British Columbia Department of Mines
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INFORMATION CIRCULAR B.C. 11

NOTES ON GERMANIUM

USES

Germanium, a metal now most useful in electronics, is also used medicinally as a specific for pernicious anaemia and sleeping sickness, in optical glass for wide-angle camera lenses and for microscope objectives, for infrared lenses, as coating on ceramic bodies to make film resistors, in an alloy with gold (12% Ge) to form a solder for jewelry and for dental inlays, and as a catalyst in the hydrogenation of coal.

In electronics germanium is used mostly in diodes, transistors, and rectifiers. These perform some of the functions of vacuum tubes and have some functions which the tubes do not perform. Germanium diodes and transistors are smaller, lighter, and cheaper than the equivalent tubes. They require less power and last longer than do vacuum tubes. They are shock resistant, a feature important in relation to use in missiles. The diode is used in various types of electronic circuits, including radio, television, telegraph, and telephone equipment, multiposition switches, and voltage-multiplier circuits. The transistor, so-named because it transfers an electrical signal across a resistor, can be used as a voice amplifier, a television-picture amplifier, a pulse amplifier, and an oscillator.

MINERALOGY

The two principal minerals of germanium are germanite and argyrodite. The most common occurrence, however, is in very small quantities in other minerals, chiefly in low-temperature sphalerite in quantities of from a trace to tenths of one per cent. Other minerals which may contain germanium are cinnabar, in tenths of one per cent; pyrargyrite, up to 1.0%; enargite, up to 0.1%; and some tin-bearing sulphides up to 0.5%. It occurs also in some coals.

Germanite: $7CuS.FeS.GeS_2$; 8.7% Ge. A dark, reddish-grey, brittle mineral with a metallic lustre and a dark grey to brown streak. Its hardness is 4 so it is readily scratched with a knife.

Argyrodite: Ag_8GeS_6; 6% to 7% Ge. A bluish- to purplish-black mineral, on a fresh fracture steel-grey with a tint of red turning to violet. The streak, or powder, is greyish-black and somewhat shining. The hardness is 2.5 and the mineral is brittle.

DEPOSITS

The principal sources of germanium are the Tri-state lead-zinc district of Missouri, Kansas, and Oklahoma and the Illinois-Kentucky zinc-fluorspar district in North America, the Tsumeb mine in South West Africa, and the Prince Leopold mine in the Katanga belt in the Belgian Congo. Germanium in coal is known in many parts of the world but commercial production, so far, has been obtained only in England.

In the Tri-state and Illinois-Kentucky occurrences germanium is a minor element within the molecular structure of sphalerite. The deposits are low-temperature replacements and fracture fillings in limestones; the sphalerite is light coloured and low in iron. The mineralogy of the deposits is simple, being predominantly sphalerite and galena with dolomite.

Germanite occurs in the ores of the Tsumeb mine in South West Africa. The orebodies are replacements of dolomite by pyrite, tennantite, enargite, galena, and sphalerite. Renierite, a variety of germanite, occurs in the Prince Leopold mine in a pipe-like replacement in limestone with bornite, chalcopyrite, and galena.

Argyrodite occurs in the Department of Potosi, Bolivia in quartz veins in slates which have been intruded by quartz-monzonite porphyry. The associated minerals are pyrite, arsenopyrite, cassiterite, sphalerite, chalcopyrite, stannite, stephanite, tetrahedrite, andorite, pyrargyrite, and jamesonite.

In coals, germanium has been found to be concentrated within the top and bottom few inches of the seams. This is in contrast to other trace elements which commonly show no such preference. It is known, too, that the germanium is more highly concentrated in the bright, woody parts of the coal (vitrain) than in the mineral charcoal (fusain), and little or none has been found in sulphides associated with the coal. Highest concentrations of

germanium are found in isolated patches of woody coal, coalified logs, and the like, in sediments. The concentration of germanium in the roofs and floors of seams may indicate precipitation from ground-water solutions. There may be some connection between the occurrence of germanium in coal and the presence or absence of sphalerite in the region.

Germanium-bearing coals have been found in British Columbia at Cape Caution and on Lang Creek, about 15 miles southeast of Powell River.

The world's largest producer of metal is the Union Miniere refinery at Hoboken, Belgium, where 200,000 to 300,000 pounds per year are refined.

TREATMENT

Germanium is extracted from flue dusts of zinc smelters and, in Britain, from the fly ash of producer gas plants. Zinc sulphide ores containing 0.01% to 0.015% germanium are of high enough grade to provide a useable flue dust. At Tsumeb the run-of-mine ore assays 3% to 4% germanium.

The three source materials of germanium, zinc smelter flue dust, germanite, and coal fly ash, require somewhat different forms of treatment. In each case the germanium is recovered as germanium tetrachloride which in turn is the raw material from which metallic germanium is extracted. Metal for the electronics industry must be very pure, to within a few parts per million, and with certain undesirable impurities present in no more than fractions of one part per million.

A process for recovering germanium tetrachloride from zinc smelter flue dust begins with roasting to remove sulphur and to convert the zinc, lead, cadmium, and copper to oxides. The oxides are sintered at a high temperature, with coal and common salt, volatilizing and so separating from the zinc the germanium, cadmium, lead, and copper which are then condensed and collected in an electrostatic precipitator. Sulphuric acid is added and the lead precipitated as lead sulphate. Zinc dust is then added to precipitate the copper and germanium, leaving the cadmium in solution. The copper-germanium precipitate is then redissolved and the germanium separated by another precipitation. The germanium precipitate is roasted and dissolved in hydrochloric acid. Germanium tetrachloride is distilled

from this solution.

Germanium is recovered from germanite by two processes. In the shorter method the ore is pulverized, roasted, and treated with hydrochloric acid. Germanium tetrachloride is distilled from the hydrochloric acid solution.

Recovery of germanium from coal fly ash is made by smelting the dust with copper oxide, soda ash, and lime to produce a regulus (impure metal) which contains most of the germanium. The regulus is leached with chlorine and ferric chloride, converting the germanium to soluble chloride. The germanium tetrachloride is then distilled off.

Metallic germanium is obtained from the tetrachloride by multiple distillation, with the addition of refluxing with copper if arsenic is present, to obtain a pure germanium tetrachloride. This is hydrolized in distilled water to germanium dioxide. The germanium dioxide is reduced by heating in hydrogen, in graphite boats, to a temperature of 650° to 675° C. until no more water is formed. When reduction is complete the temperature is raised to 1,000° C. to melt the germanium powder and so form ingots. Throughout this process scrupulous cleanliness must be maintained so as not to contaminate the final product.

PRICES

Germanium prices, per gram, as at October 29, 1959:

First Reduction		Intrinsic Quality		pricing point
1,000 gram lots	10,000 gram lots	1,000 gram lots	10,000 gram lots	
34½¢ - 35¢	33¢	35¢	35¢	f.o.b. shipping point
		37¢	35¢	delivered

BUYERS OF ORES AND CONCENTRATES

American Smelting and Refining Co., 120 Broadway, New York 5, New York.

The American Steel and Wire Div., U. S. Steel Corporation, Rockefeller Building, Cleveland 13, Ohio.
American Zinc, Lead and Smelting Co., 818 Olive Street, St. Louis, Missouri.
Eagle-Picher Co., Mining and Smelting Division, First National Bank Building, Miami, Oklahoma.
Sylvania Electric Products Inc., Towanda, Pennsylvania.

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