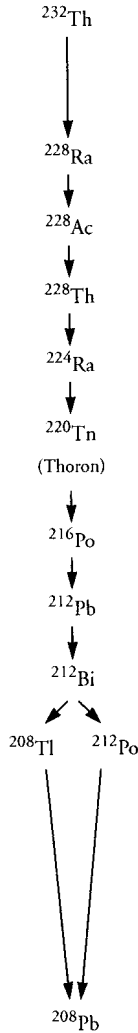
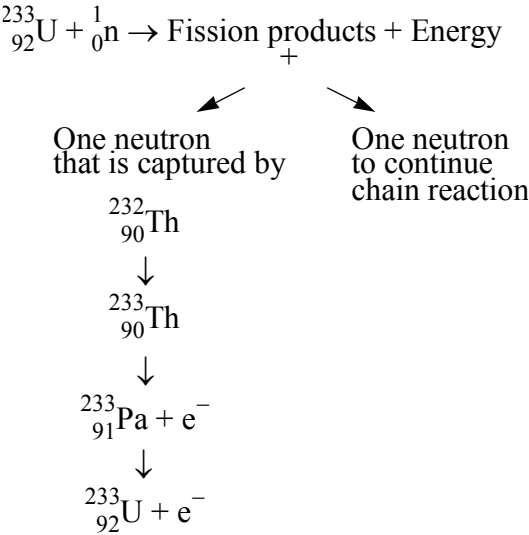


Figure 8.7.25 - Decay scheme of thorium

8.8 Lithium

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Technology	770	Uses	772
Lakes and underground brines	770		

INTRODUCTION

In 1800, Jozé Bonifacio de Andrade e Silva (1763-1838) a Brazilian scientist was sent on a journey through Europe to study chemistry, mineralogy, and metallurgy. He was appointed as the first professor of metallurgy at the University of Coimbra in Portugal. While in Scandinavia he reported that he had discovered an infusible, laminated mineral from the iron mine in Udö Island near Stockholm which he called “petalite” (Figure 8.8.1) from Greek, *leaf*, alluding to its cleavage and another which he called “spodumene” (Figure 8.8.2) from a Greek word meaning *ash colored*.

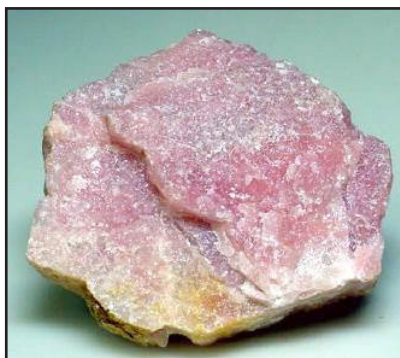


Figure 8.8.1 - Petalite
($\text{LiAlSi}_4\text{O}_{10}$)
 $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$



Figure 8.8.2 - Spodumene
($\text{LiAlSi}_2\text{O}_6$)
 $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$

After returning to Brazil in 1819 he was appointed Minister of State and

was instrumental in the independence of Brazil. He was a gifted poet and a great statesman. He was greatly honoured (Figures 8.8.3).



Figure 8.8.3 - Brazilian mineralogist
José Bonifácio de Andrada e Silva (1763–1838)

DISCOVERY

When the French chemist Vauquelin analyzed spodumene in 1801 he showed a loss of 9.5% which he could not account for. In 1818, the Swed-

ish chemist Johan August Arfwedson (1792-1841) (Figure 8.8.4) while working in Berzelius' laboratory analyzed petalite and spodumene and reported the presence of a new alkali metal which he called "lithium" to indicate that the metal was discovered in the mineral kingdom whereas the other alkali metals were found in the vegetable kingdom. Both minerals are now known to be lithium aluminum silicates. Another mineral also discovered on Udö Island was lepidolite, a word derived from Greek meaning *scale*. It has the composition $\text{K}(\text{Li,Al})(\text{AlSi}_3\text{O}_{10})(\text{O,OH,F})_2$.



Figure 8.8.4 - Johan August Arfwedson (1792-1841)



Figure 8.8.5 - Red color in a flame due to lithium

Arfwedson found that lithium differed from potassium in that it does not give a precipitate with tartaric acid, and from sodium in that its carbonate was only sparingly soluble. This last property is now used as the basis for separating lithium from sodium by precipitating it as the carbonate. The red color which lithium salts give to a flame (Figure 8.8.5) was first observed in 1818 by the German chemist Christian Gottlob Gmelin (1792-1860) (Figure 8.8.6) who worked with Berzelius in Sweden before becoming professor of chemistry and pharmacy in Tübingen.

Arfwedson and Gmelin tried in vain to isolate lithium metal by reduction of the oxide or by electrolysis of its salts. It was the British chemist William Thomas Brande (1788-1866) (Figure 8.8.7), professor of chemistry at the Royal Institution in London who used a strong battery to decompose the

oxide. Humphry Davy also obtained later a small amount of metallic lithium by the same method. In 1855 Bunsen succeeded in preparing enough of lithium by electrolyzing the molten chloride to study its properties. Later research showed that lithium is widespread in the mineral as well as in the animal and plant kingdoms.



Figure 8.8.6 - Christian
Gottlob Gmelin (1792-1860)

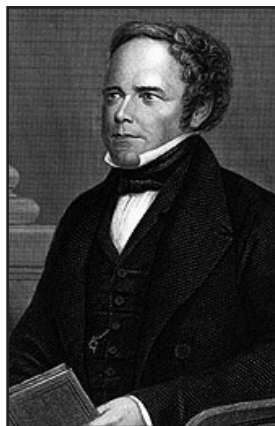


Figure 8.8.7 - William
Thomas Brande (1788-1866)

TECHNOLOGY

Lithium is recovered from two sources: lakes and underground brines, and from spodumene deposits.

Lakes and underground brines

Lithium-containing brines have become an important raw material for the production of lithium chemicals. Lithium content in this source varies from 0.07 to 1.3 g/L. Production in Searles Lake just north of Los Angeles in California started in 1938. Salar de Atacama in Antofagasta, Chile started production in 1984. The brine is pumped to the surface to fill ponds lined with nonporous membrane (Figure 8.8.8). Evaporation takes place and the concentrated brine is pumped to Antofagasta for the precipitation of lithium carbonate. Production in Salar de Uyuni in south

of Bolivia did not start yet.



Figure 8.8.8 - Brines containing lithium is pumped from underground to the ponds for concentration by evaporation in Atacama Desert

Spodumene deposits

Spodumene is a hard mineral of density 3.15 which occurs in nature in the alpha form and is not attacked by hot concentrated H_2SO_4 . However, when it is heated at 1100°C , it is converted to the beta form, which has a density of 2.4. When the hot beta form is rapidly cooled, then due to the volume change accompanying the phase transformation, the product can be easily crushed to a fine powder and will react readily with hot concentrated H_2SO_4 . Lithium is then precipitated as carbonate and recovered.

further by aluminum producers because the low density of these materials and its importance to the aircraft industry. Lithium salts have been widely used for the clinical treatment of manic-depressive illnesses. Therapeutic doses of 170 – 280 mg Li per day, mainly in the form of lithium carbonate, are administered over long periods.

Lithium batteries have lithium metal or lithium compounds as an anode. They have long life and are rechargeable. The most common type uses metallic lithium as anode and manganese dioxide as cathode, with a salt of lithium dissolved in an organic solvent. They are widely used in portable consumer electronic devices and in many long-life, critical devices, such as artificial pacemakers and other implantable electronic medical devices.

8.9 Cadmium

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DISCOVERY

In 1817 the Inspector General of Apothecaries of Hanover Friedrich Stromeyer (1776-1835) (Figure 8.9.1) noticed during one of his inspection trips a certain preparation which, according to the Hanoverian Pharmacopia ought to contain zinc oxide, contained zinc carbonate instead. He visited the manufacturing plant at Salzgitter and was informed that zinc carbonate could not be converted to oxide by heating without it turning yellow, although it was not possible to detect either iron or lead in the pure white carbonate.



Figure 8.9.1 - Friedrich Stromeyer (1776-1835)

Stromeyer took samples of this material to examine. He also acquired samples of a zinc preparation from Silesia that had been confiscated some years earlier on the supposition that it contained arsenic, because when it was dissolved in acid and then hydrogen sulfide was bubbled through, a yellow precipitate formed which was believed to be arsenic sulfide. Careful examination, however, revealed that the suspected zinc oxide did not contain arsenic.

Stromeyer then perceived that the yellow precipitate owed its existence to the presence of another metal, resembling arsenic but probably new. After extensive examination he confirmed that zinc oxide from difference sources always contained this new metal. Because this new element occurred in the zinc ore calamine, a name derived from the Latin word “*cadmia*,” he named the new element cadmium.

Stromeyer was born in Göttingen and studied chemistry and pharmacy at its University, then went to Paris to work under the famous analytical chemist Louis Nicolas Vauquelin (1763-1829). In 1802, he returned to Göttingen as assistant professor and in 1810 became professor as well as Inspector General of the apothecaries. He was Bunsen’s teacher. He authored in 1808 *Grundriss der theoretischen Chemie* in two volumes.

OCCURENCE

The average concentration of cadmium in the Earth’s crust is 1.5×10^{-5} % while zinc is 8×10^{-3} . Cadmium rarely forms its own minerals. It is always associated with zinc ores although their ionic radii differ notably. Greenockite, CdS , a rare cadmium mineral (Figure 8.9.2) was discovered in 1841 by Charles Murray Cathcart (Lord Greenock) (1783-1859), during excavating a tunnel near Port Glasgow. Lord Greenock an army officer incidentally became Governor General of Canada (1846-1847).



Figure 8.9.2 - Museum sample of greenockite, CdS , a rare cadmium mineral

THE METAL

Cadmium melts at 320.9°C , boils at 767°C , and its density is 8.64 g/cm^3 . Its crystal structure is distorted closest packed hexagonal. The metal burns at high temperature with a red-yellow flame to form brown cadmium oxide, which is poisonous. Cadmium dissolves readily in nitric acid but only slowly in hydrochloric or sulfuric acid and not at all in bases.

RECOVERY

At present cadmium is recovered from lead-zinc ores (Figure 8.9.3):

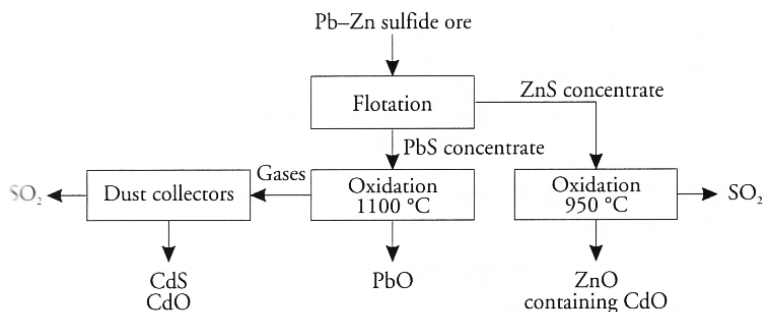


Figure 8.9.3 - Recovery of cadmium from lead-zinc ores

- The leach solutions of zinc calcines obtained by roasting zinc blende, by cementation with zinc dust
- The dust collected in the bag filters during roasting galena

Zinc blende is roasted at a lower temperature than galena; that is why cadmium is not volatilized in this case and remains in the calcines. Cadmium is recovered from solution electrolytically.

USES

After its discovery more than a century elapsed before cadmium or its compounds were employed to any significant extent. Only since the 1940's production and consumption have risen. The primary uses are electroplated cadmium coatings, nickel – cadmium storage batteries, pigments, and stabilizers for plastics.

Cadmium pigments have particularly brilliant red and yellow colors, as well as a high durability. All cadmium pigments are based on cadmium sulfide. With an increasing content of selenium, or especially mercury, the shades of the pigments change to orange, red, and ultimately to deep red. The use of cadmium is decreasing due to its toxicity. One of its new uses is in cadmium telluride solar panels.

8.10

Aluminum¹

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INTRODUCTION

Aluminum is the most abundant metallic element in the earth's crust. It occurs in a variety of minerals combined with oxygen, silicon, the alkali and alkaline-earth metals, and fluorine, and as hydroxides, sulfates, and phosphates.

DISCOVERY

The metal aluminum derives its name from alumen, the Latin name for alum found in nature (Figure 8.10.1). In 1787 Lavoisier definitely identified it as the oxide of a still undiscovered metal. Humphry Davy (1778-1829) in England attempted unsuccessfully to produce the metal by electrolyzing fused mixture of alumina and potash. When he announced in 1808 his belief that alumina, was the earth of an undiscovered metal, scientists in Europe started researches to obtain this new metal.

¹ Based on F. Habashi, *Aluminum. History & Metallurgy*, Métallurgie Extractive Québec, Québec City, Canada 2008. Available from Laval University Bookstore, www.zone.ul.ca



Figure 8.10.1 - Museum sample of aluminum alum

The metal was isolated in minute amounts for the first time in 1825 by the Danish physicist Hans Christian Oersted (1777-1851) (Figure 8.10.2) by reacting AlCl_3 with potassium amalgam; he himself prepared AlCl_3 for the first time in the same year by reaction of chlorine with Al_2O_3 .



Figure 8.10.2 - Hans Christian Oersted (1777-1851)



Figure 8.10.3 - Friedrich Wöhler (1800-1884)

The German chemist Friedrich Wöhler (1800-1884) (Figure 8.10.3) was returning home after finishing his studies with Berzelius in Stockholm, stopped in Copenhagen to see the new metal isolated by Oersted. In Berlin he repeated in 1827 Oersted's experiment using metallic potassium instead of amalgam. By this technique he obtained small metallic particles of aluminum.

ELECTROLYSIS OF FUSED AlCl_3

The electrowinning of aluminum from an aqueous solution is not possible because of the strongly negative deposition potential of this metal and the rapid hydrolysis of the aluminum ion. The first use of electric current to deposit a metal from its fused salt was demonstrated by chemistry professor Robert Bunsen (1811-1899) (Figure 8.10.4) at the University of Heidelberg. In 1852, he prepared magnesium from MgCl_2 and in 1858 lithium from LiCl using a porcelain crucible in which the carbon cathode was cut so as to form pockets inside which the metal was deposited. Unless this precaution was taken, the metal, being lighter than the fused chloride, rose to the surface and burned.



Figure 8.10.4 - Robert Bunsen
(1811-1899)

INDUSTRIAL PRODUCTION

Henri Saint Claire Deville (1818-1881) (Figure 8.10.5) professor of chemistry at Ecole Normale Supérieure in Paris produced aluminum by electrolysis of fused AlCl_3 . However, he abandoned this idea because electric current was available only from galvanic cells that were cumbersome and expensive to maintain. He then reduced aluminum chloride with sodium instead of the amalgam used by Oersted and was able to prepare a small bar of the metal to show at the meeting of the French Academy of Sciences.



Figure 8.10.5 - Henri Sainte-Claire Deville (1818-1881)

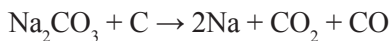


Figure 8.10.6 - Emperor Napoleon III (1808-1873)

His friend the great chemist Jean-Baptiste Dumas got an audience with Emperor Napoleon III (1808-1873) (Figure 8.10.6) the nephew of Napoleon Bonaparte, and convinced him to subsidize the researches on aluminum.

As a result Sainte-Claire Deville was also able to expose the bar at the Paris Exposition in 1855 under the title “The Silver of Clay” which attracted a great attention. He then went ahead to commercialize the process in a small plant at the Glaciere District of Paris. The plant was emitting sulfur gases and as a result of the protest of the neighbours, he was obliged to move to another location outside of Paris. In 1857 a new plant was installed at Nanterre, and in 1859 he wrote his book *De l’Aluminium, ses Propriétés, sa Fabrication et ses Applications*. Deville process involved the following steps:

- Preparation of the double chloride of sodium and aluminum by reacting a mixture of bauxite, NaCl, and coal tar with gaseous chlorine in an iron retort (Figure 8.10.7).
- Preparation of metallic sodium by heating a mixture of sodium carbonate, limestone, and coal in a retort (Figure 8.10.8):



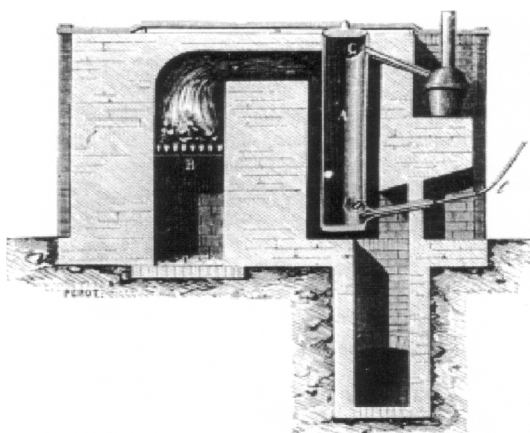


Figure 8.10.7 - Production of the double chloride $\text{AlCl}_3 \cdot \text{NaCl}$. Chlorine is introduced in the side pipe on the right and the volatilized chloride is collected into the recipient on the top right

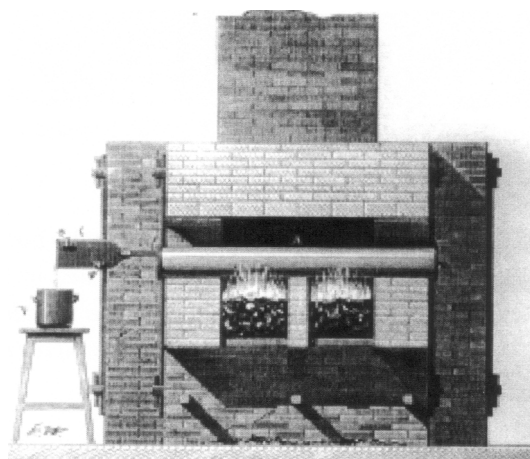


Figure 8.10.8 - Production of metallic sodium by reduction of sodium carbonate with coal. Sodium vapor is condensed in condenser C and the liquid is collected in the bucket containing oil

- Reaction metallic sodium with the double chloride $\text{AlCl}_3 \cdot \text{NaCl}$ in a reverberatory furnace to get metallic aluminum and slag (Figure 8.10.9).



Figure 8.10.9 - Production of metallic aluminum by reacting metallic sodium with the double chloride $\text{AlCl}_3 \cdot \text{NaCl}$ in a reverberatory furnace. The charge is introduced from the opening E and the product collected in the bucket J. Gases exit from H to the chimney at I



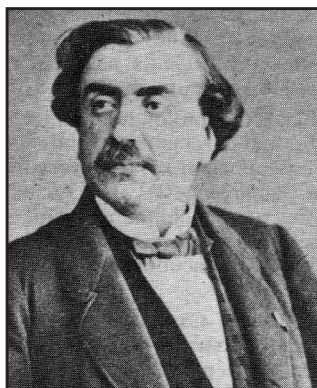
Figure 8.10.10 - A French stamp honoring Henri Sainte-Claire Deville

Deville was honoured in France as the founder of the aluminum industry (Figure 8.10.10). In 1882, one year after his death, the process was used at Compagnie des Produits Chimiques d'Alais² et de la Camargue at the Salindres plant near Nimes (Figure 8.10.11), belonging to Henry Merle (1825-1877) (Figure 8.10.12) who was fabricating sodium carbonate by the Leblanc process, H_2SO_4 by the chamber process, hydrochloric acid, and other chemicals. The plant manager was Alfred Pechiney (1833-1916)) (Figure 8.10.13) who became in full charge of operations when Marle died suddenly in 1877 at the age of 52. Marle is considered to be the founder of the inorganic chemical industry in France and his plant as the origin of Pechiney Company.

² Alais is now spelled Alès



Figure 8.10.11 - Salindres plant in the south of France

Figure 8.10.12 - Henri Merle
(1825-1877)Figure 8.10.13 - Alfred Pechiney
(1833-1916)

Hamilton Castner (1859-1890) (Figure 8.10.14) of Columbia University in New York was responsible for reducing the cost of aluminum by his invention in 1886 of a cheap method for producing sodium from molten NaOH instead of sodium carbonate by reduction with an iron-carbon mixture:



However, this was too late for the Deville process which was rapidly displaced by a new process invented simultaneously by Paul Héroult (1863-1914) in France and Charles Martin Hall (1863-1914) in the USA. The new process was based on the electrolytic reduction of Al_2O_3 dissolved in fused cryolite found in Greenland. It is the process used today world-wide.



Figure 8.10.14 - Hamilton Castner (1859-1890)



Figure 8.10.15 - Julius Thomsen (1826-1909)

PRODUCTION OF ALUMINA

Alumina from cryolite

Before the utilization of bauxite for alumina manufacture, the mineral cryolite, Na_3AlF_6 , found at Ivigtut, in south Greenland by a Danish whaler who brought a piece of it to Copenhagen, was used. The name of the mineral means frost-stone in Greek in reference to the snow-like appearance of the solid that melts easily under the flame. In 1854, i.e., one year before Le Chatelier invented his process, a process was developed by Julius Thomsen (1826-1909) (Figure 8.10.15) professor at the Technical University of Copenhagen, involving heating the cryolite with limestone followed by water leaching to extract sodium aluminate formed leaving behind CaF_2 in the residue:



Aluminum hydroxide was then precipitated from the aluminate solution by CO_2 leaving sodium carbonate in solution to be recovered as a by-product (Figure 8.10.16):

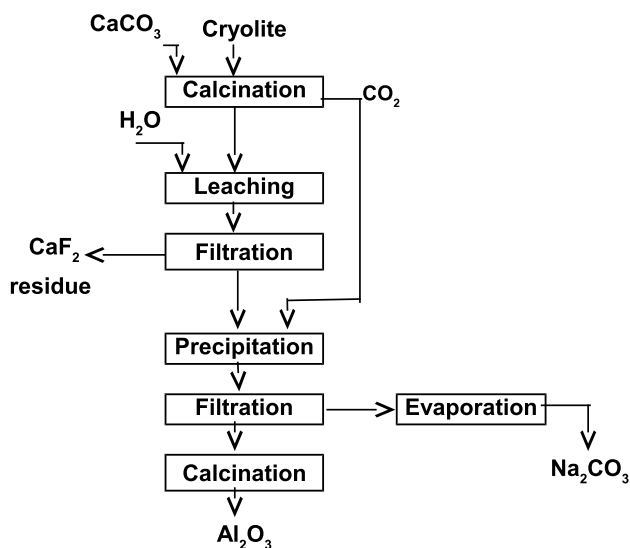
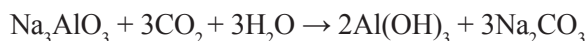


Figure 8.10.16 - Thomsen's process for the recovery of Al_2O_3 and Na_2CO_3 from cryolite

By the early 1860's a large scale soda and alumina production based on cryolite was in operation, and was one of the largest industries in Denmark. The process was also transferred to few other nearby countries as well as in USA at the Pennsylvania Salt Company at Natrona near Pittsburgh. However, in 1894 soda production from cryolite ceased in Copenhagen because of competition with the new Solvay process. In 1897 about 13 000 tons of the mineral were mined, the major part of which was delivered to the Pennsylvania Company, but three years later, the process was also abandoned in USA. Thomsen is best known for developing the principle that the heat of formation is a measure of chemical affinity and for a four volume work *Thermochemische Untersuchungen* he published between 1882 and 1886.

Later cryolite played an important role in the Hall-Hérault process when it was discovered by the German chemist Martin Kiliani (1858-1895) (Figure 8.10.17) that a cryolite sample had an exceptionally low melting point and when analyzed it was found to contain a small amount of Al_2O_3 as impurity. Thus he came to the conclusion that Al_2O_3 decreases the melting point of cryolite. This information was immediately utilized by Hérault and Hall to propose cryolite as molten salt solvent for Al_2O_3 .



Figure 8.10.17 - Martin Kiliani (1858-1895)

But before this process was invented, the German chemist Heinrich Rose and independently the British metallurgist Allan Dick devised a method for producing aluminum by reduction of cryolite with sodium. Henri Sainte-Claire Deville also considered using this method but abandoned the idea after a French expedition to Greenland in summer of 1856 headed by him found out that the cryolite deposit is of limited size, and rightly considered that the French bauxite should be a more suitable raw material for an expanding aluminum industry. In 1962 the Greenland operation ceased for good.

Alumina from bauxite

The aluminum ore known as bauxite was discovered in 1821 by Pierre Berthier (1782-1861) (Figure 8.10.18), professor at the School of Mines

in Paris, while prospecting for iron ores at Les Baux near Marseille in southern France. He called it terre d'alumine des Baux (Figure 8.10.19).



Figure 8.10.18 - Pierre Berthier
(1782-1861)



Figure 8.10.19 - A French stamp
marking the discovery of terre
d'alumine des Baux after the village of
Les Baux near Marseille

The red color of the deposit had attracted his interest as a possible iron ore for the blast furnace in the district. However, it was found to contain too much Al_2O_3 to be of value for this purpose. Bauxite was first thought to contain alumina dihydrate, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, however, later it was shown by thermal analysis to contain a mixture of the hydroxides $\text{Al}(\text{OH})_3$ and AlOOH . Discoveries of bauxite were later reported in many parts of the world including Jamaica, Surinam, Guyana, Australia, the former USSR, USA, the former Yugoslavia, and Hungary. It now represents one of the largest tonnage mineral raw material treated chemically - about 90 million tons annually world-wide (Figure 8.10.20).

Aluminum can be solubilized readily from bauxite by acids but it is difficult to get pure aluminum hydroxide from the solution because on adding an alkali to the solution a gelatinous basic salt, rather than a crystalline hydroxide is precipitated. The gelatinous precipitate is difficult to filter and wash. Furthermore, since iron and titanium are also partially dissolved in acid, the precipitate will be contaminated, creating a separation problem. As a result the acid-leaching route was never used to prepare Al_2O_3 ; it is used only on a small scale to prepare aluminum sulfate by crystallization, for water treatment.

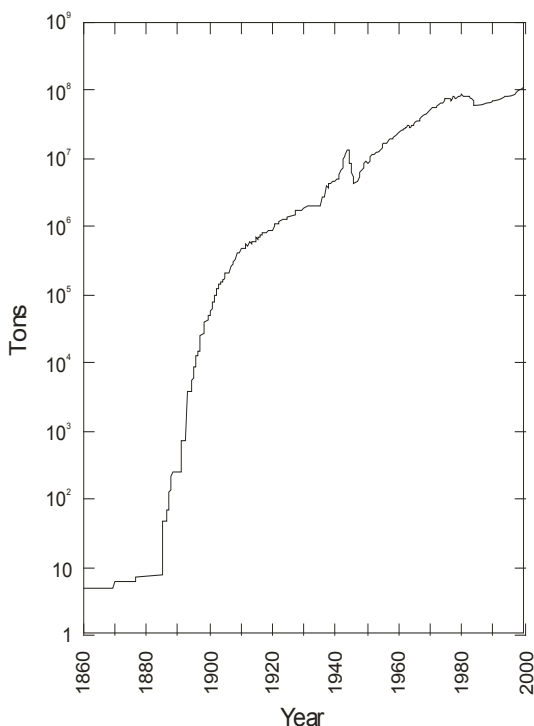
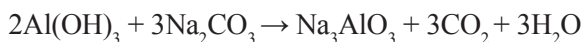


Figure 8.10.20 - Consumption of bauxite

Le Chatelier process

In 1855, the mining engineer Louis Le Chatelier (1815-1873) (Figure 8.10.21) invented the thermal process for the recovery of alumina from bauxite. He was the Chief Inspector of Mines in France whose son the chemist Henri Le Chatelier (1850-1936) is best known for the thermodynamic principle which bears his name. The process involved heating bauxite with sodium carbonate at about 1000°C to form sodium aluminate which is then leached with water. Aluminum hydroxide is then precipitated from this solution by bubbling CO₂ gas generated during the calcination step (Figure 8.10.22):



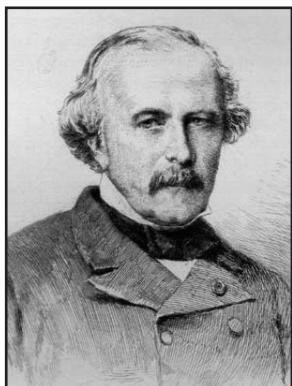


Figure 8.10.21 - Louis Le Chatelier
(1815-1873)

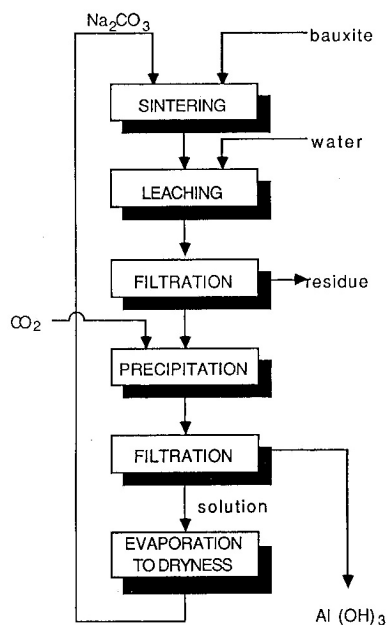


Figure 8.10.22 - Le Chatelier process,
1855

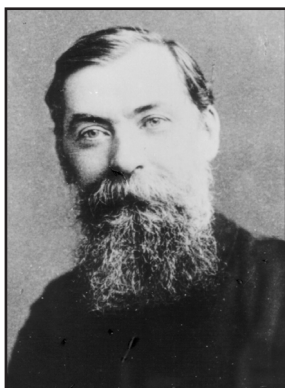


Figure 8.10.23 - Karl Josef Bayer
(1847-1904)

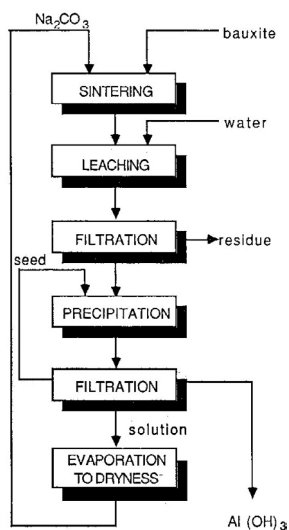


Figure 8.10.24 - Le Chatelier process
modified by Bayer, 1888

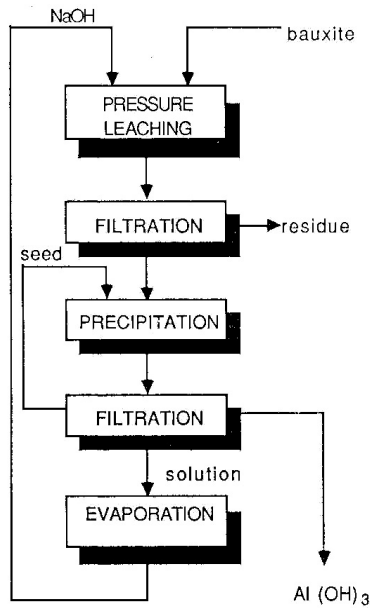


Figure 8.10.27 - Bayer process, 1892

The process involves two steps:

- The pressure leaching of bauxite with NaOH solution to obtain sodium aluminate solution.
- The precipitation of pure aluminum hydroxide from this solution by seeding with fine crystals of $\text{Al}(\text{OH})_3$ from which Al_2O_3 is obtained by calcination.

Bauxite is composed of aluminum hydroxide minerals hydrargillite or gibbsite $\gamma\text{-Al}(\text{OH})_3$, böhmite, $\gamma\text{-AlOOH}$, and diaspor, $\alpha\text{-AlOOH}$, in association with a variety of oxides of iron, titanium, and silica. Bayer process involves the selective leaching of aluminum hydroxide minerals in NaOH solutions at high temperature and pressure in autoclaves. Pure crystalline $\text{Al}(\text{OH})_3$ can then be precipitated slowly on nuclei of $\text{Al}(\text{OH})_3$ supplied for this purpose (Figure 8.10.28). After filtration and washing, the hydroxide is calcined to the oxide. Figure 8.10.29 shows a modern Bayer plant.

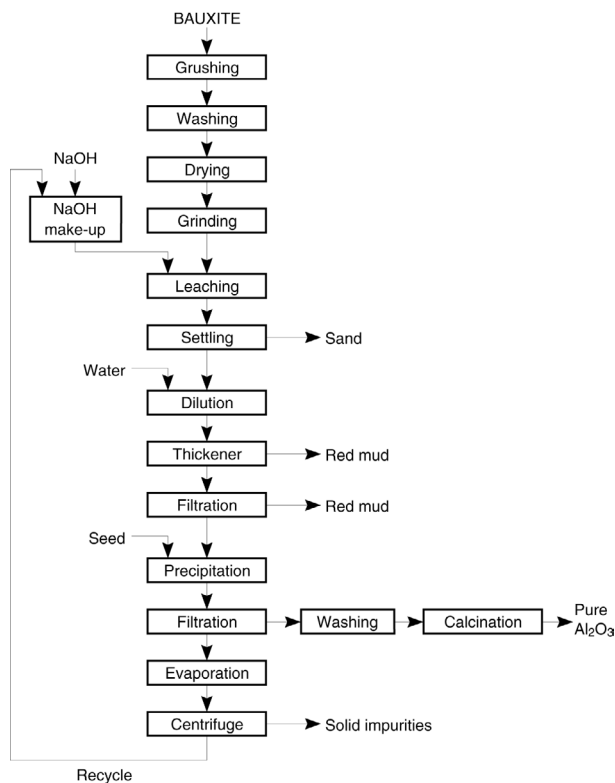


Figure 8.10.28 - Bayer process for alumina production

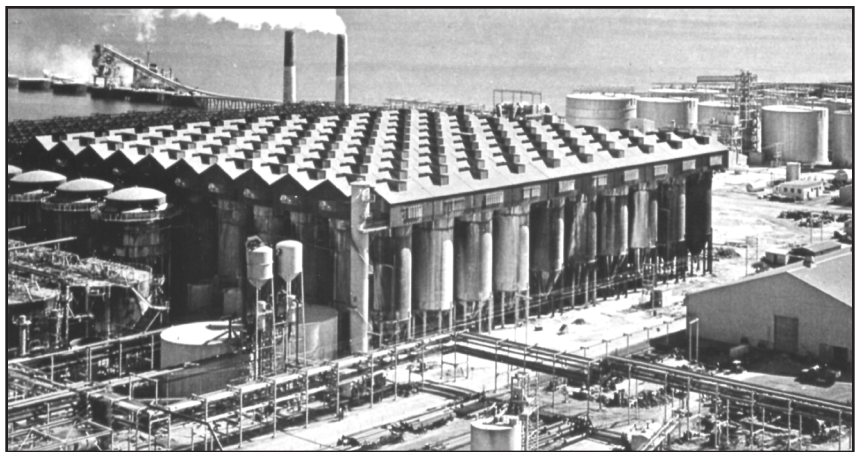


Figure 8.10.29 - A modern Bayer plant

Early German alumina plants

Three plants producing Al_2O_3 , alum, and aluminum sulfate using bauxite imported from France were erected in Germany:

1880 - Chemische Fabrik Bergius at Goldschmieden near Berslau (now Worclaw in Poland).

1885 - Giuliani at Ludwigshaven.

1914 - Martinswerk at Bergheim near Cologne.

During World War I, when the supply of French bauxite was cut off, the Vereinigte Aluminium Werke, a German state company undertook in 1917 prospection for bauxite and acquired interests in its mining in Istria in Italy, in Croatia, and in Hungary. Two more alumina plants were constructed and located in the lignite district using the sodium carbonate calcination process to treat Hungarian bauxite and Bayer's seed precipitation method. The first plant near Lauta (the Lautawerk) and the second at Grevenbroich near Duisburg (the Erftwerk) built in cooperation with Giuliani Brothers.

Alumina plants in France

The first industrial alumina plant using Bayer's patents was started at Gardanne (Figure 8.10.30) in southern France in February 1894 by the *Société Française de l'Alumine Pure* founded a year earlier for this purpose to supply 1.5 tons/day of pure Al_2O_3 to the *Société Électrométallurgique Française* owned by Paul Héroult and another associate situated at Froges near Grenoble. The choice of Gardanne was based on the availability of lignite in the region. It was estimated that it would be cheaper to transport the bauxite rather than the fuel. The region is near the important port of Marseille where the sodium hydroxide could be imported, the availability of abundant manpower, and the agreement to get water from the coal mines in case water from the local wells is not sufficient.



Figure 8.10.30 - Location of Gardanne

Bayer himself was present during the start up of the plant. There were many mechanical difficulties, e.g., explosion of a Babcock boiler that needed an additional capital to which the enterprise did not have. The precipitation process was very slow, the efficiency did not exceed 40%, and the product was not of the desired purity. A proposed fusion with Hérault's company was negotiated and accepted in February 1895. The decision was favourable for all parties since Hérault's company used to pay a high custom for the Al_2O_3 imported from Germany. Other Bayer alumina plants constructed in France were: at Salindre in 1901, at Ugine in 1908, and at Saint Auban in 1918. After overcoming the operating difficulties, fusion of plants took place which resulted in what became later *Pechiney Company*. During the Vichy Government, the Gardanne plant was occupied by the Germans and was sabotaged by the Resistance in 1944.

British alumina plants

The second Bayer process plant was built in Larne in Northern Ireland in 1895 by the *British Aluminum Company*. The Company which was formed in 1894 by Emmanuel Ristori as its director and Lord Kelvin as technical advisor, had already acquired the rights of Bayer's process and Hérault's process in the same year. The Company also built a reduction plant at Foyers in Scotland, and acquired the rolling mills from the *Cowles Syndicate* in Britain. The Foyers plant produced its first aluminum on June 15, 1896 by the electrolytic process from hydroelectric power. Lord Kelvin (1824-1907) (Figure 8.10.31) became director in 1898.



Figure 8.10.31 - Lord Kelvin [William Thomson] (1824-1907)

Bauxite had been mined at Larne for 20 years previously for the production of aluminum sulfate. The bauxite mined in the early days contained 56% Al_2O_3 , 3% Fe_2O_3 , 12% SiO_2 , 3% TiO_2 , and 26% H_2O . The mine was 56 km from the factory and the bauxite was transported by railway. Digestion took place in two 1.5m diameter x 3.3m long agitated digester, fitted with steam jackets. The autoclave was heated for 2 or 3 hours with 55 kPa. steam and then blown empty, with no flash steam recuperation. The filtered pregnant liquor was pumped into the precipitation tank in which some hydrate had been left from the previous cycle to act as seed. Six precipitators were used each was 11m diameter x 6m high. 70% of the alumina in the sodium aluminate was reported as being precipitated in 36 hours. In 1897 French bauxite was used.

In 1907, another British company, the Aluminium Corporation was founded to produce aluminum in North Wales. It secured its alumina from a plant at Hebburn-on-Tyne near New Castle operated by its subsidiary the *International Aluminium Company*. In 1913, the *British Aluminium Company* started its second Bayer plant at Burnt Island, Fifeshire, Scotland.

East Saint Louis plant, USA

The first Bayer plant in USA was constructed in 1902-1903 in East St. Louis, Illinois by the *Aluminum Ore Company* owned by the *Pittsburgh Reduction Company* founded in 1888 to exploit Hall's patent for aluminum production using Al_2O_3 imported from Silesia. Later it exploited the bauxite mined in Arkansas. In 1907 the company changed its name to the *Aluminum Company of America*, now known as *Alcoa*. Charles Martin Hall was made superintendent. The company expanded and had numerous subsidiaries in Canada, Norway, and Italy.

Alusuisse plant

The first Alusuisse Bayer plant started its operation in 1908 at Neuhausen near Schaffhausen with a capacity of 26 t/day of Al_2O_3 making it the largest plant in Europe at that time and up to World War I. The aluminum industry was already well established there by the *Schweizerische Metallurgische Gesellschaft* since 1887 which fused with *Allgemeine Elektrizitäts Gesellschaft* in 1888 to form the *Aluminum Industrie Aktiengesellschaft*.

Autoclaves

At Bayer's time synthetic dyestuffs were produced for the first time on commercial scale, and it was in this industry that high pressure reactors were first applied. Organic intermediates needed to manufacture the synthetic dyestuffs were produced in heated agitated reactors that were able to withstand the pressure required for reactions such as sulfonation, nitration, reduction, etc.

The use of tube or pipeline autoclaves began simultaneously in Germany and in the former Czechoslovakia in 1967 for the leaching of bauxite.

In this process a temperature of 300°C was used, resulting in a vapour pressure in the system of about 13 000 kPa. Due to the high temperature, a reaction time of only 2-3 minutes instead of 4-6 hours was sufficient to extract the aluminum. The process is continuous and has a high thermal efficiency due to the effective heat exchange system.

Red mud

A problem of Bayer's process is the disposal of red mud Figure 8.10.32. For each ton of Al_2O_3 about one ton of red mud is produced. Taking into consideration the large tonnage of bauxite processed, the amount of red mud produced annually world-wide is about 40 million tons. These are usually disposed of in ponds. Red mud from Gardanne is disposed of into the Mediterranean.



Figure 8.10.32 - Red mud

ELECTROLYTIC REDUCTION OF ALUMINA

All aluminum produced today is by the electrolytic reduction of Al_2O_3 invented simultaneously by Paul Héroult (1863-1914) (Figure 8.10.33) in France and Charles Martin Hall (1863-1914) in the USA (Figure 8.10.34). In 1960, aluminum production surpassed that of copper and became the second metal after iron. Its price decreased to become one fourth of that of copper instead of being higher.

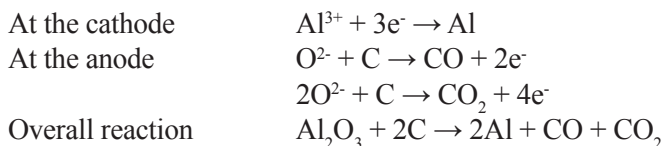


Figure 8.10.33 - Paul Héroult
(1863-1914)



Figure 8.10.34 - Charles Martin
Hall (1863-1914)

Pure aluminum oxide prepared by Bayer process is dissolved in molten cryolite, Na_3AlF_6 at 950°C to the extent of about 10% in an electrolytic cell using molten aluminum as a cathode and high quality carbon anodes. On passing the electric current, aluminum ions are reduced at the cathode while oxide ions react with carbon at the anode forming CO and CO_2 . The reaction can be represented as follows:



Anodes

Molten aluminum collected at the bottom of the cell is sucked in a vacuum container for transportation to the cast house and alloy preparation. There are two types of electrolytic cells: those using the pre-baked anodes and those using the Söderberg anodes.

Pre-baked anodes

Pre-baked anodes are made of a mixture of carbon, pitch, and tar, pressed into moulds or extruded through a die, and subsequently baked at 1000°C .

It is customary to employ petroleum coke or special low-ash anthracite, to avoid contaminating the metal with impurities. Two or more copper or aluminum busbars are supported above the electrolyte cavity of the aluminum production cells, and the anodes hang from these and dip into the molten cryolite electrolyte. They are supported by rods or bars of copper, aluminum, or iron, which are clamped onto the busbar to support the anodes mechanically and to carry current to them (Figure 8.10.35).

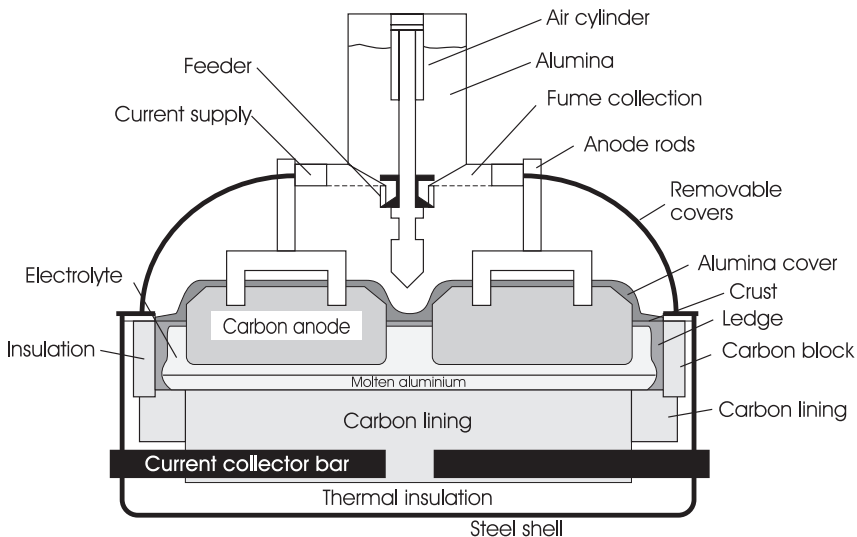


Figure 8.10.35 - Electrolytic cell for the production of aluminium

One of the important factors in the operation of the cell is the adjustment of these anodes so as to properly divide the current among them. If an anode is set too low, a projecting point may touch the metal layer in the bottom of the cell and allow part of the current to pass directly to the metal without passing through the electrolyte. If the anode is set too high, the resistance of the thicker layer of electrolyte between it and the cathode will prevent it from taking its share of the current and, consequently, increase the load on the other anodes. When the anodes are consumed they are replaced by new ones.

Søderberg anode

The Søderberg anode was invented in 1910-1912 by Carl Wilhelm Søderberg (1876-1955) (Figure 8.10.36). It consists of a cylindrical metal casing extending from the cell to a platform located directly above the cell (Figure 8.10.37).

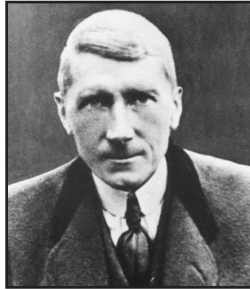


Figure 8.10.36 - Carl Wilhelm Søderberg (1876-1955)

This casing is filled with the carbonaceous mixture constituting the electrode, and serves as a mould to hold and support the carbon mix. In the lower part of the casing the electrode mix at the lower end is gradually baked by the heat from the furnace as well as by the current passing through the casing and through the carbon of the electrode (where it has baked sufficiently to become electrically conducting).

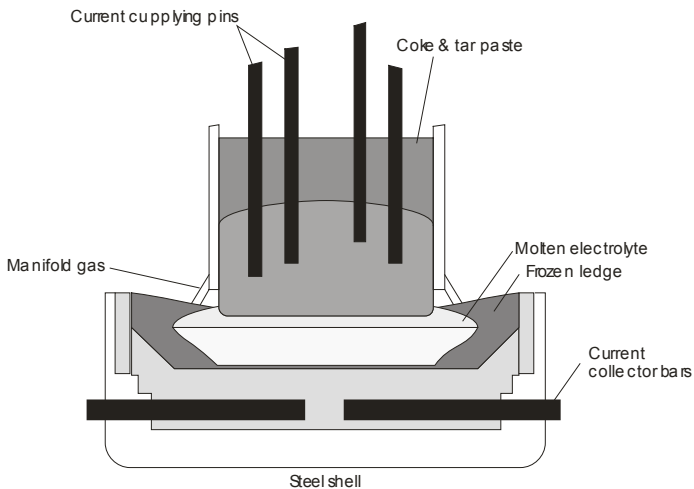


Figure 8.10.37 - Søderberg anode

In operation, as the electrode is consumed at its lower end in the cell, the electrode (but not the casing) is lowered. The baking operation is thus continuous, as the soft electrode mix gradually becomes hotter and hotter in approaching the hot zone. Instead of a multiplicity of electrodes, as in the pre-baked electrode case, only one Söderberg electrode is employed per cell. Current is led into the interior of the electrode by suitable contact stubs attached to the casing and ribs extending into the electrode mass. As the electrode is consumed, the current leads are successively moved to the next higher row of contact stubs. The electrode is a heavy structure and a substantial clamping device is necessary to hold it securely and lower it from time to time, as it is consumed, to the desired position.

Recent trends

In the 1980s the aluminum industry decided to return to the pre-baked electrodes in spite of their cost primarily to abate pollution in the vicinity of the pots.

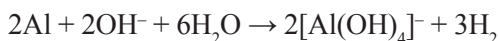
THE METAL

Physical properties

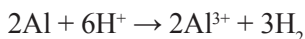
Atomic weight	26.98
Relative abundance, %	8.13
Melting point, °C	660.5
Boiling point, °C	2494
Heat of fusion, J/g	397
Heat of vaporization, kJ/g	10.8
Heat capacity, J g ⁻¹ K ⁻¹	0.90
Density, g/cm ³	2.699
Density of liquid, g/cm ³ at 700°C	2.357
Crystal Structure	Face-centered cubic
Atomic diameter, m	2.86 x 10 ⁻¹⁰
Coefficient of expansion at 20°C, K ⁻¹	23x10 ⁻⁶
Thermal conductivity at 25°C, W cm ⁻¹ K ⁻¹	2.37
Electrical resistivity of pure aluminum at 25°C, μΩ·cm	2.5

Chemical properties

Aluminum is a typical metal in the sense that when it loses its three outermost electrons it will have the electronic structure of an inert gas. Although it is one of the most reactive metals, it is widely used as a material of construction because of the continuous adherent thin oxide film that rapidly forms on its surface. It dissolves in alkaline solutions:



Aluminum is amphoteric; it reacts with mineral acids to form soluble salts with hydrogen evolution:



All aluminum compounds are colorless.

Position in the periodic table

Aluminum is usually put below boron - a metalloid with which it has little in common. When transferred to be above scandium it will form together with the alkali metals and the alkaline earth metals the typical metals group with related properties and related electronic configuration (Figure 8.10.38). They have the following characteristics:

- They have an electronic structure similar to that of the inert gases with one, two, or three electrons in the outermost shell.
- They have single valency, i.e., they lose their outermost electrons in a single step.
- They are reactive, i.e., react readily with water and oxygen. The driving force for this reactivity is the inclination to achieve maximum stability by attaining the electronic structure of an inert gas. A reactive metal such as aluminum or magnesium may be used as a material of construction because of the protective oxide film that is formed rapidly on its surface.

METALS **METALLOIDS** **NONMETALS**

Typical Metals

Transition Metals

Horizontal Similarity

Vertical Similarity

Less Typical Metals

Covalent

Monatomic

Lanthanides

Actinides

Inner Transition Metals

Figure 8.10.38 - Aluminum as a member of the typical metals

- They form only colorless compounds.
- Within a certain vertical group the atomic radius increases with increasing atomic number because of the added electron shells.
- Within a certain vertical group the reactivity increases with increasing atomic number because of the ease with which the outermost electrons will be lost since they are further away from the nucleus. Thus cesium is more reactive than rubidium, and rubidium more than potassium, etc.
- With increasing charge on the nucleus, the electrostatic attraction for the electrons increases and the outermost electrons will not be easily lost hence the reactivity decreases. Thus magnesium is less reactive than sodium, calcium less than potassium, and so on.
- With increased electrostatic attraction for the electrons as a result of increasing charge on the nucleus, the size of the atom decreases. Thus, aluminum has a smaller radius than magnesium, and magnesium smaller than sodium.

- With decreased radius and increased atomic weight the atom becomes more compact, i.e. the density increases. Thus, aluminum has higher density than magnesium, and magnesium higher than sodium.

Moving aluminum away from gallium with which it occurs in bauxite may raise objection. However, it should be recalled that there are marked differences between both metals:

- While aluminum oxidizes so rapidly that it soon forms a non-porous protective layer, gallium does not.
- Gallium can be electrodeposited from aqueous solution, while aluminum cannot.
- $\text{Al}(\text{OH})_3$ does not dissolve in ammonium hydroxide solution, but $\text{Ga}(\text{OH})_3$ does dissolve.
- Gallium is precipitated from aqueous solution by H_2S as a sulfide; aluminum does not.
- Aluminum forms carbides, gallium does not.
- Aluminum carbide, Al_4C_3 is similar to the carbides of the first three groups, being ionic colorless compound containing the C_2^{2-} anion that decomposes in water. However, it liberates methane instead of acetylene like the other members of the group:

$$\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} \rightarrow 4\text{Al}(\text{OH})_3 + 3\text{CH}_4$$
- Gallium forms a gaseous hydride, Ga_2H_6 , while aluminum forms a white solid polymer hydride, $(\text{AlH}_3)_x$
- Historically, aluminum oxide was considered an earth like the rare earths and it fits with the scandium group.
- Mendeleev successfully predicted the properties of scandium before it was discovered by linking it with aluminum.

- The chemistry of scandium is very similar to that of aluminum and the ions Al^{3+} , Sc^{3+} , Y^{3+} , La^{3+} , and Ac^{3+} form a series similar to Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} and Ra^{2+} .
- Gallium is a typical dispersed element whose relative abundance in the Earth's crust is $1.5 \times 10^{-3}\%$, aluminum is the third most abundant element with a relative abundance of 8.13% (after oxygen and silicon).

Another objection, which may arise from this transfer, is the dissimilarity of the electron orbital structure of aluminum as compared to Sc, Y and La: aluminum has 2s and 1p electrons, while the others have 2s and 1d electrons. This objection can be answered in the following. The classification of the elements in the Periodic Table according to the population of electrons in the subshells, i.e., as s-, p-, d, and f-block elements does not indicate or explain many facts such as:

- The boron group elements are in the p-block but show different chemical and physical properties, e.g., boron is a metalloid while the other elements are metals. Further, the structure of boron hydroxide (boric acid) is fundamentally different from aluminum hydroxide. In the former no oxygen atoms are shared between the $\text{M}(\text{OH})_n$ coordination groups in contrast to the latter.
- Boron group elements have three electrons in their outer shell: 2s and 1p. However, all three electrons are lost in one step except thallium and to a minor extent gallium. On the other hand the scandium group elements have also three electrons in their outer shell: 2s and 1 d, and all three are lost in one step. Hence the distinction in electron orbital is not a critical criterion for classification of the elements, and it is the total number of electrons that should be taken into consideration.
- The copper and zinc groups of elements are in the d-block which is used to be known as transition metals but differ from the other members of the same block in that the atomic radius increases with atomic number whereas in the other members it is the opposite. As a result they have

different chemical properties and should not be included in the transition metals group.

- There are many irregularities in the electron orbitals in the subshells, which arises from quantum mechanical considerations. For example:
 - Chromium and manganese, and molybdenum and technetium have the same number of d-electrons and different numbers of s-electrons instead of the reverse.
 - Europium and gadolinium have similar f- and different d-electrons instead of the reverse.

This renders the strict adherence to the s-p-d, and f-classification pointless, and it should be better to consider the total number of electrons in a shell. It should also be noted that this classification was introduced by physicists who are not necessarily interested in chemical properties.

Uses

Pure aluminum is soft but it can be alloyed with other elements to increase strength and impart a number of useful properties. Aluminum alloys containing silicon are used in casting, cylinders, pistons, and other parts of aircraft and automotive engines as they readily reproduce mould configuration; they are also light and strong.

Many of the applications of aluminum are based upon its low density, high electrical and thermal conductivities, and resistance to corrosion. Pure aluminum often replaces copper in electrical engineering. Although its electrical conductivity is only 65 % that of copper, the density of aluminum is almost three times as less (Cu 8.95, Al 2.7). This means a lesser consumption of the metal. Also suspension of aluminum conductors requires fewer poles than that for copper. Aluminum alloys combine strength, lightness, and corrosion resistance.

The large scale production of aluminium started in the first quarter of the twentieth century when aeronautics was then making its first steps. Today it finds wide application in building construction, for example in ships (Figure 8.10.39) and bridges (Figure 8.10.40).



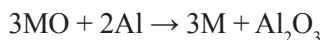
Figure 8.10.39 - The first tank vessel with entire hull from aluminum built in 1959



Figure 8.10.40 - All-aluminum highway bridge near Arvida, Canada

The surface of aluminum and of its alloys is always coated by a thin but strong layer of Al_2O_3 which protects it against further oxidation. The film is extra strong if it is obtained by anodic oxidation. The film can readily be dyed in many colours and this is widely used. The strength of the surface films and its harmlessness to users make aluminum suitable for the manufacture of various equipment in the food industry. In the form of foil it is used for packing foodstuffs.

Aluminum powder is also used in the manufacture of paint. The strong affinity of aluminum makes it suitable for preparing metals from their oxides:



where M is a divalent metal.

Because of its abundance in the Earth's crust, the metal is more likely to be used as a substitute to wood, plastics, and other construction materials. Aluminum is used to store nitric acid, concentrated sulfuric acid, organic acids, and many other reagents.

Nonmetallic applications of aluminum account for about 10 % of the element. Bauxite and alumina are used as refractories, fused alumina is used in abrasives. Alumina is a major aluminum compound produced mainly from bauxite. It is also used as a catalyst, as an adsorbent, as abrasive, in ceramics, etc.

Aluminum sulfate is used in water treatment as an important flocculating agent for purifying water. Anhydrous aluminum chloride is an important *Friedel–Crafts catalyst* in the chemical and petrochemical industries. Aluminum compounds are considered non-toxic.

8.11 Vanadium¹

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DISCOVERY

There was confusion and uncertainty for about thirty years regarding the discovery of vanadium, which resulted in the metal being discovered twice:

In Mexico

In 1801 by the Spanish mineralogist Manuel del Rio (Figure 8.11.1) who was professor at the School of Mines² in Mexico City, in a complex lead chloride mineral from Zimapan who called it erythronium because of the red color of its salts (erythros, Greek for red). This mineral became known later as vanadinite, $\text{PbCl}_2 \cdot 3\text{Pb}_3(\text{VO}_4)_2$ (Figure 8.11.2).

¹ Based on F. Habashi, “Two Hundred Years of Vanadium,” pp. 3–15 in Vanadium — Geology, Processing and Applications, MetSoc Conference published by Canadian Institute of Mining, Metallurgy, and Petroleum, Montreal 2002, edited by M. F. Taner et al. Reprinted in Metall 60(12), 804–808 (2006).

² Founded in 1792 and integrated in 1910 to the National Autonomous University of Mexico, known by the Spanish acronym UNAM, itself founded in 1553.

Del Rio was not sure that he discovered a new metal because the properties of this metal closely resembled those ascribed to a new metal called chromium discovered recently in France. In addition, a sample of the Zimapan mineral that reached the German chemist Friedrich Wöhler in 1803 through Alexander von Humboldt, who visited del Rio in Mexico, was erroneously described as containing chromium.



Figure 8.11.1 -Manuel del Rio (1764-1849)

Manuel del Rio was born in Madrid, studied at the Schools of Mines in Freiberg in Saxony and Schemnitz in Hungary (at that time part of the Austrian Empire). He was sent to Mexico City in 1775 to teach at the School of Mines there. Del Rio married a Mexican girl and made Mexico his home. He contributed greatly to the advancement of metallurgical knowledge in Mexico by translating German books on mineralogy and metallurgy in Spanish. He was a colleague and friend to the German naturalist Alexander von Humboldt.



Figure 8.11.2 - A museum sample of vanadinite



Figure 8.11.3 - Nils Sefström (1787-1854)

In Sweden

In 1830 by the Swedish chemist Nils Sefström (Figure 8.11.3) in an iron ore from the Taberg Mine in Sweden and called it vanadium in honour of the Nordic goddess Vanadis because of the beautiful colour of its compounds. The discovery was a result of an observation that brittle iron always gave a black residue on dissolution in hydrochloric acid, but the iron produced from Taberg although soft, also gave a black residue. On examining the residue after dissolving a large amount of this iron, it was found to contain a metal, which was not chromium and not uranium.

Nils Sefström (1787-1854), obtained a medical degree and practiced medicine for four years, then became professor of chemistry at the Caroline Institute of Medicine and Surgery in Stockholm. From 1820 to 1839 he taught chemistry at the newly-founded School of Mines in Falun

Berzelius clarification

It was Jöns Jacob Berzelius (1779-1848) (Figure 8.11.4) who confirmed that Sefström's new metal was the same as that discovered earlier by del Rio. This took place in Berzelius' laboratory when Sefström went there to spend the Christmas vacation and to finish his studies on the new metal that he discovered in the Taberg iron ore. Berzelius then wrote to his former student Wöhler announcing his conclusion and clarifying for him confusing vanadium with chromium.

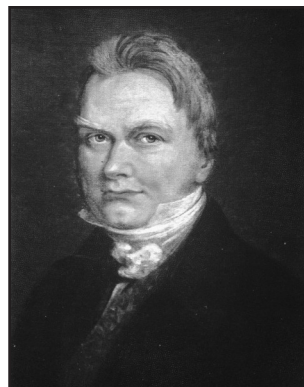


Figure 8.11.4 - Jöns Jacob Berzelius (1779-1848)

SOURCES OF VANADIUM

Vanadium is more abundant than copper and nickel, and of similar abundance to zinc. In the early 1900s, it was obtained exclusively from the rare Peruvian mineral patronite, VS_4 , which exhausted. After World War II, the sedimentary uranium- and vanadium-containing carnotite deposits of the Colorado Plateau and the marine sedimentary vanadium-bearing phosphate deposits of Idaho became important. There are also uranium-vanadium reserves in Yeellirie, Western Australia, and in the Ferghana Basin in the Kirghiz, Tadjik, and Uzbek Republics.

Carnotite, $\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$, (Figure 8.11.5) was named in 1899 by Charles Friedel in honor of Marie-Adolphe Carnot [1839 - 1920], French mining engineer and chemist, professor at École des Mines in Paris. It is valued as a uranium ore.



Figure 8.11.5 - Museum sample of carnotite

Vanadium is also a by-product of the processing of titanomagnetites, which contain 1-2% V_2O_5 . This raw material can be used directly for vanadium extraction, or treated to obtain vanadium-containing pig iron from which an oxidation slag enriched in vanadium is produced. The most important vanadium-bearing titanomagnetite deposits are the Bushveld deposit in South Africa, Katschkanor in the Urals of Russia, in the Sichwan province of China, and a deposit in New Zealand.

Titanomagnetites have been mined in the former Soviet Union and China in large quantities since the early 1960s and 1970s, respectively. The vanadium-bearing titanomagnetite deposits are of magmatic origin, and occur in many parts of the world.

Since the 1980s residues of mineral oil processing gained importance. Most crude oils contain vanadium in amounts ranging from 10 ppm (Middle East) to 1400 ppm (Central America). In petrochemical refining, vanadium is retained in boiler residues and fly ashes from incineration, with vanadium contents between a few percent and 40%. An aqueous emulsion of a highly viscous crude from the Orinoco basin in Venezuela yields on combustion fly ashes containing 10% vanadium. Other less important vanadium sources are: vanadium-containing waste from bauxite production, and spent catalysts from the chemical and petrochemical industries. The extraction of vanadium from currently available raw material sources (except direct processing of titanomagnetite) is always coupled with the production of other metals or energy. The most important sources are shown in Table 8.11.1.

Table 8.11.1. Vanadium production as a by-product

Raw material	Coupled product	Vanadium by-product
Uranium-vanadium ores	Uranium	Petrochemical residue
Titano-magnetites	Iron/steel	Vanadium slag
Mineral oils	Energy/petro-chemicals	Fly ashes, boiler residues
Bauxite	Alumina	Vanadium salt
Phosphates	Phosphorus	Vanadium-containing Fe-P salamander
Lead vanadates	Lead, zinc	Vanadium slag

South Africa

The Bushveld deposit in South Africa is an oval, bowl-shaped complex in a magmatic layer extending over an area of 65000 km². The ores were deposited in the following order: chromite, platinum ores, vanadium-containing titanomagnetites, and tin ores.

Namibia

There are a number of lead vanadate deposits in the Otavi Mountains in Namibia. Mount Aukas, near Grootfontein, has deposits of 2×10^6 t ore containing 15% Zn, 4% Pb, and 0.5% V_2O_5 . Deep mining has been discontinued since 1978. The mined ore, which was processed by flotation, yielded the following products: lead sulfide concentrate, zinc sulfide concentrate, willemite concentrate, cerussite concentrate, and a vanadium concentrate containing 17% V_2O_5 , 43% Pb, and 17% Zn.

Finland

The titanomagnetite deposits at Otanmäki and Mustavaara in Finland had reserves of 15×10^6 t ore containing 35-40% Fe, 13% TiO_2 , and 0.45% V_2O_5 , and 40×10^6 t ore containing 17% Fe, 3.1% TiO_2 , and 0.36% V_2O_5 . The production capacity of the Otanmäki deep mine was ca. 1×10^6 t/a ore. Magnetite containing 69% Fe, 2.5% TiO_2 , and 1.07% V_2O_5 together with ilmenite and pyrite were obtained by magnetic separation and flotation. Both mines were closed in the 1980s.

USA

The Colorado Plateau in the United States contains the main mining area of the Uravan mineral belt, > 1100 km long, in SW Colorado and SE Utah. This belt contains irregular lenticular ore bodies, normally < 3000 t, with 0.2-0.3% U_3O_8 and 0.85-1.4% V_2O_5 . The oxidation region contains mainly the mineral carnotite, and the unoxidized region contains the mineral pitchblende. These ores are extracted in small deep mine workings which produce ca. 0.4×10^6 t/a ore. During the early twentieth century the ores was treated principally for the recovery of radium. During World War II it was treated for uranium.

RECOVERY

From carnotite

Carnotite, $\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5$, is readily soluble in acids in the absence of oxidizing agents. After the uranium had been removed from the solution by solvent extraction, the vanadium was partially reduced with iron powder and solvent extracted. After re-extraction, the vanadium was in the form of an acid solution of vanadyl sulfate. This was oxidized with sodium chlorate at elevated temperature, and precipitated as red cake, a mixture of sodium and ammonium polyvanadate, by adding ammonia or ammonium salts. This precipitate was roasted to convert it into alkali-containing V_2O_5 .

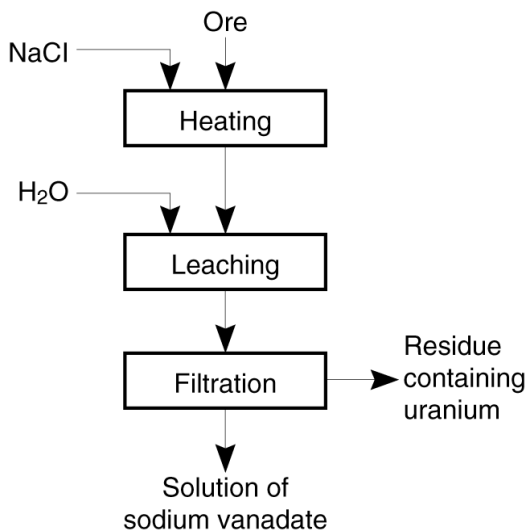


Figure 8.11.6 - Treatment of carnotite ore

Leaching of carnotite ores, however, is usually done after a preliminary salt roasting to convert vanadium minerals into a water-soluble sodium vanadate which can be recovered ahead of the acid leaching (Figure 8.11.6).

From iron ores

Pig iron from the blast furnace was first oxidized in a converter with an acid lining without adding a flux to remove all the vanadium in form of a slag. The molten charge is then transferred to a Thomas converter with basic lining to remove the other impurities with lime. The process was developed in Norway in the early 1930's but was abandoned later.

From titanomagnetites

Titanomagnetite ore containing 1.51-1.7% V_2O_5 (Mapoch mine in South Africa), is first pre-reduced by coal at 1000°C in rotary kilns then in an electric arc furnace to obtain a pig iron which contains 1.4% V_2O_5 and slag containing *ca.* 30% TiO_2 , and is deposited in heaps. In a brick-lined ladle the molten pig iron is then oxidized with oxygen lances without adding fluxes, causing the vanadium to be transferred as an iron vanadate slag containing *ca.* 25% V_2O_5 . This slag is the world's principal raw material for vanadium production. The largest slag and vanadium producer in the western world is South Africa, most of whose production is by the Highveld Steel and Vanadium Corp. Second largest producer is the Nizhny Tagil metallurgical plant in Russia; the slag contains 12-18% V_2O_5 . Another producer of vanadium slag is the Pannang steelworks in Panzihua, China.

The main process used today to produce vanadium oxide from slags is alkaline roasting. A vanadium slag has the following approximate composition: 14% V (=25% V_2O_5), 1.5% Ca, 2.5% Mg, 2% Al, 0.01% P, 9% metallic Fe, 32% total Fe, 7% Si, 3.5% Mn, and 3.5% Ti. The slag is first ground to <100 μm , and the iron granules contained therein are removed. Alkali metal salts are then added, and the material is roasted at 700-850°C in multiple-hearth furnaces or rotary kilns to form water-soluble sodium vanadate. The roasted product is leached with water, ammonium salts are added at elevated temperature to precipitate ammonium polyvanadate or sparingly soluble ammonium metavanadate in crystalline form.

These compounds are converted to high-purity vanadium pentoxide by

roasting. The presence of Ca, Mg, and Al, which form water-insoluble vanadates during alkaline roasting, leads to a reduction in yield. Silicon can cause filtration difficulties during leaching of the calcine. Phosphorus, unless removed in a separate treatment, reports to the vanadium oxide. The same process, with minor differences, is also used for processing titano-magnetite ores and vanadium-containing residues.

From ilmenite

When ilmenite is treated with concentrated hydrochloric acid in an autoclave at 110°C iron goes into solution as ferrous chloride leaving behind an enriched titanium residue known as synthetic rutile. Any vanadium in the ilmenite will report with the ferrous chloride solution from which it can be recovered by solvent extraction. Ferrous chloride is then treated by oxyhydrolysis to recover HCl for recycle and Fe_2O_3 as a by-product.

From lead-zinc ores

The Pb-Zn-V concentrates from Namibia were ground and leached with dilute sulfuric acid. This led to the formation of insoluble lead sulfate. The filtrate contained mainly ZnSO_4 and VOSO_4 , was treated with sodium carbonate to pH 1-2, and tetravalent vanadium was oxidized to the pentavalent state by heating with sodium chlorate. More sodium carbonate was added to the iron-containing solution to increase its pH to 4, precipitating a polyvanadate. This precipitate was filtered and treated with a solution of an ammonium salt to replace the sodium ions by ammonium ions. It was then dried and converted to V_2O_5 by fusion. However, the mining of these ores became uneconomic and was discontinued in 1978.

From oil residues

Appreciable amounts of vanadium are present in mineral oil, especially Venezuelan and Russian oils. The vanadium accumulates in the soot and ash of oil-fired boilers and in oil distillation residues and is sold in this form by power stations and refineries. These secondary raw materials,

sometimes contain 50% V_2O_5 . (vanadium is mainly trivalent) is pelletized with sodium carbonate then roasted at high temperature to form alkali metal vanadate, which can be leached with water. After leaching, the solutions are acidified and ammonium salts are added, precipitating the vanadium as polyvanadate, which is then converted to vanadium pentoxide by calcination.

From bauxite

Some deposits of bauxite contain high levels of vanadium, and during alumina production this ends up in the salt residue, from which V_2O_5 can be obtained. Small amounts of vanadium are obtained by this method in India and Hungary.

THE METAL AND ITS COMPOUNDS

Metallic vanadium was first produced in powder form by English chemistry professor Henry Roscoe (Figure 8.11.7) in 1867 by reduction of vanadium dichloride with hydrogen. In 1927, J.W. Marden and M.N. Rich of the research staff of the Westinghouse Lamp Company in USA obtained ductile vanadium 99.9% pure by reducing vanadium pentoxide, V_2O_5 , with calcium metal.

For the metallothermic reduction of vanadium oxide with aluminum is incomplete, while with calcium and magnesium goes almost to completion. As these metals are volatile, it is advantageous to carry out the reaction in closed vessels. Because of its high melting point [1817°C] it is considered



Figure 8.11.7 - Henry Roscoe (1833-1915) professor of chemistry at Manchester University, studied in London under Thomas Graham and in Heidelberg under Robert Bunsen

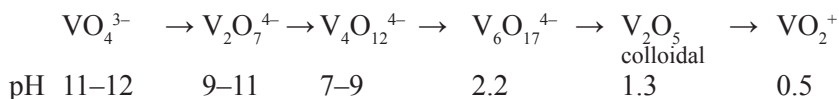
a refractory metal. It is mainly used as alloying element in steel.

Vanadium forms various colors in solution depending on oxidation state (Figure 8.11.8).

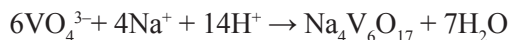


Figure 8.11.8 - Vanadium in solution: from left to right, V(II), V(III), V(IV), and V(V) [Chemical & Engineering News, 2003]

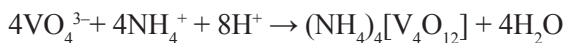
Vanadate ion, VO_4^{3-} is stable at pH 12. When the pH is gradually decreased by adding acid, divanadate and other polyions are formed until at pH of about 12 the tetravanadate is precipitated:



When the pH is decreased further, the tetravanadate dissolves forming pervanadyl ion, VO_2^+ . In industry, vanadium in ores is solubilized in form of sodium vanadate and precipitated as sodium tetravanadate known as red cake:



This is filtered, washed, and dissolved in NaOH then saturated with ammonium chloride to precipitate ammonium vanadate:



Ammonium vanadate is then decomposed by heating to vanadium pentoxide the product of commerce:



USES

Vanadium oxide, V_2O_5 , has replaced platinum as a catalyst for oxidation reactions mainly SO_2 to SO_3 (figure 8.11.9). The first major application of vanadium was in 1903 in England, where a vanadium-alloyed steel was produced on a small scale. In 1905 Henry Ford recognized the advantages of vanadium steel and promoted its use in automobile construction. Today vanadium is of major importance as an alloying component in steel and titanium alloys.



Figure 8.11.9 - Vanadium oxide catalyst for oxidation of SO_2

Ferrovanadium is a master alloy with a vanadium content of at least 50% produced by reduction of the corresponding raw materials with carbon, silicon, or aluminum. The high affinity of vanadium for carbon leads to carbide formation, so that carbothermic reduction can only be used when there is no requirement for vanadium with low carbon content. Silicothermic reduction is no longer profitable, as the process has multiple stages and gives a poor yield.

The high-vanadium grades of ferrovanadium, FeV 60, FeV 80, and FeV 90, are now usually produced by aluminothermic treatment of V_2O_5 . The mixture of V_2O_5 flakes, aluminum powder or granules, fine steel shot, and an initiating mixture, e.g., BaO_z and aluminum powder, is ignited. The reaction of V_2O_5 with aluminum is self-sustaining and the combustion time is only a few minutes. After cooling for 2-3 days, the furnace is dismantled, and the block of metal is cleaned then crushed to the desired particle size.

8.12

Lanthanum¹

Discovery	824	Lanthanides	826
The metal	824	The lanthanide contraction.....	827
Uses	825		

DISCOVERY

Toward the end of the 1830s, Swedish chemist, Carl Mosander (1797-1858) (Figure 8.12.1) became interested in an unusual black stone found near the town of Bastnas in Sweden. He found that the stone contained a new element which he called lanthanum from Greek meaning the hidden one. The material he called lanthanum later turned out to be a mixture of six new elements. Mosander is also credited with the discovery of terbium and erbium. It was not until 1923 that a pure sample of lanthanum metal was prepared.



Figure 8.12.1 - Carl Mosander (1797-1858)

THE METAL

Lanthanum is as common as copper or zinc; relative abundance is $1.7 \times 10^{-3} \%$. However, it does not occur in one place, as in copper mines. Instead, it is spread widely throughout the Earth's crust. Its most common minerals are monazite and bastnäsite. The rare earth elements are very similar to each other. The ores are first treated with sulfuric acid then

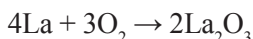
¹ See also Rare Earths

passed through a series of steps and the individual elements separated from each other. It is a transition metal. It occurs in nature in association with the lanthanides. Although it has 2 electrons in the outermost shell yttrium is exclusively trivalent.

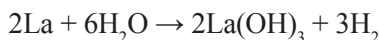
Lanthanum is a malleable, ductile, and soft metal. It is mainly used as an alloying element and in lighter flints. It undergoes phase transformation at 310°C and at 865°C:

Hexagonal $\rightleftharpoons$ Face centered cubic $\rightleftharpoons$ Body centered cubic

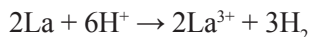
Melting point 920°C, boiling point 3457°C, and density 6.1. It oxidizes rapidly when exposed to air and burns readily at 150°C to form lanthanum oxide:



It reacts slowly with cold water and quickly with hot water to form lanthanum hydroxide:



It dissolves readily in dilute sulfuric acid liberating hydrogen:



Lanthanum is precipitated from solution as an oxalate. The oxide is obtained from the oxalate by thermal decomposition.

USES

One of the oldest uses of lanthanum is in the production of mischmetall which is an alloy that produces sparks when struck. One application is in the manufacture of cigarette lighters. Lanthanum fluoride, LaF_3 , and lanthanum oxide, La_2O_3 , are used in making phosphors in a color television set. Phosphors give off light when struck by electrons and produce colors on television sets. Compounds of lanthanum are also used to make special kinds of glass, for example, in making optical fibers. An optical

fiber is a wire-like material made of glass. It carries light in the same way a copper wire carries electricity. Optical fibers are used as methods for carrying audio, video, and digital messages. In many cases, optical fibers have replaced copper wires for this purpose. High quality lenses, for example, are often made of glass containing a small amount of lanthanum.

LANTHANIDES

The lanthanides are the metals that follow lanthanum in the Periodic Table (Figure 8.12.2). They have the same number of electrons in the two outermost shells (Figure 8.12.3) and as a result their chemical properties are nearly the same. It is also difficult to separate by chemical methods that is why physical methods are used. Earlier methods were based on fractional crystallization. Recent methods are now based on ion exchange and solvent extraction.

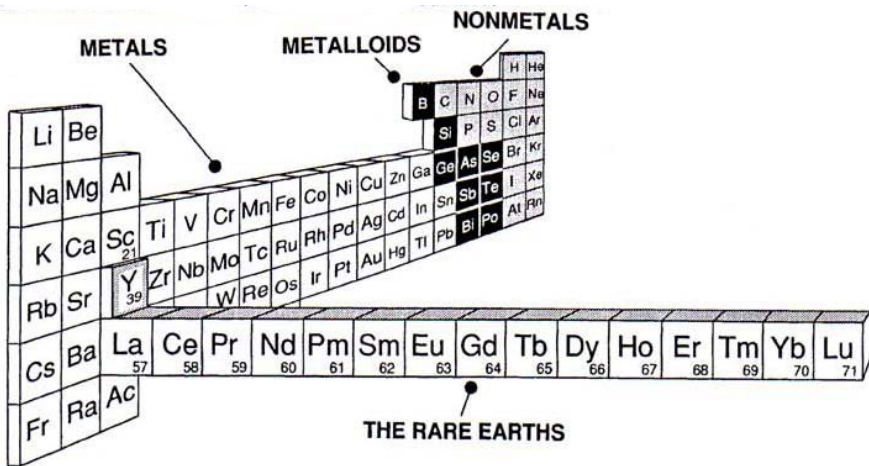


Figure 8.12.2 - The lanthanides follow lanthanum and are located in one square in the Periodic Table

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
2	2	2	2	2	2	2	2	2	2	2	2	2	2
8	8	8	8	8	8	8	8	8	8	8	8	8	8
18	18	18	18	18	18	18	18	18	18	18	18	18	18
19	20	21	22	23	24	25	26	27	28	29	30	31	32
9	9	9	9	9	9	9	9	9	9	9	9	9	9
2	2	2	2	2	2	2	2	2	2	2	2	2	2

Figure 8.12.3 - Electronic configuration of lanthanides

The lanthanide contraction

As in typical and transition metals, the atomic radius in the lanthanides gradually decreases from lanthanum to lutetium with the result that although the atomic radius of lanthanum is larger than that of yttrium, which is above it in the Table, the atomic radius of lutetium is smaller than that of yttrium, i.e., $La > Y > Lu$. This is known as the “lanthanide contraction” and is responsible for the fact that the atomic radius of hafnium equals that of zirconium, and that of tantalum to niobium, and that of tungsten to molybdenum (Figure 8.12.4).

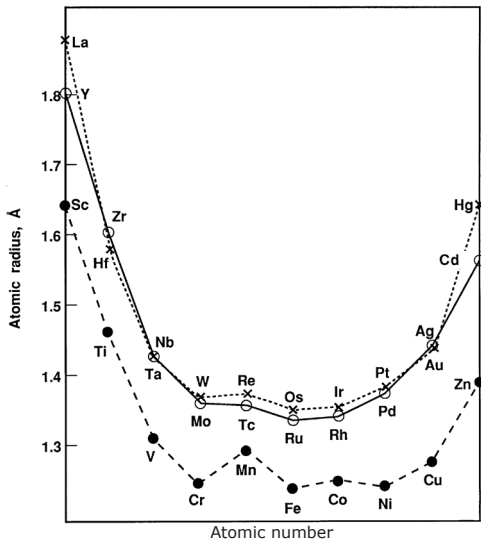


Figure 8.12.4 - The similarity of atomic radii of Zr-Hf, Nb-Ta, Mo-W, etc, due to the lanthanide contraction

Two facts emerge as a result.

- *Isomorphous substitution.* Hafnium is always associated with zirconium in their minerals, niobium with tantalum, and molybdenum with tungsten.
- *Refractory character.* Since the atomic weights of metals in the lower row are nearly double those above them in the Periodic Table, it follows that the densities of the metals in the lower row are also nearly double those above them. The atoms of those metals in the lower row are hence so compact, i.e., high density (Figure 8.12.5) and this renders them difficult to melt, i.e., refractory (Figure 8.12.6).

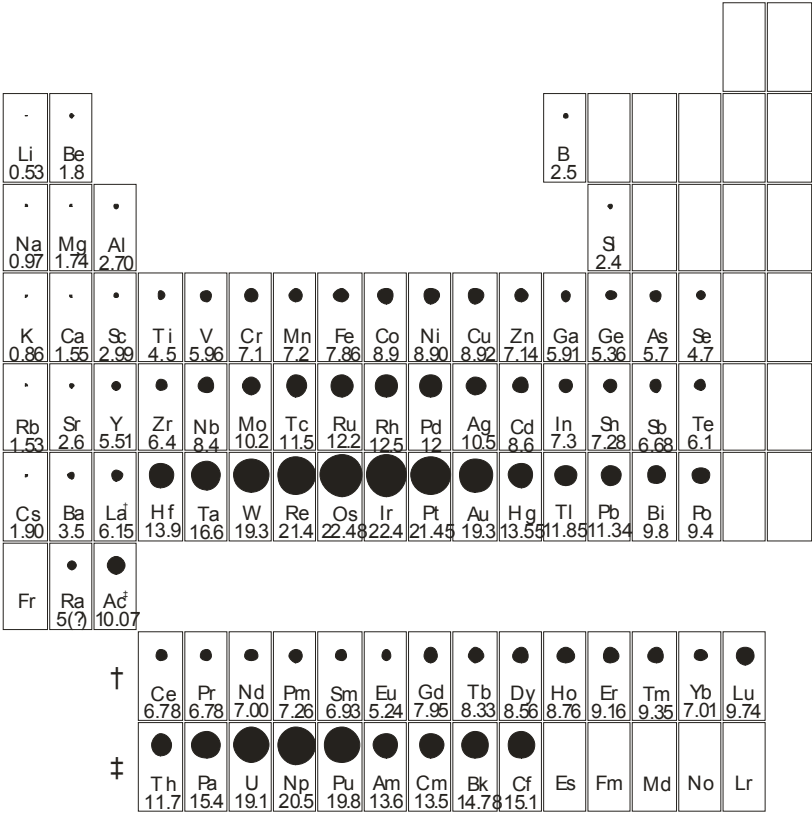


Figure 8.12.5 - Density of metals

Figure 8.12.6 - Melting points of metals

8.13

Alkali metals

cesium and rubidium

Introduction	826	Radioactive cesium	829
Cesium	827	Rubidium	829
Uses	828		

INTRODUCTION

Robert Bunsen (1811-1899) and Gustav Kirchhoff (1824-1887) (Figure 8.13.1) in Heidelberg invented chemical analysis by means of the spectroscope. This led to the discovery of new elements: rubidium and cesium (Figure 8.13.2). Later, more discoveries were made using this method.

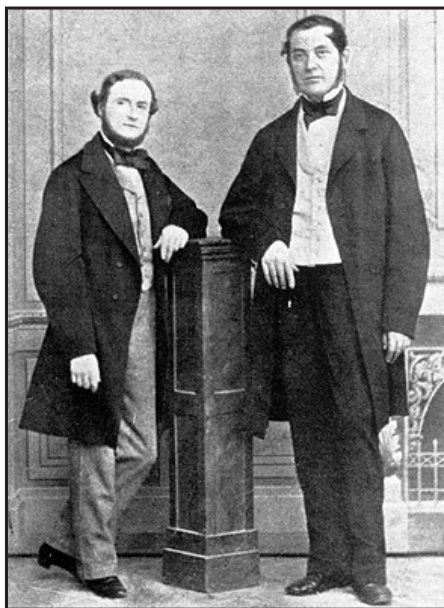


Figure 8.13.1 - Robert Bunsen (right) and Gustav Kirchhoff

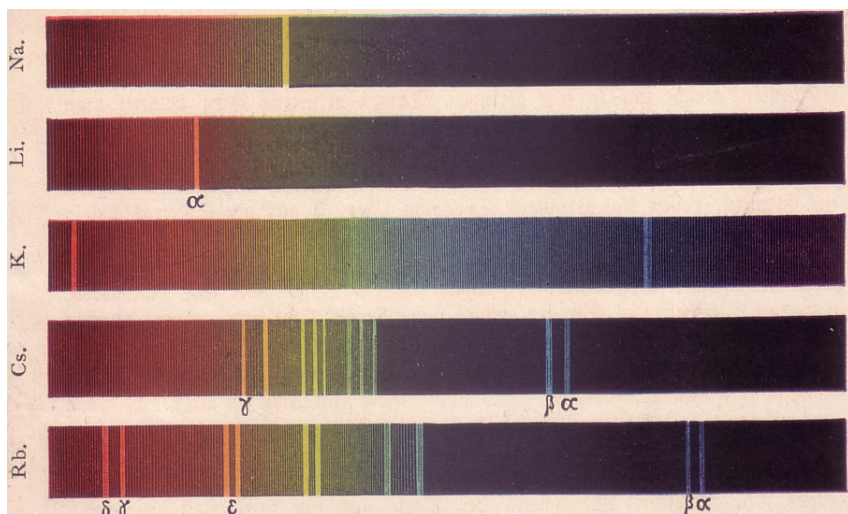


Figure 8.13.2 - Spectra of alkali metals in a publication in 1873. Characteristic yellow line due to Na, two blue lines due to Cs, and two red lines due to Rb

CESIUM

Cesium was discovered in 1860 by Bunsen in the Dürkheim mineral water using his newly invented spectroscope. He called it “cesium” from Latin caesius means sky blue because of the characteristic blue color of the two spectral lines due to this metal. Bunsen first precipitated calcium, strontium, magnesium, and lithium present in the water by known method before examining the filtrate by the spectroscope. In 1864 the French-Italian analytical chemist Felix Pisani (1831-1920) in Paris examined a silicate mineral known as pollucite and found that it contained cesium. Pollucite has the composition $(\text{Cs,Na})_2 (\text{Al}_2\text{SiO}_4)\text{O}_{12} \cdot \text{H}_2\text{O}$.

To obtain a pure sample of cesium, 44,000 Litres of mineral water were evaporated to yield 240 kilograms of concentrated salt solution. The alkaline earth metals were precipitated either as sulfates or oxalates, leaving the alkali metal in the solution. After conversion to the nitrates and adding ethanol, a sodium-free mixture was obtained. From this mix-

ture, the lithium was precipitated by ammonium carbonate. Potassium, rubidium and cesium form insoluble salts with chloroplatinic acid, but these salts show a slight difference in solubility in hot water. Therefore, the less-soluble cesium and rubidium hexachloroplatinate, $(\text{Cs,Rb})_2\text{PtCl}_6$, could be obtained by fractional crystallization. After reduction of the hexachloroplatinate with hydrogen, cesium and rubidium could be separated by the difference in solubility of their carbonates in alcohol. The process yielded 9.2 grams of rubidium chloride and 7.3 grams of cesium chloride.

The pure metal was isolated by the German chemist Carl Setterberg (1853-?) (Figure 8.13.3) while working with Bunsen. In 1882 he produced cesium metal by electrolyzing cesium cyanide.

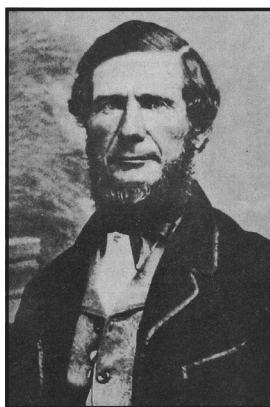


Figure 8.13.3 - Carl Setterberg (1853-?)

Uses

Few applications existed for cesium until the 1920s when it became used in radio vacuum tubes. It had two functions: as a getter it removed excess oxygen after manufacture, and as a coating on the heated cathode, it increased its electrical conductivity. In 1950s cesium was used in photoelectric cells, photomultiplier tubes, optical components of infrared spectrophotometers, catalysts for several organic reactions, crystals for scintillation counters, and in magnetohydrodynamic power generators.

Radioactive cesium

Radioactive cesium isotope, ^{137}Cs (half-life 30.1 years), is a product of atomic bomb explosions and nuclear reactors disasters, together with ^{90}Sr , and both are widely present in the biosphere.

RUBIDIUM

Few months after the discovery of cesium, Bunsen and Kichhoff announced in 1861 the discovery of a new alkali metal in the mineral lepidolite a rose colored mineral of the mica group (Figure 8.13.4) from Saxony. They dissolved a sample in alkali then precipitated potassium as hexachloroplatinate and examined it by the spectroscope. They observed the lines due to potassium. But, on washing several times with boiling water and tested it at intervals, they noticed two new red lines while those due to potassium faded away. These two new lines proved to be those of an unknown element which they named rubidium. In 1863 Bunsen succeeded in preparing elemental rubidium.



Figure 8.13.4 - Lipodolite

8.14 Thallium

Discovery	830	The metal and its compounds	832
Occurrence	831	Uses	833
Recovery from zinc sulfide	831		

DISCOVERY

The existence of thallium was noted in 1861 by William Crookes (1832-1919) (Figure 8.14.1) while studying under August Wilhelm von Hofmann at the Royal College of Chemistry in London [later known as School of Mines]. He was given a ten pound sample of residues from a lead chamber sulfuric acid plant at Tilkerode in the Harz Mountains by Professor Hofmann to extract selenium from it. After extracting selenium he thought that tellurium may also be present. All attempts to extract tellurium, however, failed.

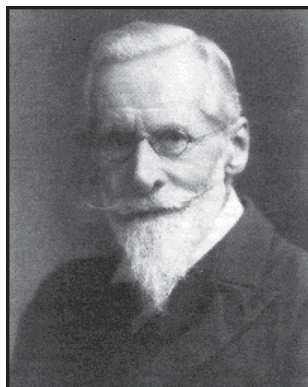


Figure 8.14.1 - William Crookes (1832-1919)



Figure 8.14.2 - Spectrum of thallium

On examining the residue with the spectroscope he found no tellurium but new green lines which could not be attributed to a known element (Figure 8.14.2). He, therefore, concluded that these lines must be due to a new element which he called thallium from Greek *thallos* means green.

Metallic thallium was isolated by Claude Auguste Lamy (1820-1878) (figure 8.14. 3) in 1862. He digested the residue from a sulfuric acid plant with aqua regia, then dissolved the material in water. As the solution cools, yellow crystalline platelets of thallium chloride form. These were then electrolyzed in the fused state to yield the metal.

William Crookes was born in Chippenham. He studied at the Royal College of Chemistry in London. In 1859 he started the publication of *Chemical News*. He worked on rarefied gases and discovered uranium X. When William Ramsay discovered helium in 1895, it was Crookes who established its identity with the helium that Norman Lockyer had observed spectroscopically in the sun's atmosphere.

Claude Auguste Lamy was born at Néry in the Jura Department of France, attended the École Normale Supérieure in Paris and at the age of 21 received his doctorate from Lille. He taught physics at Limoges and later at Lille. He recognized that thallium salts were poisonous and that thallium has two valency states: thallic and thallic.



Figure 8.14.3 - Claude Auguste Lamy (1820-1878)

OCCURRENCE

Thallium occurs as a trace element in pyrite, and is extracted as a by-product of roasting this mineral for the production of sulfuric acid. It can also be obtained from the smelting of lead and zinc sulfide ores.

RECOVERY FROM ZINC SULFIDE

During roasting of zinc sulfide concentrates in fluidized beds, the flue

dust will be enriched in cadmium, indium, and thallium, but the bulk of these metals remain in the calcine. That is why the dust is added to the calcine during processing. While cadmium and thallium are leached from the calcine (and dust) together with zinc by H_2SO_4 , indium remains in the residue.

The degree of volatilization and the water solubility of the components of the dust vary, however, if other roasting system is used. Thus when sintering machines are used (now obsolete), more metals are volatilized because of the higher temperature. The dust contains more water-soluble components due to the formation of sulfates. After leaching the calcine with H_2SO_4 , a copper-cadmium-thallium precipitate is obtained from the solution by adding zinc dust. The precipitate is re-dissolved in acid, thallium hydroxide is precipitated at pH 4, the solution is further purified, then cadmium is recovered by electrowinning from the purified solution, while the crude thallium hydroxide is dissolved in acid, the solution is purified, then pure thallium is cemented on zinc plates from which its can be easily stripped.

The residue from the main zinc circuit is processed for indium recovery by leaching with dilute HCl. Crude indium hydroxide is then precipitated from the solution by neutralization. It is re-dissolved in HCl, the solution is purified by a series of cementations. First, copper and arsenic are removed by iron, then tin and lead by indium. Indium is recovered from the purified solution by cementation on aluminum sheets from which the metal can be easily stripped.

THE METAL AND ITS COMPOUNDS

In many of its physical properties, thallium resembles its neighbor, lead. It exists in two allotropic forms: α -thallium, hexagonal close-packed, stable at room temperature; and β -thallium, body-centered cubic, stable above 226°C . Its relative abundance in Earth's crust is $3 \times 10^{-5}\%$, density $11.85 \text{ g}\cdot\text{cm}^{-3}$, melting point 303°C , boiling point 1473°C , atomic radius 170 pm.

Thallium oxidizes slowly in air, even at room temperature forming thallium (I) and thallium (III) oxides. In the presence of water, a hydroxide is formed. Thallium is therefore stored under petroleum spirit, glycerin, or de-aerated water. The metal dissolves in acids.

Tl_2O , is formed by heating thallium in air at $< 100^\circ C$. It is reddish-black to black, volatile in air at higher temperatures, being converted to Tl_2O_3 , and is hygroscopic, forming a colorless, alkaline solution of $TlOH$ with water. Thallium (III) oxide, Tl_2O_3 , can also be formed by treating thallium (III) salts with KOH or NH_3 , or treating thallium(I) salts with oxidizing agents such as $NaOCl$. It is brown to black, forms cubic crystals. Thallium is precipitated from solutions by zinc amalgam, and the relatively pure metal is obtained by an electrolytic process. Metal of the highest purity [99.9999 %] can be obtained by multistage electrorefining.

Thallium (I) hydroxide reacts with carbon dioxide forming water-soluble thallium carbonate. This is the only water soluble heavy metal carbonate. Thallium (I) bromide is a photosensitive yellow compound similar to the silver bromide.

USES

Thallium and its compounds are extremely toxic. The odorless and tasteless thallium sulfate was once widely used as rat poison and ant killer. The electrical conductivity thallium (I) sulfide changes with exposure to infrared light therefore making this compound useful in photo-resistors. Thallium selenide has been used in a bolometer for infrared detection.

8.15 Indium

Discovery	835	Indium from lead circuits.....	839
The metal and its compounds	837	Indium from tin circuits	839
Recovery	838	Uses	840
Indium from zinc circuits.....	838		

DISCOVERY

In 1863 Ferdinand Reich (1799-1882) (Figure 8.15.1) professor of physics at the School of Mines at Freiberg and his assistant Hieronymus Theodor Richter (1824-1898) (Figure 8.15.2) announced their discovery of indium. During their study of some Freiberg zinc ores from the Himmelsfürst mine, they roasted the ore to remove most of the sulfur and arsenic then decomposed it with hydrochloric acid. The solution was evaporated to dryness and the impure chlorides were examined by the spectroscope. They observed new brilliant indigo line which did not coincide with any other lines known (Figure 8.15.3). That is why they called the new element indium. Reich and Richter isolated the metal by reducing the oxide in a current of hydrogen.

Ferdinand Reich was born at Bernburg and educated at Leipzig, Freiberg, Göttingen, and Paris. He became professor at the Mining Academy in Freiberg in 1824 and in 1875 was nominated director of the academy. Hieronymus Theodor Richter was born in Dresden and became a metallurgical chemist at the School of Mines in Freiberg.

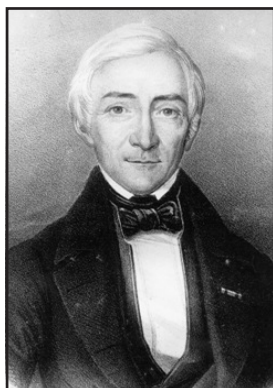


Figure 8.15.1 - Ferdinand Reich
(1799-1882)

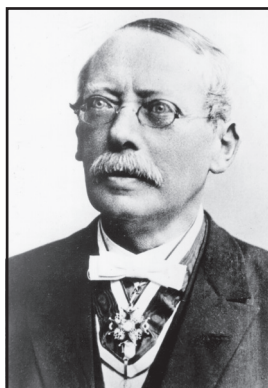


Figure 8.15.2 - Hieronymus
Theodor Richter (1824-1898)



Figure 8.15.3 - Spectrum of indium showing the indigo line on the left



Figure 8.15.4 - Plaque at the School of Mines in Freiberg commemorating the discovery of indium by Professor Ferdinand Reich at the Mining Academy

THE METAL AND ITS COMPOUNDS

Indium is a silvery-white low-melting point metal belonging to the less typical metals group, i.e., when it loses its outermost electrons it will not have the electronic structure of inert gases hence it will be not reactive at the typical metals. It is softer than lead, ductile, malleable, and retains its plastic properties at cryogenic temperatures. It becomes superconducting at 3.37 K. It does not form its own minerals but is found in trace amounts in many minerals, e.g., sphalerite, ZnS . Low-melting alloys represent a major use of indium. Indium has the highest solubility in mercury [57%].

Relative abundance $1 \times 10^{-5}\%$, melting point 156.6°C , boiling point 2072°C , density 7.31, atomic radius (coordination number 12), nm 0.162, ionic radius (In^{3+} , coordination number 6), nm 0.081, atomic volume, m^3/mol 15.73×10^{-6} , crystal structure tetragonal.

The most common valence of indium is three. Monovalent and bivalent compounds of indium with oxygen, sulfur, and halogens are also known. The lower valence compounds tend to disproportionate to give the corresponding trivalent compounds and indium metal. The semiconducting compounds indium antimonide, InSb , indium arsenide, InAs , and indium phosphide, InP , are prepared by direct combination of the high-purity elements at high temperature. Indium oxide, In_2O_3 , is yellowish white and indium sulfide, In_2S_3 , is red (Figure 8.15.5)



Figure 8.15.5 - Indium oxide (yellowish white) and indium sulfide (red)

RECOVERY

Indium from zinc circuits

Indium is recovered from zinc sulfide ores after roasting and leaching. The residue is treated further for indium and gallium recovery (Figure 8.15.6).

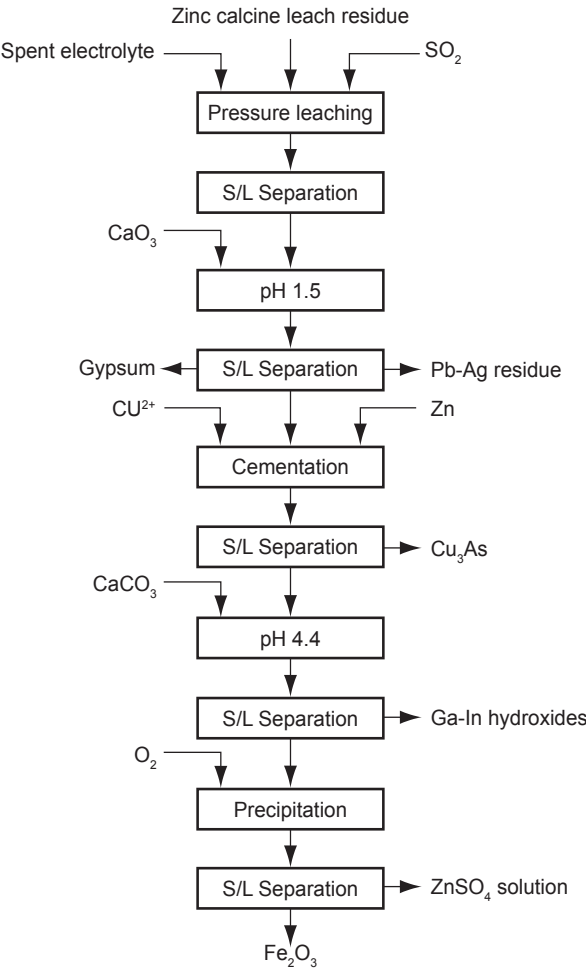


Figure 8.15.6 - Recovery of indium and gallium from zinc calcine residue in Japan

Indium from lead circuits

At Cominco's lead-zinc smelter at Trail in Canada, indium accumulates in the fumes of the continuous dressing furnace. A mixture of fumes, coke, and antimony-containing slag is melted in a direct-fired furnace. Arsenic is removed by adding scrap iron to form speiss. The residual tin-indium-antimony-lead alloy is cast into anodes and electrolyzed in a fluorosilicate solution, depositing Sn-Pb alloy on the cathode and indium-antimony in the slimes. The slimes are roasted with sulfuric acid. Indium is dissolved from the sulfated product by leaching with water. Copper in solution is removed by cementation with indium. Indium is then recovered from the solution by cementation with aluminum or zinc. The indium sponge is melted and electrorefined to give indium of 99.99% purity.

At La Oroya refinery in Peru, the lead bullion is first drossed to remove copper then tin and indium are removed at a higher temperature. The tin-indium dross is reduced to metal using coke, a mixture of lead and zinc chloride is added, and indium is recovered as indium chloride in the slag. The chloride slag is leached by water. The solution is purified by cementation of lead and tin with indium. Indium is recovered as a sponge by adding zinc. At the Hoboken smelter in Belgium, indium concentrates in a complex residue during refining of lead by the Harris process.

Indium from tin circuits

At Capper Pass in the United Kingdom, chlorination of molten electrorefined tin at 250°C gives a tin chloride slag which contains 2.7% indium. The slag which floats on the surface is collected and is leached with water. Most of the tin is precipitated in the first neutralization stage. The precipitate from the second neutralization stage, which contains some indium, is recycled for indium recovery. Indium is recovered from the filtrate as a sponge by cementation with zinc. The indium sponge of 95% purity is electrorefined to give a 99.5% indium cathode, which is recast as the anode for the second electrorefining stage, in which indium of 99.97% purity is produced.

USES

Indium is used as a coating for bearings in aircraft engines, in fusible alloys, solders, and electronics. Indium phosphide is used in semiconductors and indium tin oxide thin films for liquid crystal displays.

8.16

Gallium¹

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DISCOVERY AND ISOLATION

The metal predicted by Dimitri Ivanovitch Mendeleev (1834-1907) in 1871 when he published his Periodic Table and which he called eka-aluminum was discovered in a zinc blende sample from the Pyrenees by the French chemist Paul Emile Lecoq de Boisbaudran (1838-1912) (Figure 8.16.1) in 1877. He named it gallium in honor of his home country Gallia, as the Romans used to refer to the region now known as France. The metal was discovered by means of the spectroscope invented a few years earlier by the two German scientists Robert Bunsen (chemist) and Gustav Kirchhoff (physicist).



Figure 8.16.1- French chemist Paul Emile Lecoq de Boisbaudran (1838-1912) confirmend the prediction by discovering gallium in 1877

¹ Based on F. Habashi, "Gallium Update," pp. 141–153 in *Travaux du Comité international pour l'étude de la bauxite, de l'alumine et de l'aluminium* (ICSoba), volume 33 No. 37. Published by the Hungarian National Committee of ICSoba, Budapest 2006. Hungarian translation in *Kohászat* 140 (3), 29–34 (2007).

Boisbaudran was interested in studying the spectral lines of certain groups in the Periodic Table. He started with the aluminum group of elements and was searching for the missing element predicted by Mendeleev to be between aluminum and indium. He investigated zinc blende as a possible source of eka-aluminum because it was in this mineral that indium was discovered few years earlier by F. Reich and T.H. Richter in 1863.

In 1874 he obtained fifty two kilograms of zinc blende from a mine in the Haute Pyrénées and dissolved it in acid. When he placed a plate of metallic zinc in the solution a deposit was formed. When he heated this deposit with the oxy-hydrogen flame and examined it with the spectroscope, he saw two lines that had never been seen before which he attributed to a new metal (Figure 8.16.2). However, the material at his disposal was too small to permit separating this new metal.



Figure 8.16.2 - Emission spectrum of gallium

Later, Boisbaudran obtained from the mining company La Vieille Montagne several hundred kilograms of zinc blende which he dissolved in aqua regia. After filtering off the insoluble silicate residue he placed sheets of zinc in the filtrate to precipitate impurities such as copper, arsenic, lead, cadmium, and others. He then filtered off the residue, added hydrogen sulfide to the filtrate, and studied the spectrum of the precipitate. He confirmed the existence of gallium in the precipitate.

In 1879 Boisbaudran and Emile Clément Jungfleisch (1839-1916) (Figure 8.16.3), professor of chemistry at the École Supérieure de Pharmacie then worked up four tonnes of the zinc blende at the Javel Works in a Paris suburb and obtained 75 grams of the metal by electrolysis of an alkaline solution of gallium. They were able to study the properties of this new metal which fully confirmed that it was the missing element predicted by Mendeleev. He announced the discovery in his article «Caractères

chimiques et spectroscopiques d'un nouveau métal, le gallium, découvert dans une blende de la mine de Pierrefitte, vallée d'Argelès (Pyrénées)» published in *Annales de Chimie* in 1877.

Twenty years later, Gallium was discovered spectroscopically in 1897 in French bauxite by Walter N. Hantley and Hugh Ramage (1865-1939). In 1930 it was discovered by the Norwegian geochemist Viktor Moritz Goldschmidt (1888-1947) in a coal mine near Newcastle.

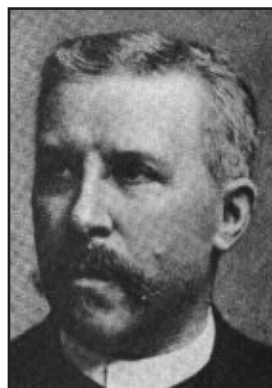


Figure 8.16.3 - Emile Clément Jungfleisch (1839-1916)

OCCURRENCE

Although gallium is as abundant as lead in the Earth's crust, it does not form deposits of its own; it is widely scattered in nature. Its relative abundance in the Earth's crust is $1.5 \times 10^{-3} \%$. It occurs in sphalerite because ZnS and GaS are isomorphous and it occurs in bauxite because the ionic radius of Ga^{3+} is nearly the same as Al^{3+} , being $0.63 \text{ \AA}$ and $0.57 \text{ \AA}$, respectively (the ionic radius of Zn^{2+} is $0.74 \text{ \AA}$). Gallium also occurs in coal deposits and in phosphate rock and is concentrated in the fly ash during the combustion of coal and the elemental phosphorus production, respectively. Gallium forms only one rare mineral -- gallite, CuGaS_2 , that was discovered in 1958 by the German mineralogist Hugo Strunz (1910-?) and co-workers in Tsumeb mine in Namibia and in Kipushi mine in Zaire.

Its concentration in bauxite is 0.003 and 0.008% . The largest reserves of gallium are contained in phosphate ores and in coal. When phosphorus is produced electrothermally from phosphate rock, the gallium is concentrated in the flue dust. Likewise, gallium may be obtained from the fly ash of coal. Gallium contained in zinc ore (sphalerite) has lost economic importance due to the change over to hydrometallurgical methods of zinc extraction.

THE METAL AND ITS COMPOUNDS

Gallium is a silvery-white low-melting point metal (Figure 8.16.4). Melting point 29.78°C , boiling point 2403°C , density of solid at 25°C is 5.9 g/cm^3 and of the liquid at 29.8°C is 6.1. There is a volume expansion of 3.2 % on solidification of the metal.



Figure 8.16.4 - Gallium is a low-melting point metal

The crude metal contains 99–99.9 % gallium. The material for semiconductor manufacture is used in purities from 99.9999 % (6N) to 99.999999 % (8N). The binary compounds, GaP and GaAs are of great industrial importance. They may be prepared by direct combination of the elements at high temperature.

Gallium dissolves slowly in dilute mineral acids, but rapidly in concentrated sodium hydroxide. In its compounds, the valency is + 3. Substances which lower the hydrogen ion concentration throw down a white gelatinous precipitate from Ga(III) salt solutions. This precipitate is amorphous to x-rays and has a variable water content (gallium oxide hydrate, $\text{Ga}_2\text{O}_3 \cdot x\text{H}_2\text{O}$). It dissolves both in acids and in strong bases, and differs from aluminum oxide hydrate in being soluble in ammonia solutions. As the precipitate ages, its solubility in caustic alkalis diminishes.

Gallium halides have covalent character and therefore have good solubility in many non-polar solvents in which they exist in dimeric form. Like aluminum, gallium is precipitated as the white oxide hydrate from solutions of its salts by reducing the hydrogen ion concentration. Gallium sulfate, $\text{Ga}_2(\text{SO}_4)_3$, crystallizes from aqueous solutions as an 18-hydrate similar to $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. It can be dehydrated by heating, and decomposes above 520°C with loss of SO_3 . With ammonium sulfate, it forms the double salt $(\text{NH}_4)\text{Ga}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, ammonium gallium alum.

INDUSTRIAL PRODUCTION

Early period

The first 50 kg of the metal were produced in Germany in 1932 from accretion formed during the smelting of copper schist in the shaft furnace at Mansfeld. At the Eagle-Picher smelter at Henryetta in Oklahoma, zinc was produced by the retort process followed by vacuum distillation to get high purity metal. Although as early as 1915, it was found at Eagle-Picher that the iron-lead residue from the distillation column contained gallium, it was not until 1944 that 6 kg of gallium were obtained from this residue by a complex process.

The lithopone industry

Lithopone is a white pigment, first developed in France in 1850, and was made by mixing solutions of zinc sulfate and barium sulfide resulting in the simultaneous precipitation of zinc sulfide and barium sulfate. The zinc sulfate was made by leaching zinc calcine in sulfuric acid and adding zinc dust to remove impurities; the barium sulfide was made by reducing barite with carbon in a furnace and extracting the product with water. Chemists at the Eagle-Picher Research Center in Joblin, Missouri became interested in gallium recovery from the lithopone plant at Argo, Illinois when they learned about the recovery of the metal at the Henryetta smelter. Gallium was found in the leach residue of the zinc calcine and was recovered as

a by-product of the pigment production by a complex process involving NaOH leaching, precipitation, and electrolysis.

Since 1950s, lithopone production has been drastically reduced as a result of the introduction of TiO_2 pigment and consequently gallium production from this source was curtailed. Eagle-Picher was also a producer of lead among other products. The lead and zinc refining plant of Eagle Picher located on the outskirts of Galena, Kansas caused extensive pollution in the neighbourhood and was forced to shut down; it was demolished few years later.

The electrolytic zinc industry

When the zinc industry shifted from the retort process to the roasting-leaching-electrowinning route, gallium was found in the iron oxide residue and this became an important source. Today gallium from zinc residues comes principally from Akita Zinc located at Akita, Japan a daughter company of Dowa Mining that has been producing zinc from sulfide concentrates since 1971. In this method, a roasted zinc concentrate is leached with sulfuric acid to produce a zinc sulfate solution, which is neutralized to remove impurities that precipitate which include gallium, aluminum, and iron. Leaching this residue with a caustic solution extracts the gallium along with the aluminum and iron. After separating the residue, the solution is neutralized to precipitate the metal hydroxides. These are leached with hydrochloric acid and the gallium is extracted by ether (Figure 8.16.5). Distillation of the ether solution yields a gallium-rich residue that still contains some iron; this is removed by treatment with a strong caustic solution to extract the gallium, while leaving the iron in the residue.

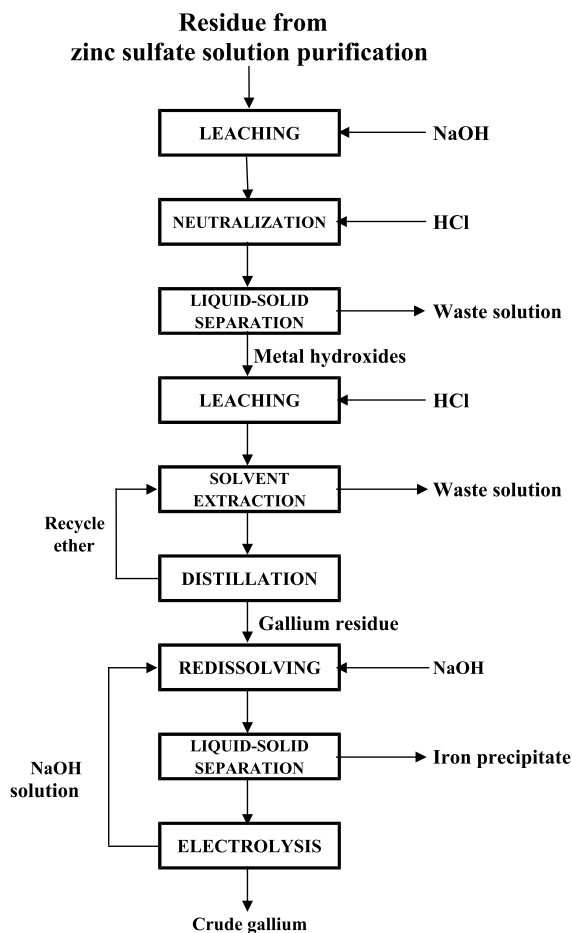


Figure 8.16.5 - Recovery of gallium from zinc concentrates

It seems, however, that the ether extraction process has been replaced by another one (Figure 8.16.6). The leach residue stockpile is now being treated by pressure leaching using SO_2 at 115°C and about 0.2 MPa pressure to decompose zinc ferrite:



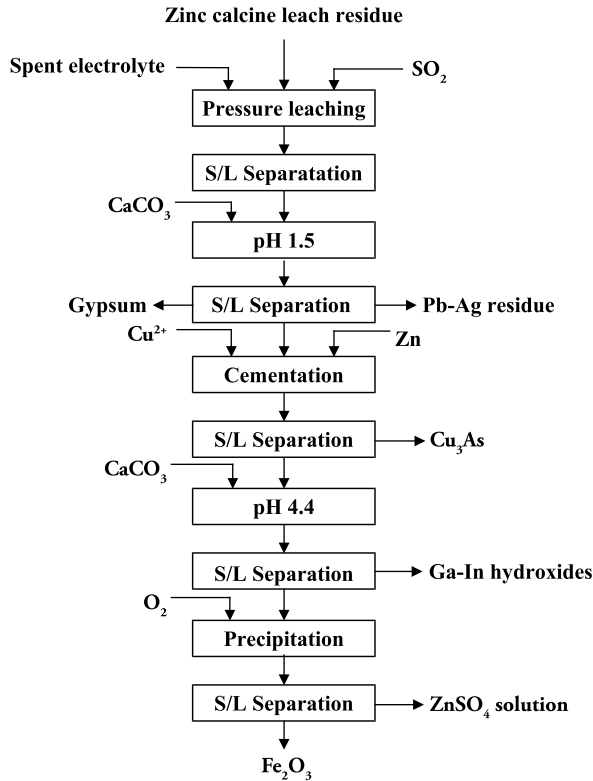
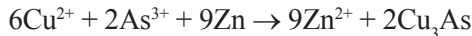


Figure 8.16.6 - Recovery of gallium from zinc concentrates

The advantage of this operation is to keep iron in the ferrous state, thus preventing its precipitation under these conditions. Hence, indium and gallium can be recovered and not lost in a ferric hydroxide (or jarosite) precipitate. The pH of the solution is then adjusted to 1.5 by calcium carbonate to produce a high grade gypsum. This is then followed by arsenic precipitation as copper arsenide using zinc dust:



The reaction is known as “copper – catalyzed zinc cementation process”. After filtering away the copper arsenide, the solution is subjected to another purification step to recover indium and gallium. This is achieved by increasing the pH to 4.3 – 4.5 with calcium carbonate to remove aluminum and more gypsum and get a product containing indium and gallium

hydroxides. These are separated from the bulk of the residue by gravity methods. The solution is now ready to precipitate nearly pure hematite by oxygen under pressure at 70°C and 1.5 – 2.0 MPa. Akita Zinc thus recovers copper arsenide, gallium, indium, gypsum, and iron oxide from the zinc leach residue in addition to gold, silver, and lead.

The aluminum industry

Bayer process

Nearly at the same time when gallium was recovered in the zinc industry, research on its recovery from bauxite was under progress. Two processes emerged from this source. Gallium is partially dissolved together with aluminum during the processing of bauxite. However, it is not removed from the solution during subsequent processing steps, and because the solution is recycled, it builds up to a concentration of 100 to 125 ppm. When gallium recovery is desired, a bleed stream is separated from the solution before it is recycled to the digestion step. Crude gallium metal, 97.0 to 99.9% pure, is recovered by the following processes:

- *Carbonation.* In this process, carbon dioxide is injected into the solution to precipitate aluminum not recovered by seeding. Aluminum hydroxide is then separated and the solution is carbonated again. In the second carbonation, a precipitate, containing 0.3-1% gallium, is formed. After its separation it is dissolved in a caustic solution and electrolysed to recover crude gallium as a liquid (Figure 8.16.7).
- *Electrolysis.* In this process, the bleed stream from the Bayer process is concentrated by evaporation then directly electrolysed using a mercury cathode. When the gallium concentration reaches about 1% in the amalgam, it is drawn off and leached with a caustic solution. This yields a concentrated gallium solution from which crude gallium can be recovered by another electrolytic step (Figure 8.16.8).

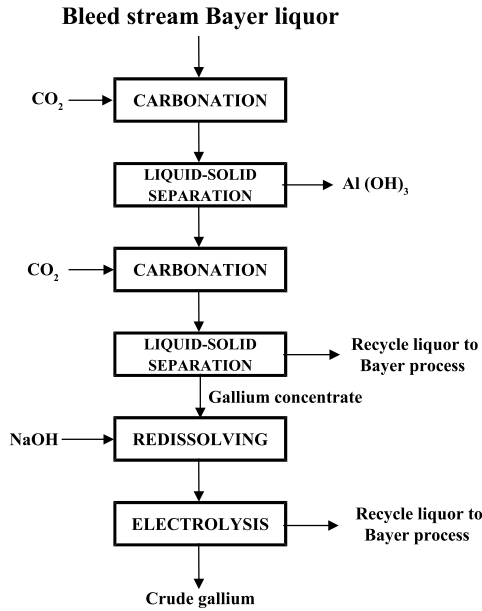


Figure 8.16.7 - Recovery of gallium from bauxite by carbonation of bleed solution

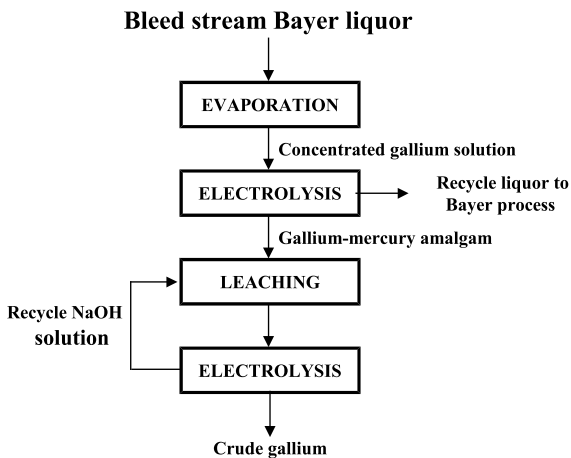


Figure 8.16.8 - Recovery of gallium from bauxite by electrolysis

- *Cementation.* Rather than preparing a gallium amalgam by electrolysis, a sodium amalgam is prepared by electrolysing the caustic solution

with a mercury cathode. Gallium is then extracted by cementation as the gallium in the aqueous phase replaces the sodium in the amalgam. Subsequent gallium recovery follows the same steps as in the previous process. This process is used in Germany and has the advantage of less mercury losses.

Gallium producers

One of the largest producers of gallium today is the US company GEO Gallium Incorporated which operates two extraction plants, one in Stade about 40 km west of Hamburg in Germany and the other in Pinjarra, Western Australia founded in 1989 with the capacity to produce 100 tonnes of 99.99% gallium per year. The feed stock to the Stade plant is pumped from Vereinigte Aluminium Werke and the feedstock to the Pinjarra plant is pumped from the nearby Alcoa plant. The company extracts the gallium as a 15 % solution of gallium chloride (i.e., equivalent to 200 g/L gallium) involving a series of steps including counter current solvent extraction process and further extraction using an ion exchange resins. The aluminate liquor is then returned to the respective alumina producers after processing. GEO Gallium also operates a purification plant in Salindres in southern France which belonged earlier to Rhodia Chimie S.A, formerly Rhône Poulenc. GEO Specialty Chemicals, founded in 1993, is headquartered in Cleveland, Ohio and is a leading producer of industrial chemicals for the semiconductor, optoelectronics, water treatment, paper, coatings and construction markets.

Shanxi Aluminum Factory, China's largest aluminum producer, with an annual capacity of 1.2 million tonnes is emerging as a large gallium producer, with a total annual capacity of around 80 tonnes from its plants:

- Great Wall Aluminum has a production capacity of 15 tonnes per year.
- Beijing JiYa Semiconductor Material provides more than 10 tonnes of 99.99% gallium per year.
- Sumitomo Chemical formed a joint venture company in China to refine

40 tonnes of gallium per year. US substrate maker AXT created a joint venture, Beijing JiYa Semiconductor Material Company to produce 4N gallium in China. AXT's partners include Shanxi Aluminum

Other leading primary producers include Pavlodar Alumina Refinery in the north-east of Kazakhstan, and several companies in both Russia and China.

Aluminum reduction cell

Dust generated from aluminum reduction cell contains about 0.5% Ga. Leaching the flue dust with hydrochloric acid extracts the gallium. Solids are filtered and the aqueous phase undergoes a series of solvent extraction stages to separate gallium from dissolved impurities. Crude gallium is recovered from the strip solution by electrolysis (Figure 8.16.9). The process is used by Elken A/S in Norway.

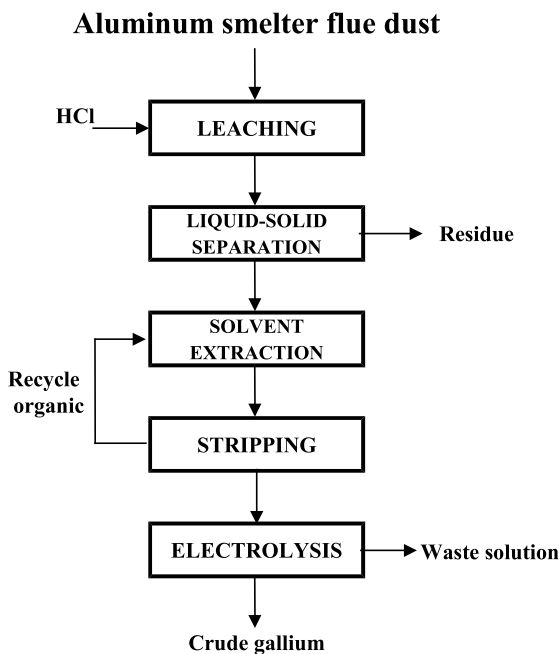


Figure 8.16.9 - Recovery of gallium from aluminum electrolytic cell flue dust in Norway

From pyrite cinder

Before the availability of large tonnage of elemental sulfur, pyrite was the main source for producing SO_2 for sulfuric acid manufacture. The Duisburger Kupferhütte in Germany imported pyrite from different countries, sold it to acid manufacturers throughout Germany, and obtained back the iron oxide residue, known as cinder, for treatment by hydrometallurgical route to obtain copper, zinc, and a large number of other metals including gallium. A small amount of gallium was produced from 1960 to 1980 from this source. Operations, however, ceased in 1980s when acid plants switched over from pyrite to elemental sulfur,

Recovery from other sources

An iron oxide deposit in Utah contains about 0.04% gallium. Crushed ore is leached with sulfuric acid containing SO_2 and fluorspar. After the insoluble impurities are separated, copper is cemented by the addition of iron and separated. Dissolved germanium is precipitated as a sulfide by H_2S and the precipitate is removed and treated to recover germanium dioxide. The solution, containing gallium, zinc, and iron, undergoes solvent extraction, where the gallium and zinc are extracted into the organic phase while iron remains in the aqueous phase. Gallium and zinc are stripped from the organic phase, and ammonia is injected into the stripped solution to precipitate gallium hydroxide. After separation it is purified and 99.999% gallium metal is recovered by electrolysis. This process is used by Saint George Mining Corporation near Saint George in Utah (Figure 8.16.10).

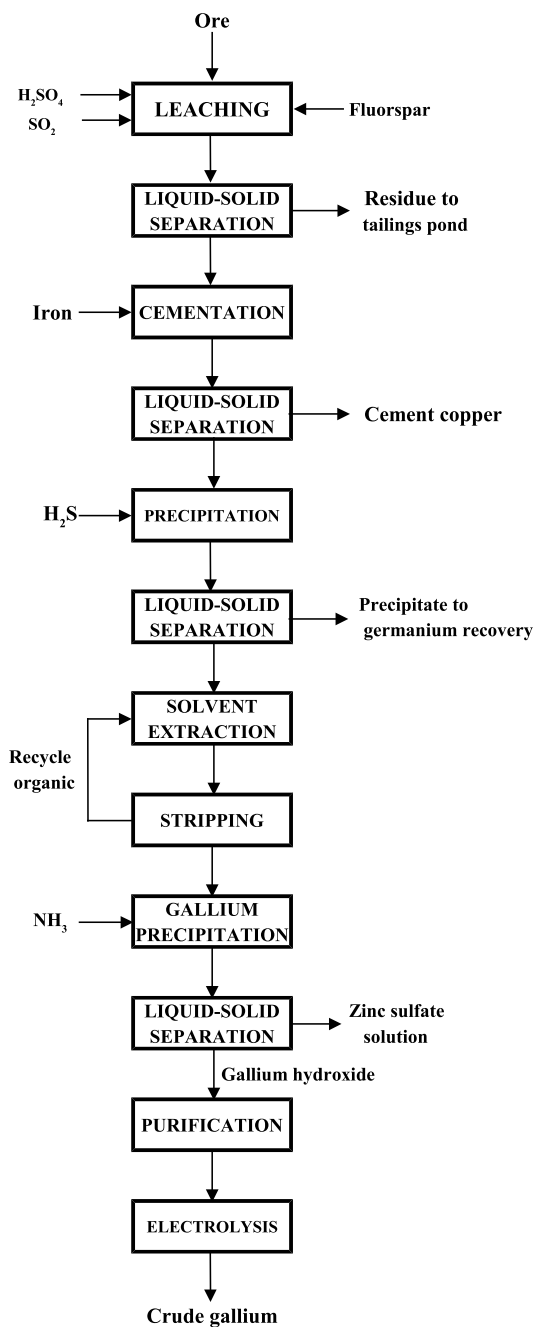


Figure 8.16.10 - Recovery of gallium from iron deposit in Utah (1986)

PURIFICATION

For most applications, purity requirements for gallium are either 6N or 7N. Crude gallium is purified in two steps, the first step produces 99.99% gallium, and the second produces the high purity desired. Liquid gallium is first filtered and heated under vacuum. Impurities can then be further reduced by sequential washing with hydrochloric acid. The principal method used to produce high purity metal is gradual crystallization of molten gallium. In this process, impurities remain in the liquid phase and do not contaminate the gallium crystal. Crystallization is repeated until gallium of the desired purity is obtained. Another method is to convert the gallium to gallium trichloride, which is then zone-refined. High-purity gallium is recovered by electrolysis of the halide compound.

STRUCTURE OF THE INDUSTRY

Today gallium is produced mainly as a by-product of extracting aluminum from bauxite, the remainder is extracted from by-products of zinc processing. Sumitomo Chemical in Japan purifies the extracted gallium to make it suitable for semiconductor applications. Recycling companies in Europe include Groupe Arnaud Electronics, MCP Group and PPM Pure Metals, which along with Furukawa is a major manufacturer of high-purity arsenic. Scrap material comes from the production of gallium arsenide and gallium phosphide substrates and other sources. In 1952 the annual world production of gallium was 350 kg; today it is about 90 tonnes.

USES

The main use of gallium is as a raw material in the manufacture of semiconductors, for example, the arsenide or the phosphide for the production of light-emitting diodes.

Gallium 99.99% is typically refined into 6N or 7N material by a third party before being used in final applications. It is widely used in doping semiconductors and producing solid-state devices such as transistors. Magnesium gallate containing divalent impurities such as Mn^{2+} is finding use in commercial ultraviolet activated powder phosphors. Gallium readily alloys with most metals, and has been used as a component in low-melting alloys.

Gallium arsenide, GaAs, is an important semiconductor, and is used to make devices such as microwave frequency integrated circuits, infrared light-emitting diodes and laser diodes. It is capable of converting electricity directly into coherent light. It has some electronic properties which are superior to silicon. Gallium arsenide devices can also be operated at higher power levels than the equivalent silicon device because they have higher breakdown voltages. These properties have made GaAs circuitry common in mobile phones, satellite communications, microwave point-to-point links, and some radar systems. Another important application of gallium arsenide is for the realisation of high efficiency solar cell. By combining gallium arsenide with germanium and indium gallium phosphide, it is possible to realise a triple junction solar cells which holds the record efficiency of over 32%. This kind of solar cell was used to power the robots which are exploring Mars surface.

Gallium and the neutrino

About 100 tonnes of gallium chloride, GaCl_3 , have been used to build the Gallium Neutrino Observatory in central Italy in the Abruzzo region, close to L'Aquila to study the neutrinos which are produced inside the sun during the process of nuclear fusion as proposed by the German physicist Hans Bethe and others in 1938. The target tank and the counting device are situated 2912 meter underground. The rock overburden shields the detector against interfering cosmic radiation. A similar experiment is being conducted in one of the underground mines in Sudbury; heavy water is used to detect the neutrinos

GALLIUM IN THE PERIODIC TABLE

Although Mendeleev predicted fairly well the atomic weight, the density, the melting point, and valency of gallium by interpolation with aluminum and indium the chemical properties of gallium are far more different from that of aluminum notwithstanding the relative abundance of gallium is $1.5 \times 10^{-3} \%$ while that of aluminum is 8.1 %. The false opinion that gallium is chemically similar to aluminum can be illustrated by the following examples:

- Gallium can be electrodeposited from aqueous solutions of its salts, but aluminum cannot
- Gallium is not precipitated with aluminum hydroxide during seeding
- Gallium hydroxide is soluble in ammonium hydroxide while aluminum hydroxide is not
- Aluminum is a typical metal that has the tendency to loose its three outermost electrons with great ease to form electronic structure of the inert gases. Gallium is a less typical metal that does not have the tendency to loose its outermost electrons with ease because in doing so it forms an 18-electron shell which does not have the inert gas structure.

8.17

Rare Earths¹

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¹ Based on

- F. Habashi, "The Discovery and Industrialization of the Rare Earths," Bull. Can. Inst. Min. & Met. 87 (976), 80–86, 87 (977), 71–76 (1993)

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See also

- Discoveries by Berzelius

- Yttrium, Lanthanum, Erbium, and Scandium

INTRODUCTION

When Mendeleev proposed the Periodic Table in 1869 only four of the rare earths yttrium, lanthanum, cerium, and erbium were known. He predicted scandium (eka boron) and it was discovered ten years later. Promethium, the last member of the group was discovered in 1945. It does not occur in nature; it was discovered among the fission products of uranium. It took over 150 years to discover and isolate all the 17 rare earth metals (Table 8.17.1).

Table 8.17.1- Discovery of rare earths

Year	Metal	Symbol	Origin of name	Discoverer	Nationality
1794	Yttrium	Y	Ytterby mine, Sweden	Gadolin	Finn*
1814	Cerium	Ce	After the planet Ceres (which in turn (named after a Greek deity)	Berzelius	Swedish
1839	Lanthanum	La	From Greek: ianthano = 1 am hidden	Mosander	Swedish
1843	Erbium	Er	Derived from Ytterby mine, Sweden	Mosander	Swedish
1878	Terbium	Tb	Derived from Ytterby mine, Sweden	Mosander	Swedish
1878	Ytterbium	Yb	Derived from Ytterby mine, Sweden	Marignac	Swiss of French origin
1879	Samarium	Sm	After a Russian mining official V.E. Smarsky	de Boisbaudran	French
1879	Scandium	Sc	After Scandinavia	Nilson	Swedish
1879	Holmium	Ho	Latin for Stockholm	Cleve	Swedish
1879	Thullium	Tm	After Scandinavian deity	Cleve	Swedish
1880	Gadolinium	Gd	In honour of Johan Gadolin	Marignac	Swiss of French origin
1885	Praseodymium	Pr	From Greek: prason = green, in reference to the colour of its salts	Welsbach	Austrian
1885	Neodymium	Nd	From Greek meaning the new one	Welsbach	Austrian
1886	Dysprosium	Dy	From Greek: dysprosodas = troublesome accessibility, in reference to the painstaking steps required in its separation	de Boisbaudran	French
1896	Europium	Eu	After Europe	Demarçay	French
1907	Lutetium	Lu	After Lutetia, Latin name for the place where Paris was founded	Urbain	French
1945	Promethium	Pm	After Prometheus, in Greek mythology, who brought fire to mankind in reference to harnessing of the energy of the nuclear fission and warning against its dangers.	Glendenin and Marinsky	American

* At that time Finland was under Swedish domination

The rare earths represent one fourth of the naturally-occurring metals. They were difficult to separate because their chemical behaviour was similar. With much laborious work the chemists separated one metal oxide after another from these minerals, only to discover later that the new 'elements' were not homogenous substances, but mixtures, which after further wearisome separation operations turned out to consist of two or more elements. During this period, an earth was a substance that could not be split further to other components by the chemical means was considered as an element.

These elements are lithophilic and are concentrated in oxidic compounds such as carbonates, silicates, titano-tantalo-niobates, and phosphates. Before the discovery of uranium fission, the rare earth metals had limited use. Their separation, based only on tedious fractional crystallizations, was extremely difficult. Their presence in the fission products of uranium and their high capacity to absorb neutrons suggested their use as control rods for nuclear reactors and prompted extensive research for their separation using ion exchange and solvent extraction. At present, they are separated on industrial scale in high purity, and find wide uses in numerous industries. It is interesting to note that many of the uses of the rare earths were developed after their commercial availability was demonstrated by Molycorp in USA on a scale which was made possible by the Mountain Pass orebody. The research and development efforts that followed created much of the economic value of the orebody.

OCCURRENCE

The rare earths always occur in nature in association with each other. The word "rare" originated from the fact it was thought that these elements could only be isolated from very rare minerals. Considering their abundance in the Earth's crust, the term is now inappropriate. When, however, a large number of minerals and rocks were analyzed, it became apparent that the earths are not rare. They constitute about 0.01% to 0.02% of the earth's crust. Cerium and yttrium, for example, are more abundant than

cadmium, mercury, antimony, and many other metals that are not usually considered rare. The abundance of the rare earth elements taken together is quite considerable. For all practical purposes, promethium does not occur in nature - - it forms only in nuclear reactors

The term “earth” was given to an oxide obtained during the chemical analysis of a mineral. For example, aluminum oxide in the German literature is Tonerde, i.e., the oxide component (Erde) of clay (Ton). In many cases, it took long time to isolate a metal from its oxide, especially those reactive metals such as aluminum, titanium, etc. There is no justification today to use the term “rare earths”. In 1925, the Norwegian geochemist Viktor Goldschmidt suggested the name “lanthanides” for those elements following lanthanum. The *Chemical Abstracts* uses the symbol Ln for lanthanides. The International Union of Pure and Applied Chemistry recommended that Sc, Y, La, and the lanthanides are called rare earths.

The rare earths always occur together in minerals; there is no mineral found that is composed of only one rare earth element. However, some minerals contain more of certain rare earths than others. For example, monazite contains a high percentage of lanthanum and the light lanthanides (Ce, Pr, and Nd) and a low percentage of the other heavy elements, while the opposite is true in xenotime. This relation is found in most rare earth minerals. That is why the early researchers in the rare earths minerals divided them into two sub-groups: the cerite group and the ytterite group, i.e., those rich in lanthanum to samarium or europium, and those rich in gadolinium to lutetium, respectively. The ytterite earth refers to the historical name of the unknown earth discovered by Gadolin in the mineral from the Ytterby mine.

While yttrium and lanthanum occur in nature together with the lanthanides [the group cerium to lutetium], scandium usually occurs in uranium ores. However, there are many similarities to justify including scandium with the rare earths metals. The major source of yttrium, lanthanum, and the lanthanides are bastnasite (a fluorocarbonate), monazite (a phosphate), and xenotime (a phosphate like monazite but of different crystalline struc-

ture). The proportion of the individual metals in each of these minerals is different. Apatite is also an important potential source of the lanthanides in which they occur in isomorphous substitution with Ca^{2+} ion.

RARE EARTH MINERALS

The first mineral discovered containing the rare earths was cerite in 1751; it was identified at that time by its discoverer the Swedish chemist Axel Cronstedt (1722-1765)² as the heavy stone from the Bastnäs mine in Sweden. Another Swedish chemist Tobern Bergman (1735-1784) in 1784 recognized the existence of an unknown earth in this mineral, but it was not until 1804 that Martin Klaproth (1743-1817) and Jons Berzelius (1779-1848) independently isolated this new earth and called it cerium oxide, naming the mineral cerite in honour of the newly discovered small planet ceres.

In 1788 a Swedish mineral collector by the name Carl Axel von Arrhenius (1757-1824) (Figure 8.17.1) discovered a remarkably heavy black stone in the feldspar quarry at Ytterby on the outskirts of Stockholm (Figure 8.17.3). Some of the properties of this mineral were described by another Swedish mineralogist Bengt Geijer (1758-1815) in 1788, and by the Finish chemist Johan Gadolin (1760-1852) (Figure 8.17.2) in 1794 and 1796 who simply referred to it as the “new stone”; he suspected in it the presence of an unknown earth to the extent of about 38%.



Figure 8.17.1 - Carl Axel von Arrhenius (1757-1824)



Figure 8.17.2 - Johan Gadolin (1760-1852)

² Discovered nickel in 1751



Figure 8.17.3 - Heavy black stone later named gadolinite
 $(\text{Ce,La,Nd,Y})_2\text{FeBe}_2\text{Si}_2\text{O}_{10}$

This discovery was confirmed a year later by the Swedish chemist Anders Ekeberg (1767-1813) (Figure 8.17.5) who called the new earth “ytter earth”. In 1801 Klaproth confirmed this discovery and named the mineral, in which the ytter earth occurred, gadolinite in honour of Gadolin who first analyzed the mineral. Thus, although cerite was discovered before gadolinite, the latter was named first.



Figure 8.17.4 - Anders Ekeberg
(1767-1813)

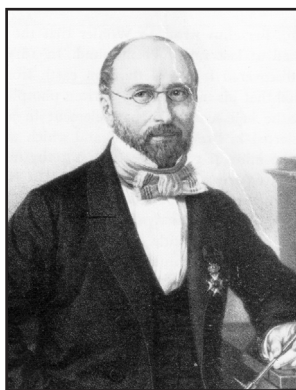


Figure 8.17.5 - Carl Gustav Mosander
(1797-1858)

Because of their similarity, the cerium earth and the ytter earth were confused and were thought to be one and the same earth, until 1839 when the Swedish chemist Carl Gustav Mosander (1797-1858) (Figure 8.17.5), a student and later a coworker of Berzelius, clarified this matter. He was able to identify and separate six new elements from these two earths:

- Cerium earth: cerium, lanthanum, and didymium
- Ytter earth: terbium, erbium, and yttrium.

The naming of the six metals reflects their origin and the circumstances during their separation. Thus, cerium was accompanied by the “hidden one”, i.e. lanthanum and its “twin”, i.e. didymium. Terbium, erbium, and yttrium are all derived from the Ytterby Mine where the mineral gadolinite was first discovered. Later research, however, has shown that the three elements didymium, terbium, and erbium were not pure metals and could be resolved further into twelve elements (Figures 8.17.6-8.17.7).

Original name of the earth was retained as one of the components. Thus, when erbium was split into three, the components became known as erbium, ytterbium, and scandium. But, then the first two later could be split further: thus, erbium became erbium, thullium, and holmium while ytterbium became ytterbium and lutetium. Holmium was later split into holmium and dysprosium.

Naming of these new elements was not a simple matter. For example, when an earth was resolved into two or three new earths, usually the original name of the earth was retained as one of the components. Thus, when erbium was split into three, the components became known as erbium, ytterbium, and scandium. But, then the first two later could be split further: thus, erbium became erbium, thulium, and holmium while ytterbium became ytterbium and lutetium. Holmium was later split into holmium and dysprosium.

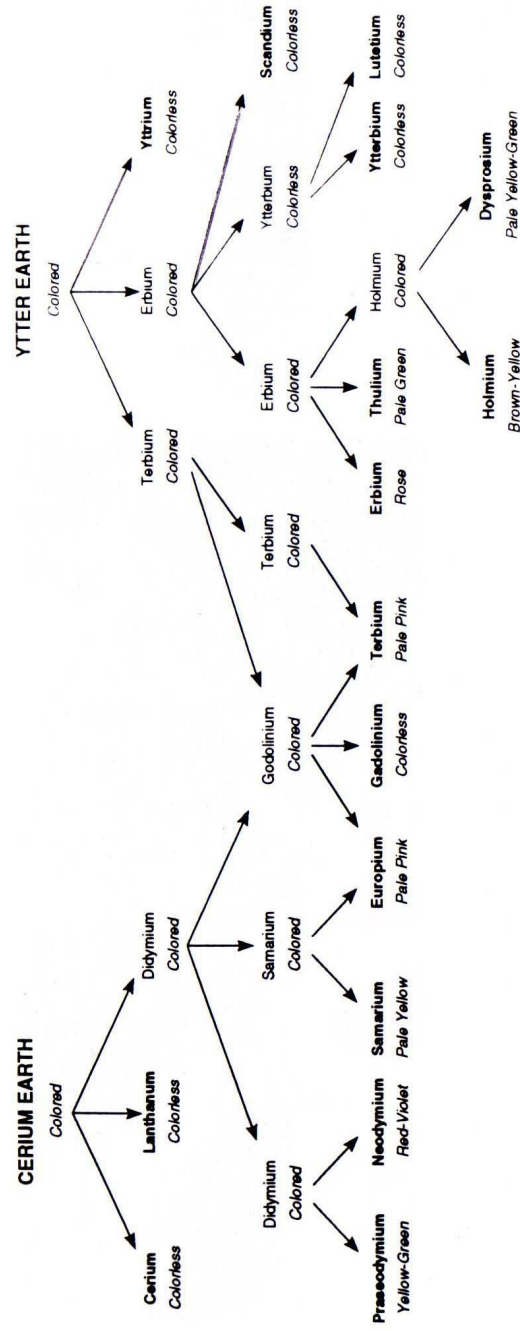


Figure 8.17.6 - The role of colour of the rare earth salts affecting their historical separation

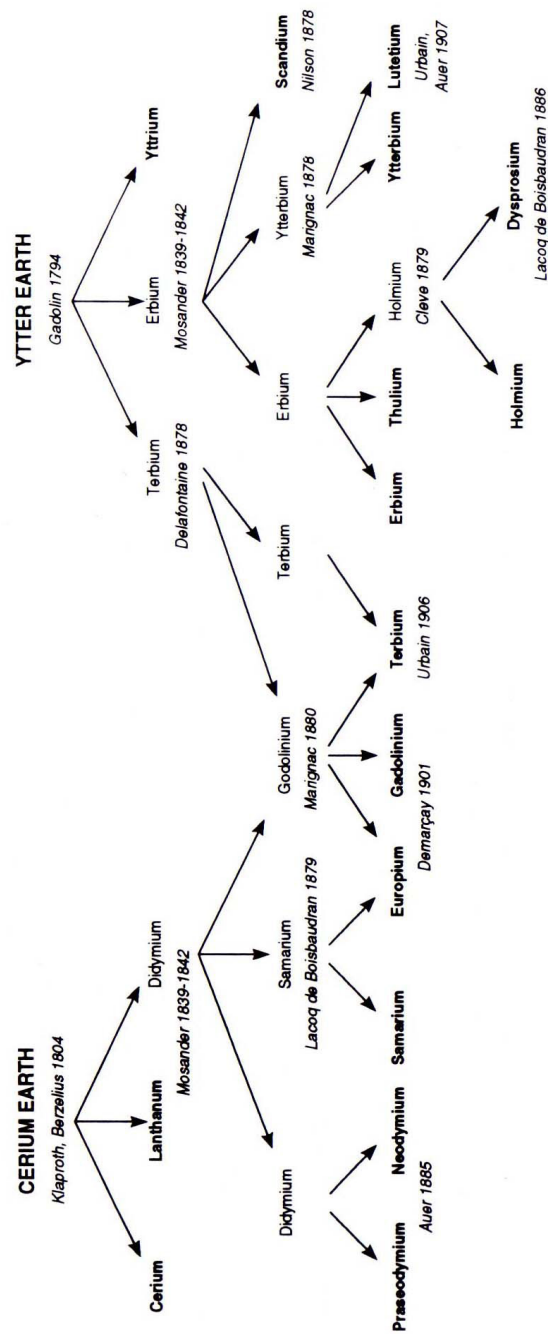


Figure 8.17.7 - Approximate chart of the history of the separation of rare earths

Europium was first found by Paul Émile Lecoq de Boisbaudran (1839-1912) (Figure 8.17.8) in 1890, who obtained basic fraction from samarium-gadolinium concentrates which had spectral lines not accounted for by samarium or gadolinium (Figure 8.17.9), but it was Eugene Anatole Demarçay (1852-1904) (Figure 8.17.10) who is credited with the isolation of europium.



Figure 8.17.8 - Paul Emile Lecoq de Boisbaudran (1839-1912)

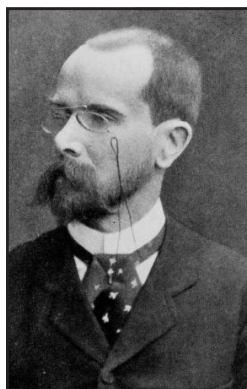


Figure 8.17.10 - Eugene Anatole Demarçay (1852-1904)

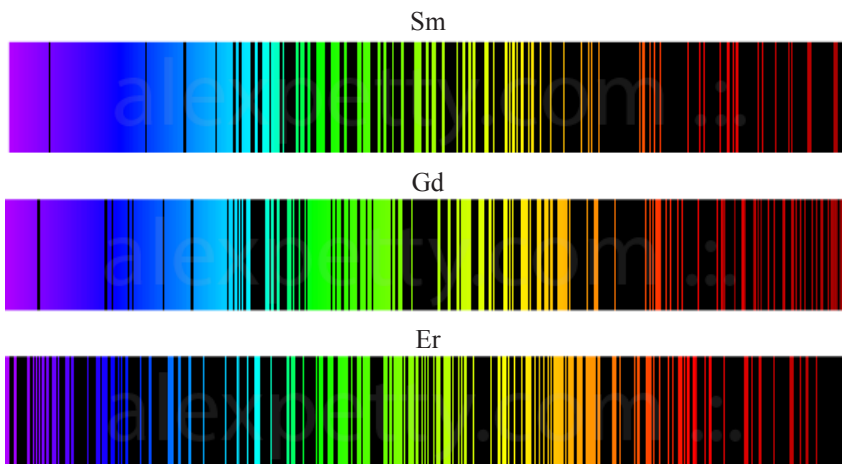


Figure 8.17.9 - Emission spectra of samarium, gadolinium, and europium

ISOLATION OF THE RARE EARTHS

The rare earth elements caused considerable confusion and problems during their discovery. The first phase of separation due to Mosander was based on colour of ions in solution and of the salts, the crystal form, and the reactivity. Thus, cerium earth was coloured, but when dissolved and recrystallized a colourless and a coloured fraction were obtained. In this way cerium and lanthanum (colourless) were separated from didymium (coloured). Similarly, ytter earth when purified by fractional crystallization a colourless fraction containing yttrium, and a coloured fraction containing terbium and erbium were obtained. Both coloured fractions, however, were complex mixtures of coloured components and, therefore it was no longer possible to identify these components visually.

Fractional crystallization

This is one of the oldest methods for the separation of rare earths and is now obsolete (Figure 8.17.12). It depends on small differences which are magnified by repeated operations. It has been replaced by ion exchange and solvent extraction which are faster and less tedious.

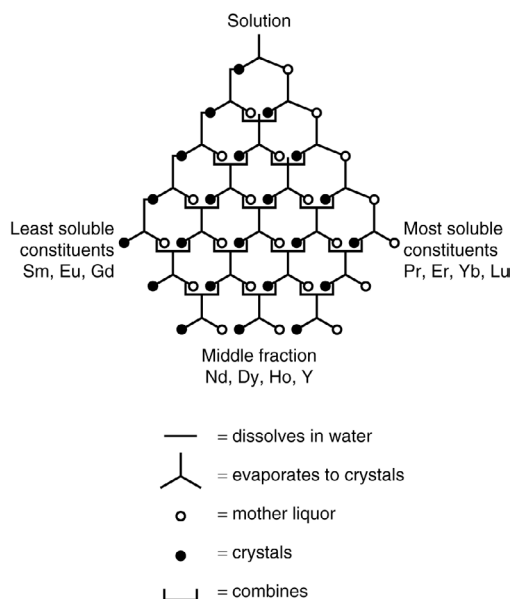


Figure 8.17.12 - separation of rare earths by fractional crystallization

New methods of analysis were necessary. Two important events that contributed to the resolution of this confusion were the discovery of spectroscopic analysis (1859) and the discovery of the Periodic Table (1869).

Spectroscopic Analysis

Spectroscopic analysis was so successful that immediately after putting it into use, the discoverers were able to find two new elements rubidium and cesium. Students visited Bunsen from all over Europe to learn this technique and chemists brought samples there to be analyzed. This method of analysis was found to be a useful tool in the discovery of new elements.

The Swiss chemist of French origin Jean Charles de Marignac (1812-1894) (Figure 8.17.13), who went to the École Polytechnique and the École des Mines in Paris, was the first to apply spectroscopic analysis to rare earths minerals. In 1878 he discovered ytterbium and in 1880 gadolinium. Around the same time Lecoq de Boibaudran became a specialist in spectroscopic analysis and set forth to study rare earths by this technique. In 1879 he discovered a new metal in the mineral samarskite which he named samarium. A few years later he discovered dysprosium (1886).

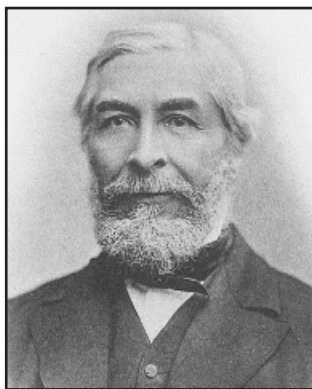


Figure 8.17.13 - Jean Charles Galissard de Marignac (1817-1894)

Spectroscopic analysis now became an essential tool in the follow-up of separations in rare earths research. However, it was Bunsen who paved

the way for all these discoveries with his invention of the burner that carries his name and is found today in most chemical laboratories. This burner permitted higher temperature in the laboratory than ever before, and hence spectroscopic analysis was possible.

Rare earths in the Periodic Table

The first Periodic Table in 1869 was very different from what we now know today. For example, cerium, lanthanum, and didymium were listed with the atomic weights of 92, 94 and 95, respectively, corresponding to bivalence at a unit $O = 16$, and also erbium and yttrium with atomic weights of 56 and 60, respectively, with interrogation marks.

In 1871 Mendeleev performed an important change with rare earth elements: he assumed that they were trivalent, and correspondingly re-calculated their atomic weights. Instead of YO and LaO he calculated with Y_2O_3 and La_2O_3 . He then listed yttrium with an atomic weight of 88, lanthanum with 137, and cerium with 138. He supported his assumption with specific heat measurements of cerium. The assumption proved true; the Swedish chemist Per Teodor Cleve (1840-1905) (Figure 8.17.14) confirmed it analytically in the following years, and the American chemist William Francis Hillebrand (1853-1925) in 1876 with specific heat determinations for lanthanum and didymium.



Figure 8.17.14 - Per Teodor Cleve (1840-1905)

The Periodic Table proved to be a useful tool in organizing the chemical elements. However, for the rare earth elements it failed. As their number increased, there was simply nowhere to put them in the Table. Numerous attempts were made to find a solution.

The Czech chemist Bohoslav Brauner (1855-1935) (Figure 8.17.15) concentrated his activity on more exact atomic weight determinations of rare earth elements. The anomalies led him to the assumption that didymium was not a homogeneous element. This was confirmed soon afterward by Carl Auer (1858-1929) in Vienna. The results of the atomic

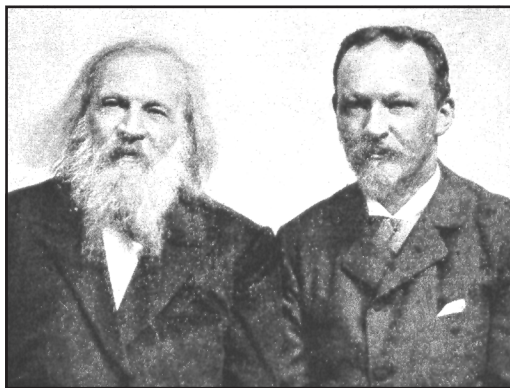


Figure 8.17.15 - Mendeleev in Prague in 1900 with Czech chemist Bohoslav Brauner (1855-1935)

weight determinations carried on for decades were: Ce 140.22, La 148.92, Pr 140.9, Nd 144.3, Sm 150.4, i.e., the values still valid today. Finally, Brauner's proposal in 1899 that all rare earth elements, with the exception of yttrium and scandium, should be placed in the Periodic Table into a single square, the square of lanthanum, remained (Figure 8.17.16).

METALS																		METALLOIDS										NONMETALS										
Li	Be																	B	C	N	O	F	Ne	Na														
Na	Mg	Al																	Si	P	S	Cl	Ar	Kr														
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Xe																				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	Rn																				
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu																						
Fr	Ra	Ac																																				

THE RARE EARTHS

Figure 8.17.16 - The rare earths are located in one square in the Periodic Table

In 1922 their position in the Periodic Table was established when Danish physicist Niels Bohr (1885-1962) (Figure 8.17.17) proposed the presence of electron shells in atomic structure (Figure 8.17.18). The chemical similarity of the rare earth elements became apparent after the clarifications made by physicists showing the same number of electrons in the two outermost shells.



Figure 8.17.17 - Danish physicist Niels Bohr (1885-1962)

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
2	2	2	2	2	2	2	2	2	2	2	2	2	2
8	8	8	8	8	8	8	8	8	8	8	8	8	8
18	18	18	18	18	18	18	18	18	18	18	18	18	18
19	20	21	22	23	24	25	26	27	28	29	30	31	32
9	9	9	9	9	9	9	9	9	9	9	9	9	9
2	2	2	2	2	2	2	2	2	2	2	2	2	2

Figure 8.17.18 - Electronic configuration of rare earths

Bohr further concluded from quantum theory that the missing element number 72 should be quadrivalent and not trivalent and must belong to the zirconium family rather than the rare earths. He advised the Hungarian chemist Georg von Hevesy (1885-1966) who was working in his laboratory at that time to search for this element in zirconium ores. This led to the discovery of hafnium in 1923.

The location of rare earth elements according to Brauner's proposal is still the most widespread solution to the problem; in most periodic tables lanthanum with the atomic number 57 is followed by hafnium with the atomic number 72, and the rare earth elements are listed separately at the bottom of the Table.

The ions rare earths are either colourless or pale colour (Table 8.17.2).

Table 8.17.2 - Color of ions of rare earths

	M ²⁺	M ³⁺	M ⁴⁺
Ce	—	colourless	orange red
Pr	—	yellow green	—
Nd	—	red violet	—
Sm	red brown	pale yellow	—
Eu	—	pale pink	—
Gd	—	colourless	—
Lu	—	colourless	—
Yb	green	colourless	—
Tm	—	pale green	—
Er	—	rose	—
Ho	—	brownish yellow	—
Dy	—	pale yellowish green	—
Tb		pale pink	

RESEARCH IN HEIDELBERG

Heidelberg on the Neckar (Figure 8.17.19), was the meeting place for chemistry students from all over Europe in the nineteenth century. Its university, founded in 1386, already had a famous Professor of chemistry and medicine in the faculty of medicine by the name Leopold Gmelin whose three-volume *Handbuch der Theoretischen Chemie* appeared in 1817-1819, and later became a multi-volume monumental work. At that time chemistry was taught mainly to medical and pharmacy students.

The separation of chemistry from medical faculties, and its inclusion in philosophical faculties as an independent discipline, was made by the poet and scientist Johann Wolfgang Goethe (1747-1832) when he was minister in Weimar in 1789. Without the consent of the administration of the University of Jena, he appointed the apothecary J.F. Götting (1753-1809) as professor of chemistry in the philosophical faculty and designated as his successor (from 1810) the gifted chemist Johann Döbereiner (1780-1849).

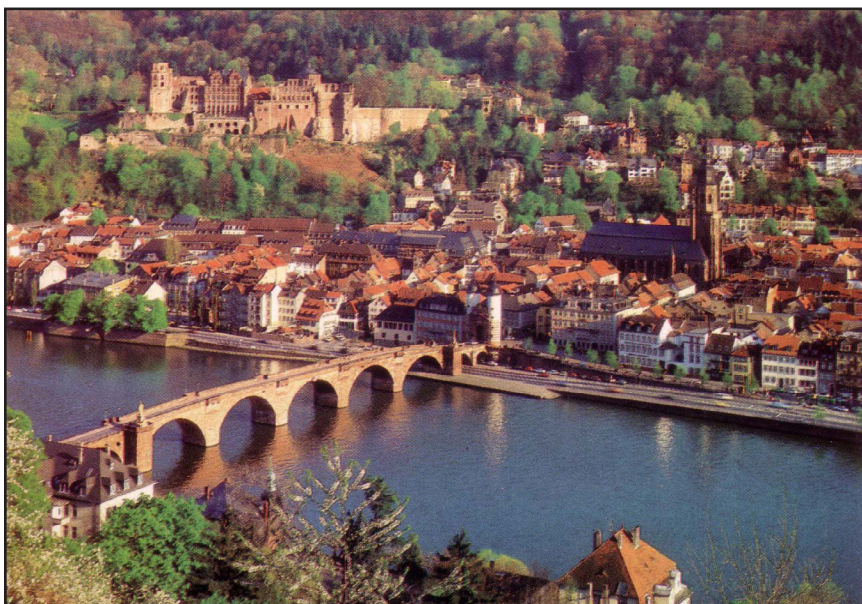


Figure 8.17.19 - Heidelberg on the Neckar

As successor to Gmelin in Heidelberg, Robert Bunsen in 1852 made this university town the Mecca of chemistry students. One of his students, Henry Roscoe (1833-1915) (Figure 8.17.20) who later became a distinguished professor in Manchester, England described him as follows: “As an investigator he was great, as a teacher he was greater, as a man and a friend he was greatest”.



Figure 8.17.20 - Robert Bunsen (sitting), on his right stands Gustav Kirchhoff and on his left Henry Roscoe. Photograph taken in Manchester in 1862

Two students who came to Bunsen played a particular role in the history of the rare earths. They were Jons Fridrik Bahr from Uppsala (Figure 8.17.21) and Carl Auer (1858-1929) (Figure 8.17.22) from Vienna. Bahr brought with him samples of rare earth minerals for analysis by Bunsen's spectroscope. He also developed a method of separation based on the selective decomposition of the nitrates. He found that the nitrates of the different earths are decomposed at different temperatures when heated gently. Bunsen later asked Auer to study different spectra of rare earths extracted from gadolinite. Auer noted that certain lines disappeared during chemical purification. Thus, he could know when an element had reached its highest degree of purity. On his return to Vienna he took samples of rare earth minerals with him and when Bunsen died, he took possession of his library.

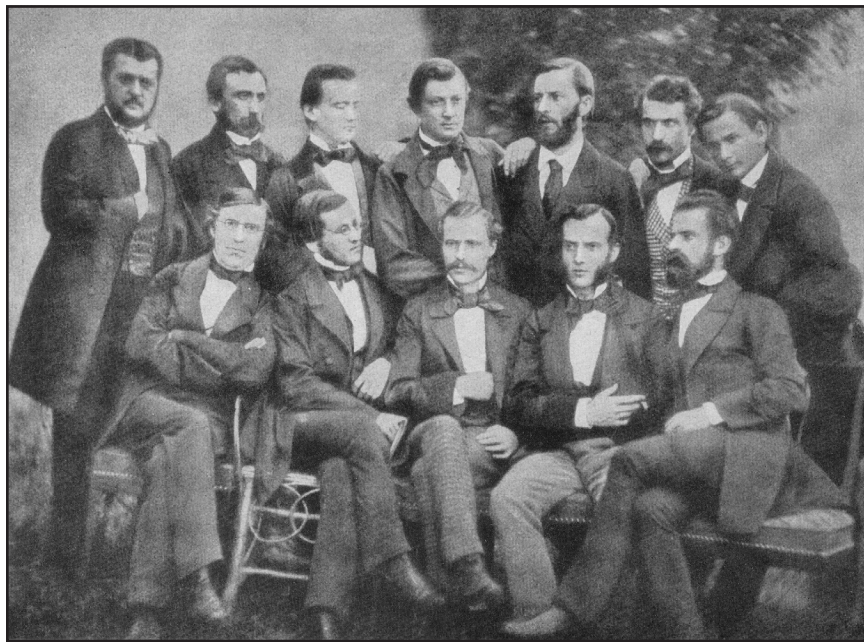


Figure 8.17.21 - Jons Fridrik Bahr (first from left seated) from Uppsala and colleagues while studying at Heidelberg³

³ Other students, sitting:

- Hans Landolt (1821-1910) from Bonn University, became famous later after compiling the multi-volume “Physikalisch-chemischen Tabellen” with Börnstein
- Heinrich Caro (1834-1910) from Berlin University, specialized in dyestuffs
- August Kekulé (1829-1896) from Bonn University, put forward the structural formula for benzene

• Pebal

Standing: Gaupilat, Frapoli, Wagner,

• Henry Roscoe (1833-1915) from London, studied under Bunsen from 1853-1857, then professor at Manchester, famous for the nine-volume work “Treatise on Chemistry” with Carl Schorlemmer

• Lothar Meyer (1830-1895) went to Heidelberg in 1854 to study medicine and Bunsen’s gas analysis methods for determining CO in blood. Put forward simultaneously and independently of Mendeleev the Periodic Table, but less fully

• Pavesi

• Friedrich Beilstein (1838-1906) born in Saint Petersburg of German Parents, studied in Heidelberg from 1853 to 1855 under Bunsen, became professor of organic chemistry at the Imperial Technological Institute in Saint Petersburg, most famous for the “Handbook of Organic Chemistry”



Figure 8.17.22 - Carl Auer (1858-1929)

CARL AUER'S RESEARCH IN VIENNA

When Carl Auer returned to the University of Vienna (Figure 8.17.23) in 1882 he had two areas of research, both were continuation of his studies and observations in Heidelberg. These were: the rare earths and the phenomenon of incandescence. Both marked the start of the rare earths industry. Later, he got involved in the formation of sparks which further advanced the rare earths industry.

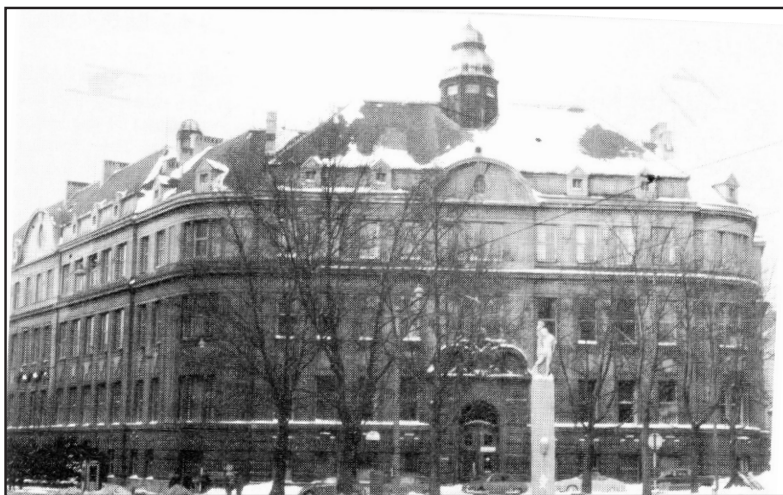


Figure 8.17.23 - Chemistry and Physics departments of the University of Vienna where Carl Auer conducted his original researches on rare earths.

Photo by Fathi Habashi 1960

Praseodymium and neodymium

In Vienna, Carl Auer introduced the fractional crystallization of the ammonium double nitrates in concentrated nitric acid and later in neutral solution, to study the separation of the rare earths. He set up a spectroscopic laboratory and studied the earths from gadolinite. Carl Auer made two discoveries in rare earth metals, one of them was, however, not credited to him because of delay in publication. Within two years of his return to Vienna he was able to report that didymium (the twin of lanthanum) was in fact two elements which he called neodymium, i.e., the new didymium and praseodymium, i.e., the green didymium in reference to the color of its salts. It was suspected long before, that didymium was not a pure element but no researcher was successful to make the separation until Carl Auer used his new method of fractional crystallization using a batch of seven kilograms of cerite. This work resulted in the accumulation of a large amount of pure lanthanum salts that played an important role later on.

The other discovery was in 1905 when he also suspected that ytterbium consisted of two elements and was able to resolve it into ytterbium and casseopeum. His report, however, appeared in 1907, forty four days after Georges Urbain (1872-1938) (Figure 8.17.24) announced his discovery of lutetium and determined its atomic weight. Because Urbain's report was more complete he was credited with the discovery.



Figure 8.17.24 - Georges Urbain (1872-1938)

BEGINNING OF THE INDUSTRY

Carl Auer got involved in the formation of sparks which further advanced the rare earth industry.

Incandescence research

As early as 1826 it was known that CaO pastilles when heated in the oxy-hydrogen flame produced light. Later, zirconium oxide was used. While in Bunsen's laboratory, Carl Auer had noted the remarkable light-emitting powers of the rare earth oxides when they were inserted into the flame of a Bunsen burner. When he returned to Vienna he found that some lanthanum oxide added to ZrO_2 improved the incandescence. He had on hand a considerable quantity of pure lanthanum salts derived from the didymium splitting. At night, he lit his laboratory window with the new light he generated attracting the attention of passers-by. For this purpose, he invented the gas mantle -- a stocking made of cotton thread and soaked in a solution of the earth metal salts. After the organic matter was burned off, a skeleton of the metal oxide was left (Figure 8.17.25). This emitted light when heated in a laboratory Bunsen burner. He demonstrated his invention to the press and gave public lectures to gain the interest of industrialists.

In 1887 Carl Auer opened a factory at Atzgersdorf, a suburb of Vienna, to prepare the rare earths salts necessary for preparing the soaking solution and to sell it to customers in Germany, England, and the United States. He engaged the 27-year old chemist Ludwig Haitinger as director. He left the manufacture of the mantle to other companies. To secure supplies of raw material for his factory he went to Sweden and Norway to buy eight tons of cerite. He sent Haitinger to the United States to get one ton of monazite, which was produced in North Carolina as a waste product of a gold operation, to be used as an experimental source for rare earths. This was suggested to Auer by his British customers. Auer did not speak English while Haitinger did.

However, after two years of success, sales declined because the light of the gas lamps was too greenish, the life of the lamps was too short, the raw material was rare and too expensive, and there was competition with the new electric light. He, therefore, had to shut down the factory in 1889 and Haitinger returned to the University of Vienna as a teaching assistant.

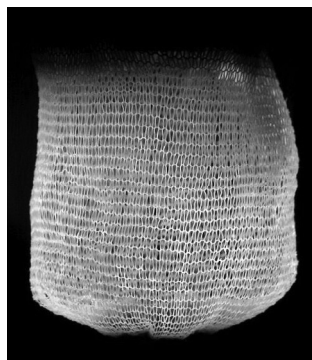


Figure 8.17.25 - Gas mantle

Carl Auer continued his research on the rare earths, but a new life came to his factory two years later. Haitinger was engaged to write a chapter on the rare earths for Dammer's *Handbook of Inorganic Chemistry*. During his literature search he came across the importance of impurities on the light emission of oxides in the cathode ray tube and in the Bunsen burner. He then performed some experiments which showed that by adding small amounts of chromium oxide to aluminum oxide, the incandescence was three times that of Auer's lanthanum - zirconium oxide mixture. However, the mixture had no practical application because the oxides were volatile in the Bunsen flame. He communicated his observation to Carl Auer on New Year's eve of 1890. Carl Auer thought of the large amounts of thorium oxalate he separated from monazite to prepare the lanthanum oxide for his lamp, and knew that ThO_2 was very stable at high temperature, he thought of using it instead of the lanthanum oxide.

After extensive research Carl Auer came to the conclusion that thorium oxide containing 1% cerium oxide gave a much brighter light in his gas lamp. In 1892 Haitinger came back to Atzgersdorf and the factory was again opened. The new light was an instant success; in one year 10 000 lamps were lighting Vienna (Figures 8.17.26-8.17.27) and more lamps were produced in the next years in competition with the new electric lamp of Edison.



Figure 8.17.26 - A historic picture showing a municipal worker lighting an Auer lamp in the street



Figure 8.17.27 - Streets in Vienna were lit by Auer's invention

First use of monazite

The mineral dealer in New York who sold Haitinger a ton of monazite had a brother who was a coffee dealer in Santos, near São Paulo in Brazil. He sent Carl Auer a sample of the heavy yellow sand from the coast of Brazil. This sand contained monazite that soon became the raw material for the growing gas mantle industry. Its inexpensive availability was an important factor in the survival of the industry in spite of competition from the electric lamp.

As a result of the working up of monazite sand for the production of thorium for the gas mantle, considerable quantities of cerium sulfate accumulated. Carl Auer recalled the preparation of metallic cerium by his colleagues at Bunsen's laboratory and the sparking of the metal when scratched or drawn over a rough surface. He conceived that this sparking action may be utilized for ignition purposes. However, cerium would be a too costly material. He, therefore, prepared a cerium-iron alloy and found out that when the alloy contained 30 % Fe it gave the best sparking effect

suitable for ignition of gases. The “Auer lighter” (Figures 8.17.28-8.17.30) soon became as famous as his incandescent mantle when it was produced on large scale in 1903. Production reached 1 000 000 kg annually in 1930; it served to prepare 500 million flints which replaced six billion boxes of matches. This work was conducted at his new factory at Treibach in Carinthia which he took possession in 1900 and which is today a successful metallurgical plant known as Treibacher Chemische Werke in Austria.

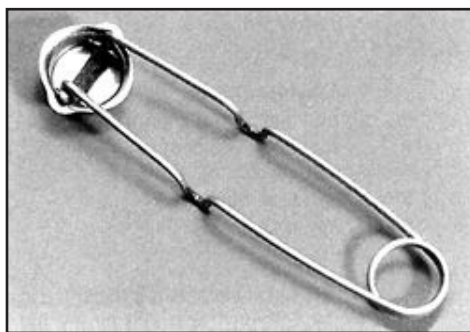


Figure 8.17.28 - Auer lighter



Figure 8.17.29 - Auer igniter in action



Figure 8.17.30 - Cigarette lighter

EXPANSION OF THE INDUSTRY

The rare earth industry that started in Austria as a small enterprise expanded to Germany and France, and in modern times to the United States, China, and other countries (Figure 8.17.31). Monazite sand occurs mainly

in Brazil, India, Australia, and the United States, while xenotime occurs mainly in South-East Asia associated with alluvial tin deposits.

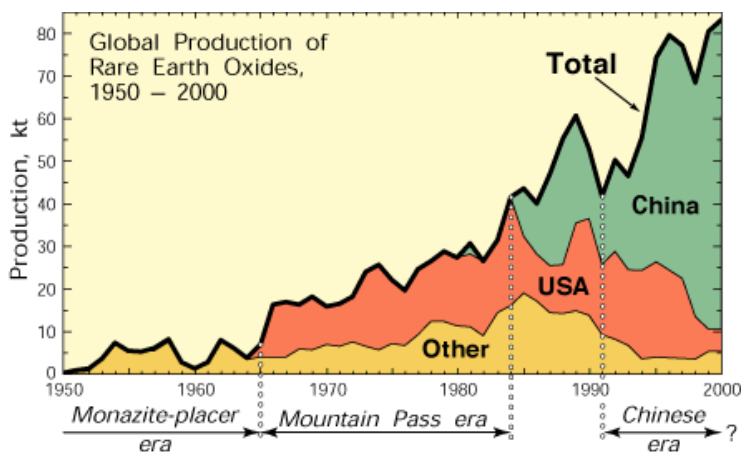


Figure 8.17.31 - Production of rare earths oxides 1950-2000

Austria

The Treibacher Chemische Werke founded by Carl Auer, started in 1903 Mischmetall⁴ and flint production. In 1916, ferroalloys were produced. After World War I, in 1929 the company became public property. In 1941, the production of artificial Corundum was started. After World War II the company diversified its products as follows: in 1949 rare earth compounds, in 1951 sodium perborate, in 1967 hard metal powders, in 1969 vanadium pentoxide, in 1978 ferronickel, in 1980 tungsten and molybdenum alloys, in 1985 rare earths metals and alloys, and in 1987 samarium cobalt magnets.

Germany

All rare earth ores shipped from Brazil and later from India arrived in Hamburg. Carl Auer founded the Auer-Gesellschaft factory in Odenburg near Berlin. In 1933, four years after Auer's death, Degussa, Goldschmidt, and Treibacher Chemische Werke merged.

⁴ German for mixed metals, the product obtained by reducing a mixture of rare earth fluorides, i.e., without separation of the individual metals.

India

Indian monazite in Travancore commenced production in 1911, and now a successful State operated enterprise.

France

At the beginning of the twentieth century, Carl Auer had a plant in France to extract thorium from monazite. During World War I, the plant was confiscated by French authorities. In 1920, the Société des Terres Rares was founded at Serquigny in Normandy and in 1924 the first industrial separation of rare earths by fractional crystallization started. In 1947, the plant was moved to La Rochefle and in 1960 was bought by the French Company Pechiney. Fractional crystallization was replaced by ion exchange and in the 1960s, by solvent extraction. Also, the H_2SO_4 method for treating monazite was replaced by the NaOH process. In 1972, Rhône-Progil was formed by the merger of Progil and the chemical activities of Pechiney Saint-Gobain. In 1975, Rhône-Progil became a part of the Rhône-Poulenc Group. In 1981, Rhône-Poulenc started a second plant for the production of rare earths in Freeport, Texas.

United States

The Lindsey Light and Chemical Company in Chicago produced thorium and cerium nitrates for gas mantles. Herbert N. McCoy (1870-1945), a professor of chemistry at the University of Chicago, arranged with Lindsey upon his retirement in 1930s, to work up some of the rare earth residues stored in a pond on the company premises. He produced kilogram amounts of europium - one of the rarest of the rare earths by a novel process he devised based on reducing Eu^{3+} to the divalent state by zinc and separating it from the other rare earths with barium as barium sulfate. The mixed barium europium sulfate was then washed with an oxidizing acid solution to remove europium in the trivalent state. This and other material was given to different laboratories for research.

During World War II when rare earths were found among the fission products of uranium, intensive research was conducted at Ames Laboratories at Iowa State College under Frank H. Spedding (1902-1984) (Figure 8.17.32) and his co-workers that resulted in preparation of pilot plant quantities of high purity rare earth salts.



Figure 8.17.32 - Frank H. Spedding (1902-1984)

The discovery of rare earth mineralization between Clark Mountain, a dominant peak in northeastern San Bernardino County, California, and interstate Highway 15 (former US 91) occurred in April 1949. The region, however, was already the site of silver mining as early as 1865. Between 1900 and 1920 many small lead, zinc, copper, gold, and tungsten mines were started and some production recorded. The Sulfide Queen gold deposit, adjacent to the Mountain Pass orebody, was not discovered until 1936. A cyanide plant was built, but only small amounts of gold were produced.

In spite of the very considerable mining exploration in the Clark Mountain area before 1949, the presence of rare earth metals was not suspected until a heavy, light-brown mineral was discovered nearly a mile north of the Sulfide Queen gold mine. The mineral identified as bastnasite. The US Geological Survey confirmed the discovery and made a public announcement in November 1949. Molycorp became interested and bought these claims in February 1950.

While the Survey was mapping the Mountain Pass Area an enormous deposit was found. Much of it was on the Sulfide Queen claims. The discovery was announced in January 1951. Molycorp bought the Sulfide Queen property, including its gold cyanide plant and other buildings. Other adjoining mining claim groups were also acquired. All of this prospecting and property acquisition led to the development and utilization of the Mountain Pass orebody and its present eminence as the only deposit

of its kind in the world mined solely for rare earths. Table 8.17.3 shows mineralogical analysis of the ore. A large plant for separating the rare earths was constructed but shut down in the late 1990's due to marked competition.

Table 8.17.3 - Mineralogical analysis of bastnasite ore at Mountain Pass

	%
Bastnasite	12
Calcite	40
Barite and/or celestite	25
Strontianite	10
Silica	8
Other minor minerals	5
	100

Canada

In Canada, uranium mines in the Elliot Lake region in Ontario (Denison Mines Limited) became the principal source of yttrium in the world in the period 1966-1970. The ores in these deposits were 0.11% U_3O_8 , 0.028% ThO_2 , and 0.057% R_2O_3 (rare earth oxides). Production was resumed between 1973 and 1977 when shut down became permanent because of competition on world markets. The pyrochlore deposits in Saint Honoré Quebec exploited by Niobec Incorporation, contain appreciable amounts of rare earths, thorium, and uranium. At present, a pyrochlore concentrate containing rare earths is exported, and a ferroniobium is produced. A complex oxide ore deposit containing about 1% rare earths is located near the Niobec mine, but is not presently being exploited.

China

Large deposits of iron ore containing rare earths in the form of a mixture of monazite (30%) and bastnasite (70%) were discovered in the 1920s, in Bayan Obo, 150 km northeast of the steel industry centre in Baotou in Inner Mongolia (Figure 8.17.33). A typical analysis of the ore is shown in

Table 8.17.4. The rare earths are recovered during the beneficiation of the iron ore and are treated with concentrated H_2SO_4 in a rotary kiln, at about 300°C at the feed end and at 800°C at the discharge end, to decompose the minerals and form rare earth sulfates to be leached subsequently with cold water.



Figure 8.17.33 - Monument to rare earths in Inner Mongolia near the town of Damao at the field of wind turbines which reads “Home of rare earths welcomes you”

Table 8.17.4 - Analysis of iron ore at Bayan Obo, Inner Mongolia, China

	%		%
Fe (total)	31.28	MgO	0.49
FeO	2.9	K ₂ O	0.1
R ₂ O ₃ *	7.02	Na ₂ O	1.6
F	9.6	TiO ₂	0.55
SiO ₂	12.2	BaO	2.69
CaO	16.9	Mn	0.15
P	0.95	Nb ₂ O ₅	0.14
S(total)0.74	ThO ₂	0.035	
Al ₂ O ₃	0.47		
	Total	87.82	

* Rare earth oxides



Figure 8.17.34 - Location of Inner Mongolia

In the late 1960s, a new type of rare earth deposits was discovered in many places of southern China in which the rare earth ions were sorbed by clay minerals. The rare earths content in these deposits is 0.05% to 0.3%; it is relatively rich in yttrium and heavy rare earths, and does not contain any radioactive elements. The rare earths can be recovered readily from such deposits by desorption with NaCl solutions.

China has the largest (over 75%) rare earths reserves in the world. Chinese rare earth researchers founded the Chinese Rare Earth Society in the early 1980s and are publishing now a specialized journal with that title.

Russia

Rare earths were recovered in Russia mainly from the mineral loparite (Figure 8.17.35), a complex oxide of titanium, niobium, and tantalum containing rare earths (Tables 8.17.5 and 8.17.6) discovered in Kola Pen-

insula in 1925. However, after the discovery of the rare earth containing phosphate deposits, also in Kola Peninsula, the rare earths were recovered from this source as a by-product of the phosphatic fertilizer industry using the HNO_3 route. The greater part of rare earths, however, are lost in the gypsum when the apatite is treated with H_2SO_4 . About 1.5 million tons of apatite containing about 1% rare earth oxides is treated per year by HNO_3 .



Figure 8.17.35 - Museum sample of loparite.

The term originates from the word Lopor, the Russian name for the indigenous inhabitants of the Kola peninsula.

Table 8.17.5 - Analysis of loparite concentrates used in the production of rare earths in Russia

	%
R_2O_3^*	32.29
TiO_2	39.24
$\text{Nb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$	11.48
ThO_2	0.67
Na_2O	9.06
K_2O	0.75
CaO	5.26
SrO	0.62
SiO_2	0.27
	99.64

* Rare earth oxides

Table 8.17.6 - Rare earths content in loparite

	%
La	25
Ce	53
Pr	6
Nd	14
Sm	0.9
Eu	0.08
Gd	0.56
Tb	0.37
Dy	0.12
Ho	0.08
Er	0.016
Tm	0.003
Yb	0.008
Lu	0.002
Y	0.008

Brazil

Brazilian monazite sand deposits near Santos, Province of São Paulo is of historical interest because it was the rare earths from these areas that the first large-scale production of the Auer gas mantles were produced. When the Brazilian government realized the importance of these sands, export was prohibited. A plant in the city of São Paulo was constructed in 1949 by Nuclemon Minero Quimica, a state-owned company, to treat the sand for the recovery of its various fractions (zircon, magnetite, rutile, etc.) as well as the production of the individual rare earths oxides by ion exchange. The monazite concentrate was attacked by NaOH because Brazil imports most of its sulfur requirement to make H_2SO_4 . The plant, however, was shut down in the late 1990's because environmental problems, being located in the center of an inhabited area.

Large deposits of complex minerals containing rare earths as well as pyrochlore, apatite, and other minerals were discovered in Araxá in the Province of Minas Gerais. Also, a pilot plant using solvent extraction is in operation (1992) at the Mineral Research Center (CETEM) in Rio de Janeiro.

RE AS SECONDARY COMPONENT

Rare earths occur as a secondary component in a large variety of minerals, mainly in isomorphous substitution for Ca^{2+} because the ionic radii are nearly identical. The major occurrence is in apatite. During the period 1965 to 1972 an industrial process was in operation in Finland for the recovery of the rare earths from Kola phosphate which contained about 1% rare earth oxides, during the production of phosphatic fertilizers

MODERN METHODS OF RECOVERY

The isolation of groups of rare earth elements or of individual elements requires costly separation processes owing to the great similarity of the chemical and physical properties of their compounds, which explains why the history of their discovery has extended over such a long period. The major raw material for rare earths is monazite sand, xenotime, bastnasite, and phosphate rock

Monazite and xenotime

Monazite derives its name from Greek meaning to be alone. The mineral monazite is a lanthanide phosphate containing some thorium and small amounts of uranium. It is widely distributed in the Earth's crust. It occurs in small proportions in granites. When such rocks are weathered, grains of monazite are carried by waters, then deposited at the mouths of rivers, together with the heavier constituents of the parent rock, to form black sands known as monazite sand. The monazite in these sands is usually present in rounded grains, showing that the grains have previously been rolled to and fro in streams of water. Monazite sands occur mainly in Brazil, India, Australia, and USA. Xenotime is also a lanthanide phosphate but the individual lanthanides occur in a different proportion from that in monazite. It occurs mainly in South East Asia associated with alluvial tin deposits.

Monazite sand and xenotime can be easily concentrated from the sands by physical methods. For example, monazite sand containing 1 % monazite can be concentrated by gravity, magnetic, and electrostatic methods to a concentrate containing 85 % monazite (Figure 8.17.36).

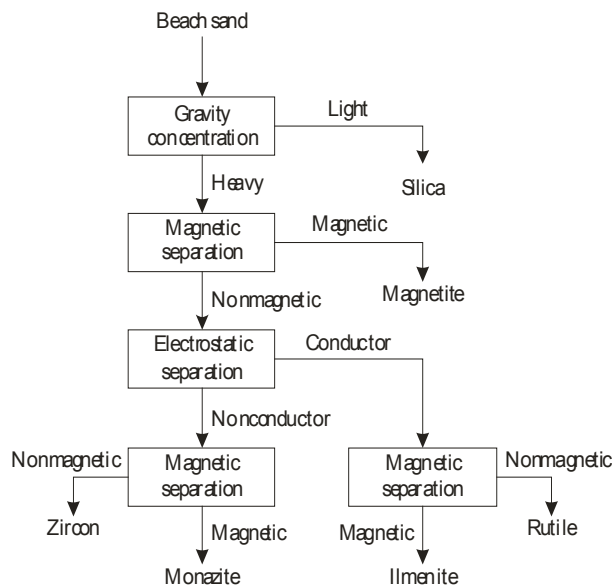


Figure 8.17.36 - Separation of the components of monazite sand

Some physical properties of monazite and xenotime concentrates are given in Table 8.17.7. A chemical analysis of the concentrates is given in Table 8.17.8. The composition of the lanthanide fraction in monazite, in xenotime, and bastnasite is given in Table 8.17.8. Monazite and xenotime are the main source of thorium and the lanthanides; uranium is recovered as a by-product.

Table 8.17.7 - Physical properties of monazite and xenotime

	Monazite	Xenotime
Color	Yellow to red brown	Pale yellow to brownish green
Specific gravity	4.9–5.5	4.5–4.6
Hardness (Mohs)	5	4.5
Crystal structure	Monoclinic	Tetragonal

Table 8.17.8 - Chemical analysis of lanthanide phosphate concentrates.

	Monazite concentrate, %	Xenotime concentrate, %
P_2O_5	24–29	
Ln_2O_3 *	55–65	52–63
ThO_2	5–10	1–3
U_3O_8	0.2–0.4	0.5–3.5
SiO_2	1–3	
CaO	0.2–0.8	
Fe_2O_3	1–2	
Al_2O_3	0.1–0.8	
ZrO_2	0.7	2–3
SnO_2	—	0–9

*Ln = Lanthanide.

Bastnasite

The most important mined rare earth deposit is at the Mountain Pass Mine in California, where up to 40 000 t/a bastnasite ore concentrate (70 % REO) is produced by ore beneficiation. Other important bastnasite deposits are in Burundi, Madagascar, and in Bayan Obo, near the town of Baotou in Inner Mongolia in China. The bastnasite, with monazite, is associated with magnetite–hematite–fluorspar. Bastnasite is a fluorocarbonate, $Ln_2(CO_3)_3$, LnF_3 , or $LnFCO_3$. A museum sample of bastnasite is shown in Figure 8.17.37.



Figure 8.17.37 - Museum sample of bastnasite.

Table 8.17.9 - Typical composition of lanthanides in monazite, xenotime, and bastnasite.

	Lanthanide oxide	Monazite %		Xenotime %		Bastnasite %	
Light	La ₂ O ₃	23.0	}	0.5	}	32.0	}
	CeO ₂	46.5		5.0		49.0	
	Pr ₆ O ₁₁	5.1		0.7		4.4	
	Nd ₂ O ₃	18.4		2.2		13.5	
Heavy	Sm ₂ O ₃	2.3	}	1.9	}	0.5	}
	Eu ₂ O ₃	0.07		0.2		0.1	
	Gd ₂ O ₃	1.7		4.0		0.3	
	Tb ₄ O ₇	0.16		1.0		0.01	
	Dy ₂ O ₃	0.52		8.7		0.03	
	Ho ₂ O ₃	0.09		2.1		0.01	
	Er ₂ O ₃	0.13		5.4		0.01	
	Tm ₂ O ₃	0.013		0.9		0.2	
	Yb ₂ O ₃	0.061		6.2		0.01	
	Lu ₂ O ₃			0.4		0.1	
	Y ₂ O ₃			60.8		0.1	

Other complex minerals

Minerals of this type are oxidic ores containing titanium, niobium, tantalum, uranium, and thorium; for example:

- Euxenite $(Y,Ce)(Nb,Ta,Ti)_2O_6$
- Samarskite $(Y,Ce)_4(Nb,Ta,Ti)_2O_6$
- Fergussonite $(Y)(Nb,Ti,Ta)O_4$
- Betafite $(U,Ca,Y,Ce,(Nb,Ta,Ti),O)_6(OH)$

Phosphate rock

Tonnage wise, phosphate rock is the most important as compared with the other material; about 120 million tons of rock are treated annually while only 30 000 tons of monazite and xenotime. However, no production of

rare earths from this source is actually conducted. Apatite is the principal constituent of phosphate rock. The mineral received its name from the Greek word meaning *I deceive* when it was realized that it was frequently confused with other mineral species, including beryl and tourmaline, prior to the latter part of the eighteenth century. Phosphate rock is the main raw material for the production of phosphatic fertilizers. Phosphate rock is composed mainly of:

- Fluorapatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$
- Hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$
- Carbonato-apatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{CO}_3$

Depending on the proportion of each component, the rock may be frankolite, kunskite, or colophanite (Table 8.17.10). Low-grade phosphate rock, may contain appreciable amounts of aluminum phosphate wavellite, AlPO_4 , and/or calcium–aluminum phosphate, crandallite.

Phosphate rock occurs either as a sedimentary deposit, e.g., in Florida and North Africa, or as igneous rock, e.g., in Kola peninsula, Russia. Sedimentary phosphates supply about 85% of the phosphate rock for the industry. Typical analyses of phosphate rocks are given in Table 8.17.11. Phosphate rock is used for the manufacture of fertilizers and elemental phosphorus. Pure phosphoric acid for other uses than fertilizers is prepared from the latter product although attempts are being made to prepare a moderate-grade phosphoric acid by leaching the rock.

Table 8.17.10 - Main types of phosphate rock.

Type	Composition
Frankolite	Isomorphous mixture of fluoroapatite and carbonate apatite in the ratio 3:1.
Kunskite	Isomorphous mixture of fluoroapatite and carbonate apatite in the ratio 2:1.
Colophanite	An ultra microcrystalline variety of frankolite.

Table 8.17.11 - Analysis of typical phosphate rock.

	%		%
P ₂ O ₅	29–38	Cl	0.01–0.7
CaO	48–52	CO ₂	2–6
MgO	0.2–0.8	SO ₃	1–3
Fe ₂ O ₃	0.2–1	SiO ₂	0.2–5
Al ₂ O ₃	0.1–1	Organic carbon	0–0.4
Na ₂ O	1–2	Uranium	0.01–0.02
K ₂ O	0.1–0.4	Ln ₂ O ₃	0.1–1
F	3.3–4.3		

RECOVERY METHODS

The preparation of the individual rare earth metals from their ores involves beneficiation of the ore to prepare an enriched mineral concentrate by mechanical, physical, and physico-chemical methods. For example, a monazite sand containing 1% monazite can be concentrated by gravity, magnetic, and electrostatic methods to a concentrate containing 90% monazite. Bastnasite is treated differently.

Monazite and xenotime

There are two methods used for treating these concentrates: the sulfuric acid and the sodium hydroxide methods (Figure 8.17.36). The decision between one or the other is an economic one; for example in Brazil, the NaOH process is used because of a shortage in sulfuric acid. However, the general tendency today is to use the NaOH process.

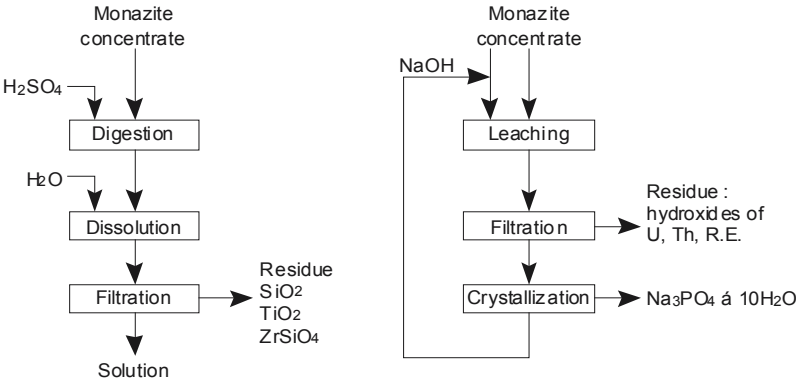
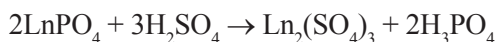


Figure 8.17.36 - Leaching methods for monazite sand.

Sulfuric acid method

This method involves two steps:

- *Digestion.* The concentrate is digested in a closed reactor or baked in a rotary kiln with 93% H_2SO_4 at about 200°C for 2–4 hours at an acid to concentrate ratio of 2:1. An acid-to-concentrate ratio lower than this, results in incomplete reaction while higher ratio interferes with subsequent operations. Also, with temperatures lower than the above, the reaction will be too slow, and if higher than 300°C , insoluble thorium pyrophosphate is liable to be formed. The reaction is exothermic and can be represented by the equation:



Thorium and uranium are also transformed into sulfates. Due to the high temperature used the product is a thick paste of anhydrous sulfates.

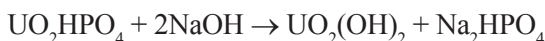
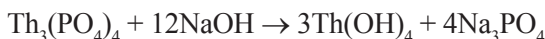
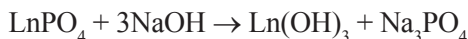
- *Dissolution of the reaction mass.* The resulting mass is allowed to cool, diluted with water to allow the insoluble material to settle, and then filtered. Typical analysis of the filtrate is shown in Table 6. The clear leach solution is then subjected to further treatment to separate thorium, uranium, and the lanthanides. The residue contains most of the radioactive decay products of uranium and thorium.

Table 6 - Typical analysis of monazite leach solution, pH = 0.05.

	g/L		g/L
Th	5.3	Nd_2O_3	7.0
U	0.2	Sm_2O_3	1.3
Ce_2O_3	16.0	SO_4^{2-}	128.0
La_2O_3	8.5	PO_4^{3-}	26.0
Pr_2O_3	1.7		

Sodium hydroxide method

The sodium hydroxide process differs from the acid process in that water-soluble phosphates are formed while the lanthanides, thorium, and uranium form insoluble hydroxides:



Optimum conditions of digestion are 40–50 % NaOH, 160°C, NaOH to concentrate 2:1, time of reaction about 3 hours. Sodium hydroxide should be free from carbonate otherwise uranium will be lost in solution, since it forms soluble carbonates. The product is a thick paste; it is slurried in water then filtered, washed, and dried. The cake obtained is composed of hydroxides of uranium, thorium, and lanthanides, containing small amounts of phosphate; it is dissolved in acid for further separation. The leach solution contains the unreacted NaOH as well as the phosphorus originally present in the concentrate. When allowed to cool to about 60°C, trisodium phosphate hydrate hydrate ($\text{Na}_3\text{PO}_4 \cdot 10\text{H}_2\text{O}$) crystallizes out. After separation, the solution typically analyse 47.4 % NaOH, 0.5 % Na_3PO_4 , 1.5 % Na_2SiO_3 , and can be recycled.

Bastnasite

In the Molycorp process, the mineral is concentrated to 60 % by flotation and then calcined, converting the cerium to the tetravalent state. It is then treated with hydrochloric acid, which causes only the trivalent rare earth elements to go into solution, leaving behind 65–80 % CeO_2 (Figure 8.17.37). The individual earths are then separated by solvent extraction (see later).

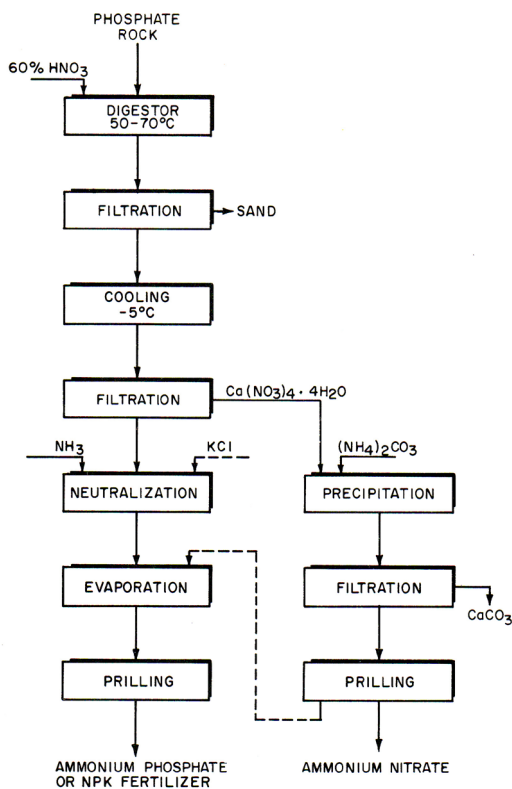
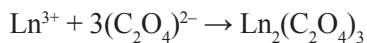
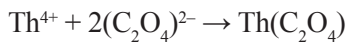


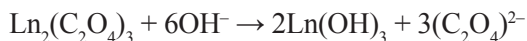
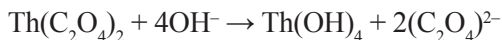
Figure 8.17.38 - Treatment of phosphate rock with nitric acid

RECOVERY FROM LEACH SOLUTION

Separation of thorium and the lanthanides from sulfuric acid leach solution of monazite and xenotime concentrates is based on oxalate precipitation:



Uranium is not precipitated. The oxalate filter cake is then digested with NaOH solution to convert the oxalates into hydroxides and recover sodium oxalate for recycle:



The hydroxides are then calcined, and the resulting oxides dissolved in nitric acid for later separation of thorium by solvent extraction.

Ion exchange

When the acid leach solution containing the lanthanides is allowed to flow through a cation exchange resin bed in hydrogen or ammonium form, they will be sorbed by the resin. However, the resin has no selectivity for one of the lanthanides as compared with the other, and therefore practically no separation can be achieved. In order to separate the different metals, use is made of their different affinities toward complexing agents in solution. When a buffered solution of some negative ion species, which forms a stable complex with the lanthanides, is passed through the column, a competition for the lanthanide ions between the aqueous phase and resin phase will be set up. When equilibrium conditions are maintained, an individual lanthanide ion continuously exchanges between the complexing ion and the resin. The positive ion in the complexing solution replaces the lanthanide ions at the rear edge of the band, so that the lanthanide band is driven down the resin bed. Because the stability constants of the lanthanide complexes differ appreciably from one lanthanide to another, the most stable complex moves faster down the column.

Different complexing agents were used as eluants for example, 5 % citric acid adjusted at pH 3 by ammonium hydroxide, 0.1 % citric acid adjusted at pH 5–8 by ammonium hydroxide, 1 M lactate at pH 3, and 0.26 M ethylene diamine tetraacetic acid (EDTA) at pH 3.6. Uniform rate of elution has been obtained by continuously varying the pH of the eluant. The eluant at pH 3.19 was neutralized at a predetermined rate with 1 M lactic acid buffered with ammonia to pH 7 to give a rate of change of pH of +0.1 unit/hour.

In the separation of the lanthanides, the concentrate is dissolved in hydrochloric acid and diluted with water to make up the feed solution for the

cation exchange columns 1.5 m long x 15 cm diameter in the ammonium form. The solution of the chlorides is loaded on four columns which are connected together in series. The sorbed band is first washed with distilled water then eluted with 0.1 % citrate solution at pH 8 at a flow rate of 0.1–1.2 L/min into a series of six similar columns. Under these conditions, the front of the adsorbed band advances at the rate of about one resin bed per day.

The light lanthanides are sorbed on the first two columns, and the heavy lanthanides are concentrated on the last two columns, while the bulk of yttrium and a considerable portion of terbium and dysprosium are concentrated on the two middle columns. Each set of two columns is further fractionated by elution through a series of eight smaller columns (1.5 m long x 10 cm diameter) at a much smaller flow rate of 0.5 L/min. Each of these small columns is loaded with a pure metal then separately eluted in a container. The pure lanthanide is recovered from the solution by precipitation with oxalic acid. Individual lanthanides up to 99.99 % purity from monazite are produced on a commercial scale based on elution with EDTA (Figure 8.17.39).

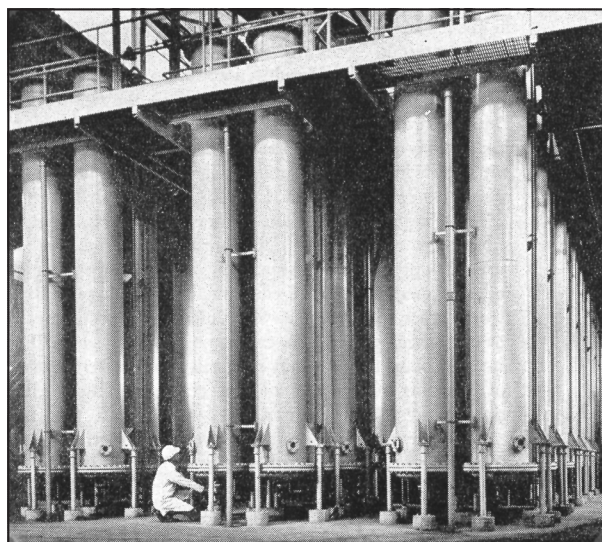
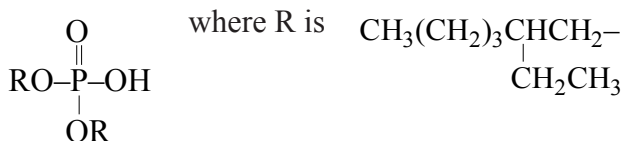


Figure 8.17.39 - Ion exchange columns for the separation of the lanthanides at Michigan Chemical Corporation, St. Louis, Michigan.

Solvent extraction

The solvent used for the separation of the lanthanides from leach solution of bastnasite concentrates is di (2-ethylhexyl) phosphoric acid known as D2EHPA:



Cerium is already separated in the leaching step since it is transformed into soluble cerium(IV) compound and is recovered from the residue. Each extraction step includes numerous stages of contact with the extractant and the stripping agent under certain conditions of organic/aqueous ratio, and extractant and stripping agent concentrations. The plant is computerized and is fully automated (Figure 8.17.40).

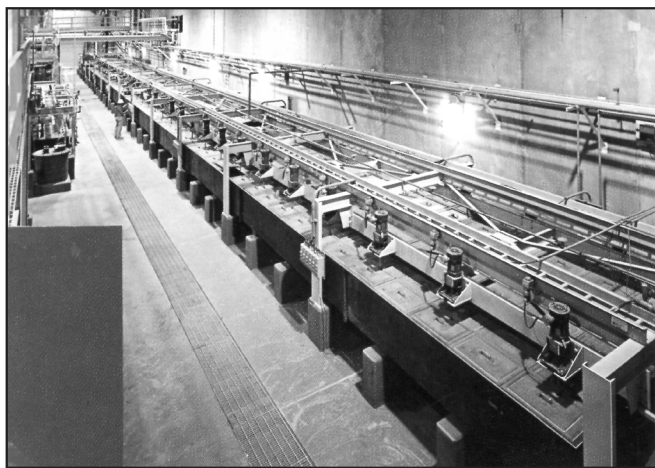


Figure 8.17.40 - Inside of Molycorp's rare earths extraction plant at Mountain Pass, California.

Cerium salts are produced by liquid–liquid extraction from rare-earth cerium-containing solutions. Cerium can be extracted out of cerium nitrate–nitric acid solutions in a few steps in the form of a cerium(IV)

nitrate complex in tributyl phosphate and therefore separated from the accompanying trivalent rare-earth elements, which form less stable nitrate complexes. Purities of 99.99% and better can be achieved.

METAL PRODUCTION

Mischmetall

Mischmetall (German: mixed metals) is an alloy of rare earth elements in various naturally-occurring proportions. Monazite-derived Mischmetall typically is about 48% cerium, 25% lanthanum, 17% neodymium, and 5% praseodymium, with the balance being the other lanthanides. Bastnaesite-derived Mischmetall is higher in lanthanum and lower in neodymium.

Mischmetall is the lowest priced rare-earth metal because no expensive chemical separation is needed to produce it. It is produced predominantly by fused-salt electrolysis of rare-earth chlorides. Mischmetall was first produced industrially in 1908 by Auer von Welsbach, who succeeded in finding an outlet for surplus rare earth in the production of lighter flints. At that time, monazite was used exclusively as the source of thorium needed for the manufacture of incandescent mantles.

Oxide Process

A process developed by the US Bureau of Mines and further improved by Santoku Metal Industries in Japan, produces mischmetal from rare-earth oxides. The process is similar to Hall–Héroult process for aluminum electrolysis. It avoids emission of chlorine and the consequent expensive purification of off-gas. Rare-earth oxides are dissolved in an electrolyte consisting of alkali fluorides (to improve conductivity), alkaline-earth fluorides (to reduce melting point), and rare-earth fluorides (to improve the solubility of rare-earth oxides) and are reduced electrolytically to the rare-earth metals.

The electrolysis cell (Figure 8.17.41) consists of a graphite crucible with graphite anode and molybdenum cathode, working under an inert-gas atmosphere to prevent oxidation of the construction materials. The electrolyte is initially melted by resistance heating. Electrolyte and electrodeposited rare-earth metals are kept liquid by the joule heat. A cell produces ca. 500 kg of metal per day. If bastnasite is a raw material, it must be specially purified prior to electrolysis.

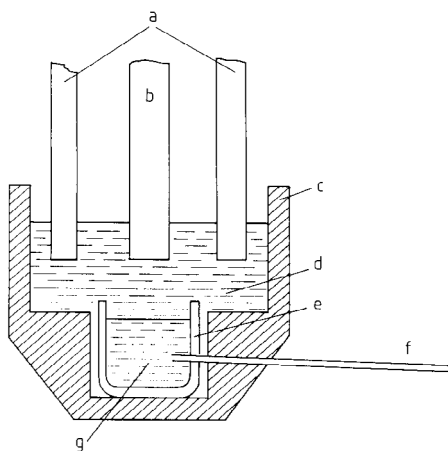


Figure 8.17.41 - Electrolysis cell for the production of misch-metal from oxides:
a) Graphite anodes, b) Molybdenum cathode, c) Graphite crucible, d) Liquid electrolyte, e) Molybdenum crucible, f) Tapping pipe, g) Molten misch-metal

Individual rare earth metals

The rare earth metals are produced, both on the laboratory and industrial scale, by molten salt electrolysis and metallothermic reduction

Fused-salt electrolysis

La, Ce, Pr, Nd can be produced by molten salt electrolysis of a mixture of anhydrous rare earth chlorides and fluorides with alkali and alkaline earth chlorides and fluorides. This process is made possible by the lower melting points of the cerium earth metals, whereas the yttrium earth metals have higher melting points and therefore do not melt during the electrolysis process. A lower melting point can be achieved by using a

cathode (e.g., Cd, Zn) that forms a low-melting alloy with the rare earth metal. This alloy can also have a lower density than the fused salt (e.g., Mg), so that it rises to the surface and can be removed from the fused salt. The alloying element can then be removed by distillation. By using molten Cd or Zn as cathode, Sm, Eu, and Yb can also be produced.

The reactivity of the rare earth metals causes problems in the choice of construction materials of the electrolysis furnace. High-purity metals can be produced by using molybdenum, tungsten, or tantalum as the crucible and cathode materials. For industrial manufacture, iron crucibles with ceramic or graphite linings are used. If halogens are liberated during the electrolysis, carbon is used as the anode material.

Metallothermic reduction

Metallothermic reduction of the rare earth oxides and anhydrous rare earth chlorides and fluorides can be used to produce high-purity rare earth metals, especially Gd to Lu, including Y. Alloys can also be produced by this process. Alkali metals, alkaline earth metals, and aluminum are suitable reducing agents, as are alloys of these elements with each other. Lithium, which forms low-melting LiF, is of special importance, as is calcium. The use of Mg or Zn has the additional advantage of producing a low-melting alloy with the rare earth metal. The alloying elements can be removed by distillation, yielding the pure rare earth metal.

For the production of La, Ce, Pr, and Nd, the metallothermic reduction of the anhydrous rare earth chlorides is preferred. The reaction is carried out in crucibles lined with MgO at temperatures up to 1100°C. At higher temperatures, reaction takes place between the rare earth metal and the MgO, and the rare earth chlorides vaporize. The process is not suitable for the production of Sm, Eu and Yb, which are merely reduced to the divalent state.

Gd to Lu and Sc, which have higher melting points, are obtained by reduction of the fluorides with Ca at 1500–1600°C. The reduction is carried out in tantalum crucibles under a protective gas or in vacuum. The

reaction temperature can be reduced by adding a booster such as iodine, which gives a slag with good flow properties that separates cleanly from the metal. Praseodymium is produced by reduction of the fluoride with lithium. The Carlson–Schmidt apparatus is shown in Figure 8.17.42. This was used between 1957 and 1959 to produce high-purity yttrium metal in 50 kg batches.

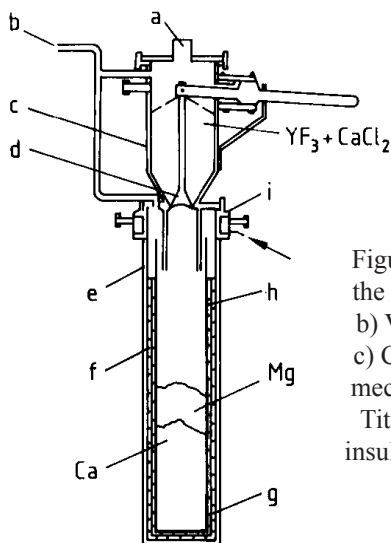


Figure 8.17.42 - Reduction apparatus for the production of yttrium: a) Sight glass, b) Vacuum connection and helium inlet, c) Charging tunnel, d) Charging shut-off mechanism, e) Steel reaction chamber, f) Titanium reaction crucible, g) Graphite insulation, h) Titanium or steel supporting crucible, i) Water cooling

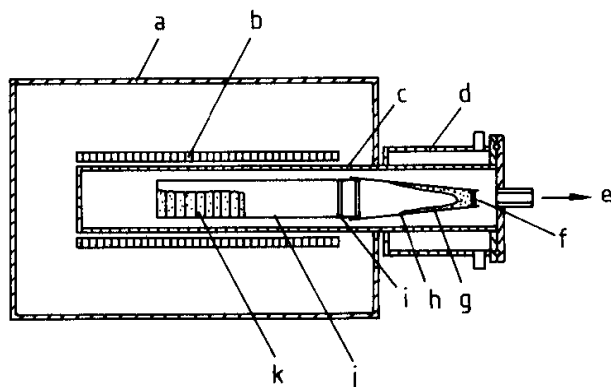


Figure 8.17.43 - Reduction–distillation apparatus for the production of samarium, europium, and yttrium: a) Furnace, b) Heating element, c) Stainless steel container, d) Water cooling, e) Vacuum, f) Baffle, g) RE metal, h) Molybdenum condenser, i) Heat shield, j) Molybdenum crucible, k) Pelletized reactants

Sm, Eu, and Yb can be produced by reduction of the oxides with La or the cheaper cerium mischmetall at 1000–1300°C. The rare earth oxides and the reducing metal are used in the form of pellets, prepared from chippings or thin disks. Sm, Eu, and Yb are volatile at the reaction temperature under vacuum ($< 10^{-4}$ bar), and can be distilled from the reaction space during the reaction and condensed on coolers. Thus, these metals can be separated from rare earth metals that are not volatile under these conditions and obtained in a pure state. Hence, the starting materials can consist of rare earth oxides in which Sm, Eu, and Yb have merely been concentrated. The principle of the reduction distillation apparatus is illustrated in Figure 8.17.43. Further purification can be carried out by a second distillation.

Purification

Production of the pure rare earth metals necessitates the removal of products of the reaction of the metals with the atmosphere, crucible materials, and co-reactants. Suitable methods include melting under a protective gas or in a vacuum. The high-boiling rare earth metals can also be purified by distillation. Alloying elements and impurities such as Mg, Cd, Zn, and Ca are distilled off under vacuum. The remaining rare earth metal is then in the form of a sponge, which can be consolidated by fusion in an electric arc furnace. Zone melting, melt extraction, and melt filtration, e.g., through tungsten powder, degassing in a high vacuum, etc., are other recommended purification methods.

USES

The most important uses of mischmetall or cerium are metallurgical. The metallurgical importance of rare-earth metals is based on reactions to form solids with oxygen, hydrogen, nitrogen, sulfur, arsenic, bismuth, and antimony, reducing the effects of these elements on the properties of the metals. Mischmetall is added as lumps, rods, or wire. The principal uses for cerium compounds are as polishing agents and as a component in

glass. The rare earth metals and their compounds are used in numerous areas of industry for a wide range of purposes. The most important of these include metallurgy, catalysts in the chemical industry, coloring of glass and ceramics, the production of magnets, and phosphors.

CARL AUER'S LEGACY

The industrialization of the rare earths started in Austria by Carl Auer von Welsbach and this was possible only because of the discovery of large economic deposits of monazite sand in Brazil in the same year. Carl Auer became a wealthy industrialist. His palace at Althofen about 13 km east of Klagenfurt in Carinthia is now a museum documenting the story of his inventions (Figure 8.17.44).



Figure 8.17.44 - Carl Auer Museum at Althofen in Carinthia, Austria

A memorial plaque (Figure 8.17.45) in honour of Carl Auer was installed in a lecture hall of the Department of Chemistry at the University of

Vienna, and a monument named “Plus Lucis”, i.e., more light commemorating his achievements was later erected near Auer’s laboratory (Figure 8.17.46-8.17.47). On his 100th anniversary in 1958 the Austrian Chemical Society celebrated this event by awarding Frank H. Spedding from Iowa University in USA the Auer Gold Medal during the Annual Meeting of the society. The Austrian National Bank issued a 20 schilling paper money bearing the picture of Carl Auer (Figure 8.17.48).



Figure 8.17.45 - A memorial plaque



Figure 8.17.46 - Monument named “Plus Lucis”, i.e., more light commemorating his achievements was later erected near Auer’s laboratory



Figure 8.17.48 - A 20-Schilling bill with Carl Auer’s portrait



Figure 8.17.47 - Details of the monument “Plus Lucis” commemorating Auer’s achievements

Carl Auer was honoured by his country on a 20-Schilling bill, a 25 Schilling silver commemorative coin with his portrait, and two postage stamps (Figures 8.17.49-8.17.50).



Figure 8.17.49 - A commemorative 25-Schilling silver coin with Carl Auer’s portrait



Figure 8.17.50 - Austrian stamps honouring Carl Auer

EPILOGUE

Minerals containing the rare earths were first discovered in Sweden in 1751 and it was there that most of the identification and separation of the individual metals took place. Two factors contributed to this effort: the discovery of spectroscopic analysis in 1859 and the discovery of the Periodic Table in 1869. In this connection Heidelberg and Paris became two centres for spectroscopic analysis.

The connection between the Swedish investigations and the Austrian industrial applications was in Heidelberg where the Swedish chemist Jons Fridrik Bahr took some rare earth minerals to Bunsen to examine them by his newly invented spectroscope. When the Austrian chemist Carl Auer went to study under Bunsen, few years later, he took with him some Swedish rare earth minerals from the Heidelberg laboratory on his return to Austria.

In Vienna, Carl Auer invented and industrialized the gas mantle for lighting purposes which was the first industrial application of the rare earths. The gas mantle for lighting purposes was abandoned a few years later, being replaced by the electric bulb. However, it is still used today in gasoline and propane camp lanterns. He also invented the cigarette lighter. Today the rare earths find wide application in modern industry.

APPENDIX

Properties of rare earth metals

Element		Melting point, °C	Boiling point, °C	Density, g/cm ³
Scandium	Sc	1540	2832	2.989
Yttrium	Y	1525	3337	4.469
Lanthanum	La	920	3457	6.145
Cerium	Ce	798	3427	6.770
Praseodymium	Pr	931	3512	6.773
Neodymium	Nd	1016	3067	7.007
Promethium	Pm	1042	(3000)	7.26
Samarium	Sm	1073	1791	7.536
Europium	Eu	822	1597	5.243
Gadolinium	Gd	1312	3267	7.900
Terbium	Tb	1357	3222	8.229
Dysprosium	Dy	1409	2562	8.550
Holmium	Ho	1470	2695	8.795
Erbium	Er	1522	2862	9.066
Thulium	Tm	1545	1927	9.321
Ytterbium	Yb	816	1194	6.965
Lutetium	Lu	1663	3397	9.840

8.18 Scandium¹

Introduction	933	Extraction from bauxite	938
Occurrence	935	Extraction from laterites	938
Recovery	936	Extraction from ilmenite	938
Extraction from uranium ores	937	Preparation of metallic scandium	939
Extraction from wolframite	937	Applications	939

INTRODUCTION

When the Russian chemist Dmitri Ivanovich Mendeleev (1834-1907) proposed the Periodic Table in 1869 he predicted the existence of eka-boron, which would have an atomic weight between 40 of calcium and 48 of titanium. The element was discovered by Swedish chemist Lars Fredrik Nilson (1840-1899) (Figure 8.18.1) in 1878 by spectroscopic analysis of the minerals euxenite and gadolinite, which had not yet been found anywhere except in Scandinavia.



Figure 8.18.1 - Lars Fredrik Nilson (1840-1899)



Figure 8.18.2 - Per Teodor Cleve (1840-1905)

¹ Based on F. Habashi, "Scandium," *Metall* **62** (12), 814–816 (2008).
See also Rare Earths

By processing 10 kg of euxenite and other residues of rare-earth minerals, Nilson was able to prepare about 2 g of the oxide of the new metal in high purity and called the metal scandium in honour of his fatherland. It was another Swedish chemist Per Teodor Cleve (1840-1905) (Figure 8.18.2) who later pointed out that Nilson's scandium was identical with Mendeleev's eka-boron. The emission spectrum of scandium is shown in Figure 8.18.3.



Figure 8.18.3 - Emission spectrum of scandium

Scandium has a unique position in the modern Periodic Table. (Figure 8.18.4). It is a transition metal like yttrium and lanthanum, however it resembles aluminum more than it resembles the other transition metals. For example, it has a single valency like aluminum while the transition metals have multiple valencies. All its compounds are colorless like yttrium, lanthanum, and aluminum thus not resembling the transition metals which all have colored ions in solution. Mendeleev successfully predicted the properties of scandium by linking it with aluminum. Although scandium has two electrons in the outermost shell and one would expect that it would form divalent compounds, yet its most common valency state is three resembling aluminum.

Li 2 1	Be 2 2		
Na 2 8 1	Mg 2 8 2	Al 2 8 3	
K 2 8 8 1	Ca 2 8 8 2	Sc 2 8 9 2	Ti 2 8 10 2
Rb 2 8 18 8 1	Sr 2 8 18 8 2	Y 2 8 18 9 2	Zr 2 8 18 10 2
Cs 2 8 18 18 8 1	Ba 2 8 18 18 8 2	La [†] 2 8 18 18 9 2	Hf [†] 2 8 18 32 10 2

Figure 8.18.4 - A portion of the Periodic Table showing the position of scandium

Scandium is usually associated with the lanthanides and the metal has hexagonal structure like the yttrium, lanthanum, and the lanthanides. On the other hand aluminum has face-centered cubic structure. Scandium

forms an insoluble hydroxide, fluoride, or oxalate under proper conditions, similar to the rare earths.

OCCURRENCE

Scandium is widespread in nature but in small concentrations; its relative abundance is $5 \times 10^{-4} \%$ like the lanthanides. It occurs in association of with the lanthanides, with uranium ores, in laterites, in bauxite, in wolframite, and in ilmenite. Thortveitite, euxenite, and gadolinite are the only known concentrated sources of this element. The present main source of scandium metal is from the military stockpiles of the former Soviet Union (mainly in Ukraine), which were themselves extracted from uranium tailings. Scandium was also extracted in the former Soviet Union from ilmenite. It is believed however that all these operations are no longer functioning. Scandium ion, Sc^{3+} , has ionic radius close to that of Fe^{2+} , Mg^{2+} , Ti^{4+} , and Zr^{4+} thus isomorphism is possible. The only naturally occurring isotope of scandium is ^{45}Sc .

- *Thortveitite*. In 1911, Schetelig, in Norway, discovered a silicate mineral, that he called thortveitite, contained 30 to 40% of Sc_2O_3 . This mineral was also found later, in Madagascar. It has the composition $(\text{Sc},\text{Y})_2\text{Si}_2\text{O}_7$.
- *Bazzite*. $\text{Be}_3(\text{Sc},\text{Al})_2\text{Si}_6\text{O}_{18}$ is another silicate mineral containing scandium discovered in 1915.
- *Euxenite*. $(\text{Y},\text{Ca},\text{Ce},\text{U},\text{Th})(\text{Nb},\text{Ta},\text{Ti})_2\text{O}_6$ occurs in granite pegmatites and detrital black sands. It is commonly partially amorphous due to radiation damage. It was first described in 1870 and named from the Greek word meaning hospitable or friendly to strangers, in allusion to the many rare elements that it contains. It is found in many locations worldwide, notably its type locality in Jølster, Sunnfjord, Norway. Other locations include the Ural Mountains, Sweden, Minas Gerais in Brazil, Ampangabe in Madagascar. Ontario, Canada; and in Arizona, Wyoming and Colorado in the USA.

• *Gadolinite*. $(\text{Ce}, \text{La}, \text{Nd}, \text{Y})_2\text{FeBe}_2\text{Si}_2\text{O}_{10}$ is a silicate mineral nearly black in color with vitreous luster. Gadolinite was named in 1800 in honor of Johan Gadolin, the Finnish mineralogist - chemist who first isolated an oxide of the rare earth element yttrium from the mineral in 1792. However, gadolinite does not contain more than trace amounts of gadolinium.

RECOVERY

Scandium is present in all rare earth minerals, although only in trace amounts. Because it has similar chemical properties to the other rare earth elements, it cannot be obtained by selective precipitation as the oxalate or a double salt. The most effective separation is by solvent extraction, scandium behaving quite differently from the other rare earth metals. For example, it is readily extracted by diethyl ether from thiocyanate solution. Tributylphosphate (Figure 8.18.5), known as TBP is an effective extractant from chloride solutions, while the other rare earth elements are hardly extracted. Organo-phosphoric acids such as diethylhexyl phosphoric acid (Figure 8.18.6), known as D2-EHPA are much more effective extractants for scandium than for the other rare earth elements.

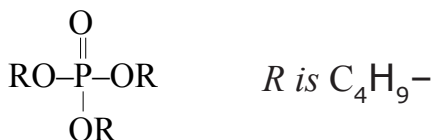


Figure 8.18.5 – Tributyl phosphate

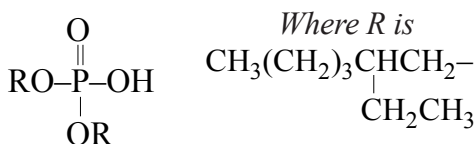


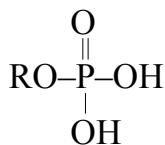
Figure 8.18.6 - Di (2-ethylhexyl) phosphoric acid

Scandium is not recovered from rare earth minerals such as monazite or bastnasite but it recovered mainly as a by-product from two main sources:

- Uranium ores in Canada and USA
- Uranium and ilmenite processing in the Former Soviet Union

Extraction from uranium ores

In 1954 traces of scandium in uranium ores of the Blind River deposit in Ontario, Canada were detected by spectrum analysis. In 1959 a unit was installed for the extraction of thorium compounds from the spent solution. This was followed in 1960 by the extraction of 0.9 kg of scandium oxide from which the metal was prepared. Discovery of scandium in the late 1950s in the Vitro solvent extraction plant for uranium in Salt Lake City, Utah led to its commercial recovery as a by-product. Micro amounts of scandium were extracted with uranium from the acid leach solution by dodecyl phosphoric acid (Figure 8.18.7), but failed to follow uranium into the hydrochloric acid strip solution and were eventually concentrated in the organic phase. A fluoride strip system was developed to recover scandium from the solvent as a cake containing 10% Sc_2O_3 and 20% ThO_2 . High purity scandium oxide was then prepared in multi-pound lots by chemical separation techniques.



Where R is (1,2-methylpropyl)-3,5-dimethyl hexyl phosphate



Figure 8.18.7 - Dodecyl phosphoric acid

Extraction from wolframite

Wolframite, $(\text{Fe,Mn})\text{WO}_4$, concentrates contain 500–800 ppm scandium. Two methods have been proposed for the recovery of scandium:

- When digested with acid, iron, manganese, and scandium go into solution while tungstic acid, H_2WO_4 , is precipitated. The solution can then be treated further to recover scandium.
- When wolframite is digested with sodium carbonate, water-soluble sodium tungstate is formed. The residue is then dissolved in hydrochloric acid and scandium is preferentially extracted by tributyl phosphate and stripped with 8 M hydrochloric acid. Scandium is then precipitated with ammonia in presence of ammonium chloride, and final purification of the scandium by TBP extraction.

Extraction from bauxite

In the production of alumina from red mud by Bayer process scandium remains in the red mud. A pilot plant was constructed which includes acid leaching of the red mud, ion-exchange separation of scandium and lanthanides from iron, and subsequent liquid-liquid extraction of the eluate for further scandium purification and enrichment.

Extraction from laterites

Scandium can be recovered from laterites during the sulfuric acid leaching process at high temperature and high pressure. It will dissolve together with nickel but will not be precipitated by hydrogen sulfide like nickel. By adjusting the pH of the solution after separating the nickel sulfide, scandium hydroxide or carbonate can then be precipitated.

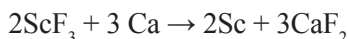
Extraction from ilmenite

A process for extracting scandium from titanium ore by feeding the

titanium ore to a fluidized bed chlorinator at about 1000°C to produce a vapors of TiCl_4 and FeCl_3 . Scandium remains in the residue and can be recovered by leaching the residue with hydrochloric acid, followed by extraction with tributyl phosphate. Scandium is then precipitation from the strip solution by an ammonium hydroxide. Scandium hydroxide is then calcined to oxide. The residue generally also contains yttrium and lanthanides, and the yttrium and lanthanides can also be recovered from the residue as a part of the scandium recovery process.

Preparation of metallic scandium

Fischer, Brunger, and Grieneisen prepared metallic scandium for the first time in 1937 by electrolysis of a eutectic melt of potassium, lithium, and scandium chlorides at a temperature of 700 to 800°C. Tungsten wires in a pool of liquid zinc were the electrodes in a graphite crucible. Pure scandium is now produced by reducing scandium fluoride with calcium metal:



The production of the first pound of 99% pure scandium metal was announced in 1960.

APPLICATIONS

The metal has little commercial importance. In 1970 pure scandium cost several thousand dollars per pound. The current price of refined scandium is in the order of US \$600 per kilogram. World production of the metal is in the order of 2,000 kg per year, generally as a by-product of uranium processing. Greater consumption would allow additional price reductions. Scandium oxide finds use as a catalyst and in making crucibles and other ceramic parts. Scandium sulfate in very dilute aqueous solution is used in agriculture as a seed treatment to improve the germination of corn, peas, wheat, and other plants.

However, the major application is expected to be as an alloying element

with aluminum since it is a light metal. Approximately 15 different commercial Al-Sc alloys have been developed in Russia, and some of them are used for aerospace applications. The Russian military aircrafts Mig 21 and Mig 29 used aluminum scandium alloys. In Europe and the U.S., scandium-containing alloys have been evaluated for use in structural parts in airplanes. The combination of high strength and light weight makes Al-Sc alloys suitable for a number of applications. However, titanium being much more common, and similar in lightness and strength, is much more widely used.

8.19

Germanium

Discovery	941	The metalloid and its compounds ..	946
Recovery	942	Uses of germanium	947
Refining	944		

DISCOVERY

In 1885, Clemens Alexander Winkler (1838-1904) (Figure 8.19.1) professor of metallurgy at the Mining Academy in Freiberg analyzed a newly discovered silver mineral called argyrodite (Figure 8.19.2) that was found in the old Himmelsfürst Mines at Saint Mickleis near Freiberg. Argyrodite gets its name from the Greek words that translate into “rich in silver”. The mineral resembled argentite (silver sulfide), yet differed from it because it contained 75% Ag and 18% S with the remaining 7% unaccounted for. After further research he concluded that the mineral contained a new metal which resembled arsenic and antimony.



Figure 8.19.1 - Clemens Alexander Winkler (1838-1904)



Figure 8.19.2- A museum sample of argyrodite

Winkler then fused a pulverized portion with sodium carbonate, took up the melt with water, and filtered off the residue, acidified it then precipitated the sulfides of arsenic and antimony by hydrogen sulfide. The new element however, did not appear in the precipitate. Adding more acid to the filtrate, resulted in the formation of a white precipitate – the sulfide of the new element. The new element, which he called “germanium” in honor of his country, was isolated by heating the dry sulfide in a current of hydrogen.

The mineral from which the new element was isolated is now known to be a double sulfide of silver and germanium, $\text{GeS}_2 \cdot 4\text{Ag}_2\text{S}$ or Ag_8GeS_6 . It is a rare mineral that its ores have already been exhausted. The properties of germanium fully agreed with those predicted by Mendeleev in 1871 for eka-silicon.

In 1920 a complex copper germanium sulfide mineral was discovered in the Tsumeb Mine, Otavi in Southwest Africa. It was named germanite and became an important source of germanium. Winkler is also famous for his innovations in gas analysis, for example, the special burette known by his name.

RECOVERY

Germanium is generally found as a sulfide associated with other minerals in particular those of zinc, and is recovered as a by-product during the process of recovering the primary metal. The first major recovery of the metal was made in 1952 from the zinc ores of the Tri-State (Missouri, Oklahoma and Kansas) deposits in the USA. The zinc ores of Katanga in the Congo have also in recent years yielded significant amounts of germanium. On sintering the zinc ores, cadmium and germanium are volatilized and collect in bag houses or electrostatic precipitators, this material forming the raw material for production of the metal.

The British source of germanium is the dust found in flues of gas-producer

plants. Many British coals contain germanium of the order of 10-12 parts per million. During the process of using the coal to make producer gas, germanium in the form of oxide or sulfide passes out with the gas and on burning the gas the dust accumulates in the flues containing up to 1% Ge. A preliminary concentration is given by smelting in a small reverberatory furnace with coal dust as a reducer, soda ash and lime, slagging off the alumina and silica, copper oxide being present to collect the germanium in a regulus. This regulus containing about 4% germanium is granulated by pouring into water and then subjected to treatment with chlorine in the presence of ferric chloride. Distillation of the chloride solution in the presence of sulfuric acid results in germanium tetrachloride containing up to 15% arsenic trichloride. This forms the raw material in the production of the metal. Production in Britain was initiated in 1950 by Johnson Matthey & Company.

In 1917 G.H. Buchanan devised a process for separating germanium obtained from zinc ores based on the volatility of the tetrachloride. The crude material was heated with hydrochloric acid in a distillation flask, and the distillate treated with H_2S . The germanium compound so obtained was contaminated with arsenic. Using a fractionating column, GeCl_4 which boils at 85°C can be separated from AsCl_3 boiling at 122°C (Figure 8.19.3).

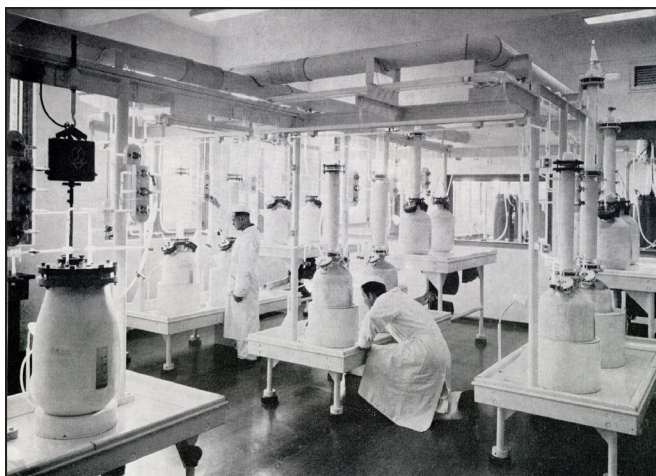


Figure 8.19.3 - Distillation room of GeCl_4

Hydrolysis of the tetrachloride with water results in the precipitation of the dioxide which is washed and dried. The reduction to metal is achieved by heating in a current of hydrogen. Reduction takes place in two stages, the dioxide being first heated to below 700°C above which temperature, the monoxide which is first formed is volatile. When water ceases to be evolved the temperature is slowly raised to 1000°C at which temperature the powder consolidates into metal.

REFINING

The metal still contained traces of such impurities as arsenic, antimony, indium, sulfur and iron, and further purification is necessary in order to achieve the high level of purity required for electronic needs. This has been achieved by zone refining introduced in 1952 by William Gardner Pfann (1917–1982) (Figure 8.19.4) of the Bell Telephone Company.



Figure 8.19.4 - William Gardner Pfann (1917–1982)

The method is based on the fact that in many metals segregation of the impurities between a molten and solid part of the material can be induced under the influence of heat, the impurities being more soluble in liquid than in solid metal. Thus, if an ingot of metal is fused for a narrow portion of its length and this zone of fusion is moved along the ingot, pure metal will concentrate to the cooling portion whilst the impurities will be carried forward in the molten portion towards one end of the bar in the direction of zone movement (Figure 8.19.5).

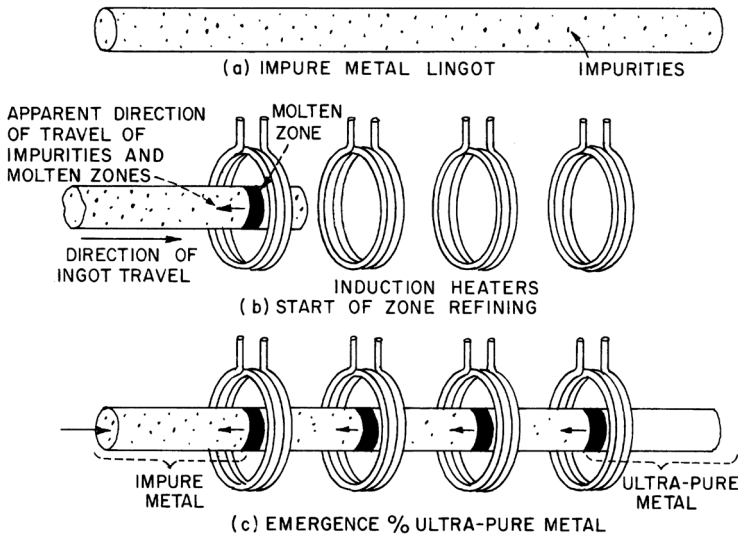


Figure 8.19.5 - Zone refining

By a repetition of this process it is possible to obtain a metal in which most of the impurity is concentrated at one end, the purity increasing with distance towards the other end.

In its application an ingot of the metal contained in a crucible of pure graphite or pure silica is placed in a long quartz tube through which is passed an inert gas such as argon. The tube is surrounded at intervals by three or four electrical induction coils which are arranged to travel together slowly from one end of the ingot to the other, so causing three or four molten zones about an inch wide to move along the ingot in one operation.

The impurities present tend to remain in the liquid metal rather than move across the liquid/solid interface at the trailing end of the zone and this results in their being swept to that end of the ingot towards which the coils are moving. The zone containing the impurities is then discarded by cutting off the end at a suitable point.

THE METALLOID AND ITS COMPOUNDS

Germanium is a hard, grayish-white element, has a metallic luster but is brittle like glass. It is classified as a metalloid having the same crystal structure as diamond. It does not form minerals but is present in the lattices of certain sulfides such as sphalerite, ZnS . It is a semiconducting element.

In 2010, the world's total production of germanium was between 100 and 120 tonnes. This comprised germanium recovered from zinc concentrates, fly ash from burning coal, and recycled material. The main producers of germanium end products are located in the United States, Belgium, France, Germany, and Japan.

Relative abundance	$7 \times 10^{-4} \%$
Density	5.3
Melting point	938.4°C
Boiling point	2833°C

Germanium is stable in air. At temperatures above 400°C in oxygen, a passivating oxide layer is formed. It resists concentrated hydrochloric and hydrofluoric acids even at their boiling points, but reacts slowly with hot sulfuric acid. It dissolves at room temperature in nitric acid to form nitrate and in alkaline media in the presence of an oxidizing agent, e.g., hydrogen peroxide to form germanates. Germanium and silicon are miscible and form a continuous range of alloys.

Germanium can have valences of two or four. The divalent compounds are less stable and oxidize easily to the tetravalent compounds, which are similar to their silicon analogs. Germanium reacts readily with halogens to form tetrahalides. Germanium tetrachloride is obtained by reaction of chlorine gas with elemental germanium and of hydrochloric acid with GeO_2 or germanates. Germanium tetrachloride is soluble in carbon tetrachloride. All the tetrahalides are readily hydrolyzed to hydrated germanium dioxide.

Germanides can be produced by melting metals with germanium and freezing the melt, e.g., Mg_2Ge . Germanes (germanium hydrides) are evolved

when germanides react with acids: mono-germane, GeH_4 , di-germane, Ge_2H_6 , and tri-germane, Ge_3H_8 , can be separated by fractional distillation. Mono-germane is similar in structure to methane is a colorless, highly inflammable, toxic gas of low stability with a characteristic unpleasant odor. Polygermanes are similar to alkanes with formula $\text{Ge}_n\text{H}_{2n+2}$ containing up to five germanium atoms are known. The germanes are less volatile and less reactive than their corresponding silicon analogues. The germanium hydrohalides with one, two, and three halogen atoms are colorless reactive liquids.

Most germanium compounds are comparatively low in toxicity because of pharmacological inertness and rapid excretion. However, some exceptions exist, the most important being germanium hydrides. Germanium tetrafluoride and tetrachloride vapors irritate the eyes and mucous membranes of the respiratory tract. Gaseous germanium hydride is the most toxic of germanium compounds when inhaled.

USES OF GERMANIUM

Research had shown in 1942 that the metalloid had semi-conducting properties. When used in conjunction with suitable electrical contacts some of the ions are free to move giving rise to a current in a particular direction, current flowing much more readily in one direction than the other. In effect the current becomes uni-directional, alternating current being rectified to direct. This is the principle of the crystal diode rectifier.

Its first industrial application was in 1947 with the development of the transistor. Until the early 1970s, it was used extensively in the solid-state electronics industry, although it has been replaced almost entirely by the cheaper silicon. The main use of metallic germanium currently is for infrared optics. Germanium tetrachloride is used in optical fiber production. Germanium dioxide is used mainly as a catalyst in the production of polyester and synthetic textile fiber.

8.20 Polonium and Radium

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INTRODUCTION

The discovery of radioactivity at the end of the 19th century opened up an entirely new era that has dominated scientific research for many decades. It started with Antoine Henri Becquerel who discovered what he called “uranic radiation” emitted from uranium salts. Then it was the Polish-born physicist Marya Skłodowska-Curie (1867–1934) (Figure 8.20.1) who found that uranium-containing minerals were more active than pure uranium salts. Marie and her husband, French physicist Pierre Curie (1859-1906) (Figure 8.20.2) discovered the increased radioactivity in uranium ore pitchblende. Their experiments led them to the conclusion that the radioactivity was coming for the most part from unknown trace radioelements in the samples not from the uranium itself.



Figure 8.20.1 - Marya Skłodowska-Curie (1867–1934)

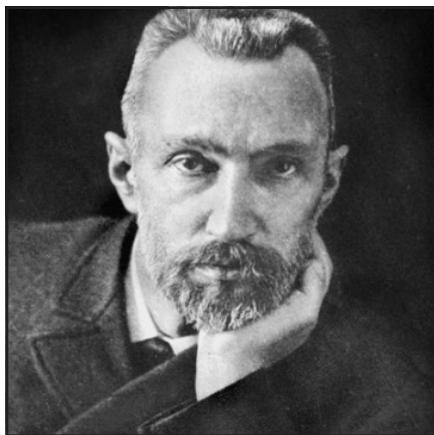


Figure 8.20.2 - Pierre Curie (1859-1906)

The first new radioelement discovered by the Curies was polonium, in July 1898. The Curies' claim for the existence of the new element was unique in chemical history at that time in that they were not able to isolate and characterize the element, as would normally be required for such a

proposal to be considered valid. Instead, the claim was based solely on the strong radioactivity of a polonium fraction isolated from pitchblende. The sample studied by the Curies likely contained only about 6 ng of polonium — far below the limits of sensitivity of the spectroscopic techniques available at that time.

In December 1898, the Curies also reported the existence of radium — in this case working with a sample that probably contained only about 30 mg of the element. Marie Curie's work to purify radium from pitchblende to determine its atomic mass and prove it was an element was later described in the book *Madame Curie* by the Curies' daughter, Ève Curie.

For their work on radioactivity, Becquerel and the Curies shared the 1903 Nobel Prize in Physics. Marie Curie later also received the 1911 Nobel Prize in Chemistry for the discovery of polonium and radium and chemical studies on radium.

Uranium and thorium are two naturally-occurring radioactive elements which spontaneously decay to give a variety of radioactive products until a non-radioactive lead isotope is reached (Figure 8.20.3). Historically, the actinium series was thought to begin by actinium but research showed that actinium itself was a decay product of the newly discovered uranium 235. In the middle of all the series, radium isotopes are formed which disintegrate to a radioactive inert gas: radon, actinon, and thoron, respectively. These decay further to a solid radioactive polonium isotopes.

POLONIUM

The discovery of polonium (Table 8.20.1) in uranium ores was possible only because of its radioactivity. The concentration in uranium ores is $7.4 \times 10^{-11} \text{ g } ^{210}\text{Po/g } ^{238}\text{U}$. There is no stable isotope of polonium and the longest-lived isotope is ^{209}Po ($t_{1/2} = 102 \text{ years}$). Polonium may enter the respiratory system of human beings as a result of inhaling radon gas generated from radium.

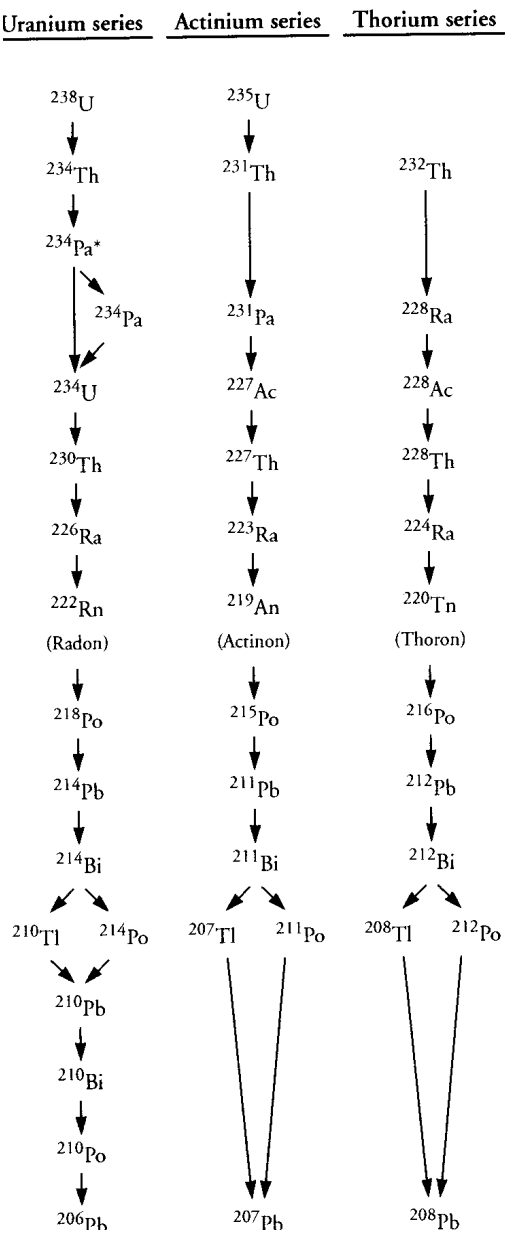


Figure 8.20.3 - Naturally-occurring polonium isotopes [210, 211, 212, 214, 215, 216, and 218] and radium isotopes [226, 224, 223]

Table 8.20.1 - Properties of polonium

Atomic number	84
Atomic weight	208.95
Relative abundance in the Earth's crust, %	3×10^{-14}
Melting point, °C	~250
Boiling point, °C	962
Atomic radius, pm	164
Crystal structure a-Po (< 18°C) b-Po (> 54°C)	Cubic Rhombohedral
Density, g/cm ³ a-Po b-Po	9.14 9.35
Vapor pressure (438–45°C), Pa	$\log p = (964.36 \pm 0.9064) - (716\,860 \pm 893)/T(^{\circ}\text{C})$

Polonium 210 is isolated either from old radium samples or by irradiation in a nuclear reactor. One year of irradiation of 1 kg bismuth at a neutron flux of $10^{14} \text{ n cm}^{-2}\text{s}^{-1}$ gives 25 mg ^{210}Po (ca. $4 \cdot 10^{12} \text{ Bq}$). Polonium is then separated by vacuum distillation. Final purification is accomplished by cementation on silver or copper powders. Metallic polonium is then prepared by sublimation of this deposit at about 700°C. It is also obtained by reduction of polonium sulfide with hydrogen at 500°C. Polonium sulfide itself is precipitated from an acid solution of polonium ion by H_2S .

Chemical properties

Polonium is a metalloid, chemically similar to its neighbors in the Periodic Table bismuth and tellurium. Its oxidation states +2, +4, +6, and -2 are known, but Po(IV) is the most stable one. Po(VI) is easily reduced to a lower oxidation state by its own radiation. Polonium is soluble in HCl to form Po(II) and in HNO_3 to form Po(IV).

The presence of polonium in tobacco smoke has been known since the early 1960s. Radioactive polonium-210 contained in phosphate fertilizers as a result of the presence of uranium in phosphate rock is absorbed by the

roots of plants (such as tobacco) and stored in its tissues. Tobacco plants fertilized by rock phosphates contain polonium-210.

Polonium problem

Capper Pass plant west of Hull in England specialized in smelting low grade Bolivian tin ore. Other metals produced included silver, cadmium, lead, copper, antimony, bismuth, indium, and gold. The plant employed blast furnaces for tin production, with additional electrorefining. In 1970 Rio Tinto Zinc acquired the plant and in 1980 it became the largest smelter of tin from secondary sources, and contributed 10% of the world capacity for tin production.

In 1984 a bismuth alloy was found to be radioactive due to the presence of polonium 210. After smelting in a blast furnace, most of the polonium reported in the metal phase. As a result of the high temperature, polonium volatilized and condensed within the plant. Following refining processes and a tin electrolysis process, polonium reported in the tin electrolysis slime.

The lead anode slimes were smelted in a small rotary furnace and then liquated to produce a bismuth rich alloy and a silver rich alloy. Being volatile, polonium which was present in the lead anode slime ultimately reported in the bismuth-lead alloy product.

The behaviour of polonium is similar to that of tellurium. Sodium was added to the stirred kettle at 370°C. The dross produced was agglomerated and removed using a perforated shovel. It was stored until the polonium activity was less than 15 Bq/g whereupon it was sold for tellurium recovery. In 1985 the world tin price collapsed making the plant un-economic, and the plant closed in 1991, and was decommissioned.

Uses

^{210}Po is used as an α -emitter for (α ,n) neutron sources. A BeO- ^{210}Po source emits up to 93 neutrons per 10^6 α particles.

RADIUM

Radium (Table 8.20.2) is a radioactive alkaline earth metal that is found in trace amounts in uranium and thorium ores. One gram uranium contains 0.33×10^{-6} g Ra. Uranium 235 is present to the extent of 0.7% in uranium ores, was once called actino-uranium because it produced actinium hence the actinium series. Radium and its salts exhibit luminescence (Figure 8.20.4) and impart a carmine color to flame.

Table 8.20.2 - Properties of radium

Atomic number	88
Atomic weight	226
Density	5.5
Relative abundance in Earth's crust, %	1.3×10^{-10}
Melting point, °C	700
Boiling point, °C	1737
Heat of fusion, kJ·mol ⁻¹	8.5
Heat of vaporization, kJ·mol ⁻¹	113
Crystal structure	Body-centered cubic
Electrical resistivity at 20°C, μΩ·m	1
Thermal conductivity at 25°C, W·m ⁻¹ ·K ⁻¹	18.6



Figure 8.20.4 - Luminescence of radium salts on a French postage stamp

Its most stable isotope, Ra 226, has a half-life of 1601 years. Radium 223 has a half life of 11.43 days and that of Ra 224 is 3.363 days. Radium loses about 1% of its activity in 25 years, being transformed into elements of lower atomic weight with lead being the final product of disintegration.

The unit of radioactivity is the becquerel (Bq), equal to one disintegration per second. The curie is defined as that amount of radioactivity which has the same disintegration rate as 1 gram of Ra 226 (3.7×10^{10} disintegrations per second, or 37 G Bq).

Radium has the electronic structure 2, 8, 18, 32, 18, 8, 2. When it loses its two outermost electrons it will attain the inert gas electronic structure hence it is a typical metal. Infinitesimal amounts of radium in sulfate solution can be co-precipitated with barium sulfate as $(\text{Ba,Ra})\text{SO}_4$, when barium chloride solution is added.

Commercial production of radium

The discovery in 1903 that radium emitted gamma rays was put into practice for treatment of cancer by the so-called « Curie Therapy », hence the production of radium became in great demand. A small plant was erected east of Paris to treat on a non-profit basis the Joachimsthal residue shipped from Bohemia, for its recovery.

When the Curies together with Becquerel were awarded the Nobel Prize in 1903, the attention was drawn to Joachimsthal. In the same year, the Austrian Government declared an embargo on the export of ore and residue and asked Carl Auer von Welsbach (1858-1929) (Figure 8.20.5) the famous Austrian chemist specialized in the recovery of rare earths to devise a method for radium recovery. At the same time the Austrian Academy of Sciences founded an Institute for Radium Research, the first such organization in Europe, with the physicist Stefan Meyer (1872-1949) as its director (Figure 8.20.6).



Figure 8.20.5 - Carl Auer von Welsbach
(1858-1929)



Figure 8.20.6 - Stefan Meyer
(1872-1949)

As a result of the boycott, exploration for radium was launched world wide. Ores were discovered, plants were erected and small amounts of radium were produced at a very high cost — \$100,000/gram.

In 1907 a radium separation unit was installed in the same building in Joachimsthal that was used for preparing uranium yellow pigment. It became the leading radium producer in the world (Table 8.20.3).

Table 8.20.3 - Radium production at Joachimsthal.
Total production 1904 to 1936 was 61.271 grams

Year	Grams	Price \$/g
1910	1.120	100 000
1920	(2.2)	-
1930	3.759	-
1938	-	25 000

Radium spa

In 1905, Stefan Meyer proved that the Joachimsthal mine waters indicated high content of radium. In 1906, the first radium spa in the world was opened there which attracted a large number of wealthy tourists. The gradually developing spa business resulted in the construction of the lux-

ury Radium Palace Hotel (Figure 8.20.7) in 1912 in Joachimsthal which became one of the best spa hotels in Europe and the town became a spa resort of global importance. In 1913, the number of guests was about 2500. However, on the outbreak of World War I in 1914, the number greatly declined which reflected badly on the economy. During the war, many hotels were transformed into military hospitals for the wounded soldiers.



Figure 8.20.7 - Radium Palace Hotel

In June 1925, Marie Curie visited the town in company of Thomas Masaryk the president of the Czechoslovak Republic. Their guide was Dr. F. Behounek a former student at the Sorbonne in Paris and a scientist at the Austrian Academy of Science. Since then, the number of tourists increased and in 1930 they amounted to 9000. At that time, the town had a population of 18 000 of whom 95% were German.

The magic metal

During the heydays of Joachimsthal, radium was the magic word, for example, the radium beer in the pubs, the radium soap, etc. However, the death of the American Senator M. Byers changed all that. The senator,

who was suffering from certain disease, was recommended to him to drink radioactive water from a special kit available on the market composed of a small reservoir containing a radium salt in water. After one month drinking this water, however, he died. Autopsy showed that his bones were high in radium. Immediately the Congress ordered the removal of all products containing radium from the market.

Research and applications

When late in 1903 the Austrian government declared an embargo on the export of uranium ore and residue from Joachimsthal the demand for radium became great and increasing rapidly. Thus the stage was set for the exploitation of new sources of radium and for the development of the radium-extraction industry in other countries. Exploration was in most instances done by prospectors who relied on surface indications of mineralization, such as brightly coloured outcrops while simple chemical tests gave further evidence of uranium content.

The most important instruments for determining radium content, however, relied on measurements of the radioactivity of the specimen. Radiation-detection devices of various kinds were used for screening and assaying. For example, photographic plate sealed in light-proof paper registered any exposure to radiation. The radioscope which was composed of glass jar with a zinc sulfide-coated screen that emitted light when it was struck by alpha particles, was also used.

In 1910, Debierne and Marie Curie prepared metallic radium by electrolyzing an aqueous solution of radium chloride using mercury cathode. The amalgam was then heated in a boat to drive off mercury leaving radium metal behind.

In September 1910 the International Radiology Congress was held in Brussels in which leading scientists in the field of radioactivity considered for the first time the question of preparing standard samples for comparison of measurements carried out at different laboratories (Figure 8.20.8).



Figure 8.20.8 - International Radiology Congress in Metropole Hotel in Brussels in 1910

Britain

Intensive research was underway at numerous research establishments and universities. In 1903 the British scientists William Ramsay and Frederick Soddy showed that radium emitted the inert gas helium. Britain entered the radium market in about 1910 with British Radium Corporation, which worked the Trenwith mine in the St. Ives district of Cornwall and shipped the ore to London for processing.

In 1922 a plant was built at the South Terras mine site, where the processing of the low-grade ore continued until 1925. Radium Institute was founded in London in 1911 with Lord Rayleigh, William Bragg, and J.J. Thomson among the members of the executive committee. The Irish Radium Institute was founded in Dublin in 1914.

Russia

Russia entered radium research in 1910, when the *Fergana Company for the Production of Rare Metals* began processing low-grade ore from the Fergana region of Turkestan, now known as Uzbekistan. After producing the first gram of radium, mining operations were suspended in 1914. After the revolution, a Radium Institute was inaugurated in 1922 in Saint Petersburg (at that time was known as Petrograd) with Academician Vladimir I. Vernadsky (1863-1945) (figure 8.20.9), as its director, and a government extraction plant was constructed on the Kama River and a new plant was built in Moscow in 1931.



Figure 8.20.9 -
Vladimir I. Vernadsky
(1863-1945)

Germany

In 1900, Friedrich Ernst Dorn (1848-1916) (figure 8.20.10), professor of physics at Darmstadt and at Halle discovered radon - - an inert radioactive gas emanating from radium and was first known as “radium emanation”. Friedrich Giesel¹ (1852-1927) was the first in Germany to produce radium salts commercially while working at the Quinine Works in Braunschweig. He independently discovered actinium in 1902 two years after Debierne.



Figure 8.20.10 - Friedrich Ernst Dorn (1848-1916)

In 1911, the Radium Institute was founded in the Mining Academy in Freiberg which later became attached to the Physics Institute. In 1913 Kasimir Fajans and O. Göhring discovered protactinium, and the discovery was confirmed by Otto Hahn and Lise Meitner in 1917 from pitchblend residue and who later prepared pure samples from residues at the Quinine Works. This was pursued further by Arstid von Grosse (1905-1985)² who in 1927 prepared two milligrams of the oxide.

¹ Born in Winzig, Germany, studied in Berlin and Göttingen employed at Chininfabrik Braunschweig, was a pioneer in radiochemistry in Germany, discovered that beta rays were deflected by a magnetic field.

² Born in Riga, Latvia, studied in Berlin, worked at Kaiser-Wilhelm Institute for Chemistry, emigrated to USA in 1930 was associated with a variety of jobs, e.g., Manhattan Project in Columbia University, in petroleum research with Vladimir N. Ipatieff, and cosmic ray research with Walter Libby. He settled down at Temple University in Philadelphia.

Poland

In 1911 a society of Polish scientists created a Laboratory of Radioactivity in Warsaw which was inaugurated by Madame Curie in 1913. Poland at that time was under Russian occupation. After World War I when Poland, became independent Madame Curie went again to Warsaw in 1925 to lay the cornerstone for the Polish Radium Institute (Figure 8.20.11). She had been collecting money for this project many years before which also included funds for the purchase of one gram radium. Most of the donation came from USA. In 1929, she travelled again to USA to thank the American people for their gift. She was received by President Hebert Hoover and was his guest at the White House. On May 29, 1932, Madame Curie went to Warsaw to inaugurate the Radium Institute of Warsaw.



Figure 8.20.11 - Polish Radium Institute in Warsaw



Figure 8.20.12 - Madame Curie in Polish Radium Institute in 1932



Figure 8.20.13 - Madame Curie statue in Radium Institute in Warsaw, 1935

The Curies chose not to patent their radium-extraction procedure; instead they shared its details with other workers. In 1904, with the Curies' technical assistance, Armet de Lisle, a French industrialist began commercial radium production at a factory in Nogent-sur-Marne, east of Paris from ore discovered in 1907 in Portugal. La Société Industrielle du Radium acquired the South Terras mine near St. Austell in Cornwall in 1913 and shipped the ore to another plant near Paris.

Other countries

Uranium-bearing alum shales from Sweden and pitchblende from Norway were the raw materials for radium production at a plant near Stockholm. Ore from the arid interior of South Australia was shipped to Sydney and Adelaide for radium extraction.

Major industrial operations

The United States, Belgium, and Canada became heavily involved in radium production. The industry was still unaware of the perils of radioactivity. Technicians engaged in purifying radium were not protected from inhaling dangerous doses of radiation when handling solutions containing radium (Figure 8.20.14)



Figure 8.20.14 - Workers in a radium production factory

USA

Numerous extraction companies were established in Colorado, Illinois, New Jersey and Pennsylvania, and the U.S. became prominent in the international radium market, producing about 200 grams between 1913 and 1923.

- *Rare Metals Reduction Company.* Commercial radium production in the U.S. was first attended by Stephen T. Lockwood in 1906 but his Rare Metals Reduction Company lasted only until 1908. The efficiency of radium recovery was poor, there was little demand for the uranium and vanadium by-products and Lockwood was unable to secure adequate

supplies of ore. Although this early venture failed, it helped to bring attention to vast reserves of carnotite ore in Colorado and Utah.

- *Standard Chemical Company.* In 1910 Joseph M. Flannery (1865-1920), organized the Standard Chemical Company to extract radium from the carnotite ores at Uravan in Colorado (8.20.15). By 1913, when radium production was under way at the company's plant in Canonsburg, PA, and its refining laboratory in nearby Pittsburgh, Standard Chemical was the leader in the American radium industry. It was from there that US president Warren Harding presented Madame Curie with one gram radium when she visited America.

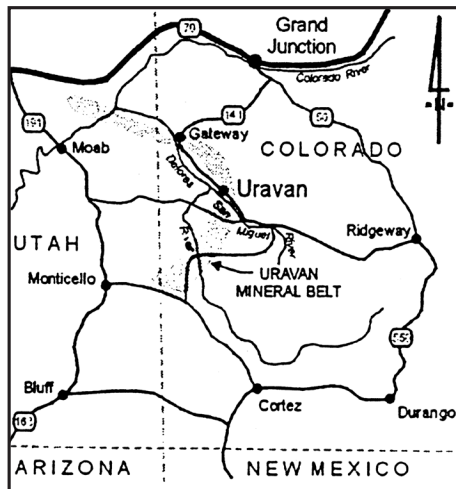


Figure 8.20.15 - Standard Chemical Company extracting radium from the carnotite ores at Uravan in Colorado

- *Carnotite Reduction Company.* Herbert N. MacCoy of the University of Chicago established the Carnotite Reduction Company.
- *US Radium Company.* Herman Schlundt of the University of Missouri provided technical advice on radium extraction to Government agencies including the Bureau of Mines and the Bureau of Standards and to several commercial concerns including the U.S. Radium Company.

- *Radium Company of Colorado.* The collaboration of Henry Koenig of the University of Pittsburgh and Willy A. Schlesinger of the University of Heidelberg at the Radioactive Laboratories of Princeton in 1914 and 1915 led to the founding of the Radium Company of Colorado in Denver. Funds given by Thomas Walsh, a Denver gold magnate, to the Colorado School of Mines sponsored geologic and metallurgical work on the carnotite deposits of Colorado.
- *National Radium Institute.* The National Radium Institute was established in 1913 by a cooperative agreement among the U.S. Bureau of Mines, James Douglas, a New York mining industrialist and philanthropist, and Howard A. Kelly, a gynecologist who operated a private hospital in Baltimore and was a member of the faculty of the Johns Hopkins University Medical School. The undertaking was intended to supply radium to the General Memorial Hospital for the Treatment of Cancer and Allied Diseases in New York and to Kelly's hospital in Baltimore and to investigate ways of reducing the cost of radium production from domestic carnotite ore. When the Denver extraction plant built by the Institute closed in 1916, about 8.5 grams of radium had been produced.

Belgium

Important pitchblende deposits were discovered in what became known as Shinkolobwe (Figure 8.20.16) in the Haut Katanga district of the Belgian Congo between 1913 and 1915, but wartime pressure of maximum production of copper prevented their exploitation. After the armistice in 1919 the Société Générale de Belgique got as a ransom, two German operations: a desilvering plant at Hoboken in Belgium, and an arsenic residue treating plant at Limburg in Germany. As a result a new company under the name Société Générale Métallurgique de Hoboken was formed to manage them together with its small plant for treating imported chromium minerals at Olen near Antwerp.

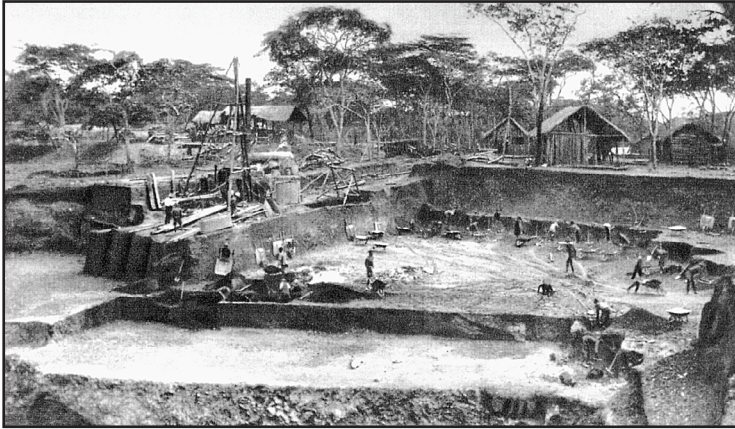


Figure 8.20.16 - Shinkolobwe in the Haut Katanga district of the Belgian Congo

In 1921 the Union Minière du Haut Katanga began shipping the high-grade ore (averaging about 50% uranium oxide) to Olen (Figure 8.20.17) for the extraction of radium. Production began in mid-1922 and forced an immediate and final shutdown of almost all radium-extraction operations in USA. Sensing the inevitable, two of the largest American companies, the Standard Chemical Company and the Radium Company of Colorado, provided guidance in setting up the Olen plant and later served as the agents for the sale of the Belgian radium in USA.

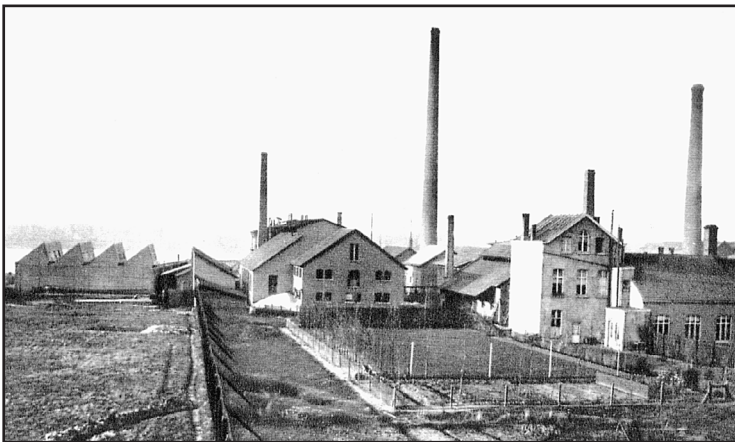


Figure 8.20.17 - Olen plant in Belgium in 1921

Demand for new stocks of radium fluctuated widely between 1922 and 1933 and annual production at Olen reflected this, ranging from 6 to 60 grams with a total production of 326 grams for the period.

On the generous initiative of Baron Henri de Rothschild, the Curie Foundation was created in 1920 as an independent institution to collect gifts and subsidies and to support the scientific and medical work at the Radium Institute. In 1923, the Foundation celebrated 25th anniversary of the discovery of radium.

In spring of 1921, Marie Curie, a widow since 1905, accompanied by her daughters Irene, 24, and Eve, 16, was invited to the United States where she received many honours and a gram of radium from the hands of President Warren Harding to pursue her research (Figure 8.20.18). In 1929 she was invited again to the USA by President Herbert Hoover (Figure 8.20.19).



Figure 8.20.18 - Madame Curie and US President Warren Harding in 1921



Figure 8.20.19 - Madame Curie and US President Herbert Hoover in 1929

Canada

The existence of uranium in outcrops along the shores of Great Bear Lake in northwestern Canada had been discovered in 1900 by a pioneering geo-

logical survey of the area. In 1931 Edgar A. LaBine (1890-1977) (Figure 8.20.20) announced that the extensive of pitchblende deposits included ores containing 30 to 60% uranium oxide. He developed the deposit under the name of Eldorado Gold Mines. The ore was rich in silver and cobalt. Radium at that time was selling at \$120,000/gram and therefore the discovery was of great significance. A shaft was sunk and a gravity plant constructed; the site was named appropriately “Port Radium” (Figures 8.20.22-8.20.23).



Figure 8.20.20 - Edgar A. LaBine (1890-1977)

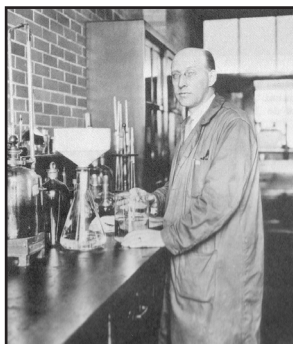


Figure 8.20.21 - R. J. Traill at the Bureau of Mines in Ottawa



Figure 8.20.22 - Location of Port Radium in the Canadian North

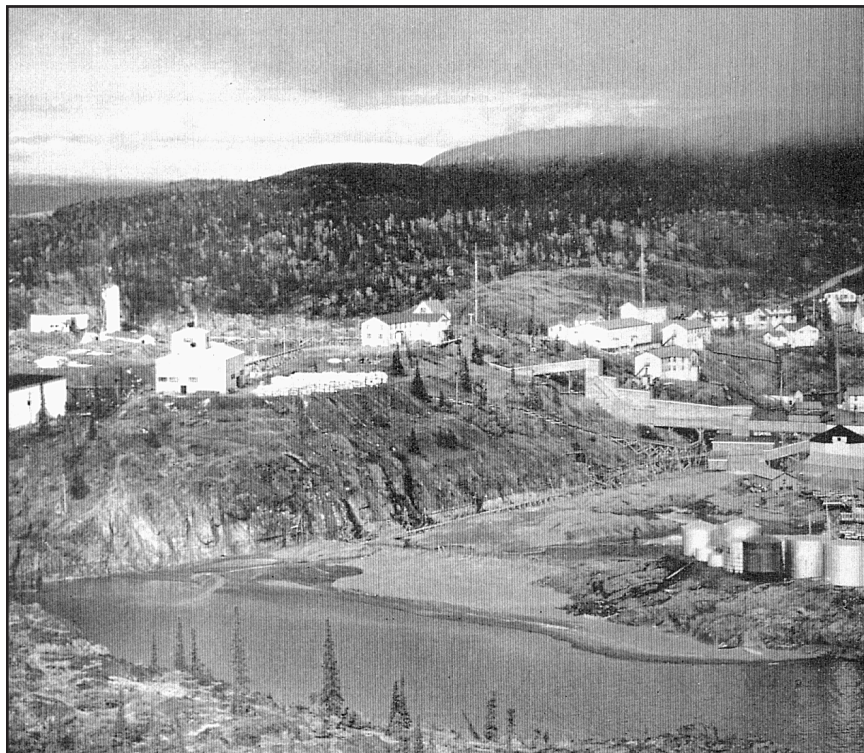


Figure 8.20.23 - Port Radium plant

In 1933 Labine found a place and a person to handle the complicated radium processing. The place was an old plant on the waterfront of Port Hope, Ontario (Figure 8.20.24), and the person was Marcel Pochon, a former co-worker of Madame Curie. The reactions took place in glazed earthenware vessels manually agitated with wooden paddles. Buckets were used to add the seven tons of corrosive chemicals needed for every ton of 40% uranium concentrate to get 0.1 gram of radium. The production capacity of about two grams of radium/ month was completed by the end of 1933 which more than doubled by 1938.

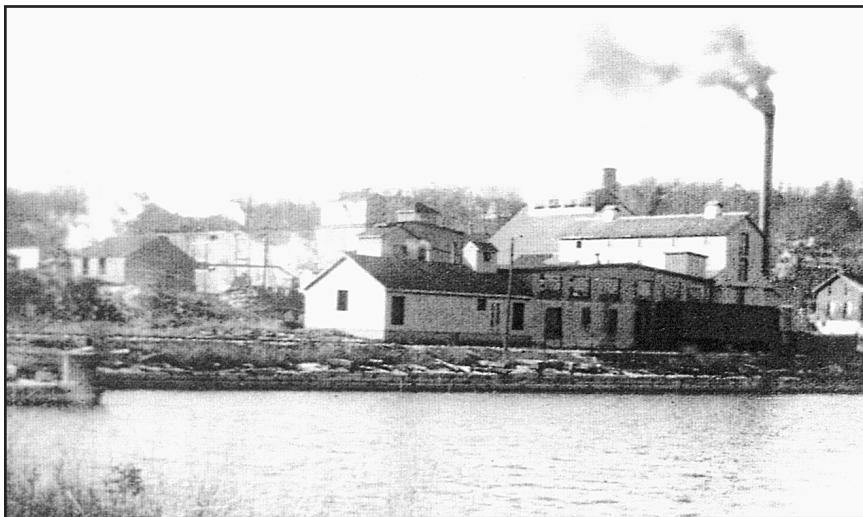
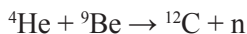


Figure 8.20.24 - Radium processing at Port Hope, Ontario

Uses

Radium salts produce neutrons when mixed with beryllium. Alpha particles from radium bombard beryllium to produce neutrons:



Radium salts were also used in painting watch dials with glow-in-the-dark paint (Figure 8.20.25). The salt was mixed with glue, water and zinc sulfide, then used brushes to apply the paint onto dials. The radiation from radium caused the sulfide to fluoresce. During World War I, demand for glowing dials, watches, and aircraft instruments were in great need. Several hundred grams of radium salts were used for this purpose.



Figure 8.20.25 - Radium in dials

The end of the radium industry

The magic metal radium turned into nuisance. Whereas it took between 300 and 400 tons of a typical American carnotite ore to produce one gram of radium, less than 10 tons of the Katanga ore was needed to yield the same amount. In the aftermath of the Belgian emergence, the pattern of radium production throughout the world changed drastically. The US Radium Company continued to extract radium until 1926. The remaining American operations were either abandoned completely or were converted to the treatment of carnotite ore for the recovery of vanadium. A limited amount of mining and extraction of radium was done in Britain and France through at least 1925 and in Australia through about 1930.

Joachimsthal became part of Czechoslovakia after World War I and was renamed Jáchymov; radium production was sustained there through 1937. In the former USSR radium processing continued in spite of ores that now had to be classified as low grade, and it was even expanded in 1931. The high output from the factories at Olen and Port Hope rapidly forced down the price of radium, and in 1938 an agreement that divided up the world market and attempted to stabilize the price at \$40,000/gram was negotiated by Belgium and Canada. Later, after World War II radionuclides such as cobalt 60 and cesium 137 became available for radiation therapy sources. To-day radium is classified as a waste and methods are devoted to fix it in a form suitable for long-term burial.

In 1938, the National Socialists started to propagate the idea of the union of Joachimsthal and the Sudetenland with Germany. This resulted in the invasion of Czechoslovakia by the Nazi troops. During the German occupation, the Radium Palace Hotel became a branch of the Berlin Hospital, the small hotels transformed into military hospitals, and the mine shafts into prison.

Radium was once used for cancer treatment because of its gamma rays. When cheap cobalt 60 became available by irradiation of cobalt in nuclear reactors the importance of radium declined. Uranium ores especially

carnotite in USA which was used to recover radium at high cost was abandoned.

All three isotopes of radium decay into radon gas which then decays to polonium which is a solid product hence the danger of respiring radon - - once it enters the lungs it will never leave and may cause lung cancer because of the bombardment of the tissue with alpha particles.

Since radium is chemically similar to calcium, it has the potential to cause great harm by replacing it in bones. Inhalation, injection, ingestion or body exposure to radium can cause cancer and other disorders. Stored radium should be ventilated to prevent accumulation of radon. Emitted energy from the decay of radium ionizes gases, affects photographic plates, causes sores on the skin, and produces many other detrimental effects.

Radium is present in filter cakes of uranium recovery and in phosphate rock treatment with sulfuric acid (Figure 8.20.26).



Figure 8.20.26 - Radioactive gypsum disposal in phosphate rock treatment with sulfuric acid containing radium in Florida

8.21 Actinium

Discovery and isolation	978	Actinides	980
Properties	979		

DISCOVERY AND ISOLATION

André Louis Debierne (1874-1949) (Figure 8.21.1) discovered the radioactive element actinium in 1899 in the residue from Joachimsthal. Actinium was isolated by Friedrich Oskar Giesel (1852–1927) (figure 8.21.2) a German organic chemist during his work in a quinine factory in the late 1890s. He started the production of radium from the waste of uranium production in the chemical plant E. de Haën in Hanover. In the period between 1902 and 1904 he was able to isolate a new element which he called *emanium*. Later it was found to be identical to actinium already discovered by Debierne. He produced large quantities of pure radium and polonium for commercial applications from uranium ore.



Figure 8.21.1 - André Louis Debierne (1874-1949) born in Paris, studied at the École de Physique et Chimie, appointed professor then director of the school, succeeded Marië Curie as director of Institut du Radium.



Figure 8.21.2- Friedrich Oskar Giesel (1852-1927)

PROPERTIES

Actinium is soft, silvery-white radioactive metal, reacts rapidly with oxygen and moisture in air forming a white coating of actinium oxide that prevents further oxidation. Owing to its strong radioactivity, actinium glows in the dark with a pale blue light. Actinium assumes oxidation state +3 in nearly all its chemical compounds. The Ac^{3+} ions are colorless in solutions.

Actinium is found only in traces in uranium ores as the isotope ^{227}Ac , which decays with a half-life of 21.772 years, predominantly emitting beta particles. Relative abundance of actinium in earth's crust is 3×10^{-14} . One tonne of uranium ore contains about 0.2 milligrams of actinium. Naturally occurring actinium is composed of one radioactive isotope: Ac 227 which is the most stable. Thirty-six other radioisotopes have been identified.

There is close similarity of physical and chemical properties of actinium and lanthanum which are neighbors in the Periodic Table (Figure 8.21.3). Solvent extraction and ion chromatography are commonly used for its separation. The element is prepared, in milligram amounts, by the neutron irradiation of its neighbor ^{226}Ra in a nuclear reactor.

Figure 8.21.3 - Position of actinium in the Periodic Table

Actinium trifluoride can be produced either in solution or in solid reaction. The former reaction is carried out at room temperature, by adding hydrofluoric acid to a solution containing actinium ions. In the latter method, actinium metal is treated with hydrogen fluoride vapors at 700°C in an all-platinum setup.

ACTINIDES

Actinides are a group of metals following actinium in the Periodic Table (Figure 8.21.4). The first member is thorium (discovered in 1829) followed by protactinium (discovered in 1917), then uranium (discovered in 1789). The trans-uranium elements do not occur in nature and were prepared artificially. They became an important group of metals after the discovery of the phenomenon of fission in 1939. Only thorium, uranium, and plutonium are of technical importance for nuclear energy. The electronic configuration of actinides is similar to the lanthanides in that the two outermost shells are the same [with minor exceptions due to quantum chemistry considerations].

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw
2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
18	18	18	18	18	18	18	18	18	18	18	18	18	18	18
32	32	32	32	32	32	32	32	32	32	32	32	32	32	32
19	20	21	22	23	24	25	26	27	29	30	31	32	32	32
9	9	9	9	9	9	9	9	9	9	8	8	8	8	9
2	2	2	2	2	2	2	2	2	2	2	2	2	2	2

Figure 8.21.4 - Electronic structure of actinides

Part 9 - Twenty century metals

9.1 Introduction

New metal discovery.....	969	Advances in radiochemistry	975
The quantum theory.....	970	Uranium fission.....	976
X-ray analysis.....	972	Cyclotron.....	977
The discovery of the neutron.....	973	Trans-uranium metals.....	978
Eka-rhenium.....	974		

[illegible]

Cr	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

Ancient metals
Medieval metals
Eighteenth century metals
Nineteenth century metals
Twentieth century metals

Figure 9.1.1 - Metals in the twentieth century

NEW METAL DISCOVERY

The twentieth century opened with the discovery of the quantum theory which allowed the understanding of the movement of electrons in the atom and the formation of electron shells. The elements europium and lutetium were discovered after careful examination of spectrum analysis of certain rare earths while protactinium and francium were also discovered, although they occur in infinitesimal quantities in nature, thanks to perfection in radioactivity and radioactive techniques.

In the 1920s hafnium and rhenium were discovered - - the first due to the quantum theory and the second thanks to the discovery of x-ray analysis. In the 1930s the neutron was discovered which was responsible for the discovery of uranium fission. The construction of the cyclotron led to the discovery of technetium. Few years later in the 1940s, during the Manhattan Project for the production of atomic bomb in USA, the last member of the rare earths promethium was discovered in fission products although it does not occur in nature. It was also during this period that plutonium was discovered and isolated as well as other trans-uranium elements (Table 9.1.1).

Table 9.1.1 - Metals discovered in the twentieth century.

Year	Metal	Discoverer	Remarks
1907	Lutetium	Urbain	Discovered in France
1917	Protactinium	Hahn and Meitner	Isolated by von Grosse in 1934.
1923	Hafnium	Coster and Hevesy	Isolated by van Arkel and de Boer in 1925
1924	Rhenium	Noddack, Tacke, and Berg	Discovered in Germany
1937	Technetium	Segre	By bombardment of molybdenum with α -particles; later on found in uranium fission components
1939	Francium	Perey	Discovered in France
1940-1961	Trans-uranium metals	Seaborg et al.	Discovered in USA
1945	Promethium	Glendenin and Merinsky	Discovered in USA

THE QUANTUM THEORY

The quantum theory by Max Planck (1858-1947) (Figure 9.1.2) is based on the principle that energy like matter is also composed of minute quantities called quanta, i.e., energy is not continuous but occurs in small parcels (Figure 9.1.3). This allowed the understanding of the movement of electrons in the atom by Niels Bohr (1885-1962) (Figure 9.1.4) and the hypothesis of the formation of electron shells.



Figure 9.1.2 - Max Planck (1858-1947)

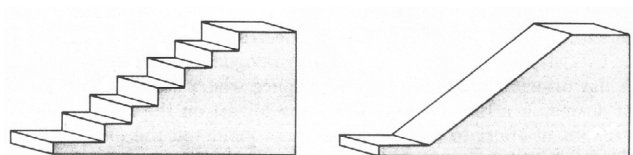


Figure 9.1.3 - Representation of the discontinuity of energy



Figure 9.1.4 - Niels Bohr (1885-1962)

Following the discovery of lutetium in 1907 and its identification by Bohr as a rare earth and not as a member of Group IV, search for the missing element in Group IV was started in his laboratory. By means of x-ray analysis Dirk Coster and Georg Hevesy in 1923 discovered hafnium in zirconium ores. As a result, a major change in the Periodic Table took place. In 1922 the electronic structure of the rare earths was elucidated by Bohr (Table 9.1.2).

Table 9.1.2 - Electronic structure of lanthanides

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
2	2	2	2	2	2	2	2	2	2	2	2	2	2
8	8	8	8	8	8	8	8	8	8	8	8	8	8
18	18	18	18	18	18	18	18	18	18	18	18	18	18
19	20	21	22	23	24	25	26	27	28	29	30	31	32
9	9	9	9	9	9	9	9	9	9	9	9	9	9
2	2	2	2	2	2	2	2	2	2	2	2	2	2

X-RAY ANALYSIS

In the same year of 1923 Henry Moseley (1887-1915) (Figure 9.1.5) by means of x-ray analysis he discovered the atomic number of the elements and came to the conclusion that it was the fundamental principle of the Periodic Table and not the atomic weights as was suggested by Mendeleev. His method of analysis became a useful tool in discovering new metals, for example hafnium and rhenium.



Figure 9.1.5 - Henry Moseley (1887-1915)

THE DISCOVERY OF THE NEUTRON

When in 1911 Ernest Rutherford (1871-1937) bombarded metal foils with positively charged helium ions (alpha particles) and observed the rebounding of some of these particles, he realized that the atom must have a tiny positive nucleus containing nearly all the mass of the atom. Between 1930 and 1932, some physicists including Frédéric Joliot (1900-1958) and Irène Curie (1897-1957) in Paris noted that when certain light elements such as beryllium were exposed to alpha particles, some kind of radiation was formed, which showed its presence by ejecting protons from paraffin. They were unable to interpret their results.

It was James Chadwick (1891–1974) (Figure 9.1.6) in Cambridge in 1932 who repeated these experiments and explained the phenomenon by supposing that alpha particles were knocking neutral particles out of the nuclei of the beryllium atom and that these neutral particles were in turn knocking protons out of the paraffin. In this way the neutron was discovered. He was awarded Nobel Prize for physics in 1935.



Figure 9.1.6 - James Chadwick
(1891-1974)



Figure 9.1.7 - Enrico Fermi
(1901-1954)

In 1934, Enrico Fermi (1901-1954) (Figure 9.1.7) in Rome discovered that neutrons may be captured by atoms and that the frequency of capture increases when they are slowed down by passing them through a hydro-

eliminated before one could claim to have found a trans-uranium element. She went further and suggested that: *“When heavy nuclei are bombarded by neutrons, it would be reasonable to conceive that they break down into numerous large fragments which are isotopes of known elements but are not neighbours of the bombarded elements”*¹.

Her argument was as follows: when atoms are bombarded by protons or alpha particles, the nuclear reactions that take place involve the emission of an electron, a proton, or a helium nucleus and the mass of the bombarded atom suffers little change. When, however, neutrons are used, new types of nuclear reaction should take place that are completely different from those previously known.

ADVANCES IN RADIOCHEMISTRY

Radiochemists played an important role in separating the individual radioelements, their identification, and their arrangement in radioactive series. New methods of measurements such as the Geiger counter and the gamma scintillation counter replaced the gold leaf electroscope (Figures 9.1.9-9.1.11). Radiations from radioactive substances were identified as alpha, beta, and gamma. For example, alpha particles were collected in a special thin glass container and examined by the spectroscope and identified as helium (Figures 9.1.12).

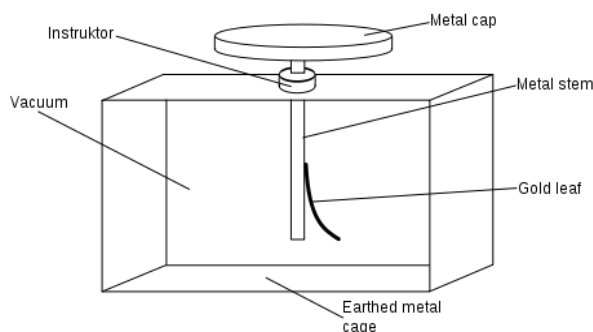


Figure 9.1.9 - Principle of gold leaf electroscope

¹ Translation by the writer



Figure 9.1.10 - Gold leaf electroscope

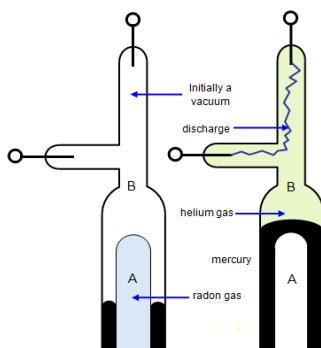


Figure 9.1.11 - Collecting alpha particles [left] and measuring their spectrum [right]

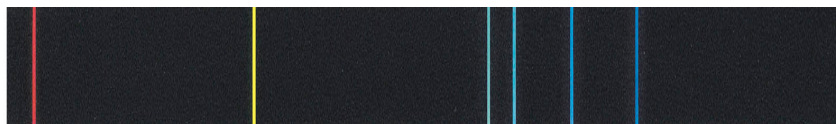


Figure 9.1.12 - Spectrum of helium

URANIUM FISSION

Fermi's experiments were repeated by Otto Hahn (1879-1968) (Figure 9.1.13) and his coworkers in Berlin. They confirmed his conclusions and published a series of papers on extensive radiochemical separations of the so-called trans-uranium elements. The results, however, became so contradictory that after five years of intensive research and extensive publication the concept of trans-uranium elements had to be abandoned. Hahn then announced in January 1939 the definite formation of barium during the bombardment of uranium and started speculating about the mechanism of its formation.



Figure 9.1.13 - Otto Hahn (1879-1968)

Hahn was 55 and already director of the Kaiser Wilhelm Institute for Chemistry (now Max Planck Institute). He apparently could not accept the new idea that the uranium atom was split into two fragments. It was Lise Meitner who finally explained the results of the work as fission, a few months after she was forced to leave Germany in 1939.

Cyclotron

The cyclotron was invented by Ernest O. Lawrence (1901-1958) (Figure 9.1.14) of the University of California, Berkeley, where it was first operated in 1932. By its means technetium and the trans-uranium metals were discovered.

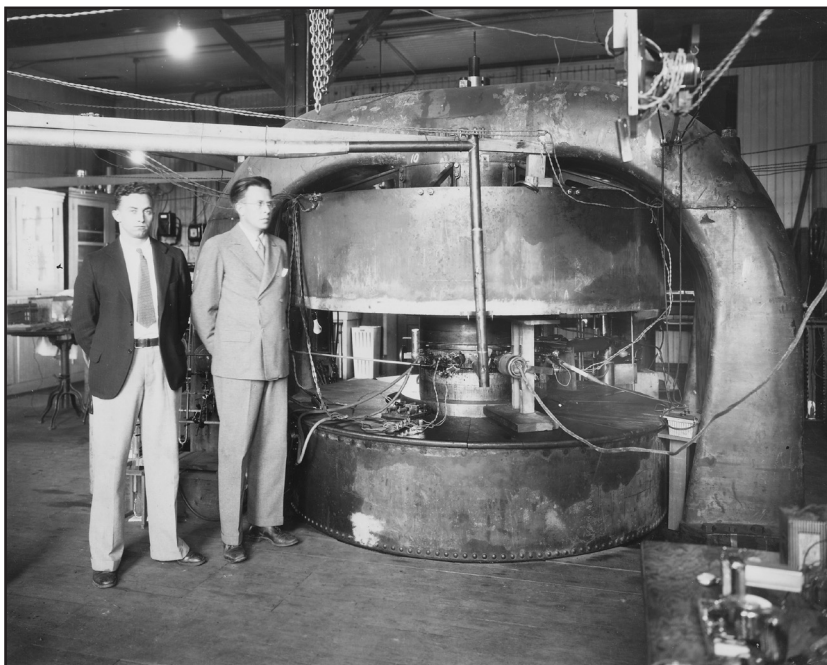


Figure 9.1.14 - Ernest Lawrence (1901-1958) [right]
standing next to the cyclotron

In 1937 the Italian physicists Emilio Segrè (1905-1989) and C. Perrier announced the detection of the element with atomic number 43 in trace

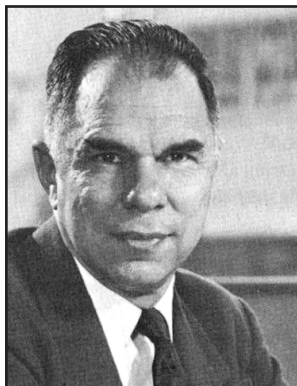


Figure 9.1.16 – Glenn T. Seaborg (1912-1999)

																H	He	
Li	Be												B	C	N	O	F	Ne
Na	Mg	Al												Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	Ga	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	*La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	**Ac																

*

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
----	----	----	----	----	----	----	----	----	----	----	----	----	----

**

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
----	----	---	----	----	----	----	----	----	----	----	----	----	----

Figure 9.1.17 - Periodic Table after 1945

The existence of a rare earth element between neodymium and samarium was predicted by Brunauer. This was discovered by Glendenin and Marinsky in 1945 in uranium fission products and named “promethium”. The 14 rare earth elements were identified as “inner transition metals” and were assigned a special place in the Periodic Table that became known as “lanthanides”. In this group the two outermost electronic shells are filled with the same number of electrons, and it is in the third shell that the number of electrons is increased gradually. This explained the close similarity of the members of this group in their chemical behaviour.

9.2 Protactinium

Discovery	995	The metal	997
Isolation	996		

DISCOVERY

In 1871, Dmitri Mendeleev predicted the existence of an element between thorium and uranium he left the space below tantalum empty. For a long time chemists searched for eka-tantalum as an element with similar chemical properties to tantalum. In 1900, William Crookes (1832-1919) (Figure 9.2.1) isolated as an intensely radioactive material from uranium and named it uranium-X (UX). Kasimir Fajans (1887-1975) (Figure 9.2.2) and Oswald Helmuth Göhring encountered an isotope during their studies of the decay chains of uranium-238 and named the new element *brevium* (from Latin, *brevis*, meaning brief) because of its short half-life, 6.7 hours.

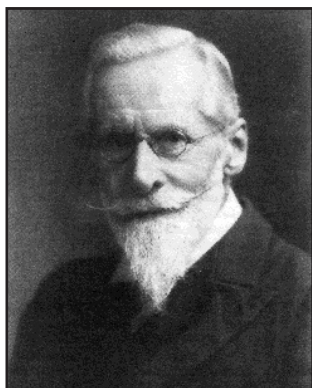


Figure 9.2.1 - William Crookes
(1832-1919)



Figure 9.2.2 - Kasimir Fajans
(1887-1975)

In 1917-18, Otto Hahn (1879-1968) and Lise Meitner (1878-1968) (Figure 9.2.3) in Germany discovered another isotope much longer half-life of about 32,000 years. Thus the name *brevium* was changed to *protoactinium* as the new element was part of the decay chain of uranium-235 before the actinium. Frederick Soddy and John Cranston in England independently made the same discovery. The name was shortened to *protactinium* by the IUPAC in 1949 and Hahn and Meitner were confirmed as discoverers.

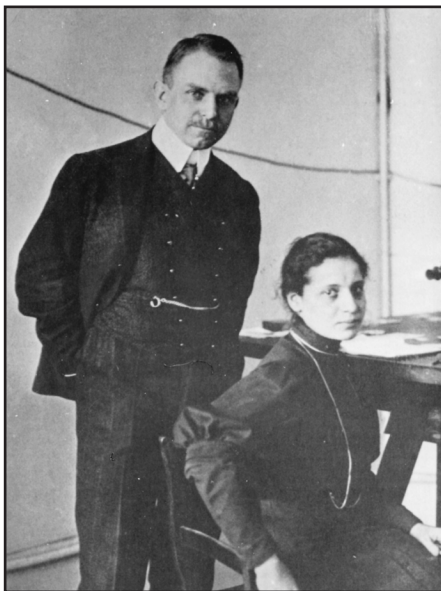


Figure 9.2.3 - Otto Hahn (1879-1968) and Lise Meitner (1878-1968)

ISOLATION

Aristid von Grosse (1905-1985) (Figure 9.2.4) produced 2 milligrams of Pa_2O_5 in 1927, and in 1934 first isolated metallic protactinium from 0.1 milligrams of Pa_2O_5 . He used the van Arkel–de Boer process in which the oxide was chemically converted to iodide and then reduced in a vacuum with an electrically heated metallic filament. In 1961, the United Kingdom Atomic Energy Authority produced 125 grams of 99.9% pure protactinium by processing 60 tonnes of waste material in a 12-stage process.

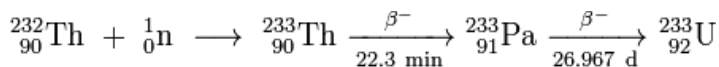


Figure 9.2.4 - Aristid von Grosse (1905-1985)

THE METAL

Protactinium is a silvery-gray metal which readily reacts with oxygen, water vapour and inorganic acids. It forms compounds mainly in the oxidation state +5. Because of its scarcity, high radioactivity, and high toxicity there are currently no uses for it. It is mostly extracted from spent nuclear fuel.

Before the advent of nuclear reactors, protactinium was separated from uranium ores. Nowadays, it is mostly produced as an intermediate product of nuclear fission in thorium high-temperature reactors:



Atomic number	91
Atomic weight	201.04
Relative abundance, %	8×10^{-11}
Atomic radius, pm	163
Density, g/cm ³	15.37
Melting point, °C	1568
Boiling point, °C	4027

Protactinium is a radioactive metal formed in the decay chain of uranium but not thorium (Figure 9.2.5). It exists in two crystalline forms: α -Protactinium is tetragonal-body centered and β protactinium is cubic face-centered. Protactinium isotope ^{231}Pa ($t_{1/2} = 32\,480$ years) is the most important of all 24 known isotopes.

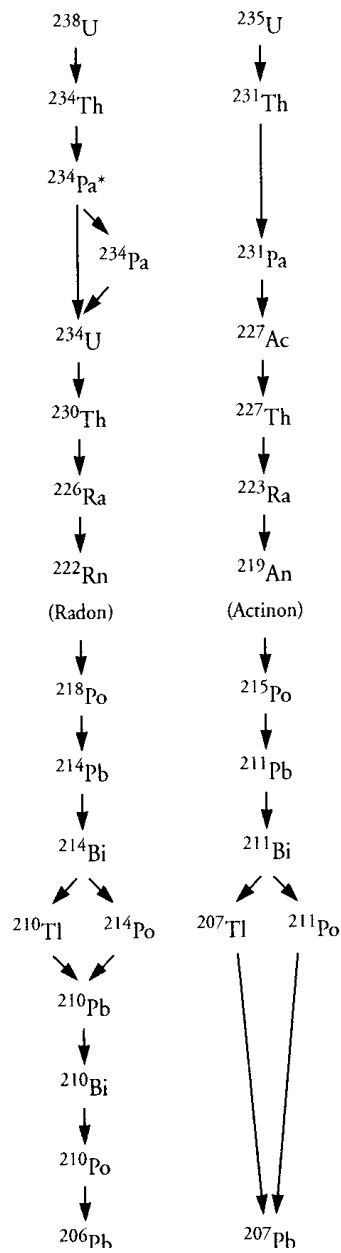


Figure 9.2.5 - Decay chain of uranium

9.3

Hafnium¹

Introduction	986	Hafnium and its compounds	987
Discovery and isolation	986	Uses	988

INTRODUCTION

When Henry Moseley discovered the relationship between the X-ray spectrum of an element and its atomic number, there were seven unfilled spaces in the Periodic Table for elements 43, 61, 72, 75, 85, 87, and 91. Georges Urbain who in 1907 discovered the rare earth lutetium (atomic number 71) searched for element 72 in the rare earth residue he was working with but without success. On the basis of his quantum theory of atomic structure Niels Bohr argued that element 72 must be quadri-valent rather than trivalent and must belong to the zirconium family and not the rare earths. Bohr therefore advised Georg von Hevesy in his laboratory to search for this element in zirconium ores.

DISCOVERY AND ISOLATION

It was in 1923, that Dirk Coster (1889-1950) (Figure 9.3.1) and Georg von Hevesy (1885-1966) (Figure 9.3.2) in Copenhagen brought their search to a successful conclusion. They discovered element 72 in a Norwegian zircon and later in all the zirconium minerals and all the commercial zirconium preparations they investigated, even those which had previously been believed to be pure, was made possible by Moseley's method of X-ray analysis. This metal was named hafnium for the city of Copenhagen.

¹ See also Zirconium, Eighteenth Century Metals



Figure 9.3.1 - Dirk Coster
(1889-1950)

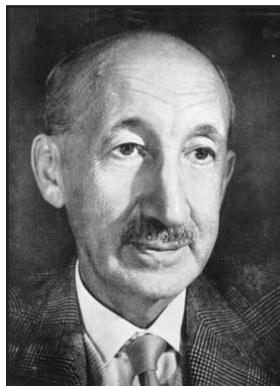


Figure 9.3.2- Georg von Hevesy
(1885-1966)

Hafnium had lain hidden for long, not because of its rarity but because of its close similarity to zirconium. It is far more abundant than silver or gold. Since the earlier chemists were unable to prepare zirconium compounds free from hafnium, the discovery necessitated a revision of the atomic weight of zirconium. Hevesy and his coworkers then isolated hafnium oxide from zirconium oxide by repeated re-crystallization of the double ammonium or potassium fluorides. They also prepared the metal. Van Arkel and de Boer prepared the pure metal in 1925 by passing the vapor of the tetra-iodide over a heated tungsten filament.

HAFNIUM AND ITS COMPOUNDS

Hafnium is a refractory metal with a high melting point. It occurs mainly in association of zirconium in the mineral is zircon, ZrSiO_4 , in a concentration of about 1%. Although hafnium has two electrons in the outermost shell and it would have been expected that to have valency of 2, yet its valency is 4.

Relative abundance, ppm	2.8-4.5
Melting point, °C	2227
Boiling point, °C	4602
Density, g/cm ³	13.3

Elemental hafnium reacts with hydrogen ($>250^{\circ}\text{C}$), carbon ($>500^{\circ}\text{C}$), and nitrogen ($>900^{\circ}\text{C}$) to form brittle, nonstoichiometric interstitial compounds with metal-like conductivity. In molten salts, hafnium is normally quadrivalent, but in anhydrous molten halide salts, it can be reduced to hafnium(III) and hafnium(II). In aqueous solution, hafnium is always quadrivalent. In dilute acid, hafnium slowly hydrolyzes and polymerizes. Hafnium hydrous oxide precipitates from aqueous solution at ca. pH 2. The only inorganic compounds with significant solubility in neutral or slightly basic aqueous solution are the ammonium – hafnium carbonate and potassium – hafnium carbonate complexes.

USES

Hafnium is used in nuclear reactors as control rods because of its high neutron cross section.

Rhenium¹

Introduction	989	Industrial production of rhenium	992
Confirmation by x-rays	990	The metal and its compounds	994
Search for the missing element	990	Uses	995

INTRODUCTION

Manganese is the ninth most abundant metal in nature; its relative abundance in the Earth's crust is 0.1%. It was recognized by the Swedish chemists Carl Wilhelm Scheele (1742-1786) and Tobern Bergman (1735-1784) and was isolated in 1774 by Johan Gottlieb Gahn (1745-1818) another Swedish chemist. When the Russian chemist Dimitri Ivanovitch Mendeleev (1834-1907) discovered the Periodic Table in 1869 he put it in Group VII and left two gaps below it which he marked eka-manganese (Em) and dvi-manganese (Dm). He predicted new elements to fill these and other gaps he left in his Table (Figure 9.4.1).

																H	
Li	Be											B	C	N	O	F	
Na	Mg	Al											Si	P	S	Cl	
K	Ca		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			As	Se	Br	
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	
Cs	Ba	*La		Ta	W		Os	Ir	Pt	Au	Hg	Tl	Pb	Bi			
			Th		U												
*	Ce											Er					

Figure 9.4.1 - Mendeleev's Periodic Table of 1869 in modern form. Shaded areas were predicted elements, empty spaces were unknown

¹ Based on F. Habashi, *Ida Noddack (1896–1978). Personal Recollections on the Occasion of 80th Anniversary of the Discovery of Rhenium*, Métallurgie Extractive Québec, Québec City, Canada 2005. Distributed by Bookstore Université Laval, Quebec City, www.zone.ul.ca

In his prediction of the existence of the three elements eka-boron, eka-aluminum, and eka-silicon Mandeleev was able to describe their properties with fair accuracy by interpolation. This facilitated the work of chemists greatly because they knew for what they were looking for. Hence, scandium, gallium, and germanium were discovered within 10 years of Mendeleev's prediction.

When, however, he predicted eka-manganese and dvi-manganese, he was unable to predict much of their properties because it was not possible to interpolate. For eka-manganese he predicted an atomic weight of 100, and for dvi-manganese 190 -- values that are very near to the actual values of 98 and 182.2, respectively. He also predicted that their compounds would be coloured and there would be a series of oxides corresponding to the oxides of manganese. Because these were the last two members of Group VII, their properties could not be interpolated. These gaps were not filled for more than 50 years.

CONFIRMATION BY X-RAYS

The existence of the two missing elements was later confirmed by Henry Moseley (1887-1915) when he discovered the atomic numbers of the elements. For example, he established that the atomic number of molybdenum was 42 and that of ruthenium was 44. Thus, it was shown that the space left in Mendeleev's Table for eka-manganese was real and that a definite element should occupy that space-element 43.

SEARCH FOR THE MISSING ELEMENT

In their search for the two missing elements of the manganese group, Ida Tacke (1896-1978) and Walter Noddack (1893-1962) (Figure 9.4.2) of the Physico-Technical Testing Office came to the conclusion from the very beginning, that these elements must have properties different from manganese and should be similar to their horizontally-occurring neighbours. This

proved to be quite accurate. Thus, the two elements eka-manganese and dvi-manganese are extremely rare as compared to manganese and further, technetium (eka-manganese) has properties very similar to rhenium and not to manganese. Rhenium should occur in molybdenum and tungsten ores and not with manganese ores.



Figure 9.4.2 - Ida Noddack [born Tacke] (1896-1978)
and Walter Noddack (1893-1962)

Ida Noddack decided to investigate the mystery of these two missing elements with her husband. They made a tedious and systematic study of properties of the elements near these two gaps. They found that, although usually there was a gradual change in properties in the vertical groups, there were also sharp changes. From comparisons with other groups they concluded that such sharp changes would occur between manganese and the two elements below it. For example, they believed that the sulfides of the missing elements would be insoluble in dilute acid in contrast to manganese disulfide which is acid-soluble. They also predicted that the eka-manganese should be relatively less abundant than ruthenium and osmium. Certainly, they would not be as abundant as manganese which is nearly of the same order of magnitude as iron, its horizontal neighbour.

This explains why previous investigators had failed to discover the

missing elements - - they were searching for them in manganese ores on the assumption that the missing elements would resemble manganese in chemical properties. The Noddacks did not make this assumption; their research for the missing elements centred on ores containing minerals of the metals molybdenum, tungsten, ruthenium, and osmium, the horizontal neighbours of eka- and dwi-manganese. They prepared more than 400 enriched products from different ores for examination.

Moseley's work from 1912-14 had firmly established the periodicity of the wave lengths of the X-ray emission lines of the elements and it was that phenomenon, which Tacke and Noddack utilized as their main technique in looking for the unknown elements. In June 1925, with the help of Otto Berg, an X-ray specialist at Siemens-Halske in Berlin, they identified in a Norwegian columbite a new element which they called rhenium in honour of the River Rhein. A year after the discovery of rhenium, Ida Tacke, now Frau Noddack, prepared the first gram of the metal from 660 kg of molybdenite ore and, later, wrote numerous papers on its chemistry.

INDUSTRIAL PRODUCTION OF RHENIUM

The first industrial production of rhenium took place in Leopoldshall in Germany in the late 1920s. The raw material was furnace crust from carbonaceous copper schist ore (Kupferschiefer) from the Mansfeld District. About 100 kg of the metal was produced by a complicated process, but the price was so high that production was discontinued. In the early 1950s production started again at the Mansfeld Kombinat "Wilhelm Pieck" (former German Democratic Republic) from a lead-zinc flue dust.

An important advance in rhenium technology was the production of the element from flue dusts from the roasting of molybdenite. The amount recovered from the dusts was, however, only 10-15% of the total rhenium content of the MoS_2 concentrate. The introduction of accurate analytical methods enabled material balances for rhenium extraction to be established. These showed that most of the rhenium was lost up the stack, and

only a small amount remained in the flue dust or in the roasted product. The flue gas was therefore scrubbed intensively to ensure that the volatile oxides of rhenium were recovered when the molybdenite concentrate was roasted.

In the USA, 17 tons of dust from a molybdenite roasting furnace were treated over a period of 10 years at the University of Tennessee to recover 109 kg rhenium in the form of potassium perrhenate. Large-scale production was then started by Kennecott in Salt Lake City, Utah (Figure 9.4.3) and in Waterbury, Connecticut. Rhenium production started in the USSR in 1948 also from molybdenite roasting dust. In 1960, world production (excluding the former USSR) reached 10 tons; production figures for today are withheld by producers.

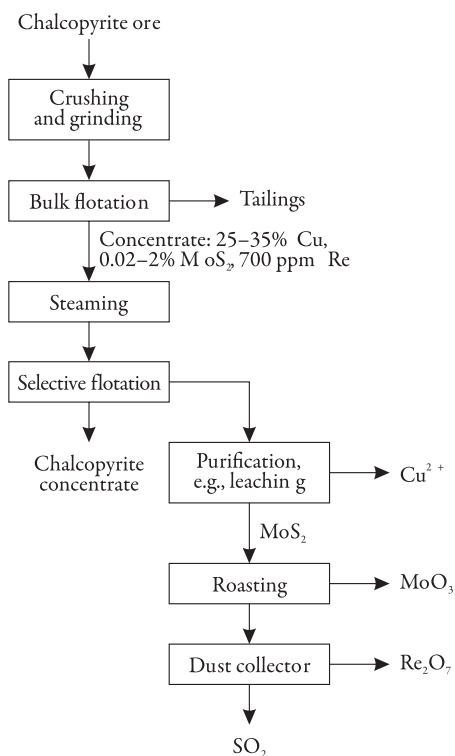


Figure 9.4.3 - Recovery of rhenium from the sulfide fraction of porphyry copper ores

Molybdenite associated with the porphyry copper ores are the most important commercial sources of rhenium, while molybdenite veins in quartz are rhenium-free. Rhenium is extracted from flue gases during the roasting of molybdenite concentrates separated by flotation from chalcophyrite concentrates. Recovered rhenium is then treated in ion exchange systems, precipitated as ammonium perrhenate and reduced by hydrogen to form a metal powder. The powder was compacted, vacuum pre-sintered, and then hydrogen sintered at high temperatures.

THE METAL AND ITS COMPOUNDS

Rhenium is present in the earth's crust at a very low concentration (ca. 7×10^{-8} %, 0.7 ppm). Having a melting point of 3180°C , it is the highest melting metal next to tungsten (3380°C). It has also a high specific gravity (21.4) next only to Os, Ir, and Pt. Its characteristic valence stage is 7 but it can also form compounds with valency -1, 1, 2, 4, 5, and 6. While similar in many respects to other refractory metals, rhenium's unusual combination of properties from both a chemical and metallurgical point of view makes it unique even among its close relatives. For example, it is the only refractory metal which does not form carbides.

Rhenium has a hexagonal close-packed structure which it retains to its melting point and hence does not undergo a ductile-brittle transformation, in contrast to other refractory metals. It has very high strength at high temperature, as well as extremely good ductility and cold working properties. It is therefore a very useful high-temperature material. Rhenium is a very heat-resistance metal, provided it does not come in contact with oxidizing agents. It is practically insoluble in hydrochloric and hydrofluoric acids. In oxidizing acids, it dissolves to form perrhenic acid.

Rhenium forms volatile oxides with oxygen at high temperature. In air at 350°C , the heptoxide, Re_2O_7 , is formed. The stability of rhenium metal components is limited due to oxide formation. When rhenium is heated with fluorine or chlorine, the fluorides or chlorides are formed. Rhenium

reacts with silicon, boron, and phosphorus at elevated temperature to form silicides, borides, and phosphides, respectively.

USES

Rhenium is highly desirable as an alloy addition to other refractory metals; such addition greatly enhances ductility and tensile strength even after heating above the re-crystallization temperature. Rhenium alloys are gaining acceptance in nuclear reactors, semi-conductors, electronic tube components, and other commercial and aerospace applications.

Tungsten-rhenium alloys are used to surface molybdenum targets in x-ray tube manufacture. Other rhenium alloys (with tungsten or molybdenum) are used for filaments, grid heaters, cathode cups, and ignitor wires in photo-flash bulbs. Surprisingly, the most important use of rhenium is as a chemical rather than as a metal. Rhenium has found important applications in catalysts for such processes as alkylation, dealkylation, dehydrochlorination, dehydrogenation, dehydroisomerization, hydrocracking, hydrogenation, oxidation, and reforming. The outstanding property of rhenium catalysts is their high selectivity particularly in hydrogenation reactions. They also display unusually high resistance to such catalyst poisons as nitrogen, sulfur, and phosphorus.

When rhenium is used as an alloying component with the metals tungsten and molybdenum, which are difficult to work, ductility and strength are improved. This is caused by alloy softening, which is defined as the reduction in the yield stress or hardness at low temperature. This effect is observed especially in body-centered cubic alloys. In addition to the improvement in ductility at low temperature, the strength at high temperature increases. Tungsten rhenium alloys containing 25-30% Re have good cold ductility. Rhenium is soluble in tungsten, its solubility reaching 28% at 1600°C and 37% at 3000°C. Tungsten is also soluble in rhenium: 11% at 1600°C and 20% at 2825°C.

The addition 1-3% Re to a nickel-base alloy improves its toughness at high temperature and prevents fatigue fracture. Such alloys are used mainly in the production of aircraft turbine blades. They are monocrystalline and have high strength and resistance to oxidation. When these turbine blades are used in the hot zones of an engine, operating temperature can be increased, giving higher efficiency (lower fuel consumption). Similar effects are achieved by coating the gas turbine blades with rhenium-containing (1-20% Fe).

Rhenium in the form of the powdered metal or pellets is incorporated into alloys by various methods. The W-Re and Mo-Re alloys are used mainly in the manufacture of thermo-elements. Other uses include semiconductors, heating elements, electrical and electronic applications, high-temperature welding rods, and metallic coatings. Tungsten-rhenium alloys (W5Re, W10Re) are used in the manufacture of rotating X-ray anodes.

The largest world reserves of rhenium are located in Chile which is today the world's largest producer. Other producers include Germany, Commonwealth of Independent States, Sweden, the United States, and Japan. In Germany, rhenium is obtained from molybdenum concentrates, spent catalysts, and rhenium-containing scrap, and processed to produce high-purity NH_4ReO_4 , HReO_4 , and Re metal powder or pellets. The largest consumer of rhenium is the United States, which imported ca. 15 t of rhenium in 1990. Rhenium is used for aircraft turbine blades (60%), reforming catalysts (30%), and other applications (10%).

9.5 Technetium

Masurium	997	Preparation	999
The cyclotron	997	Conclusion	1001
Spontaneous fission	998		

MASURIUM

In the same paper announcing the discovery of rhenium Tacke, Noddack, and Berg also announced the discovery of the other missing element in the manganese group, because the X-ray spectrum of rhenium always showed some weak lines of another element. They called it masurium after Masuria, a district in Eastern Prussia (now in Poland), famous for its lakes, and from where Walter Noddack originates. While Ida Noddack was able to isolate few milligrams of rhenium she was unable to do the same thing for masurium. The discovery was also contested by many chemists because of the absence of strong evidence.

THE CYCLOTRON

Few years later, in 1937, the Italian physicists Emilio Segrè (1905-1989) (Figure 9.5.1) and C. Perrier announced the detection of the element with atomic number 43 in trace amounts in a molybdenum target which has been bombarded in the cyclotron for several months with a strong deuteron beam. They called this new element technetium deriving the name from the Greek word for “artificial”. In 1940, element 43 was found among the fission products of uranium, and since then larger amounts were isolated from this source and studied.



Figure 9.5.1 - Emilio Segrè (1905-1989)

SPONTANEOUS FISSION

In 1961, Kenna and Kuroda suspected and detected element 43 in uranium minerals due to the phenomenon of *spontaneous fission*, a phenomenon that was already predicted by physicists in 1940. During 1972, research workers of the French Commissariat à l'Energie Atomique made an astonishing discovery: fission chain reactions had been triggered spontaneously in the very remote past within a uranium deposit in Gabon and parts of the deposit had behaved like a modern nuclear reactor for hundreds of thousands of years. Subsequent investigations showed that the reaction sites had remained in a remarkable state of preservation, so that detailed study was possible.

The discovery began with the observation of a very slight isotopic anomaly in a natural uranium sample during a routine analysis in the laboratory. A series of checks was carried out. Then, when these had revealed other anomalous samples, a systematic program was started, to find the origin of what was thought to be artificial contamination.

It was discovered that uranium ore with a concentration of fissionable nuclei below the normal had been received from Gabon, and inquiries revealed that it came from the Oklo deposit. In addition, it was found

that large amounts of the depleted ore had already been supplied to the nuclear industry. Fission products discovered in the ore pointed clearly to the origin of the anomaly. It was decided, accordingly, that the part of the deposit yielding anomalous uranium should be reserved for scientific research. Parts of the reaction sites were studied in detail through boreholes and sampling.

Of the two principal isotopes of uranium, which are naturally radioactive, U^{235} has a shorter half-life than U^{238} (7.1×10^8 years as against 4.51×10^9 years). Consequently, the concentration of U^{235} in natural uranium is decreasing constantly with time; in the very remote past it was much higher than it is now (3.65% two thousand million years ago as against 0.72 % now). It was therefore suggested some time ago that fission chain reactions might have been triggered spontaneously within uranium deposits in the very remote past, given the existence of certain conditions: high concentrations of uranium, the absence of strongly neutron-absorbing elements, and the presence of water.

PREPARATION

As it is known today technetium does not occur in nature and it is radioactive; fourteen isotopes of this element with atomic masses ranging from 92 to 105 are known. Technetium 97 g has a half-life of 2.6×10^6 years, and Tc 98 has a half life of 1.5×10^6 years.

First obtained by irradiation of molybdenum with deuterons at the Berkeley cyclotron. The isotope ^{93}Tc ($t_{1/2} = 4.2 \times 10^6$ years) is the longest-lived isotope but it cannot be obtained in weighable amounts. The isotope ^{99}Tc ($t_{1/2} = 2.14 \times 10^5$ years) is obtained by fission of ^{235}U with thermal neutrons in about 6 % yield and used for chemical and physical studies of the metal. This corresponds to formation of 2.8 g technetium per day and 100 MWth power of a nuclear reactor (i.e., about 30 kg/year in a modern 1300 MWe nuclear power reactor). ^{99}Tc can be recovered from high active waste solutions after reprocessing of spent fuel by the PUREX process.

The most important technetium isotope, however, is ^{99m}Tc ($t_{1/2} = 6$ hours) which is currently the most frequently used radionuclide in nuclear medicine. Due to its short half-life, it must be separated from its mother nuclide ^{99}Mo ($t_{1/2} = 66$ hours) by the use of a generator at the place of application. Several types of $^{99}\text{Mo}/^{99m}\text{Tc}$ generators exist which can supply sterile ^{99m}Tc in high purity and good yield, e.g., by elution of technetium with NaCl solution from an alumina column loaded with ^{99}Mo . ^{99}Mo itself can be produced in a nuclear reactor.

The second type of production is preferred because it yields ^{99}Mo with a high specific activity so that the eluted ^{99m}Tc is obtained in high concentration. In contrast, the product of ^{98}Mo irradiation only delivers ^{99}Mo with a much lower specific activity and, therefore, requires larger generators. Nowadays, an adequate supply of ^{99m}Tc is provided by the so-called ^{99m}Tc generators. These generators are efficient and reliable and differ principally from common generators in the technique of separating technetium from molybdenum. Technetium is hexagonal close-packed has a melting point 2250°C and density 11.47.

The chemical properties of technetium are more similar to rhenium than to manganese. Valency states between 1– and 7+ are known, the most stable ones being Tc (IV) and Tc (VII). Solid technetium is resistant to oxidation, but in sponge or powder form it is readily oxidized to the volatile heptaoxide when heated in air. The metal dissolves in dilute or concentrated nitric acid, concentrated sulfuric acid, and bromine water, but not in hydrochloric acid. It also dissolves in aqueous acid hydrogen peroxide solutions. It is oxidized by these solvents to pertechnetate, but in the case of bromine water $[\text{TcBr}_6]^{2-}$ is also formed. Contrary to rhenium, no heptafluoride of technetium is known - - only TcF_5 and TcF_6 are obtained. Sulfur reacts with technetium at elevated temperature to give the disulfide, and carbon to give TcC . Oxidation of technetium metal by oxygen at 500°C yields pale yellow Tc_2O_7 (m.p. 119.5°C , b.p. 310.6°C) which reacts with water vapor to form dark red HTcO_4 .

CONCLUSION

Pieter Van Assche a scientist at the Belgian Nuclear Research Establishment in Mol examined the experimental results of Tacke, Noddack, and Berg, and observed that masurium was reported only in those samples containing appreciable amounts of uranium and no masurium was found in samples which did not contain uranium. He came to the conclusion that masurium should have been present in these samples and attempted to rehabilitate Tacke, Noddack, and Berg. However, it is clear that this conclusion is erroneous, since even at 5% uranium in a sample the amount of masurium (technetium) is still unweighable and cannot be detected by any other method except radioactive measurements.

Kenna reported processing 3.5 kg of pitchblende containing 50% U and he obtained activity equivalent to 1×10^{-9} g technetium, i.e., a uranium ore containing 50% U will contain 0.3×10^{-3} ppb, hence a uranium ore containing 5% U will contain 0.03×10^{-3} ppb. This concentration is far beyond any other detection method. The question was settled by Kuroda (Figure 9.5.2) : Tacke, Noddack, and Berg did not discover masurium.



Paul Kazuo Kuroda (1917-2001)
Professor of Physics at the University of Arkansas

9.6 Francium

Francium, element 87 occurs in nature in minute amounts as the radioactive element ^{223}Fr ($t_{1/2} = 21.8 \text{ min}$) which is the most stable of all 27 isotopes. It decays into astatine, radium, and radon. Francium is only monovalent and shows a very similar behaviour to the other heavy alkali elements. It has the most negative standard potential of all elements.



Figure 9.6.1 - Marguerite Perey
(1909-1975)

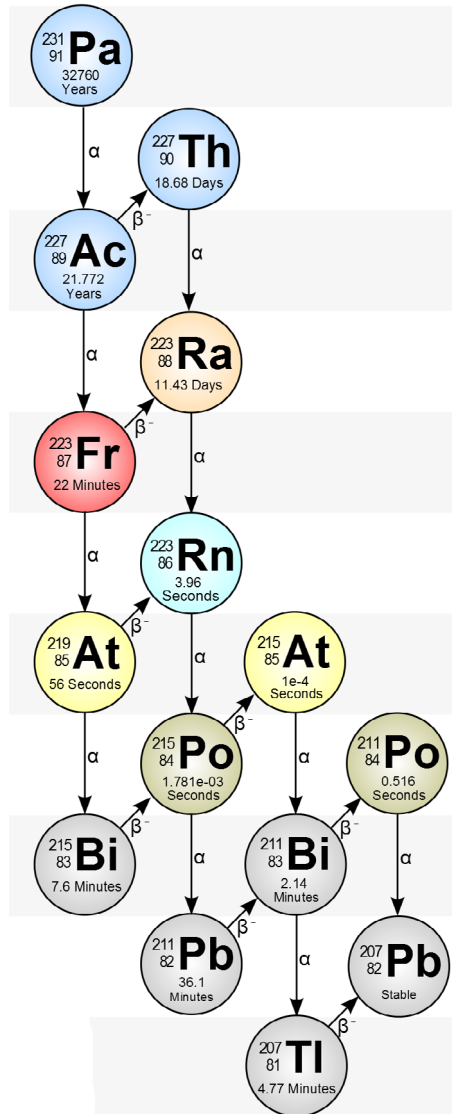


Figure 9.6.2 - Francium in the decay
chain of protactinium

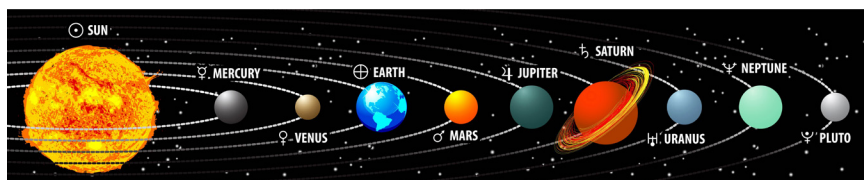
Relatively pure ^{223}Fr solutions are obtained by its elution with $\text{NH}_4\text{Cl} - \text{CrO}_3$ from a cation exchanger loaded with ^{227}Ac . The solution is further purified by passing it through a SiO_2 column loaded with BaSO_4 .

Francium was discovered in 1939 at Curie Institute in Paris, France by Marguerite Perey (1909-1975) (Figure 9.6.1) from which the element takes its name. It was discovered during the purification of a sample of actinium 227 (Figure 9.6.2). It was the last element discovered in nature. It is extremely rare, with trace amounts found in uranium and thorium ores, where the isotope francium-223 continually forms and decays.

9.7

Neptunium and Plutonium

Neptunium	1006	The metal and its compounds.....	1010
Plutonium	1009		



Solar system and naming of the elements

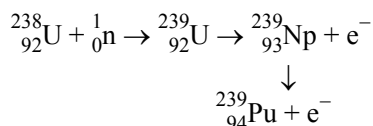
In 1934, Enrico Fermi (1901-1954) in Rome discovered that neutrons may be captured by atoms and that the frequency of capture increases when they are slowed down by passing them through a hydrogen-rich material such as paraffin or water. He was thus able to produce atoms of higher atomic weights than those bombarded. For example, on bombarding cobalt with neutrons he was able to produce nickel.

When, however, he and his coworkers bombarded uranium with neutrons, they obtained more than one radioactive product. Following the same line of thought as in their previous experiments they suggested that one of these products was formed by neutron capture, i.e., that it was a trans-uranium element or element number 93. Fermi put the new element under rhenium in the Periodic Table and called it eka-rhenium.

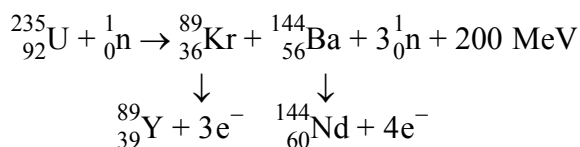
Fermi's experiments were repeated by Otto Hahn (1879-1968) and his coworkers in Berlin. They confirmed his conclusions and published a series of papers on extensive radiochemical separations of the so-called trans-uranium elements. The results, however, became so contradictory that after

five years of intensive research and extensive publication the concept of trans-uranium elements had to be abandoned.

Indeed uranium 238 absorbs neutrons forming uranium 239 which is a beta emitter with a short half-life. Its daughter neptunium 239 also emits an electron to form plutonium 239:



The previous experiments were further clouded by the fact that uranium also undergoes fission by slow neutrons. For example:



This is exactly what Ida Noddack suggested in 1934 when she commented on Fermi's experiments. Her argument was as follows: when atoms are bombarded by protons or alpha particles, the nuclear reactions that take place involve the emission of an electron, a proton, or a helium nucleus and the mass of the bombarded atom suffers little change. When, however, neutrons are used, new types of nuclear reaction should take place that are completely different from those previously known. She wrote that "*When heavy nuclei are bombarded by neutrons, it would be reasonable to conceive that they break down into numerous large fragments which are isotopes of known elements but are not neighbours of the bombarded elements*". This was confirmed later in 1939 and became known as fission.

NEPTUNIUM

The element was first synthesized by Edwin McMillan (1907-1991)

and Philip H. Abelson (1913-1004) (Figures 9.7.1-9.7.2) at the Berkeley Radiation Laboratory, California in 1940 by bombarding uranium by slow neutrons in a cyclotron. The team produced the neptunium isotope ^{239}Np (2.4 day half-life). Neptunium is silvery metal which tarnishes when exposed to air. It occurs in three allotropic forms. It exhibits five oxidation states, ranging from +3 to +7 (Figure 9.7.3). Neptunium (VI) fluoride, NpF_6 , is volatile like uranium hexafluoride.

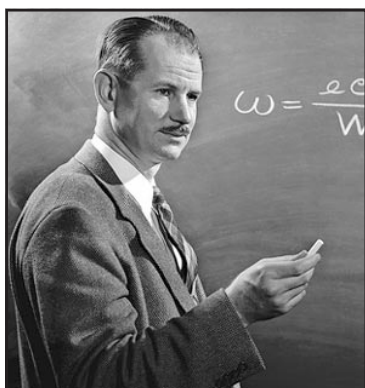


Figure 9.7.1 - Edwin McMillan
(1907-1991)



Figure 9.7.2 - Philip H. Abelson
(1913-1004)

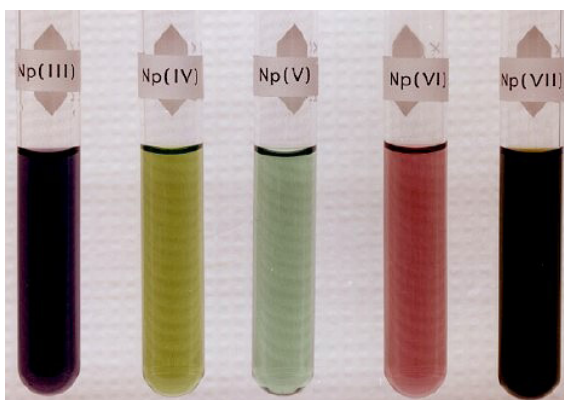
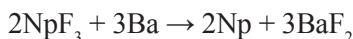


Figure 9.7.3 - Solutions of neptunium
(Courtesy of the University of California, Berkeley)

Neptunium has a unique decay chain ending with thallium and not lead as in the other series (Figure 9.7.4).

Neptunium 237 the most stable isotope is generated in nuclear reactors as a precursor for the formation of plutonium-238. It is extracted from spent nuclear fuel rods in kilogram amounts as a by-product in plutonium production. The metal is produced through a reaction of $^{237}\text{NpF}_3$ with barium or lithium at 1200°C:



It is found in at least three allotropes:

- α -neptunium, orthorhombic, density 20.45
- β -neptunium (above 280°C), tetragonal, density (313°C) 19.36
- γ -neptunium (above 577°C), cubic, density (600°C) 18

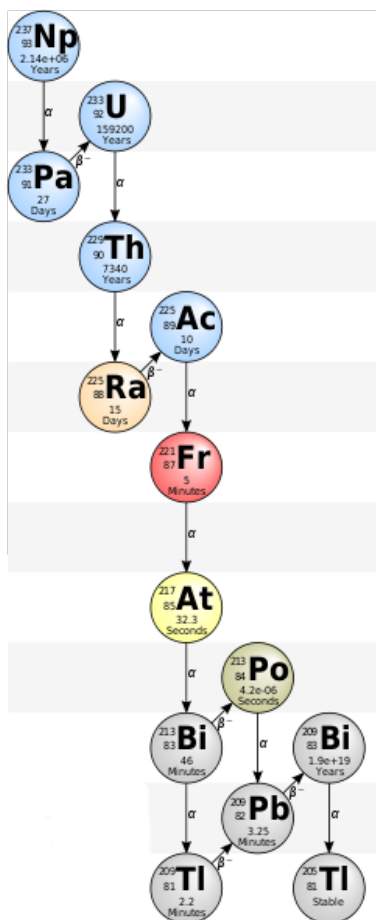


Figure 9.7.4 - Neptunium decay chain

Neptunium has the largest liquid range of any element: melting point 637°C and boiling point 4000°C. The isotopes neptunium-237 and neptunium-239 are also found in trace amounts in uranium ores due to neutron capture reactions and beta decay.

PLUTONIUM

Plutonium 238 was first produced and isolated on December 14, 1940, and chemically identified on February 23, 1941, by Glenn T. Seaborg (1912-1999), Edwin M. McMillan (1907-1991) (Figure 9.7.5), Joseph W. Kennedy (1916-1957) (Figure 9.7.6), and Arthur C. Wahl (1917-2006) (Figure 9.7.7) by

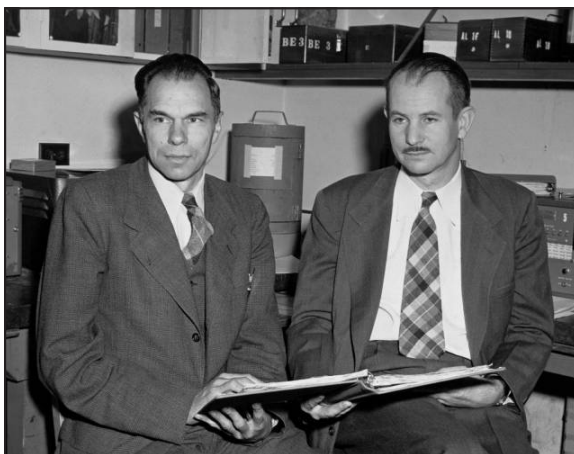


Figure 9.7.5 - Glenn T. Seaborg (1912-1999) and Edwin M. McMillan (1907-1991)

deuteron bombardment of uranium in the cyclotron at the University of California, Berkeley. The first atomic bomb test, code named “Trinity” and detonated on July 16, 1945, near Alamogordo, New Mexico, used plutonium as its fissile material. The bomb that destroyed Nagasaki had also a plutonium core. It was only after the dropping of the first atomic bomb in Japan that the existence of plutonium was made public.



Figure 9.7.6 - Joseph W. Kennedy (1916-1957)



Figure 9.7.7 - Arthur C. Wahl (1917-2006)

During World War II the US government established the Manhattan Project to develop an atomic bomb. The three primary research and production sites of the project were the plutonium production facility at what is now the Hanford Site, the uranium enrichment facilities at Oak Ridge, Tennessee, and the weapons research and design laboratory, now known as Los Alamos National Laboratory. The first production reactor that made plutonium-239 was the X-10 Graphite Reactor. It went online in 1943 and was built at a facility in Oak Ridge that later became the Oak Ridge National Laboratory.

Plutonium 239 (half life 2.4×10^4 years) is an alpha emitter and undergoes fission with the emission of several neutrons and can maintain a chain reaction. Thus, a nuclear reactor using uranium as a fuel, not only produces energy, but also produces another nuclear fuel. Under certain conditions it is possible to generate fissionable material at a rate equal to or greater than the rate of consumption of the uranium. Such a reactor is known as a *breeder reactor*. Plutonium-238 has a half-life of 88 years and emits alpha particles.

The metal and its compounds

Plutonium is silvery-gray appearance that tarnishes when exposed to air. It exhibits six allotropes and four oxidation states (Figure 9.7.8). When exposed to moist air, it forms oxides and hydrides that expand the sample up to 70% in volume, which in turn flake off as a powder that can spontaneously ignite. It is radioactive and can accumulate in the bones.

Fifteen isotopes of plutonium have been synthesized; long-lived isotopes. About 400 tonnes of plutonium have been produced in nuclear power stations excluding the former Eastern-bloc countries. The ^{239}Pu stockpiled in weapons is estimated to exceed 100 tonnes. About 10 tonnes of plutonium are distributed on earth as a result of military activities (bomb tests, satellite accidents, bombers, rockets, etc.) and releases from nuclear facilities.

Plutonium oxide, PuO_2 , is used for the production of the metal by reduction with calcium. Its half life is 2.4×10^4 years and decays by α -emission. No less than five phases existed in the metal between room temperature and the melting point, with densities between 15.9 and 19.8. Plutonium 239 melts at 639.5°C . Since plutonium is highly toxic all work had to be done in glove-boxes (Figure 9.7.9) and an elaborate ventilation system. Today, a large supply of plutonium is stored under strictly-controlled conditions at Rocky Flats in Colorado (Figure 9.7.10).



Figure 9.7.8 - Solutions of plutonium
(Courtesy of the University of California,
Berkeley)

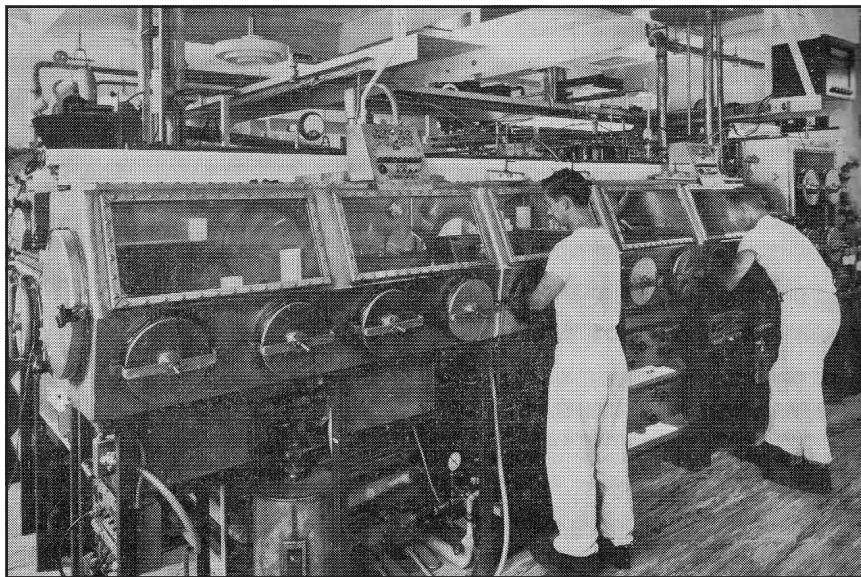


Figure 9.7.9 - Handling plutonium in dry boxes

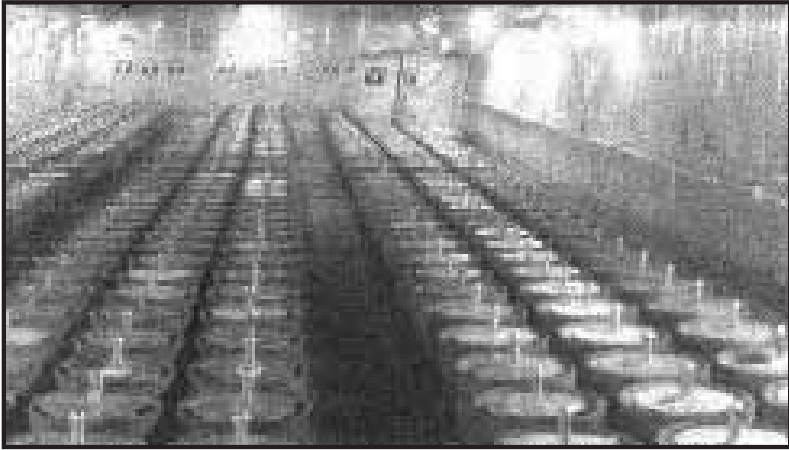


Figure 9.7.10 - Plutonium storage facility in USA

Plutonium from spent nuclear fuel is recovered by extraction with tri-n-butyl phosphate. Recovery by electrorefining from molten alkali-metal and alkaline earth metal chlorides is an alternative for metallic fuels. Plutonium metal is prepared from its oxide by reduction with calcium in molten CaCl_2 or $\text{CaCl}_2\text{--CaF}_2$.

9.8 Promethium

The metal promethium, the last member of the rare earths, was named after Prometheus (Figure 9.8.1), the Titan in Greek mythology who stole fire from Mount Olympus and brought it down to humans, to symbolize both the daring and the possible misuse of mankind's intellect - - the atomic energy.



Figure 9.8.1 - Prometheus

In 1902, the Czech chemist Bohuslav Brauner (1855-1935) (Figure 9.8.2) suggested that there should be an element with properties intermediate between those of neodymium and samarium (Figure 9.8.3). This was confirmed in 1914 by Henry Moseley who, having measured the atomic numbers of all the elements then known, found there was no element with atomic number 61.



Figure 9.8.2 - Bohuslav Brauner (1855-1935)

Ce	Pr	Nd		Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
58	59	60	61	62	63	64	65	66	67	68	69	70	71

Figure 9.8.3 - Element 61 missing in the rare earths

Promethium does not occur in nature, it was first produced and characterized at Oak Ridge National Laboratory in 1945, by Jacob A. Marinsky (1918-2005) (Figure 9.8.4), Lawrence E. Glendenin (1918-2008) (Figure 9.8.5), and Charles D. Coryell (1912-1971) (Figure 9.8.6) by separation and analysis of the fission products of uranium fuel irradiated in the graphite reactor. However, due to military-related research during World War II, they did not announce their discovery until 1947. A sample of the metal was made only in 1963.



Figure 9.8.4 - Jacob A. Marinsky (1918-2005)

Promethium can be formed in nature as a product of spontaneous fission of uranium-238. Only trace amounts can be found in naturally occurring ores. It is synthesized by bombarding enriched uranium with thermal neutrons. The most stable isotope of the element is promethium-145, which has a half-life of 17.7 years via electron capture.



Figure 9.8.5 - Lawrence
E. Glendenin (1918-2008)



Figure 9.8.6 - Charles D. Coryell
(1912-1971)

Promethium has a double hexagonal close packed structure. This low-temperature alpha form converts into a beta, body-centered cubic phase upon heating to 890°C. Promethium compounds tend to be pink or red in color. Treatment of acidic solutions containing Pm^{3+} ions with ammonia results in a gelatinous light-brown sediment of hydroxide, $\text{Pm}(\text{OH})_3$. The sulfate is slightly soluble, like the other cerium group sulfates.

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