#108 May 2011

ELECTRONIC METALS

AND RARE EARTH OXIDES

Barton G. Stone
Chief Geologist, PAH

Several years ago, the author used a historic 15th century Portuguese bookcover in a college lecture. The picture illustrated the dangers of world exploration with a two mast sailing ship breaking up near shore, and all the crew jumping overboard to swim to safety. The picture illustrated nails from the ship's construction being pulled into the water by the magnetic forces of a submarine magnetite outcrop (lodestone). At that time, the earth's magnetic field was just becoming more familiar to some elements of Portuguese society and the artist and author obviously included this fiction as a potential threat for explorationists.

The remarkable and sometime magical characteristic of some metals and minerals has always been of fascination to mankind. We now know that the effect of sunshine on tellurium metal will create an electric current in the metal which can be harnessed for use in solar energy panels. The discovery, in the 20th Century, that cesium is an essential material for photo-electrical devices allowed the problem of television to be practically solved. The use of gallium in lamps allows a light to transmit which is very similar to natural sunlight.

Pincock Allen & Holt (PAH) in the past ten years have had numerous opportunities to evaluate and examine some of the more exotic metal and mineral deposits belonging to a group of metals which are referred to as "electronic metals." Although both gold and silver would typically be included because of their superior conducting properties, they have been left out because they are well described elsewhere. The author is indebted to the staff and senior scientists of the United States Geological Survey who maintain an annual yearbook "Minerals Information" of all of the metal groups and elements' usage, and from whom much of this material has been collected. Additional contributions have come from A. Betekhtin's classic Russian textbook "A Course of Mineralogy." The author would like to thank his employer for the opportunity to collect and assimilate internal files for this Perspective article.

Beryllium (Be) is one of the lightest of all metals and has one of the highest melting points of any light metal. Beryllium metal is used principally in aerospace and defense applications because of its stiffness, light weight, and dimensional stability over a wide temperature range. Beryllium-copper alloys are used in a wide variety of applications because of their electrical and thermal conductivity, high strength and hardness, good corrosion and fatigue resistance, and nonmagnetic properties. Beryllium oxide is an excellent heat conductor, with high strength and hardness, and acts as an electrical insulator in some applications. The United States supplies most of the rest of the world with these products.

Bismuth (Bi) is mainly a byproduct of lead ore processing. It has a metallic luster and is silver-white with an iridescent tarnish. Among the heavy metals, it is the heaviest and the only non-toxic. Bismuth has been used in solders, a variety of other alloys, metallurgical additives, medications, and in atomic research. In the early 1990s, research began on the evaluation of bismuth as a nontoxic replacement for lead in such uses as ceramic glazes, fishing sinkers, food processing equipment, free-machining brasses for plumbing applications, lubricating greases, and shot for waterfowl hunting. The USA is entirely dependent on imports for all of its required bismuth.

Cadmium (Cd), a soft, malleable, ductile, bluish-white metal, was discovered in Germany in 1817, and Germany remained the only important producer for 100 years. Cadmium is generally recovered as a byproduct from zinc concentrates. Zinc-to-cadmium ratios in typical zinc ores range from 200:1 to 400:1. Sphalerite (ZnS), the most economically significant zinc mineral, commonly contains minor amounts of other elements; cadmium, which shares certain similar chemical properties with zinc, will often substitute for zinc in the sphalerite crystal lattice. A significant amount of cadmium is also recovered from spent nickel cadmium batteries.

Cadmium is primarily consumed for the production of rechargeable nickel cadmium batteries; other end uses include pigments, coatings and plating, and as stabilizers for plastics. Solar cell manufacturing may become another significant market for cadmium in the future. Cadmium telluride thin-film photovoltaics are an alternative to the traditional silicon-based solar cells and are a preferred photovoltaic technology for commercial rooftop applications and for large-scale, ground-mounted utility systems.

Cesium (Cs), the most electropositive and least abundant of the five naturally occurring alkali metals, was discovered spectroscopically in 1860. The first cesium metal was produced in 1881. Because cesium is not mined domestically, the United States is completely dependent on imports. Historically, the most important use for cesium has been in research and development, primarily in chemical and electrical applications.

Cobalt (Co) is a metal used in numerous diverse commercial, industrial, and military applications, many of which are strategic and critical. On a global basis, the leading use of cobalt is in rechargeable battery electrodes. Superalloys, which are used to make parts for gas turbine engines, are another major use for cobalt. Cobalt is also used to make airbags in automobiles; catalysts for the petroleum and chemical industries; cemented carbides (also called hardmetals) and diamond tools; corrosion- and wear-resistant alloys; drying agents for paints, varnishes, and inks; dyes and pigments; ground coats for porcelain enamels; high-speed steels; magnetic recording media; magnets; and steel-belted radial tires.

Niobium (Nb) and columbium are synonymous names for the chemical element with atomic number 41; columbium was the name given in 1801, and niobium (Nb) was the name officially designated by the International Union of Pure and Applied Chemistry in 1950. Niobium in the form of ferroniobium is used worldwide, mostly as an alloying element in steels and in superalloys. Appreciable amounts of niobium in the form of high-purity ferroniobium and nickel niobium are used in nickel-, cobalt-, and iron-base superalloys for such applications as jet engine components, rocket subassemblies, and heat-resisting and combustion equipment.

Gallium (Ga) is not produced in the United States, and demand is satisfied by imports, primarily high-purity material from France and low-purity material from Kazakhstan and Russia. More than 95% of gallium consumed in the United States is in the form of gallium arsenide (GaAs). Analog integrated circuits are the largest application for gallium, with optoelectronic devices [mostly laser diodes and light-emitting diodes] as the second largest end use.

Germanium (Ge) is mainly a byproduct of zinc ore processing. It is a hard, grayish-white element; it has a metallic luster and the same crystal structure as diamond; and it is brittle, like glass. In addition, it is important to note that germanium is a semiconductor, with electrical properties between those of a metal and an insulator. The development of the germanium transistor opened the door to countless applications of solid-state electronics. From 1950 through the early 1970s, this area provided an increasing market for germanium, but then high purity silicon began replacing germanium in transistors, diodes, and rectifiers. Meanwhile, demand for germanium in fiber optics communication networks, infrared night vision systems, and polymerization catalysts increased dramatically. These end uses represented 85% of worldwide germanium consumption for 2000. World germanium consumption has been greater than primary production in recent years, but releases of germanium from government stockpiles and increased recycling have provided adequate supply.

Indium (In) is produced mainly from residues generated during zinc ore processing. It was named after the indigo line in its atomic spectrum. The first large-scale application for indium was as a coating for bearings in high-performance aircraft engines during World War II. Afterwards, production gradually increased as new uses were found in fusible alloys, solders, and electronics. In the middle and late 1980s, the development of indium phosphide semiconductors and indium-tin-oxide thin films for Liquid Crystal Displays (LCD) aroused much interest. By 1992, the thin-film application had become the largest end use. The amount of indium consumed is largely a function of worldwide LCD production. Increased manufacturing efficiency and recycling (especially in Japan) maintain a balance between demand and supply.

Mercury (Hg) is the only common metal that is liquid at room temperature. It occurs either as native metal or in cinnabar, corderoite, livingstonite, and other minerals. Mercury has uniform volumetric thermal expansion, good electrical conductivity, and easily forms amalgams with almost all common metals except iron. Most mercury is used for the manufacture of industrial chemicals and for electrical and electronic applications.

Molybdenum (Mo) is a refractory metallic element used principally as an alloying agent in steel, cast iron, and superalloys to enhance hardenability, strength, toughness, and wear and corrosion resistance. The versatility of molybdenum in enhancing a variety of alloy properties has ensured it a significant role in contemporary industrial technology, which increasingly requires materials that are serviceable under high stress, expanded temperature ranges, and highly corrosive environments. Moreover, molybdenum finds significant usage as a refractory metal in numerous chemical applications, including catalysts, lubricants, and pigments. Few of molybdenum's uses have acceptable substitutions.

Platinum Group Minerals (PGMs). Naturally occurring platinum and platinum-rich alloys have been known for a long time. The Spaniards named the metal "platina," or little silver, when they first encountered it in Colombia. They regarded platinum as an unwanted impurity in the silver they were mining.

The catalytic properties of the six platinum group metals (PGM): iridium, osmium, palladium, platinum, rhodium, and ruthenium are outstanding. Platinum's wear and tarnish resistance characteristics are well suited for making fine jewelry. Other distinctive properties include resistance to chemical attack, excellent high-temperature characteristics, and stable electrical properties. The chemical industry uses a significant amount of either platinum or a platinum-rhodium alloy catalyst in the form of gauze to catalyze the partial oxidation of ammonia to yield nitric oxide, which is the raw material for fertilizers, explosives, and nitric acid. In recent years, a number of PGMs have become important as catalysts in synthetic organic chemistry. Platinum supported catalysts are used in the refining of crude oil, reforming, and other processes used in the production of high-octane gasoline and aromatic compounds for the petrochemical industry. Since 1979, the automotive industry has emerged as the principal consumer of PGMs used as oxidation catalyst in catalytic converters to treat automobile exhaust emissions. A wide range of PGM alloy compositions is used in low-voltage and low-energy contacts, thick- and thin-film circuits, thermocouples and furnace components, and electrodes.

Rare Earth Oxides (REOs). Rare earths are those elements with atomic numbers 58 through 71 generally known as the lanthanide group. These include the following elements: cerium, dysprosium, erbium, europium, gadolinium, holmium, lanthanum, lutetium, neodymium, praseodymium, promethium, samarium, terbium, thulium, ytterbium, yttrium, and usually also include scandium (atomic number 21).

The principal economic sources of rare earths are the minerals bastnasite, monazite, and loparite and the lateritic ion-adsorption clays. The rare earths are a relatively abundant group of 17 elements composed of scandium, yttrium, and the lanthanides. The elements range in crustal abundance from cerium, the 25th most abundant element of the 78 common elements in the Earth's crust at 60 parts per million, to thulium and lutetium, the least abundant rare-earth elements at about 0.5 part per million. The elemental forms of rare earths are iron gray to silvery lustrous metals that are typically soft, malleable, and ductile and usually reactive, especially at elevated temperatures or when finely divided. The rare earths' unique properties are used in a wide variety of applications.

Rhenium (Re), the last naturally-occurring element to be discovered, was discovered in Germany in 1925. The process was so complicated and the cost so high that production was discontinued until early 1950 when tungsten-rhenium and molybdenum-rhenium alloys were prepared. These alloys found important applications in industry that resulted in a great demand for the rhenium produced from the molybdenite fraction of porphyry copper ores. Important uses of rhenium have been in platinum-rhenium catalysts, used primarily in producing lead-free, high-octane gasoline and in high-temperature superalloys used for jet engine components.

Rubidium (Rb) was discovered in 1861 but had extremely limited industrial use until the 1920s. Small quantities of rubidium-containing minerals were mined in the United States prior to mid-1960, but rubidium is no longer mined domestically. Historically, the most important use for rubidium has been in research and development, primarily in chemical and electronic applications.

Selenium (Se). Commercial quantities of selenium are recovered as a byproduct of the electrolytic refining of copper where it accumulates in anode residues. Growth in consumption was driven by the development of new uses, including applications in rubber compounding, steel alloying, and selenium rectifiers. By 1970, selenium in rectifiers had largely been replaced by silicon, but its use as a photoconductor in plain paper copiers had become its leading application. During the 1980s, the photoconductor application declined (although it was still a large end-use) as more and more copiers using organic photoconductors were produced. In 1996, continuing research showed a positive correlation between selenium supplementation and cancer prevention in humans, but widespread direct application of this important finding would not add significantly to demand owing to the small doses required. In the late 1990s, the use of selenium (usually with bismuth) as an additive to plumbing brasses to meet no-lead environmental standards became important.

Strontium (Sr) commonly occurs in nature, averaging 0.034% of all igneous rock; only two minerals, celestite (strontium sulfate) and strontianite (strontium carbonate), however, contain strontium in sufficient quantities to make its recovery practical. Of the two, celestite occurs much more frequently in sedimentary deposits of sufficient size to make development of mining facilities attractive. Strontianite would be the more useful of the two common minerals because strontium is used most often in the carbonate form, but few deposits have been discovered that are suitable for development. The primary usage is in television tubes and the bright red colors in fireworks.

Tantalum (Ta) is ductile, easily fabricated, and highly resistant to corrosion by acids and a good conductor of heat and electricity, and has a high melting point. The major use for tantalum, as tantalum metal powder, is in the production of electronic components, mainly tantalum capacitors. Major end uses for tantalum capacitors include portable telephones, pagers, personal computers, and automotive electronics. Alloyed with other metals, tantalum is also used in making carbide tools for metalworking equipment and in the production of superalloys for jet engine components.

The United States does not have a niobium or tantalum mining industry because resources are of low grade, and the United States must import all of its niobium and tantalum source materials for processing.

Tellurium (Te) is a relatively rare element, in the same chemical family as oxygen, sulfur, selenium, and polonium: oxygen and sulfur are nonmetals, polonium is a metal, and selenium and tellurium are semiconductors (i.e., their electrical properties are between those of a metal and an insulator). Nevertheless, tellurium, as well as selenium, is often referred to as a metal when in elemental form. Tellurium production, like selenium is mainly a byproduct of copper processing. The 1960s brought growth in thermoelectric applications for tellurium, as well as its use in free-machining steel, which became the dominant use. The use of high-purity tellurium in cadmium telluride solar cells is very promising. Some of the highest efficiencies for electric power generation have been obtained by using this material, but this application has not yet caused demand to increase significantly.

Thallium (Tl), a soft, bluish-gray, malleable heavy metal, was discovered by Sir William Crookes in 1861 while he was making spectroscopic determinations for tellurium on residues from a sulfuric acid plant. Although the metal is reasonably abundant in the Earth's crust at a concentration estimated to be about 0.7 part per million, it exists mostly in association with potassium minerals in clays, soils, and granites and, thus, is not generally considered to be commercially recoverable from those forms. The major source of commercial thallium is the trace amounts found in copper, lead, zinc, and other sulfide ores and their smelting.

Thallium metal and its compounds are consumed in a wide variety of applications; for example, thallium is used in semiconductor material for selenium rectifiers, in gamma radiation detection equipment, in infrared radiation detection and transmission equipment, in crystalline filters for light diffraction for acousto-optical measuring devices, in a mercury-thallium alloy for low-temperature measurements, in glass to increase its refractive index and density, in the synthesis of organic compounds, and in a high-density liquid for sink-float separation of minerals. In addition, research activity with thallium is ongoing to develop high-temperature superconducting materials for such applications as magnetic resonance imaging, storage of magnetic energy, magnetic propulsion, and electric power generation and transmission. Also, the use of radioactive thallium compounds for medical purposes in cardiovascular imaging to detect heart disease is increasing.

Zirconium (Zr) The principal economic source of zirconium is the zirconium silicate mineral, zircon ($ZrSiO4$). Zircon is the primary source of all hafnium. Zirconium and hafnium are contained in zircon at a ratio of about 50 to 1. Zircon is a coproduct or byproduct of the mining and processing of heavy-mineral sands for the titanium minerals, ilmenite and rutile, or tin minerals. The major end uses of zircon are refractories, foundry sands (including investment casting), and ceramic opacification. Zircon is also marketed as a natural gemstone, and its oxide is processed to produce the diamond simulant, cubic zirconia. Zirconium is used in nuclear fuel cladding, chemical piping in corrosive environments, heat exchangers, and various specialty alloys. The major end uses of hafnium are in nuclear control rods, nickel-based superalloys, nozzles for plasma arc metal cutting, and high-temperature ceramics.

The human genius for invention, substitution, replacement and time-savings will ensure further developments and uses to all of these "electronic metals."