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Scandium

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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) in 1878 by spectroscopic analysis of the minerals euxenite and gadolinite, which had not yet been found anywhere except in Scandinavia. By processing 10 kg of euxenite and other residues of rare-earth minerals, Nilson was able to prepare about 2 *q* 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) who later pointed out that Nilson's scandium was identical with Mendeleev's eka-boron.

S candium has a unique position in the modern Periodic Table. 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 alumi-



Lars Fredrik Nilson (1840-1899)

num. 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.

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.

Occurence

Scandium is widespread in nature but in small concentrations; its relative abundance is 5 x 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, Sc3+, has ionic radius close to that of Fe2+, Mg2+, Ti4+, and Zr⁴⁺ thus isomorphism is possible. The only naturally occurring isotope of scandium is ⁴⁵Sc.

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 $(Sc,Y)_2Si_2O_7$.

Bazzite: $Be_3(Sc,Al)_2Si_6O_{18}$ is another silicate mineral containing scandium discovered in 1915.

Euxenite: (Y,Ca,Ce,U,Th)(Nb,Ta,Ti)₂O₆ 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: $(Ce,La,Nd,Y)_2FeBe_2Si_2O_{10}$ 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, known as TBP is an effective extractant from chloride solutions, while the other rare earth



Per Teodor Cleve (1840-1905)

elements are hardly extracted. Organophosphoric acids such as diethylhexyl phosphoric acid, known as D2-EHPA are much more effective extractants for scandium than for the other rare earth elements.

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, 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% Sc₂O₃ and 20% ThO₂. High purity scandium oxide was then prepared in multi-pound lots by chemical separation techniques.

Extraction from wolframite

Wolframite, (Fe,Mn)WO₄, 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, H₂WO₄, 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 tita-

nium ore to a fluidized bed chlorinator at about 1000 °C to produce a vapors of TiCl₄ and FeCl₃. 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:

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2 ScF<sub>3</sub> + 3 Ca \rightarrow 2 Sc + 3 CaF<sub>2</sub>
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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 AI-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 AI-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.

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