

MAHDOLLISISTA GERMANIUM-KONSENTRAITUMISTA SUOMESSA

OKFY:n taholta on esitetty kysymys mahdollisten Ge-konsentroitumien esiintymisestä yhtiössä ja/tai Suomessa. Varsin suppean aineiston pohjalta allekirjoittanut on laatinut seuraavan selvityksen. Liitteessä 1 on esitetty tunnetut pääasiat Ge:n esiintymisestä. Mukaan on liitetty kaksi artikkelia (liitteet 2 ja 3), jotka antanevat lukijalle, joskin hieman vanhentuneen, yleiskuvan "Ge-taloudesta".

Vuonna 1971 maailman Ge-tuotanto on ollut 88 000 kg (USA 12 250 kg). Primäärisinä Ge-lähteinä ovat eräät sinkkivälkerikasteet (Tri-state, Mississippi Valley, USA) ja Cu-sulfidirikasteet (Katanga), Ge-sulfidirikaste (Tsumeb Mine, SW-Afrikka), kivihiilipolton lentopöly (Englanti) ja jäteromu. Ge saadaan yleensä sivutuotteena. Sen erottaminen ja puhdistaminen lienee varsin kallista. Tuotanto on sovitettu vastaamaan kysyntää. Germaniumin saanti em. Zn- ja Cu-sulfidirikasteista sekä kivihiilen lentopölystä on taloudellisesti kannattavaa vain, koska niiden käsittelyprosesseissa Ge konsentroituu sivutuotteisiin. Ilman ko. rikastumista sen taloudellinen erottaminen tuskin olisi mahdollista.

Tiedot germaniumin esiintymisestä Suomen kallioperässä ovat jokseenkin olemattomat. Muualla saatujen tietojen valossa (vrt. liitteet) lienee perusteltua huomioida mahdollisina Ge-konsentroitumina (ja potentiaalisina lähteinä?) seuraavat seikat:

1. Kokkolan tehtaan käyttämät sinkkivälkerikasteet ja Zn-prosessin sivutuotteet.
2. Harjavallan tehtaiden käyttämät Cu-rikasteet ja Cu-prosessin sivutuotteet.

Yhtiön keskuslaboratoriossa on analysoitu ao. rikasteita myös Ge:n suhteen. Analyysitietoja ei allekirjoittaneella ole ollut käytettävissään.

Toissijaisina kohteina, joilla tuskin lienee taloudellista merkitystä, tulisivat lähinnä kysymykseen:

3. Kompleksiset falertsipitoiset sulfidijuonet (Pyhäsalmi, Vihanti)
4. Rapakivigraniittien reunavyöhykkeisiin liittyvät Sn-pitoiset greisen-muodostumat (toht. I Haapalan, GTL, tiedonannon mukaan Eurajoen esiintymän sinkkivälkkeessä ei ole todettu Ge:a).

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5. Kompleksiset graniitti-pegmatiitit (etenkin topaasi-pitoiset; esim. Eräjärvi).

Seuraavat ulkomaiset lähteet saattavat osoittautua antoisiksi:

6. Yhtiön piirissä eräänä potentiaalisena Ge-kantajana tulisi huomioida La Plata'n (Toachi, Ecuador) kaivoksen rikasteet. Ko. rikasteet lienee syytä analysoida myös muiden harvinaisempien metallien suhteen. Kaivos on mineralogialtaan jne. merkittävästi samankaltainen kuin muut ko. alueen (Peru, Chile) kaivokset, joiden Cu-rikasteissa on todettu Ge-konsentroitumia (vrt. liite 1).
7. Mielenkiintoisena ja ehkä todennäköisimpänä Ge-konsentroitumana tulisi harkita voimaloissamme jne. käytettävän puolalaisen (ja muualtakin tuodun) kivihiilen polttotuotteiden (lähinnä lentopölyn) analysointia. Eräitä tietoja puolalaisten kivihilten Ge-pitoisuuksista löytynee artikkeleista Winnicki (1964) ja Ryczek (1959). Winnicki on todennut pitoisuudet 0.05-37 ppm Ge kivihielessä (coal) ja 1-812 ppm Ge tuhka-aineksessa (ash). Allekirjoittaneella ei ole ollut tilaisuutta tutustua em. julkaisuihin.

Koska Ge näyttää konsentroituvan fossiilisiin orgaanisiin kerrostumiin, niin mahdollisten Ge-rikastumien suhteen lienee syytä myös huomioida seuraavat kaksi seikkaa:

8. Neste Oy:n öljynjalostamot.  
9. Seinäjoen turvekoksitendas.

Kiertäneekö näissä prosesseissa (7-9) Ge mukana ja onko havaittavia konsentroitumia? Allekirjoittaneen käyttämässä suppeassa lähdeaineistossa ei ole esiintynyt mitään mainintoja raakaöljyn ja turveaineksen ja niiden sivutuotteiden Ge-pitoisuuksista.

Joulukuun 1976 alussa metallisen germaniumin hinta (UK, zone refined, 30 ohm/cm) oli 121.00 £/kg eli noin 775 mk/kg. Hintaa on muutettu viimeksi 5.2.1974 (Metal Bulletin No. 6149, Dec. 7, 1976).

*World Mining, Nov. -76. Ge diamonds \$ 293,-/kg*

Viitteet (puolalaiset kivihiiilet):

Ryczek, M. (1959) Występowanie germanu w węglu kamiennym oraz sposoby jego wzbogacania (The occurrence of germanium and gallium in Polish coals, and methods for their concentration) Przegląd Gorniczy 15(46), 420 - 426.

Winnicki, J. (1964) German a nieorganiczna substancja mineralna w węglu pokladu 510 w Górnośląskim Zagłębiu Węglowym (Germanium and inorganic matter in coal of seam 510 in the Upper Silesian coalfield) Prace Głównego Inst. Gornictwa, Komun. No. 352 - 360, 159 - 195.

Olari 27.12.76

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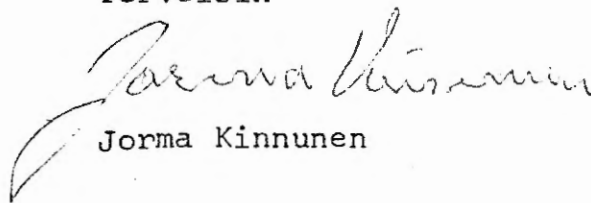
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Keskuslaboratoriosta ei löydy Ge-arvoja Outokummun tuotteista.

Mahdollista on, että Vuorelainen on aikoinaan kerännyt Pyhäsalmeilta tiettyjä mineraalityyppejä, joissa ehkä olisi voinut olla germaniumia.

Terveisin

  
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Ko. raportissa olen maininnut eräänä potentiaalisena Ge-kantajana yhtiön piirissä La Plata'n (Ecuador) kaivoksen rikasteet. Asian suhteen huomioitakoon seuraava lisäselvitys.

Raportin "La Plata, Ecuador-malminäytteiden rikastustutkimus" (M Saari & K Salminen, 24.08.1976), joka käsittelee ko. kaivoksen kahden malminäytteen Ecuador C (normaalimalmi) ja Ecuador D (sivumalmi) vaahdotuskokeita, liitteessä 2 on mainittu seuraavat Ge-pitoisuudet:

Malmi	Ge (ppm)
näyte C	70
näyte D	20
Selektiivinen vaahdotus (SO <sub>2</sub> )	
näyte C/CuPbKR3	70
näyte C/ZnKR3	150
näyte D/CuPbKR3	20
näyte D/ZnKR3	50
Yhteisvaahdotus + Zn-erotus (ei kerrattu)	
näyte C/CuPbR	70
näyte C/ZnR	100
CuPbZn-yhteisrikaste	
näyte C	70
näyte D	30
Ba-rikaste	
näyte D	10

Havaittavissa on heikko, mutta selvä, konsentroituminen Zn-rikasteisiin.

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GERMANIUM'IN ESIINTYMISESTÄ LUONNOSSA

Seuraavassa on lyhyesti tarkasteltu germanium'in esiintymistä luonnossa. Pääasiallisina lähteinä ovat olleet Wittmann & Hörmann (1970), Weeks (1973) ja Goldschmidt (1950).

Kontinentaalisen kuoren keskimääräinen Ge-pitoisuus on noin 1.5 ppm ollen likimain samaa luokkaa kuin molybdeenin ja tinan vastaavat pitoisuudet. Vallitsevana piirteenä on Ge:n esiintyminen 4-koordinaatiossa Si:n paikalla silikaateissa. Syntetisoituja, tyyppillisten silikaattirakenteiden kanssa analogisia germanaatteja tunnetaan huomattava määrä, mutta niitä ei ole tavattu luonnon kivistä (vrt. esim. Wittmann & Hörmann, 1970, Table 32-A-1). Taloudellisesti merkittävin piirre on Ge:n piiloutuminen eräiden sulfidien hiloihin ja muutaman Ge-sulfidin harvinainen esiintyminen.

Meteorittien keskimääräisen Ge-pitoisuuden on laskettu olevan 55 ppm. Eri meteorittityyppien Ge-pitoisuuksien on todettu vaihtelevan seuraavissa rajoissa:

rautameteoritit	0.30 - 470 ppm
chondriitit	5 - 48 "
tektiitit	0.15 - 0.62 "

Fe-meteoriteissa faasiin keskeisen jakauman on todettu olevan likimain seuraavan:

metallifaasi (FeNi)	300 ppm
troiliitti	30 "
silikaatit	< 5 "

Silikaattikivien Ge-pitoisuudet vaihtelevat yleisimmin välillä 0.5-3 ppm. Emäksisten ja graniittisten kivien Ge-pitoisuuksissa ei ole mitään merkittäviä eroja kuten ilmenee oheisista pitoisuusrajoista:

Syväkivet:

gabrot	0.7 - 1.7 ppm
dioriitit	1.2 - 6 "
syeniitit	0.6 - 2.0 "
granodioriitit-kvartsimon-	
zoniitit	0.9 - 2.3 "
alkaliset syväkivet	1.3 - 2.1 "

Laavakivet:

basaltit	0.9 - 3.2 "
andesitit	1.2 - 2.3 "
kvartsiporfyyrit	0.9 - 2.0 "
ryoliitit	1.0 - 1.3 "
alkaliset laavakivet	0.9 - 3.5 "

Tavallisten kivissä esiintyvien silikaattimineraalien Ge-pitoisuudet ovat likimain samaa suuruusluokkaa:

oliiviini	0.4 - 3.4 ppm
pyrokseenit	0.25 - 3.8 "
sarvivälke	1.5 - 3.4 "
biotiiitti	1.2 - 8.5 "
muskoviitti	1.1 - 6.5 "
talkki	1.3 - 13.0 "
granaatti	1.5 - 6.0 "
kloritoidi	7.0 - 18.6 "
plagioklaasi	0.1 - 3.6 "
alkalimaasälpä	1.0 - 3.8 "
kvartsi	0.8 - 2.1 "

Fe-oksidiin, magnetiitin ja hematitiin, Ge-pitoisuudet ovat 0.X-XO ppm.  
Magmakivissä magnetiitin Ge-pitoisuus kasvaa kiven SiO<sub>2</sub>-pitoisuuden kasvaessa. Sedimenttisten rautamuodostumien Fe<sub>2</sub>-oksidiin Ge-pitoisuudet ovat korkeampia kuin magmakivissä.

Karbonaatti-, sulfaatti- ja kloridimineraalien Ge-pitoisuudet ovat yleensä alle 1 ppm.

Graniittipegmatiittien keskimääräisen Ge-pitoisuuden oletetaan olevan noin 10 ppm. Pääasiallisena Ge-kantajana on topaasi. Pegmatiiteissa esiintyvien mineraalien Ge-pitoisuuksien keskiarvojen on todettu vaihtelevan seuraavissa rajoissa:

topaasi	200 - 700 ppm
granaatti	7 - 70 "
turmaliini	10 "
spodumeni	5 - 28 "
lepidoliitti	5 - 70 "
muskoviitti	19 - 36 "
maasälvät	2 - 15 "
kvartsi	0 - 6 "

Greisen-muodostumissa tavatut Ge-pitoisuudet ovat noin 2 - 50 ppm topaasi-pitoisten greisenien ollessa Ge-rikkaimpia. Keskimääräiset Ge-pitoisuudet lienevät noin 20 - 30 ppm. Ge- ja F-pitoisuuksien on todettu omaavan positiivisen korrelaation.

Hydrotermiset sulfidimuodostumat ovat selvästi tärkeimmät taloudellisina Ge-lähteinä. Niissä Ge esiintyy muiden sulfidien hiloissa (etenkin sinkkivälkkeessä) ja harvoin muodostaa pienessä määrin tavattavia Ge-sulfideja.

USA:ssa (suurin Ge-kuluttaja) on Ge saatu sivutuotteena pääasiassa Tri-State (Missouri-Kansas-Oklahoma) Zn-Pb-alueen ja Mississippi Valley'n sinkkivälkerikasteista, joissa Ge-pitoisuudet vaihtelevat 0.008 - 0.026 %. - Zn-malmien ohella Ge on myös konsentroitunut eräisiin Cu-sulfidimalmeihin, etenkin enargiittia, borniittia ja tennantiittia sisältäviin (esim. Butte, Montana; Chuquicamata, Chile; Cerro de Pasco, Morococha, Quiruvilca ja Casapalca, Peru; Bor, Jugoslavia).

Eräiden sulfidien Ge-pitoisuusrajoja on annettu seuraavassa:

sinkkivälke ZnS	5 - 1850	ppm
lyijyhohde PbS	0 - 10	"
kuparikiisu CuFeS <sub>2</sub>	0.5 - 900	"
enargiitti Cu <sub>3</sub> AsS <sub>4</sub>	10 - 5000	"
borniitti Cu <sub>5</sub> FeS <sub>4</sub>	0 - 1000	"
tennanttiitti Cu <sub>12</sub> As <sub>4</sub> S <sub>13</sub>	0 - 5000	"
tetrahedriitti Cu <sub>12</sub> Sb <sub>4</sub> S <sub>13</sub>	0 - 500	"
kovelliitti CuS	0 - 40	"
kalkosiitti Cu <sub>2</sub> S	0 - 30	"
pyriitti FeS <sub>2</sub>	0 - 100	"
molybdeenihohde MoS <sub>2</sub>	2 - 10	"
stanniitti Cu <sub>2</sub> FeSnS <sub>4</sub>	6 - 20	"
arsenikiisu FeAsS	1 - 50	"

Em. sulfidien ohella hydrotermisissä kiteytymissä on Ge-konsentroitumista tavattu kassiteriitissa (5 - 200 ppm), sinoberissa (< 0.X %), canfieldiitissa (aina 1.8 %), pyrargyriitissa (jopa n. 1 %), bertrandiitissa (50 - 160 ppm), willemitissa (47 - 350 ppm), hematitissa (X0 - X00 ppm) ja sideriitissä (< 50 ppm). Kalsiitti, magnesiitti, strontianiitti, witheriitti, baryytti ja fluoriitti sisältävät alle 1 ppm Ge. - Sulfidien Ge-pitoisuudet eri alueiden ja mineralisaatioiden kesken vaihtelevat huomattavasti. Korkeimmat Ge-pitoisuudet (aina 0.X %) on tavattu polymetallisten mineralisaatioiden borniitissa ja tennantiitissa, kun Ge-sulfidit, renieriitti ja germaniitti ovat läsnä. Sinkkivälkeen Ge-pitoisuudet ovat korkeammat alhaisen lämpötilan kiteytymissä.

Ge-mineraalit ovat harvinaisia ja liittyvät hydrotermisiin kiteytyksiin. Muutamia sulfideja ja sekundäärisiä hapettumistuotteita tunnetaan. Ne liittyvät polymetallisiin hydrotermisiin borniitti-kalkosiitti-kuparikiisu-tennanttiitti-energiitti-luzoniitti-sinkkivälke parageneeseihin. Tunnetuin esiintymispaikka on Tsumeb Mine Lounais-Afrikassa. Tunnetut mineraalit ja niiden Ge-pitoisuudet ovat:

Sulfidit:

argyrodiiitti Ag <sub>8</sub> GeS <sub>6</sub>	7	%
germaniitti Cu <sub>3</sub> (Ge,Fe)S <sub>4</sub>	6.2 - 11.4	"
renieriitti (Cu,Fe,Ge,Zn)S	5.9 - 9.6	"
briariitti Cu <sub>2</sub> (Fe,Zn)GeS <sub>4</sub>	13.7 - 16.9	"

Sekundääriset hapettumistuotteet (Tsumeb Mine)

stottiitti Fe <sub>4-5</sub> H <sub>8-6</sub> [GeO <sub>4</sub> ] 4·8H <sub>2</sub> O	29	%
fleischeriitti Pb <sub>3</sub> [Ge(OH) <sub>6</sub> /(SO <sub>4</sub> ) <sub>2</sub> ] ·3H <sub>2</sub> O	6.7	%
itoiitti Pb <sub>3</sub> [GeO <sub>2</sub> (OH) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ]		
schaurteiitti Ca <sub>3</sub> [Ge(OH) <sub>6</sub> (SO <sub>4</sub> ) <sub>2</sub> ] ·3H <sub>2</sub> O	14.8	%

Tsumeb Mine'n ohella Ge-sulfideja ja kokeita Ge-pitoisuuksia muissa sulfideissa on tavattu Katangan Cu-malmeissa ja Bolivian Ag-sulfidimineralisaatioissa. Tsumeb'issa saadaan Ge-rikaste



selektiivisellä vaahdotuksella. Katangalaisissa Cu-malmeissa Ge joutuu Cu-rikasteeseen, jonka metallurgisen käsittelyn sivutuotteena saadaan Ge-rikaste. Ko. Ge-rikasteet käsitellään Belgiassa ( ja Länsi-Saksassa ?).

Sedimenttikivissä Ge-pitoisuudet ovat pieniä ja riippuvat mineralogisesta koostumuksesta. Suhteellista rikastumista savimineraaleihin on todettavissa. Seuraavat pitoisuusvaihtelut ja keskipitoisuudet on todettu:

savet ja saviliuskeet	0 - 3.9 ppm	(keskipit. 2.2 ppm)
hiekat ja hiekkakivet	0 - 3.5 "	( " ~1 ppm)
karbonaattikivet	0 - 0.8 "	( " ~0.3 ppm)
bauxiitit	1 - 3.6 "	(keskipit. ~2 ppm)

Luonnonvesissä Ge-pitoisuudet ovat häviävän pieniä kuten oheisista numero-tiedoista ilmenee:

valtamerien vesi	0.05-0.07 ppb	(keskipit. 0.06 ppb)
jokivedet	0.03-0.11 "	( " 0.05 ppb)
pohjavedet	0 - 24 "	(keskipit. 0.3 ppb?)
kuumat lähteet	0.4 - 44 "	(keskipit. 10 ppb)

Vesien suhteen on todettu että Ge-pitoisuus kasvaa Na- ja/ tai F-pitoisuuden, lämpötilan ja alkaalisuuden kasvaessa ja pienee Ca- ja/ tai Cl-pitoisuuden kasvaessa.

Kasvien Ge-pitoisuus on alle 10 ppm, joka on niiden "toxic level".

Kivihiilikerrostumissa on todettavissa selvää Ge:n rikastumista. Tavallisesti Ge-pitoisuudet vaihtelevat likimain seuraavissa rajoissa:

kivihiili (coal)	1 - 150 ppm	Ge
tuhka-aines (ash)	5 - 11000 ppm	Ge

Tuhka-aineksen (coal ash) määrä on yleensä välillä 1-38 %. Tuhka-aineksessa on poikkeuksellisesti todettu jopa 5-7.5 % Ge. Hiiltyneen puu- tai muun kasviaineksen havaittu maksimi Ge-pitoisuus on ollut 0.4 %. Yksityisissä kerroksissa Ge on jakautunut epätasaisesti. Ge on sidottu pääasiassa orgaaniseen ainekseen ja alhaisimman tuhka-aineksen määrän sisältävät kivihiilet omaavat korkeammat Ge-pitoisuudet. Eräiden kokeiden mukaan germaniumista noin 12 % on adsorboituneena ja noin 88 % kemiallisesti sidottuna kivihiilen orgaaniseen ainekseen. Kasvien maksimi Ge-pitoisuus 10 ppm ei yksin voi selittää kivihiilten korkeita Ge-pitoisuuksia, vaan todennäköisesti osa on tuotu systeemin ulkopuolelta ja sidottu orgaaniseen ainekseen mahdollisesti humushappojen myötävaikutuksella. - Kivihiilen polttotuotteet sisältävät huomattavia Ge-määriä; mm. lentopöly (flue dust) saattaa sisältää useita prosentteja tai prosentin kymmenesosia Ge. Polttotuotteiden hyväksikäyttöä Ge-lähteenä on tutkittu etenkin Englannissa ja USA:ssa. Englannissa on Ge-tuotanto aloitettu v. 1950 (Johnson Matthey & Co) ja primäärisenä raakaaineena on kivihiilipolton lentopöly (vrt. Harner, 1961,

s. 189). On arvioitu, että käytetyn kivihiilen Ge-pitoisuuden seurauksena Englannissa vuosittain n. 1.8 milj. kg Ge sisältyy teollisuuden savukaasuihin, lentopölyihin ja tuhkiin (Paone, 1970, s. 566).

### Viitteet

Goldschmidt, V. M. (1954) Geochemistry. - Clarendon Press, Oxford.

Harner, H. R. (1961) Germanium. - Hampel, C. A. (ed.) Rare metals handbook. Reinhold, New York, ss. 188 - 197.

Paone, J. (1970) Germanium. - Mineral facts and problems. U. S. Bureau of Mines Bull. 650, ss. 563 - 571.

Weeks, R. A. (1973) Gallium, germanium, and indium. - Brobst, D. A. & Pratt, W. P. (eds) United states Mineral Resources. U. S. Geol. Survey Prof. Paper 820, ss. 237 - 246.

Wittmann, A. & Hörmann, P. K. (1970) Germanium. - Wedepohl, K. H. (ed.) Handbook of Geochemistry. Vol. II-1, Ch. 32.

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*Rare metals handbook, 2nd ed.  
New York, 1961. pp. 188-197.*

## 11. GERMANIUM

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### INTRODUCTION

In working on the relation of properties of the elements, Newlands<sup>58</sup> noted that, if his theories were correct, there seemed to be a missing element between silicon and tin. Seven years later Mendeleeff<sup>51</sup> predicted the discovery of the three "eka" elements and listed the properties to be expected for each. One of these was expected to belong to the silicon family; this was his eka-silicon. In 1886 Winkler was asked to analyze a sample of argyrodite. Repeated analyses did not account for about 7 per cent of the composition, and he finally concluded that the missing portion was a new element. Winkler<sup>54</sup> finally isolated the new element and named it germanium, after his native country.

Further investigation of the properties definitely fixed the position of germanium in the atomic table and confirmed the predictions of Mendeleeff. Germanium is in Group IV, Period 4, of the periodic table. The atomic number is 32; the atomic weight is 72.60.

Although germanium has been known for many years and there has been considerable study of it and its compounds, only recently has it attained importance. Commercial production in the United States began only twenty years ago.

### OCCURRENCE

It has been estimated that a ton of the earth's crust contains from 4 to 7 g of germanium.<sup>1,19</sup> Minute amounts have been detected in many silicate minerals.

Only a very few minerals contain appreciable amounts of germanium.<sup>63</sup> Argyrodite (from which it was first isolated) contains from 5 to 7 per cent germanium; only small amounts of this mineral (a silver-germanium sulfide) have been located. Canfieldite, a silver-tin-germanium sulfide mineral containing about 1.8 per cent germanium, is found in Bolivia, but only in small quantities. Enargite, a copper-arsenic sulfide, is found in some quantity in western United States and is reported to contain as much as 0.03 per cent germanium.<sup>62</sup> None of these minerals is presently utilized for recovery of germanium, presumably because of the small quantities available.

Germanite, a complex copper-zinc-arsenic-germanium sulfide, has been mined at Tsumeb, Southwest Africa; it has been found associated with the lead-zinc-copper ores of that district. True germanite contains 10 per cent germanium,<sup>61</sup> but the run-of-mine ore assays only 3 to 4 per cent germanium. Some pockets of germanite have been found, but it is usually dispersed in the lead-copper ores. This is the only known mineral from which germanium is recovered as the primary metal. Renierite, a complex copper-iron-germanium-arsenic sulfide, was first discovered in the Belgian Congo.<sup>62</sup> Analysis of clean renierite crystals showed an average of 7 per cent germanium.<sup>61</sup> It is found intimately mixed with the copper-zinc ores in Katanga, Belgian Congo.<sup>4</sup> It has also been reported in association with germanite in the copper-lead-zinc ores in Tsumeb, Southwest Africa.<sup>3</sup>

Some zinc ores in the United States contain

small amounts (0.01 to 0.1 per cent) of germanium;<sup>6</sup> zinc ores from other parts of the world also contain traces of germanium. Silver, tin, copper, and iron ores sometimes have small amounts of germanium.

The first major recovery of germanium from ores was from the zinc ores of the Tri-State (Missouri-Oklahoma-Kansas) field;<sup>60</sup> subsequently, germanium was recovered from zinc ores of the Mississippi Valley.<sup>6</sup>

Recovery of the germanium content of the Tsumeb ores<sup>3</sup> and the Katanga ores<sup>4</sup> in recent years has added measurably to the world supply of germanium.

The presence of germanium in coals has been known for some time;<sup>18</sup> numerous references in recent years have reported the finding of germanium in coals from many different parts of the world.<sup>48,63</sup> British coals and combustion by-products have been investigated<sup>55</sup> and the germanium contents reported in some detail; these by-products comprise one source of raw material for recovery in England. (See under the heading "Derivation".) The United States Geological Survey has compiled data on the concentration of germanium in some American coals.<sup>73</sup> Data on the germanium content of coals have been reported in West Virginia,<sup>25</sup> Illinois,<sup>49</sup> and Kansas.<sup>69</sup> Recovery of germanium from American coals has been intensively studied, but to date there has been no commercial recovery.<sup>16</sup>

Recovery of germanium from zinc and other ores is economically feasible only because the germanium is concentrated in by-products during the process of recovering the primary metals; without such initial concentration of the germanium, it would not be economically possible to separate and purify it. Similarly, recovery of germanium in coal is dependent on the concentration of germanium in coal by-products (primarily flue dusts); these by-products must contain sufficient germanium to make its recovery profitable.

#### PRODUCTION AND ECONOMIC STATISTICS

In 1959 the consumption of germanium (metal and oxide) in the United States was estimated at 45,000 lb.<sup>16</sup> Actual production figures have not been released.

Production of germanium in England started in 1950;<sup>54</sup> no production figures are available. Belgium is a major European producer, the

raw material coming from Tsumeb and the Belgian Congo.

The major producer in the United States is The Eagle-Picher Company which recovers it from zinc ore.<sup>60</sup> The American Zinc Company and Sylvania Electric Products, Inc., are also suppliers. American Metal Climax, Inc. is beginning production. In England, Johnson Matthey & Company is a producer; flue dusts from coals are their primary raw materials. In Belgium, germanium metal and oxide are produced at Olen by the Societe Generale Metallurgique de Hoboken and at Balen by the Societe de la Vielle Montagne S.A. The price of electronic-grade germanium metal in the United States is currently about \$185/lb for large quantities. Germanium dioxide is about \$110/lb.

#### DERIVATION

Commercial recovery of germanium has been chiefly from zinc and zinc-copper-lead ores, germanite, and flue dusts from coals.

Ores from the Tri-State district (Missouri, Oklahoma, and Kansas) are concentrated and roasted to a crude zinc oxide by conventional means. Roasted ores mixed with salt and coal are sintered at a high temperature; germanium, cadmium, and some other impurities are vaporized; and the vapors are condensed and collected in an electrostatic precipitator. This by-product fume is chemically treated to obtain crude fractions of germanium, cadmium, and the other impurities.<sup>60</sup>

The germanium concentrate is reacted with strong hydrochloric acid. The resultant germanium tetrachloride [b.p. 86°C (187°F)] is distilled off. The crude tetrachloride is given additional purification and finally distilled with chlorine (to hold back arsenic). The purified, redistilled tetrachloride is then hydrolyzed in water to form germanium dioxide, which is reduced to a powdered metal by heating to 650°C (1200°F) in an atmosphere of hydrogen. The powdered metal is melted at 1100°C (2012°F) in an inert atmosphere to form ingots. This method of recovery from germanium concentrates and reduction to the metal is used, with modifications, in practically all processes.

Zinc ores from the Mississippi Valley are concentrated, and the concentrate roasted and sintered in much the same fashion as the Tri-State ores; a by-product fume contains the

recoverable germanium. This fume is leached with sulfuric acid under conditions which dissolve the zinc and cadmium and leave the lead, germanium, and other impurities as a sludge. The sludge is reacted with hot, strong sulfuric acid, the germanium being dissolved. The germanium in this liquor is precipitated with hydrogen sulfide, and the sulfide precipitate is roasted. The roasted material is then reacted with concentrated hydrochloric acid, and the distillation and purification are performed as described in the previous paragraph.<sup>6</sup>

At Balen, Belgium, lead and zinc ores are smelted in a complex circuit; germanium is concentrated in a crude zinc oxide. Leaching of this crude zinc oxide under appropriate conditions dissolves the germanium. The germanium is precipitated, and the resulting germanium concentrate reacted with hydrochloric acid and distilled from the solution as germanium tetrachloride. Further purification steps follow essentially the same procedure as described for zinc ores.<sup>8</sup>

The presence of germanium in zinc solutions for electrowinning of the zinc is highly detrimental. This is one of the reasons for the separation of germanium in the Balen process, since the zinc is recovered there by electrolysis. Another method for purification of the zinc solution yields a sludge which contains the germanium, copper, and arsenic. This sludge is smelted with excess sulfur to fume off the germanium for subsequent recovery.<sup>17</sup>

At Tsumeb, Southwest Africa, germanium occurs as germanite and renierite intimately mixed with the copper-lead-zinc ore of this district. By selective flotation a germanium concentrate is made, and the material is shipped to Olen, Belgium. Here the concentrate is processed in a vertical retort furnace under reducing conditions to obtain a germanium sulfide fume which is condensed. The fume is given an oxidizing roast; a crude germanium dioxide is obtained for the purification stages.<sup>3</sup>

Germanium, as renierite, is dispersed through some of the copper-zinc ores from Katanga, Belgium Congo. In the flotation process for concentration of these ores, the germanium follows the copper. During the smelting of the copper, dusts and fumes which contain appreciable amounts of germanium are collected. These dusts and fumes are baked with sulfuric acid, and the baked dust is leached with weak

acid to obtain a germanium-bearing solution. After oxidation of the solution, germanium is precipitated with magnesia and copper hydrate to give a concentrate for further purification.<sup>1</sup>

The germanium concentrates made at Tsumeb and Katanga (described in the preceding paragraphs) are shipped to Hoboken, Belgium, for recovery and purification of the germanium.<sup>5</sup> Distillation of the germanium tetrachloride, hydrolysis of the tetrachloride to the dioxide, and reduction and purification of the metal are essentially as previously described.

At Tsumeb, some pockets of germanite ore have been found which have been mined separately and the germanite processed for recovery of germanium and gallium. In one process<sup>66</sup> the pulverized germanite ore is reacted with 50 per cent sodium hydroxide solution, and the mixture is evaporated to dryness. The dry mass is leached with hot water, and the leach solution is brought to pH 8 with sulfuric acid. Under controlled conditions, nitric acid is added to the boiling solution to give 5 per cent of free acid in the solution; after filtering, this solution is brought to pH 3 with sodium hydroxide (to precipitate the gallium), the precipitate is filtered off, and the germanium is precipitated (as dioxide) by neutralization with ammonia. The germanium dioxide is then filtered from the solution and dissolved in strong hydrochloric acid, and the resultant germanium tetrachloride is distilled and purified. Hydrolysis of the tetrachloride to germanium dioxide and subsequent reduction and melting follow the same steps as previously described.

To recover germanium (and gallium) from flue dusts,<sup>66</sup> the dust is smelted with soda ash, lime, copper oxide, and coal dust to form a regulus and a slag. These products can be separated; practically all of the germanium (and gallium) is concentrated in the regulus. The regulus is reacted with chlorine under a dilute solution of ferric chloride; after the reaction is complete, the solution is made strongly acid, and the crude germanium tetrachloride is distilled off. The germanium tetrachloride so formed contains appreciable quantities of arsenic chloride and is refluxed with copper turnings (for 12 hr or longer) to eliminate this impurity. Otherwise, the purification and final production of the metal follow the usual steps discussed in the processes for zinc ore and germanite.



TABLE 11.1. PHYSICAL CONSTANTS OF GERMANIUM  
(Superscript numbers refer to references.)

Atomic number	32
Atomic weight	72.60 <sup>76</sup>
Isotopes and abundance	
Mass No. 70	20.4% <sup>21</sup>
Mass No. 72	27.4% <sup>21</sup>
Mass No. 73	7.8% <sup>21</sup>
Mass No. 74	36.6% <sup>21</sup>
Mass No. 76	7.8% <sup>21</sup>
Color	Silvery
Crystal structure	Octahedral <sup>50</sup>
Index of refraction	4.068-4.143 <sup>9</sup>
Hardness, Mohs scale (s)	6.25 <sup>50</sup>
Ductility	Frangible
Density (s) at 25°C (77°F) (g/cc)	5.32 <sup>76</sup>
Specific volume (s) at 25°C (77°F)	0.188
Melting point	936°C (1717°F) <sup>22</sup>
Boiling point	2700°C (approx.) (4890°F) <sup>56</sup>
Latent heat of fusion (g-cal/g)	111.5 <sup>22</sup>
Latent heat of vaporization (g-cal/g)	1,200 <sup>71</sup>
Specific heat at 25°C (77°F) (cal/g)	0.086 <sup>38</sup>
Volume resistivity at 25°C (77°F) (microhm-cm)	60 × 10 <sup>6</sup> <sup>44</sup>
Electrochemical equivalent Ge <sup>++++</sup> (mg/coulomb)	0.1881 <sup>26</sup>
Electrode potential Ge <sup>++++</sup> (H <sub>2</sub> = 0.0 volts)*	-0.15 (est'd) <sup>34</sup>

\* National Bureau of Standards nomenclature.

GeO<sub>2</sub>. The latter, germanium dioxide, is the type sold commercially.

Johnson<sup>37</sup> has compiled an excellent summary of the published work on the inorganic compounds of germanium; a similar digest by the same author<sup>36</sup> covers the extensive work on organometallic compounds of germanium.

In detection of germanium, the sample is usually fused with sodium carbonate or caustic soda. Germanium is separated from most of the other elements by dissolving the fused mass and distilling from a strong hydrochloric acid solution. The distillate is tested by the appropriate method.

Qualitative analysis for small amounts of germanium is best made by reacting with phenylfluorone. An intense rose color is formed in the presence of even traces of germanium.<sup>13</sup>

Precipitation as the sulfide from strong sulfuric acid solution can be used for larger quantities of germanium.

For quantitative determination, the sample is fused with caustic soda or sodium carbonate, the fused mass is reacted with hydrochloric acid, and the resultant germanium tetrachloride is distilled off in the presence of chlorine. The tetrachloride is dissolved in 6*N* sulfuric acid and precipitated as the sulfide. The sulfide is oxidized to the dioxide with hydrogen peroxide and weighed.<sup>35</sup>

The tetrachloride can also be reduced with sodium hypophosphite and the divalent germanium determined by titration with potassium iodate.<sup>30</sup>

For very small amounts of germanium, colorimetric determination with phenylfluorone<sup>13</sup> or oxidized hematoxylin<sup>57</sup> is more satisfactory than the gravimetric or titrimetric methods.

Spectrographic methods of analysis are widely used. Strock<sup>77</sup> has used beryllium oxide as an internal standard, carbon powder as a dispersing agent, and a crater-type electrode, burning in a d-c arc and using the 2651.1 Å line. A variation of this procedure uses lithium carbonate as an internal standard, completely vaporizing the sample at 10 amp (d-c), which requires 2 to 3 min.<sup>50</sup> Another method uses a pegmatic diluent without an internal standard.<sup>20</sup>

A critical review of analytical methods for germanium has been published by Krause and Johnson.<sup>41</sup>

Chemical methods for analysis of impurities in germanium for electronic use are not satisfactory. Spectrographic methods can be employed, but it is more usual to make electrical-resistivity measurements. Neutron-activation analysis has also been used.

Germanium or germanium dioxide shows no evidence of toxicity.<sup>24</sup> Germanium tetrachloride is irritating when inhaled; this is believed to be due to hydrolysis of the compound to GeO<sub>2</sub> and HCl; the released acid is probably the cause of the irritation.

**Alloys.** Some pertinent information on the alloys of germanium is given below.

*Aluminum*—The binary system germanium-aluminum forms a eutectic at 55 per cent by weight of germanium which melts at 423°C (793°F).<sup>43,74</sup> In the solid state, aluminum is slightly soluble in ger-

from strong sulfuric  
for larger quantities

ination, the sample  
or sodium carbonate,  
with hydrochloric  
anium tetrachloride  
nce of chlorine. The  
in 6N sulfuric acid  
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electrode, burning in  
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germanium which  
)<sup>43,74</sup> In the solid  
htly soluble in ger-

manium; similarly, germanium is slightly  
soluble in aluminum.

*Antimony*—The system germanium-  
antimony forms a eutectic melting at  
588°C (1090°F) and containing 28.5 per  
cent by weight of germanium.<sup>68</sup> In the solid  
state, germanium is slightly soluble in  
antimony and antimony is slightly soluble  
in germanium.<sup>75</sup>

*Arsenic*—The germanium-arsenic system  
indicates two compounds, GeAs and  
GeAs<sub>2</sub>.<sup>75</sup>

*Bismuth*—A eutectic is formed which  
melts at 271°C (520°F) and is almost 100  
per cent bismuth.<sup>68,75</sup>

*Cobalt*—A germanium-cobalt alloy, con-  
taining 41 per cent germanium by weight,  
is reported.<sup>46</sup>

*Copper*—This system has received con-  
siderable study.<sup>28,70</sup> Only one compound,  
Cu<sub>3</sub>Ge, has been identified. A eutectic is  
formed at 650°C (1202°F) and about 39  
per cent by weight germanium. Alpha  
copper will dissolve about 10 per cent of  
germanium in the solid state.<sup>27</sup> The ternary  
system Cu-Ge-Au has been investigated.<sup>31</sup>

*Gold*—The system gold-germanium forms  
a eutectic containing 12 per cent ger-  
manium by weight which melts at 356°C  
(673°F);<sup>33</sup> 0.8 per cent germanium is  
soluble in gold at 350°C (662°F); it is  
very slightly soluble at room temperature.  
Ternary systems have been investigated.<sup>31</sup>

*Iridium*—A compound IrGe is re-  
ported.<sup>64</sup>

*Iron*—Two compounds are reported.<sup>46,68</sup>  
Fe<sub>2</sub>Ge melts at 1180°C (2156°F) and  
FeGe<sub>2</sub> at 866°C (1591°F).

*Lead*—Germanium and lead are mutu-  
ally soluble in the liquid state, but the  
germanium precipitates out almost com-  
pletely on cooling.<sup>10</sup>

*Magnesium*—A compound Mg<sub>2</sub>Ge is  
known; it melts at 1115°C (2039°F) and  
contains 59.9 per cent germanium by  
weight.<sup>40</sup> Two eutectics are formed, one  
at 635°C (1175°F) (3.4 per cent ger-  
manium by weight) and another at 680°C  
(1256°F) (83 per cent germanium by  
weight).

*Nickel*—The binary system is complex;  
only one compound has been definitely  
identified.<sup>46,64,65</sup> This compound is Ni<sub>2</sub>Ge,

melting at 1200°C (2192°F). Another com-  
pound is mentioned, NiGe, but there seems  
to be some doubt of its existence. Two  
eutectics are formed; one melts at 1130°C  
(2066°F) (33 per cent germanium by  
weight), the other at 775°C (1427°F)  
(66 per cent germanium by weight).  
Nickel dissolves approximately 12 per cent  
of germanium in the solid phase.

*Palladium*—A compound PdGe is re-  
ported.<sup>64</sup>

*Platinum*—A compound PtGe is re-  
ported.<sup>64</sup>

*Selenium*—Two compounds GeSe and  
GeSe<sub>2</sub> have been prepared.<sup>29</sup>

*Silicon*—Silicon and germanium form a  
continuous series of solid solutions.<sup>75</sup>

*Silver*—The silver-germanium system in-  
dicates no compounds;<sup>11</sup> the single eutectic  
contains 18 per cent germanium by weight  
and melts at 650°C (1202°F).

*Sodium*—An alloy corresponding to the  
formula NaGe has been prepared;<sup>14</sup> it  
slowly decomposes in moist air.

*Tellurium*—One compound GeTe is re-  
ported;<sup>39</sup> it melts incongruently at 725°C  
(1337°F).

*Tin*—Tin and germanium form a eutec-  
tic which melts at 232°C (450°F) and is  
almost 100 per cent tin.<sup>75</sup> Germanium is  
only slightly soluble in solid tin; likewise,  
tin is only slightly soluble in solid ger-  
manium.

*Zinc*—A eutectic is formed melting at  
398°C (748°F), which contains 6 per cent  
germanium by weight. No compounds ap-  
pear to be formed. Germanium and zinc  
have only slight solubility in each other  
in the solid state.<sup>17</sup>

## FABRICATION TECHNIQUES

The reduction of germanium dioxide to pow-  
dered metal and subsequent melting to ingots  
has been described under the heading "Deriva-  
tion." Further purification of the metal by  
recrystallization under vacuum or in an inert  
atmosphere is likewise covered in that section.

Germanium is supplied in ingots of 15 to 26  
in. (38 to 66 cm) and of varying cross sections,  
as demanded by the industry. Cross-sectional  
areas of as much as 1 sq in. are available.  
Attempts have been made to fabricate the



metal in ribbon form, but no such material has yet been offered for sale. Pure germanium does not lend itself to fabrication into wire, rod, or rolled shapes.

Single crystal germanium is also supplied. It is produced<sup>61</sup> by "seeding" a melt of germanium (held only slightly above the melting point) and slowly withdrawing the crystal from the furnace.

To obtain the desired properties for electronic applications, pure germanium must be further processed. Pressure or heating and quenching are sometimes employed. The usual one, however, is "doping" or alloying with minute amounts of appropriate metals. Many alloys have been patented for these purposes.<sup>45,82</sup> Alloying is usually done in an inert atmosphere or under vacuum. Several ingenious methods of incorporating these very small amounts of other metals have been devised. Diffusing of the appropriate metal into the germanium is one of these; another is electroetching.

Electrodeposition of germanium from 3*N* potassium hydroxide solution on copper cathodes produces a thin, coherent coating, but deposition stops as soon as the cathode is covered.<sup>23</sup> A bath of germanium tetraiodide in ethylene glycol at 150°C (302°F) is reported to deposit germanium.<sup>15</sup> Some success has been achieved in electrodeposition from germanium tetrachloride dissolved in propylene glycol.<sup>78</sup>

### APPLICATIONS

The science of solid-state physics, and particularly that phase of it relating to semiconductors, has found many practical applications in the past decade. The first major strides in utilizing semiconducting properties were due primarily to the availability of high-purity germanium. While many other and diverse semiconducting materials have been or are being developed,<sup>83</sup> germanium is still one of the most important. It is in this field that germanium finds its major use.

The semiconducting properties of germanium first led to its use as a crystal diode rectifier<sup>79</sup> in World War II. In 1948 the germanium triode or transistor was developed.<sup>7</sup> Since that time, continuous developments and improvements have been made on germanium semiconducting devices which have opened entirely new fields for their utilization. The first germanium diode was a fine wire of appropriate

metal pressing against a thin wafer of properly prepared germanium (analogous to the old galena whisker detector). The wire and germanium wafer were soldered to separate electrical conductors, and the unit was embedded in plastic or enclosed in glass. This assembly was scarcely larger than a grain of corn.<sup>61</sup> Advances in technology have improved and miniaturized the original diodes; for many special applications, present-day diode assemblies are scarcely thicker than the wire in a paper clip and less than ½ cm long.

Germanium diodes, besides acting as crystal rectifiers, perform the same general functions as vacuum tube diodes. They have very small power consumption, very little heat emission, start up immediately (since there is no filament to heat), and are quite rugged. Many diverse types of germanium diodes are commercially available. One interesting property of germanium diodes<sup>79</sup> is their photoelectric effect, which is commercially utilized in the photodiode.

The first transistors had much the same size as the germanium diodes, except that two wires made contact with the germanium wafer instead of one; this was called a point-contact transistor. Later, another type was developed which was made up of a single tiny block of germanium suitably treated to give different properties to the end sections, in comparison with the center section: this was called a junction or area transistor. Each of these types has its advantages and limitations. These first transistors were quite small (about a ¼-in. cube); like the diodes, improvements in technology and manufacture have allowed further reduction in size and major improvements in performance. Power transistors are, of course, much larger.

The first transistors were used as amplifiers and oscillators. As new developments were made, their utility was greatly increased until, in 1959 alone, 125 million semiconducting devices were manufactured.<sup>16</sup> It has been only in the last 4 or 5 years that mass-production techniques have been developed which made these devices available for widespread use.

These devices have allowed miniaturization and improvements in radios, hearing aids, and communication equipment. Replacement of vacuum tubes by transistors has allowed direct long distance dialing in our telephones. Communications of all types depend heavily on

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such semiconducting devices. Military equip-  
 ment has been vastly improved and mini-  
 aturized. These developments, which are so  
 important to the Defense Forces, have also  
 benefited civilian and commercial operations.  
 The use of specialized germanium devices has  
 allowed major advances in astronautics and  
 missile guidance.

The theory of semiconductors and the mech-  
 anism of the behavior of germanium diodes  
 and triodes are beyond the scope of this chap-  
 ter. Shockley<sup>72</sup> gives an excellent theoretical  
 treatment; O'Connor<sup>61</sup> gives a lucid description  
 of the mechanism for transistors.

Germanium power rectifiers are in commer-  
 cial use and have many advantages over the  
 older types.<sup>12</sup> In 1956 alone, rectifiers for  
 50,000 KW were installed. Many types are com-  
 mercially available, and their use is increasing  
 rapidly.

Germanium is transparent to infrared light.  
 This property is utilized in the infrared spectro-  
 scope and other optical instruments. Special  
 germanium devices are also used in extremely  
 sensitive infrared detectors supplementing radar  
 for detection purposes. The high index of re-  
 fraction and high dispersion of germanium  
 glasses (in which germanium dioxide replaces  
 silicon dioxide) has led to their use in special-  
 ized optical equipment. Magnesium germanate  
 is used as a phosphor in fluorescent lamps.<sup>42</sup>  
 A germanium resistance thermometer which  
 will operate at temperatures near absolute zero  
 has been developed. Germanium is being studied  
 as a catalyst and shows considerable promise  
 for some applications.

Gold-germanium alloys have been suggested  
 for use in dental work or precision casting<sup>33</sup>  
 because of their expansion upon solidification.  
 The low melting gold-germanium eutectic could  
 be used as an improved gold solder or in the  
 reduction of the melting temperature of gold-  
 containing alloys.

Resistors made by deposition of germanium  
 on a thin film of silver have interesting prop-  
 erties.<sup>32</sup> Such films, formed by first depositing  
 silver on "Pyrex" glass and subsequently de-  
 positing germanium on the silver, have resis-  
 tivities from 1,000 ohms to several megohms  
 and extremely good temperature coefficients.

The ready availability of germanium has  
 spurred further research with it, both in the  
 electronic field and for other applications.

### References

1. Ahrens, L. H., *S. African J. Sci.*, **41**, 152-160 (1945).
2. Anon., *Eng. and Mining J.*, **157**, #5, 75 (1956).
3. Anon., *Eng. and Mining J.*, **157**, #5, 79 (1956).
4. Anon., *Eng. and Mining J.*, **157**, #5, 83 (1956).
5. Anon., *Eng. and Mining J.*, **157**, #5, 85 (1956).
6. Anon., *Eng. and Mining J.*, **157**, #5, 88 (1956).
7. Bardeen, J., and Brattain, W. H., *Phys. Rev.*, **74**, 230-1 (1948); *ibid.*, **75**, 1208 (1949).
8. Boving, Theophile and Andre, Jean, *J. of Metals*, **10**, 659 (1958).
9. Briggs, H. B., *Phys. Rev.*, **77**, 297 (1950).
10. Briggs, T. R., and Benedict, W. S., *J. Phys. Chem.*, **34**, 173-77 (1930).
11. Briggs, T. R., McDuffie, R. O., and Willisford, L. H., *J. Phys. Chem.*, **33**, 1080-96 (1929).
12. Burton, L. W., and Thurell, J. R., *Power*, **101**, #7, 73 (1957).
13. Cluley, H. J., *Analyst*, **76**, 525 (1951).
14. Dennis, L. M., and Skow, N. A., *J. Am. Chem. Soc.*, **52**, 2369-72 (1930).
15. Fink, C. G., and Dokras, V. M., *Trans. Electrochem. Soc.*, **95**, 80 (1949).
16. Fisher, Frank L., "Germanium," pp. 341-346 in "Mineral Facts and Problems," Bulletin 585, U.S. Bureau of Mines, Washington, D.C., Government Printing Office, 1960.
17. Gebhardt, Erich, *Z. Metallkunde*, **34**, 255-57 (1942).
18. Goldschmidt, V. M., *Ind. Eng. Chem.*, **27**, 1100-2 (1935).
19. Goldschmidt, V. M., and Peters, Cl., *Nachr. Ges. Wiss. Göttingen, Math. physik. Kl.*, III: IV, 141 (1933).
20. Gordon, Mackenzie, and Murata, K. J., *Econ. Geol.*, **47**, 170 (March-April 1952).
21. Graham, R. P., Macnamara, J., Crocker, I. H., and MacFarlane, R. B., *Can. J. Chem.*, **29**, 89-102 (1951).
22. Greiner, E. S., *J. of Metals*, **4**, 1044 (1952).
23. Hall, J. I., and Koenig, A. E., *Trans. Electrochem. Soc.*, **65**, 215 (1934).
24. Harrold, G. C., and Meek, S. F., *Ind. Med.*, **13**, 236-8 (1944).
25. Headlee, A. J. W., and Hunter, R. G., "Germanium in Coals of West Virginia," Geological and Economic Survey, Report of Investigations No. 8, Morgantown, West Virginia, 1951.
26. Hodgman, C. D., "Handbook of Chemistry and Physics," Cleveland, Ohio, Chemical Rubber Publishing Co., 1951-1952.
27. Hume-Rothery, Wm., Mabbott, G. W., and Channel-Evans, K. M., *Phil. Trans. Royal Soc.*, **233A**, 1-97 (1934).
28. Hume-Rothery, W., Raynor, G. V., Reynolds,

- P. W., and Packer, H. K., *J. Inst. Metals*, **66**, 209-39 (1940).
29. Ivanov-Emin, B. N., *J. Gen. Chem. (USSR)*, **10**, 1813-18 (1940).
30. Ivanov-Emin, B. N., *Zavodskaya Lab.*, **13**, 161 (1947).
31. Jaffee, R. I., and Gonser, B. W., *A.I.M.E. Tech. Pub. 1998* (1946).
32. Jaffee, R. I., McMullen, E. W., and Gonser, B. W., *Trans. Electrochem. Soc.*, **89**, 277-90 (1946).
33. Jaffee, R. I., Smith, E. M., and Gonser, B. W., *Trans. A.I.M.E.*, **161**, 366 (1945).
34. Jirsa, Franz, *Z. anorg. u. allegem. Chem.*, **268**, 84-8 (1952).
35. Johnson, E. B. and Dennis, L. M., *J. Am. Chem. Soc.*, **47**, 790-3 (1925).
36. Johnson, O. H., *Chem. Revs.*, **48**, 259-297 (1951).
37. Johnson, O. H., *Chem. Revs.*, **51**, 431 (1952).
38. Kelley, K. K., "Contributions to the Data on Theoretical Metallurgy. XI. Entropies of Inorganic Substances. Revision (1948) of Data Methods of Calculation," *Bur. Mines Bull. 477*, p. 98, Washington, Government Printing Office, 1950.
39. Klemm, W., and Frischmuth, G., *Z. anorg. Chem.*, **218**, 249-51 (1934).
40. Klemm, W., and Westerlinning, H., *Z. anorg. Chem.*, **245**, 365-80 (1941).
41. Krause, H. H., and Johnson, O. H., *Anal. Chem.*, **25**, 134 (1953).
42. Kroeger, F. A., and van den Boomgaard, J., *J. Electrochem. Soc.*, **97**, 377-82 (1950).
43. Kroll, W., *Metall u. Erz*, **23**, 682-84 (1926).
44. Lark-Horovitz, K., and Whaley, R. M., "The Preparation of Pure Germanium and Its Semi-conducting Alloys," Paper presented before the Ninety-Fifth Meeting of The Electrochemical Society, Philadelphia, May, 1949.
45. Lark-Horovitz, K., and Whaley, R. M., U.S. Patent 2,514,879 (July 11, 1950).
46. Laves, F., and Wallbaum, H. J., *Z. angew. Mineral.*, **4**, 17-46 (1942).
47. Lebedeff, E. Yurii, and Wetherill, Wm. H., U.S. Patent 2,889,196 (June 2, 1959).
48. McCabe, Louis C., *Ind. Eng. Chem.*, **44**, 113a (1952).
49. Machin, J. S., and Witters, Juanita, *Ill. State Geol. Survey Circular 216*, 1956-13 pages.
50. Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 7, New York, Longmans, Green and Co., 1930.
51. Mendeleeff, D. E., *Ann.*, Supplementband, **8**, 196-206, (Heft 2) (1871).
52. "Minerals Yearbook," (U.S. Bur. Mines) Washington, D.C., Government Printing Office, 1948.
53. *Ibid.*, 1949.
54. *Mining J. (London)*, **234**, 5982, 367-8 (1950).
55. Morgan, G., and Davies, G. R., *Chemistry & Industry*, **56**, 717-21 (1937).
56. National Research Council, "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," Vol. 1, p. 102, New York, McGraw-Hill Book Co., Inc., 1926.
57. Newcombe, H., et al., *Anal. Chem.*, **23**, 1023 (1951).
58. Newlands, *Chem. News*, **10**, 59, (July 30, 1864).
59. Noyes, A. A., and Bray, W. C., "A System of Qualitative Analysis for the Rare Elements," New York, The Macmillan Co., 1927.
60. O'Connor, Joseph A., *Chem. Eng.*, **59**, No. 4, 158-160 (1952).
61. *Ibid.*, No. 5, 154-6, 370-6 (1952).
62. Papish, Jacob, Brewer, F. M., and Holt, Donald A., *J. Am. Chem. Soc.*, **49**, 3031-2 (1927).
63. Petar, Alice V., "Gallium, Germanium, Indium and Scandium," *U.S. Bur. Mines Inform. Circ. 6401*, 5, (Nov. 1930).
64. Pfisterer, H., and Schubert, K., *Naturwissenschaften*, **37**, 112-13 (1950).
65. Pilkington, E. S., *Australian J. of Applied Science (Melbourne)*, **8**, #2, 98-111 (June, 1957).
66. Powell, A. R., Lever, F. M., and Walpole, R. E., *J. Applied Chem.*, **1**, 541-51 (1951).
67. Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S., and Jaffe, I., "Selected Values of Chemical Thermodynamic Properties," *Natl. Bur. Standards Circ. 500*, p. 151, Washington, Government Printing Office, 1952.
68. Ruttewit, K., and Masing, G., *Z. Metallkunde*, **32**, 52-61 (1940).
69. Schleicher, John A., State Geol. Survey of Kans., Bulletin 134, part 4, U. of Kans. Publications, Lawrence, Kansas (1959).
70. Schwarz, R., and Elstner, G., *Z. anorg. Chem.*, **217**, 289-97 (1934).
71. Searcy, Alan W., *J. Am. Chem. Soc.*, **74**, 4789 (1952).
72. Shockley, Wm., "Electrons and Holes in Semiconductors," New York, D. Van Nostrand Co., Inc., 1950.
73. Stadnichenko, T., Murata, K. J., Zubovic, P., and Hufschmidt, E. L., U.S. Geol. Survey, *Circ. No. 272* (1953).
74. Stohr, H., and Klemm, W., *Z. anorg. Chem.*, **241**, 305-23 (1939).
75. Stohr, H., and Klemm, W., *Z. anorg. u. allgem. Chem.*, **244**, 205-23 (1940).

ment Printing Office,

5982, 367-8 (1950).

G. R., *Chemistry & Physics*, 23, 330-34 (1952).

International Council, *International Tables for X-ray Crystallography*, Vol. 1, p. 102, McGraw-Hill Book Co., Inc., 1926.

*J. Chem. Phys.*, 23, 1023 (1955).

*Ann. Chem.*, 59, July 30, 1864).

W. C., "A System of the Rare Elements," McGraw-Hill Book Co. 1927.

*Chem. Eng.*, 59, No. 4, 1952).

M., and Holt, Donald, *Metals Technol.*, 49, 3031-2 (1927).

Germanium, Indium, *Mines Inform. Circ.*, 1952).

rt, K., *Naturwissenschaften*, 1952).

*Australian J. of Applied Science*, #2, 98-111 (June, 1952).

M., and Walpole, *J. Chem. Phys.*, 19, 541-51 (1951).

D. D., Evans, W. H., "Selected Values of the Properties," *Natl. Bur. of Standards*, p. 151, Washington, 1952.

G., *Z. Metallkunde*, 1952).

Geological Survey of the United States, *Publications*, 1959).

G., *Z. anorg. Chem.*, 1952).

*Chem. Soc.*, 74, 4789 (1952).

and Holes in Semiconductors, Van Nostrand Co., 1952).

K. J., Zubovic, P., *Geol. Survey, Circ.*, 1952).

*Z. anorg. Chem.*, 1952).

*Z. anorg. u. allgem. Chem.*, 1952).

76. Straumanis, M. E., and Aka, E. Z., *J. Appl. Phys.*, 23, 330-34 (1952).

77. Strock, L. W., *Am. Inst. Mining Met. Engrs., Tech. Publ. No. 1866* (1945). (Published in *Metals Technol.*, April, 1945).

T., Murata, K. J., Zubovic, P., and Hufschmidt, E. L., (1953).

73. U.S. Geol. Survey, *Circ. No. 272* Stadnichenko, 57. Newcombe, H., et al, *Anal. Chem.* 23, 1023 (1951).

78. Szekeley, G., *J. Electrochem. Soc.*, 98, 318-34 (1951).

79. Torrey, H. C., and Whitmer, C. A., "Crystal

Rectifiers," New York, McGraw-Hill Book Co., 1948.

80. Unpublished data from the Research Laboratories of The Eagle-Picher Company, Joplin, Missouri.

81. Vaes, J. F., *Ann. soc. géol. Belg.*, T LXXII, B19-B32 (Oct. 1948).

82. Whaley, R. M., U.S. Patent 2,447,829 (Aug. 24, 1948).

83. Willardson, R. K., *Battelle Tech. Rev.*, 6, #8, 8 (1957).

84. Winkler, C., *Ber.*, 19, 210-1 (Feb. 8, 1886).

Mineral facts and problems.

U.S. Bureau of Mines Bull. 650, 563-571. 1970.

GERMANIUM

By James Paone <sup>1</sup>

Because germanium is a minor byproduct of ores mined primarily for zinc, the supply of primary germanium in the United States is wholly a factor of the domestic zinc production rate. The element also occurs in some coals, which are a commercial source of germanium in Great Britain. A major component of the U.S. supply of germanium is derived from recycled scrap from manufacturing processes. Currently, domestic supply is equal to demand. Large stocks are accumulated in residues containing germanium.

Most germanium consumption is currently in the electronics industry, where it is used predominantly as a semiconductor. However, there is strong competition from alternate materials in this market, which is tending to reduce the demand for germanium in this end use. Although sales of germanium have only a small effect upon the economics of extracting and producing the primary product, the available supply of refined germanium has been significant enough to prompt industry inquiry into potential new uses.

Based on contingency forecasts of demand for germanium, an interval range of possible demand for primary in the year 2000 is between 33,000 and 65,000 pounds. Rest-of-the-world demand for primary germanium is forecast at 120,000 to 220,000 pounds in 2000. Projected domestic supply from lead-zinc operations is adequate to meet the low of the forecast range of cumulative demand during 1968-2000, although at a price somewhat higher than current levels, reaching an estimated \$120 per pound in the year 2000. However, recovery of germanium

from processing certain coals may be necessary to meet the high forecast range. The high range would probably be met at an indicated price of \$150 per pound in 2000. A parallel situation exists for the rest of the world. Secondary germanium will continue to be a major factor in the supply-demand picture, but this factor will begin a slight downward trend as technological improvements in manufacturing emerge and as a higher proportion of germanium is used dissipatively for massive items such as nuclear radiation detection devices, special optical glass, and infrared transmitting lenses, and as a consumed catalyst in the production of polyester fibers.

Solid state technology, brought about through widespread utilization of semiconductors for transistors, diodes, and rectifiers, will find increasing application in many aspects of consumer electronics, communications equipment, and control and computing equipment. Similarly, rapid growth is expected in infrared technology for thermal mapping and surveillance. Such areas of growth could result in increased demand for germanium. The use of germanium in electronic nuclear detection systems is expected to show a positive growth rate throughout the forecast period. Based on these considerations, the demand for germanium could be expected to approach the high of the forecast demand range by the year 2000. The major contingency which would lead to the forecast low would be the substitution of other materials for germanium in electronic applications.

BACKGROUND

In 1871, Mendeleev, a Russian scientist, predicted a missing element between silicon and tin in the periodic table. Fifteen years later, Clemens Winkler, a German scientist, isolated the element from the mineral argyrodite and named it germanium in honor of his native country. Investigation of the properties of germanium confirmed the prediction of Mendeleev (8).<sup>2</sup>

Germanium remained little more than a scientific curiosity until the early 1920's when

extensive studies were conducted on possible applications of the element. In 1922, the therapeutic value of germanium oxide in treating anemia was reported. The first commercial producer of germanium dioxide was the Otavi Co. in Frankfurt, Germany, in 1930. The source of this material was germanite ore obtained from

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<sup>2</sup> Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

the Tsumeb mine in the then-German colony of the Territory of South-West Africa.

The zinc ores of the Kansas-Missouri-Oklahoma area contain a small amount of germanium. Germanium, an impurity in refined zinc, is removed by a difficult and costly process. The Eagle-Picher Co. initiated a research program to determine what, if any, commercial application could be developed for this byproduct. Fundamental research programs at the Bell Telephone Laboratories and Purdue University resulted in the development of semiconductor applications for germanium; and by 1941 a germanium-recovery facility was in operation in connection with the Henryetta, Okla., zinc smelter of The Eagle-Picher Co.

The semiconductor properties of germanium were first utilized extensively for crystal diode rectifiers during World War II. In 1948, the germanium transistor was developed and expanded research and availability of high-purity germanium has revolutionized the communications industry. The semiconductor devices currently utilized—diodes, transistors, and rectifiers—have permitted miniaturization of radios, television, hearing aids, and telephone dialing equipment, and have resulted in major advances in astronautics, missile guidance, and worldwide communications systems.

#### INDUSTRY PATTERN

One domestic refinery produces germanium by refining residues from zinc concentrates from domestic mines and from residues from other zinc refineries; these residues are not traceable to individual mines. In addition to the primary refinery, Eagle-Picher, Miami, Okla., three secondary refineries in Pennsylvania and New Jersey process new scrap generated in the manufacture of semiconductor devices.

None of the domestic processors operates mines in foreign countries. Germanium is a minor aspect of the producers' base metal or manufacturing activities. One producer is fully integrated from mining through end-product application.

Foreign production is centered at two base-metal mines, one in the Congo (Kinshasa) and one in the Territory of South-West Africa. From these sources, germanium is exported either as a concentrate or as the dioxide for refining to metal in western Europe, the United States, or Japan. Germanium is a minor activity of these base-metal mines and of other refineries operating on germanium derived from base-metal ores. Germanium production in the U.S.S.R. is likewise a byproduct of importance only to the degree of self-sufficiency desired.

#### TECHNOLOGY

##### Definition of Terms, Grades, and Specifications

Germanium is metallic-looking but displays the physical and chemical properties of a metal only under special conditions. It is a semiconductor with properties ranging between those of a metal and of an insulator. Structurally, germanium has the cubic symmetry of the diamond crystal lattice and four valence electrons (5).

Germanium is available in three forms—as reduced ingots, purified ingots, and single crystals. Standard ingots are 15 to 17 inches long and weigh approximately 1,750 grams. Mono, or single, crystals grown are supplied in sizes up to 3 inches in diameter and weights up to 2,000 grams. These crystals are normally grown in the 1:1:1 orientation.

The standard measurement of purity of electronic-grade germanium is resistivity. These measurements are made using a four-point probe on an abraded surface at 25° C. In the polycrystalline form, measurements are made along the bottom of the ingot.

Specifications for marketable electronic-grade germanium have changed as the requirements of the electronic industry became more rigid. It is typical for germanium to be offered to consumers under the following resistivity specifications:

	<i>Ohm centimeters (minimum)</i>
As-reduced .....	5
Purified .....	40
Monocrystalline .....	40

Germanium is also offered commercially in the form of the dioxide and compounded with other metallic and nonmetallic substances.

Test procedures for determination of volatile content and bulk density of germanium dioxide have been accepted by the American Society for Testing and Materials (2).

The widely manufactured germanium alloy transistor is cut out from a single germanium crystal. It consists of a pellet of semiconductor metal about 4 square millimeters in area and about 0.2 millimeter thick. It has three zones behaving differently electrically; the different electrical properties are obtained by alloying with, or diffusing in, small quantities of certain elements. In a diode, the area of the semiconductor is only about one-fourth the size of the transistor, for rectifiers, the area may be many times larger, depending on the magnitude of the current to be rectified. The average single-junction diode is estimated to weigh 0.0007 gram, or 0.000025 ounce; the transistor units are estimated to be about eight times heavier.

### Current Technology

**Geology.**—There are no native occurrences of germanium, and its abundance in the earth's crust is 1 part in 150,000 (or 6.7 parts per million). The most common occurrence of germanium is in minute quantities within the molecular structure of other minerals. It occurs most abundantly in sphalerite (ZnS) in quantities ranging from traces to tenths of 1 percent. Germanium is generally supposed to be most concentrated in sphalerites, where the temperatures of formation are lowest; recent studies have shown the cold water diagenetic sphalerites of central Kentucky are virtually free of germanium (9). Cinnabar sometimes contains germanium in tenths of 1 percent, and enargite may have up to 0.1 percent. Pyragyrite from the silver mines of Bolivia contains up to 0.1 percent, and some tin-bearing sulfides contain 0.5 percent. Germanium has also been said to occur in calamine, pyrites, euxenite, cassiterite, and tantalum and columbium ores. However, the amounts recorded are small, usually about 0.001 percent or less.

Extensive studies have been made on the germanium content as well as techniques used for analysis and detection of germanium in coal (1, 4).

**Mining and Metallurgy.**—No mines are operated solely for recovery of germanium. Germanium is obtained commercially as a byproduct of zinc production and from germanium-bearing minerals as a coproduct of base-metal refining.

In the metallurgical recovery of germanium from the Tri-State zinc sulfide concentrates, the sulfur is first removed by roasting, and the zinc, germanium, and cadmium are converted to oxides. The oxides are given a chloridizing roast to convert cadmium and germanium to chlorides which are volatilized. These are condensed and collected electrostatically to yield a product from which germanium can be distilled as the tetrachloride.

The copper-zinc ores of Katanga contain germanium as the mineral renierite. In selective flotation of the ores, the renierite reports with the copper concentrate. Part of the renierite is then recovered by magnetic separation. This product is treated in an electric furnace to obtain a fume containing germanium dioxide. Germanium-bearing fume and dust, recovered from the copper smelting, are then baked with sulfuric acid and leached to obtain a germanium-bearing solution from which, after oxidation, the germanium is precipitated with magnesia and copper hydrate to form a concentrate which is then shipped to Belgium for further refining.

Flue dusts are smelted with soda ash, lime, copper oxide, and coal dust to form a regulus and slag. The regulus, containing germanium,

is reacted with chloride under a dilute solution of ferric chloride, and the crude germanium tetrachloride is distilled. Arsenic chloride accompanying the germanium is eliminated by refluxing with copper turnings.

Controlled purity is essential in germanium for electronic uses. Less than 1 part per 100 billion of some impurities has an observable effect. Germanium tetrachloride is purified by distilling it from strong hydrochloric acid solution. After distillation it is hydrolyzed in ice water to obtain pure germanium dioxide, which is washed completely free of chloride and is then ready for reduction to the metal.

Germanium dioxide is reduced by heating in hydrogen. The dioxide is packed in graphite boats and heated to 650° C in an electric furnace in a current of hydrogen until no more water is evolved. The hydrogen is then replaced by helium or nitrogen, and the temperature is raised to 1,000° C to melt the resulting powder.

When germanium is used as a semiconductor, it is necessary to have an ultra-high purity which is measurable in parts per billion and which is achieved by zone refining. A germanium ingot 12 to 20 inches in length and 1 to 1½ inches in diameter is passed through a series of induction-coil heaters, each of which produces a molten zone. Relatively pure germanium crystallizes at the trailing edge of each molten zone; impurities remain in the molten zone and are gradually isolated toward one end as the bar moves through the heaters. After the desirable number of passes are made through the induction stages, the end of the ingot containing the impurities is cut off.

The ultrapure germanium ingot thus produced is polycrystalline, and for semiconductor use it must be in the form of a single crystal. Two methods of single-crystal growth were developed for growing germanium crystals. The first, originated by Czochralski, is called the vertical-pulling method. A crystallographically oriented seed crystal is dipped into molten germanium in a graphite crucible and slowly withdrawn. By adjusting the heat input and heat losses, and under proper conditions and synchronization, the germanium will grow on the seed and extend its crystal lattice until the charge has been converted to one crystal.

The second method, called the horizontal or zone-leveling technique, is a modification of zone melting. The crystal seed is placed at one end of a horizontal, carbon-coated silica crucible filled with ultrapure polycrystalline germanium. The whole may be converted into a single crystal with the controlled addition of a desired impurity by carefully moving a molten zone toward the seed, melting into it, and then slowly withdrawing the molten zone (6).

### Research

Large-scale research on germanium was focused first on removing the element from zinc concentrates and later on the development of a process for refining the extracted germanium on a commercial basis. Later, research programs were directed toward finding industrial applications for the metal.

The search for significant industrial applications was successful in introducing the germanium diode during World War II. The transistor developed in 1948 by W. Shockley, J. Bardeen, and W. Brattain at the Bell Telephone Laboratory provided a major advance for germanium. These men received the Nobel Prize for their significant contribution to knowledge of solid-state physics which revolutionized electronic theory and design.

Research conducted on the commercial recovery of germanium from coals and other hydrocarbons has not yet resulted in a competitive process (10, 14).

A Germanium Research Committee was formed in 1959 by six domestic and foreign producers. The purpose of this group is to unite their research efforts to develop new uses for germanium and to disseminate information on germanium and its applications. Research being sponsored by the group is conducted by many organizations throughout the world (5).

Recent research has been on electrorefining, electrolytic slicing in preparing semiconductor wafers, growing of large (500 cubic centimeters), high-purity monocrystals, developing detector-grade germanium for use in nuclear detection instruments, improving doped germanium for infrared transmission and detection devices, and developing methods for calibrating germanium resistors for low-temperature thermometry (3, 11-13).

### APPARENT RESERVES

The germanium reserves of the United States have not been seriously studied. The lead-zinc-fluorspar ores of the Mississippi Valley are currently the only exploited source. Data on production from these ores are not available, but Bureau of Mines sampling has shown 0.008 to 0.026 percent germanium in zinc concentrates of this area. Additionally, a potential supply exists in other domestic base-metal ores, the industry evaluation of which was terminated in 1952 when further supply expansion was deemed unwarranted. Sampling of ore deposits in New Mexico indicates a range of 3.5 to 78 parts per million (0.00035 to 0.0078 percent) in certain deposits. Various domestic coals contain a concentration of up to 0.05 percent germanium in the ash.

The potential of the United States for germanium production as a byproduct from various sources of primary material has been indicated at 55,000 pounds of germanium annually. Recovery at this rate is believed possible for at least 15 years (an apparent reserve of 825,000 pounds). An apparently larger resource for germanium is in coals.

World reserves are unknown but have been evaluated at an annual production potential of 154,000 pounds which amounts to over 3 million pounds when projected over a 20-year period. The Territory of South-West Africa has the largest potential (57 percent), followed by the Congo (Kinshasa) (36 percent). Japan, Italy, France, the United Kingdom, and the U.S.S.R. are considered relatively self-sufficient.

A relatively large potential source of world germanium is the germanium compounds found in certain coal ashes and flue dusts. It has been estimated that in the United Kingdom 4 million pounds of germanium yearly may be present in stack gases, flue dusts, and ashes at plants burning germanium-bearing coal.

### SUPPLY-DEMAND RELATIONSHIPS

#### Production, Consumption, and Trade

Domestic production of primary germanium from domestic sources was estimated at 21,000 pounds in 1968, with a total consumption of primary plus reprocessed scrap of 75,000 pounds. Two-thirds of the domestic demand was met from supplies refined from scrap sources.

U.S. production of primary germanium in 1968 was augmented by imports of germanium concentrates from Belgium-Luxembourg, Italy, West Germany, and the United Kingdom. Germanium dioxide and concentrates from the Congo (Kinshasa) are exported to two firms in Belgium; one of which, the Société Générale Métallurgique de Hoboken, Belgium, is the world's largest producer and has an annual capacity of 1.65 million pounds of germanium dioxide and 224,000 pounds of germanium metal. As no transistors or diodes are produced in Belgium, all of the germanium production is for export. The Tsumeb Corp. Ltd., Territory of South-West Africa, one of the world's largest sources of germanium with a reported annual capacity of 330,000 pounds, exports germanium in blister copper principally to West Germany for refining; germanium in zinc concentrates produced at the Tsumeb mine may contribute to U.S. supply, but no data are available on the quantity derived from this source (7).

Imports of germanium dropped from over 30,000 pounds in 1961 to about 900 pounds in 1964; since then imports have remained between 3,000 and 4,000 pounds per year.

The estimated demand of 63,500 pounds for



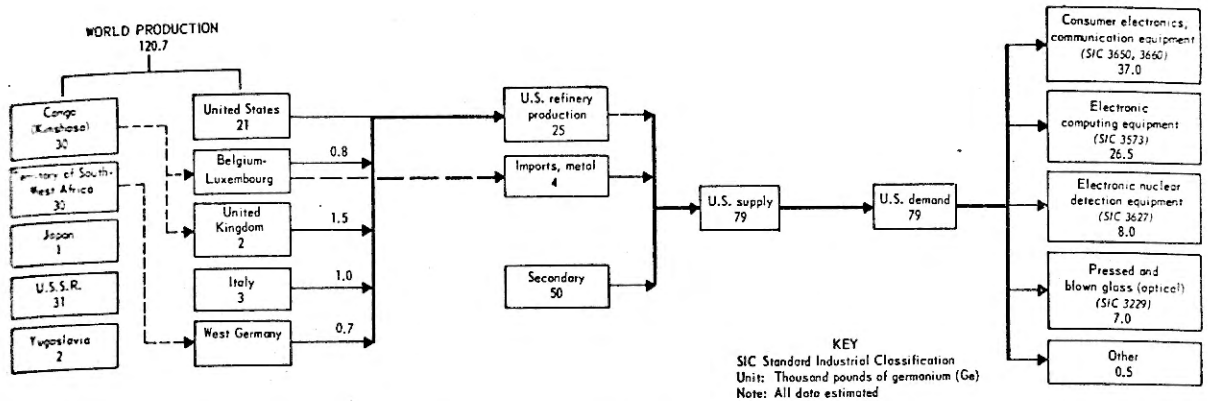


FIGURE 1.—Supply-Demand Relationships for Germanium, 1968.

single-crystal germanium ingot for the electronics industry in 1968 dropped from the steady level of about 70,000 pounds per year noted for 1965-67; the decline was attributed to increased use of alternate materials and technological changes in semiconductors. The number of semiconductor devices has shown a remarkable growth in recent years, and the volume of such devices using germanium accounts for about 80 percent of the total germanium consumption; consumption of germanium for semiconductors probably will stabilize at the 1968 level for some time.

#### Secondary Sources and Conservation

The major secondary source and conservation practice for germanium is through recovery from scrap cuttings and grindings in the manufacture of semiconductor devices.

#### BYPRODUCT-COPRODUCT RELATIONSHIPS

Germanium is commercially recognized as a byproduct, necessarily eliminated when present in refined zinc from domestic sources and from copper-zinc ores in Africa. It commonly exists within the molecular structure of other minerals.

Germanium is recovered from coal residues in the form of flue dusts and ashes in the United Kingdom; this source of germanium has been largely undeveloped in the United States and could probably have a significant impact on domestic supply.

#### CONSUMPTION PATTERN

##### Uses

The major use of germanium in end products is as a single-crystal high-purity metal used principally in the manufacture of semiconductor devices including transistors, diodes, and rectifiers; this end use accounts for about 90 percent of the total demand. Germanium semiconductor

usage is distributed in consumer electronics and communication devices and equipment (47 percent); electronic computing and data processing equipment (33 percent) and electronic nuclear measuring instruments, principally as a radiation detection crystal (10 percent). The remaining 10 percent is utilized in the manufacture of specialized optical glass, infrared equipment, and minor uses. Germanium is used as an alloying constituent in copper, aluminum, and magnesium to increase hardness and improve rolling properties of the alloys, and in gold solder and jewelry manufacture. Germanium is also used in phosphors in certain lights, and a minor amount is used in research. Germanium is used to a large extent in Europe and Japan as a catalyst in textile (polyester) manufacture. This type of catalyst makes the material whiter and imparts the permanent press characteristics. U.S. manufacturers presently do not use germanium as a catalyst.

##### Alternate Materials

Germanium transistors, diodes, and rectifiers have replaced the vacuum tube or electron tube in many applications where cost-performance ratios have been competitive and where size requirements necessitate solid-state devices. However, semiconductor materials with comparable performance characteristics such as high-purity silicon and certain tellurium, selenium, indium, and gallium bimetals can be substituted for germanium.

#### ECONOMIC FACTORS

##### Prices and Costs

In 1952, the price of germanium reached a high of \$488 per pound in constant 1968 dollars. Subsequently, the price declined and remained at \$79.65 per pound from the last quarter of 1966 until mid-1969. The price increased in June

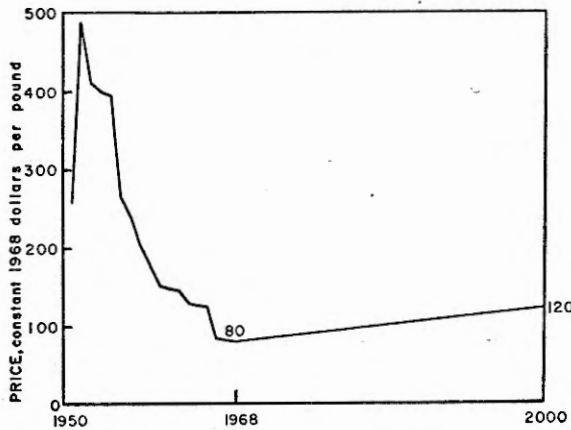


FIGURE 2.—Time-Price Relationship for Germanium.

to \$85.50 per pound and again in October to \$93 per pound. The downward trend since 1952 is indicative of the competition between germanium and silicon for the semiconductor market. The price increases in 1969 largely reflect demand for catalytic use in polyester fiber production.

The 1968 price of electronic-grade germanium dioxide continued at about \$40 per pound until June 1969 when it was raised to \$43 per pound. In October 1969 the price was again increased

to \$48 per pound. The price-time relationship for germanium in constant 1968 dollars is shown in figure 2.

The total value of domestic primary production of germanium in 1968 was about \$1.7 million, and demand amounted to \$6 million.

#### Taxes and Tariffs

Domestic producers are granted a depletion allowance of 15 percent on either domestic or foreign production of germanium. Effective January 1, 1969, the tariffs on imported germanium dioxide and metal are respectively 8 and 14 percent ad valorem on manufactured articles. Transportation costs are of little significance in movement either of feed material or refined product.

#### Government Programs and Strategic Considerations

Germanium has not been included in the Government stockpiling program or in Government-sponsored exploration assistance programs. However, some research has been conducted by the Bureau of Mines and the Geological Survey.

Although germanium may be considered of some strategic importance through its use as a semiconductor for solid state applications, particularly in the field of communications, the availability of alternate materials tends to minimize germanium for strategic considerations.

## OUTLOOK

Demand for primary germanium dropped from 78,000 pounds in 1960 to 16,000 pounds in 1964, doubled in 1965 to nearly 33,000 pounds, and has since been on a general decline. However, during this time, the demand for semiconductors has continued to climb. The disparity between a decrease in demand for primary germanium and an increase in demand for semiconductors is attributed to advances in manufacturing technology and the use of alternate materials, especially silicon. Technological shifts in the prospective use pattern during the forecast period of 1968–2000 should result in a departure from the principally semiconductor use, which currently accounts for 80 percent of total demand, to a more diversified use pattern. The semiconductor use of germanium is expected to drop to about 60 percent of total demand in year 2000. Domestic germanium consumption should grow during 1968–2000 at average annual rates ranging between 0.9 and 3.0 percent. Based on projected domestic supply, domestic demand for germanium can be met throughout the forecast period from primary sources and from recycled scrap.

Rest-of-the-world consumption of primary is

expected also to grow during the forecast period at average annual rates ranging between 0.9 and 3.0 percent, the same rates predicted for the United States. Technological shifts and other contingency influences predicted for the United States will be paralleled in evolving use patterns in rest of the world. The consumption of recycled scrap is also expected to be similar to that predicted for the United States.

If supply from coal sources is considered, both domestic and world supply potential is adequate to meet forecast demands.

#### DEMAND

The domestic forecast demand for germanium in the year 2000 is expected to range between 97,000 and 195,000 pounds. The contingency forecasts of demand for germanium are shown in table 1. A forecast base for each end use in 2000 was established by correlating demand in each category with the projected growth of such variables as gross national product (GNP) and total population. Probabilistic and multiple contingency analyses of technologic, economic, and other contingency assumptions were con-

sidered for each of the major end uses of germanium in the year 2000. The high and low ranges of the forecast represent the outer range of positive or negative influences of the foregoing factors on each end use. A summary of the forecast range follows:

		Forecast range of demand for germanium (thousand pounds)	
		1968	2000
<b>United States</b>			
Total:			
High	} 79		{ 195
Low			{ 97
(Median)			{ (146)
Primary:			
High	} 25		{ 65
Low			{ 33
(Median)			{ (49)
<b>Rest of the world</b>			
Primary:			
High	} 90		{ 220
Low			{ 120
(Median)			{ (170)

TABLE 1.—Contingency forecasts of demand for germanium by end use, year 2000 (Thousand pounds)

End use	Demand 1968	U.S. forecast base 2000	Demand in year 2000			
			United States		Rest of the world <sup>1</sup>	
			Low	High	Low	High
Consumer electronics, communication equipment ...	37.0	60	35	70	NA	NA
Electronic computing equipment ...	26.5	40	25	50	NA	NA
Electronic nuclear detection equipment ...	8.0	30	20	40	NA	NA
Pressed and blown glass (optical) ...	7.0	25	15	30	NA	NA
Other uses ...	.5	2	2	5	NA	NA
<b>Total</b> ...	<b>79.0</b>	<b>..</b>	<b>97</b>	<b>195</b>	<b>120</b>	<b>220</b>
			(Median 146)		(Median 170)	

NA Not available.  
<sup>1</sup> Rest-of-the-world demand for primary only.

**Consumer Electronics and Communication Equipment**

The forecast base for the category was projected at the anticipated annual growth rate for total population of 1.6 percent for 1968-2000, resulting in a forecast demand base of 60,000 pounds of germanium. A high demand for germanium in 2000 may result from the continued high growth rate of consumer electronics and communication broadcasting and receiving equipment utilizing germanium, and by a technological shift to solid state devices for ignition systems and control of land vehicles, aircraft, and other mobile equipment. Based on these considerations, the demand for germanium in 2000 could be as high as 70,000 pounds. Alternatively, the future growth rate for germanium in these end uses could be reduced through such changes as increased substitution for semi-

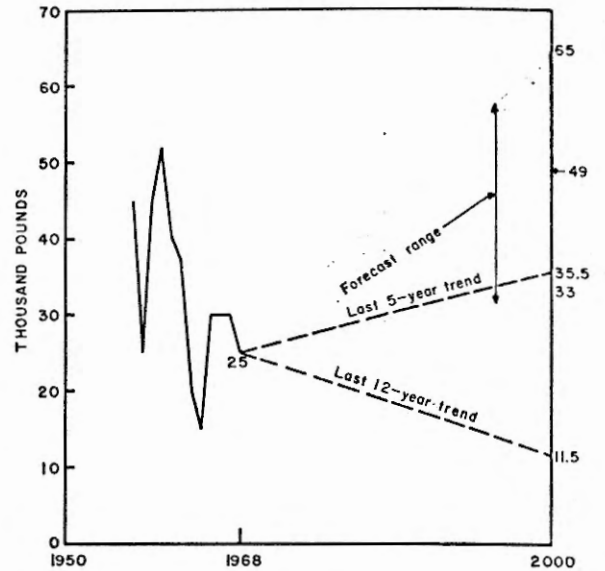


FIGURE 3.—Comparison of Trend Projections and Forecasts for Primary Germanium Demand.

conductors by silicon and other materials, by developments in microminiaturization which would require less semiconducting material per unit, or by greater efficiency in utilizing semiconductors and their components. These contingencies could result in a forecast low of 35,000 pounds for this end use in 2000.

**Electronic Computing Equipment**

Demand in 2000 for germanium for electronic computing equipment was related to the projected annual growth rate for total population, 1.6 percent, resulting in a forecast base of 40,000 pounds of germanium. The growth of germanium demand for this end use could reach a forecast high of 50,000 pounds in 2000, assuming that the rapid computer growth continues during the forecast period. However, contingencies similar to those that would contribute to a forecast low for consumer electronics, such as substitution for semiconductor materials and microminiaturization for components, could result in a forecast low of 25,000 pounds of germanium in electronic computing equipment.

**Electronic Nuclear Detection Equipment**

The demand in 2000 for germanium in electronic nuclear detection equipment was related to the anticipated growth in GNP, 4.0 percent for 1968-2000, resulting in a forecast base of 30,000 pounds for this end use. Increased demand by medical, industrial, and research laboratories, particularly those working with low-level radioactivity, widespread monitoring for radiation in response to public awareness of radiation hazards, and a general increase in

usage of nuclear technology could result in a forecast high of 40,000 pounds of germanium for nuclear detection in the year 2000. Moreover, this end use will probably be less sensitive to inroads by substitute materials than the other uses of germanium. However, microminiaturization of components as well as more efficient use of detection crystals that would reduce the quantity of germanium per unit could result in a forecast low of 20,000 pounds.

#### Pressed and Blown Glass (Optical)

Germanium should find continued and growing usage in infrared optics, which is currently a strongly defense-oriented demand. The forecast base of 25,000 pounds for germanium in glass in 2000 was related to the projected growth in GNP of 4 percent for the forecast period. The demand for germanium in this end use could reach a forecast high of 30,000 pounds of germanium if military demands for infrared products continue, and if peaceful uses of infrared devices expand to meet demands for nighttime surveillance of property. Additionally, infrared or thermal mapping from satellites and aircraft which may be useful in minerals prospecting, in forest and agricultural control, and in highway and construction planning activities may also contribute to the high demand. On the other hand, decreased military demands for germanium, brought about by relaxation in world conflict or because of substitute materials that may be developed during the forecast period, could result in a forecast low of 15,000 pounds.

#### Other Uses

The forecast base of 2,000 pounds for this category in 2000 was related to the projected annual growth of GNP of 4 percent. If these end uses are sustained throughout the forecast period and if research results in the development of new applications for germanium, a high forecast demand of 5,000 pounds may result in the year 2000. The low demand for germanium in 2000 is not expected to fall below the projected forecast base of 2,000 pounds.

#### SUPPLY

Domestic resources of germanium are associated with lead-zinc resources principally in ores in Wisconsin, Illinois, and Oklahoma. Potential sources of germanium include other lead-zinc ores and ash from certain domestic coals.

The projected domestic availability for germanium, figure 5, is estimated at over 1.2 million pounds from recovery as a byproduct of lead-zinc ores, from flue dusts and residues from base-metal refining, and from certain coals and coal

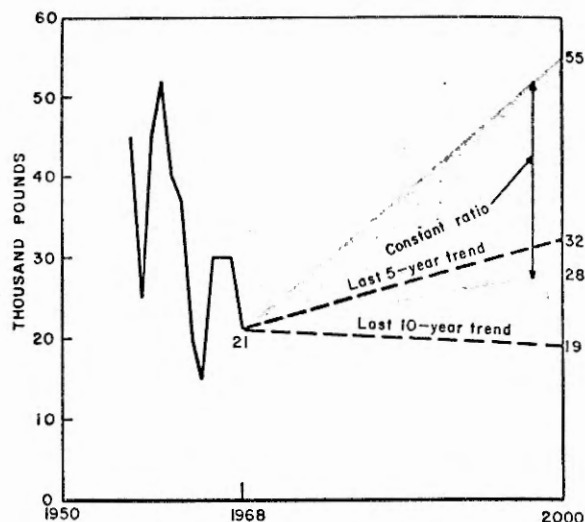


FIGURE 4.—Comparison of Trend Projections and Forecasts for Primary Germanium Production.

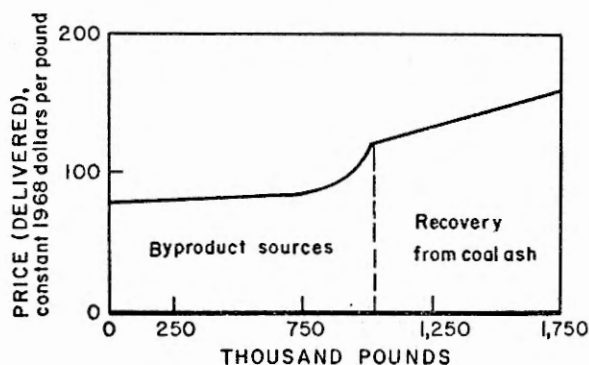


FIGURE 5.—Projected Domestic Availability of Germanium.

fly ash. Although rest-of-the-world supply of germanium is unknown, it might be conservatively estimated at over 10 million pounds if germanium-bearing coals are included.

#### POSSIBLE ADVANCES IN TECHNOLOGY

Research and development may result in reliable and highly effective methods for growing high-purity germanium monocrystals for widespread use in nuclear particle detection and analysis systems. Studies on properties of germanium and development of efficient techniques for making superconductors and more versatile semiconductors could result in new solid state circuitry and applications. Demand for specialized glass should stimulate and intensify research and development in use of germanium glasses for transmission of infrared radiation.

### FUTURE SUPPLY-DEMAND RELATIONSHIPS

The median demand for primary germanium in 2000 is expected to be 49,000 pounds, valued at nearly \$6 million in constant 1968 dollars. The projected low and high demands of 33,000 to 65,000 pounds are valued at \$4 million and \$7.8 million, respectively. The values of constant ratio production for high and low range in 2000 are \$6.6 million and \$3.4 million, respectively.

The constant ratio for the high and low production requirement to meet domestic demand for primary for 1968-2000 indicates a supply requirement of 1.25 million and 0.8 million pounds, respectively, during the forecast period (fig. 4). The constant ratio low domestic pro-

duction requirement for 1968-2000 could be met entirely from supply originating in base-metal ores. However, the constant ratio for the high forecast domestic production requirement for 1968-2000 would have to be met to some extent by germanium recovered from coal ash during part of the forecast period.

The rest-of-the-world supply is adequate to meet the cumulative rest-of-the-world demand for 1968-2000 of 3.4 million pounds at the low of the range and 5 million pounds at the high range. However, a situation analogous to the forecast domestic supply-demand picture could prevail so that it is likely that a larger proportion of world supply will be recovered from coal ash because of the depletion of base-metal deposits.

### PROBLEMS

The major problem facing the germanium industry is the lack of diversified industrial application for the element. As such, demand for germanium is sensitive to its use in the semiconductor market and to inroads by competitive materials. Research is needed to develop new and diverse applications that utilize significant quantities of the element.

Domestic germanium output is dependent

upon zinc production. Coals and flue dusts of other metallurgical operations are sources of germanium in foreign countries. These sources have not been utilized for recovery of germanium in the United States, principally because of the lack of markets for the element.

Comprehensive resource information and statistical data on domestic and world supply and demand of germanium are lacking.

### REFERENCES<sup>3</sup>

- Almond, H., H. E. Crowe, and C. E. Thompson. Rapid Determination of Germanium in Coal, Soil and Rock. U.S. Geol. Survey Bull. 1036-B, 1955, 17 pp.
- American Society for Testing and Materials. Volatile Content of Germanium Oxide. F5-58T in 1958 Book of ASTM Standards: Part 2, Nonferrous Metals (Specifications), Electronic Materials. Philadelphia, Pa., 1958, pp. 784-786.
- Cataland, G., and H. H. Plumb. Calibration of Germanium Resistors at Low Temperatures (2-20° K). J. Res. NBS, Sec. A—Physics & Chemistry, v. 70a, No. 3, May-June 1966, pp. 243-252.
- Dressel, W. M. Field Test for Germanium. BuMines Rept. of Inv. 5907, 1962, 4 pp.
- Germanium Information Center, Midwest Research Institute (Kansas City, Mo.). Bulletin, 1962, 35 pp.
- Grubel, Ralph. Metallurgy in the Semiconductor Industry. J. Metals, v. 19, No. 1, January 1967, pp. 13-17.
- Gunzel, H., and B. Knorr. Der Markt für Reinstgermanium un-silizium unter dem Einfluss der Produktion elektronischer Halbleiter-Bauelemente (The Market for Super-Purity Germanium and Silicon, Under the Influence of the Production of Electronic Semiconducting Components.) Metall., v. 20, No. 2, February 1966, pp. 169-176 (in German); trans. available from Metal Information Services Ltd., Winchcombe House, Winchcombe Street, Cheltenham, Gloucestershire, England.
- Harner, H. R. Germanium. Ch. in Rare Metals Handbook, ed. by C. A. Hampel. Reinhold Pub. Corp., New York, 1961, pp. 188-197.
- Jolly, Janice L., and Allen V. Heyl. Mercury and Other Trace Elements in Sphalerite and Wallrocks From Central Kentucky, Tennessee and Appalachian Zinc Districts. U.S. Geol. Survey Bull. 1252-F, 1968, 29 pp.
- Mah, Alla, and L. H. Adami. Heats and Free Energies of Formation of Germanium Dioxide. BuMines Rept. of Inv. 6034, 1962, 7 pp.
- Minden, Henry T. Recent Advances in Gallium Arsenide Materials Technology. Solid State Technol., v. 12, No. 4, April 1969, pp. 25-35.
- Sheff, S. Electrolytic Slicing of Germanium; Characteristics of the (111), (110), and (100) N- and P-Type Surfaces. Electrochem. Technol., v. 5, No. 1-2, January-February 1967, pp. 47-52.
- Swiggard, E. M., and H. Shenker. Preparation of Doped Germanium for Far Infrared Detectors. J. Electrochem. Soc., v. 113, No. 1, January 1966, pp. 92-93.
- Waters, R. F., and H. Kenworthy. Extraction of Germanium and Gallium From Coal Fly Ash and Phosphorus Furnace Flue Dust. BuMines Rept. of Inv. 6940, April 1967, 33 pp.

<sup>3</sup> Titles enclosed in parentheses are translations from the language in which the item was published.