Information Circular 8570

The Economics of Byproduct Metals

(In Two Parts)

2. Lead, Zinc, Uranium, Rare-Earth, Iron, Aluminum, Titanium, and Lithium Systems

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March 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR
Rogers C. B. Morton, Secretary

BUREAU OF MINES
Elburt F. Osborn, Director

This publication has been cataloged as follows:

Petrick, Alfred

The economics of byproduct metals (in two parts). 2. Lead, zinc, uranium, rare-earth, iron, aluminum, titanium, and lithium systems, by Alfred Petrick, Jr. [and others. Washington] U.S. Dept. of the Interior, Bureau of Mines [1973]

99 p. illus., tables. (U.S. Bureau of Mines. Information circular 8570)

Includes bibliography.

1. Metals. 2. Lead. 3. Zinc. 4. Uranium. 5. Rare-earth metals. 6. Iron. 7. Aluminum. 8. Titanium. 9. Lithium. I. Title: The economics of byproduct metals, Pt. 2. (Series)

TN23.U71 no. 8570 622.06173

U.S. Dept. of the Int. Library

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Stock No. 2404-01342

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THE ECONOMICS OF BYPRODUCT METALS

(In Two Parts)

2. Lead, Zinc, Uranium, Rare-Earth, Iron, Aluminum, Titanium, and Lithium Systems

by

Alfred Petrick, Jr.,[1] Harold J. Bennett,[2] Karl E. Starch,[3]
and Robert C. Weisner[2]

ABSTRACT

This report analyzes the byproducts systems of lead, zinc, uranium, rare earths, iron, aluminum, titanium, and lithium. Specific byproduct metals covered are cadmium, germanium, indium, and thallium from the zinc system; antimony and bismuth from the lead system; vanadium, radium, and scandium from the uranium system; rare-earth oxides from the rare-earth system; and cobalt, gallium, hafnium, and rubidium from other systems. The report discusses various metallurgical systems, marginal and incremental production costs of byproduct subsystems, industry structure and organization, and historical data on price, consumption, and supply.

INTRODUCTION

This is the second report of a two-part Bureau of Mines study concerning an analysis of 24 byproduct metals. Part 1 analyzes byproduct metals from the copper system.[4] Part 2 completes the study and covers an analysis of byproduct metals from the lead, zinc, and other systems. A review of the complex ore and rare-earth systems and their component byproducts is included.

American industry is increasingly dependent upon a number of economically and strategically important metals with rather unique supply characteristics. These are the so-called byproduct metals whose supply is wholly or largely dependent upon the production of some other major metals. The byproduct metals are a near universal phenomenon in the mineral industries and are becoming daily a more important source of metal supplies, yet relatively little is known about their supply potential. The object of this study is to examine the relationships between prices, costs, and supply of the principal metals

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[4] Petrick, Alfred, Jr., Harold J. Bennett, Karl E. Starch, and Robert C. Weisner. The Economics of Byproduct Metals (In Two Parts). 1. Copper System. BuMines Inf. Circ. 8569, 1973.

and their byproducts. Through analysis of such relationships, it is hoped that a more accurate picture of the supply for individual byproduct metals can be determined.

This project is an initial effort in the economic analysis of byproduct minerals production. It is part of a larger effort having the long-range objective to determine the potential production of metal or mineral products as byproducts.

A major effort was made to develop an analytical approach useful in later studies of byproducts. Marginal and incremental cost analysis appeared promising in the early stages of the study. As the study progressed it became apparent that economic rent and opportunity costs were also important. Production cost analysis can only provide a part, sometimes a small part, of the information needed to construct supply curves for the byproduct metals. In many cases, factors such as pricing to sell scarce commodities and the costs of holding high value inventories are more important in determining sales price.

If we designate production systems by the major metal produced, a study of byproduct metals quickly leads us to the copper, lead, and zinc systems. Because of the size and economic importance of these systems to the U.S. economy, it is easy to identify a number of byproduct metals within them--metals produced incidentally to the major metal. Seventeen of the 24 byproduct metals included in this two-part study can be classified in these three systems. The remaining seven metals are byproducts of other less familiar systems. This analysis focuses on these systems, their byproduct subsystems, and the technical-economic relationships between them. Byproduct metals are split-off from the major system for additional processing. From the copper system comes selenium, tellurium, arsenic, gold, silver, platinum, palladium, molybdenum, rhenium, and the potential for production of uranium and aluminum. From the lead and zinc systems come antimony, bismuth, cadmium, arsenic, silver, gold, germanium, and indium. Iron-ore processing is the source of the only domestic supply of cobalt, and the uranium system yields scandium and vanadium and has a potential to yield radium. The processing of aluminum ores yields gallium and the production of nuclear-grade zirconium metal yields hafnium. Rubidium is derived from a lithium processing system. Recycled scrap mixed with primary material also yields its byproduct metals. The burning of uranium in nuclear reactors also yields its manmade byproduct metals. Intersystem transfers confuse the source of byproduct supply. For example, bismuth or precious metals turning up as a lead byproduct might actually have originated in copper ores.

This analysis covers the definition of the supply-demand patterns for the 24 byproduct metals and the construction of their price-supply schedules where possible. To adequately express relationships between byproduct supply and the factors affecting it, the analysis includes geological and technical relationships, the effect of market size, and the economies of scale, incremental cost-incremental revenue relationships.

In this study, it was necessary to choose those specific metals to be characterized as byproduct metals, define the supply-demand patterns of the specific metals, develop a systems analysis of byproduct producing systems, and finally, to summarize the analysis in terms of the supply curves for byproduct metals. The data for the analysis were provided by an extensive literature search, compilation of production and consumption data, interviews with experts in mineral industry management and engineering, and visits to 19 mills, smelters, and refineries producing byproduct metals.

Part 1 of the two-part study contains chapters on the conceptual framework for analysis, classification of byproduct metals, the economics and strategic importance of byproduct metals and mineral supply systems, and an analysis of individual byproduct metals in the copper system. Part 2 contains the analysis for byproduct metals in the lead and zinc systems and for several byproduct metals of the uranium, rare earth, iron, aluminum, titanium and lithium systems. Conclusions of the study are also listed in Part 2. Each part contains a bibliography.

Zinc System

Zinc ore occurs in nature most abundantly as a sulfide. The deposits usually contain some lead associated with lesser quantities of iron and copper sulfides. The sulfides are separated from the waste and to a certain extent from each other by differential flotation. A typical zinc concentrate prepared for smelting may contain 52 to 60 percent zinc, 30 to 33 percent sulfur, and 4 to 11 percent iron. There are also a small amount of lead and minor quantities of cadmium, copper, and other metals.

The zinc system is likely to produce a byproduct lead sulfide at the flotation stage of mineral processing because of the common association of lead and zinc.

Several different combinations of processes are used by zinc smelters to prepare the ore concentrates for extraction of zinc. Choice of methods depends on physical and chemical properties of the raw material and the extraction process to be used. Extraction of zinc requires that the raw material first be processed to convert the zinc content to a dense form of zinc oxide. Roasting, sintering, and calcining are three preextraction operations that accomplish this. Some plants both roast and sinter zinc sulfide concentrates while others may use only sinter machines which, in effect, both roast and sinter the concentrate in one operation. Calcining is performed only on oxide ores or on material that has been oxidized by roasting. Gases containing sulfur oxides are generated in large quantities during the roasting and sintering operation but very little during calcining.

There are three processes that account for all U.S. slab zinc production. The two most used processes are incorporated in the simplified systems diagram of figure 1. In 1970 the leach-electrolytic process accounted for 43 percent of total U.S. slab zinc capacity. The continuous distilling vertical retort process accounted for the largest portion of the remainder. The information summarized in figure 1 came from a number of publications describing the

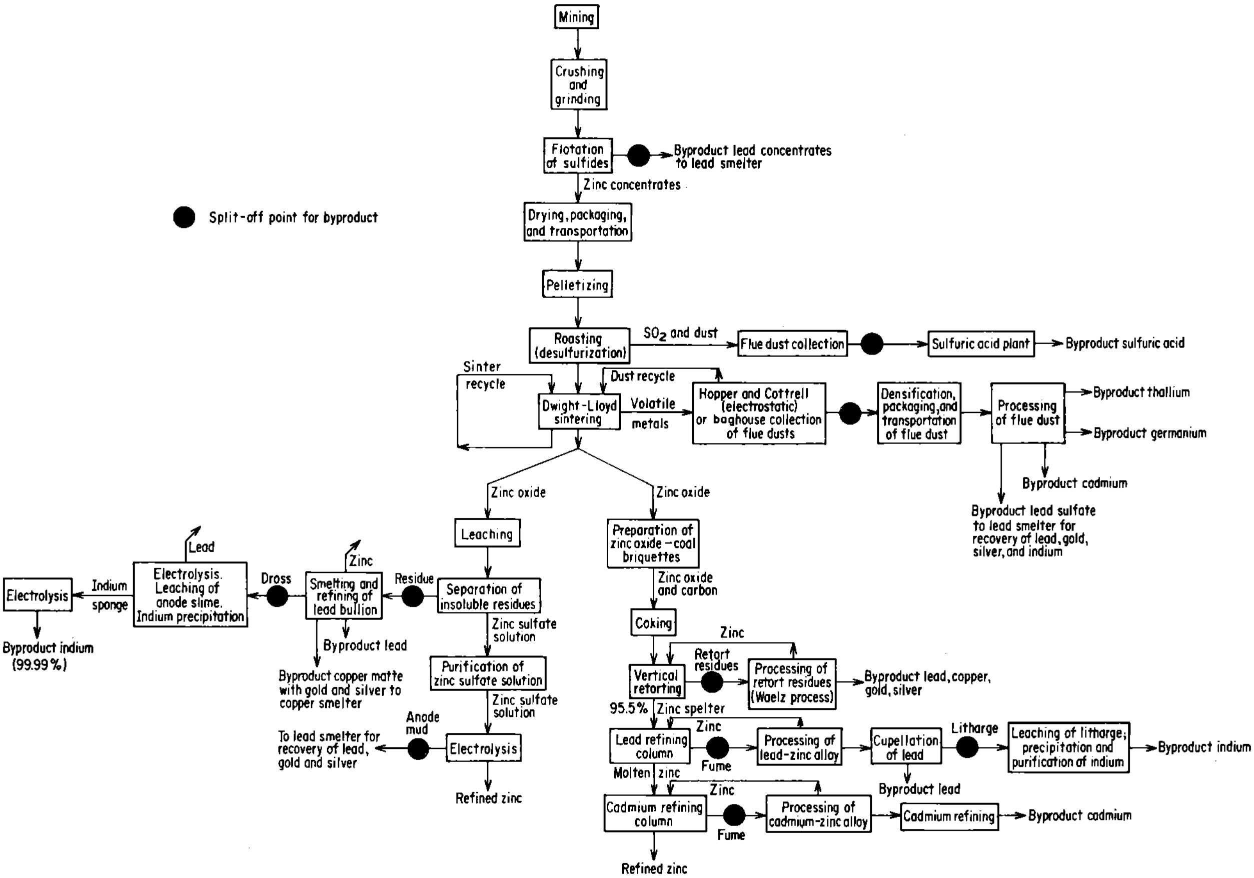

FIGURE 1. - Zinc System Showing Principal Byproduct Metals.

metallurgy of zinc (18; 44, pp. 343-379; 44, pp. 444-472; 13, pp. 861-867; 61, pp. 73-77).[5]

After pelletizing to minimize flue dust losses, the concentrates from the milling operation are roasted to remove sulfur. The roasting process results in sulfur dioxide gas which may be used to produce byproduct sulfuric acid as shown in figure 1.

If volatile metals are present, sintering is likely to follow the roasting stage. At this point, flue dust containing volatile impurities is collected. Further processing of the flue dust is a major source of the zinc system. Processing of the flue dust may yield cadmium, germanium, and thallium as well as a lead sulfate product containing gold, silver, and indium. The lead sulfate product is often shipped to a lead smelter for recovery of lead and precious metals.

If the leach-electrolytic process is used, the zinc oxide calcine moves from sintering to leaching and separation of insoluble residues from a zinc

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[5] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

sulfate solution. This stage of processing yields a residue which upon further processing results in byproduct lead, copper, gold, silver, and indium. The electrolysis of the zinc sulfate solution yields an anode mud, a source of byproduct lead, gold, and silver.

If the continuous vertical retort process is used, retort residues may yield byproduct lead, copper, gold, and silver. In the refining columns, the fume from the lead column yields byproduct lead and is the major source of byproduct indium. The cadmium column product can be further refined to recover cadmium. The cadmium produced at this point, however, is small compared to that recovered from the sinter fume.

It is estimated the 650,000 tons of sulfur equivalent was generated at zinc smelters in 1970, of which 59 percent, or 383,500 tons, was recovered as a byproduct.

Six of the eight zinc smelters in this country recover sulfur oxides from offgas. Two are smelting material that contains very little sulfur. Smelters with recovery units recover sulfur oxides as sulfuric acid only from the roaster gas. No sulfur is recovered from the sintering process, primarily because 93 to 97 percent of the sulfur is oxidized to sulfur dioxide in the roasting process.

The cost of producing a sulfur byproduct is dependent upon the quantity of sulfur in the flue gas, the size of the plant, and the process used to recover the sulfur.

Zinc System Byproducts

Cadmium

Sources of supply

Greenockite (CdS), the most common cadmium mineral, is usually found associated with primary sphalerite (ZnS). The supply of cadmium is almost wholly dependent upon the processing of such zinc ores. While some ores of lead and copper, containing zinc, may have enough cadmium to allow economic recovery, the supply of cadmium is essentially a byproduct of the zinc system. The total U.S. supply of cadmium in 1970 as shown in figure 2 indicates a small secondary recovery, imports, industry stock releases, and Government stockpile releases as sources of cadmium supply. The bulk of cadmium (62 percent), however, was derived from the processing of domestic and foreign base metal concentrates and smelter flue dusts.

Figure 2 indicates that foreign sources of cadmium are important. In addition to cadmium metal, a large portion of cadmium-bearing concentrates and smelter residues are also of foreign origin. Domestic sources provided about one-third of the primary cadmium supply during 1970.

In the roasting of zinc ores to oxidize the zinc and remove the sulfur, cadmium is also volatilized. The fume and dust are collected in baghouses

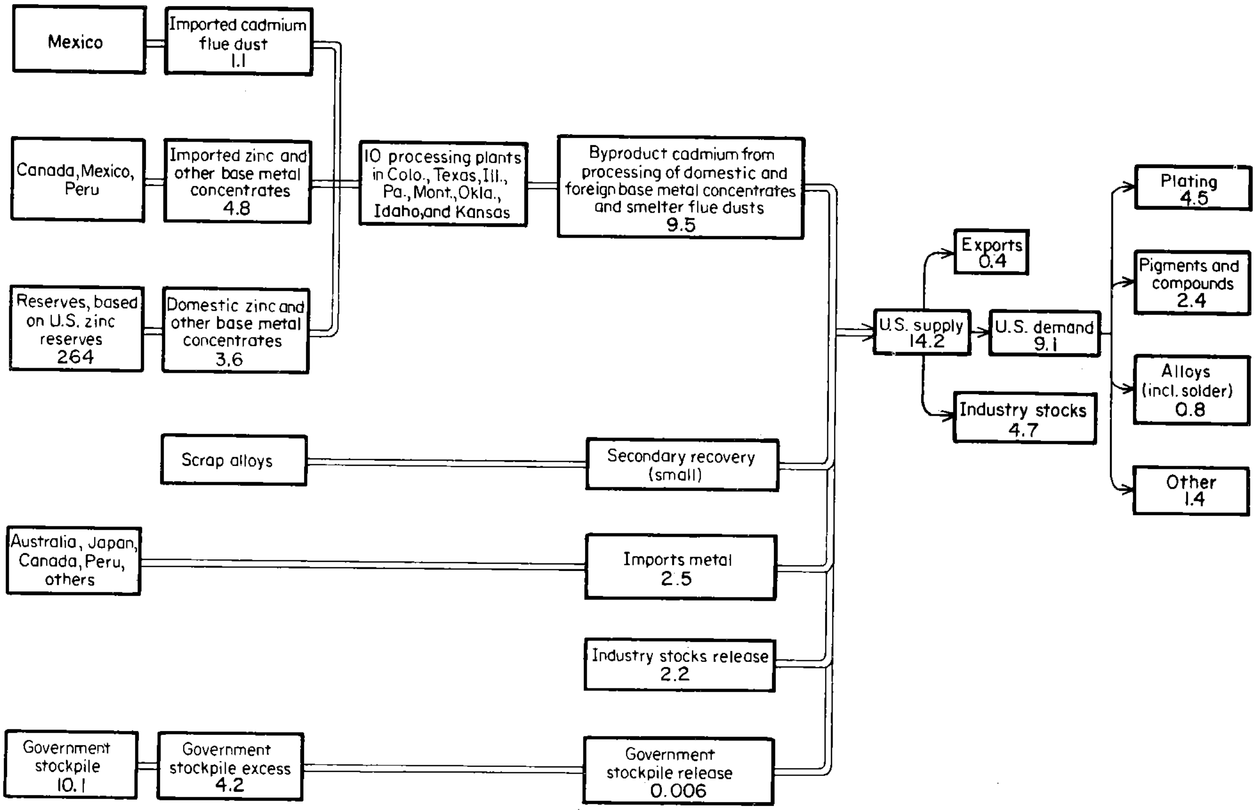

FIGURE 2. - Cadmium Supply and Demand (Million Pounds, Metal and Content, 1970).

or electrostatic precipitators. The processing of such fumes and dusts as indicated in figure 2 is the primary source of byproduct cadmium.

After roasting, the zinc ores proceed to further pyrometallurgical or hydrometallurgical recovery processes. These processes may be adapted to allow further recovery of cadmium. The purification of zinc-sulfate solution preparatory to electrolytic recovery of zinc involves the addition of zinc dust to precipitate copper or cadmium. The resultant copper-cadmium sludge may be further treated to recover cadmium, a second byproduct source of the metal.

A third source of byproduct cadmium, though also small relative to that recovered from fume, occurs when a pyrometallurgical process is used to recover zinc. In this process cadmium is recovered by distillation from the cadmium column.

The 10 processing plants that produce byproduct cadmium are listed in table 1. The list includes only those plants recovering the final cadmium product. It does not include other zinc smelters that produce cadmium-bearing fume. Concentration of cadmium refining takes place by intracompany and intercompany transfers of cadmium-bearing materials in a manner similar to the production of other byproduct metals. In the case of cadmium, transfers are often international. The volume of international shipments of both concentrates and residues distorts any statistical relationship between domestic zinc production and byproduct cadmium production.

TABLE 1. - Byproduct cadmium producers

Plant:	Location
Blackwell Zinc Co., Inc., Division of American Metals Climax, Inc.	Blackwell, Okla.
American Smelting and Refining Co.	Denver, Colo.
American Smelting and Refining Co.	Corpus Christi, Tex.
American Zinc Co.	East St. Louis, Ill.
The Anaconda Co.	Great Falls, Mont.
The Bunker Hill Co.	Kellogg, Idaho
Eagle-Picher Industries, Inc.[1]	Galena, Kans.
National Zinc Co.	Bartlesville, Okla.
New Jersey Zinc Co.	Palmerton, Pa.
St. Joe Minerals Corp.	Monaca, Pa.

[1] Closed end of 1971.

In 1970 the firms listed in table 1 operated 10 zinc smelters, electrolytic refineries, or zinc oxide plants, having an estimated zinc metal capacity of nearly 1 million short tons annually (71, pp. 18-21). The raw materials for a number of the zinc plants are ores and concentrates purchased from other domestic or foreign companies or subsidiaries.

Reserves-Resource Base

Reserves of cadmium have been calculated as a function of zinc reserves. Cadmium reserves of the United States were estimated at 264 million pounds of the total world reserve of 922 million pounds. Canadian reserves were estimated to be 168 million pounds.

Demand (48; 20; 38; 33, pp. 82-92)

The most important applications of cadmium are in electroplating. Electrodeposited cadmium has good adherence to ferrous metals and excellent corrosion resistance. It competes successfully with zinc-plating in some applications because thinner coatings provide equal protection. Regarding other advantages, cadmium has a higher rate of deposition relative to zinc at a given current amperage, the electric resistance of cadmium-plated contacts is lower than zinc-plated contacts, cadmium retains its metallic luster longer than zinc, cadmium-plated parts are easily soldered, cadmium has great resistance to alkali corrosion, cadmium has a superior ability to deposit on intricately shaped objects, and the corrosion of cadmium by galvanic action is more efficiently minimized than it is for zinc plating. Common uses of cadmium plating are in building automotive and marine hardware, such as nuts, bolts, screws, springs, and in electrical and electronic parts. As indicated in figure 2, consumption in electroplating was about 4.5 million pounds of cadmium, about 50 percent of the total demand in 1970.

Cadmium compounds are used in pigments, the most important of which are the sulfide and the sulfoselenide. Cadmium-based pigments are desirable where extreme color retention is required, such as in machinery and automotive enamels, artificial leather coloration, rubber, paper, printing inks, ceramic glazes, and in artists' oil and water colors. A growing use of cadmium compounds is in the production of thermoplastics such as polyvinylchloride.

Cadmium is used in bearing metals because it imparts to the base metal excellent mechanical strength, hardness, tensile strength, a high-melting point, antifriction characteristics, and corrosion resistance. These bearing materials find use in high-speed automotive, aircraft, and marine engines that operate at high temperatures.

Low-melting-point cadmium alloys are used in fire detection apparatus, automatic sprinkler systems, and in automatic shutoffs for heating systems. Other alloys such as Cerrobend[6] are used to fill thin-walled tubes to allow bending without distortion. Woods metal, an alloy of bismuth, tin, lead, and cadmium, is used to seal joints in glass apparatus used in laboratories. Another cadmium alloy, low cadmium copper, has found wide use in telegraphic, telephonic, and power transmission wires. Still other alloys such as cadmium-silver and cadmium-zinc are used for soldering aluminum.

Other smaller markets for cadmium include the nickel-cadmium battery used in preference to the lead battery in some heavy-duty applications. Cadmium is also a neutron absorber useful in nuclear reactors as a control mechanism. High-purity cadmium sulfide is used in photovoltaic cells, radiation detection devices, infrared windows, and photosensitive elements in cameras. Another intriguing use of cadmium-sulfide is in solar cells used for the conversion of sunlight to electrical energy.

Production, Consumption, and Price Statistics

Cadmium production, consumption, and price all showed generally rising trends during the 1945-69 period, but the curves for production and consumption broke sharply in 1970 (fig. 3). Sharp swings in the curves were related to adjustments in inventory and general industrial activity. In the 1960's cadmium shortages were met by stockpile sales; strikes at zinc smelters decreased the cadmium supply in 1967, and increased imports of metal in 1970 created an oversupply.

Continuous pressure on cadmium supply caused an increase in the $2.65 per pound price established in January 1967. The American Smelting and Refining Company in December 1968 raised the price to $2.80 per pound for anodes, balls, and shapes in ton lots. The U.S. Smelting Refining and Mining Co., the Amax Lead and Zinc Division of American Metals Climax, Inc., The American Zinc Co., and the St. Joe Minerals Corp. followed the ASARCO price in January 1969. Government prices for stockpiled cadmium were increased from $2.53 to $2.68 per pound for ton lots. In March 1969, the price of cadmium again

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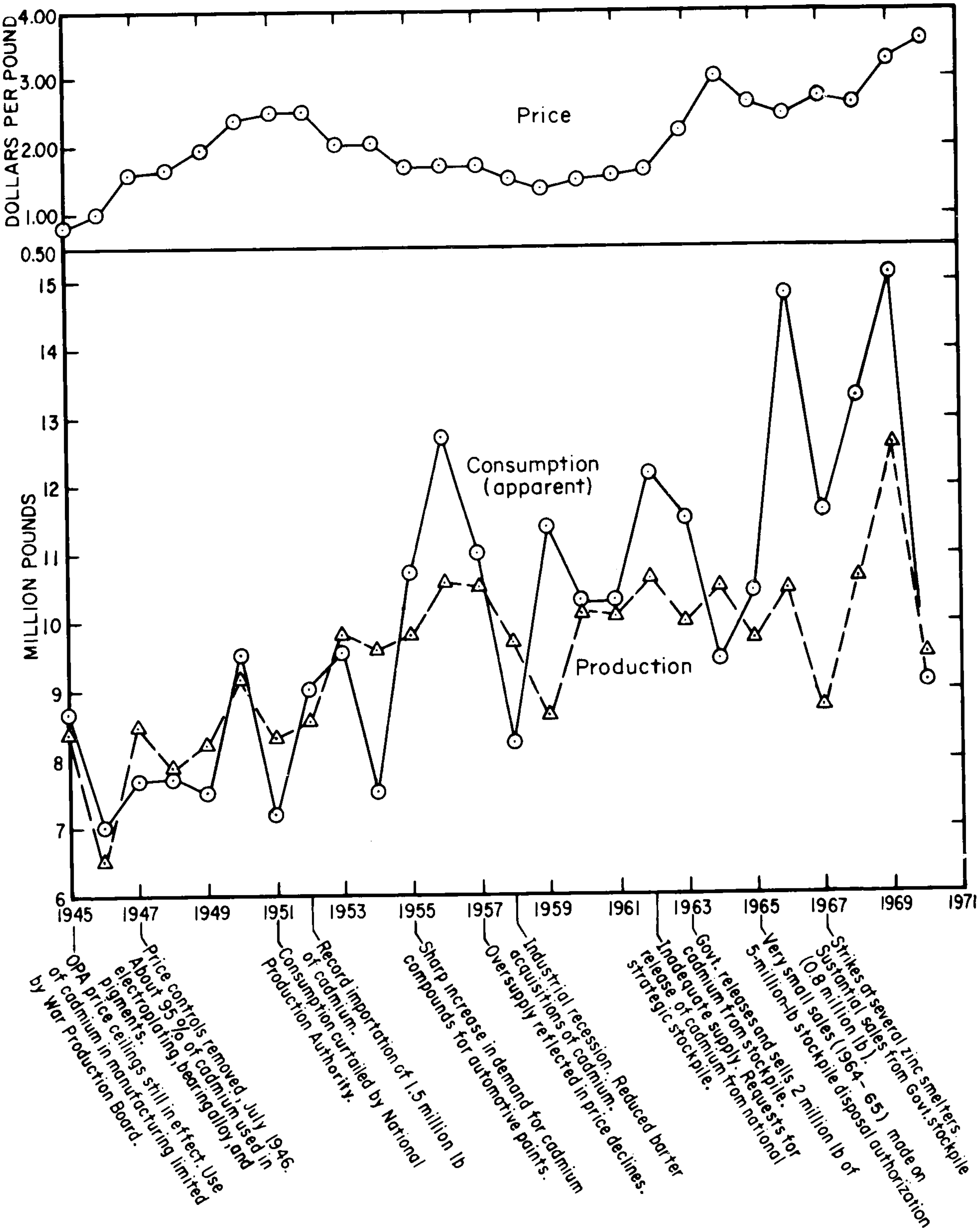
[6] Reference to specific brands, makes of equipment, or trade names in this report is done to facilitate understanding and does not imply endorsement by the Bureau of Mines.



OPA price ceilings still in effect. Use of cadmium in manufacturing limited by War Production Board.

Price controls removed, July 1946. About 95% of cadmium used in electroplating, bearing alloy, and pigments.

Consumption curtailed by National Production Authority.

Record importation of 1.5 million lb of cadmium.

Sharp increase in demand for cadmium compounds for automotive paints.

Oversupply reflected in price declines.

Industrial recession. Reduced barter acquisitions of cadmium.

Inadequate supply. Requests for release of cadmium from national strategic stockpile.

Govt. releases and sells 2 million lb of cadmium from stockpile.

Very small sales (1964-65) made on 5-million-lb stockpile disposal authorization.

Strikes at several zinc smelters. Sustantial sales from Govt. stockpile (0.8 million lb).

FIGURE 3. - Cadmium Production, Consumption, and Price History, 1945-70.

went up, this time to $3.00 per pound; a further rise in price to $3.50 became effective July 1, 1969, and the price again rose to $4.00 December 1, 1969. In April 1970, the price fluctuated between $3.25 and $4.00, and stabilized at $3.25 per pound in August. The price was further reduced to $2.75 in October, and to $2.25 per pound in December 1970.

Cadmium consumption is expected to increase. Anticipated increases in electroplating consumption for automotive and construction applications may be an important contribution to the demand pattern. In addition, cadmium phosphors for television and the nickel-cadmium battery are growth markets. The Bureau of Mines projects cadmium at a 4.1-percent compounded annual growth rate from 1970 to 2000. The probable demand projection of 30.8 million pounds in 2000 signifies more than a threefold growth over demand in 1970.

Incremental Costing (12, pp. 83-245; 33, pp. 83-85)

There are two methods for producing zinc--pyrometallurgy and the hydrometallurgical process. Both methods are illustrated in figure 1, which shows the zinc system and its byproduct metals. Both methods involve roasting and/or sintering the zinc concentrates to convert ZnS to ZnO. Common salt or calcium chloride is usually added to the concentrates being roasted to increase the degree of volatilization of cadmium during roasting and sintering.

The hydrometallurgical processing of fume from roasting and sintering of zinc concentrates shown in figure 4 is selected as the subsystem for calculation of marginal and incremental costs of cadmium production. The hydrometallurgical process shown for cadmium production is distinguished by its universality. It is commonly applied to a wide variety of cadmium-bearing materials (12, p. 111). Cadmium-bearing materials obtained as byproducts by zinc, lead, and copper processing include the dusts from roasters, sintering machines, furnaces, fuming, and Waelz kilns. They also include the blue powder from the distillation of zinc, the cadmium fraction in the rectification of zinc, and the copper-cadmium filter cakes derived from purification of sulfate by cementation. The hydrometallurgical process may be used on any of these materials.

The hydrometallurgical process for cadmium involves leaching the cadmium-bearing materials with sulfuric acid to transfer the cadmium to solution. Subsequently, the cadmium sulfate solution is treated to remove impurities such as arsenic, antimony, and iron. The cadmium sponge is then precipitated, usually with zinc, or it is electrodeposited from the solution. The sponge is then further treated by electrolytic or distillation methods, yielding a final product of high-purity cadmium. Special high-purity cadmium may be obtained by vacuum distillation, zone recrystallization, ion exchange, and other techniques.

Chizhikov (12, p. 223) describes the flowsheet for cadmium production at the American Smelting and Refining Co.'s plant at Denver, Colo., Anaconda's cadmium plant at Great Falls, Mont., the American Smelting and Refining Co.'s electrolytic cadmium plant at Corpus Christi, Tex., the St. Joe Minerals Corp.'s plant at Monaca, Pa., and the Bunker Hill Co.'s cadmium plant at Kellogg, Idaho. He also describes a number of other plants in the United

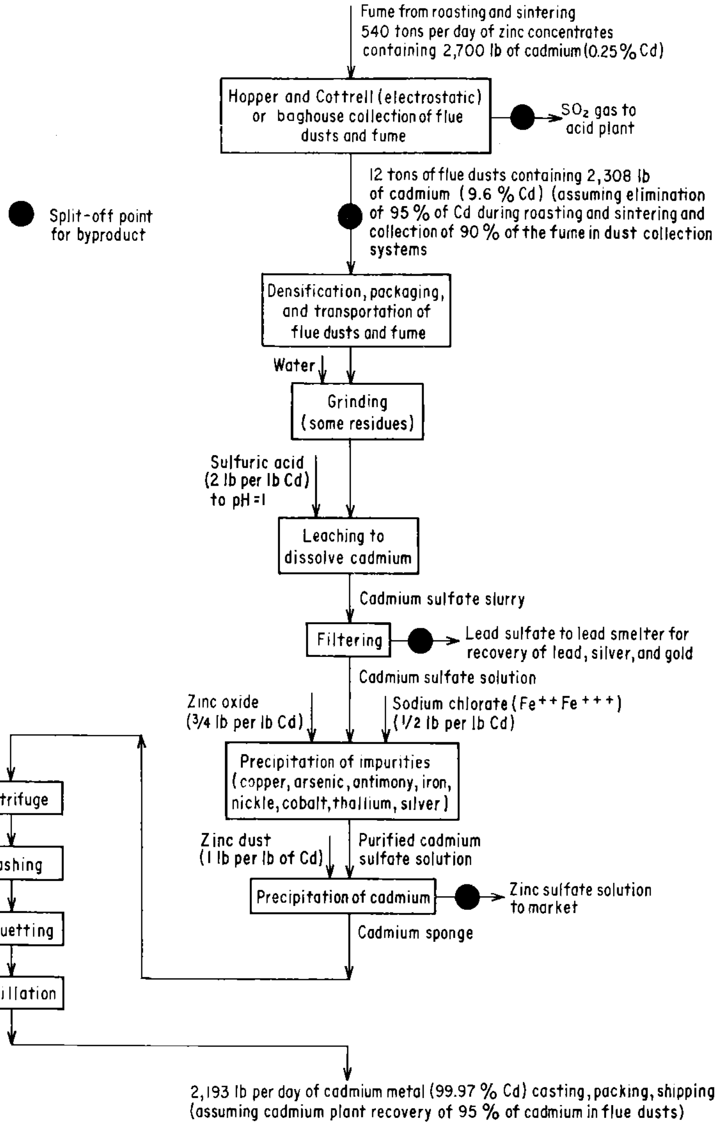


FIGURE 4. - Byproduct Cadmium Subsystem.

States, Canada, Australia, and other countries. The results of review of the above material, plant visits, and discussion of cadmium technology is the hypothetical subsystem shown in figure 4.

It is perhaps worth noting that the metallurgy of cadmium pinpoints the split-off point for processing cadmium residues at the dust collectors. This is the point of economic decision where additional costs must be balanced by expected revenues from the cadmium metal. However, this point is not entirely dependent of what has gone before. The amount of cadmium in the zinc concentrates is determined not only by the cadmium grade in ores but also by prior metallurgical processes. Chizhikov (12, p. 84) points out that selective flotation practices will determine how much cadmium passes to the zinc concentrate during the milling of lead-zinc ores. For maximum transfer of cadmium into the zinc concentrate it is necessary that the depression of the zinc-cadmium minerals in the lead flotation cycle should be as effective as possible. It is then equally necessary that vigorous prolonged activation take place before zinc flotation. Likewise, the degree of saturation of individual particles in the flotation process affects the concentration of cadmium in the separate products of flotation. The metallurgy and the economics of cadmium, therefore, begins at the mill though the actual economic decision to produce cadmium is made at the smelter or refinery.

The first step in the processing of cadmium-bearing materials shown in figure 4 is the densification, packaging, and transportation of the cadmium fume. Inclusion of this step may be questioned because many cadmium plants are in close proximity to the source of raw material. Nevertheless, there

The above calculations indicate expansion of optimum plants would be at an incremental cost level of about $1.12 per pound of cadmium.

These factors tend to bracket unit costs of suboptimum and optimum plants between 45 cents and $1.34 per pound of cadmium.

Supply Curves

A supply curve for cadmium can be derived empirically because of the availability of firm and industry production data. The data for individual firms are reflected in the industry production curve shown in figure 5. It exhibits a relatively constant cadmium output, inelastic with respect to price.

The production limit for shortrun production appears to be the 10.6 million pound cadmium output achieved in 1956. Shifts to the left from that production level can be explained by changes in grade, changes in availability of foreign cadmium-bearing materials, and changes in the output of zinc and other cadmium-bearing concentrates.

The present recovery level for cadmium in zinc concentrates was estimated at 81 percent in the calculation of marginal and incremental costs. Conceivably additional investment, particularly in the area of dust and fume collection but also in cadmium recovery and in the elimination of cadmium from concentrates, could push recovery close to the 100-percent level. Such an achievement would place the longrun supply of cadmium in the vicinity of 13 million pounds as shown in figure 5. This as before assumes constant production of zinc concentrates and other main product materials.

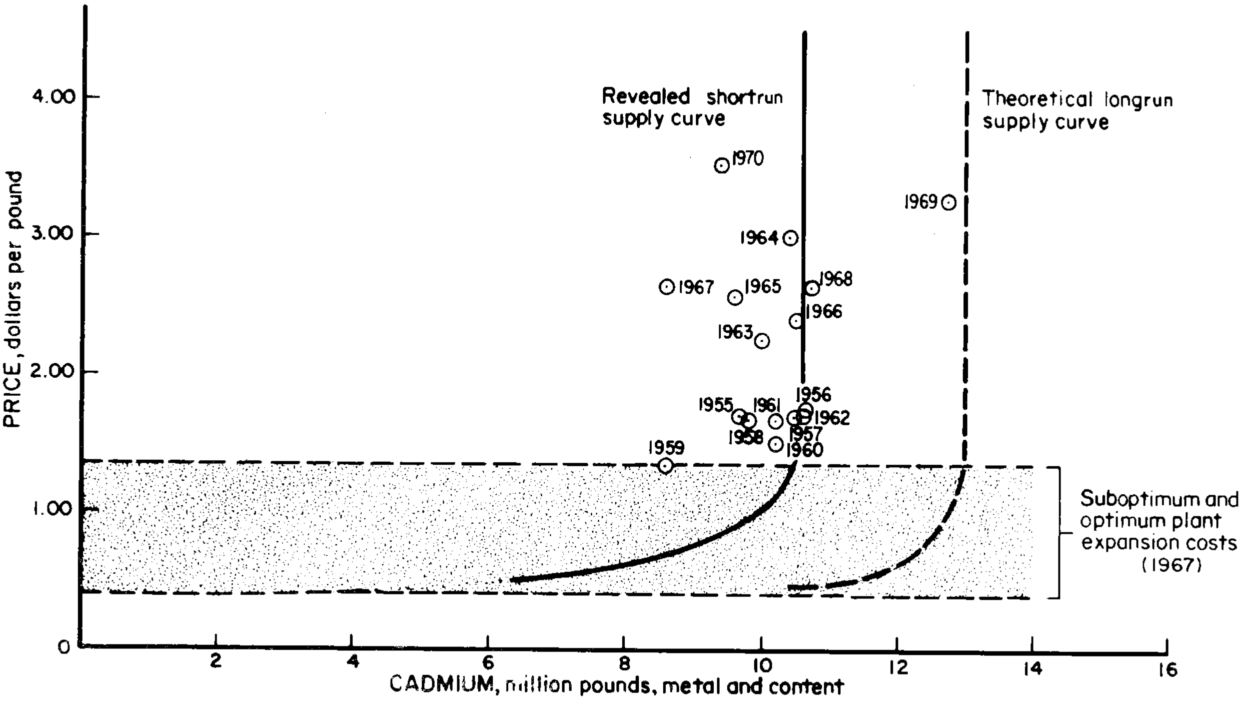


FIGURE 5. - Byproduct Cadmium Production and Supply Curves.

In the case of cadmium, the upper limit of marginal and incremental production costs is close to the price during the years 1958-60. The marginal and incremental cost range of 45 cents to \$1.34 per pound of cadmium includes the 22 cents per pound cadmium cost of purchased cadmium-bearing material. It is likely that the foreign supply would be cut off first if price fell below the high limit of the cost range. Declines below that point would tend to eliminate cadmium-bearing materials requiring transportation. Last to cut back in production would be the lowest cost cadmium plants located at the zinc smelters or other smelters having low marginal costs. The latter are estimated at 45 cents per pound in developing the theoretical supply curve.

Other Variables

Two regression equations were calculated for cadmium, the first relating cadmium output to zinc production and the second relating cadmium to zinc production and cadmium price.[7] The coefficients in both equations were significant as determined by the T-test but the equations explain only 57 percent and 64 percent, respectively, of the variation in cadmium output.

It is obvious that only a beginning has been made in statistical analysis. No attempt has been made to relate cadmium output to lead production, copper production, grade of concentrates processed, imports of cadmium-bearing materials, or stockpiling of cadmium-bearing residues.

In an attempt to eliminate the zinc variable from the cadmium supply curve, figure 6 plots cadmium per ton of zinc versus cadmium price. The results are still clouded by the effects of imported flue dusts and the failure to exclude noncadmium-bearing zinc ores.

Two supply curves are drawn in figure 6, the first applying to 1967 and the second, to production in 1970.

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[7] Equation 1: $Y = -1.723 + 0000696X_1$
Dependent variable Y = Cadmium production (1947-67), thousand pounds
Independent variable X_1 = Zinc production, thousand short tons
Multiple correlation coefficient squared (r^2) = 0.569
Degrees of freedom = 20
T-test (X_1) = 5.262

Equation 2: $Y = -2.982 + 0.0000687X_1 + 0.00014X_2$
Dependent variable Y = Cadmium production (1947-67), thousand pounds
Independent variable X_1 = Zinc production, thousand short tons
Independent variable X_2 = Cadmium price, dollars per pound
Multiple correlation coefficient squared (r^2) = 0.643
Degrees of freedom = 20
T-test (X_1) = 5.571
T-test (X_2) = 2.046

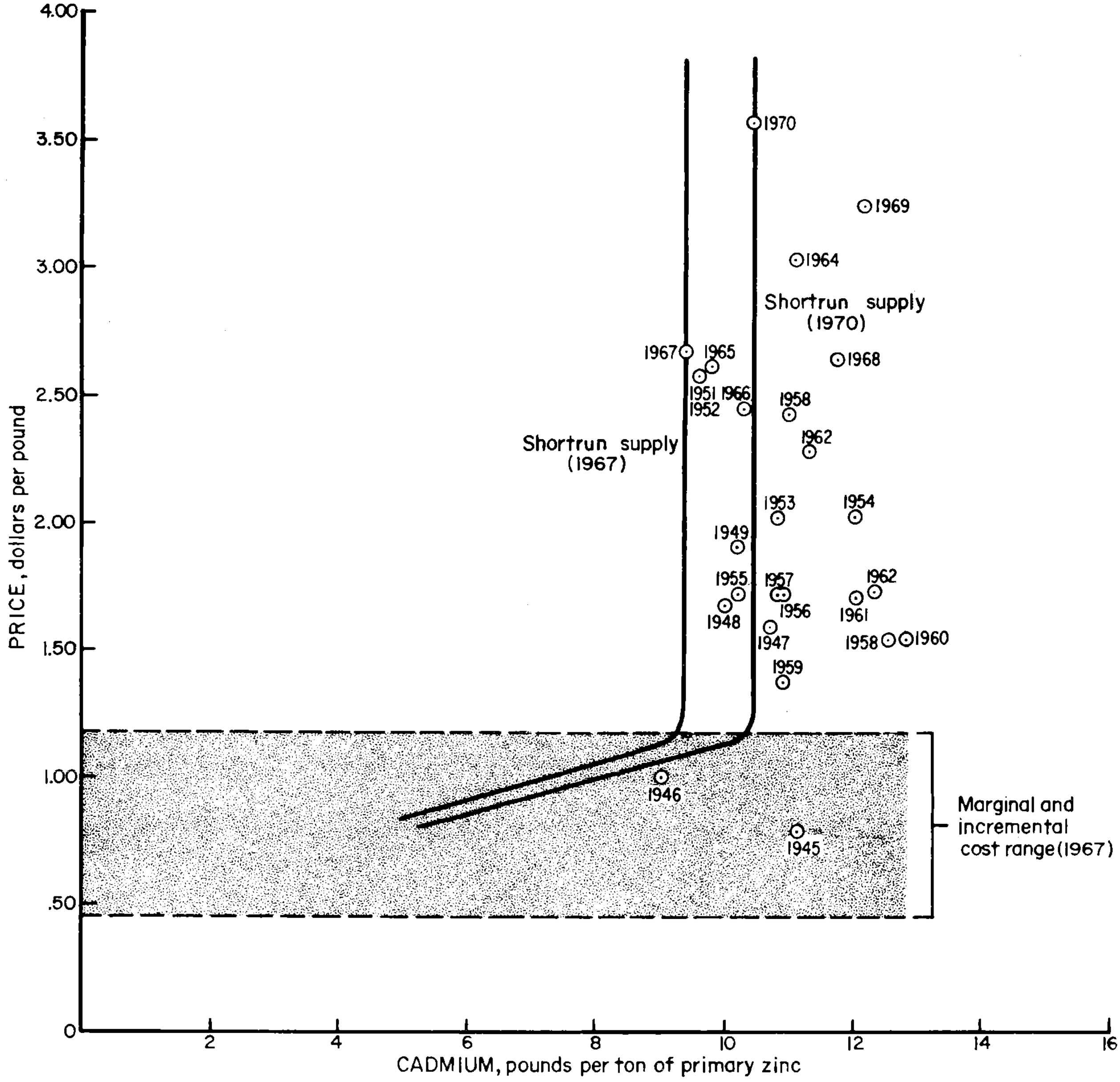

FIGURE 6. - Byproduct Cadmium per Ton of Zinc Supply Curves, 1967, 1970.

Germanium

Sources of Supply

Germanium is found in sulfide ores of copper, lead, tin, and antimony. In sphalerite (ZnS), small and varied amounts of germanium are substituted for zinc atoms in the lattice structure. Living plants concentrate germanium, and perhaps as a result coal and its byproducts, are potential sources of the metal. The content of germanium in coal is low, and consequently, the coal source is considered uneconomic at the present time.

Because of its association with zinc ores, the U.S. supply of germanium has been entirely derived from zinc smelter residues, as indicated in figure 7. The residues left from the smelting of zinc-lead ores of the Kansas-Oklahoma area and fluorspar-zinc-lead ores of the Kentucky-Illinois area are the historical sources of germanium. Germanium tends to report in certain cadmium-rich dusts or in residues of zinc retorts. Zinc sulfides containing 0.01 to 0.015 percent germanium constitute the resource base for germanium production. The fume produced during roasting and sintering are processed in a manner similar to that used for cadmium recovery. When germanium is to be recovered, a residue is separated from the cadmium-germanium solution by partial precipitation with zinc. Treatment of a copper-germanium residue includes redissolving the residue, reprecipitation of the germanium, roasting and dissolution of the germanium concentrate, and production of a germanium tetrachloride suitable for purification by solvent extraction and redistillation.

Recovery of germanium varies considerably from that described because sources and form of germanium differ. The germanium in the copper-zinc ores of the Republic of Zaire reports in the copper concentrate separated by selective flotation methods. Renierite, a complex sulfide of copper, iron, germanium, and arsenic containing 7.8 percent germanium, is recovered as a magnetic portion of the copper concentrate. The magnetic concentrate is smelted and treated by wet methods for recovery of a germanium precipitate.

During 1970, smelter residues were processed in Oklahoma by the Eagle Picher Industries, Inc.

The production and consumption figures of figure 7 are rough estimates because statistical data are not available on domestic production of germanium dioxide or metal. The figures shown are taken from estimates made in the Bureau of Mines Minerals Yearbook.

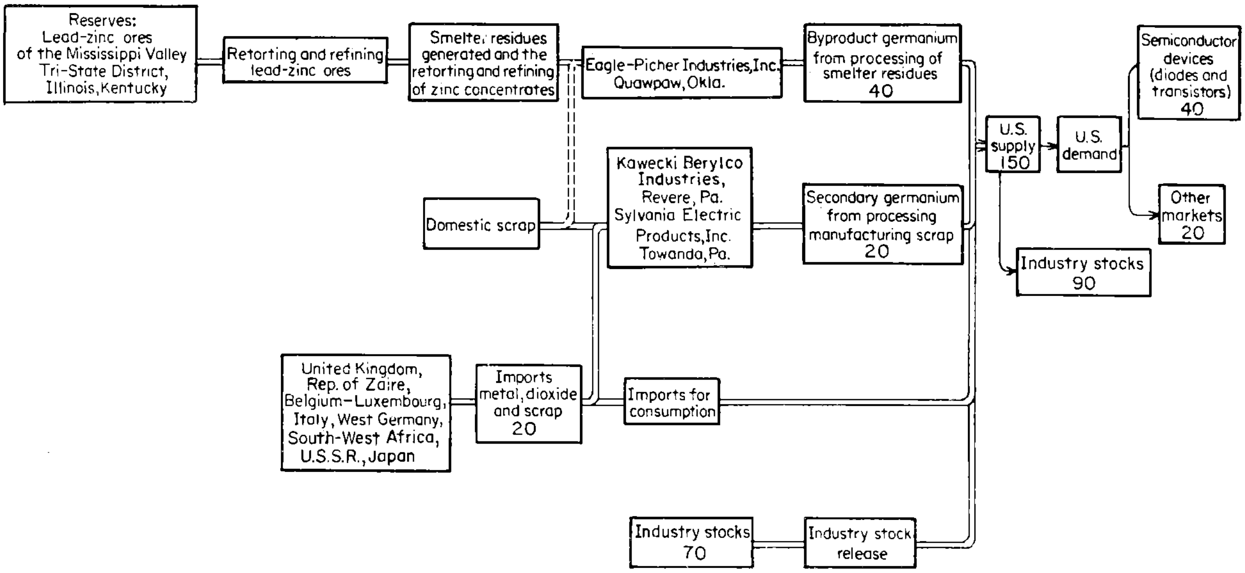

FIGURE 7. - Germanium Supply and Demand (Thousand Pounds, Metal and Content, 1970).

The recovery of germanium scrap from manufacturers' waste material, transistors, and other rejected semiconductor devices is an important segment of the germanium industry. Disregarding industry stocks, one-fourth of the 1970 supply of germanium came from these secondary sources. Many manufacturers process their own scrap. The processors indicated in figure 7 purchase scrap outright or process it on a toll basis. The material is returned to the refinery for processing by leaching, chemical purification to produce germanium dioxide, and reduction of the dioxide to germanium metals. Manufacturers' residues and sludges returned to the refinery for treatment are a result of the processes of etching, slicing, and lapping of the germanium crystal.

Reserves-Resource Base

The current exploitable sources of germanium are the lead-zinc fluorspar ores of the Mississippi Valley. These ores are estimated to contain 0.01 to 0.1 percent germanium. The total U.S. germanium reserve, at a zinc price of 15 cents per pound, is estimated at 900,000 pounds. The total resource, available at a zinc price of 25 cents per pound, is 1.5 million pounds. The corresponding rest-of-world reserves and resources are 3.1 million pounds and 6.7 million pounds, respectively.

Coal and coal fly ash are also potential sources of germanium. Since germanium concentrates in the fly ash of coal, a study of the commercial potential of coal-derived germanium was based on the possible exploitation of fly ash sources (16). In testing fly ash from powerplant hoppers, the germanium content of samples ranged from 15 to 60 parts per million. The content of the original coal ran 2.4 to 9.0 parts per million. Germanium from coal is generally considered uneconomic under present conditions. If antipollution controls are imposed on powerplants in the future, installation of high-efficiency dust precipitators may assume the major portion of the cost of germanium recovery. Likewise, there are apparently geographic concentrations of germanium-bearing coal that may be more economic than those tested. Furthermore, germanium has been found to concentrate at the top and bottom of coal seams in amounts that may be sufficient to warrant commercial recovery (35).

Demand (29; 76; 34; 33, pp. 188-197; 58; 43, p. 130)

Throughout its short and explosive growth history, germanium demand has been dominated by its use as a semiconductor in the manufacture of electronic equipment. In fact, the first major strides in utilizing semiconducting properties were due to the availability of high-purity germanium. The first germanium diode was a fine wire of appropriate metal pressing against a thin wafer of properly prepared germanium. Current flow through a semiconductor is controllable by varying the number of electron-carrying atoms. This variation is achieved by changing the electronic structure, for example, by introducing certain impurities.

The first transistors, dating back to the late 1940's, were used in amplifiers and oscillators. Their utility over the years was rapidly increased, allowing miniaturization in electronic equipment. Replacement of vacuum tubes by transistors made possible direct long-distance dialing. Other special germanium devices resulted in major advances in astronautics and missile guidance. By 1959 the germanium semiconductor market totaled 125 million devices despite strong competition from high-purity silicon. Although there are many other semiconductors, germanium and silicon are the two that possess the optimum electrical properties that meet the requirements for electronic devices and rectifiers.

By 1970, two decades after the start of the growing demand for transistors, the market for germanium semiconducting devices totaled 505 million devices. Demand for silicon devices in 1970 totaled 1.7 billion, which gives some idea of the impact of the late-comer silicon on the demand for germanium. While germanium monopolized 80 to 90 percent of the diode and transistor market in the early years, it had dropped to 27 percent of the diodes produced and 15 percent of the transistors produced by 1970.

In other electronic applications, the photoconductive properties of germanium are utilized in construction of photodiodes and photoelectric cells. Germanium is also used in rectifiers. A molecular digital computer has been built using blocks of etched germanium. Germanium is also used in strain gages that are more sensitive than conventional strain gages.

The largest market by far for germanium has been the semiconductor. There are, however, other potentially very important applications. Several transistorized ignition systems have appeared in the automotive industry, as have germanium diode voltage regulators, transistor radios, speed control devices, and devices that warn of icy road conditions and low tire pressure. Germanium is used to measure exceedingly low temperatures down to a few degrees Kelvin in resistance thermometers.

Germanium like most semiconductors transmits light in the infrared region; hence, it is useful as a detector and as a window or lens.

Germanium silicon alloys are being investigated for thermoelectric properties. Thermoelectric materials convert heat into electrical work.

Another potential application of germanium is as a catalyst in manufacturing polyester fibers.

Gallium-doped germanium is a most sensitive detector of radiation. This use is growing and may become a major consumer of germanium.

Small markets for germanium include production of glass with special properties. Glass in which silicon dioxide is largely replaced by germanium dioxide has an unusually high refractive index and is useful in manufacturing wide-angle camera lenses and microscope objects.

Projection of germanium demand is not possible using conventional projection indices. This is the result of the great variety of new potential applications. The tie of germanium to electronics through the transistor is threatened by continued market erosion due to competition from silicon. The Bureau of Mines has projected germanium demand to increase at a 2-percent compound annual growth rate. Such a projection puts U.S. demand at 75,000 pounds by the year 2000.

Production, Consumption, and Price Statistics

The production, consumption, and price history of germanium is summarized in figure 8. The spectacular rise in consumption between 1945 and 1956 can be attributed to germanium domination of the transistor market and rapid application of the transistor in electronics. The check to germanium consumption and the price decline after 1956 primarily reflects the impact of competition introduced by the availability of silicon for transistors. The rapidly widening gap between production and consumption shows how a slow growth in the market and a rapid buildup of secondary germanium cut primary demands on production.

The price decline of germanium after 1956 undoubtedly resulted from both silicon competition and reaching the limits of explosive market growth after the early 1950's. High prices failed to slow down germanium growth during its early period of expansion. Likewise, declining prices failed to spur consumption significantly after silicon competition was introduced. The three price increases in early 1970 reflected the rising cost of raw material.

Production declines reflect both the impact of changes in zinc production and the cutbacks in production necessary because of overexpanded inventories and the slower growth rate of germanium markets.

The germanium consumption trend subsequent to the silicon competition from 1956 through 1970 increased at an average 0.8 percent compound rate annually.[8]

Incremental Costing

The most relevant byproduct subsystem for germanium includes all processing of germanium-bearing residues after their precipitation with zinc dust and separation from cadmium-bearing solution. The production of germanium can be viewed as a byproduct of the byproduct cadmium system if the cadmium system is profitable in itself.

The flow diagram shown in figure 9 is based primarily on an article by Thompson and Musgrave printed in 1952 (76). The processing is essentially unchanged today. Some additional technical material was reviewed to assure consistency with modern practice (34, 29, 40, 56, 23).

The process shown in figure 9 begins with the collection of the cadmium-germanium-bearing fume from the roasting and sintering operation in processing zinc sulfide concentrates.

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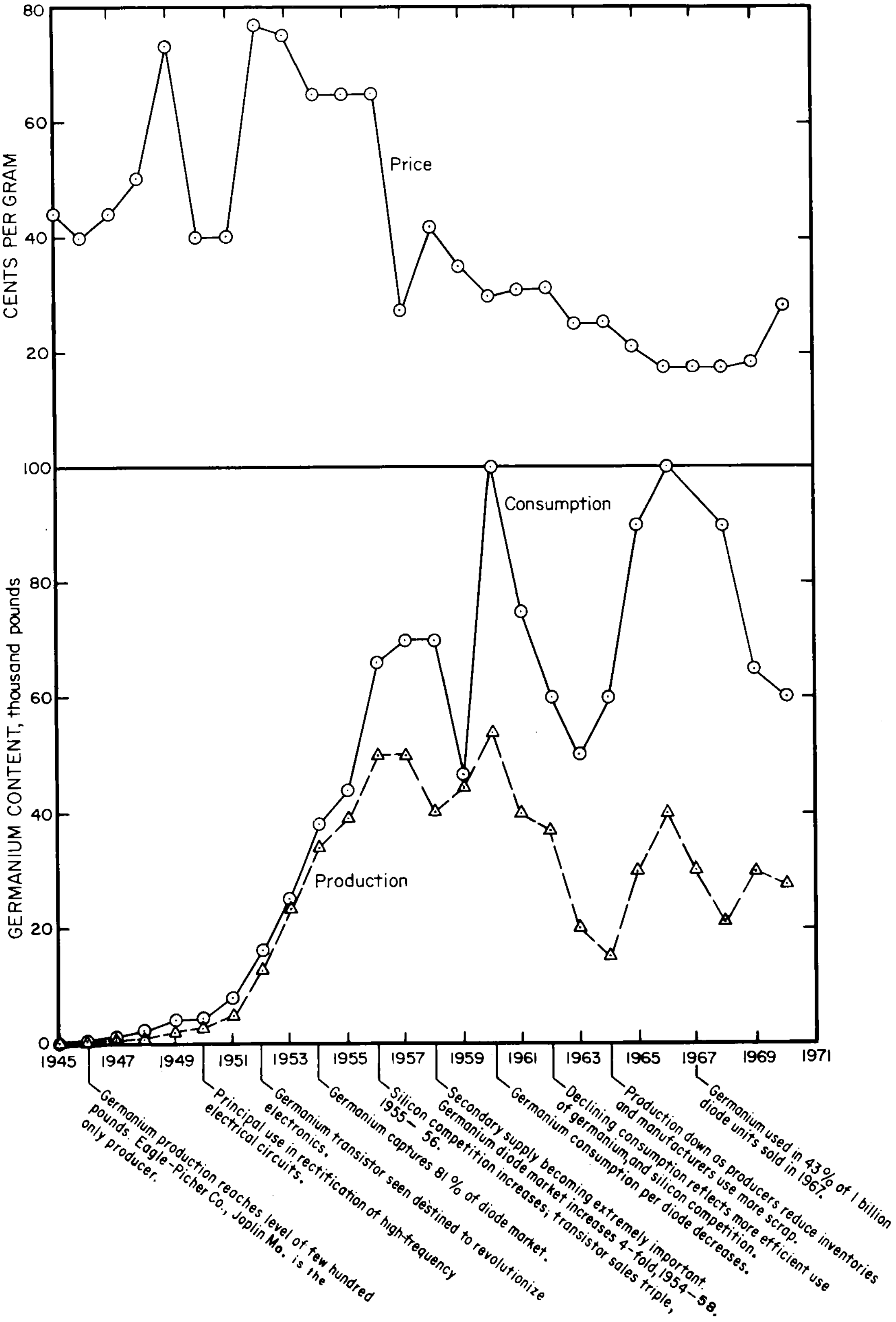
[8] Straight line trend equation is $Y = 622.08X + 68{,}593.06$ where Y is germanium consumption and X is the year. $X = 1$ in 1956 and $X = 15$ in 1970.



Germanium production reaches level of few hundred pounds. Eagle-Picher Co., Joplin Mo. is the only producer.

Principal use in rectification of high-frequency electrical circuits.

Germanium transistor seen destined to revolutionize electronics.

Germanium captures 81 % of diode market.

Silicon competition increases; transistor sales triple, 1955– 56.

Secondary supply becoming extremely important. Germanium diode market increases 4-fold, 1954–58.

Germanium consumption per diode decreases.

Declining consumption reflects more efficient use of germanium, and silicon competition.

Production down as producers reduce inventories and manufacturers use more scrap.

Germanium used in 43% of 1 billion diode units sold in 1967.

FIGURE 8. - Germanium Production, Consumption, and Price History, 1945-70.

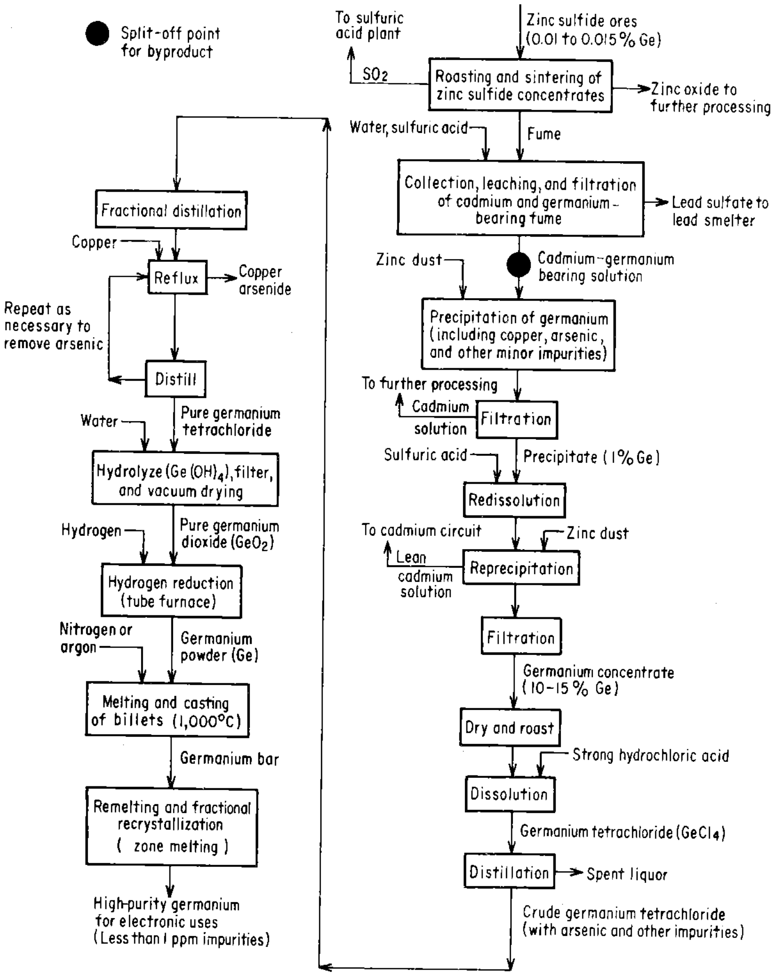


FIGURE 9. - Byproduct Germanium Subsystem.

The split-off point for germanium separates the collection, leaching, and filtration of the fume from the first partial precipitation which was done expressly to separate the germanium-bearing precipitate from the cadmium-bearing solution. This partial precipitation is achieved by adding zinc dust sufficient to precipitate copper and germanium without precipitating the cadmium. Some other impurities, principally arsenic, are also thrown down with the copper-germanium precipitate. From this point on, the process is similar whether the 1 percent germanium product comes from zinc smelter residues, zinc flue dusts, or coal ashes.

The germanium-bearing sludge is redissolved in sulfuric acid, and the germanium is concentrated by a second precipitation. The germanium concentrate is dried and roasted and is then dissolved in strong hydrochloric acid. The resulting germanium tetrachloride and arsenic chloride are distilled from the solution and are then ready for purification. Purification involves multiple distillation of the tetrachloride, hydrolyzing with water, and calcination to produce a pure germanium dioxide. The metal is produced by hydrogen reduction of the germanium dioxide in a tube furnace. The resulting germanium metal powder is melted in an inert atmosphere to prevent oxidation and is cast into bars. The product is not pure enough for electronic applications and must be further purified by such techniques as zone refining.

Zone refining relies on the fact that impurities are more soluble in a melted substance than in a solid substance. The melted zone in a bar of germanium is made to travel from one end of the bar to the other so as to carry the impurities to one end. The bar of metal is surrounded during refining by an atmosphere of inert gas to prevent oxidation.

Single crystals of germanium may be produced by seeding melted germanium and slowly withdrawing the crystals from the furnace. Other processes include pressure, heating and quenching, or alloying of germanium with minute amounts of other metals.

The economic importance of some of the final stages of germanium purification is indicated in the price structure of the metal. Purified germanium dioxide, before hydrogen reduction, was priced at a low level in 1970 of $105.00 per kilogram (2.2 pound). Three subsequent price increases resulted in a final price of $167.50 per kilogram. The first hydrogen reduction of germanium, without zone refining, includes the cost of the hydrogen reduction process. This processing changes the price to $272 per kilogram. The $293 per kilogram price of intrinsic or ultrahigh-purity polycrystalline germanium metal includes zone refining. In other words, hydrogen reduction costs the consumer $104.50 per kilogram, and zone refining of the metal costs $21 per kilogram. Single crystal germanium prices are likely to be double the prices for the ultrahigh-purity polycrystalline form.

The germanium process illustrated in figure 9 has not been subjected to cost calculations. There are several indications that incremental processing costs are somewhat irrevelant just as they are for many of the byproduct metals. Germanium is similar to rhenium in that its application requires small amounts of the metal resulting in insensitivity to price changes. Consumption is more a function of technical performance among competing materials rather than a function of relative price.

Supply Curves

The germanium supply curves shown in figure 10 are sketched on the assumption of a marginal cost level equal to two-thirds of the 1967-70 price level.

The long-term supply curve is not drawn and would require considerably more detailed examination of alternative sources of germanium. It is possible, for example, that air pollution regulations requiring more complete collection of powerplant dusts would bring germanium from this source into commercial production. If it does, the long-range supply curve may be far to the right for small increments in price.

Other Variables

The effect of variation in zinc output on germanium output could be eliminated by plotting germanium per ton of germanium-bearing zinc versus germanium price. In figure 11, germanium per ton of recoverable zinc contained in domestically produced ore is plotted versus germanium price. The result is not completely satisfactory because only a small portion of total zinc ores is a potential source of germanium.

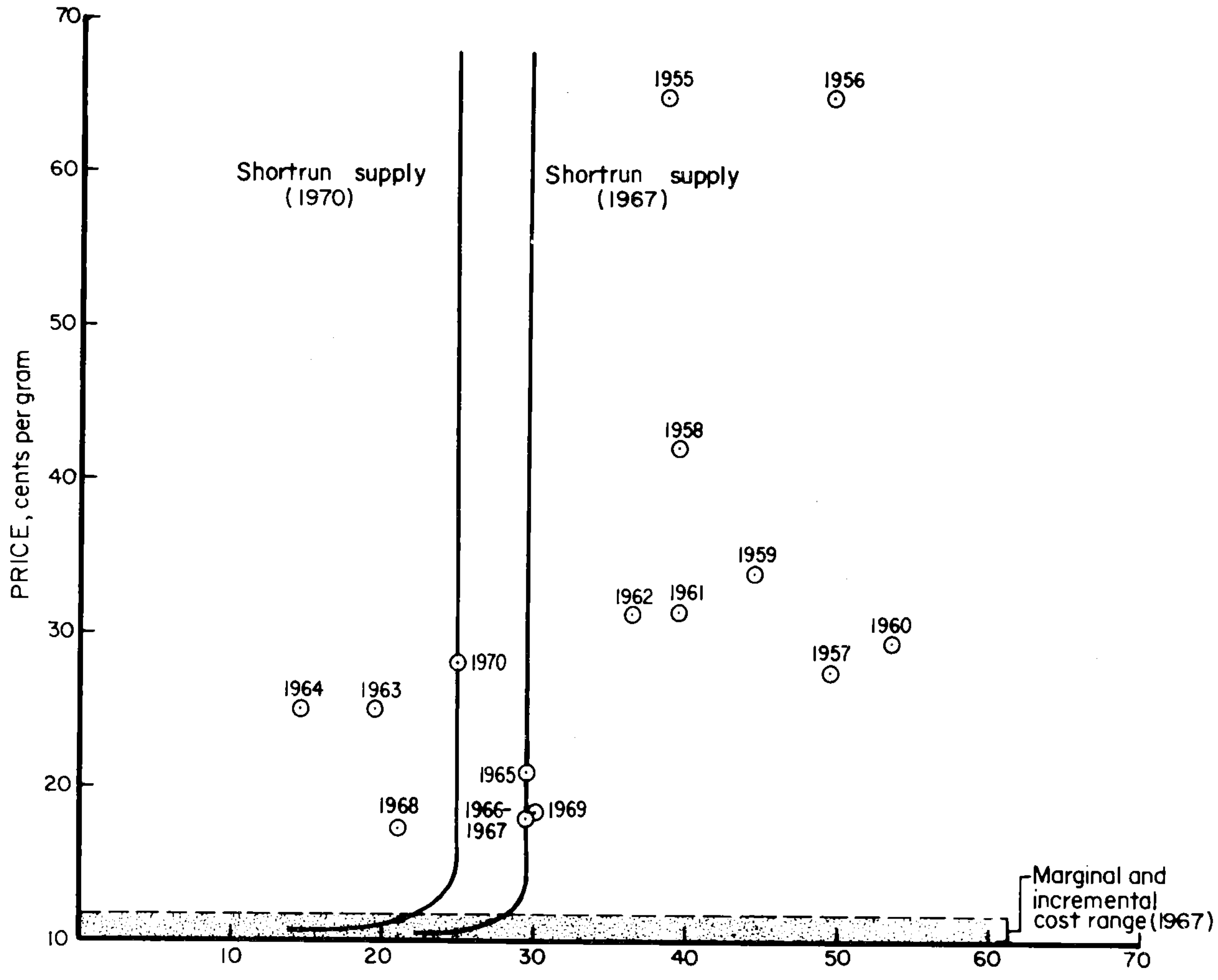


FIGURE 10. - Germanium Production and Supply Curves, 1967, 1970.

Indium

Sources of Supply

One gram constituted the world's available supply of indium in 1924. Today, thanks to the development of byproduct production techniques and to the development of industrial uses for the metal, domestic demand totals in the thousands of ounces.

Indium is widely distributed in minute quantities. The earth's crust is estimated to contain 0.1 parts per million of indium, found in minute quantities (less than 0.1 percent) in many minerals. Often, indium is associated with lead and zinc minerals. It is most frequently associated with zinc, and for this reason it is considered a part of the zinc-processing system. Indium is recovered from zinc smelter residues and slags, the only presently commercial source of the metal. Indium reports at several points in the zinc

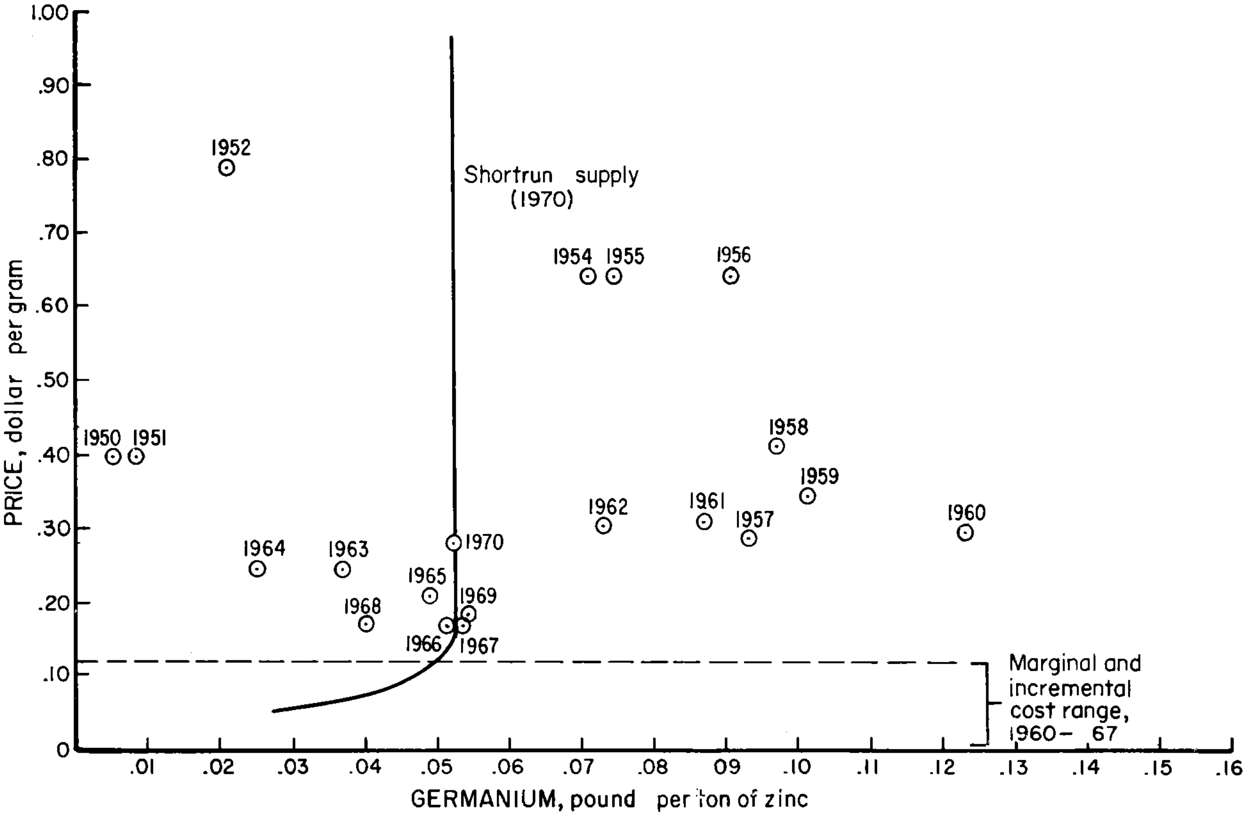


FIGURE 11. - Byproduct Germanium per Ton of Zinc Supply Curve, 1970.

processing system. It is recovered from lead blast furnace slags, from crude lead containing zinc and indium as impurities, from insoluble residues produced during the leaching of zinc oxide for the electrolytic zinc process, during the purification of crude zinc, and from zinc-plating solutions.

American Smelting and Refining Company patents cover two processes for the recovery of indium. The first process involves leaching residues with acid and precipitating indium as a phosphate. The second patent describes a process for recovering indium from crude zinc-lead metal.

An Anaconda Co. patent covers recovery of indium from zinc calcine or zinc oxide fume produced in the treatment of lead blast furnace slag.[9]

As indicated in figure 12, two U.S. plants controlled by one company produced all domestic indium in 1970. Total production data are confidential. The only company production data published are those of The Anaconda Co., which ceased production in 1969. These data showed production of 177,000 ounces of indium in 1966, 61,000 ounces in 1967, 86,000 ounces in 1968, and 63,000 ounces in 1969. The most recent figure on the total U.S. supply of indium is that for 1957, a peak year in which 640,000 troy ounces were supplied.

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[9] Patents are summarized in Hampel (33, p. 222).

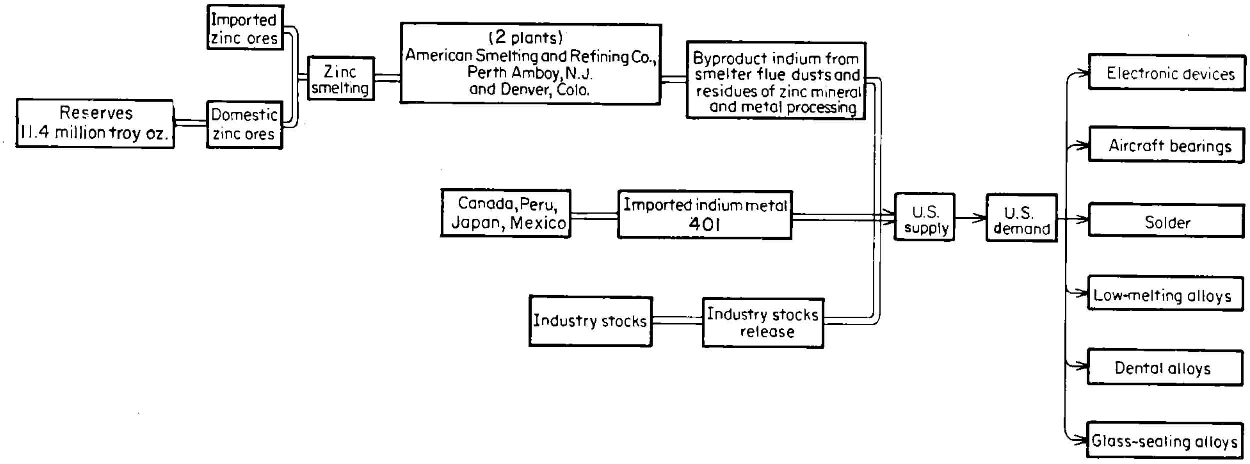

FIGURE 12. - Indium Supply and Demand (Thousand Troy Ounces, Metal, 1970).

Mine sources of indium-bearing zinc concentrates have not been traced, but they are of both foreign and domestic origin. Domestic ores and foreign ores each accounted for 50 percent of the U.S. zinc ore supply during 1970. Sources of indium probably approximate this distribution. As figure 12 indicates, imported indium metal from Canada, Peru, Japan, and Mexico also accounted for a substantial portion of the U.S. supply in 1970.

Reserves-Resource Base

In 1970 domestic reserves of indium were estimated at 11.4 million troy ounces based on zinc at 15 cents per pound. At a 25-cent-per-pound price for zinc, indium reserves were estimated at 17.0 million troy ounces.

Demand (72)

Indium is used chiefly in electronics, and in measuring and controlling instruments. Indium is used with germanium in semiconductor devices, and is also used to solder leads in the manufacture of germanium transistors. Indium phosphide has application in high-temperature transistors. Indium arsenide and antimonide are used in low-temperature transistors, thermistors, and optical devices. Infrared detectors and magnetoresistors using indium antimonide are available. Indium has been found to make excellent low-resistant contacts with oxides, such as titanium oxide and barium titanate. It may therefore be useful in piezoelectric units.

Indium is used also in automobile and other motor bearings. The addition of indium to bearings improve strength and hardness, increases corrosion resistance, and affords improved wettability with resultant increases in antiseizure properties. The use of indium in bearings is not of great importance in the United States, but this use remains popular in Europe.

Indium and its alloys adhere well to a large number of metals and nonmetals. For this reason, special solders containing indium find many applications. Mentioned before is the important market in the manufacture of transistors.

A number of low-melting point alloys containing indium have been developed. These alloys are used in surgical casts, foundry patterns, and fusible safety plugs. An alloy of tin and indium is capable of wetting glass and can therefore be used to seal glass joints.

Other uses for indium include use as an oxygen scavenger in gold dental alloys. Indium alloys in jewelry and silver keep the metals bright, and a silver-indium-cadmium alloy is used in nuclear reactor control rods.

The Bureau of Mines projection for indium is based on a 1.3-percent growth rate compounded annually between 1970 and the year 2000. The rate reflects present small markets for indium, as well as the effect of limited supply on incentive to develop new markets.

Production, Consumption, and Price History

The sparse data on the production and consumption of indium limit analysis. The best available and publishable data indicating production and consumption are the 640,000-troy-ounce production figure of 1957 and the 401,000-troy-ounce imports for 1970.

The price for indium, based on 99.97 percent pure indium in 30- to 90-ounce sticks, was constant at $2.25 per troy ounce from 1945 to 1963. The average price rose to $2.40 per troy ounce in 1964 and to $2.75 per troy ounce in 1965, where it remained until September 1968 when it dropped back to $2.50 per troy ounce and remained at this price through 1970. In larger quantity sales, ingots in lots of 10,000 ounces were quoted at $1.75 per troy ounce in 1970.

Incremental Costing

Available data on the metallurgical techniques of indium production used in the United States are very limited. Therefore, no attempt is made to define the indium subsystem in detail or to calculate marginal or incremental cost. A flowsheet for Canadian indium production and data on electrolytic recovery of indium from slag are available (26; 45, pp. 194-195).

Supply Curves

There are insufficient data to develop supply curves for indium.

Thallium

Source of Supply

Trace amounts of thallium are found in sulfide ores. Because of this, it is commonly a byproduct of the roasting of pyrite ores in the production of sulfuric acid or a byproduct of the smelting of lead and zinc concentrates. Spectrographic analysis of residues from a sulfuric acid plant was responsible for the discovery of thallium in 1862. The potash minerals probably contain more thallium than the sulfide minerals. However, the metallurgy of the sulfide minerals is more adaptable to the recovery of thallium as a byproduct. Demand for thallium is too small to provide incentives for the recovery of the metal from other sources or even full recovery from the present source.

The U.S. supply of thallium as indicated in figure 13 is derived principally from the processing of zinc concentrates. The American Smelting and Refining Company at Denver, Colo., has been the sole domestic producer of thallium for many years.

Commercial thallium is derived generally from flue dusts generated in the roasting of sulfides or from cadmium-rich material derived from zinc ores. It is commonly associated with the cadmium byproduct system, as indicated in the zinc system diagram of figure 13. The first steps of thallium recovery are part of the cadmium subsystem. The final steps of thallium recovery involve precipitation with zinc, purification by reprecipitation and subsequent electrolytic recovery of the metal.

Reserves-Resource Base

Thallium reserves are estimated to total 150,000 pounds based on zinc reserves at 15 cents per pound for zinc and production experience of recovered thallium.

Demand (33, pp. 529-535)

Thallium markets are smaller than those of any of the other byproduct metals. The historical market for thallium, rodenticides and insecticides, declined sharply beginning in 1965. Electronics and solder and alloy manufacturing applications are important consumers of the metal. Certain salts of thallium have unique photosensitivity properties that make the metal

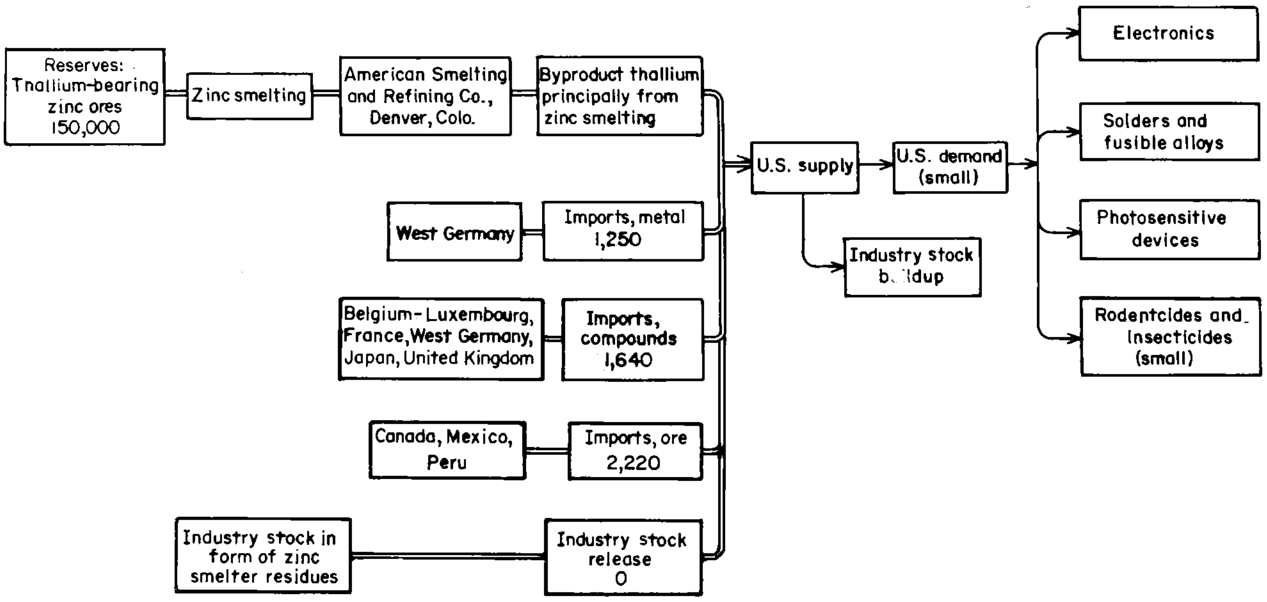

FIGURE 13. - Thallium Supply and Demand (Pounds, Metal and Content, 1970).

important in modern warfare applications. Conductivity of oxidized thallium sulfide changes on exposure to light. Incorporated in cells, the compound is particularly sensitive to infrared light. During World War II, mixed thallium bromide-iodized crystals were used to transmit infrared radiation and were employed in military equipment designed for sniper detection and in signaling where visible radiation could not be used (33, p. 533).

Several types of alkaline earth silicates and phosphates activated with thallium give good erythemic (suntan) range radiation.

Thallium has some interesting potential markets that may expand in the future. Thallium alloys have unique properties. The addition of lead to thallium raises the melting point above that of the components making it of limited use in fuses. A mercury-thallium alloy has the property of freezing below the freezing point of mercury, making it a potential substitute material for mercury in low-temperature applications.

Because of the very small size of present markets and the relatively large stocks of thallium-containing residues, a thallium supply curve can be expected to be more elastic than a more typical byproduct curve.

The Bureau of Mines projects the consumption of thallium at an annually compounded rate of 1 percent to the year 2000. Curtailment of the rodenticide market and the expanding use of thallium in electronics contribute to future uncertainties.

Production, Consumption, and Price Statistics

There are virtually no quantitative data on thallium production or consumption.

At the end of World War II, thallium had little use other than as a rodenticide or insecticide. At that time there was some experimental use of thallium in alloys with lead, copper, and silver. There was interest in the unique physical properties of the compounds of thallium, such as the bromoiodide of thallium which transmits wavelengths in the infrared region.

In 1949 a new and much enlarged thallium recovery unit was put into operation at the American Smelting and Refining Company Globe smelter. The American Smelting and Refining Company was the only domestic producer of thallium during the postwar period.

During the early 1950's, the output of thallium metal and sulfate was estimated to be a few thousand pounds per year.

Sales to the public of thallium sulfate, an odorless, tasteless, and very poisonous sulfate of thallium, were restricted during the 1950's because of extreme toxicity to men and animals. This tended to change the consumption pattern for thallium, and shifted the demand to the bromoiodide form. The bromoiodide crystals found important application in military equipment designed for detection and signaling.

However, in the early 1960's thallium sulfate was still the principal product, and rodenticides and insecticides were still the principal markets. In August 1965, the U.S. Department of Agriculture prohibited further private use of thallium for the control of insect and rodent pests. The ruling limited the usage of thallium compounds to qualified personnel in Federal, State, or local governments. As a result, use of thallium was further curtailed. Electronic, solder, alloy, and other minor markets increased substantially and partially offset the pesticide losses.

The price of thallium declined rapidly from the post-World War II levels of $15 to $20 per pound. The price of thallium in 25-pound lots was quoted at $7.50 per pound during 1970. The last price change was in December 1957 when the price of $12.50 per pound, in effect between 1949 and 1957, declined to the present level of $7.50 per pound.

Incremental Costing (65, p. 55; 33, pp. 529-531)

Costs of the thallium subsystem were not estimated. A number of byproduct subsystems for thallium are described in the literature. Several depend upon the extraction of thallium from flue dust by boiling it in acidified water. The dissolved thallium is precipitated with zinc. Traces of zinc, copper, lead, cadmium, and indium are removed by dissolving thallium in dilute sulfuric acid and precipitating the impurities with hydrogen sulfide. A saturated solution of thallium can be readily electrolyzed using platinum cathodes. The metal is then washed, compressed into blocks, melted in a hydrogen atmosphere, and cast into sticks.

Another thallium process makes it a byproduct of the cadmium subsystem. The crude flue dust is leached with sulfuric acid, forming both cadmium and thallium sulfates. Impurities are precipitated as sulfides and hydroxides, and the purified solution is electrolyzed for the deposition of cadmium. When the thallium content of the electrolytes reaches a 1:10 ratio with the cadmium content, cathodes are removed and replaced. The continued electrolysis precipitates a cadmium-thallium alloy. The alloy is subsequently treated with boiling water and steam. The solution contains thallium hydroxide and minor amounts of cadmium. Cadmium is precipitated with sodium carbonate and leaves a solution of thallium carbonate. Precipitation from this solution separates the thallium as a sulfide. The sulfide is dissolved in sulfuric acid producing a pure thallium sulfate ready for market or for further processing by electrolysis.

Supply Curves

There are insufficient data on thallium to sketch supply curves. The shortrun curve now operating in the level of several thousand pounds is estimated to have a potential capacity of 30,000 pounds annually by one author (33, p. 531).

The price stability of thallium over the last 13 years and the general decline over the past 20 years suggests that the trend toward rising production costs has been offset by new technology or that there is sufficient margin between incremental cost and price to absorb increases in the cost level.

Lead System

All lead ores contain substances other than lead minerals, and these become the basis for the byproducts of the lead system. The simplified diagram shown in figure 14 shows the split-off points for byproducts, zinc, copper, thallium, cadmium, arsenic, gold, silver, and antimony. Figure 14 is the result of a review of a number of metallurgical references (47; 48; 18, pp. 234-238; 44, pp. 144-215; 30; 44, pp. 139-143; 44, pp. 94-103; 44, pp. 104-138).

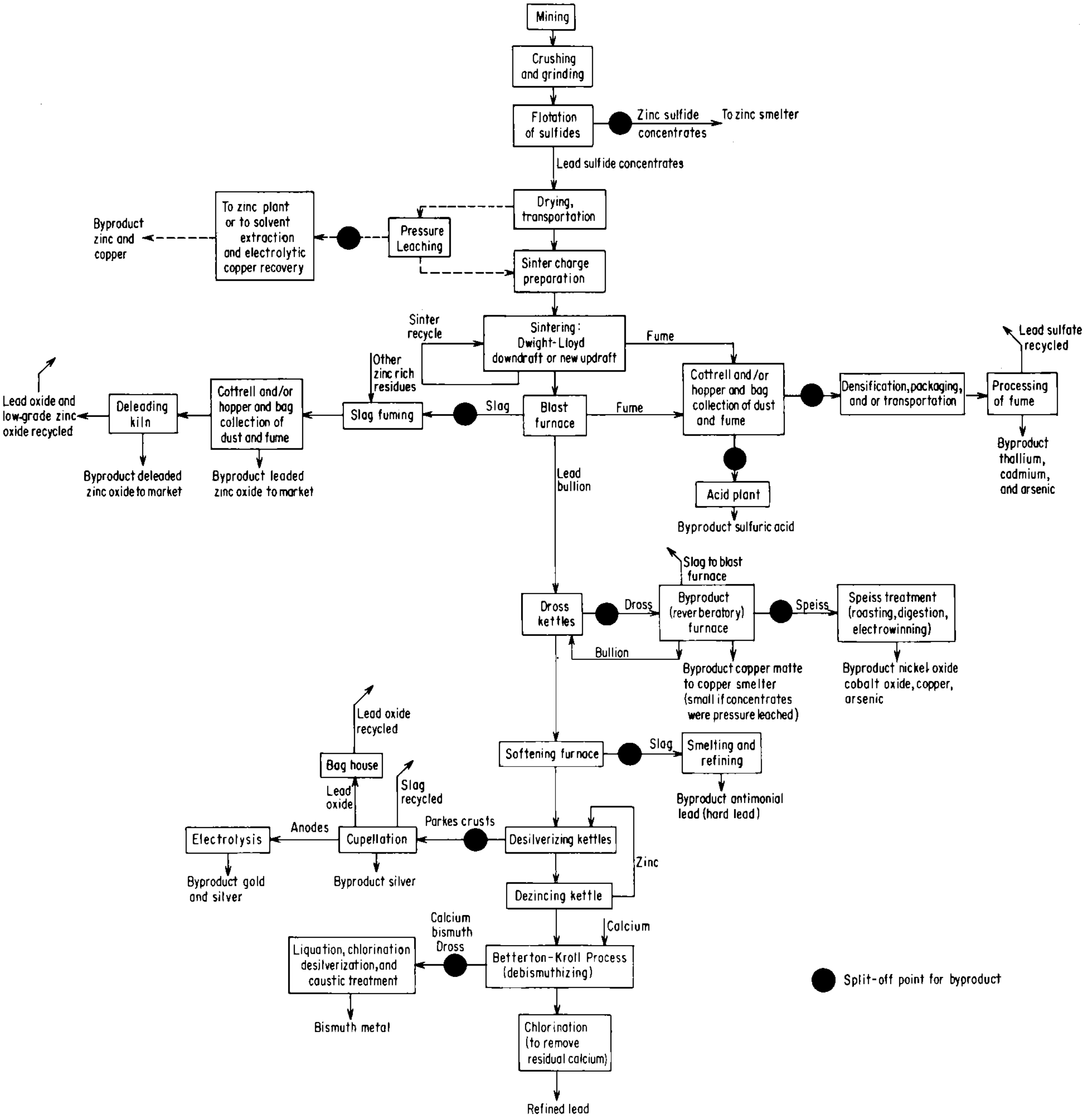

FIGURE 14. - Lead System, Showing Byproduct Metals.

The various commercial grades of lead have maximum allowable impurities of silver, copper, arsenic, antimony, tin, zinc, iron, and bismuth. Separation of these impurities from the refined lead is part of the refining process designed to meet standard specifications for lead (44, p. 145).

Antimony is retained in lead because it imparts hardness and expansibility upon solidification, qualities which are essential in the production of type metal (3 to 8 percent antimony) and storage battery grids (3 to 5 percent antimony) and casting metals generally. Likewise, small amounts of copper (0.04 to 0.06 percent) are retained in lead used for cable sheathing while small amounts of tellurium and calcium are retained in other lead grades. Because of these demands for byproduct metals in the form of alloys with lead, incremental processing is often not carried to the point of producing a metallic byproduct. Processing is limited to concentration of the byproduct metal in the lead.

Arsenic is generally minimized in the lead product except in the production of lead shot. Arsenic usually finds its market in the form of an oxide fume. It is concentrated during the roasting and smelting operations, and occurs in the flue product in the trioxide form in concentrations up to 30 percent arsenic. The split-off for arsenic occurs at the blast furnace and dross kettles. The arsenic is recovered from subsequent treatment of fume and speiss. Further processing includes repetitive resublimation to remove impurities and results in a product that is 99-percent-pure arsenic trioxide. Incremental costs are identical whether the arsenic originated in the copper system or the lead system in the form of flue dust.

Lead and zinc are commonly associated in mineral deposits. Since galena, lead sulfide, is the most common of the lead minerals, and sphalerite, zinc sulfide, is the most common of the zinc minerals, separation of the two is often achieved through selective flotation of sulfides during the milling stage. Thus, flotation is the location of the first split-off point in the lead system--at the point where the zinc system and the lead system are separated.

Typical analysis of a lead concentrate, a product of the flotation process, is from 55 to 70 percent lead, up to 6.5 percent zinc, 0.5 to 4.0 percent copper, 13 to 18.5 percent sulfur, up to 5.0 percent iron, and minor amounts of silica, lime, cadmium, silver, gold, arsenic, and other metals depending on the source.

A second split-off point occurs if the sulfide concentrates are subjected to pressure leaching. If they are, byproduct zinc and copper will be produced as indicated on figure 14.

The procedures used to process lead concentrates are sintering, reduction in a blast furnace, and refining. Refining includes operation of the dross reverberatory furnace.

In smelting any type of lead ore, sulfur must be removed first. It is commonly removed by roasting to reduce the sulfur content to less than

4 percent. At the same time other volatile impurities are driven off in the form of gas and fumes. The gas, fume, and dust from lead-sintering operations are combined with blast furnace gas, fume, and dust. The result is a byproduct subsystem yielding sulfuric acid, thallium, cadmium, and arsenic. Sintering is the prime source of byproduct fume. Downdraft and updraft techniques are used (30).

The function of the blast furnace in lead smelting is to reduce the concentrates to metal and combine the impurities in a slag so that a separation can be made. These slags from the lead blast furnace yield additional byproduct zinc in the form of zinc oxide. Generally, the process is slag fuming. Benefits include increased lead recovery through return of lead in the slag to the furnace.

Dross from the lead drossing kettles is processed first to recover entrained lead in the slag. Processing may also yield byproduct nickel and cobalt oxides, copper, and arsenic. The Bunker Hill plant at Kellogg, Idaho, now has a facility using an alternative method for processing drosses. The method results in the production of electrolytic copper while lead is recycled back to the blast furnace. Copper, lead, and precious metals are recovered in the dross (47).

Softening of lead bullion refers to the removal of arsenic, antimony, and tin, which are the elements that increase the hardness of pure lead. Softening can be accomplished by the reverberatory process, the kettle process, or the continuous process (46, pp. 226-227). The reverberatory process shown in the flow diagram is common because of its adaptability to softening lead bullion having a wide range of impurities in day-to-day operation.

Slags resulting from the softening operation are transferred to the antimony plant where they are reduced or treated. Antimony is usually marketed as antimonial lead, but it may also be converted to antimony oxide or metallic antimony. Tin recovered from the skim may be sold as lead-antimony-tin bearing alloy or other tin alloys. Arsenic contained in the softening skim is usually discarded as sodium arsenate.

After softening, the lead bullion goes to the desilverization kettles. Zinc is added and forms oxide crusts containing lead, zinc, gold, and silver. The crusts from the desilverization kettles are processed to remove gold and silver. Recycled lead oxide increases lead recovery and is included in the benefits of the precious metal subsystem.

The dezincing kettle shown in the flow diagram is for recovering the zinc used in desilverization. About 90 percent is recovered and recycled back to the desilverization kettle.

Bismuth, being very resistant to oxidation, is not removed from the lead bullion during the softening process. It is separated from the lead bullion in a number of ways, including the Betts electrolytic process, Pattinson or Hall crystallization processes, Sperry electrolytic production of white lead, and the Betterton-Kroll process. Because the Betterton-Kroll process is probably the most common for domestic bismuth production, it is the one indicated on the flow chart. It involves treating the desilverized lead with metallic calcium and magnesium, cooling, and dross removal. The calcium-bismuth dross skims are melted to remove entrained lead and are treated with chlorine or chlorides to remove the calcium and magnesium. The impure bismuth is then desilverized using the Parkes process, is chlorinated to remove lead, and is treated with caustic soda to dissolve other impurities. The resulting product is high-purity bismuth (99.95 percent pure).

Sulfuric acid recovered from lead smelter offgases is often quite dark in color because of the organic vapors from flotation reagents. The acid color may vary from yellow to black, and as a result, the acid has usually sold at a lower price than acid from brimstone. The dark acid can be bleached by adding hydrogen peroxide, which can be expensive.

The cost of producing a sulfur byproduct is dependent upon the sulfur content of the flue gas, the size of the plant, and the process used to recover the sulfur.

Lead System Byproducts

Antimony

Sources of Supply

The world supply of antimony comes mainly from the mineral stibnite (Sb_2S_3). Currently, the domestic supply of antimony, however, is obtained from the mineral tetrahedrite ($Cu_8Sb_2S_7$).

About 25 percent of the U.S. reserves of antimony are in the ores of the Yellow Pine district of northern Idaho (39). The ore bodies have three main mineral values. One is stibnite, which is closely associated with gold.

The Sunshine mine in Idaho is the principal antimony producer (31). The chief economic mineral there is argentiferous tetrahedrite. Concentration by flotation results in three concentrates, a silver-copper concentrate containing about 20 percent antimony, a lead concentrate with 2.3 percent antimony, and an iron-silver concentrate. The silver-copper concentrate is leached to dissolve the antimony, and the electrolytic method is used to recover the antimony metal.

In both cases, antimony is a byproduct or coproduct partially separated at the milling stage of processing with final separation in smelting and refining. Involved are the gold and silver production systems, which were not included within the scope of the present analysis.

A second system, the lead system, is also a source of byproduct antimony and is within the scope of this analysis. Byproduct antimony from the lead system is nearly all produced as antimonial lead. The split-off for the byproduct is at the softening furnace of the lead system.

The drosses from lead softening may be divided into two classes--those that contain mainly copper and those that contain mainly antimony. The drosses and slags containing mainly antimony are treated in a small blast furnace. The production of this furnace is antimonial lead, a marketable product that averaged 9.2 percent antimony in 1970.

The two major domestic byproduct sources of antimony, the silver antimony and gold antimony ores of Idaho and the byproduct antimonial lead, provided 8 percent of the total U.S. antimony supply in 1970. The balance of the supply as indicated in figure 15 came primarily from secondary sources and from imports of antimony ore, concentrates, or metal.

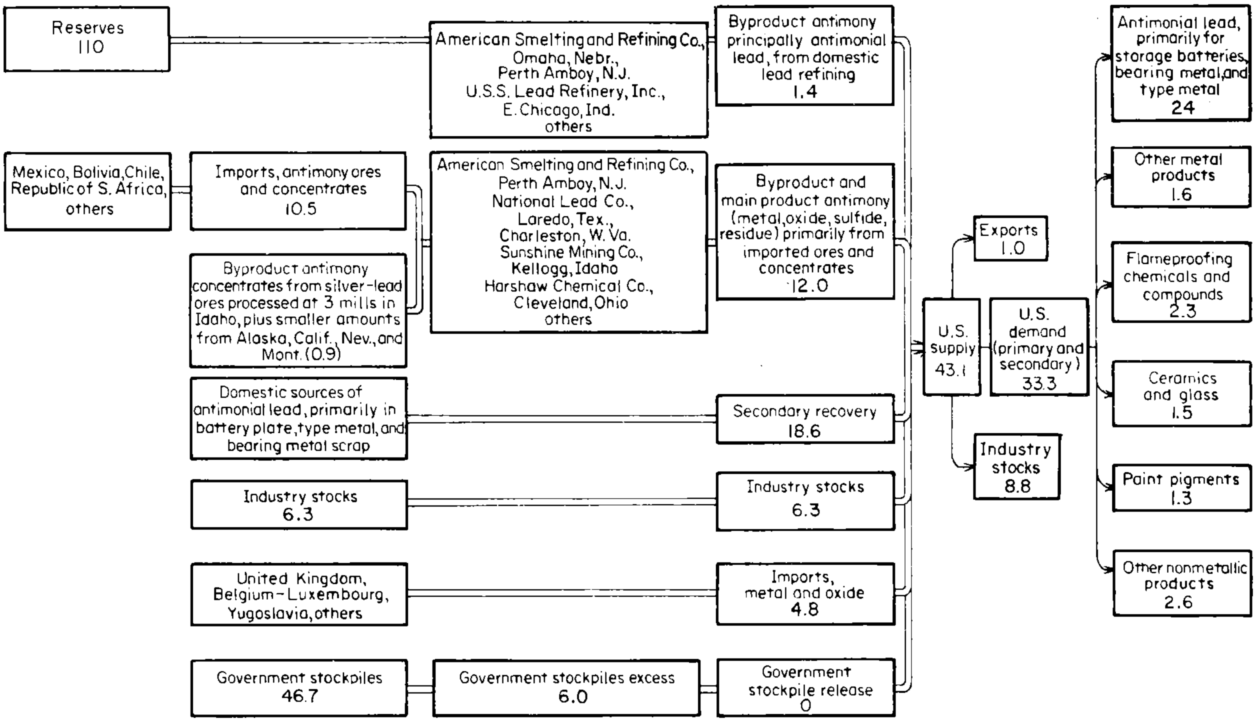

FIGURE 15. - Antimony Supply and Demand (Thousand Short Tons, Metal or Content, 1970).

Reserves-Resource Base

The U.S. Geological Survey estimates that ore in deposits of the type found in the Yellow Pine district of Idaho contains about 55,000 short tons of antimony metal. About one-half of the reserves is located in the Yellow Pine district. The other commercial source of antimony comprise the reserves found in base and precious metal ores usually processed at lead smelters. The Geological Survey estimates that this resource is an additional 55,000 short tons of recoverable antimony metal, resulting in a total reserve of 110,000 short tons. The grade of the ore varies from up to 60 percent in hand-sorted antimony ores to parts per million in some base metal ores.

Demand (18, p. 460; 19, pp. 5-22; 49)

Virtually all metallic antimony goes into remelt antimonial lead alloys to build up antimony content. Even here high-antimony-content antimonial lead is used because most users are not equipped to handle antimony metal. Antimonial lead for battery grids is the largest market. The alloy runs from 3 to 5 percent antimony, and the base price is determined by the prices of the metal constituents.

The lead-acid battery is the leader in the battery industry, and the addition of antimony to lead gives it the hardness and rigidity necessary for this application. The automotive battery is the largest single component of battery sales, and there is little question that the lead-acid battery will continue to be the power source for internal combustion engines. It is probable that the lead-acid battery will not be the power for electric cars because of its weight. A trend toward the electric car could eliminate this market for antimony in the more distant future. The industrial lead-acid battery shows more certain growth potential than does the automotive battery. Manufacture of materials handling equipment, railroad equipment, trucks and other transportation equipment, and in addition, the utility market, offer potential growth for antimony. Government applications such as standby power for missile lauching, submarines and undersea vehicle power are also important.

Type metal containing 3 to 8 percent antimony is another large consumer of antimonial lead. Antimony is used to harden and sharpen the type.

The third major consumer of antimonial lead is the bearing manufacturing industry. Lead base babbitt metal for automotive bearings contains 3 to 15 percent antimony plus tin, arsenic, and lead. Tin base babbitt for specialty, aircraft, and marine bearings contains 7 to 10 percent antimony plus copper, nickel, and lead. Other antimonial lead alloys are used in automobile body fillers and in other minor applications.

In its pure form antimony has few applications. As a fine powder, it is used in fireworks and tracer bullets. Modern electronics have created a demand for small amounts of superpure antimony, thermoelectric grade (99.95 percent). It is alloyed with bismuth or bismuth and tellurium. Semiconductor grade antimony (99.999+ percent) is alloyed with indium.

Antimony oxide is added to paints for its flame retardation, antichalking, and high hiding power as a white pigment. Various chemical compounds of antimony yield the present pigments of black, vermillion, and yellow-orange. Infrared reflecting characteristics of certain antimony sulfide pigments led to their use in camouflage paints. Antimony oxide is also added to plastics and to fabrics for flame retardation. Plastics are a new and potentially important growth market for antimony. In other fabric uses, antimony oxide is used in a finishing additive to fibers.

In ceramics and glass, antimony adds hardness and acid resistance to enamel coverings. The trioxide is a glass former like silica and is valued because of its peculiar light transmitting characteristics.

A Bureau of Mines forecast for antimony is based on a probabilistic and multiple contingency analysis of technologic, economic, and other contingency assumptions. The projection places antimony consumption between 63,000 and 115,000 tons in the year 2000. The probable forecast is 87,000 tons, corresponding to an average growth rate of 3.3 percent between 1970 and the year 2000.

Production, Consumption, and Price Statistics

The production, consumption, and price history of antimony is summarized in figure 16. This chart shows antimony price, consumption of primary antimony, smelter production of primary antimony and antimonial lead, and secondary recovery of antimony principally in antimonial lead. The data on secondary antimony is included because of the importance of this source to total supply. Both the production and consumption graphs would shift upward by approximately the amount of secondary production shown if total production and consumption were plotted.

It will help clarify antimony production and consumption data by correlating the historical data in figure 16 for the year 1970 with the structural relationship of supply and demand shown in figure 15. The consumption data shown in figure 16 are taken directly from the 1970 Minerals Yearbook. The figure shown in the Yearbook for industrial consumption of primary antimony is 13,937 short tons or 27.9 million pounds antimony content. The structure chart, figure 15, includes

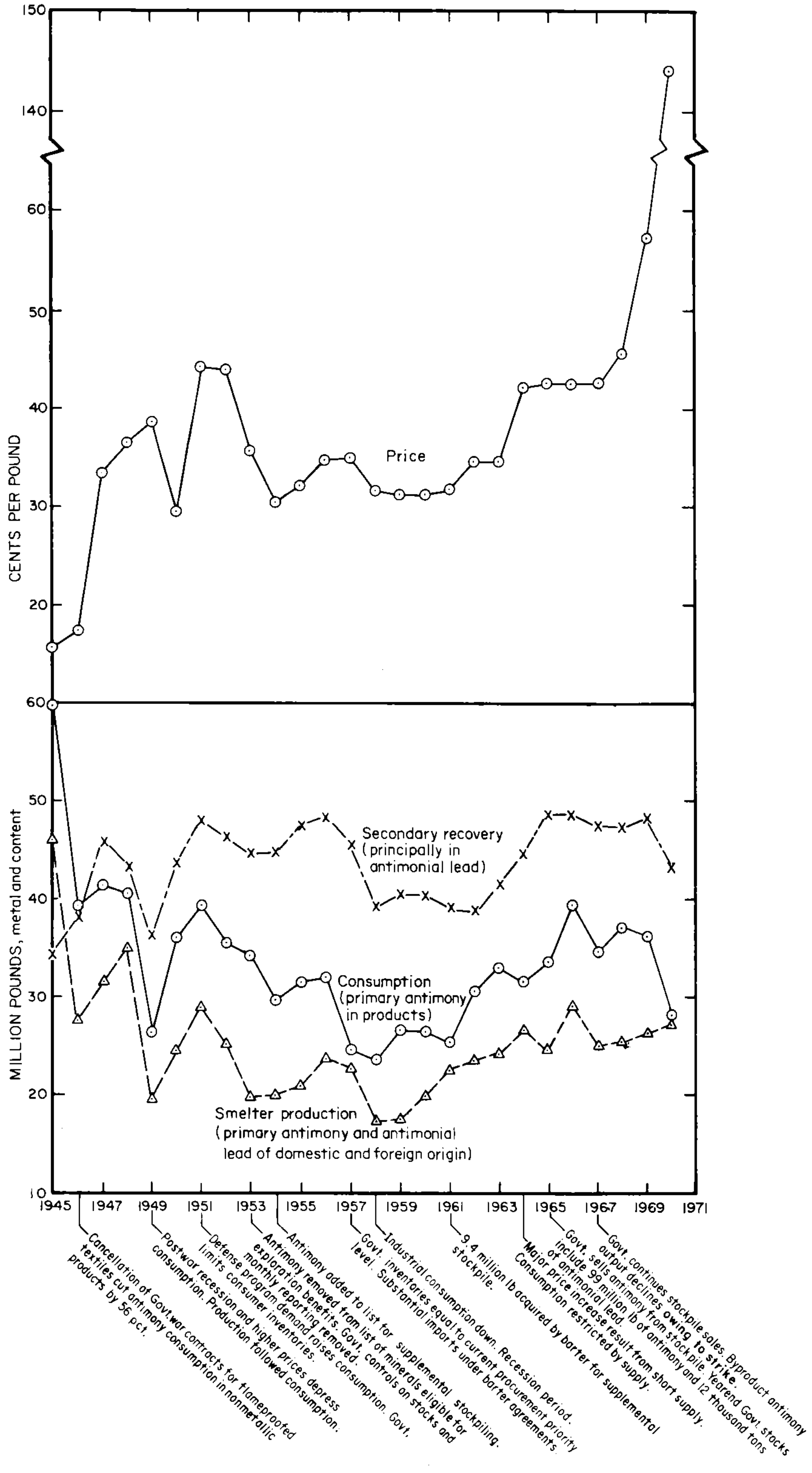

FIGURE 16. - Antimony Production, Consumption, and Price History, 1945-70.

all of the 13,937 short tons plus an additional 19,413 short tons of antimony estimated contained in antimonial lead used for the manufacture of storage batteries, type metal, and bearing metal. The sum of the last two numbers is 33,300 short tons, the total U.S. demand shown in figure 15.

In reviewing the production data of figure 15, most of the total supply of antimony is either main product antimony derived from foreign ores and concentrates or is of secondary origin. Thus, factors other than the byproduct nature of a portion of antimony supply dominate the price-consumption-production data shown.

The sharp downward trends in production and consumption of antimony in the 1945-49 period reflect post-World War II adjustments. One in particular worth noting is the steep drop in the consumption of antimony for flameproof textiles in 1946.

Production throughout the entire 1945-70 period shows good correlation with consumption as production was adjusted to balance with demand. This is in part a result of

Government regulations, which controlled inventories and disposition of antimony in the immediate postwar (1945-52) period. It is also a result of supplementing production with stockpile disposals during the 1965-70 period. The General Services Administration completed sale of the authorized antimony in December 1970 after 5 years of sales. A total of 5,000 tons of antimony was sold between late 1964 and December 1970. A total of 46,746 short tons of antimony in the present Government stockpile includes 6,047 short tons excess held pending Congressional authorization to resume sales.

The high prices of 1947-52 and 1964-70 are the result of spirited bidding for limited supplies. Production and consumption show the price elasticity expected more with a main product metal with substantial secondary and stockpile sources of raw material. The price elasticities have no relevance to byproduct antimony elasticities.

Incremental Costing

An incremental cost analysis of the byproduct antimonial lead system is not within the scope of this report. It involves treatment of drosses and slags from the softening furnace of the lead smelter. These drosses and slags are treated in a small blast furnace. The charge is made up of various antimony-bearing materials produced in the lead refining, proper fluxes, and 8 to 14 percent coke. The product is marketable antimonial lead (6, pp. 310-311; 44, pp. 193-210).

Supply Curves

Although there appears to be a degree of price elasticity somewhat greater than unity in the supply curves of primary, main product antimony, and of secondary antimony, the revealed byproduct antimony curve is essentially a vertical distribution of points at a low production level that indicates little or no elasticity with respect to price. The curve for total primary antimony is made less elastic by including the byproduct output.

Bismuth

Sources of Supply

Bismuth is generally obtained as a byproduct of the smelting of lead, copper, molybdenum, tin, silver, or gold ores. In the United States, bismuth is a byproduct of refining domestic and imported lead bullion and from the smelting and refining of copper.

In the copper system, byproduct bismuth is one of the products derived from the processing of leady flue dusts generated in the copper converting process. These dusts are caught in the Cottrell precipitator and transferred to a lead smelter for processing. The major portion of the bismuth, however, remains with the copper and reports in the leady residues during electrolytic refining. These residues are shipped to a lead smelter for recovery. Most of the incremental costs of bismuth production show up in the lead system even though the bismuth may have originated in the copper ore.

The diagram of the lead system indicates a split-off point for bismuth in the processing of calcium-bismuth drosses from the Betterton-Kroll (debismuthizing) process.

As indicated in figure 17, only two companies in the United States are engaged in the production of primary domestic bismuth. For this reason nearly all company data are confidential. Domestic production is primarily in the hands of the American Smelting and Refining Company. One other company, the U.S.S. Lead Refinery, Inc., at East Chicago, Ind., produces bismuth that is derived from zinc mining and lead refining.

One can infer from figure 17 that imports of bismuth metal dominated the bismuth supply picture during 1970. There is very little business in bismuth scrap. Bismuth supply has been tight for several years in the face of an unprecedented demand.

Reserves-Resource Base

The most recent domestic bismuth reserve estimates by the Bureau of Mines place bismuth reserves at 26.4 million pounds recoverable from lead, zinc, and copper reserves (64). An additional 9.9 million pounds is estimated contained in potential resources of lead, zinc, and copper. In recent years, all bismuth production has been a byproduct of lead production. The bismuth reserve with economically producible lead reserves is estimated at 13 million pounds.

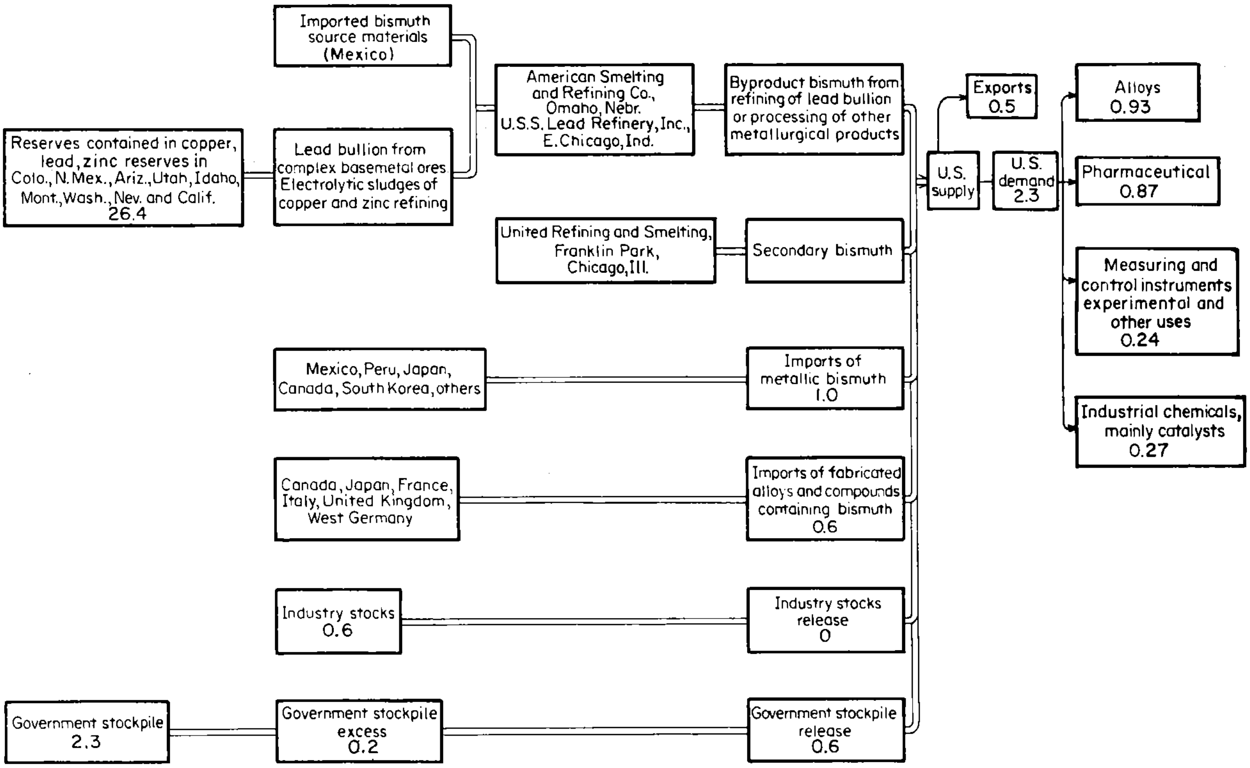

FIGURE 17. - Bismuth Supply and Demand (Million Pounds, Metal and Content, 1970).

Demand (33, pp. 58-68; 21, pp. 5-16; 3)

In 1970, the United States consumed 2.3 million pounds of bismuth. Consumption during 1967 was restricted by the tight supply situation, which resulted from a surging demand for bismuth compounded by a strike at the major producing refinery during 1967. Consumption in 1966 of bismuth totaled 3.2 million pounds and even this level involved allocation of limited supplies to the extent that dealer prices rose from $2.25 per pound in 1963 to as high as $4.50 per pound during 1967. Producer prices were stable.

The reason for the boom in demand for bismuth prior to 1966 was the use of bismuth as a catalyst in acrylonitrile production; since 1966 it has been replaced by other compounds. An estimated 1.5 million pounds of bismuth was used in catalyst production in 1965. The figure for 1966 was 1.0 million pounds and for 1970, 270,000 pounds. The drop was explained in part by completion of stock building by manufacturers but primarily by the commercial availability of a less expensive uranium catalyst. Bismuth has been used in many medicinal and cosmetic preparations, and up to 1930 these applications used 90 percent of bismuth produced. Today the medical uses of bismuth are estimated at 800,000 to 900,000 pounds.

Alloys are the traditional and steady market for bismuth. Bismuth is used in fusible alloys in combination with lead, tin, cadmium, indium, silver, and antimony. Such alloys contain 40 to 99 percent bismuth. Fusible alloys are now used in plugs for compressed gas cylinders, automatic sprinkler systems, fire door releases, electric fuses, and other heat-operated safety devices. Low-melting-point alloys also find use in pattern making, tools, fixtures, and dental alloys.

In other small and expanding markets, bismuth is used in thermoelectrics for heat pumps and power generators. Bismuth introduced into malleable iron improves machinability, suppresses mottling, and yields better surface characteristics. One of the smallest and most compact heat modules contains eight bismuth telluride thermocouples. Because of its extremely small size (about 1/3-inch square) the unit is suited to applications where space is of primary importance. These units are used in air conditioning, electronic equipment, instrumentation, refrigeration, medical and laboratory hardware, and in other equipment.

Bureau of Mines projections for bismuth place consumption in the United States between 2.9 and 5.2 million pounds by the year 2000. The probable forecast is 4.2 million pounds corresponding to an average annual growth rate of 2.0 percent. The forecast is a probabilistic assessment of technologic, economic, and other influences affecting demand for bismuth. The projection relies most heavily on continued growth in fusible alloys.

Production, Consumption, and Price Statistics

No publishable production data are available on bismuth. Production has generally correlated well with consumption over the period shown in figure 18. The exception is the period 1962-67 when imports increased substantially.

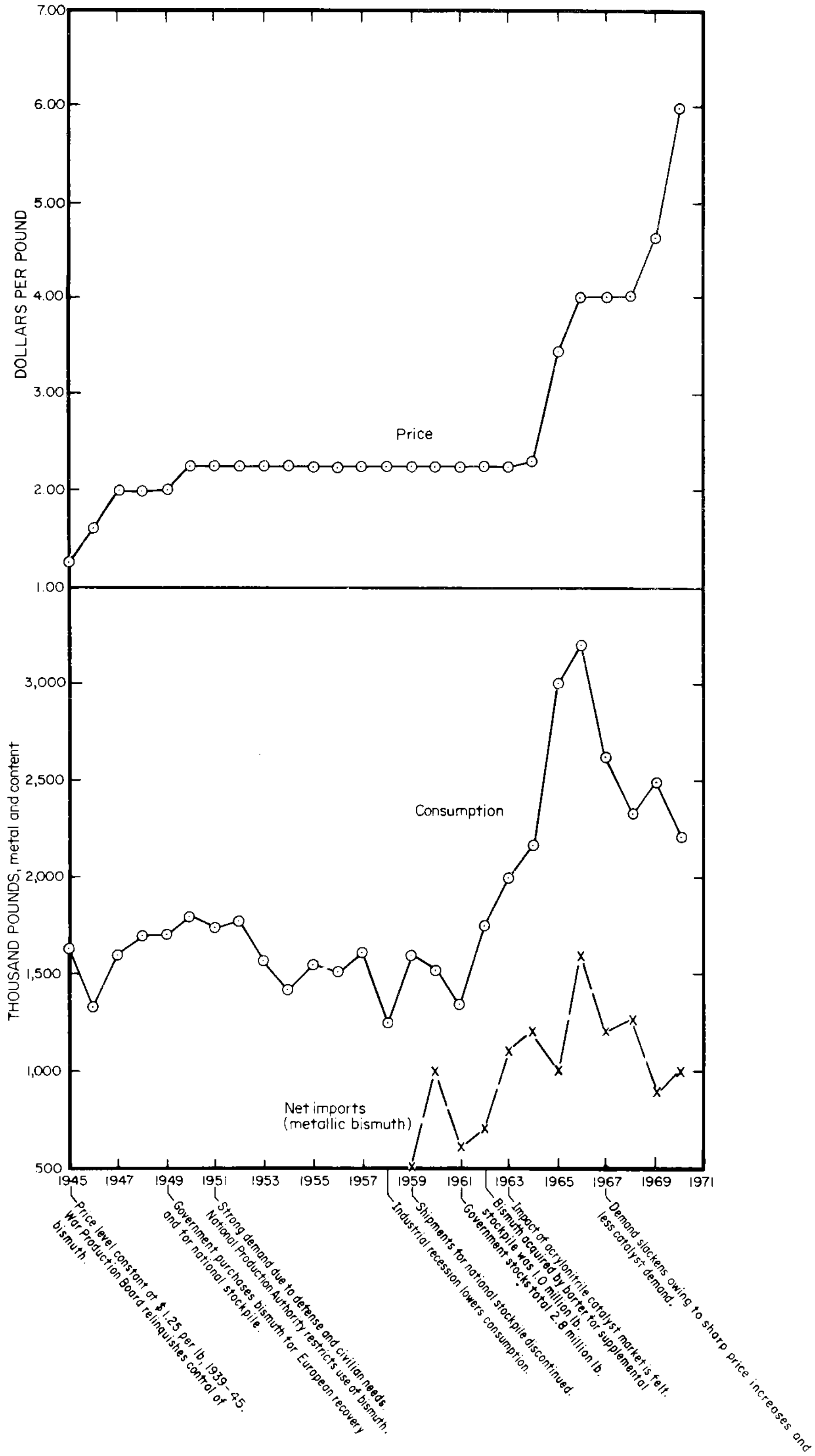

FIGURE 18. - Bismuth Consumption and Price History, 1945-70.

The impact of supply-demand imbalance brought about by the acrylonitrile catalyst boom is evidenced in the price increases and the sharp increase of imported bismuth.

The sag in consumption between 1952 and 1961 separates two periods of high demand--for defense and European recovery, and for the recent expansion linked to plastics. During this period, the price of bismuth was stable for 14 consecutive years.

Incremental Costing

The calculation of incremental costs of bismuth production is not within the scope of this report. The processes for refining of byproduct bismuth are described in several publications (33, pp. 58-60; 18, pp. 521-529; 44, pp. 139-143).

The Betterton-Kroll process is representative of byproduct bismuth metallurgy. Other processes used to separate bismuth from lead are (1) electrolytic refining of lead bullion, (2) Pattinson or Hull crystallization, and (3) electrolytic process for white lead.

The Betterton-Kroll process depends on the characteristic of bismuth following the lead through the blast furnace, drossing, softening, desilverization, and dezincing. When high bismuth lead (>0.05 percent bismuth) is ready for debismuthizing, a high calcium and magnesium compound is added to the kettles, and the resultant calcium-magnesium-bismuth dross is skimmed. The incremental costs of the bismuth subsystem apply to the processing of such drosses. The dross is skimmed and additional amounts of calcium and magnesium are stirred in with the remaining molten lead. The charge is cooled, and the liquating bismuth dross is skimmed. The amounts of calcium and magnesium (and sometimes antimony) added determine the purity of the lead.

Bismuth dross is processed by smelting in a small 25-ton kettle and separating the dross from the entrained lead. The dross is treated with chlorine or lead chloride to remove calcium and magnesium, desilverized using the Parkes' process, and deleaded with chlorine. Final treatments with caustic soda produce high-purity bismuth (99.995 percent +).

Supply Curves

A plot of bismuth production versus price yields a cluster of points in the $2.25 per pound price area that indicates a rather constant output at the $2.25 per pound price level. The jump to $4 per pound in 1966 indicates a very inelastic curve.

Uranium System Byproducts

Uranium is derived from various ores. The most important domestic ores are the carnotite ores found in sandstone deposits of the Colorado Plateau and the uraninite and coffinite ores of New Mexico and Wyoming. Elsewhere in the world, uranium has mostly been obtained from uraninite (pitchblende), autunite, and torbernite. The major byproducts from the system include vanadium, molybdenum, scandium, thorium, and radium. Some ores processed for uranium also yield silver, copper, selenium, and gold. Uranium is also produced as a byproduct of such other minerals as gold, copper, and phosphate.

The description of some of the ores yielding uranium from the uranium system is somewhat arbitrary as the mineral of principal value in these ores may be other than uranium. The carnotite ores for example were originally processed for vanadium. When radium was sought, vanadium became a byproduct in treating these same ores. Later still, the ores were sought for their uranium content, which averages about 0.2 percent of the ore. The status of vanadium in the current economics of processing these ores is now that of a coproduct.

Since radium is a daughter product of uranium, it exists in all uranium ores, generally in a fixed proportion to the uranium content. However, because no demand for radium exists, no uranium ores are treated to recover the radium content nor have they been since 1925.

Until 1968 thorium was produced as a byproduct from uranium-bearing ores of the Elliot Lake district, Ontario, Canada, and has been imported into the

United States via the United Kingdom. There is also potential for byproduct thorium production from uranium-bearing ores in the Somali Republic, Africa. No thorium is recovered from uranium ores mined in the United States. Because the potential for domestic production of thorium as a byproduct of the uranium system seems rather remote, no further discussion of it will be made in this study.

The byproduct molybdenum split-off occurs after the pregnant eluate from the resin-in-pulp circuit is passed through a solvent extraction step; the resulting organic solution is stripped of its uranium and molybdenum values, and the uranium and molybdenum pregnant strip solution is filtered to remove the molybdenum content. The solution containing uranium is returned to the uranium processing system. The molybdenum is stripped from the charcoal filter and is precipitated as calcium molybdate.

Scandium in trace amounts is also associated with most uranium ores. In the solvent extraction process of treating uranium ore, the scandium accumulates in the organic solvent and can be removed periodically, although it does not strip out with the uranium.

The uranium and associated elements are removed from sandstone ores by either the solvent extraction or resin-in-pulp (ion exchange) methods. In either case, the uranium and other metallic content of the ore is solubilized after grinding by either an acid or alkaline leaching process depending upon the nature of the particular ore. Some carnotite ores are first roasted to convert the vanadium content to water soluble sodium vanadate to permit separation of the vanadium before the acid leach. Sulfuric acid is the most commonly used leaching agent. With 95 percent or more of the uranium content of the ore in solution, the leached pulp is separated from the uranium pregnant solution by countercurrent decantation with the uranium-barren slime solids going to the waste tailings. The split-off point for vanadium is in the following step, that of solvent extraction, in which the mineral-bearing aqueous solution is mixed with an organic solvent, generally kerosine, which has a greater affinity for the uranium. The vanadium content remains in the now uranium-barren aqueous solution, which can then be passed through a vanadium extraction circuit. This has been the major domestic source of vanadium over the past two decades. The uranium is stripped from the organic solvent by precipitation through use of a soda ash solution. The molybdenum content remains in the uranium-barren organic solvent and can be split off at this point.

The resin-in-pulp method substitutes an ion exchange step for the solvent extraction step. With this technique, the uranium is recovered from the sulfuric acid solution by passing the solution through beds of resin until the uranium is all adsorbed on the resin. The uranium is then removed from the resin by a nitric acid solution, and is precipitated, filtered, and dried.

The material obtained through either technique is "yellow cake," 75 to 85 percent uranium oxide (U_3O_8). Uranium is converted to uranium hexafluoride (UF_6) for isotope U_{235} enrichment before being further processed into nuclear reactor fuel. Uranium has unique environmental and disposal problems related to its radioactive characteristics at all stages of its production and use.

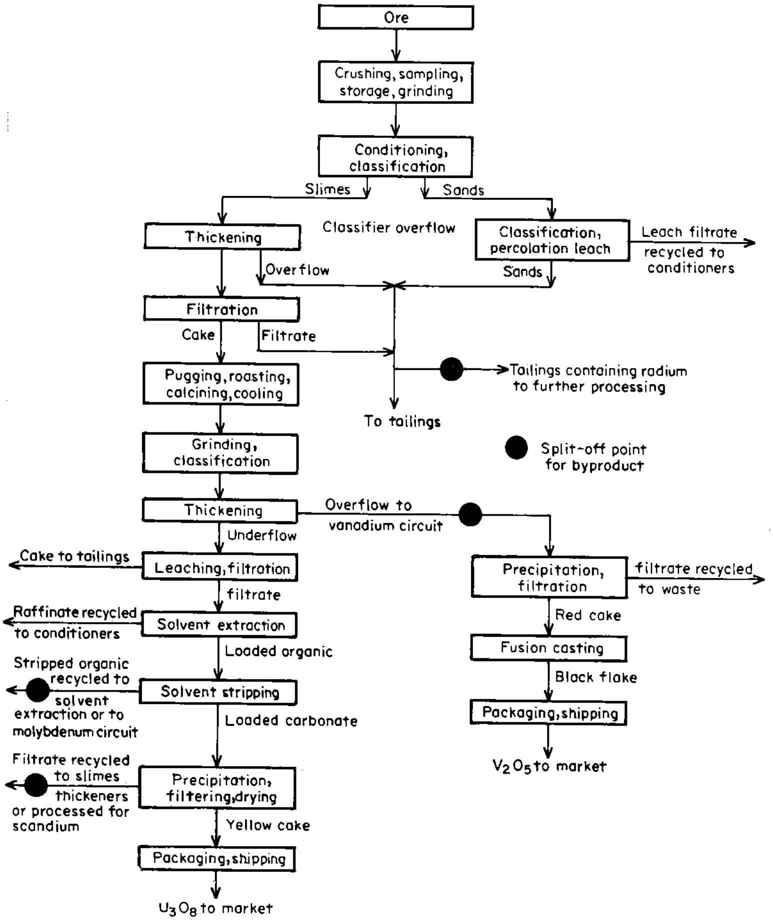

FIGURE 19. - Uranium System, Showing Principal Byproduct Metals.

The processing method investigated in considerable detail in order to estimate costs for the production of byproduct vanadium and outlined in figure 19 deviates from the two general methods of processing uranium ore because it was patterned after the only mill currently producing uranium and vanadium from the same ore as coproducts.

Vanadium

Sources of Supply

Although vanadium is relatively abundant in the earth's crust, it is so widely and thinly distributed that ores of present commercial value are somewhat limited and production of vanadium is typically tied to the production of other minerals (44, pp. 428-443; 44, pp. 542-581; 66; 7). The most important source of vanadium in the United States in 1970 (fig. 20) as in prior years was as a byproduct of uranium production from the carnotite and roscoelite ores of the Colorado Plateau. The balance of the vanadium output was derived from three sources. In order of importance these were: the processing of ores in which vanadium was the primary product; as a byproduct of the processing of phosphate rock mined in Idaho and Utah; and the processing of secondary materials such as oil and coal residues and spent catalysts.

In the past 2-1/2 decades, the quantity of vanadium produced has been very largely a function of the demand for and production of uranium. It appears unlikely, however, that this relationship between vanadium and uranium production will remain as close in the future as it has been in the past. The curtailment of carnotite-type uranium production will require vanadium production to come from other sources. A trend in this direction may be seen in the 1968-70 data, which indicate a significant increase in the output of vanadium as a primary product and in the byproduct output from phosphate rock. (One mill processing uranium-vanadium ore in early 1970 viewed its vanadium output more as a coproduct than a byproduct.) Uranium-vanadium ores of the Colorado Plateau are more costly to mine for uranium than the uraninite ores, and vanadium values do not offset the higher costs. Therefore, fewer of these ores are being worked.

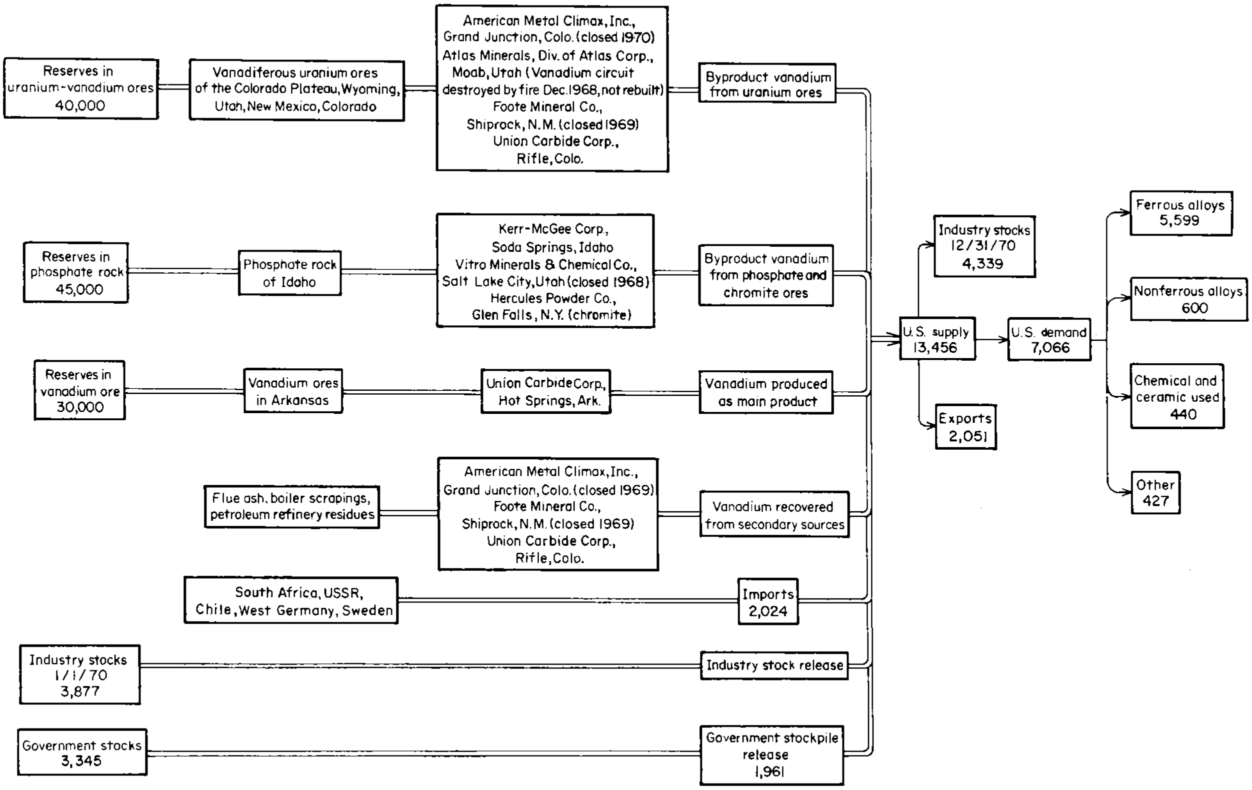

FIGURE 20. - Vanadium Supply and Demand (Short Tons Contained Vanadium, 1970).

The number of plants producing vanadium has declined since 1968. Of the four plants producing vanadium as a byproduct of uranium processing in 1968, only the Union Carbide Corp. plant at Rifle, Colo., remained in operation in early 1970. This plant also is the only plant currently producing vanadium from secondary materials. Union Carbide Corp.'s plant at Hot Springs, Ark., is the only plant producing vanadium as a primary product. The Kerr-McGee Corp. produces vanadium as a byproduct of its Soda Springs, Idaho, phosphate operation. Hercules Powder Co. produces vanadium as a byproduct from chromite ores at Glen Falls, N.Y.

Reserves-Resource Base

The U.S. reserves of vanadium are estimated to be about 115,000 tons. Of these, 40,000 tons are in the vanadiferous uranium ores of the Colorado Plateau in Utah, New Mexico, and Colorado. Another 45,000 tons is believed to exist in the phosphate rock of Idaho, with an additional 30,000 tons in the vanadium ores of Arkansas. The Government stockpile of vanadium at yearend 1970 consisted of 3,345 tons of vanadium, with industry inventories at 4,339 tons.

Comparing reserves of ores from which vanadium is likely to be produced as a byproduct with those in which it would be the primary product, it appears that nearly 75 percent of the known vanadium reserves of this country are in ores that will probably be mined with vanadium as a byproduct or coproduct.

The total potential resource of vanadium in the United States is estimated to be about 3.5 million tons of vanadium. Most of this resource occurs in the form of vanadiferous phosphatic shales in Idaho and Wyoming and in titaniferous magnetites in New York, Wyoming, Rhode Island, and Minnesota. There has been no commercial production of vanadium from these deposits. In addition to the important vanadium deposits existing in sedimentary iron ores, important quantities are present in some coals and petroleums. The vanadium content of these materials is enriched during oxidization, and consequently, the most noteworthy concentrations of vanadium are often found in the slags of iron ore and phosphorous smelting furnaces, coal ash, and the petroleum residues found in smokestack scrapings.

Columbium, molybdenum, and tungsten, and to a lesser extent, nickel and platinum, compete with and can substitute for vanadium in various applications.

Demand

The major demand for vanadium is as an alloying element for steel, to which it gives added toughness and durability by refining the grain size of the steel. This use, plus small amounts in cast iron and other ferrous alloys, constitutes more than 79 percent of the demand for vanadium; nonferrous alloys--another 9 percent; chemical and ceramic uses--6 percent; and all other uses--about 6 percent.

The desirable characteristics given to steel by the small amount of vanadium added--usually between 0.1 and 0.4 percent--include improved tensile strength, greater wear and impact resistance, improved machinability and weldability, reduced distortion, greater flexibility in heat treatment, and better finish. The largest markets for vanadium steel are in the construction industry where it is applied in structural members and pipelines; in the transportation industry, with extensive use in automobiles, locomotive axles, armor plate; and in metal working machinery and tools. Because of its ability to maintain strength and hardness at moderately high temperatures--around 1,200° C--vanadium alloys are in demand for aircraft and space applications as in jet engines and aircraft frames and coverings. In this field, the use of vanadium alloyed with titanium and aluminum had increased dramatically by 1970. Finally, vanadium added to steel, copper, or aluminum permits easier continuous casting by producing a more freely flowing metal.

The chemical industry has long used vanadium as a catalyst, most notably in manufacturing sulfuric acid and in petroleum refining. More recently, there has been increased chemical use in such applications as coloring glass, ceramic glazes, driers in paint, and in the processing of colored film and phosphors used in color television tubes. Potential uses are as an adsorbent in control of automobile exhaust fumes, as a fuel element cladding in nuclear reactors, and as an element in a heart attack control drug.

Production, Consumption, and Price Statistics (22; 68; 43; 67; 17; 81)

The presence of vanadium in the carnotite and roscoelite ores of the Colorado Plateau was discovered in 1900, and the first important market for the metal in this country was in the automobile industry after 1905. Production of vanadium rarely exceeded 1,000 tons annually from that time until 1937, and during the depression years of 1933-36, production virtually ceased. In 1937, output began a rapid increase, which has continued to the present with only three short periods of declining production. The Atomic Energy Commission uranium purchase program, which began at the end of World War II, included the purchase of the vanadium content of the ores until 1963. The resulting potential for a relatively large supply of vanadium encouraged an expanded search for uses for vanadium through the 1950's. Figure 21 illustrates vanadium production, consumption, and price statistics.

Although most of the vanadium produced in this country has been as a byproduct of ores processed for their uranium content, actual production of vanadium in any given year is more closely related to steel production. (A zero order correlation coefficient of 0.77 was found for the period 1943-68.) Vanadium steel has been the fastest growing alloy of steel in the past decade. This is reflected in the ratio of vanadium consumed per ton of total steel production, which has increased from 0.058 pound in 1955 to 0.081 pound in 1960 and to 0.092 pound per ton in 1962, and in the relative average annual growth rates of steel--1.9 percent--and vanadium--2.7 percent--between 1943 and 1970.

Part of the increased production of vanadium after 1950 may be due to the substitution of vanadium for molybdenum in steel as molybdenum prices rose.

Imports met half the domestic demand for vanadium during the first period of growth, but after 1941, when the United States replaced Peru as the major producer of vanadium, imports declined to virtually nil in 1956. A renewal of imports began after 1961. The first significant export of vanadium began in 1955 and peaked in 1961 when European steelmakers, in a desire to produce improved grades of steel, turned to the United States as the major producer of vanadium. Increased output by Finland and South Africa soon filled this demand.

The price of technical grade vanadium pentoxide, the form most used in making alloy steel, remained steady at $1.10 per pound from 1941 to late 1947 when it rose to $1.20 per pound, where it remained for 2 years before falling to $1.00 and then increasing to $1.06 in 1950. It rose slightly again to the $1.06 to $1.28 range in 1951, and to the $1.28 to $1.30 range in 1952-54. In 1955, the price rose from approximately $1.28 to $1.38, where it remained until 1963 when it fell to $1.25, and then to $1.15 the following year. Actual prices, especially for large lots, were probably lower, perhaps in the $0.80 to $0.95 range. Prices returned to the $1.30 range in 1966-68, and continued to rise into 1970.

Incremental Costing

The vanadium subsystem portion of the uranium system covers the processing of the uranium-vanadium ores, and the roasting process converts the insoluble vanadium compounds contained in the ore, to water-soluble sodium vanadates. The production system upon which the following cost calculations

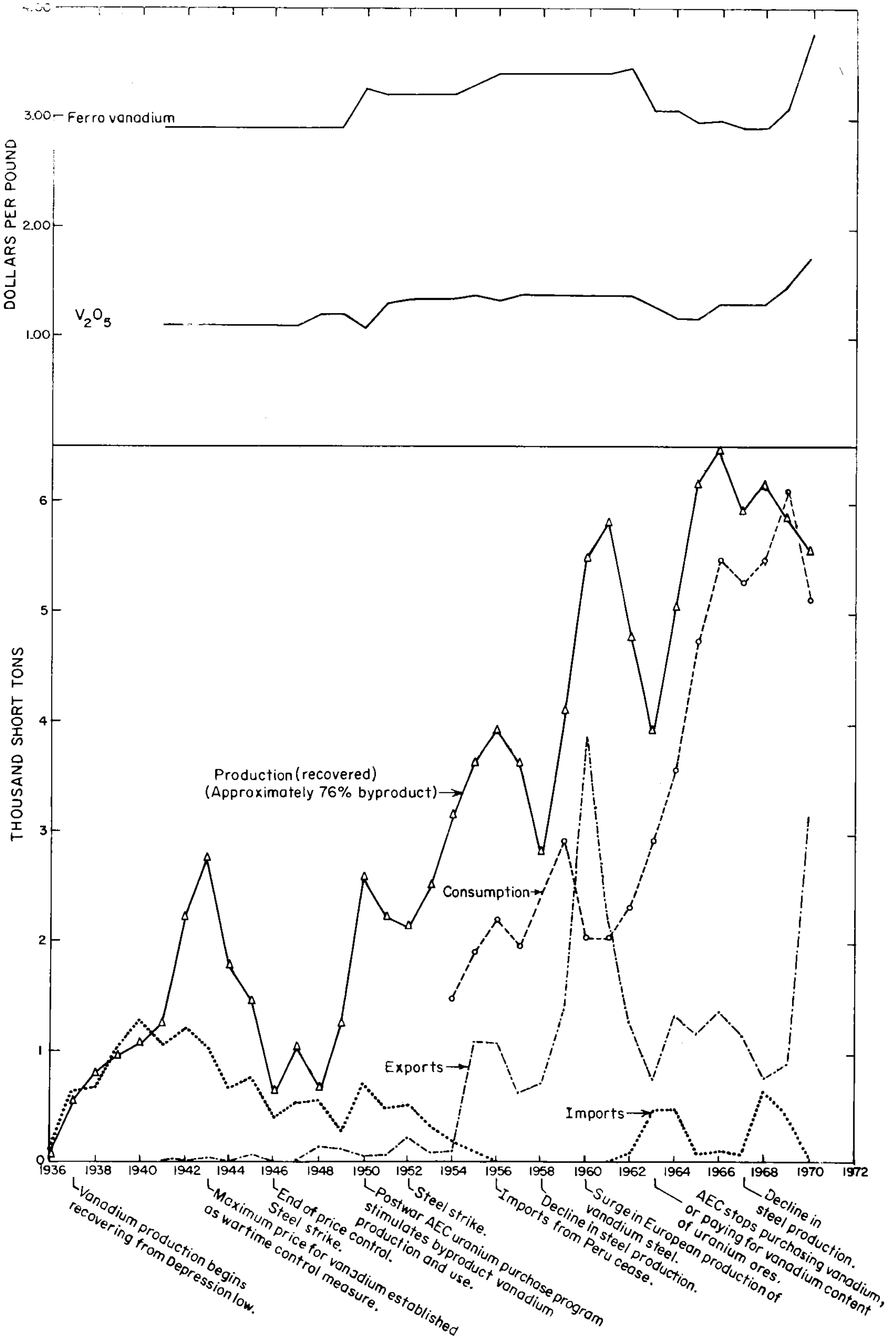

FIGURE 21. - Vanadium Production, Consumption, and Price Statistics, 1936-70.

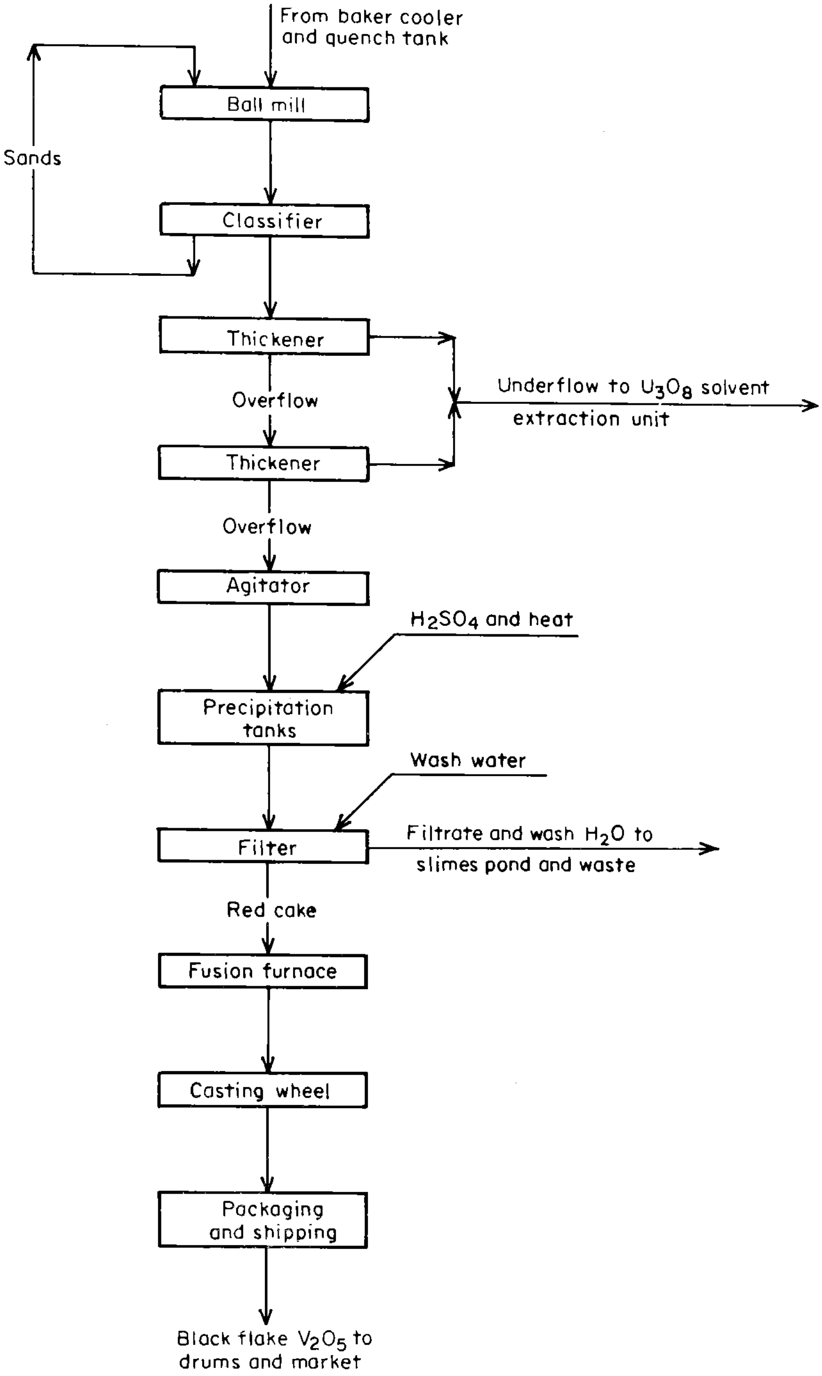

FIGURE 22. - Byproduct Vanadium System.

are based was chosen as the one most closely approximating the only uranium-vanadium plant in current operation, and it is designed to treat the vanadium more as a coproduct than as a byproduct.

A model of the byproduct vanadium system is shown in figure 22. The hypothetical system shown assumes as its raw material 330 tons of uranium-vanadium ore per day. The ore is assumed to contain 1.50 percent V_2O_5 (30 lb V_2O_5 per ton ore) and an unspecified quantity of U_3O_8. It is also assumed that approximately 73 percent of the contained vanadium pentoxide (V_2O_5) in the ore is recovered.

Calcines from the roaster are cooled and reground in a ball mill in closed circuit with a spiral classifier. The classifier overflow is thickened and processed for vanadium; the underflow is processed for uranium.

The thickener overflow feeds five vanadium precipitation tanks of 7,100-gallon capacity each. Precipitation is carried out on a batch basis. The time required for this may vary from 1/2 to to 3 hours depending on the grade and characteristics of the liquor. A typical operation in any tank is when the tank has been filled with the thickener overflow, agitation is begun, and the content of the tank is brought almost to the boiling point by the injection of steam. Concentrated sulfuric acid is then added to lower the pH to below 4.0. The tank content is agitated until precipitation of vanadium as sodium polyvanadate (red cake) is completed. The tank contents are filtered, and the filtrate is discharged to waste. The red cake is washed with water and is fused at 650° C in a fusion furnace. The molten product is discharged to a casting wheel, where it is cooled prior to being drummed for shipment.

A rough estimate of investment costs can be made on the basis of the foregoing hypothetical flowsheet. Estimated direct costs are shown in table 3. The direct costs are rough approximations based on limited information in the literature. Direct costs of $616,100 or $0.234 per pound include all raw materials, direct labor, maintenance labor, supervision, payroll overhead, and operating supplies. The depreciation of equipment is not included.

TABLE 3. - Unit cost estimate--byproduct vanadium production (2,637,855 pounds V_2O_5 per year)

Cost category	Man-hours	Assumed wage rate, dollars per man-hour[1]	Cost, dollars
Direct labor:			
Vanadium roasting, precipitation, filtering, fusion, casting, and packaging. One-third of the labor cost charged for sampling, crushing, conditioning, classifying, leaching, and thickening. Including maintenance. 24 men per day × 8 hours per shift × 365 days per year.	70,080	4.69	328,500
Supervision (20 percent of labor)...............	-	-	65,700
Total direct labor and supervisory...........	-	-	394,200
Raw materials, utilities, and operating supplies:			
Power and fuel..................................	-	-	29,700
Chemicals and reagents..........................	-	-	122,000
Water and operating supplies....................	-	-	70,200
Total...	-	-	221,900
Grand total.....................................	-	-	616,100

[1] The $4.69 per hour wage rate is based on an assumed base rate of $3.75 per hour plus 25 percent for fringe benefits.

$$\text{Direct costs} = \frac{\$616,100}{2,637,855} = \$0.234 \text{ per pound } U_2O_5.$$

Calculation of the approximate investment required to produce 2,637,000 pounds of byproduct vanadium pentoxide annually indicates that the total investment would probably be about $2,068,000. Such an investment spread over an economic life of 10 years would indicate a depreciation rate of $0.065 per pound of vanadium pentoxide produced.

A rate of return of 30 percent before taxes on the $2,068,000 investment over 10 years would require an annual revenue of $669,100 above direct costs and depreciation. At a production rate of 2,637,000 pounds of vanadium pentoxide annually, this amounts to $0.254 per pound of vanadium pentoxide.

This indicates that the incremental cost of producing vanadium in the uranium-vanadium system is at least $0.55 per pound of vanadium pentoxide in the optimum output plant. For plants working below optimum capacity shortrun marginal costs might run as low as the cost of raw materials, utilities, and operating supplies alone. These average about $0.09 per pound.

Supply Curves

As with most byproduct materials, the supply of byproduct vanadium from uranium has depended more upon the rate of production of uranium than on the price of vanadium. Consequently, it would be expected that the supply of byproduct vanadium would result in an inelastic price. In addition, the major use of vanadium is as an alloying element in steel, which represents a relatively small portion of final cost. This, too, suggests price inelasticity. There is little in the production and price time series for vanadium that implies behavior counter to these expectations.

Construction of the supply curve of figure 23 is based on the costs developed for the representative uranium-vanadium plant in the preceding section on incremental costs and on actual price and production data. The curve shown is for 1968, and the production-price point on the vertical

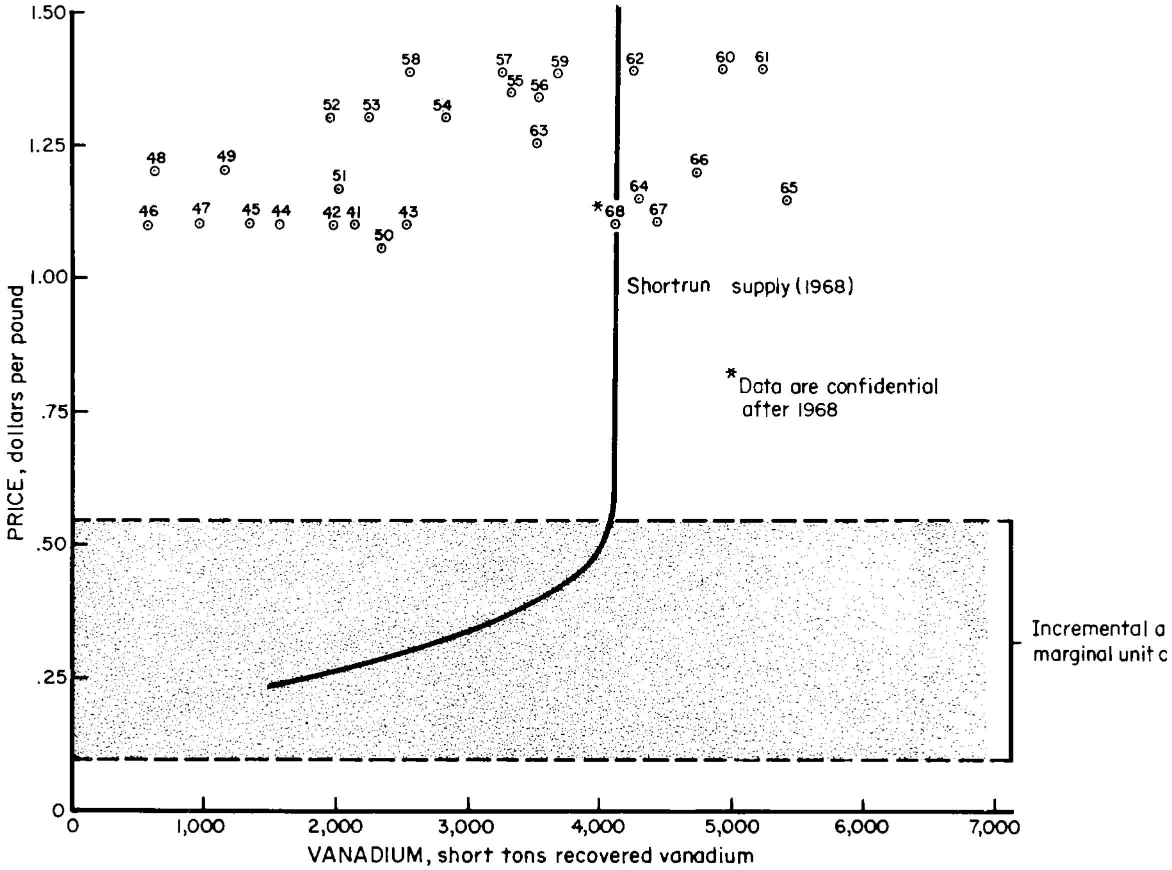

FIGURE 23. - Byproduct Vanadium (From Uranium System) Supply Curve, 1968.

portion of the supply curve indicates the point of intersection of supply and demand for that year. All other points represent supply and demand intersections for corresponding years. The curve is assumed to become less inelastic in the price range between $0.09, which is the marginal cost of producing additional units of byproduct vanadium with the existing plant and below which absolute losses would occur, and $0.55, which is the average cost of production. It is assumed that production costs of individual firms vary between these two points. The vertical distance between the upper cost level and the intersection of supply and demand can largely be explained as economic rent accruing to the byproduct producer because of his unique position in the industry. The declining role of byproduct vanadium produced from uranium ores appears as shifts to the left in the supply curve in recent years.

Radium

Sources of Supply

Radium production in the United States as a byproduct is entirely potential. There has been no production of radium either as a main product or a byproduct reported by the Bureau of Mines since 1925. U.S. production virtually came to a halt in 1925 under the impact of cheaper Congolese radium. Radium is included in the list of byproduct metals because past production was and future production is potentially as a byproduct of the uranium production system.

The most production of radium in the United States was during World War II. At that time some small quantities of radium were produced in connection with the war effort.

Radium is always associated with uranium, though only a few deposits are sufficiently rich in radium to justify mining for radium alone. In the digestion of carnotite (uranium) ore, the pulverized mineral is heated with sulfuric acid, and the resulting solution is filtered. A residue of barium-lead-radium sulfate called "white cake" remains on the filter after the uranium solutions pass through. The residual material is leached with sodium chloride to remove lead. Then the barium-radium-sulfate residue is reacted with hydrobromic acid and is subjected to fractional crystallization. The resulting product is 90-percent-pure radium bromide crystals. Ion exchange and solvent extraction methods then separate the radium from the remaining barium. Radium metal may also be produced by electrolytic methods.

The U.S. supply of radium has been entirely imported since World War II. The major part of the imported supply has come from the Republic of Zaire (formerly Democratic Republic of the Congo), with Canada, the United Kingdom, the Netherlands, and Colombia supplying lesser amounts. Little, if any, new primary supply enters the U.S. market; encapsulated radioisotope is recycled. Demand is small, and other less expensive, and better suited radioisotopes are substituted for radium.

Reserves-Resource Base

The U.S. supply of radium is in the reserves of uranium ores. Radium occurs in all uranium ores in a ratio of approximately one part radium to three million parts uranium. No quantitative estimates of radium in uranium reserves have been made.

Demand

The principal use for radium is in radium therapy for cancer. The second largest use is in industrial radiography, where it has been useful in the nondestructive (radiographic) inspection of metal castings and welds. These two markets for radium have generally deteriorated since World War II. A consumption level of 173 grams of radium in the United States during 1952 declined to about 12 grams in 1970. The principal reason for the decline is the competition from the less expensive radioisotopes, which are the result of expansion in the field of atomic energy.

Production, Consumption, and Price Statistics

From the discovery of radium in uranium ore in 1898 up to about 1940, the demand for uranium was essentially a direct function of the use of radium. In fact, in the immediate pre-World War II years the expanding use of radium tended to create a surplus of uranium products. The reversal of the position of main product radium and byproduct uranium after the atomic bomb and with the development of nuclear power is one of the spectacular examples of the effect of market on the economics of the byproduct metals.

Beside replacing radium as the main product of radioactive ores, uranium and the related nuclear technology have produced the radioisotopes that compete with radium for its traditional markets. A large number of artificially produced isotopes such as cobalt-60, Californium-252, strontium-90, thallium-204, cesium-137, krypton-85, and tritium have slowly displaced radium from many major applications in medical therapy and radiography.

Overall consumption of radium has declined from the 100-gram level of the 1947-52 period to about 12 grams during 1970. The potential for radium production in contrast has risen tremendously as production of U_3O_8 has increased. Prior to World War II, radium production approximated 100 grams per 500 short tons of U_3O_8. If this ratio were applied to the 1970 U.S. production of 13,037 short tons of U_3O_8, then 2,600 grams of radium were discarded as waste by uranium producers. Such material poses an as yet unappraised environmental problem.

The price of radium has declined with lessening demand. It slipped from \$25 to \$30 per milligram in 1950 and increased from \$16 to \$21.50 per milligram in 1951. The price remained at this level for 14 years, it dropped to \$15.50 to \$16 per milligram during 1965-67 and as low as \$2 per milligram by 1970. Even at its present level, radium is the highest priced of all known metals traded commercially. Because of efforts to license and limit the use of radium, some former users have offered radium salts at low prices or free of charge in order to dispose of the material.

Supply Curves

There is a supply curve for domestic radium, and it is related to the incremental costs of byproduct radium production from uranium processing. The lack of a domestic supply is due to the low volume demanded and the current relatively low prices. Construction of the supply curve would involve calculation of the probable incremental costs of byproduct radium from uranium. Such an analysis is beyond the scope of the present report.

The lack of production in the United States would indicate that the flat portion of the shortrun curve and longrun curve is above the present price level. The potential production from uranium would indicate that the longrun curve turns upward in the production range of 2,000 to 2,500 grams annually.

Scandium

Sources of Supply

Scandium is a rare metal found in trace amounts in the earth's crust. Production was restricted to very small quantities of a handpicked mineral, thortveitite, in Norway, Madagascar, and Italy from the date of its discovery in 1911 until 1952. Since 1952 the rapid expansion of uranium processing has created a potentially large byproduct source for scandium.

As recently as 1960 there was no reported commercial market for scandium. Since 1960 the use of the metal in radioisotope tracers in alloys with several other metals has been reported, and there is active research in these and other applications.

Scandium was detected in the organophosphate extractant used by the Vitro Chemical Co. in processing uranium ores by solvent extraction methods at Salt Lake City, Utah (42). The scandium followed the uranium into the solvent, but it did not strip with the uranium nor did other impurities, thorium or titanium. This caused a buildup of scandium, thorium, and titanium in the organic phase of the solvent extraction process. The solvent became unable to properly extract uranium because the exchange sites were progressively filled with nonstrippable metal. A hydrofluoric acid stripping section was incorporated into the plant to remove thorium and titanium poisons. The special stripping section was found to also remove the scandium. Steps were then taken to optimize scandium recovery, and resulted in a thorium-scandium cake byproduct. The byproduct was subsequently refined to high-purity scandium oxide.

A second byproduct source of scandium metal was developed in the processing of byproduct wolframite concentrate from the Climax Molybdenum Co. plant in Colorado. A method for its recovery was developed in a cooperative effort between the Bureau of Mines and the Climax Molybdenum Co. (69-70).

Domestic uranium mills have not produced scandium-bearing solutions since 1964. As indicated in figure 24, output of scandium has come from the producers' stocks of concentrates imported from Australia and Canada, with

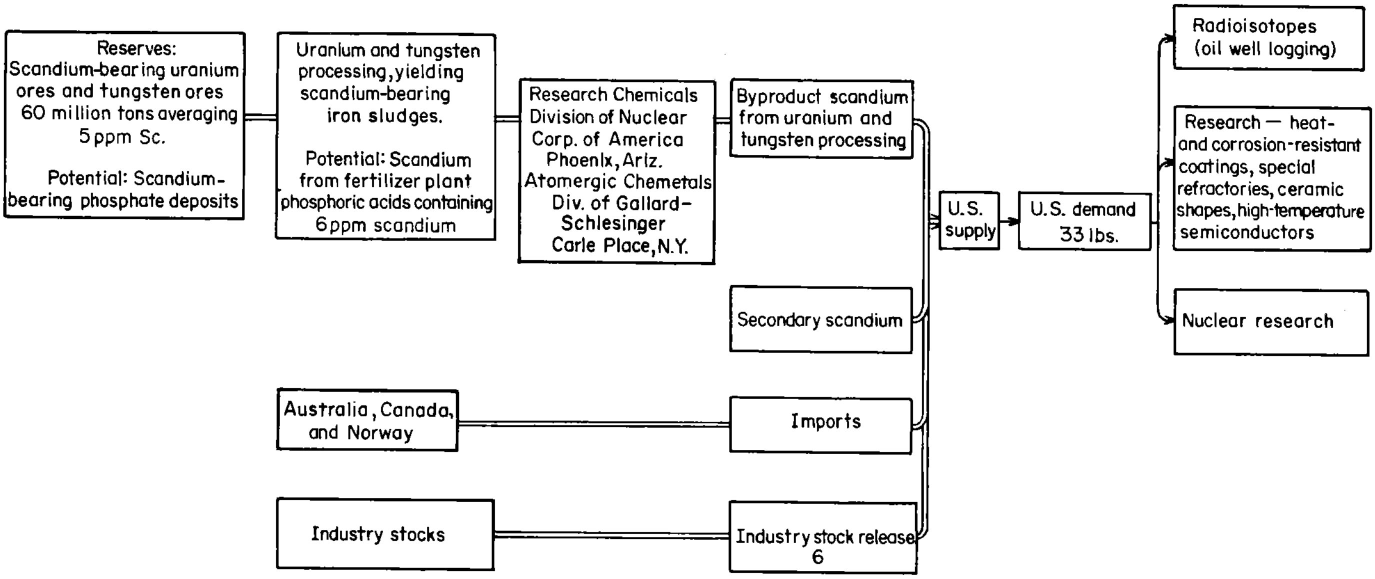

FIGURE 24. - Scandium Supply and Demand (Pounds, Metal and Content, 1970).

small amounts of thortveitite imported from Norway. Secondary sources of scandium are also a significant portion of the total supply.

The Research Chemical Division of the Nuclear Corporation of America, Phoenix, Ariz., and Atomergic Chemetals Co. Div. of Gallard-Schlesinger, Carle Place, N.Y., were the only suppliers of primary scandium in 1970.

Iron-bearing sludges from U.S. uranium plants and tungsten plants form the raw material for scandium production. No information is available on intercompany transfers. They tend to concentrate scandium production in much the same way that other small volume byproduct metal production is concentrated.

Reserves-Resource Base

Reserves of scandium are unknown. Research points to the probability of large quantities of scandium in uranium ores and also in phosphate rock deposits.

Uranium ores usually contain less than 5 ppm scandium. The uranium reserves of the United States, which are producible at $8 per pound U_3O_8, are estimated to be 246,000 short tons of measured ore reserves, and 490,000 short tons of potential ore reserves. Conversion of these figures to scandium reserves suggests a 7,000-pound potential of scandium metal. Sales of scandium oxide in 1970 were about 33 pounds. At current consumption rates, reserves of the metal are believed quite adequate.

Recent studies on the recovery of scandium from fertilizer plant phosphoric acids reveal them to contain up to 6 ppm scandium. Based on resources of 16 billion tons of phosphorous pentoxide in the United States, scandium reserves could be estimated to be several hundred thousand tons in phosphate deposits. Recovery of scandium from the phosphate deposits would be limited by the rate at which these ores are mined.

Demand

Scandium has few commercial applications. Research continues to be the major consumer of the metal.

Scandium-46 radioisotope is used as a tracer in analytical work and oil-well drilling. When subjected to neutron bombardment, water soluble salts of scandium can be used to trace underground flows of liquids. The stable isotope scandium-45 found in nature will form scandium-46 when irradiated in a nuclear reactor. The highly radioactive isotope was produced by the Oak Ridge National Laboratory of the Atomic Energy Commission.

Scandium has some useful alloying characteristics and is probably being used in nuclear energy applications. Scandium added to titanium almost doubles its hardness at room temperature. Plutonium-scandium alloys are also a subject of research. Ternary zircon alloys with scandium are said to be superior to those with yttrium, and therefore, they have relatively long life in high-temperature applications.

Scandium has potential as a high-temperature semiconductor, and scandium-oxide has been used in glass to reduce density and to open up the structure. The oxide has also been used as a flame spray material for various services to reduce heat and thermal shock.

Other uses for scandium include its use in growing garnets for microwave applications. Scandium also finds use in TV tube phosphors in conjunction with europium oxide. Ultraviolet light on scandium doped with europium yields a bright red fluorescence while scandium doped with terbium gives a bright green fluorescence. This property may find use in color television and cathode ray tubes. In 1969, the manufacture of a high-density mercury vapor lamp incorporating small quantities of high-purity scandium metal was reported. Estimated scandium demand for use in this lamp was advanced to 4,000 grams in 1970.

Production, Consumption, and Price Statistics

Production and consumption statistics have not been collected for scandium during its relatively short sales history.

Thortveitite concentrates from Norway and Madagascar were the only sources of scandium until 1959. Richer Norwegian sources appear to be exhausted, and Madagascar thortveitite was sold only to the Atomic Energy Commission of France.

Scandium oxide became available from uranium waste liquors in 1960. After that the dependence upon the foreign supply of the metal became less important. Research in applications for scandium has accelerated, but a volume market still does not exist.

The price for scandium oxide was quoted at $10 to $52 per gram between 1952 and 1958, and at $15 to $30 per gram in 1959. Prices vary widely between individual contracts, which depend mainly upon the quantity and purity of the metal sold. In 1960, improved processing techniques and expanded production facilities led Vitro Chemical Co. to cut the price of scandium oxide.

Prices ranged from \$6 to \$8.60 per gram in 1960, and from \$2.80 to \$5 per gram in 1970. The range of domestic refinery prices for the metal was from \$23 to \$32 per gram in 1968 and from \$4.40 to \$10 in 1970.

Metallurgy and Incremental Costing

The relationship of the scandium byproduct subsystem to the uranium production system is illustrated in figure 25. The simplified flow diagram is based on the Vitro process described by Lash and Ross in 1962 (42) and the description of the recovery of scandium from uranium plant sludge by Ross and Schack in 1965 (70). Two split-off points for byproduct scandium are shown. In the Vitro Chemical Co. process, thorium and titanium and scandium building up in the organic stream of the uranium solvent extraction system are selectively tapped and subjected to a special stripping with hydrofluoric acid. The "white cake" precipitated from this cleanup system contains 10 percent scandium oxide and is further refined to produce high-purity scandium oxide.

The system described by Ross and Schack is based on processing of an iron sludge containing scandium, titanium, thorium, uranium, and iron. This sludge

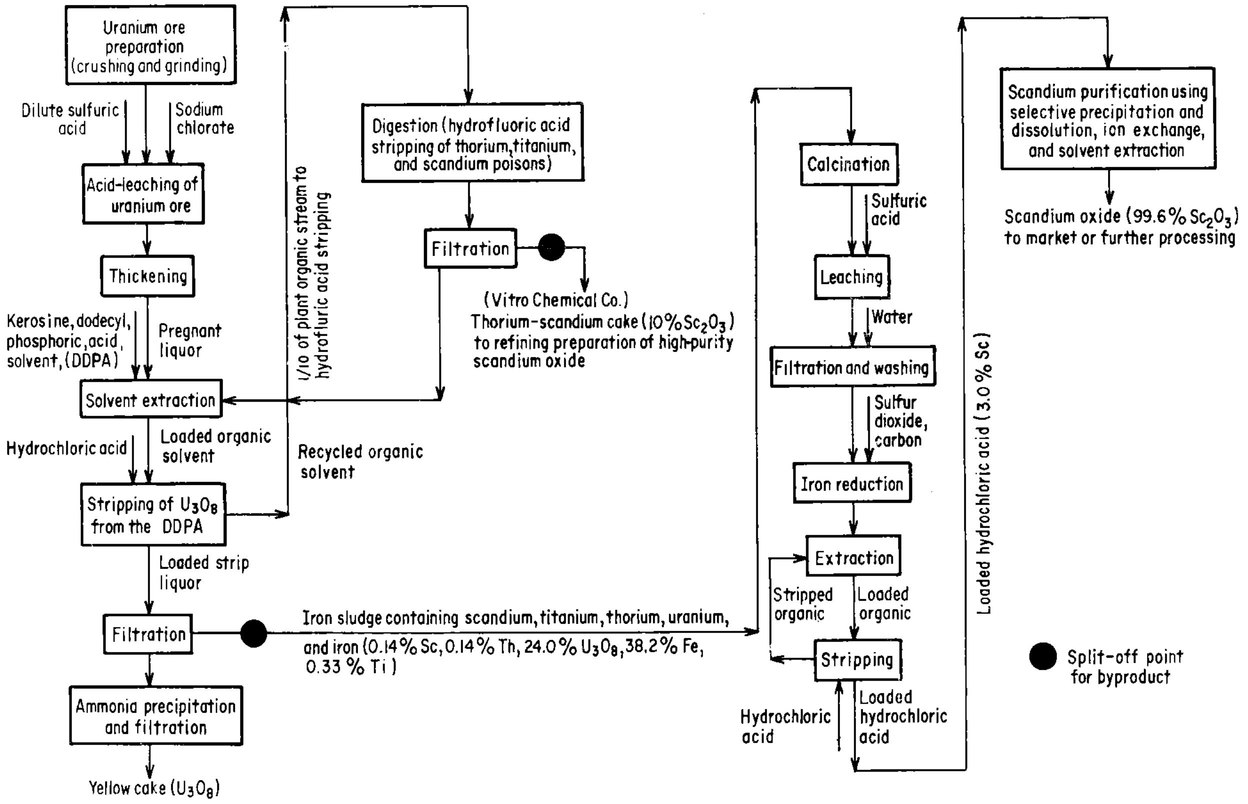

FIGURE 25. - Byproduct Scandium Subsystem.

is filtered from the loaded strip liquor and is either recycled to recover uranium, discarded, or is used as a raw material for scandium recovery as shown.

Incremental costs for the scandium recovery system depicted have not been calculated. The cost of chemicals for processing the iron sludge was estimated to be $25.67 per pound of scandium recovered in a product containing 99.6 percent scandium oxide. Major chemical costs were sulfuric acid ($11.85 per pound scandium), ammonium thiocyanate ($5.40 per pound scandium), and sulfur dioxide ($3.16 per pound scandium) (70, p. 12).

The system shown is based on the most recent available information on scandium processing. One major improvement since publication of the Bureau data is the production of high-purity scandium about 99.99 percent pure. High-purity scandium has physical characteristics considerably different from those of the less pure material. Formability is significantly improved.

Supply Curves

Insufficient data do not permit construction of supply curves for scandium. The longrun potential appears much larger than present output, but the relationship of price and cost is undetermined. One would expect a fairly large spread between price and incremental cost to interest producers in such a small volume market.

There is evidence that there may be a need to develop new sources of scandium-bearing materials to meet future demands for the metal. If this proves to be true the problem of shifting the shortrun curve to the right is one of interesting additional uranium plants in the delivering of such residues from waste or recycling to the scandium recovery circuit. Such interest involves reorganization of plants and additional investment that is not always attractive to the uranium producer because of the small market for the byproduct metal.

Rare-Earth System

The rare-earth elements, sometimes known as the lanthanides, comprise the series of 15 chemically similar elements with atomic numbers 57 through 71. Yttrium, with atomic number 39, is often included in the group because its properties are similar and because it more often than not occurs associated with the lanthanides.

The lanthanides include the following elements arranged sequentially as to atomic numbers 57 to 71: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). Promethium, atomic number 61, is a highly radioactive fission product of uranium with a half-life of only 2.6 years. Its occurrence in nature is questionable.

The first seven members of the lanthanide series (La through Eu) are often referred to as the cerium subgroup of the rare-earth elements because cerium is their most abundant member. The remaining eight elements (Gd through Lu) together with yttrium are called the yttrium subgroup. The two subgroups are also referred to as the light and heavy rare-earth elements, respectively.

Analyses of rare-earth ores and compounds are usually reported as rare-earth oxide, frequently abbreviated to the pseudochemical symbol REO.

The lanthanides are present in more than 100 minerals, but monazite concentrates and bastnaesite ores are the most common sources. Monazite and bastnaesite contain the cerium or light rare-earth elements, principally lanthanum, cerium, praseodymium, samarium, europium, and gadolinium. Bastnaesite ore, mined primarily for its rare-earth content, contains practically no yttrium or thorium, but byproduct monazite concentrates usually contain from a trace to as much as 5 percent yttria. Byproduct xenotime concentrates, uranium residues, and apatite are important sources of yttrium (62).

Byproduct monazite is recovered from heavy mineral sands primarily mined for ilmenite, zircon, and rutile minerals; xenotime is usually present in monazite concentrate and is also a byproduct of alluvial tin mining and processing. Uranium residues are a byproduct from ores processed primarily for their uranium content. Bastnaesite ore is mined primarily for the rare-earth content.

Production of rare-earth products from these sources is unique in that one to about 12 separate products can be produced from a single type ore. In most instances, the process used to produce the high-purity individual rare earths is sequential. One product is produced or dropped out, and the reaction is continued until all are separated. Intermediate low-purity products or compounds can be produced requiring less processing.

For example, mischmetal, an established product of the rare-earth industry, is an alloy produced from a rare-earth compound in which the elements occur in the same ratio as in nature. The alloy contains about 50 percent cerium and 45 percent of the other elements combined.

Because processing requires separation of individual rare-earth products whether or not they have a market, the marginal cost of producing products in quantities greater than current demand is zero. These products are generally stockpiled in the expectation that they can be sold in the future. Revenues from the salable coproducts usually are greater than total costs while the uncertain revenues from the stockpiled products constitute an expected addition to profits. In the past, producers have directed research and market development efforts toward establishing or increasing demand for the stockpiled commodities.

In the production of rare earths it is difficult to designate the individual products as coproducts or byproducts. Most companies processing rare-earth concentrates consider the rare-earth compounds produced as coproducts.

Small quantities of heavy rare earths produced when processing bastnaesite concentrates may be a byproduct.

Figure 26, a simplified diagram, shows the split-off point for the byproduct monazite. This system is typical of most gravity methods used to separate the heavy minerals (62).

The principal source of rare-earth oxides is bastnaesite. In this system, the ore is concentrated, and various rare-earth compounds and metals are sequentially separated (fig. 27).

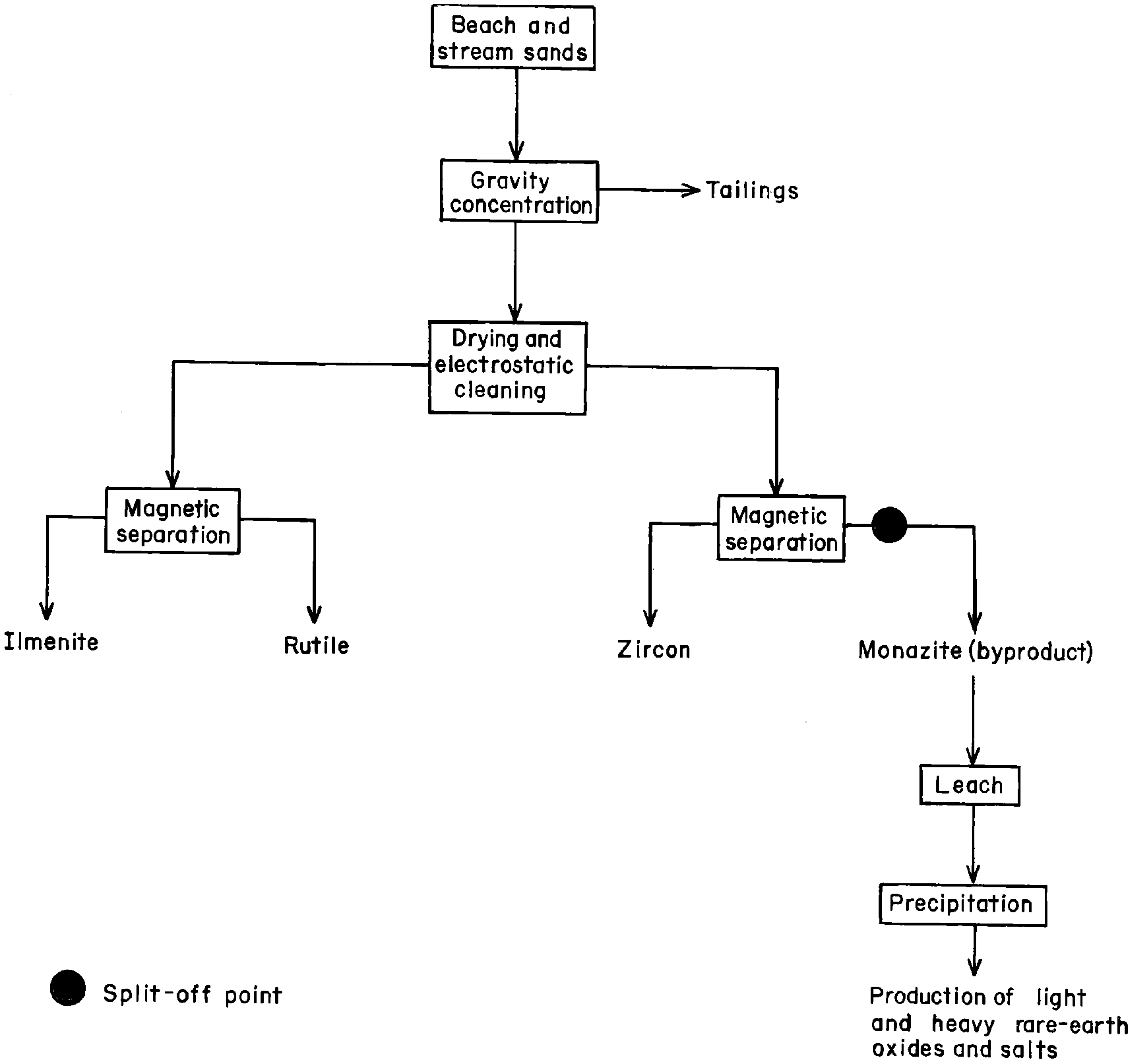

FIGURE 26. - Heavy Sands System Showing Byproduct Monazite Production.

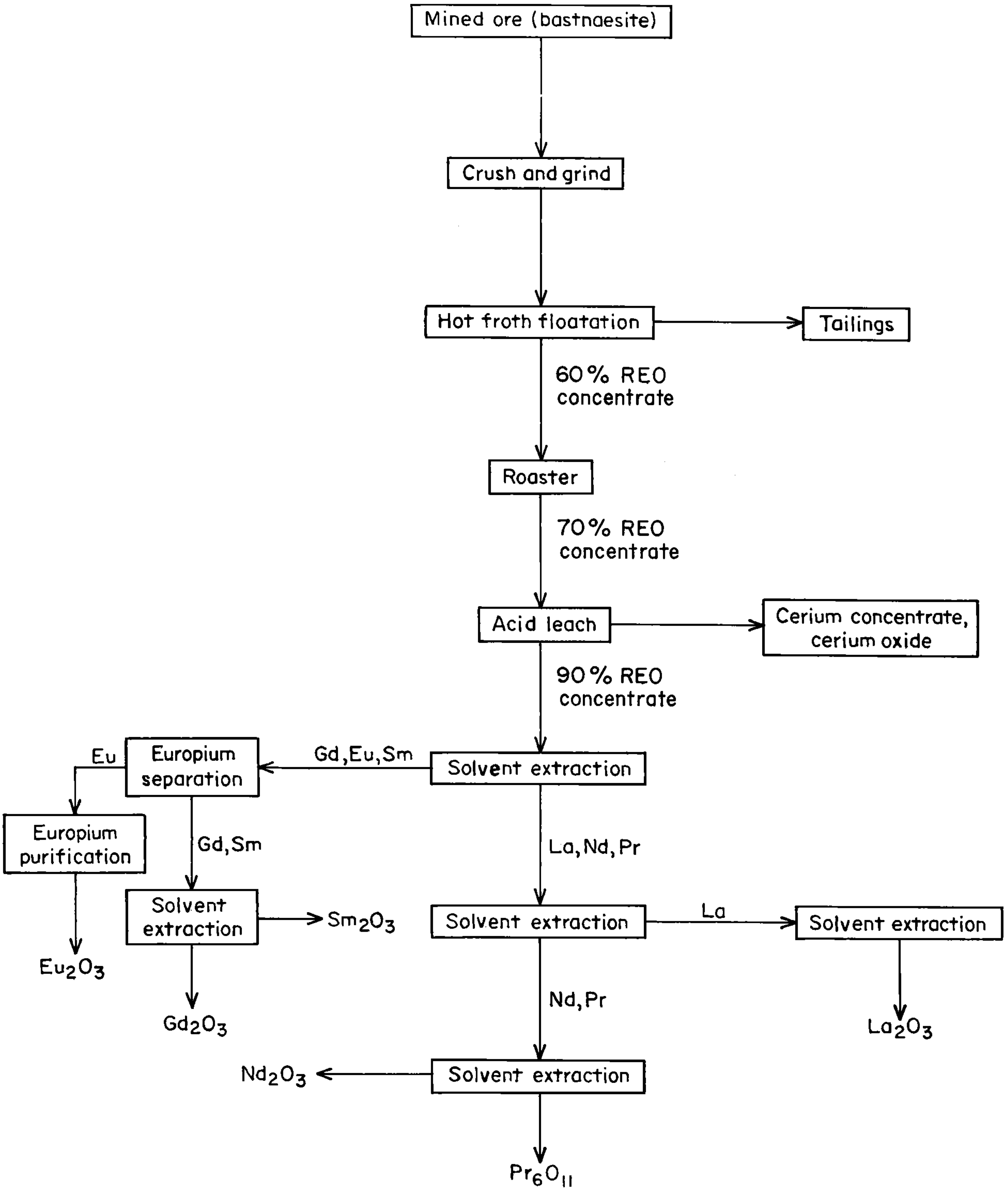

FIGURE 27. - Rare-Earth Production From Bastnaesite Ore.

Rare-Earth System Byproducts and Coproducts

Rare-Earth Oxides

Sources of Supply

Bastnaesite ore has been the principal source of rare earths in the world in recent years. The world's largest and richest known bastnaesite deposit was discovered in 1949 in San Bernardino County, Calif. Most of the mineralized area was acquired by the Molybdenum Corporation of America, which has mined and milled the ore since 1952. The ore is mined by open-pit methods and is concentrated by flotation employing heated conditioning of the pulp. The rare-earth oxide (REO) content of the concentrates varies in tenor according to the degree of beneficiation and subsequent processing of the concentrate. Natural material subjected to flotation is enriched to a 60-percent REO concentrate and is then roasted to produce a 70-percent REO concentrate. The acid is leached to a 90-percent REO concentrate. The cerium is removed in the acid leach process; further processing using solvent extraction techniques produces compounds of various rare-earth elements and metals. Figure 27 is a simplified diagram of the sequential procedure to produce these products.

In 1970, the Molybdenum Corporation of America at Mountain Pass, Calif., produced the entire domestic bastnaesite production. This company produces concentrates that are sold to other companies for further processing and also produces rare-earth compounds. The plant at Mountain Pass produces the commercial concentrates of cerium, lanthanum, neodymium and praseodymium, gadolinium and samarium, and europium oxide. The company has a plant at Louviers, Colo., which further processes the material using solvent extraction techniques to produce rare-earth pure chemicals of the light elements. It also processes heavy rare-earth concentrates to produce rare-earth chemicals of the heavy elements. The company plants at York, Pa., and Washington, Pa., further process the material from Mountain Pass, Calif., and produce mixed chemical compounds (chlorides, nitrates, carbonates, acetates, and oxylates), mischmetal, and alloys.

Other major companies that process bastnaesite concentrates are Lindsay Rare Earths, West Chicago, Ill., W. R. Grace & Co., Chattanooga, Tenn., Michigan Chemical Corp., St. Louis, Mich., and Transelco, Inc., Penn Yam, N.Y.

Monazite, a rare-earth phosphate, is the second most significant source of rare earths. Its occurrence is widespread throughout the world. A detailed study of the occurrence of monazite has been made by the U.S. Geological Survey (60). Actual production is limited and is usually a byproduct of minerals recovered from alluvial deposits, such as beach or river sands. Current domestic production is limited and reported as a byproduct of rutile-ilmenite mining at Folkston, Ga. Production of titanium minerals, zircon and monazite, from a large heavy mineral sand deposit near Green Cove Springs, Fla., is scheduled to begin in July 1972.

In 1970, 3,448 tons of monazite concentrates were imported, primarily from Australia and Malaysia. The imports were estimated to average about 55 percent REO.

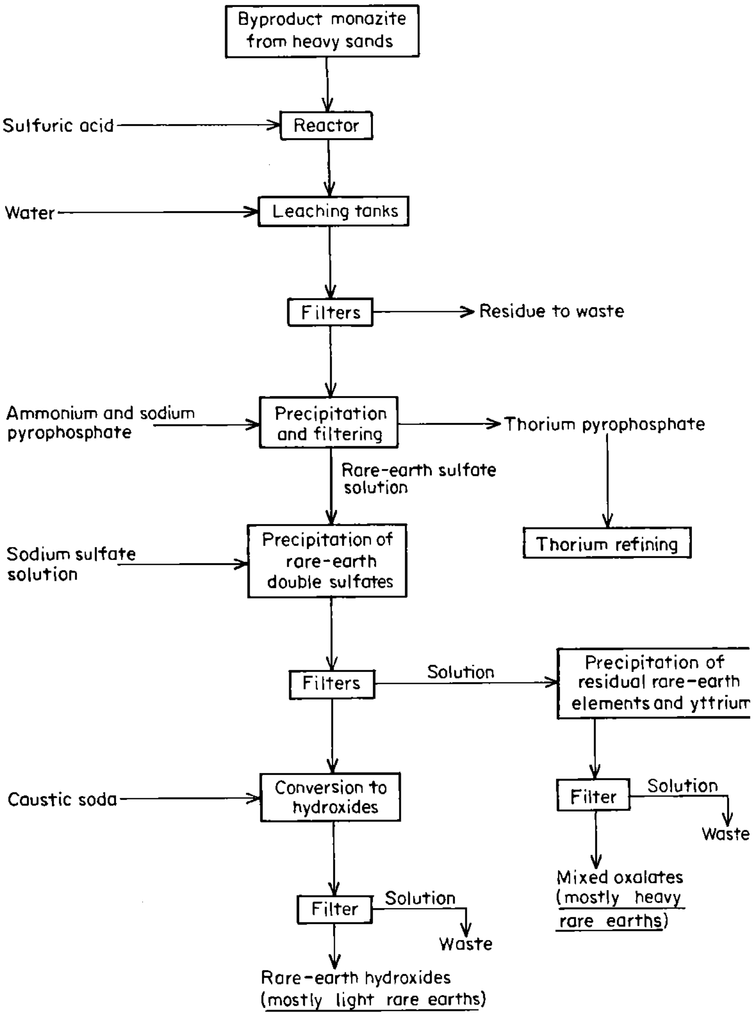

FIGURE 28. - Rare-Earth Production From Monazite Concentrates.

The heavy minerals in the sands are concentrated by using jigs, shaking tables, or Humphrey spirals. Separation of monazite from the other heavy minerals is accomplished with magnetic and electrostatic separators (fig. 28).

The monazite concentrates are fairly clean and contain 55 to 60 percent REO. The concentrate is processed by either the caustic or acid method. The latter is preferred by the principal chemical processors of this mineral. The finely ground mineral is reacted with warm sulfuric acid, and when cool the mixture is leached with cold water. The insoluble minerals are separated by filtration from the soluble rare-earth and thorium sulfates. The thorium is then precipitated and separated, and the rare-earth sulfates are commonly separated as oxalates or as double sulfates, which are the intermediate products of the largest monazite processor. From these products, other rare-earth compounds are separated as commercial-grade products, such as rare-earth chloride, fluoride, or oxide, or are purified further by solvent-extraction or ion-exchange methods (62).

The principal domestic processors of monazite are Lindsay Rare Earths, West Chicago, Ill., and W. R. Grace & Co., Chattanooga, Tenn., and Pompton Plains, N.J.

As bastnaesite and monazite contain mostly the light rare earths, heavy rare earths are obtained from different sources (table 4). Until 1964 monazite was the only source of the heavy rare earths and yttrium. In 1964, the development of the new red phosphor for color television tubes employing yttrium as well as europium stimulated the search for other rare-earth materials. Many uranium ores have rare-earth potential, and yttrium concentrate is an important byproduct of the Canadian uranium industry. The Elliot

Lake conglomerate deposits contain an average of 0.5 percent rare-earth oxide. Yttrium occurs as a large percentage of the total rare-earth content.

TABLE 4. - Rare-earth contents of minerals
(percent of total R_2O_3)

	Bastnaesite, California	Monazite, South Carolina	Monazite, Australia	Xenotime, Malaysia	Uranium residues, Ontario, Canada
La_2O_3.......	32.0	19.5	20.2	0.5	0.8
CeO_2........	49.0	44.0	45.3	5.0	3.7
Pr_6O_{11}......	4.4	5.8	5.4	.7	1.0
Nd_2O_3.......	13.5	19.2	18.3	2.2	4.1
Sm_2O_3.......	.5	4.0	4.6	1.9	4.5
Eu_2O_3.......	.1	.17	.05	.2	.2
Gd_2O_3.......	.3	2.0	2.0	4.0	8.5
Tb_4O_7.......	.1	.2	2.0	1.0	1.2
Dy_2O_3.......		1.3		8.7	11.2
Ho_2O_3.......		.1		2.1	2.6
Er_2O_3.......		.5		5.4	5.5
Tm_2O_3.......		-		.9	.9
Yb_2O_3.......		.2		6.2	4.0
Lu_2O_3.......		-		.4	.4
Y_2O_3........	.1	3.0	2.1	60.8	51.4
Total..	100.0	100.0	100.0	100.0	100.0

Another source of yttrium is xenotime, an orthophosphate of the yttrium earths. Material recovered at low cost from Malaysian tin mining is an acceptable source of yttrium and other rare earths.

Major domestic processors of the uranium residues for the rare-earth content include the Michigan Chemical Corp., St. Louis, Mich. (11).

As shown in figure 29, the major portion of the domestic supply in 1970 was provided by the bastnaesite ores.

The 5.7-million-ton reserve and resource of rare-earth oxides indicated in figure 29 are contained mostly in the bastnaesite ores, with monazite the next most significant source. Numerically the values are estimated as follows: 5 million tons in bastnaesite ores of Mountain Pass, Calif., 660,000 tons in monazite material in the Southeastern United States, and 55,000 tons in the Northwestern United States.

Estimated foreign reserves and resources are mostly in monazite material with the major portion (3 million tons) contained in Indian beach sands. The uranium ores in the conglomerate in Canada contain an estimated 50,000 tons. Other countries containing rare-earth material are Australia, Brazil, Ceylon, Malagasy Republic, Malawi, Republic of South Africa, South Korea, Taiwan, United Arab Republic, and U.S.S.R. (62).

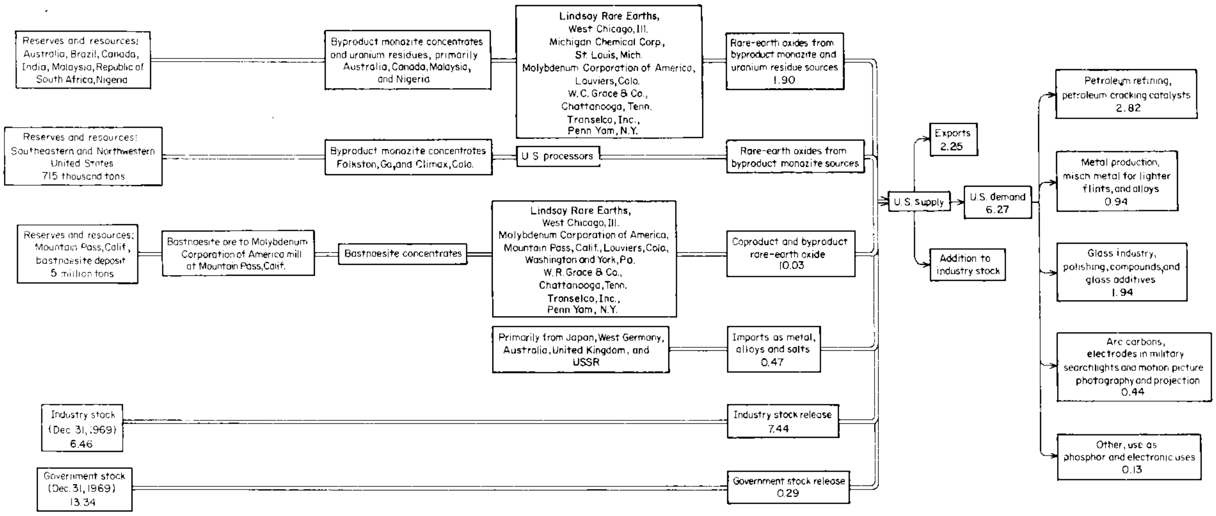

FIGURE 29. - Rare-Earth Supply and Demand (Thousand Tons, Rare-Earth Oxide (REO) Equivalent, 1970).

Rare-earth compounds, metals, and alloys are marketed under various trade names or sold by purity designations. The lowest purity materials are usually referred to as commercial-grade or production chemicals. The undifferentiated rare-earth compounds are chemical mixtures containing rare-earth elements in about the same ratio as in the original ore material; they are the least expensive rare-earth materials and can be supplied in ton quantities. Most of the rare-earth compounds supplied commercially are in the form of powder; others are sold in polycrystalline lumps, in granules, and in flakes and cast solids (62).

In 1970, it was estimated that approximately 6,270 tons of REO having a value of $11 million was consumed. The consuming industries and quantities used were: 45 percent as rare-earth and lanthanum chlorides used to manufacture gasoline cracking catalysts; 15 percent usually as chloride in metal production, mostly for mischmetal, which is used primarily in lighter flints; 31 percent as the oxide and hydrate used in the glass industry, mostly as polishing compounds with increasing amounts as glass additives; 7 percent as fluoride and oxide used in the manufacture of arc carbons; and 2 percent used in other applications including a small quantity for phosphor and electronic uses.

Tables 5 and 6 contain data of the established and developing uses of rare-earth compounds, concentrates, metals, and alloys (9).

The production, consumption, and price history of rare-earth oxides is summarized in figure 30. The price is the average value per pound of the rare-earth oxide (REO) equivalent found in the compounds and high-purity metals consumed. Price fluctuation in part is the result of the change in the mix of the type of rare-earth products consumed. Particular examples occurred in 1965, 1966, and 1967 when europium oxide and yttrium were in demand for the manufacture of color television tubes; demand for these high-purity products increased the average price. In 1968 the price declined as there was a rapid increase in the consumption of low-cost, mixed rare earths, principally by the petroleum refining industry, and continuing sharp decline in consumption of high dollar value yttrium and europium. The decline in yttrium and europium primarily reflects a threefold improvement in efficiency of application of rare-earth phosphor by television tube manufacturers (41).

TABLE 5. - Developing uses for rare-earth metals and alloys

	Ductile iron	Lighter flints	Rolled steel	Cast steel	Super-alloys	Magnesium alloys	Cobalt magnets	Aluminum alloys
Pure metals:								
Yttrium......	-	-	-	-	X	X	X	X
Lanthanum....	-	-	-	-	-	X	X	-
Cerium.......	-	-	-	-	-	-	X	X
Praseodymium.	-	-	-	-	-	-	X	-
Samarium.....	-	-	-	-	-	-	X	-
Mixed metals and concentrates:								
Natural......	X	X	X	X	-	-	X	X
Cerium.......	X	-	X	-	-	-	-	-
Neodymium-praseodymium	-	-	-	-	X	-	-	-
Yttrium and heavies.....	-	-	-	-	X	-	-	-
Master alloys:								
Yttrium......	-	-	-	-	X	X	-	-
Lanthanum....	-	-	-	-	-	X	-	-
Cerium.......	-	-	-	-	-	X	-	-
Neodymium-praseodymium	-	-	-	-	X	-	-	-

TABLE 6. - Established uses of rare-earth compounds and concentrates

Mixed compounds and concentrates	Catalysts	Glass additives	Glass polishers	Arc carbons	Capacitors	Nuclear
Natural..............	X	-	X	X	-	-
Cerium...............	X	X	X	X	-	-
Lanthanum-neodymium-praseodymium........	X	-	-	-	X	-
Neodymium-praseodymium........	-	-	-	X	X	-
Samarium-gadolinium..	-	-	-	-	-	X

Price fluctuation also results if demand for a particular product slackens and an inventory develops; cost of separating this product must be borne by those elements sold. The industry must sell a balance of all products produced to attain a minimum price for each. The overall trend in price has

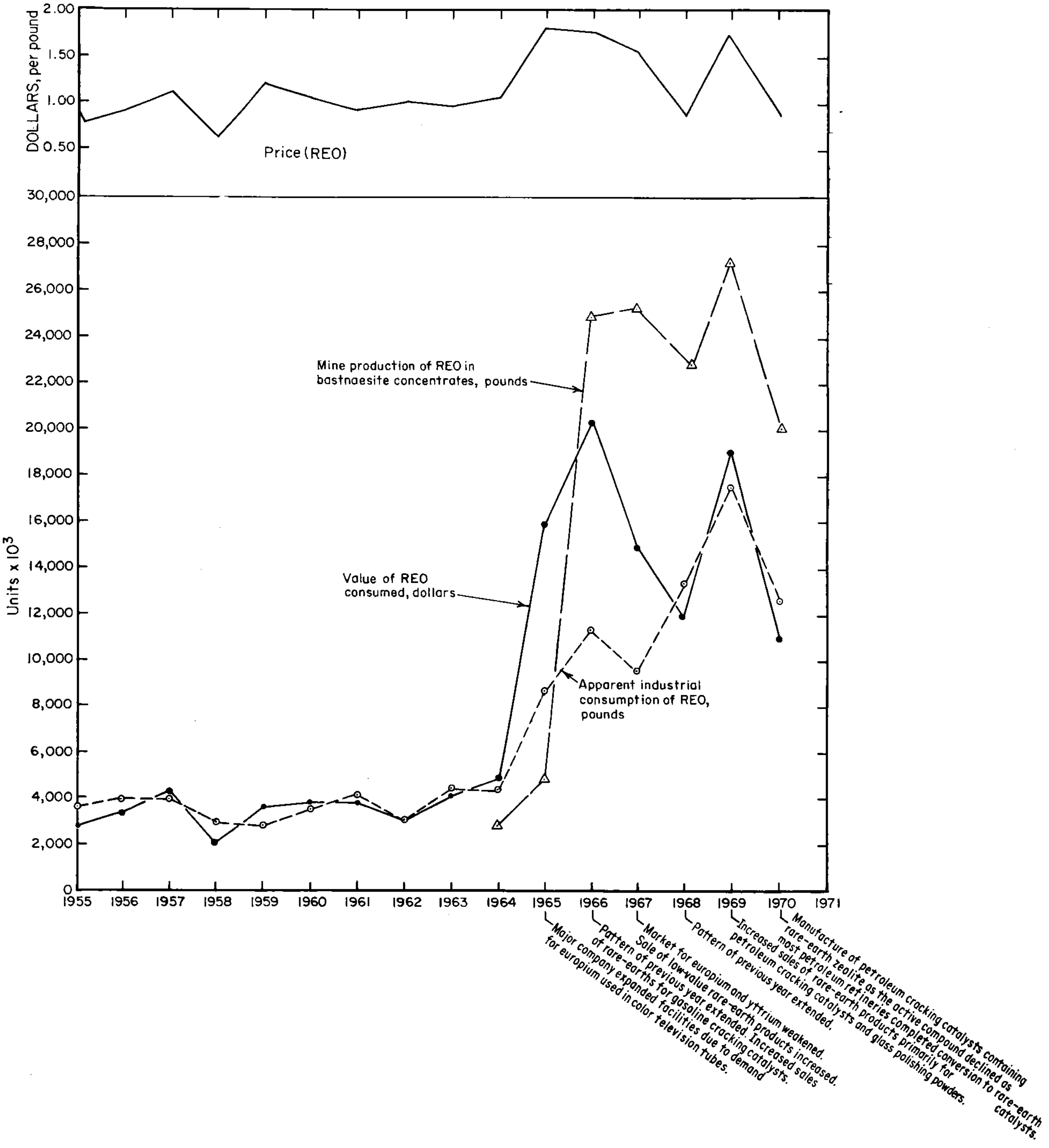

FIGURE 30. - Rare-Earth Oxide Production, Consumption, and Price History, 1955-70.

increased at a rate of approximately 3.0 percent from 1955 through 1970.[10] The average annual price was obtained by dividing annual sales value of rare-earth products by apparent industrial consumption.

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[10] Straight line trend 1955-70 is given by Y = 0.0373X + 0.8746 where Y = price and X = number of years where 1955 = 1 and 1970 = 16.

The trend in consumption of REO equivalent based largely on shipments from chemical processors to domestic consumers has been upward since 1955, averaging approximately 15 percent annually over the 1955-70 period.[11] During 1964-70, it increased annually about 11 percent.[12]

Consumption data for individual compounds and high-purity products are not available. Prices for these materials have declined mainly because markets and improved processing techniques have been developed. Table 7 contains an average annual price for various high-purity rare-earth products.

TABLE 7. - Typical prices of high-purity rare-earth oxides, dollars per pound

Element	Percent purity	1960[1]	1961[2]	1962[3]	1963[3]	1964[3]	1965[3]
Lanthanum............	99.99	-	5.50	5.50	5.50	8.77	7.80
Cerium...............	99.9+	-	-	-	-	6.50	6.50
Praseodymium.........	99.9	40.00	50.00	50.00	40.00	40.00	45.00
Neodymium............	99.9	37.50	40.00	37.50	30.00	30.00	30.00
Samarium.............	99.9	50.00	60.00	50.00	45.00	45.00	45.00
Europium.............	99.9	-	740.00	740.00	640.00	-	-
Gadolinium...........	99.9	100.00	100.00	100.00	80.00	79.00	85.00
Terbium..............	99.9	720.00	440.00	440.00	390.00	390.00	390.00
Dysprosium...........	99.9	100.00	100.00	100.00	85.00	70.00	70.00
Holmium..............	99.9	100.00	100.00	100.00	115.00	165.00	200.00
Erbium...............	99.9	100.00	100.00	100.00	85.00	85.00	85.00
Thulium..............	99.9	720.00	900.00	900.00	1,250.00	1,450.00	1,450.00
Ytterbium............	99.9	160.00	180.00	160.00	150.00	150.00	150.00
Lutetium.............	99.9	1,200.00	-	-	-	-	-
Yttrium..............	99.9	60.00	60.00	60.00	54.00	52.00	53.00

Element	Percent purity	1966[4]	1967[4]	1968[4]	1969[5]	1970[6]
Lanthanum..	99.9	9.50	7.80	7.80	5.00	5.00
Cerium...............	99.9	9.00	7.50	7.50	7.50	7.50
Praseodymium.........	99.9	50.00	45.00	45.00	38.00	38.00
Neodymium............	99.9	35.00	37.50	37.50	25.00	25.00
Samarium.............	99.9	55.00	50.00	50.00	38.00	40.00
Europium.............	99.9	1,000.00	1,350.00	850.00	519.00	519.00
Gadolinium...........	99.9	125.00	85.00	95.00	75.00	75.00
Terbium..............	99.9	500.00	925.00	925.00	320.00	320.00
Dysprosium...........	99.9	100.00	100.00	100.00	80.00	80.00
Holmium..............	99.9	185.00	210.00	210.00	160.00	160.00
Erbium...............	99.9	100.00	150.00	150.00	96.00	96.00
Thulium..............	99.9	2,000.00	2,000.00	2,000.00	1,376.00	1,376.00
Ytterbium............	99.9	150.00	285.00	285.00	192.00	192.00
Lutetium.............	99.9	-	3,500.00	3,500.00	3,000.00	3,000.00
Yttrium..............	99.9	55.00	50.00	55.00	38.00	38.00

[1] In quantities of 2 to 99 pounds quoted by American Potash & Chemical Corp. Price list published November 1960.

[2] In quantities over 10 pounds quoted by Michigan Chemical Corp. Price list published August 1961.

[3] In quantities of 2 to 99 pounds quoted by Michigan Chemical Corp. Price lists published September 1962, December 1963, June 1964, May 1965, and July 1966.

[4] In quantities of 2 to 99 pounds quoted by American Metal Market. Price lists published January 1967 and November 1968.

[5] In quantities of 1 to 99 pounds quoted by American Metal Market. Price list published September 1969.

[6] In quantities of 2 to 99 pounds quoted by American Metal Market. Price list published December 1970.

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[11] Straight line trend 1955-70 is given by $Y = 800.2X + 806.2$ where Y = apparent consumption and X = number of years where 1955 = 1 and 1970 = 16.

[12] Straight line trend 1964-70 is given by $Y = 1217.5X + 7674.3$ where Y = apparent consumption and X = number of years where 1964 = 1 and 1970 = 7.

Production data of REO equivalent is that of Molybdenum Corporation of America mine production at Mountain Pass, Calif. (54). Considering the period 1955-70, mine production has trended upward averaging about an 11-percent increase per year; from 1964 through 1970 the increase has been about 7 percent per year.

Byproducts of Other Systems

Cobalt (Iron)

The United States is almost entirely dependent upon foreign sources for its present supply of cobalt. As shown in figure 31, imports of cobalt metal provide the bulk of the current U.S. supply.

Cobalt is widely diffused in the earth's crust, occurring primarily in sulfides, arsenides, and oxidized compounds. Worldwide, little cobalt ore is mined as a primary product. Most of the cobalt metal is recovered as a byproduct of treating ores of copper and nickel. Prominent foreign sources are the cobalt-bearing ores (0.2 to 0.3 percent cobalt) of the Republic of Zaire, the Zambian copper ores (0.1 to 0.2 percent cobalt), and the Canadian nickel-sulfide ores of Ontario (0.5 to 2.0 percent cobalt) (33, pp. 114-117)

Though the United States has potential cobalt resources in Idaho and Missouri, the present domestic supply of cobalt as indicated in figure 31 is almost entirely derived as a byproduct of iron ore mined in Pennsylvania. Actual company production figures are confidential. A cobalt output of

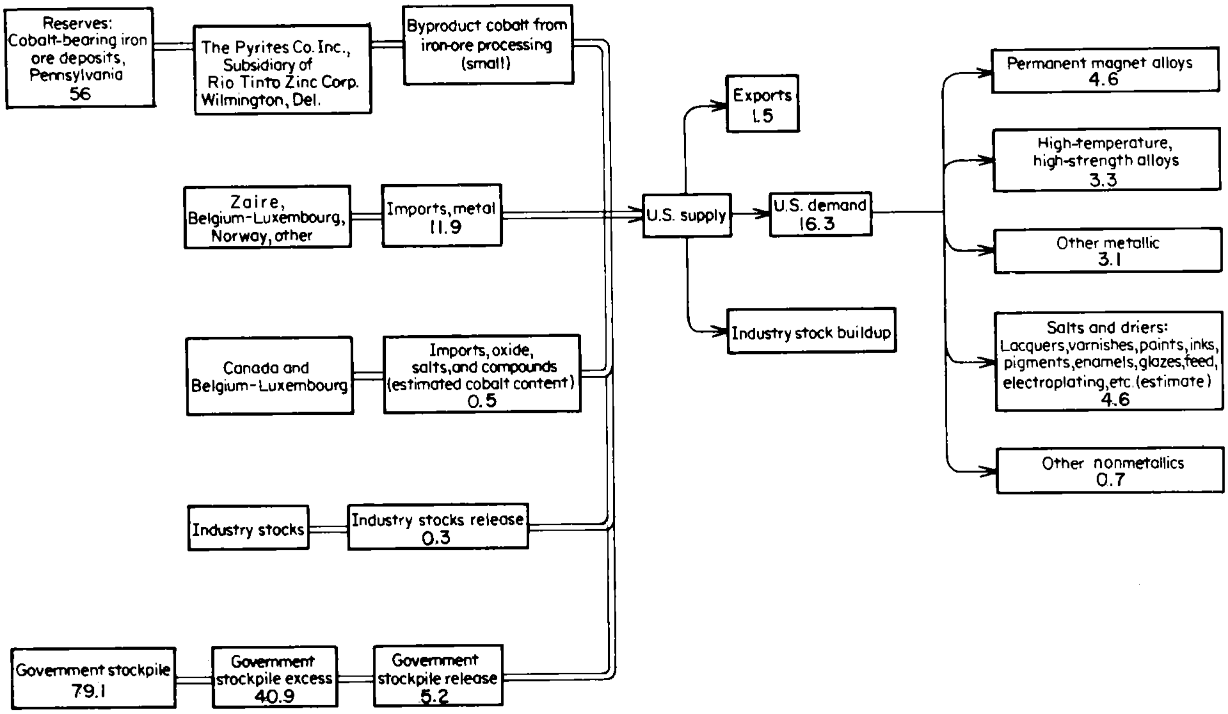

FIGURE 31. - Cobalt Supply and Demand (Million Pounds, Metal and Content, 1970).

640,000 pounds in 1966 was estimated in a survey by Battelle Memorial Institute (55); a more recent estimate given by the Institute was 324,000 pounds in 1970 (15).

A flotation concentrate of cobaltous pyrite from two magnetite iron mines is processed first to recover sulfur, which is used in the manufacture of byproduct sulfuric acid. The byproduct of the sulfuric acid manufacturing operation is a desulfured cobalt-bearing material which is water-quenched, yielding a solution containing primary cobalt. The solution is then processed to recover copper and cobalt. Electrolytic methods remove the bulk of the copper, which is followed by chemical precipitation of iron, manganese, and the remaining copper in that order. Calcination of the cobalt-containing precipitate results in two products, a cobalt hydrate and a cobalt oxide.

The United States was a major producer of cobalt only during the mid-1950's when production was expanded at the instigation of the U.S. Government. Peak production reached 4 million pounds of recoverable cobalt. The United States held this position as the second largest cobalt producer in the world only 1 year because of the uneconomic nature of most U.S. deposits.

Reserves-Resource Base

The present output of cobalt is backed by a reserve of magnetite iron ores. These ores occur in the Bethlehem Cornwall Corp.'s Grace and Cornwall mines in Pennsylvania. There are substantial ore reserves in the Grace mine, but the cobalt content is low. The Cornwall ore is relatively rich in cobalt, but reserves are much more limited. As production shifts from the Cornwall to the Grace mine, the Pyrites Company will be required to look elsewhere for cobalt-bearing raw materials in order to maintain the present output of cobalt.

The magnetite ores probably constitute the second largest cobalt resource in the United States. The ore bodies contain 40 to 60 percent magnetite and about 3.5 percent pyrite. The pyrite fraction contains 1.5 percent cobalt. Thus, the ore contains an average of 0.05 percent cobalt. In 1962, the reserves of the Bethlehem Cornwall Corp. mines were estimated to total 50 million tons of ore containing 56 million pounds of cobalt metal (5, p. 26). This survey did not indicate the distribution of cobalt reserves between the Cornwall and Grace mines.

Other potential resources of cobalt in the United States include the cobalt ores of Idaho and the cobalt-bearing lead ores near Fredericktown, Mo.

The largest known resources of cobalt ores are those of Calera Mining Co. in the Blackbird District of Lemhi County, Idaho. These ores were developed from 1899 to 1902, operated during World War I, were explored during World War II, and again in 1951. Under Government contract they came into production in June 1951. The cobalt resources of the Idaho ores have been estimated to be 200 million pounds of contained cobalt metal (5, p. 26). The Calera Mining Co. permanently closed its cobalt plant at Garfield, Utah, in 1960 when deliveries under Government contracts were completed.

The cobalt-bearing lead ores of the National Lead Co. near Fredericktown, Mo., are estimated at approximately 16 million pounds of contained cobalt metal. Work on these ores commenced in 1906, and minor amounts of cobalt have been produced. The National Lead Co. plant at Fredericktown, constructed in 1955, closed in 1961.

Demand (5, pp. 1-15; 33, pp. 122-139)

Cobalt possesses unique magnetic properties, making it an important component of permanent magnets. The most famous of these magnets are the Alnico magnets first developed by the General Electric Co. in 1936. The composition of these magnets is 14 to 30 percent nickel, 6 to 12 percent aluminum, 5 to 35 percent cobalt, and the balance iron. Some also contain copper and titanium. Other magnetic copper alloys use cobalt with tungsten, molybdenum, chromium, vanadium, and platinum. The largest single use for Alnico magnets is the construction of loudspeakers. They are also used in such devices as automobile speedometers, magnetic tachometers, magnetic chucks and holding plates, TV receivers, telephones, and hundreds of other applications.

Cobalt also has important applications in the manufacture of high-temperature alloys. Cobalt is used in toolsteel, allowing tools to be used at higher speeds and for deeper cuts than would be possible if they were constructed of a noncobalt alloy. Iron-nickel-cobalt alloys are used extensively for glass-to-metal seals. By blending the metals the expansion properties of the alloys can be made to equal or approach those of the glasses. Another use for high-temperature cobalt metal alloys such as iron-nickel-chromium-cobalt-tungsten-molybdenum alloy is in the construction of gas turbine blades.

Cobalt is used in the manufacture of cemented carbides, particularly tungsten carbides. Cobalt fulfills the role of a binder in carbide manufacture. The cemented tungsten carbides are used in cutting tools, dies, masonry and rock drills, and in other wear-resistant applications. In cutting tools, cobalt ranges from 3 to 13 percent content. Cobalt contents of up to 30 percent are used in the manufacture of tungsten carbide dies. Another type of hard, wear-resistant material is used in "hard facing," a welding process by which a hard alloy is deposited on a softer metal. Cobalt is used in the cobalt base nonferrous hard-facing alloy.

It is now practical to metal-spray cobalt base alloys onto carbon and low-alloy steel. The spray is held in contact by a mechanical bond that is acceptable for some applications. In other applications, the spray must be metallurgically bonded to the steel. Applications include pump shafts, sleeves, pump plungers, fan blades, and similar equipment.

Dental and surgical alloys also employ cobalt because it is not attacked by body fluids. These alloys employ 20 to 70 percent cobalt with carbon, chromium, molybdenum, iron, silicon, manganese, nickel, vanadium, and beryllium.

Cobalt-60 is used as a radiotherapeutic agent. This isotope emits two gamma rays, accompanied by beta radiation. In addition to therapy application it is used in feed sterilization and food preservation, chemical research and analysis, thickness determination, and other applications.

Cobalt salts and driers find use in specialty blue and violet paints and dyes. It is used by the ceramic industry as a decolorizer and to impart blue color to pottery, glazes, enamels, and glass. Cobalt oxide is used in white enamels to neutralize yellow tinge due to iron.

Driers accelerate the drying of paint, varnish, and inks. Cobalt is the strongest and most effective metal used for this purpose. It acts as a rapid oxidation catalyst.

Other nonmetal uses for cobalt include use as a catalyst in synthesis, hydrogenation, hydration, desulfurization, oxidation, and reduction. Cobalt has been found a necessary ingredient in animal feed.

Production, Consumption, and Price Statistics

The historical record of cobalt production, consumption, and price in figure 32 outlines the rise of the United States to the position of the second largest cobalt producer in the world and its subsequent decline. During the peak year of 1956 the United States produced more than 50 percent of U.S. consumption. In contrast, when imports from the Congo were cut off in 1967, domestic demand was met mainly by withdrawals from the national stockpile.

Between 1949-56, cobalt prices rose from $1.80 per pound to $2.60 per pound, and declined to $2.48 per pound by 1956. Two new producers joined Bethlehem in cobalt production. One of them, the Calera Mining Co., operated on a Government contract to supply 6.5 million pounds of cobalt for the national stockpile. When stockpile commitments were complete, Calera shut down in the face of declining cobalt prices. In 1961 National Lead closed operations at their Fredericktown, Mo.,plant. During 1960-65, imports, chiefly from the Republic of the Congo, fell back close to U.S. consumption because of reduced deliveries to the Government stockpile.

The price declines, import declines, and production declines of the 1959-61 period appear related to reduced Government stockpiling, while the rising prices, imports, and production levels of the 1950-56 period were strongly influenced by Government buying for stockpiles and by the rising demand for cobalt in the private sector.

High cobalt prices of the 1950-59 period appear to have slowed growth and consumption. There is a definite indication of a response in the form of higher consumption to the lower prices for cobalt after 1960. The longrun growth trend for cobalt consumption, 1945-70, is 5.0 percent annually.[13] Uncertainty of supplies and price levels is highlighted by the cutoff of the Congo cobalt supply and the price rises during 1967.

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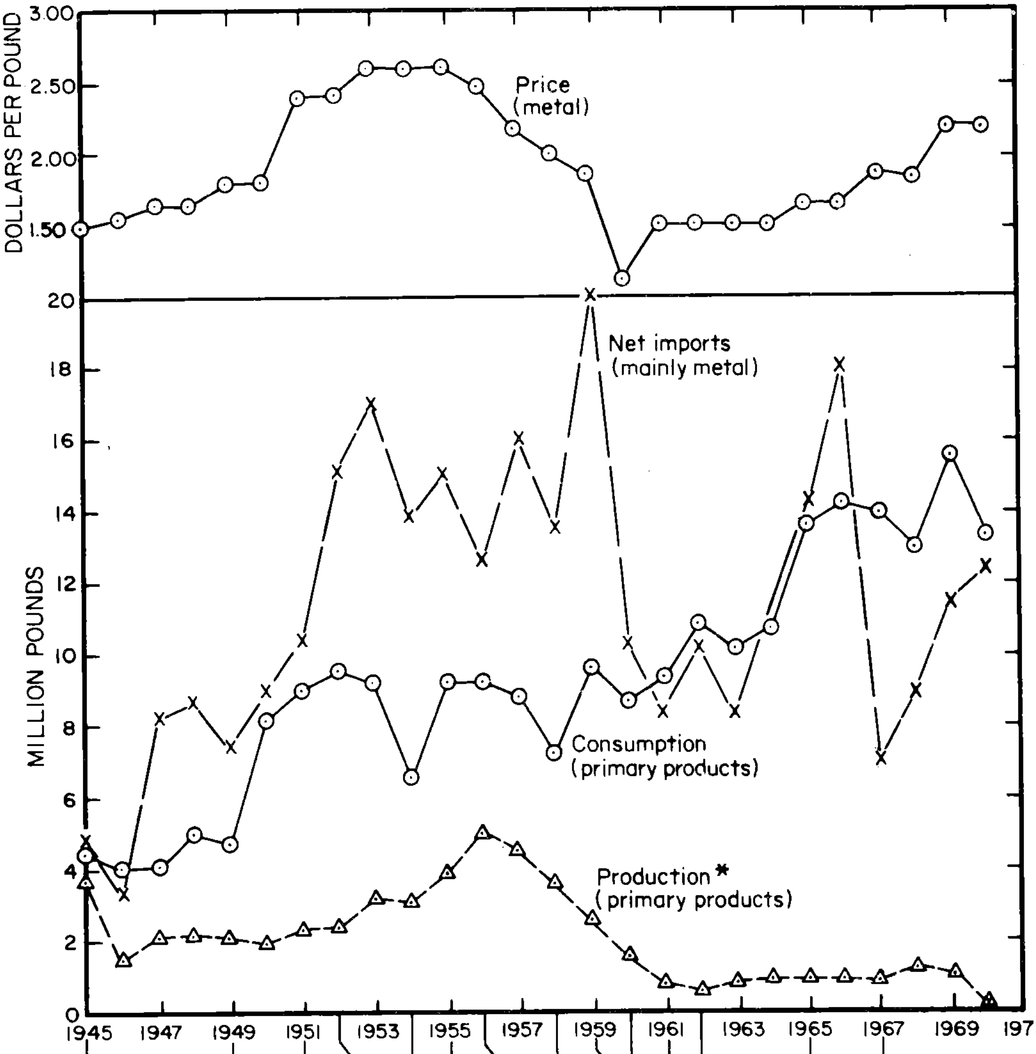
[13] Trend equations are $Y = 384.8X + 4{,}481.0$ for 1945-70 where Y = cobalt consumption in thousands of pounds and X = year where $X = 1$ for 1945 and $X = 26$ for 1970 and $Y = 500.5X + 9{,}762.0$ for 1960-70 where Y = cobalt consumption in thousands of pounds and X = year where $X = 1$ for 1960 and $X = 11$ for 1970.



1945 War demand subsides. Production from Missouri, Pennsylvania, and Idaho.

1949 Bethlehem Steel Co. only commercial cobalt producer. Cobalt-bearing residues stockpiled in Idaho and Missouri. Calera Mining Co. develops mine in Idaho, refinery in Utah.

1951 Calera begins production, June 1951.

Cobalt demand up for high-temperature alloys, cobalt steels, and cemented carbides. Calera becomes chief producer at Cobalt, Idaho. Concentrator at 40% of capacity. Technical problems at refinery delay full production of 3 million lb per year.

Heavy deliveries to national stockpile. 82% of imports from Belgian Congo.

1955 Production from National Lead Co., Fredericktown, Mo., 1955-61

Production peak. Calera chief producer from copper-cobalt ore, Bethlehem second from iron ore, National Lead third from iron ore

Niagara Falls refinery closes. Mine production still expanding. Consumption down owing to industrial recession.

1959 Calera closes Idaho mine after completion of Govt. contract to deliver 6.5 million lb of cobalt to stockpile.

Cobalt price drops from $2.60 per lb in 1955 to $1.15 per lb in 1960.

1961 National Lead closes down at Fredericktown, Mo.

Bethlehem Cornwall Corp is the only producer, 1962-67

1965 Consumption up sharply for magnet alloys, high-temperature, high-strength alloys, and metal to glass seals.

1967 Congo cuts off exports of cobalt, December, 1966. Sales from national stockpile surplus total 6 million lb.

* Production data after 1959 are company confidential. Data from 1960-70 taken from alloy and concentrate consumed by refiners and processors.

FIGURE 32. - Cobalt Production, Consumption, and Price History, 1945-70.

Incremental Costing

Calculation of the incremental costs of cobalt production is not included in the present analysis.

The byproduct cobalt subsystem that existed in the United States until 1970 is shown in figure 33. It is a simplified flow diagram of the Pyrites Co. processing of cobalt-bearing solutions derived from sulfuric acid manufacture, which is a byproduct of the concentration of magnetite iron ores. If a more detailed investigation indicated that sulfuric acid production is not independent of the cobalt system, the sulfuric acid and cobalt would have to be classified as coproducts.

In the systems shown, Bethlehem Cornwall Corp. transports its pyrite concentrates from the Grace and Cornwall mines and concentrators to the sulfuric acid plant at Sparrows Point, near Baltimore, Md. At this plant the pyrite concentrate is roasted, and the sulfur dioxide is used in the manufacture of sulfuric acid.

The desulfurized concentrate is then water-quenched. This process results in a waste residue and a copper-bearing solution. The solution is shipped to the Wilmington, Del., plant of the Pyrites Co., Inc. This solution contains 25 to 35 grams per liter of cobalt plus copper, manganese, ferrous iron, zinc, nickel, and sulfate ion.

The Pyrites process begins with electrolytic recovery of the bulk of contained copper. The remaining processing steps eliminate iron, manganese, and the balance of the copper in that order by precipitation and filtration. The cobalt is then precipitated and calcined, resulting in two products depending upon calcine time, a cobalt hydrate and a cobalt oxide. Major cobalt losses occur in the solution discarded after cobalt precipitation. Another source of loss is during manganese precipitation where one part of cobalt is lost for each part of manganese eliminated.

The only other source of cobalt available to Pyrites other than the Bethlehem concentrates is a small amount of secondary cobalt in cobalt catalyst residues obtained from the petroleum industry.

The economics of cobalt differs from the economics of many other byproduct metals simply because of the industrial organization of cobalt production. At $1.70 per pound, cobalt does not offer the same spread between incremental cost and revenue offered by some of the other byproduct metals. Furthermore, since Pyrites must bid for its raw material, the cost of raw material itself is a factor in the production decision. Presumably the cobalt solution is valued in the market place at approximately the selling price for cobalt, less incremental processing costs and profit for Pyrites.

The processing shown in figure 33 became obsolete in April 1970 when the entire Pyrites plant shifted to a solvent extraction technique. Pyrites system could also become nonrepresentative of the industry if other cobalt-bearing ore deposits such as those in Idaho or Missouri were to be developed

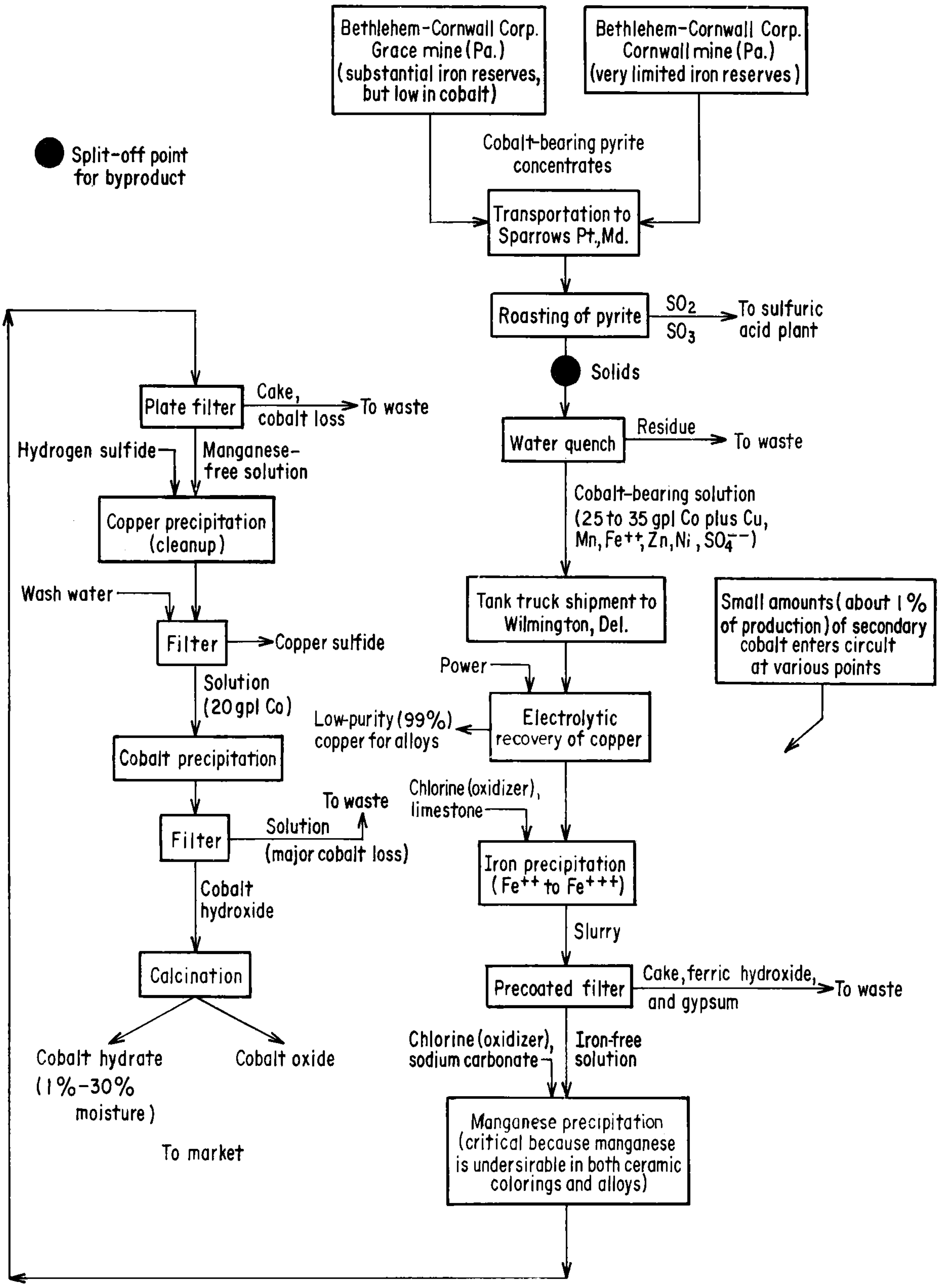


FIGURE 33. - Byproduct Cobalt Subsystem.

again. Some of the metallurgy of the Calera Mining Co. processing plant in Idaho is described in the literature (52; 53; 24).

Supply Curves

As might be inferred from an examination of the organization and history of cobalt production, the supply curve during the period of rapid expansion exhibits considerable elasticity with respect to price. The production of primary products (cobalt metal content) versus price is plotted in figure 34. The industry curve exhibits elasticity reflecting the Government stimulation to production and high prices of the 1950 decade.

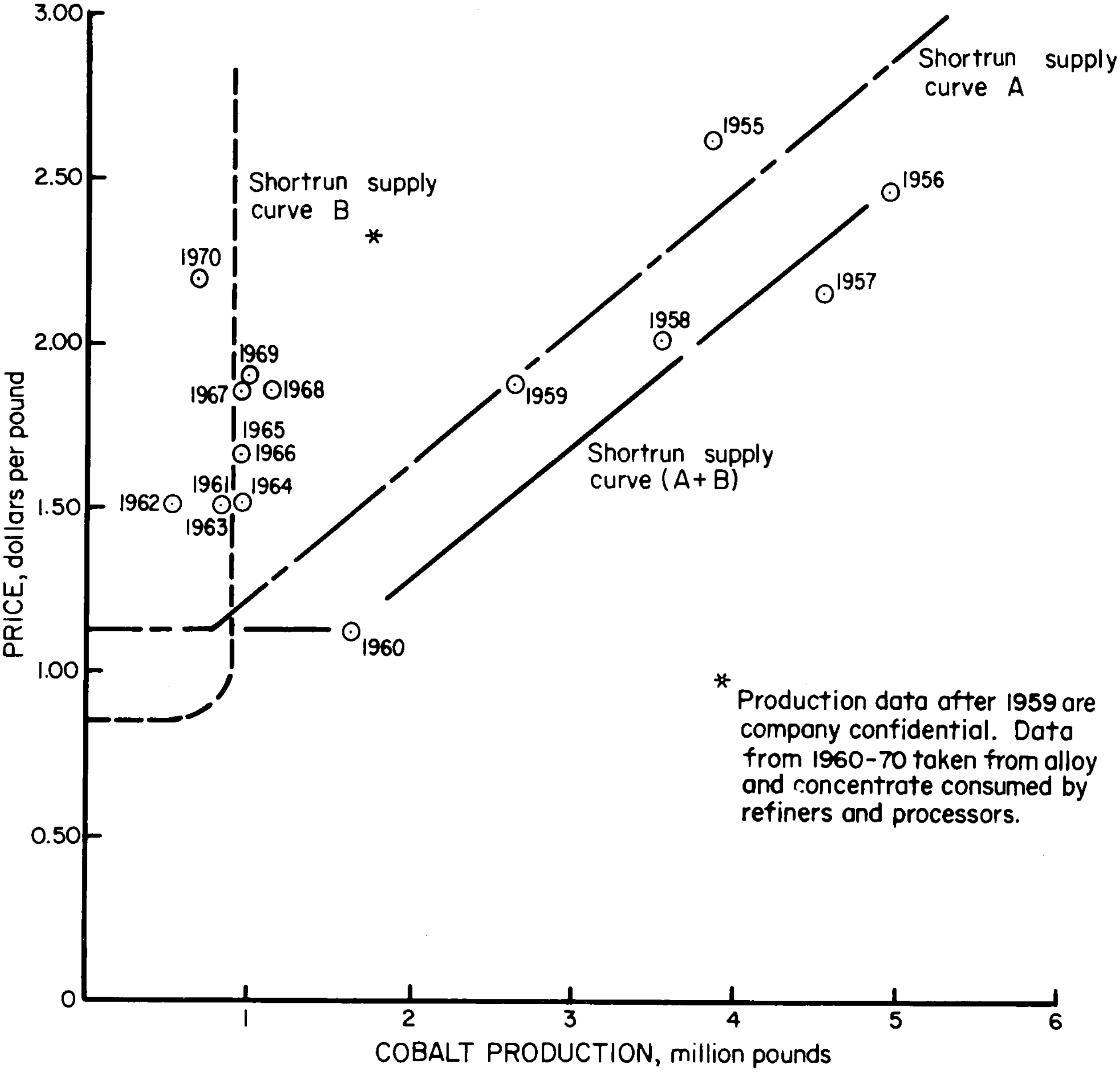


FIGURE 34. - Cobalt Supply Curves, 1955-70.

We might infer from what has been discussed that the elasticity in cobalt output is a result of the availability of cobalt materials from sources other than Bethlehem ores, which are controlled to a great extent by the price of cobalt. The elasticity of the industry curve may be the result of adding a supply curve such as A sketched in figure 35 to the original byproduct supply curve B. The industry curve is the summation of the two. Identification of the two distinct supply curves is possible in the case of cobalt because of the drastic change in the nature of production over the period plotted.

Actually, curve A might better be described as a summation of several rather inelastic byproduct curves as shown in figure 35. The result of adding several price inelastic sources of material leads to a more elastic industry curve.

The peculiar nature of economic conditions in the case of cobalt highlights the desirability of being familiar with the byproduct curves for all sources of byproduct metals, including those that are not presently exploited. Such investigations identify sources of incremental output at higher prices and help to quantify price supply relationships.

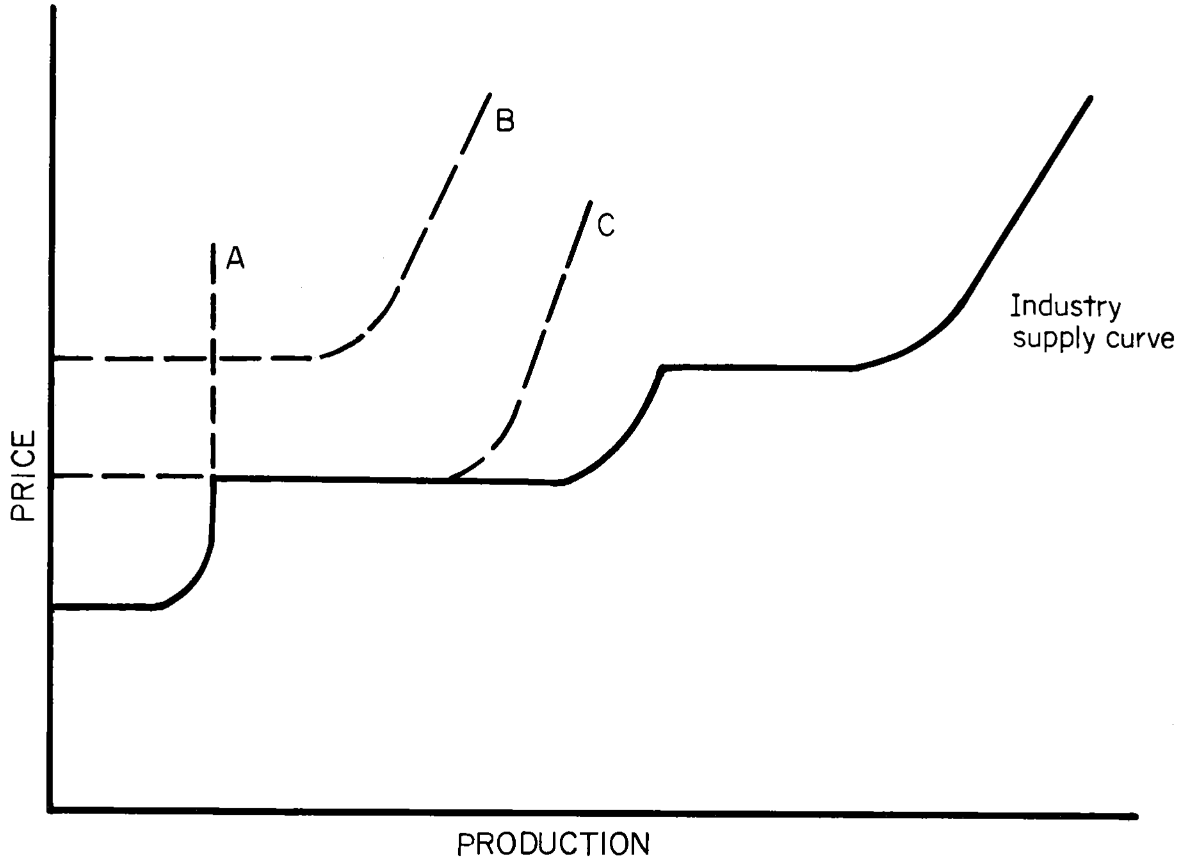


FIGURE 35. - Industry Supply Curves.

Gallium (Aluminum)

Sources of Supply

Gallium occurs widely in nature, particularly in aluminous minerals. It occurs in very low concentrations (0.002 to 0.01 percent gallium). As a consequence the major sources of commercial gallium are as a byproduct of the Bayer process for producing alumina from bauxite and occasionally as a byproduct of the production of zinc from sphalerite.

The domestic supply of gallium as illustrated in figure 36 is derived entirely from two U.S. plants: the Aluminum Company of America (Alcoa) alumina plant at Bauxite, Ark., and the zinc processing plant of the Eagle-Picher Co. at Quapaw, Okla. Production data are confidential.

The domestic production of gallium was supplemented by imports of gallium metal totaling 2,331 pounds in 1970. The reported value of gallium imports suggests that most imports were in the form of low-grade material or waste.

Reserves-Resource Base

Gallium reserves in Arkansas bauxite are estimated at 2,200 short tons, and the gallium reserves in the Tri-State area zinc ores are estimated at 770 short tons. The Bureau of Mines discussed reserves of recoverable gallium in fly ash and flue dusts generated during the industrial burning of coal (80).

Demand (33, pp. 182-186)

Demand for gallium was only a few grams in 1952. Although the majority of uses are still in the development state, current demand is probably about several hundred kilograms annually.

The largest market for gallium in 1970 was in intermetallic compounds used in the manufacture of semiconductors. Intermetallic compounds have applications in rectifiers, transistors, solar batteries, and other devices.

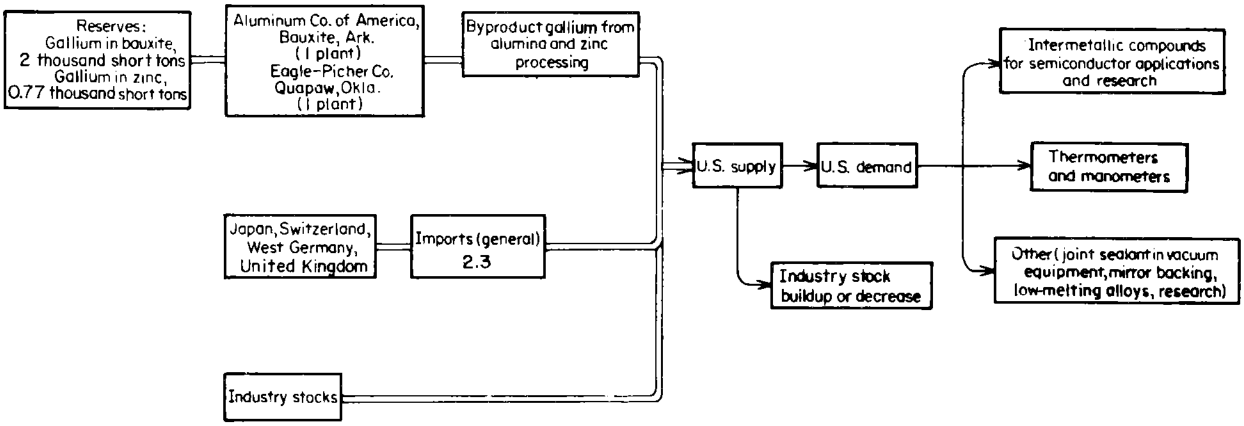


FIGURE 36. - Gallium Supply and Demand (Thousand Pounds, 1970).

Gallium was the basic construction material used in the initial development of semiconductors. Presently, silicon and germanium are used extensively in semiconductors. However, gallium still has application where temperature and upper frequency limits of silicon and germanium make gallium more desirable. Gallium is used principally in the form of gallium-arsenide or gallium-phosphide. Because both gallium and arsenic are available in states of extreme purity (up to 99.9999 percent for gallium) it is possible to obtain finished gallium arsenide crystals pure enough for high-frequency, high-temperature applications. Gallium arsenide is also used in tunnel diodes. The tunnel diode is a doped junction diode displaying negative resistivity effects. Application of tunnel diodes are in oscillators, switching circuits, FM transmitter circuits, and amplifiers. Gallium arsenide is also used in solar cells for satellite power systems.

Gallium oxide has been used for vapor doping of other semiconductor materials. Gallium ammonium chloride is used in plating baths for electrodeposition of gallium on whisker wires for leads of transistors.

Gallium at room temperature is a solid gray white metal, but at 85.6° F it becomes liquid and changes to a silver color. The metal remains a liquid up to 4,595° F, its estimated boiling point. It thus has one of the longest liquid phases among elements or compounds. Early applications of gallium made use of this property in direct reading fused quartz thermometers for high-temperature applications. Its possible use as a heat-transfer liquid also relies on the long liquid-phase properties. One major drawback for this application is its extremely corrosive nature at high temperatures.

Other uses for gallium include applications in the manufacture of optical mirrors, as a catalyst, in radioactive compounds, and in dental alloys. Other gallium alloys are used in vapor arc lamps, in low-resistance contact electrodes, in selenium rectifiers, as a sealant for glass joints, and in laboratory equipment such as the mass spectrometer.

Production, Consumption, and Price Statistics

Production and consumption data on gallium are not available. A few thousand grams was produced by The Anaconda Co., Great Falls, Mont., between 1943 and 1945, in processing indium. In 1954, gallium production was reported as fewer than 100 pounds per year.

The price of gallium ranged from \$3 per gram to \$3.75 per gram between 1945 and 1960. After 1960, the price dropped rapidly to \$1 per gram in 1969, where it remained through 1970. General imports (unwrought, waste, and scrap) reported in 1970 totaled 2,331 pounds, but an average valuation of 40 cents per gram indicates that most imports were not refined gallium metal.

Incremental Costs

Calculation of incremental costs for gallium are not included in this analysis. However, the alumina system and the relationship of the byproduct gallium subsystem is depicted in figure 37.

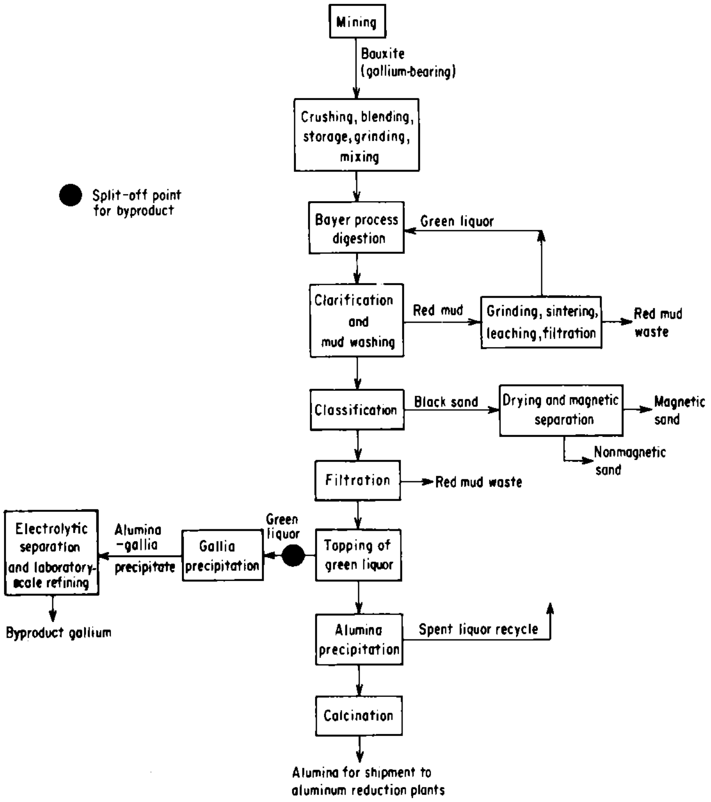


FIGURE 37. - Alumina System, Showing Gallium Byproduct.

Gallium, a byproduct of the aluminum system, is produced by tapping a portion of the green liquor generated in the production of alumina (Al_2O_3). Gallia (Ga_2O_3), present in bauxite, dissolves along with the alumina during the digestion of the bauxite ore. The soluble gallia builds up in recycled plant liquors by dissolving to saturation (about 0.2 gram per liter) and partial precipitation. After the solution is saturated with gallia, its concentration in the liquor remains relatively constant with the excess exiting the process via the red mud waste.

Gallia is produced by withdrawing a small portion of the plant liquor and subjecting it to a separate precipitation. In this process, a small amount of alumina is lost equal to about 100 parts alumina for each part of gallia produced. Once the alumina-gallia precipitate is obtained, the gallium is separated from it electrolytically and is refined by subjecting it to as many as 16 steps of processing on a laboratory scale.

The sand removed in classification prior to filtration of the green liquor is of interest because it is an example of the variety of minerals contained in the plant liquor. The black sand is presently considered waste, though it might some day be considered worthy of byproduct processing. If the sand removed by the classifier is subjected to magnetic separation, a black (magnetic) portion can be separated from the total. A sample of this material at Alcoa's Bauxite, Ark., plant assayed 40 percent iron oxide and 3.8 percent titania with smaller amounts of zircon, manganese, magnesium, vanadium, nobium, gallium, chromium, molybdenum, nickel, lead, and copper oxides.

The system depicted in figure 37 is based on the alumina plant of the Aluminum Company of America at Bauxite, Ark.

Gallia is produced by extracting a very small portion of plant liquors, which flow through the plant at 300,000 gallons per minute. Labor is by far the major item of cost in the production of gallium. Even the methods of packing and shipping have significant impact on incremental costs. There is no fulltime labor devoted to gallium production. The labor force that extracts gallia is also concerned with the production of several other specialty products.

Because there is a market for only small quantities of gallium, large quantities are discarded in the red mud wastes. Bauxites are known to contain up to 0.01 percent gallium or 0.22 pound per long ton. Fifty-percent recovery of contained gallium would yield 0.11 pound per ton, and 90-percent recovery would yield 0.20 pound per ton. The U.S. production of bauxite in 1970, principally by Aluminum Company of America and Reynolds Mining Co. in Arkansas, totaled 2,082,000 long tons. On this basis, a potential production of 229,000 to 416,000 pounds of gallium is indicated. Present recovery of gallium from aluminum production is far below this figure.

Supply Curves

The main characteristics of the gallium supply curves are indicated in figure 38. In this instance, the shortrun supply is determined by the Aluminum Company of America facility. Discussions with management indicate that the shortrun supply curve would turn up after a 50-percent expansion in production at the present facility. After such an expansion, additional plant investment would be required to shift the shortrun supply curve to the right.

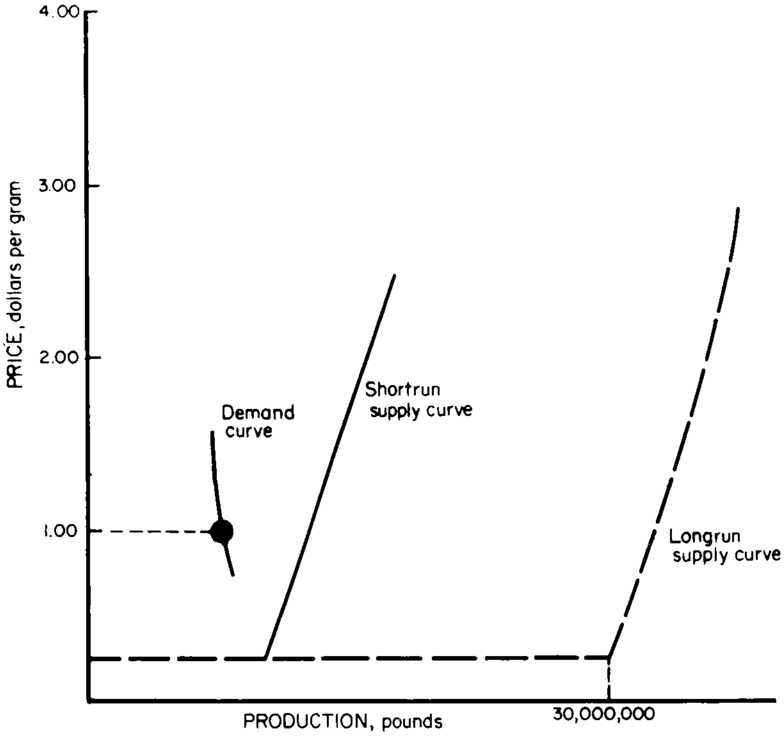


FIGURE 38. - Byproduct Gallium Supply Curves.

Demand is shown as inelastic owing to limited applications of the metal and compounds. Price is shown well above marginal costs and is likely to remain so.

The horizontal axis of figure 38 is left without dimension because of the lack of publishable data.

The vertical portion of the longrun supply curve is turned up at the 30-million-pound output level, based on the calculations for gallium in bauxite.

Examination of the byproduct gallium supply curve leads one to infer that supply is likely to be infinitely elastic at the current price level and is likely to expand with demand without price increases until output is much larger than it is at present.

Hafnium (Titanium)

Sources of Supply

Hafnium occurs in nature in small to moderate amounts associated with zirconium in all zirconium-bearing materials. Only one mineral, thortveitite, is reported to contain more hafnium than zirconium, but there are no known commercial concentrations of this mineral.

Byproduct hafnium is a product of a relatively complex system that might be labeled the titanium system. Initial milling separates the zircon (zirconium silicate) product and provides raw material for a subsystem producing a particular grade of zirconium metal. This subsystem in turn has a split-off point for byproduct hafnium. The present domestic source of the metal hafnium as indicated in figure 39 is as a byproduct of the production of nuclear-grade zirconium. Nuclear-grade zirconium metal is one of several products derived from zircon. Most zircon is used in the production of refractories, ceramics, alloys, and nonnuclear zirconium metals and chemicals.

Zircon itself is a byproduct or coproduct of the dredging of heavy mineral sands, chiefly the beach sand deposits of Florida, California, New Jersey, South Carolina, Georgia, and other States. These sands are worked chiefly for the titanium minerals ilmenite and rutile associated with zircon, monazite, garnet, staurolite, and other minerals of high specific gravity. The economic recovery of zircon is, therefore, dependent upon the existence of monazite, staurolite, or titanium minerals in the deposit. Domestic reserves of

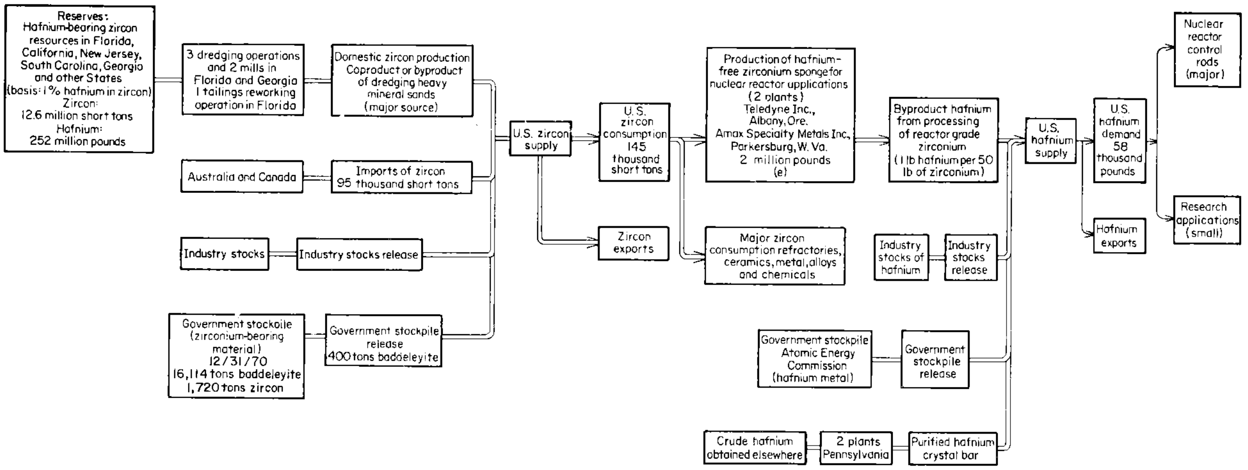


FIGURE 39. - Hafnium Supply and Demand, 1970.

zircon are large, but they cannot be economically exploited for the zircon alone. Ilmenite has traditionally been the principal titanium mineral product. Rutile also is a titanium mineral. It contains more titanium than ilmenite, but it is less abundant. It commands a higher price. Zircon is also found with some gold gravels of central California and gold-monazite gravels of central Idaho. They are also readily concentrated by gravity methods. In addition to the dredging and gravity concentration operations for titanium mineral sands, zircon was recovered during 1970 from old tailings in Florida, reworked principally for recovery of monazite-xenotime.

As shown in figure 39, substantial amounts of zircon are imported from Australia. The U.S. Government stockpile excess of zircon-bearing materials is a third potential source of zircon in periods of tight supply or emergency. The 16,114 tons of baddeleyite in the stockpile contains a maximum of 0.8 percent hafnium oxide.

Byproduct hafnium production is a result of successful attempts to develop high-purity zirconium, which has particular value as a construction material in nuclear reactors. The fact that zirconium has a very low tendency to absorb slow neutrons, combined with its relatively high melting point (1,860° C) and its ease of formability and corrosive resistance, makes zircon of much interest in the field of atomic energy.

Two U.S. plants are engaged in producing nuclear-grade (hafnium-free) zirconium. These two plants use a small portion of the U.S. zircon and zirconium supply. Most zircon is consumed in applications not requiring the elimination of hafnium.

Other hafnium compounds, particularly the refractory oxides, carbides, and nitrides, have been of slight commercial interest.

To separate hafnium from zircon requires complicated metallurgical processes, a costly but necessary separation to produce hafnium-free zirconium required for nuclear reactors. Hafnium and zirconium are companion metals in zircon, but hafnium is zirconium's nuclear opposite, having a thermoneutron cross section over 600 times that of zirconium. Whereas zirconium allows free passage of neutrons, hafnium acts as a barrier. Thus, the same properties that make these metals attractive for their individual applications also necessitate that they be separated. Ordinary zirconium made without hafnium separation and containing 2- to 3-percent hafnium is suitable for most nonnuclear uses.

Solvent extraction has been adopted to the greatest extent for separating hafnium and zirconium. As a light methyl isobutyl ketone solvent enters the bottom of a column containing the heavier aqueous solution of ammonium thiocyanate, the ketone rises to the top, extracting hafnium thiocyanate preferentially on the way to the top. The hafnium thiocyanate leaves the column at the top, holding most of the hafnium and a small part of the zirconium. The remaining zirconium is then removed, and the hafnium is recovered by precipitation of hafnium hydroxide. Further processing of hafnium oxide results in hafnium sponge, ready for additional purification necessary for marketing.

and averaged 83,000 pounds annually for the years 1958-63. Production of zirconium sponge over the same period averaged 2.7 million pounds per year or about 32.5 pounds of zirconium for each pound of hafnium. The range of the Zr:Hf production ratio varied from 40 in 1962 to less than 20 in 1963. Subsequent to 1963 when 130,000 pounds of hafnium oxide was produced, production figures were withheld because they were company confidential information.

The price of reactor-grade hafnium sponge stabilized at $75 per pound in 1963 and remained there until it dropped to $72.50 in 1968; the price returned to $75 in 1969 and 1970. Rolled bar and plate hafnium were priced at $138 per pound in 1963, but dropped to $130 during 1967, to $120 in 1968, and remained constant through 1970.

Incremental Costing (10; 27; 75, pp. 35-82; 75, pp. 83-106; 75, pp. 107-137; 33, pp. 199-204; 37; 57, pp. 756-761; 25; 74)

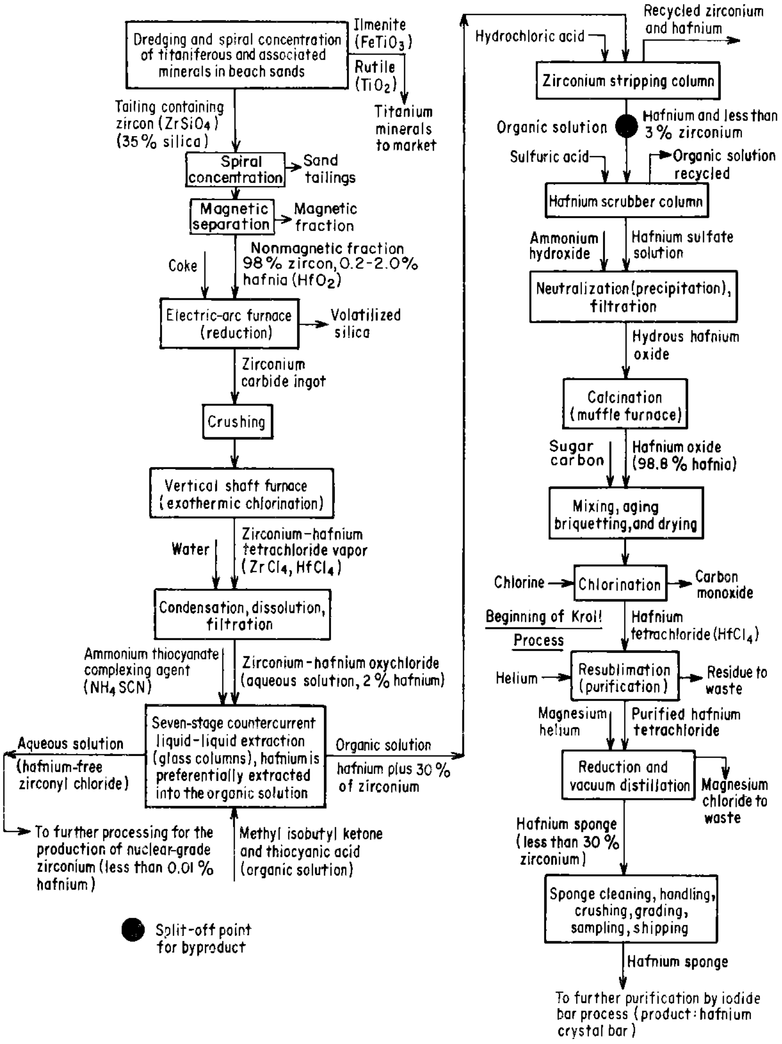


FIGURE 40. - Byproduct Hafnium Subsystem and Titanium System.

The titanium mineral and zirconium production systems responsible for byproduct hafnium and the byproduct hafnium system itself are illustrated in the simplified metallurgical diagram in figure 40. Zircon is shown as the byproduct of dredging and concentration of heavy mineral sands for ilmenite and rutile. After additional concentration, the zircon destined to be raw material for the production of nuclear-grade zirconium is reduced to zirconium carbide in an electric-arc furnace. It is then chlorinated to produce a zirconium-hafnium tetrachloride and is dissolved in water to convert the tetrachloride to an aqueous solution of zirconium and hafnium oxychloride. This aqueous solution contains about 98 percent zirconium and 2 percent hafnium. It is the feed for countercurrent liquid-liquid extraction that separates the zirconium and hafnium.

The hafnium is trapped in the organic solvent as a result of the liquid-liquid extraction process. Subsequently, the remaining zircon is removed from the organic solution, and the hafnium is stripped from the organic solvent with sulfuric acid. The result is hafnium sulfate, which is precipitated by neutralization, filtered, and calcined to produce hafnium oxide.

The hafnium oxide is briquetted with carbon and sugar and is chlorinated to produce hafnium tetrachloride. Hafnium tetrachloride forms the feed for the Kroll process treatment resulting in hafnium metal.

Briefly, the Kroll process consists of a purification step for the hafnium tetrachloride and then a reduction of the tetrachloride with magnesium in a helium atmosphere to produce hafnium sponge. The hafnium sponge is further purified by the iodide bar process in order to produce high-purity hafnium metal for hafnium control rods in nuclear reactors. A typical analysis of the Kroll process and iodide bar process hafnium indicates that the zirconium content of the hafnium remains at 2.6 percent, but that other impurities are reduced by the iodide treatment (57, p. 760).

The costing of the hafnium subsystem is not included in this report.

Supply Curves

There are little data upon which to base hafnium supply curves. The price of hafnium sponge has been stable at $72 to $75 per pound since 1952. Output is entirely dependent on the output of nuclear-grade zirconium since the birth of the industry.

According to one author the price of hafnium is cost related, and the current price is determined by apportioning about one-half of the extraction and separation costs to each of the metals, zirconium and hafnium. Since 2 pounds of hafnium oxide are produced for each 100 pounds of zirconium oxide, a price of $1.50 per pound for zirconium oxide translates to $74 per pound for hafnium oxide. This pricing is based on the current practice of apportioning the costs of production entirely between each metal (57, p. 761). The cost of converting zirconium oxide to reactor-grade zirconium sponge is $3.50 to $5.50 per pound. Assuming equal costs for the conversion of hafnium oxide to reactor-grade hafnium sponge would result in an expected price level of $78.50 to $80.50 per pound. Such reasoning assumes price to be closely related to production costs.

Earlier prices for zirconium and by inference the prices of hafnium were higher. In 1952, the Atomic Energy Commission and Carborundum Metals Co., Inc., Akron, N.Y., executed a contract to produce 150,000 pounds of zirconium sponge annually for 5 years at a price of less than $15 per pound, or 3,000 pounds of hafnium sponge per year at a price of less than $150 per pound. During the same year, the Rust Process Design Co., Pittsburgh, Pa., designed a plant reported to cost $2.5 million and scheduled to produce 150,000 pounds of zirconium sponge annually at a capital cost of about $17 per pound of annual zirconium sponge capacity. The division of the investment equally between zirconium and hafnium production indicated that $1.25 million would be applied to the hafnium sponge production. Since the output would be approximately 3,000 pounds annually, the capital cost indicated for hafnium was $417 per pound of annual capacity. The distribution of this investment over 5 years would mean about $83 per pound of hafnium produced. The location of the split-off point, as shown in figure 84, and the knowledge that zirconium and hafnium metallurgy is similar lead to speculation that incremental costs are less than would be expected by dividing costs equally. The split-off point assumes that zirconium is economically self-sufficient. Incremental costs of hafnium production, therefore, exclude the initial liquid-liquid separation and the zirconium stripping of the organic solution. This is logical because these operations would be performed to produce nuclear-grade zirconium, whether or not hafnium was produced as a byproduct.

The high investment cost for hafnium is related to the high rate of depreciation imposed by the 5-year economic life assumed. This is perhaps justified where markets and processes are as uncertain as they were for hafnium in 1952.

Rubidium (Lithium)

Sources of Supply

Rubidium is not found as a principal constituent in any mineral. It occurs widely dispersed in potassium minerals in low concentration. Large quantities of rubidium are reported in lepidolite and pollucite deposits in Canada, Southern Rhodesia, Southwest Africa, and Mozambique. Rubidium, found in the lepidolite ores of the pegmatites of Southwest Africa, is imported by U.S. companies for extraction of lithium. Extensive processing of lithium ores in the past resulted in increased availability of rubidium and cesium in byproduct concentrates. One operation based on African lepidolite produced a 70-percent potassium byproduct, which contained 23-percent rubidium concentrate and 2-percent cesium carbonate. The material was marketed under the trade name Alkarb (33, p. 434). In addition to being the commercial source of rubidium, Alkarb has applications in glass, ceramic glazes, and in porcelain enamels.

The current U.S. supply of rubidium as indicated in figure 41 is derived entirely from Alkarb. Lepidolite is no longer used to produce lithium compounds

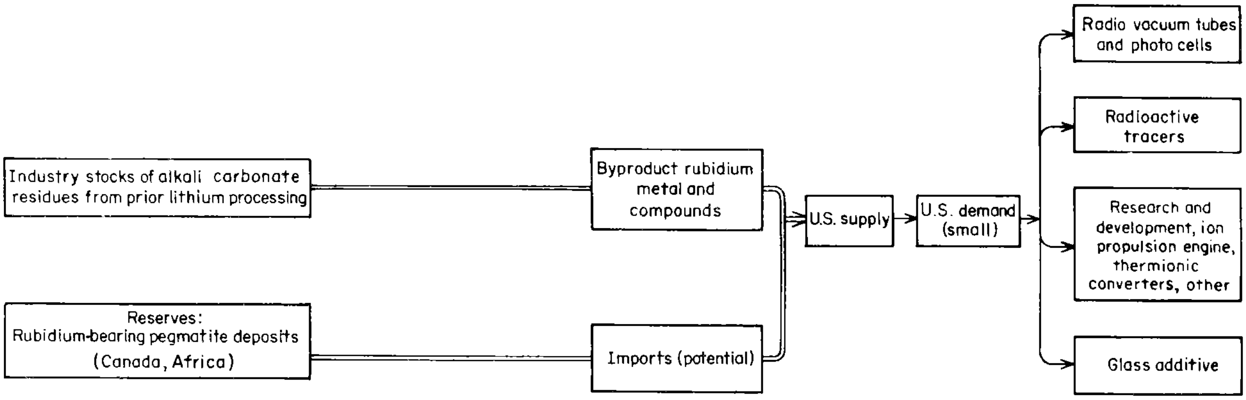


FIGURE 41. - Rubidium Supply and Demand, 1970.

in the United States. As a result, Alkarb production has ceased, but supplies are still available from accumulations. Consumer stocks are sufficient for short-term but not long-term demand.

Reserves-Resource Base

There are no estimates of U.S. rubidium reserves other than ample short-term supplies in the lepidolite residues. Rubidium is also known to occur in the United States in feldspars, brines, and in saline deposits.

Foreign sources of rubidium include large quantities of rubidium in lepidolite and pollucite deposits of Southern Rhodesia, Southwest Africa, and Mozambique. The largest reserves of rubidium in North America are in the pegmatite deposits of Bernic Lake, Manitoba, Canada. The deposits contain 350,000 tons of pollucite averaging about 20 percent cesium and 0.7 percent rubidium oxide, and 100,000 tons of rubidium in lepidolite averaging about 1.5 percent rubidium oxide.

Demand

Rubidium has few industrial applications. Rubidium compounds are used in radio vacuum tubes and photocells. Small additions of rubidium to glass make it more stable and durable. Alkarb also has uses in ceramic glazes and porcelain enamels.

Radioactive rubidium has been used in medical testing as a tag element to trace the flow of blood.

The potential uses for rubidium are more exciting. Cesium followed by rubidium is the most easily ionized element. There is, therefore, a potential for rubidium as a substitute or supplement to cesium as an important source of material fuel for the ionic propulsion engine being developed for long distance space travel. In the ionic propulsion engine, cesium atoms are ionized to give them a positive charge. The ions are accelerated tremendously by an electrical field, and thrust is developed by exhausting the stream of ions through a nozzle.

Cesium and rubidium have applications in thermionic converters. When a hot electrode or plate containing cesium or rubidium vapor is heated, electrons leave the hot electrode and pass to a cold electrode so that an electrical current is generated.

Another form of the thermoelectric generator utilizes the magnetohydrodynamic principle. Cesium ions formed by heat are passed at high temperature through a magnetic field. The ion stream is similar to the armature of a conventional generator in generating electricity.

It is apparent that demand possibilities for rubidium are largely potential and that cesium is more promising for its potential applications. A Bureau of Mines forecast places the range of rubidium demand in the United States between 1,200 and 3,400 pounds annually by the year 2000.

Production, Consumption, and Price Statistics

There are no publishable statistics on the production or consumption of rubidium. The long-term trend in production and consumption has been upward.

The market for rubidium metal is very small. The carbonate or chloride is usually demanded for present applications. High-purity (99.8 percent) rubidium, in 1- to 4-pound lots, sold for $375 per pound in 1970, and standard grade (99.5 percent) sold for $300 per pound. Prices for high-purity rubidium compounds, in 50- to 100-pound lots, ranged from $73 to $83 per pound, and prices for standard-grade compounds ranged from $44 to $51 per pound. Price quotations on rubidium and its compounds are seldom changed.

Because of the widely differing markets and the very small market volume, little can be inferred from the sparse data on price-output relationships for rubidium. Most of the metal production continues to be used in research and development sponsored chiefly by the National Aeronautics and Space Administration or the Atomic Energy Commission. The research is primarily with the ion propulsion engine and thermoelectric generators.

Metallurgy and Incremental Costs

Description of the metallurgy and incremental costs of rubidium production is not included in this study. A number of references are given in Hampel (33, p. 440; 63).

Supply Curves

About all that can be inferred from the very sparse data on rubidium is that any expansion in demand is likely to cause a shift to an entirely different supply system than the one now functioning. The present system is based on the processing of rubidium from Alkarb. The new system may also be based on the processing of lepidolite to lithium, or it may be based on the processing of pollucite to cesium. Both systems should be investigated to determine the character of future supply.

CONCLUSIONS

Supply Curve Generalizations

This analysis of byproduct metals supply relies on a calculation of unit production costs and estimation of marginal opportunity costs. The first is achieved by costing portions of the metallurgical production systems, and the second is achieved by a review of the empirical production data and the historical record of market conditions. The general objective of sketching improved supply curves is realized by fitting the cost calculations to a model based on workable competition, except for those metals for which there are insufficient data.

Most observations of the results of the supply curve are summarized in the chapters dealing with the individual byproduct metals. A few generalizations are as follows:

(1) Market-related opportunity costs are important in locating the horizontal portion of the shortrun supply curve. Silver, gold, rhenium, germanium, and tellurium are good examples.

(2) Opportunity costs will probably continue to influence the supply curve even under longrun conditions because the static equilibrium of the long run is never reached. Instead we proceed from one shortrun condition to another shortrun condition. The question is raised first with the discussion of the selenium longrun supply, and again with the supply of tellurium and rhenium.

(3) The varying, sometimes declining byproduct metal content of major metal ores can upset the general concept of the longrun supply curve being to the right of the shortrun curve. Declining byproduct content may shift it to the left. Gold and silver provide examples of a leftward shift while byproduct molybdenum is a good example of a rightward shift toward a longrun equilibrium.

(4) Inventory balancing and stockpiling reflect opportunity cost decisions. Their effects are sometimes difficult to separate from grade changes. Selenium, tellurium, and germanium provide examples.

(5) Imported byproduct-metal-bearing raw materials and the assumption of one major byproduct source sometimes make supply relationships hazy. The cadmium curve and cadmium production data provide an example.

Other observations relate to specific metals--the minute exploitation of longrun supply (gallium), the importance of technical relationships (hafnium), the crucial question of economies of scale (scandium), and the general insufficiency of available data (indium, thallium, bismuth, radium).

Classification

The group selected for most intensive study in this analysis consists of the 19 metals that were most obviously byproducts because they were incidental to a main product. This initial classification separated the main product and a set of byproduct metals, but it did not separate what might be termed the several levels of byproduct production. Rhenium, a byproduct of byproduct molybdenum, is an example. Another example is silver, which in turn is a byproduct of copper production. But the silver system itself produces byproduct gold, and the platinum metals are a byproduct of the gold production. Germanium is likely to be a byproduct of byproduct cadmium from zinc processing. Cobalt is a byproduct of sulfuric acid production, which in turn is a byproduct of iron ore processing. The level of byproduct production depends upon the economics of the metal upon which its production is directly dependent as well as upon the main product involved. The economics of the higher level byproduct makes production of the lower level byproduct possible because only marginal or incremental costs are involved. This aspect of byproduct metal classification appears useful to identify metals whose costs of production appear initially far too high to justify extraction, but whose incremental costs of production may turn out to be unexpectedly low because of the possibility of separating other intermediate products.

In this analysis, byproduct metals from secondary sources and from manmade sources (nuclear technology) were essentially ignored, and warrant further study.

Economic and Strategic Importance

Four of the 19 byproduct metals, cadmium, gold, molybdenum, and silver, are most important when measuring the value of production and consumption. Antimony, bismuth, cobalt, selenium, and hafnium would be added to the list if it were to include those metals that form part of the strategic stockpile program of the United States.

Probably most neglected in the classification by economic and strategic criteria are the metals with few present applications but with possible important future application. A better means of classifying these metals might be the projection of future needs compared with a relatively sophisticated projection of supply. Perhaps econometric models can now be constructed to project supply and calculate the ratio of future supply and demand. These ratios could then be ranked by both size and by weighting of the strategic or economic importance of demand.

Data Problems

This study was limited by some substantial data gaps. There are little data on potential byproduct sources or reserves. There are practically no data on the inventory of waste materials resulting from minerals being processed today nor is there any information on the probable costs of recovering metals from these waste materials.

Sufficient time series data were unavailable on some metals to draw inferences about revealed supply curves. Where time series data were available, as for selenium, tellurium, and cadmium, it was used for purposes of comparing actual supply curves with the theoretical curve.

The study of some of the metals was made more difficult by lack of supply-demand information. The data on molybdenum and antimony were particularly difficult to unravel. A complete balanced supply and demand account for each metal, even if it required some estimating, would be extremely helpful.

Methodology

The system-subsystem approach was helpful in identifying split-off points and the costs relevant to the production of the byproducts. There were problems of overlapping systems and of choosing one of several subsystems as representative for the purposes of costing and analysis. It is hard to see how this could be overcome by a different approach. The approach might be improved by calculating incremental costs of alternative metallurgical systems where two or more systems are important in production.

The usefulness of the marginal cost or incremental cost analysis in drawing supply curves depends on including opportunity costs in the estimates. In other cases, such as selenium, the price dips closer to the incremental production cost and provides a complete explanation of supply.

Other variables probably should be given more attention in subsequent studies, particularly the problem of organizing production to make byproduct production attractive. Considerable byproduct molybdenum, rhenium, germanium, and scandium are diverted to waste because the volume of byproduct production is too small to interest the main product producer in recovery. If economies of scale could be introduced by concentrating production, some of these metals might be recovered.

Effect of Limited Scope

The limited scope of the present analysis prevented calculation of incremental costs for all of the metals. It also prevented full development of the potential sources of supply of byproduct metals, the marginal costs involved with new metallurgical systems, and the expansion of reserves connected with their exploitation. There is a trend toward metallurgical techniques that more fully exploit a wide range of potential metal products in a given ore. The new ion exchange techniques are examples. These are now used in connection with processing rare earths and similar groups of metals. While the present analysis has been limited to the conventional byproduct recovery systems, there is a wide field for investigation in total extraction metallurgy.

The present analysis includes little information on the relationship of main product and byproduct metallurgy. To what extent does main product technology limit or increase the cost of byproduct recovery? Most metallurgical techniques studied focus on the main product up to the split-off point for the byproduct. An interesting postscript would be the benefits and costs of total extraction metallurgy versus the main product extraction. This question becomes more relevant for metals whose demand appears to be surging ahead of byproduct supply, and for those metals that occur in a coproduct rather than a byproduct relationship.

A Plan for Additional Study

The emphasis of this study was on those metals now recovered as byproducts. It examines cost-revenue relationships, traces the byproduct metals from ore reserves to final product, and defines the economics of supply. Additional work might adopt the following objectives:

(1) Determine the relationship of new sources of supply to the present supply curve. At what prices do new byproducts, coproducts, or main product sources become economic? What technical and economic problems are involved?

(2) Expand the analysis to additional Group II metals produced in minor amounts as byproducts, and to additional Group III metals whose byproducts and/or coproducts are not completely defined.

(3) Extend the analysis of byproduct supply to the manmade byproduct metals that are byproducts of nuclear power generation. What industrial needs would they fulfill? What are the costs involved?

(4) Show how the problems of the scale of operation result in a loss of byproduct metals to waste. Examples are the magnetic sands in alumina processing, rhenium in molybdenum processing, germanium in zinc processing, scandium in phosphate fertilizer manufacture.

(5) Determine the relationship of secondary sources of byproduct metals to the present supply curves.

(6) Relate losses of byproducts to the economics of the process involved. The recovery of byproduct metals is dependent on the metallurgical process used. The process used in turn is designed not for the byproduct metal but for the main product metal. Assuming rising demands for byproducts are there better metallurgical alternatives designed for recovery of a number of coproduct or byproduct metals?

(7) Use the details on the economics of byproduct metals developed in the present study for computer simulation of the copper, lead, and zinc systems, which would provide forecasts of byproduct output under alternate assumptions affecting the system.

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