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Review Article

Metals and Metallurgy

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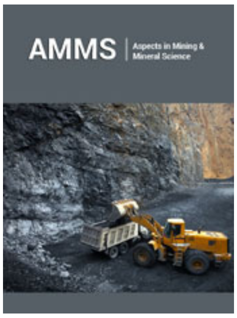
ISSN: 2578-0255



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Submission: March 20, 2019

Published: May 29, 2019

Volume 3 - Issue 1

How to cite this article: Fathi H. Metals and Metallurgy. Aspects Min Miner Sci.3(1). AMMS.000551.2019.
DOI: 10.31031/AMMS.2019.03.000551.

The Commercial Classification of Metals

Elements can be arranged conveniently in the Periodic Table and described as metals, non-metals, and metalloids. Metals are further classified as typical and less typical, transition and inner transition (Figure 1). While this classification is useful for the chemists and physicists it does not show the economic value of the metals. For the metallurgist however, a more useful form is the commercial classification of metals: ferrous and nonferrous (Figure 2). This classification is well justified because the annual production of iron and steel in one year exceeds the production of all other metals combined in about ten years. Ferrous metals include wrought iron, cast iron, and steel. Nonferrous metals, on the other hand, is classified into primary, secondary, light, precious, etc., as shown in (Table 1).

Table 1: Commercial classification of nonferrous metals and metalloids.

Group	Metals	Remarks
Primary	Cu, Pb, Zn, Sn, Ni	Extensively used; second in importance to iron.
Secondary	As, Sb, Bi, Cd, Hg, Co	Mainly by-products of the major metals but also form their own deposits. Used in almost equal amounts (10-20 thousand tons annually).
Light	Be, Mg, Al, Ti	Low specific gravity (below 4.5), used mainly as material of construction.
Precious	Au, Ag, Pt, Os, Ir, Ru, Rh, Pd	Do not rust; highly priced.
Refractory	W, Mo, Nb, Ta, Ti, Zr, Hf, V, Re, Cr	Melting points above 1650 °C. Mainly used as alloying elements in steel but also used in the elemental form. Some resist high temperature without oxidation.
Scattered	Sc, Ge, Ga, In, Tl, Hf, Re, Se, Te	Do not form minerals of their own. Distributed in extremely minute amounts in the earth's crust.
Radioactive	Po, Ra, Ac, Th, Pa, U, Pu	Undergo radioactive decay. Some of them (U, Pu, and Th) undergo fission. Plutonium prepared artificially in nuclear reactors.
Rare earths (lanthanides)	Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	Always occur together, similar chemical properties. Not rare as the name implies.
Ferroalloy	Cr, Mn, Si, B	Were once mainly used as alloying elements to steel, but now also used in elemental form.
Alkali	Li, Na, K, Rb, Cs	Soft and highly reactive.
Alkaline earths	Be, Mg, Ca, Sr, Ba	Beryllium is more similar to aluminum, and magnesium is more similar to lithium (Diagonal similarities)

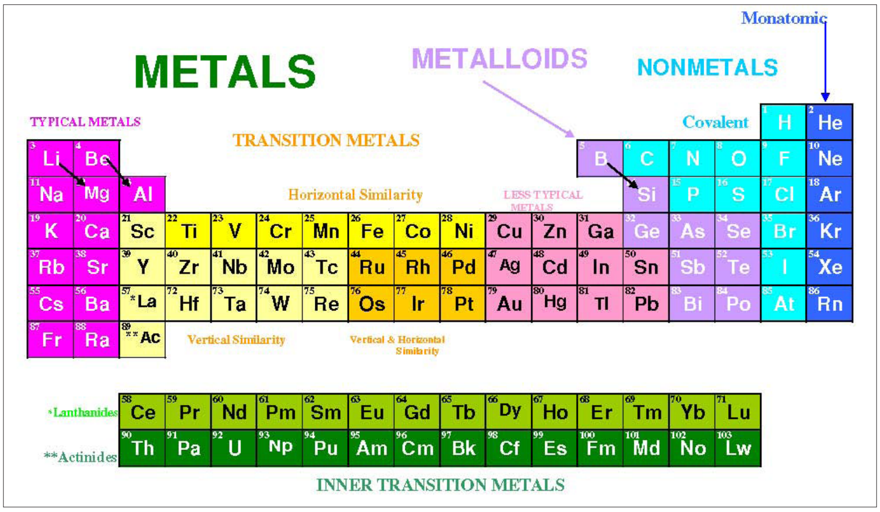

Figure 1: Periodic table showing metals, nonmetals, and metalloids and the different types of metals.

Figure 2: Ferrous and nonferrous metals.

Discovery of Metals

Seven metals were used by the ancient people, then in the Middle Ages the alchemists knew aqua regia for dissolving gold and in the 13th and 14th centuries three metalloids: arsenic, antimony, and bismuth were discovered. The East supplied two metals: zinc and boron in form of borate. The bulk of metals became known in the 17th and 18th centuries.

Smelting

In the 17th 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 [1], 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:

Ore (oxide)+Phlogiston (from coal) →Metal

It was the French chemist Antoine Laurent Lavoisier (1743-1794) 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.

Tools of Discovery

The platinum metals became known in Europe from Ecuador in South America and this was followed by many other metals (Table 2). The blowpipe (Figure 3) played an important role in the discovery. In the 19th century the metals discovered was a result of the discovery of electric current and the development in analytical chemistry and chemical theory.

Table 2: 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_30_8 with carbon. Infact 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	Titani-um	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	Berylli-um	Vauquelin	Isolated by Wöhler and Bussy in 1828 by the reduction of the fluoride with sodium.
1797	Chro-mium	Vauquelin	Isolated by Wöhler in 1859 by reducing molten chromium chloride with zinc

It was Robert Bunsen (1811-1899) at the University of Heidelberg, who paved the way for the great discoveries in the 19th century (Table 3) with his invention of the burner in 1852 that carries his name and is found today in most chemical laboratories (Figure 4). This burner permitted higher temperature to be achieved in the laboratory when conducting a test. Before this burner [2] the flame of a candle or from alcohol was used. The Bunsen burner flame permitted performing the flame tests (Figure 5) and later spectroscopic analysis (Figures 6 & 7).

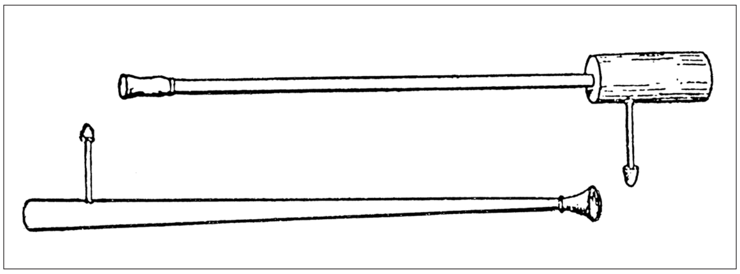

Figure 3: The blowpipe.

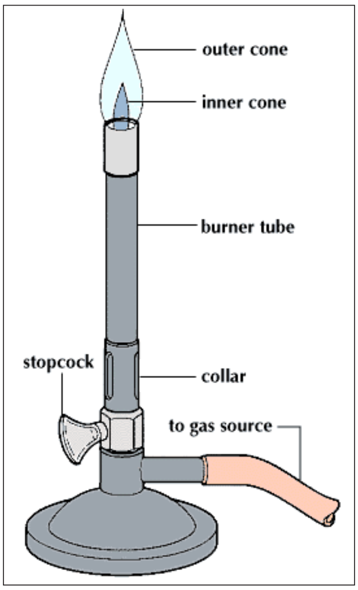

Figure 4: Bunsen burner.

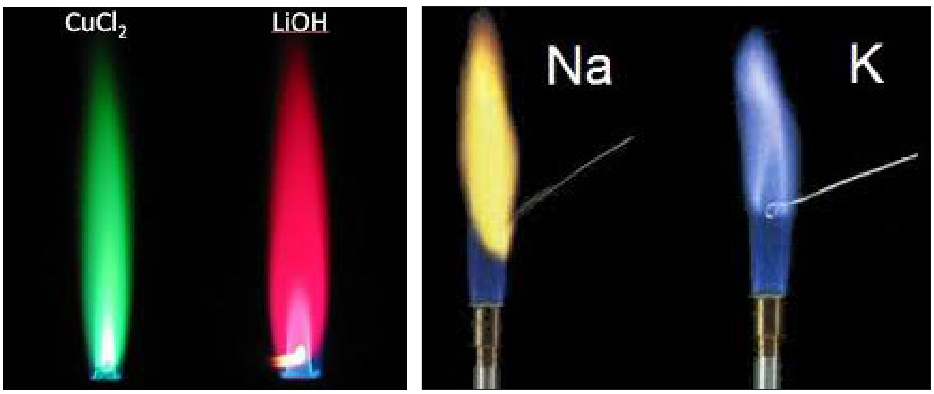

Figure 5: Examples of coloured flames in flame tests.

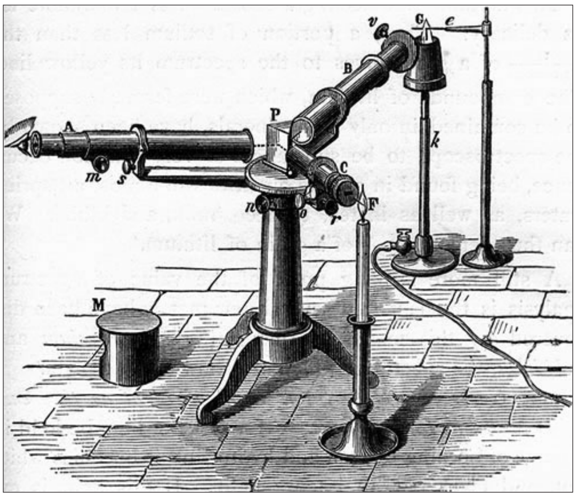

Figure 6: A first spectroscope.

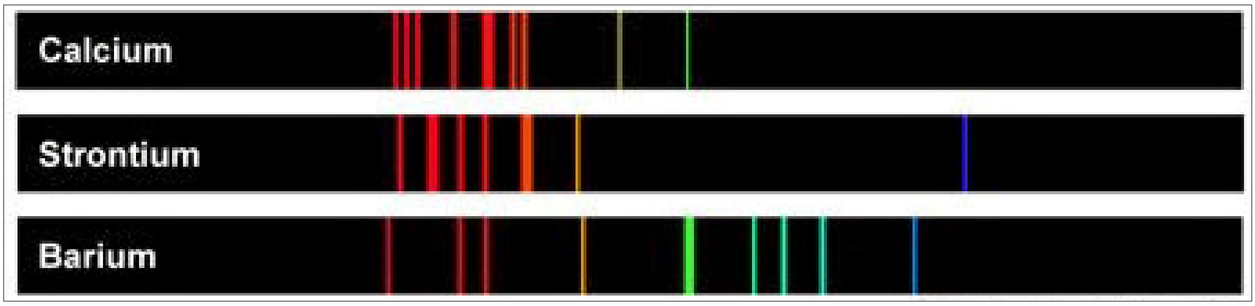

Figure 7: Examples of emission spectra: calcium, strontium, and barium.

Table 3: Metals discovered and isolated in the nineteenth century.

Year	Metal	Discoverer	Remarks
1801	Niobium	Hatchett	Isolated by Blomstrand in 1864 by reduction of $NbCl_5$ with H_2 and by Moissan in 1901 by carbon reduction of Nb_20_5 in an electric furnace
1802	Tantalum	Ekeberg	Discovered in Sweden
1803	Iridium	Tennnat	Discovered in England
	Osmium		
	Palladium	Wollaston	Discovered in England
	Rhodium		
1807	Potassium	Davy	Discovered in England
	Sodium		
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	Discovered in Germany
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	Praseodym-ium	Auer von Welsbach	Discovered in Austria
	Neodymuim	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 Industrial Production of Aluminum

A great technological advance was the invention of the dynamo in the 1870's that made available electricity in bulk which encouraged the expansion of electrolytic copper refining to supply the pure copper needed for the electrical industry. Another important application of electricity was in the electrolytic production of aluminum. Once aluminum was available inexpensively, it was used for reducing other oxides to metals. Thus, chromium and manganese were prepared a few years later by this technique.

X-Rays and Radioactivity

In 1895 x-rays were discovered by Wilhelm Conrad Roentgen (1845-1923) followed by the discovery of radioactivity in 1898 by Antoine Henri Becquerel (1852-1908) which was responsible for the discovery of polonium and radium [3] shortly afterwards by Marie Curie (1867-1934). A year later, André Debièrne (1874-1949) a co-worker with Curie discovered and isolated actinium.

Metals of the Twentieth Century

Elements discovered in the 20th century are those which are very rare or do not occur in nature (Table 4). Elements beyond plutonium were discovered at the Lawrence Radiation Laboratory, University of California from 1944 to 1961 by Seaborg, McMillan, and Ghiorso:

A. 1944, americium and curium

B. 1949, berkelium

C. 1950, californium

D. 1952, einsteinium

E. 1956, nobelium

F. 1961, lawrentium

Table 4: Twenty century metals.

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

Development of Radiochemistry

Radiochemists played an important role in separating the individual radioelements, their identification, and their arrangement in series. New methods of measurements such as the Geiger counter and the gamma scintillation counter replaced the gold leaf electroscope. Radiations from radioactive substances were identified as alpha, beta, and gamma. As a result, two very rare radioactive metals: protactinium and francium were discovered. Protactinium was discovered in 1917-18 by Otto Hahn (1879-1968) and Lise Meitner (1878-1968) in Germany the new element was part of the decay chain of uranium-235.

Francium was discovered in 1939 at Curie Institute in Paris, France by Marguerite Perey (1909-1975) from which the element takes its name. It was discovered during the purification of a sample of actinium 227. It is extremely rare, with trace amounts found in uranium and thorium ores, where the isotope francium-223 continually forms and decays.

The Discovery of Lutetium

Lutetium, element 71, was discovered spectroscopically in 1907 by the French chemist Georges Urbain (1872-1938) (Figure 3) who named it after Lutia the Roman name of the place where Paris was founded. It was identified by Bohr as a rare earth and not as a member of Group IV.

Quantum Theory

The quantum theory by Max Planck (1858-1947) 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. This allowed the understanding of the movement of electrons [4] in the atom by Niels Bohr (1885-1962), the hypothesis of the formation of electron shells, and the explanation of emission spectra.

Electronic Structure of Rare Earths

In 1922 Bohr elucidated the electronic structure of the rare earths. 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 behavior. Bohr concluded that element 72 which occurs after lutetium must be tetra-valent rather than trivalent and must belong to the zirconium family and not the rare earths. He advised his co-workers in his laboratory to search for this element in zirconium ores.

X-Ray Analysis

X-ray spectrum analysis by Henry Moseley (1887-1915) in 1914 led to the discovery of two metals: hafnium and rhenium.

Discovery of The Neutron

James Chadwick (1891-1974) in Cambridge in 1932 explained the experiments of Frédéric Joliot (1900-1958) and Irène Curie (1897-1957) in Paris 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.

Neutron Capture

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 (Figure 8).

																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	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	*43*	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	*85*	Rn
87	Ra	Ac	Th	Pa	U	*93*											
	†	Ce	Pr	Nd	*61*	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		

Figure 8: Eka-rhenium according to Fermi, 1934.

Fermis' paper naturally attracted the attention of Ida Noddack the discoverer of rhenium because it dealt with another element in the manganese group. Soon afterward, she published a paper which showed that Fermi's experimental evidence was incomplete. 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 It would be reasonable to propose that they break down into numerous large fractions. Here she conceived the idea of nuclear fission.

Discovery of Uranium Fission

Fermi's experiments were repeated by Otto Hahn (1879-1968) and his coworkers in Berlin. They confirmed Fermi's 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. Hahn could not accept the new idea that the uranium atom was split into two fragments. It was Lise Meitner in Sweden 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) of the University of California, Berkeley, where it was first operated in 1932. By its means technetium and the trans-uranium metals were discovered. In 1937 the Italian physicists Emilio Segrè (1905-1989) and his co-worker 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".

Transuranium

After elucidating the electronic structure of the trans-uranium which resembled that of the lanthanides, Seaborg (1912-1999) proposed a second series of inner transition metals similar to the lanthanides that became known as "actinides". He changed the Periodic Table of 1945. Thus, uranium was removed from Group VI to become a member of this new group.

Promethium

The existence of a rare earth element between neodymium and samarium was predicted by Brunauer. 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. This element was discovered by Glendenin, Marinsky, and Coryell in 1945 at Oak Ridge National Laboratory in uranium fission products and named "promethium". Promethium does not occur in nature.

Metallurgy in the Past Decades

Word War II ended by the use of atomic bomb. The bomb was the result of Manhattan Project in USA in 1940s which played an important role in developing extractive metallurgy for the production of uranium. It was responsible for advancing the technology of metallothermic reactions, introducing new leaching processes, new precipitation methods, new reagents, ion exchange technology, and solvent extraction.

For the peaceful uses of atomic energy, uranium and trans-uranium elements were thoroughly studied, and the chemistry of other metals such as beryllium, boron, cadmium, zirconium, hafnium, rare earths, etc., became widely known. For the sake of conveniently outlining these developments, extractive metallurgy is divided into three sectors: pyro-, hydro-, and electrometallurgy. However, it is not possible to separate the three sectors since in general all three may be involved in the recovery of a particular metal.

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