

Information Circular 8790

# Occurrence and Recovery of Certain Minor Metals in the Processing of Lead and Zinc

By John G. Parker



UNITED STATES DEPARTMENT OF THE INTERIOR  
Cecil D. Andrus, Secretary  
BUREAU OF MINES

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# OCCURRENCE AND RECOVERY OF CERTAIN MINOR METALS IN THE PROCESSING OF LEAD AND ZINC

by

John G. Parker<sup>1</sup>

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## ABSTRACT

Many of the so-called minor metals are derived as byproducts from the processing of lead and zinc concentrates in which they occur as minor constituents. Concentrates from some lead-zinc mineral deposits are more enriched in metals such as cadmium, arsenic, bismuth, silver, and selenium than are others, and these sources offer a continuing, assured supply of certain of these metals. Despite the age of the data collected, the Bureau of Mines feels it to be highly desirable to publish due to its relevance to the objective of the study which was to ascertain the flow of minor metals from certain smelter feeds. Efforts to trace these metals through the complicated lead and zinc processing steps included trying to ascertain losses and mode of loss of these metals. Losses of some metals in processing may be surmised as occurring in gaseous and other emissions, or possibly in slags and residues.

## INTRODUCTION

This report assesses the importance of domestic and foreign lead and zinc concentrates and other smelter feed materials as sources of certain minor metals, some of which are of strategic importance. Efforts were made to determine the flow of these metals from entering the processing plants as feed materials through subsequent processing products. Pertinent data and representative samples were collected from the plants shown in figures 1-3. It may be seen in these figures and in figures 4-5 that some of these plants, principally those processing zinc, have ceased operating and some have been closed since 1971. Nevertheless, because of the increasing importance of trace and minor elements, the data represented by these materials flows are useful in various analyses of the industries. Accordingly, this study is more specific than the broad, extensive economic study of major metal systems and byproduct minor metal subsystems published by the Bureau of Mines in 1973 (104-105).<sup>2</sup>

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<sup>1</sup> Physical scientist, Intermountain Field Operations Center, Bureau of Mines, Denver, Colo.

<sup>2</sup> Underlined numbers in parentheses refer to items in the bibliography at the end of this report.

Byproduct metals studied in the lead-zinc industry include: arsenic, antimony, bismuth, cadmium, gold, silver, and platinum-group metals. Also studied are selenium, tellurium, and thallium peculiar to the lead industry, and gallium, germanium, and indium peculiar to the zinc industry.

It was determined that the quantities of process material, with assays, were not available at various process points, and that quantities recovered, lost or yet in process, could not be ascertained. Available published data proved inadequate (3, 8, 20, 24, 49, 75, 86). The only feasible approach to solving a very complex problem was to ask companies in the industry to furnish analyses and weights of materials in process. If analyses were not available, the companies were asked to furnish samples for analyses by the Bureau of Mines. Some companies provided flowsheets of lead and zinc processing. Combining these with other information, specific flowsheets were transformed into generalized flowsheets for the lead and zinc industries. Precise metallurgical balances were determined to be infeasible due to variability of mill feed, byproduct impurities, recycling procedures, limitations on sampling and assay methods, and restrictions imposed by company confidentiality requirements.

As a result of legislation to minimize environmental pollution, numerous reports have been prepared on metallurgical plant emissions. Typical of these is a report on the disposition of arsenic in smelting and another on sulfur oxide emissions from lead, zinc, and copper smelters (4, 136).

In the United States, all lead is produced by the blast furnace method. Procedures are discussed in a number of publications (79, 104). The four major methods used to produce zinc domestically are: the horizontal retort, the vertical retort, the electrolytic process, and the electrothermic process (51, 82, 130). Currently there are no horizontal retort plants in operation, the last having been closed in mid-1976.

#### ACKNOWLEDGMENTS

The need for comprehensive data on the lead and zinc industry in this project entailed the procurement of information from many people knowledgeable in the geology of lead-zinc deposits in this country and abroad, in the industrial processing of lead and zinc metal and oxides, and in research activities associated with them. Lead and zinc plant management personnel, without whose contributions this study would not have been possible, include: M. M. Anderson, R. D. Symonds, and L. Welborn of AMAX, Greenwich, Conn.; K. D. Loughridge, C. F. Bates, W. R. Kelly, S. M. Lane, H. L. Montague, R. Paul, S. Y. Stennis, L. C. Travis, and C. B. White of American Smelting and Refining Co. (ASARCO), J. A. Marvin, R. Mercer, H. N. Ord, and T. Paige of The New Jersey Zinc Co., a subsidiary of Gulf & Western Industries, J. G. Sevick, R. G. Redelfs, and J. W. Sherman of St. Joe Minerals Corp., and J. Garrison of U.S. Smelting Lead Refinery, Inc., a division of UV Industries, Inc., all located in New York, N.Y.; K. A. Phillips of American Zinc Co. (now Azcon Corp.), East St. Louis, Mo.; A. J. Alf (now retired), J. L. Owings, W. J. Roberts, and N. C. Whitehouse of The Anaconda Co., Denver, Colo.; J. A. Anderson, G. P. Bollwerk, and P. A. Jensen of Blackwell Zinc Co., Blackwell, Okla.; T. D. Hymas and M. K. Weiss of The Bunker Hill Co., Kellogg, Idaho; R. L. Bockstahler and

M. A. Dodd of Eagle-Picher Industries, Inc., Cincinnati, Ohio; J. S. Van Aken of National Zinc Co., Bartlesville, Okla.; and R. H. Kindrick of Sherwin Williams Chemicals, Cleveland, Ohio.

#### STRUCTURE OF THE BYPRODUCT MINOR METALS INDUSTRY

Each of the byproduct minor metals is recovered to various degrees in primary lead and zinc smelting and refining plants.

Smelter byproduct antimony recovered at primary lead smelters, usually less than 10 percent of total primary antimony production, was consumed mostly at the smelters in the production of antimonial lead; a remaining very small quantity was recycled in residues or processed to oxide. The recycled residues are eventually converted to oxides or sulfides. In 1974 primary lead smelters recovered 658 tons of byproduct antimony from domestic lead ores. Antimony and antimonial lead also were produced at the lead refineries (99). At one time, the lead-silver ores of the Coeur d'Alene district in Idaho accounted for 96 percent of the domestic mine production of antimony but in 1974 these ores accounted for about 80 percent.

Arsenic (as trioxide) was produced domestically only by the American Smelting and Refining Co. (ASARCO)<sup>3</sup> plant at Tacoma, Wash., using as feed arsenical smelter aggregates (such as slag and fume) which usually are derived from copper smelters but also from lead smelter flue dusts (101, 104).

Bismuth was produced domestically as a refinery byproduct from both domestic and foreign lead bullion and certain zinc and copper smelter byproducts. The major production was at ASARCO's Omaha, Nebr., refinery and UV Industries' East Chicago, Ind., refinery. The latter plant was forced to depend upon secondary lead as a bismuth source when the Tooele, Utah, lead smelter was closed. Bismuth extraction and refining methods include the Betts and Betterton-Kroll processes (3, 8, 49, 57, 102).

In 1974 cadmium was produced at eight domestic plants, most of which also produced zinc metal. Petrick described the hydrometallurgical processing of cadmium from zinc plant flue dusts (105). Others discuss the recovery of cadmium at horizontal and vertical retort plants and at electrolytic plants (77, 87, 92). Production of cadmium metal in 1974 was 3,333 short tons, considerably less than the record production of 6,323 tons in 1969.

Gallium metal, oxide, and chloride were produced from certain zinc plant residues by Eagle-Picher Industries, Inc., Quapaw, Okla. In 1974, Aluminum Co. of America (ALCOA) also produced gallium metal as a byproduct of alumina production at Bauxite, Ark. Descriptions of gallium extraction methods have been published (32, 123).

Primary germanium was produced solely at Eagle-Picher's Quapaw, Okla., plant from zinc smelter residues. Production techniques for germanium were discussed (24, 70, 105).

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<sup>3</sup>Reference to specific manufacturers or trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

In recent years, indium has been recovered only at refinery plants owned by ASARCO at Denver, Colo., and Perth Amboy, N.J., where the feed materials are zinc plant flue dusts and residues. The New Jersey plant was closed in 1976. Extraction techniques have been described (24, 41, 120).

Domestic selenium production in 1974 was 644,000 pounds, down 19 percent from the previous year. Practically all primary selenium was produced at four electrolytic copper refineries. Small amounts of selenium are also derived from copper and lead smelter flue dusts, lead refinery slimes, and sulfuric acid manufacturing (104). A byproduct selenium subsystem for gases and dross as well as soda-nitre slag also is shown. Other workers discuss selenium extraction in more detail (8, 24).

Tellurium was produced by three of the four electrolytic copper refineries producing selenium and by UV Industries' East Chicago, Ind., lead plant. Domestic tellurium production in 1974 was 191,000 pounds, 21 percent below that of 1973. Refinery sludges containing primary tellurium also were produced at other copper refineries. The tellurium subsystem, its relationship to that of selenium, and other data on tellurium recovery were described (8, 104).

Thallium was produced at only one location, the Globe refinery at Denver owned by ASARCO. Thallium metal recovery was discussed (24, 42, 105).

The major part of silver production was recovered as a byproduct in treating base metals, especially lead. Information is available on removal of silver and other precious metals from electrolytic slimes (24).

Using data available from Bureau of Mines canvass schedules and other sources, figures 1-3 (input, output, and distribution flowsheets) indicate the types of materials fed to lead, zinc, and zinc oxide plants and the various plant products. The figures show intraplant, intracompany, and intercompany transfers such as zinc plant residues shipped to lead smelters, lead smelter matte and speiss shipped to copper smelters, and lead bullion shipped to lead refineries. The lead flowsheet (fig. 1) also shows the combined general input and output at three refineries. U.S. primary lead smelter and refinery capacity in thousands of short tons of metal and sources of supply, 1973, and U.S. primary zinc capacity in thousands of short tons of metal and sources of supply, 1973, are shown in figures 4-5.

Figure 4 indicates that domestic concentrates formed about 84 percent of total lead in ores and concentrates used in 1973. About 81 percent of domestic ores and concentrates came from Missouri, 10 percent from Idaho, and the rest from Colorado, Utah, and other States. Peru supplied 26 percent of lead in foreign concentrates followed by Australia, Honduras, Canada, and other countries.







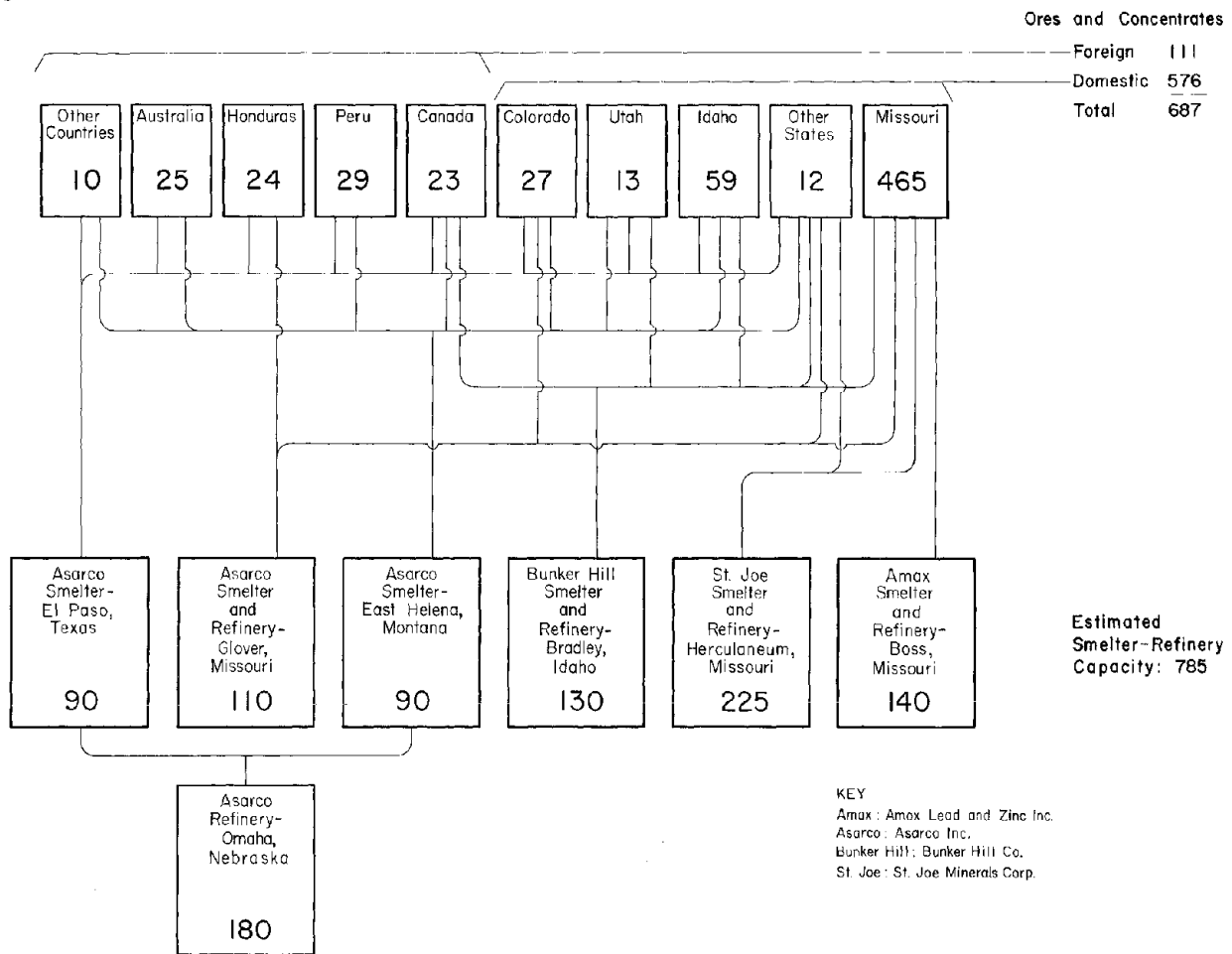


FIGURE 4. - U.S. primary lead smelter and refinery capacity (thousands of short tons of lead content) and sources of supply, 1973. (Source: Lead chapter, BuMines Bull. 667.)

Figure 5 shows that domestic mines supplied nearly 71 percent of total zinc in ores and concentrates in 1973. About 17 percent of domestic materials each came from Missouri and New York State. Tennessee supplied over 13 percent; Colorado and Idaho also were major sources. Canada provided 62 percent of foreign zinc in ores and concentrates and Mexico provided 17 percent.

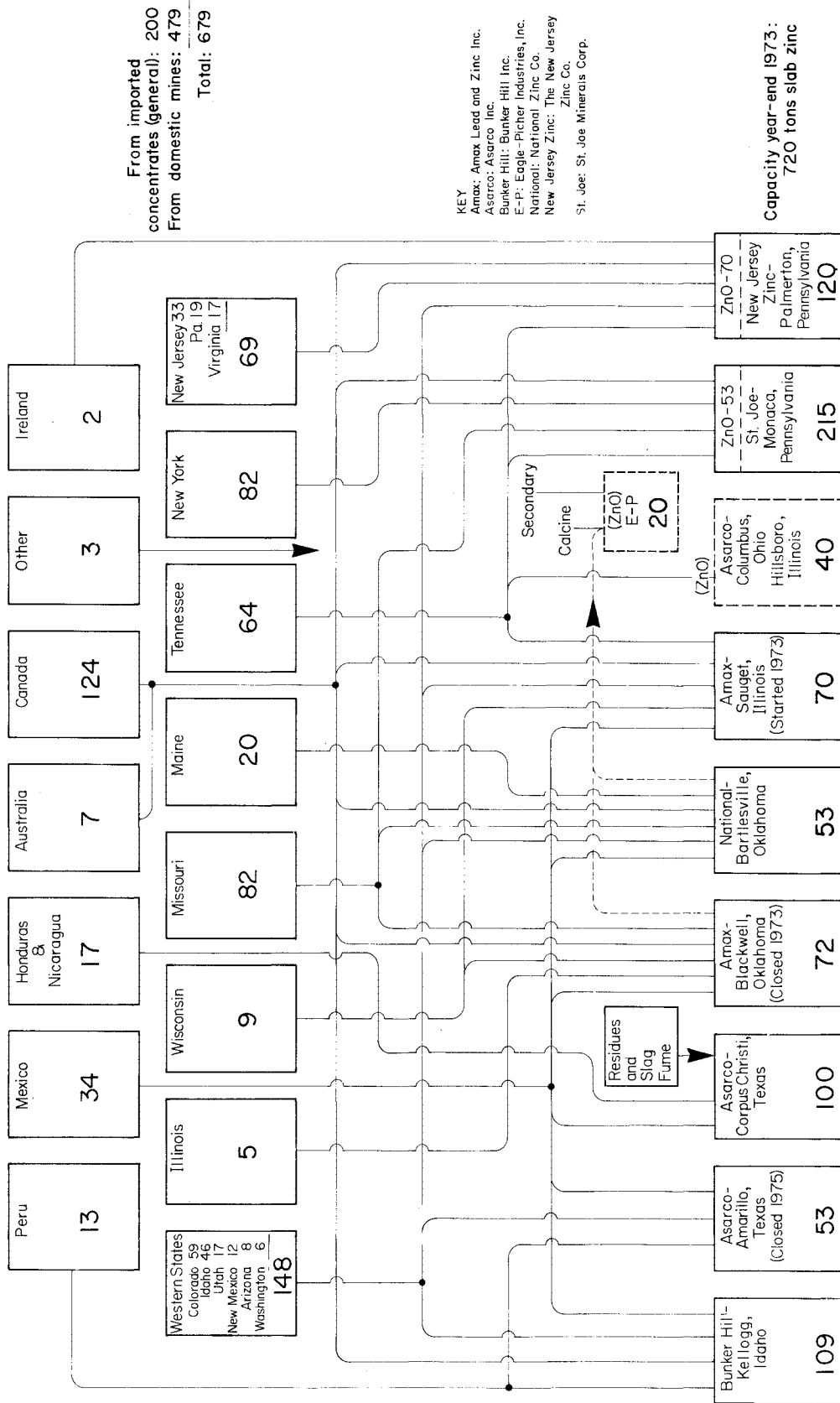


FIGURE 5. - U.S. primary zinc capacity (thousands of short tons of zinc content) and sources of supply, 1973.  
 (Source: Zinc chapter, BuMines Bull. 667.)

GENERALIZATIONS ON FLOW OF MATERIALS

The complex smelting and refining problems involved with the recovery and production of copper, lead, and zinc and associated byproducts have been solved partially by improvements in analytical methods. Phillips describes the complicated metallurgy which requires the circulation of products between lead and copper, lead and zinc, and, at least in one case, a direct circulation between copper and zinc circuits (106). Figure 6, which is from Phillips' paper, shows the flow among combined lead, zinc, and copper circuits. According to this diagram, copper processing contributes the following to the lead and zinc circuits: zinc in slag fuming; lead, antimony, bismuth, and thallium in converter fume; and lead, antimony, arsenic, and bismuth in litharge from electrolytic slimes to the lead charge. In turn, lead dressing matte and speiss with contents of copper, gold, silver, arsenic, selenium, and sulfur are shipped to the copper smelters.

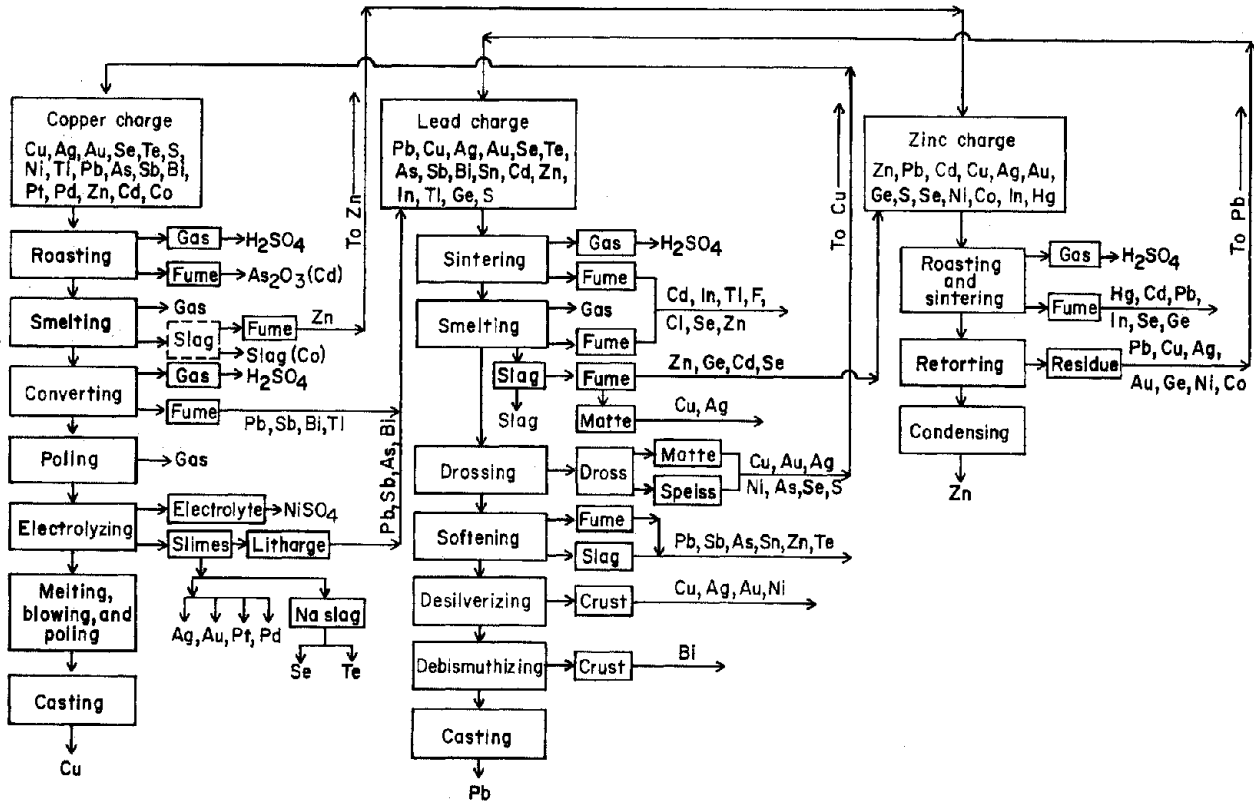


FIGURE 6. - Combined copper, lead, and zinc circuits (106).

Lead processing and its byproducts are diagrammed in figure 7 and zinc processing in figure 8. Zinc processing was divided into two general categories: (1) Pyrometallurgy including horizontal and vertical retorts and the electrothermic process, and (2) electrometallurgy with the electrolytic process. Figures 7-8 show "strategic locations" or "split-off points" (104-105). A precise determination of minor metals at such strategic locations should reflect the loss of these metals at any intermediate point; for example, between presence of metal "X" in roaster input and metal "X" in calcines, the intermediate point showing loss of metal "X" in dust and fume from the roasting operation.

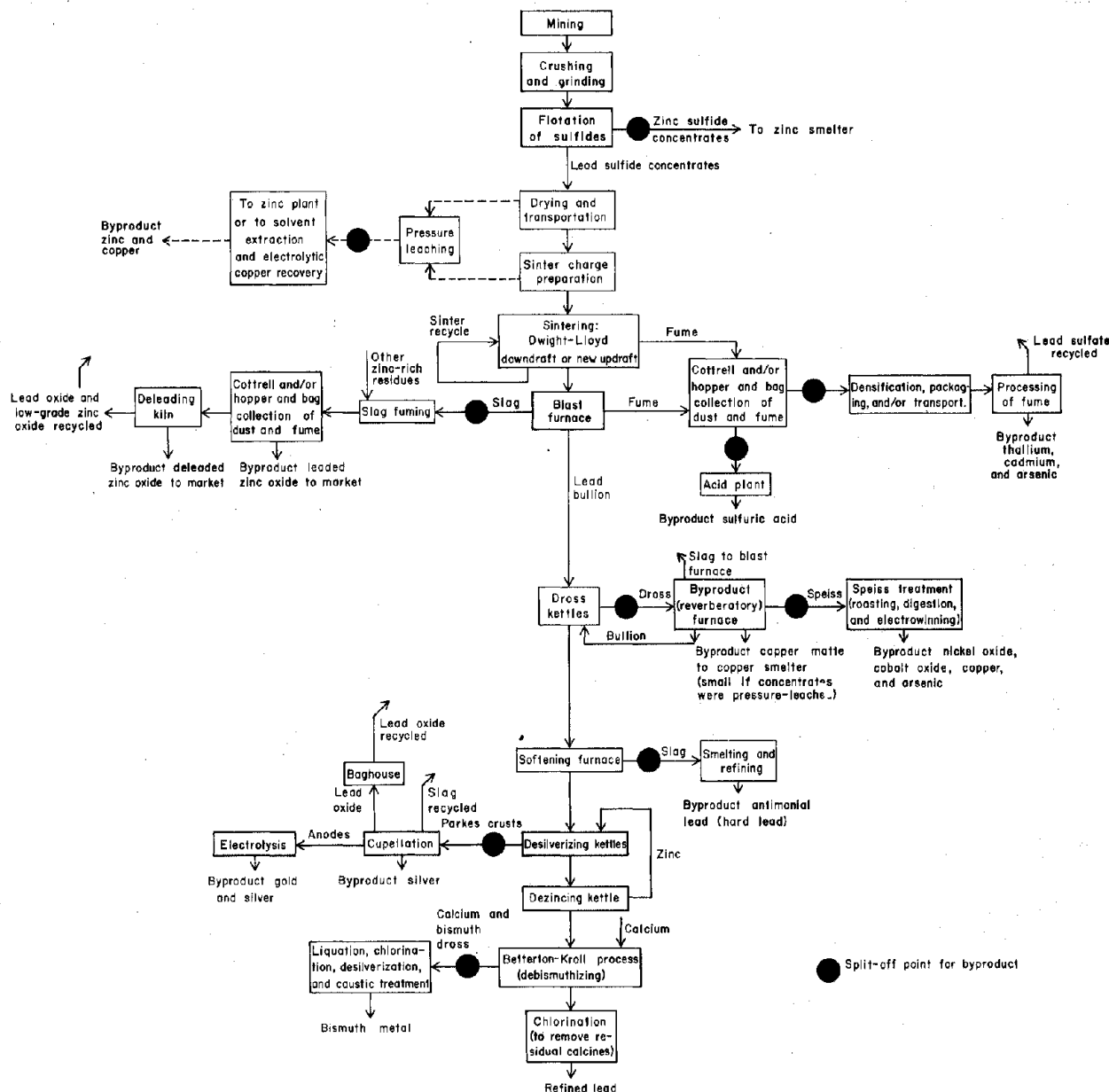


FIGURE 7. - Lead system showing byproduct metals.

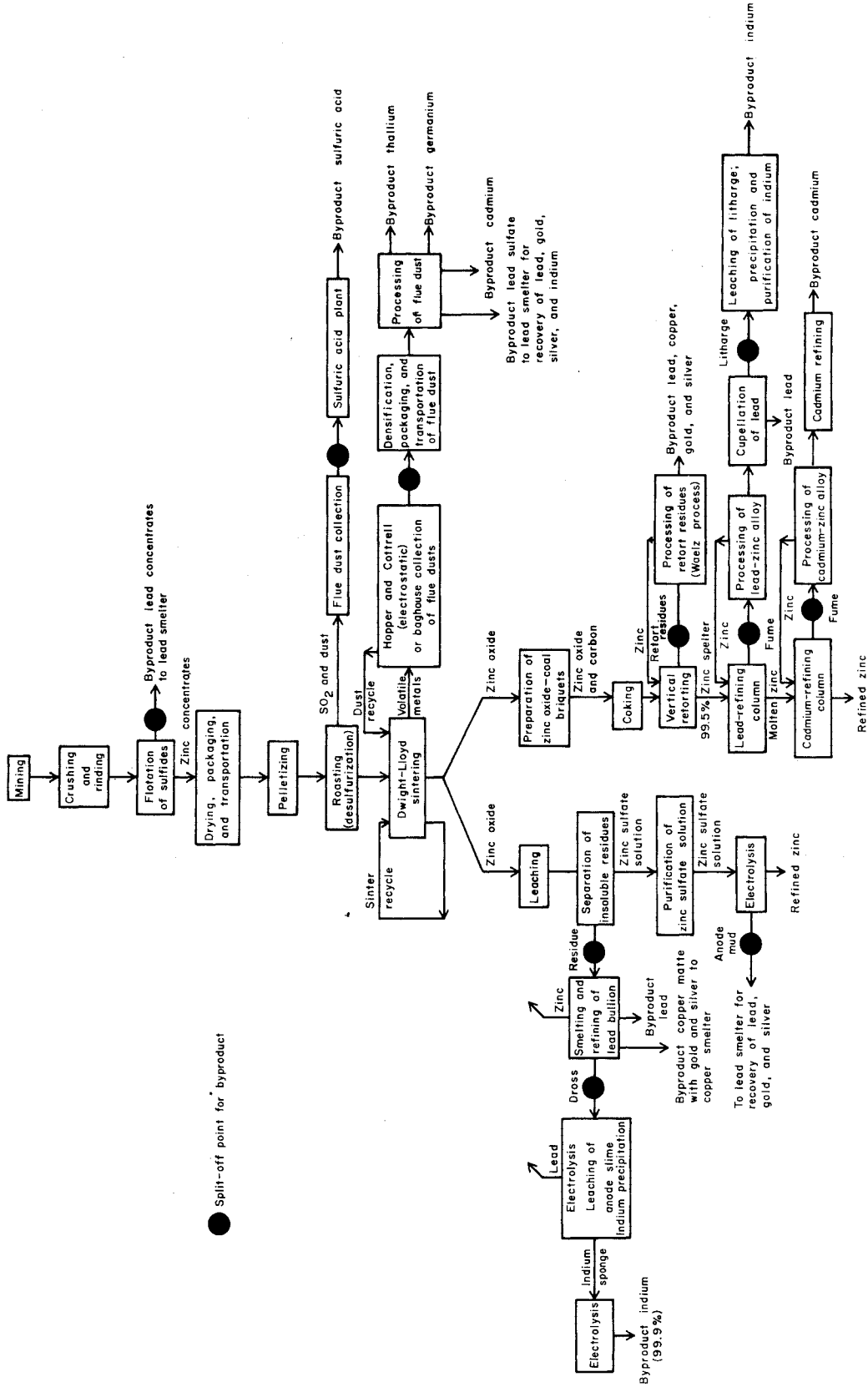


FIGURE 8. - Zinc system showing principal byproduct metals.

LEAD-ZINC DEPOSITS OF THE WORLD

Figures 9-12 show locations of recent and current districts and mines supplying lead and zinc concentrates to U.S. industry. More recent data on States and countries supplying lead and zinc concentrates and on their gold and silver contents are shown in pertinent following sections.

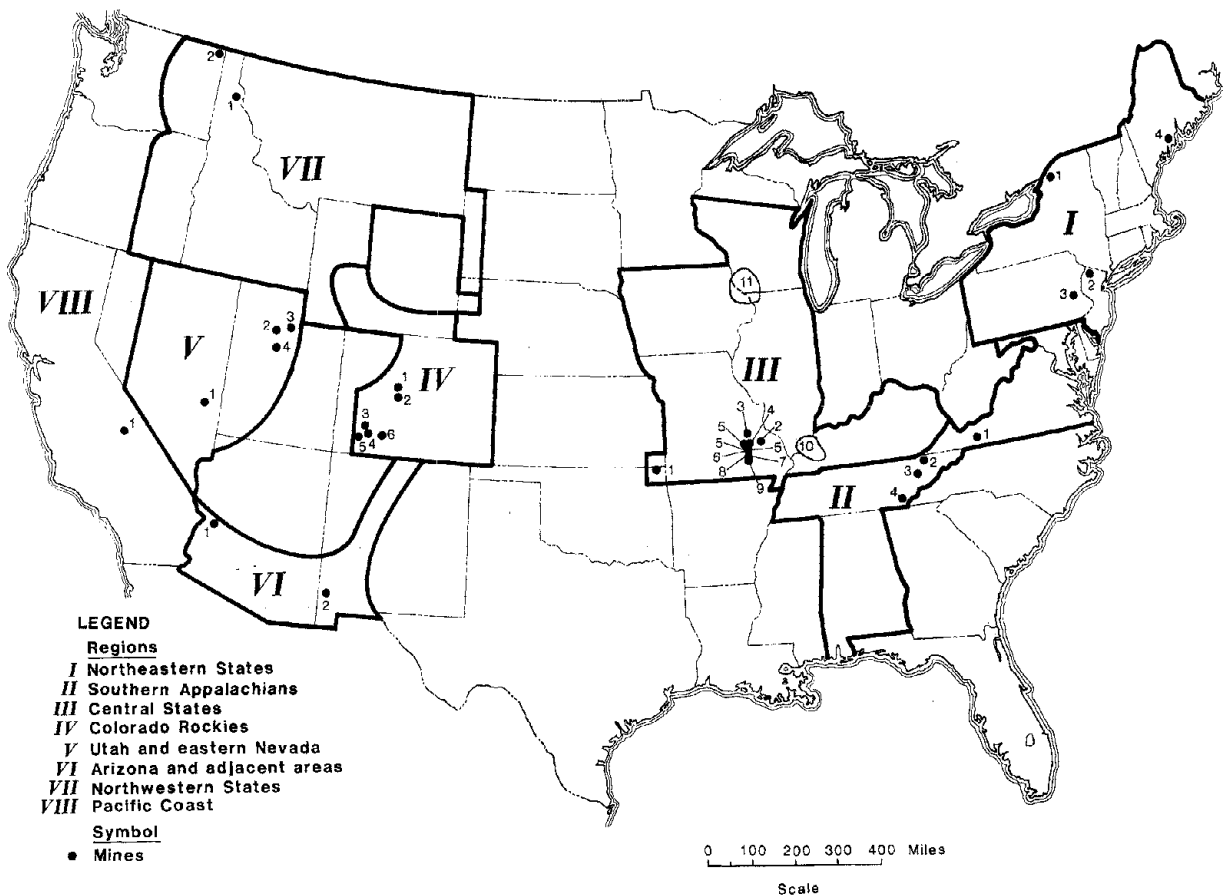


FIGURE 9. - Lead-zinc deposits of the United States, by regions and mines.

LEGEND

- A-Buchans Unit
- B-Walton
- C-Bathurst
- D-Newcastle
- E-Mafagami
- F-Orchan Mines, Ltd.
- G-Manitou-Barvue Mines, Ltd.
- H-Noranda-Rouyn Area
- J-Noranda Mine
- K-Timmins Area
- L-Geco Deposit
- M-Zenmac Deposit
- N-Rath Vermont Mine
- O-Silmonac Mine
- P-Jersey Mine, Reeves MacDonald Mine, Annex Mine
- Q-Highland-Bell Mine
- R-Western Mines, Ltd.
- S-Pine Point Mines, Ltd.
- T-Port Radium Area
- U-United Keno Hill Mines, Ltd.
- V-Anvil Mining Corp., Ltd.
- W-Senus Mines, Ltd.
- X-Sturgeon Lake Area
- AA-Uchi Lake Area
- BB-Lynn Lake (Granville Lake Dist.)
- CC-Rubin Mine
- DD-Fission Area
- EE-Wollaston Lake Area
- FF-Robb Lake Area
- GG-Tom Cicims
- HH-Placer Development, Ltd.
- KK-Bathurst Inlet
- LL-Arvik ML Deposit
- MM-Strathcona Sand Deposit

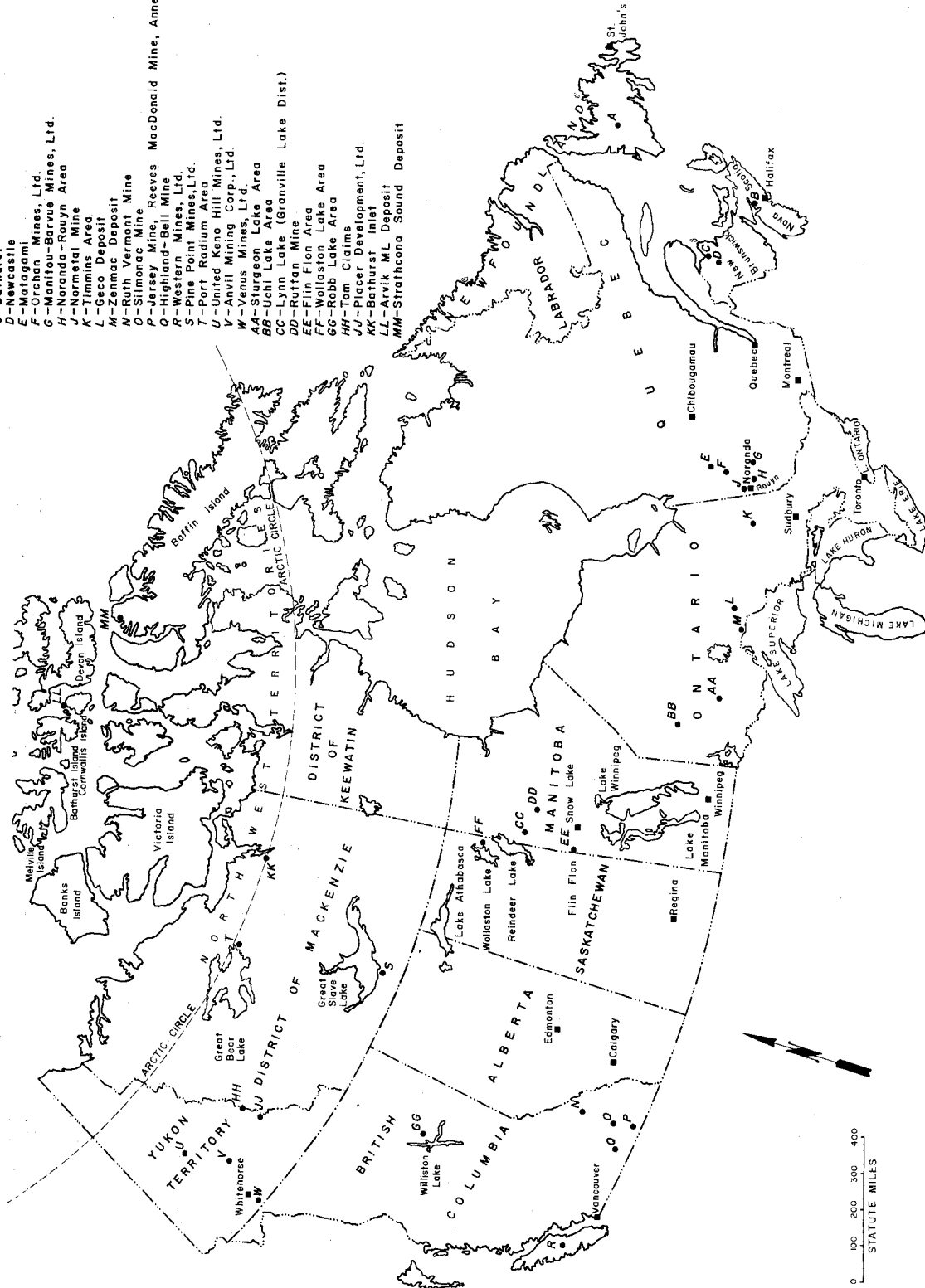


FIGURE 10. - Producing and potential lead-zinc areas and mines of Canada.



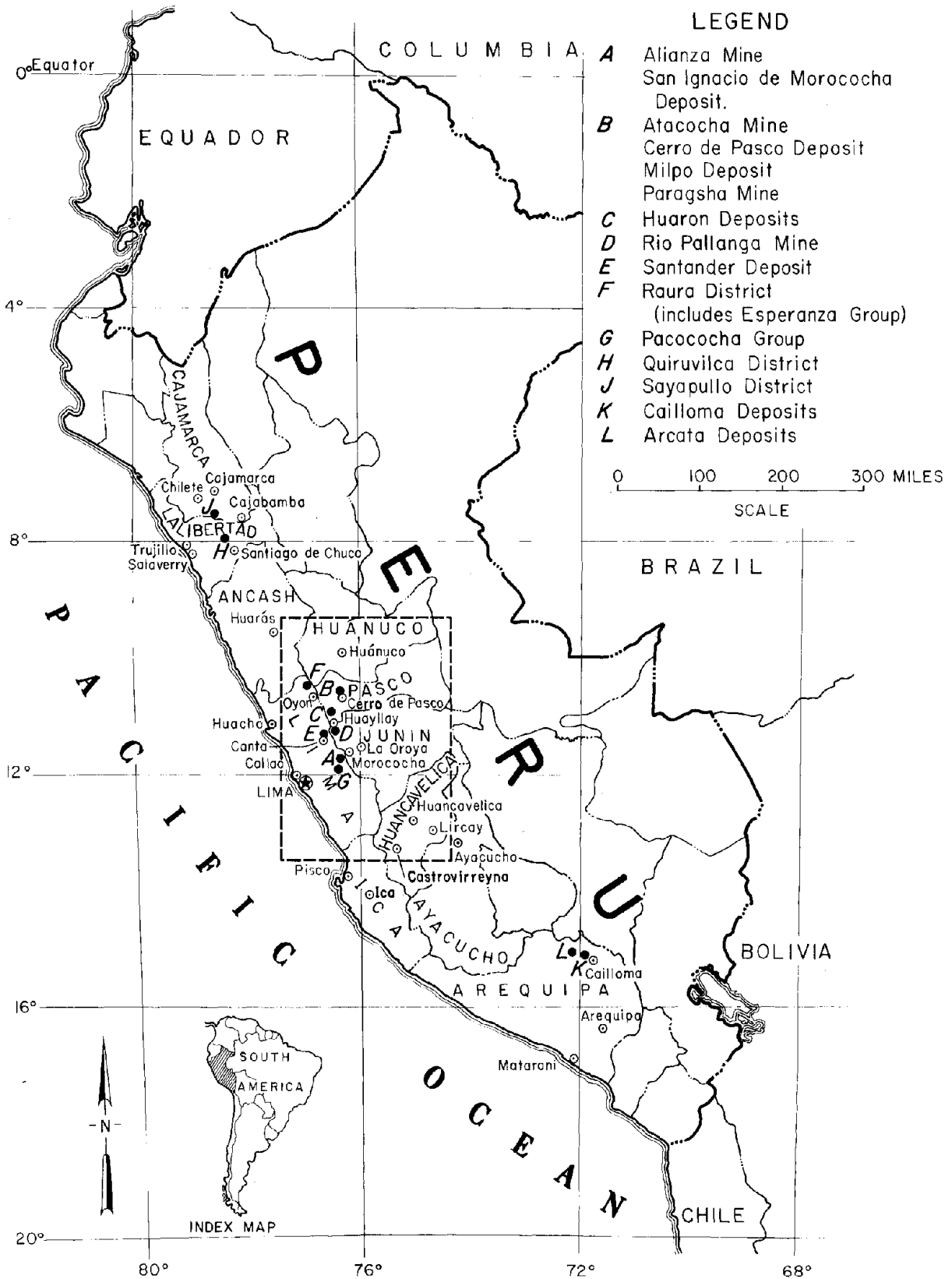


FIGURE 12. - Lead-zinc mines and mining areas of Peru.

## LEAD PROCESSING

The material flow in lead processing is shown in some detail in figure 7 and can be summarized as consisting of three major steps: (1) mining, crushing and grinding, and beneficiation to produce the lead concentrates; (2) sintering, followed by blast furnace smelting to produce lead bullion; and (3) refining the lead bullion through a number of metallurgical operations to produce commercially pure lead.

### Mining Through Beneficiation

For the purpose of this paper, which is concerned with minor metal flow during smelting and refining operations, discussion of the physical and mechanical operations involved in lead and zinc concentrate production is not included. The flow of minor metals is followed to the extent possible, even in cases where a commercial byproduct is not ultimately recovered.

### Sintering Operations

Most of the feed to sintering in the lead industry consists of domestic and foreign concentrates. The feed materials and products from sintering and from the various subsequent processes used in whole or in part in lead smelting plants are shown in figure 13 and table 1.

By weight, about 82 percent (924,000 tons) of total concentrates (1,133,500 tons) used by the industry in 1971 were of domestic origin, with Missouri supplying about 66 percent of the domestic materials; Idaho, about 13 percent; Utah, about 11 percent; Colorado, less than 5 percent; and Montana, about 2 percent. Other minor suppliers, in order, were Washington, California, Virginia, New Mexico, Illinois-Kentucky-Wisconsin, New York, Nevada, Arizona, Kansas, North Carolina, and Wyoming. In 1975, domestic lead concentrates received at six plants owned by four companies totaled 795,837 dry tons containing 552,039 tons of lead, the figures being respectively about 81 percent and 86 percent of total domestic and foreign lead concentrates received. The States supplying principal quantities of lead in domestic concentrates in 1975 were Missouri, 82 percent; Idaho, 9 percent; Colorado, nearly 5 percent; and Utah, nearly 2 percent. Other States included New York, Nevada, Virginia, New Mexico, Washington, Illinois, Arizona, Oklahoma, Montana, and California.

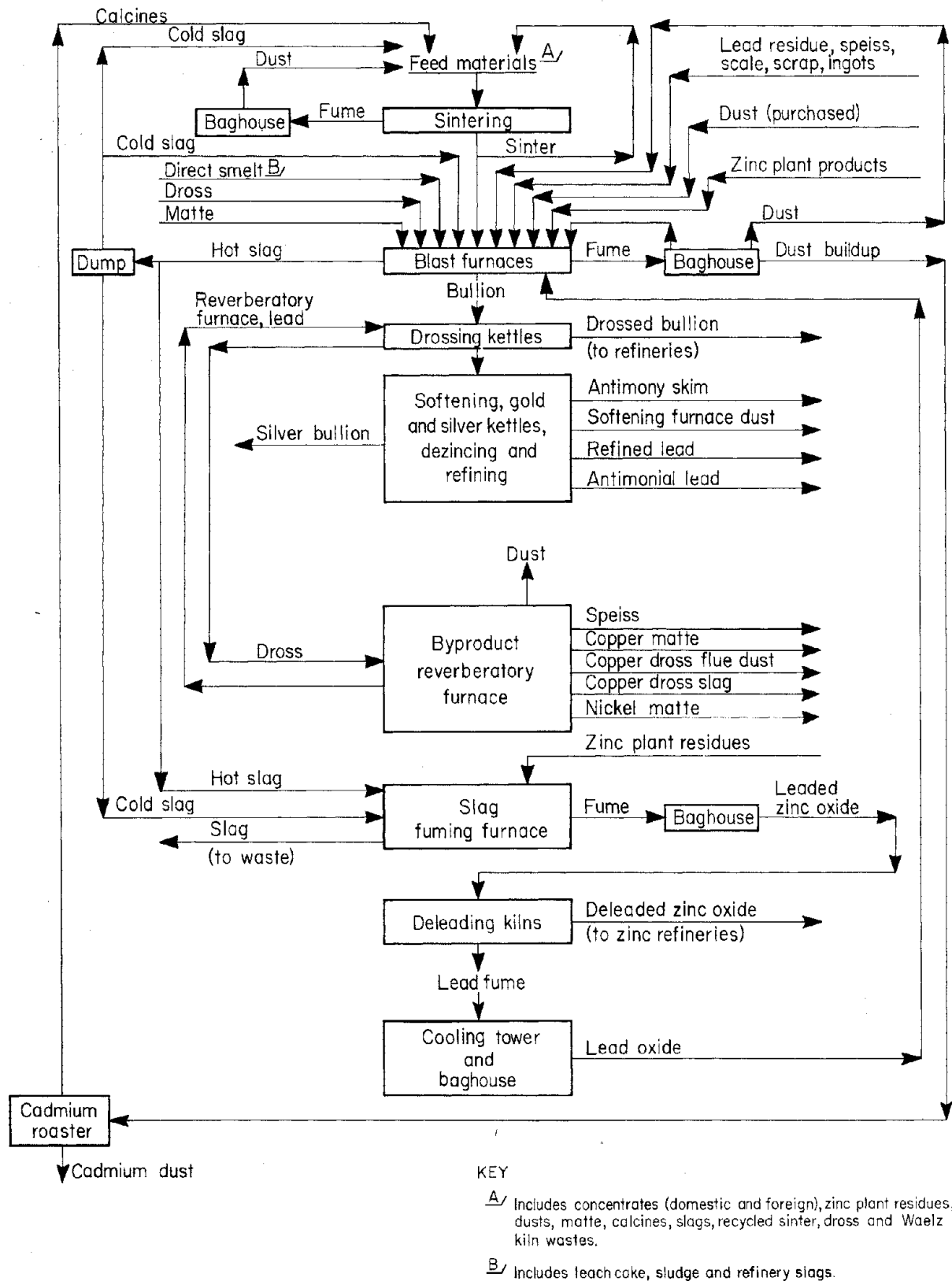


FIGURE 13. - Flowsheet for lead processing.

TABLE 1. - Byproduct minor metals in lead processing--inputs, outputs, plants, and weights

(Key to figure 13)

Process	No. of plants <sup>1</sup>	Short tons							Troy ounces	
		As	Sb	Bi	Cd	Se	Te	Tl	Au	Ag
Sintering:	7									
Input: Feed materials <sup>2</sup>		4,220	3,651	382	1,014	14	54	6-7	51,000	13,400,000
Output: Sinter.....	7	NA	NA	NA	NA	NA	NA	NA	NA	NA
Blast furnace:	7									
Input:										
Sinter.....	7	NA	169	90	NA	NA	NA	NA	42,798	2,445,789
Recycled fume.....		219	59	<sup>3</sup> 7	1,266	.3	.3	.3	22	16,845-
Purchased dust.....	3	283	52	209	74	NA	NA	NA	395	19,965
Lead residue, etc...	1	9	72	3	NA	NA	NA	NA	2,150	56,057
Zinc plant products.	1	Neg	1	.1	.1	NA	NA	NA	NA	270,678
Cold slag.....	1	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )
Direct smelt.....	1	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )
Dross.....	3	48	37	1.0	4.0	NA	NA	NA	90	3,337
Matte.....	1	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )
Output:										
Fume.....	2	219	69	7	1,266	.3	.3	.3	22	<sup>5</sup> 16,845-
Hot slag.....	6	72	325	13	17	<sup>6</sup> 8	<sup>6</sup> 11	<sup>6</sup> .4	1,071	19,965
Bullion.....	4	315	1,135	<sup>7</sup> 31-125	<sup>7</sup> 7-8	<sup>7</sup> 12	NA	<sup>7</sup> 1	85,270	<sup>8</sup> 45,623
Drossing kettles:	7									
Input: Bullion.....		315	1,135	<sup>8</sup> 11-105	<sup>7</sup> 7-8	2	NA	1	85,270	<sup>7</sup> 11,435,122-
Output:										
Dross.....	5	76	46	1	16	.1	.1	NA	NA	10,670
Drossed bullion....	3	<sup>9</sup> 38	<sup>9</sup> 1,052	<sup>9</sup> 377	NA	NA	43	NA	11,640	2,327,000
Softening furnace products:	4									
Output:										
Antimony skim.....	1	NA	NA	NA	NA	NA	NA	NA	NA	NA
Softening furnace dust.....	1	NA	NA	NA	NA	NA	NA	NA	NA	NA
Refined lead.....	4	0.1	<sup>10</sup> 1.5	12.5	6.5	Neg	NA	.22	NA	<sup>10</sup> 170,000
Antimonial lead.....	2	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )
Silver bullion.....	1	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )
Reverberatory furnace:	6									
Input: Dross.....	4	8	4	NA	3	<.1	<.1	NA	NA	2,350
Output:										
Speiss.....	4	3,107	1,525	NA	2	1.9	.1	NA	564	142,000
Copper matte.....	5	<sup>11</sup> 308	<sup>11</sup> 127	1	<sup>11</sup> 8	Tr	Tr	NA	3,801	144,500
Copper dross flue dust	1	} 125-229	40-97		2	2.4	.1	Tr	17	17,300
Copper dross slag...	1									
Nickel matte.....	1	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )	( <sup>4</sup> )
Slag fuming plants:	4									
Input:										
Hot slag.....	4	59	368	11	8	<sup>12</sup> 6	2	.2	1,070	<sup>12</sup> 48,600
Cold slag.....	3	25	4	.3	( <sup>4</sup> 3)	NA	NA	NA	NA	5,310
Zinc plant residues.	1	60	24	Neg	43				460	<sup>14</sup> 374,400
Output:										
Waste slag.....	4									49,791
Fume.....	4									
Deleading kilns.....	3									

NA Not available. Neg Negligible. Tr Trace.

<sup>1</sup> Plants using processes and showing quantities or assays on materials.<sup>2</sup> Includes 2 plants feeding calcines and 1 feeding cold slag.<sup>3</sup> Includes 0.22 and 0.24 percent bismuth at 2 plants.<sup>4</sup> Company confidential.<sup>5</sup> Includes 1.6 to 18.2 ounces silver per ton.<sup>6</sup> Includes 0.003 and 0.0005 percent selenium at 2 plants; 0.0005, 0.0008, 0.001, and 0.11 percent tellurium; 0.0001 and 0.0003 percent thallium at 2 plants; and 0.08 and 0.35 ounce silver per ton at 2 plants.<sup>7</sup> Includes 0.0003 to 0.07 percent bismuth; 0.0009 to 0.003 percent cadmium; 0.016 and 0.0015 percent selenium; 0.0006 percent thallium; 2.3 to 141.1 ounces silver per ton at 3 plants.<sup>8</sup> Includes 0.0003 to 0.33 percent bismuth at 3 plants.<sup>9</sup> Includes 0.025 percent arsenic; 0.32 to 1.08 (average 0.7) percent antimony; 0.075, 0.245, and 0.39 percent bismuth.<sup>10</sup> Includes 0.0005 percent antimony; 0.2 to 1.6 ounces silver per ton at 3 plants.<sup>11</sup> Copper matte at these plants totaled 40,300 tons with assays ranging from 0.2 to 1.05 percent arsenic at 4 plants; 0.1 to 0.44 percent antimony; 0.02 percent cadmium.<sup>12</sup> 0.003 percent selenium at 1 plant; 0.08 and 0.33 ounce silver per ton at 2 plants.<sup>13</sup> See hot slag and section, Cadmium in Fuming Operations.<sup>14</sup> Includes 12,200 ounces in zinc plant secondaries.

Of 209,500 tons of foreign concentrates in 1971, Canada was the foremost source, supplying about 46 percent largely from Ontario and British Columbia, Canada. Other countries and percents were: Peru, about 26 percent; Honduras, less than 13 percent; Australia, about 12 percent; and Mexico, most of the rest, largely from the State of Coahuila. By comparison in 1975, shipments of lead in foreign concentrates were 38 percent from Canada, 21 percent from Honduras, more than 18 percent from Peru, almost 14 percent from Australia, 7 percent from Greenland, and small percentages from Nicaragua and Colombia.

Sinter products include sinter, fume, and dust. Fume consists of volatilized metals or metallic compounds which are condensed as the temperature is lowered and carried by furnace gases into the flues. Sulfur trioxide and elemental sulfur are also classed as fume. In general, fume includes all the volatile constituents of the ore charge.

Sinter goes to the blast furnace; fume and dust goes to a Cottrell precipitator or baghouse. Flue dust is a simple recirculating load, but the fume can be recycled to sintering or reconcentrated and sent to another circuit or circuits for recovery of certain byproduct metals.

Quantitative data on these products at some plants are available through calculations based both on published information and personal communications. Sinter recycling was varied. Most of the dust and fume from sintering is recycled to the sintering plant. Only some analytical data are available for sinter.

Samples or assays on dust and fume were obtained from five of seven plants. Assays and weights were reported by most of the plants; samples of fume and dust also were assayed by the Bureau of Mines. Variations were noted in quantities and assays on Cottrell and baghouse dust received from the plants. Some of the plants reported total fume and dust collected, two operations indicated the quantities were for sinter dust and fume with both plants recycling the materials. Assays were varied, low contents of minor metals, for example, arsenic, occurring in the total dust and fume reported for each plant, and higher contents for those from sintering collected at Cottrell precipitators. Some of the high assays, for example, arsenic and antimony, were probably from sintering concentrates from complex ores relatively high in contents of these metals. Further details on these dusts and fumes will be given in discussions under the various minor metals in these products.

#### Sinter Feed and Products in Specific Lead Plants

Seven lead plants consumed domestic concentrates; three of these also consumed foreign concentrates.

About 59 percent of the domestic concentrates consumed at a large plant came from Colorado, the rest in order were from Missouri, New Mexico, Idaho, Virginia, the Illinois-Kentucky-Wisconsin district, California, Arizona, North Carolina, and Nevada. The largest suppliers of foreign concentrates to this plant were Honduras, 38 percent; Peru, 33 percent; and Australia, 14 percent; followed by Canada, 8 percent; and Mexico, 7 percent.

At this plant, in addition to concentrates, other sinter feed including in-plant generated sinter, slag, and dusts, and zinc plant residues, dusts, matte, and calcines from other sources totaled about 117,000 tons. Company assays on arsenic, antimony, bismuth, and cadmium were available on practically all the nonconcentrate feed materials. In general, slags (considered as primary lead-bearing byproducts) had a high content of antimony; some residues, sludge, and particularly calcines and speiss were high in arsenic; bismuth seemed to be concentrated in calcines and cadmium mostly in certain dusts or fumes.

One plant has recycled as much as 70 percent and as little as 30 percent of its blast furnace slag to sinter; another plant recycled nearly 70 percent of its sinter and also used dust, calcines, and matte in its sinter feed. Two other plants recycled slag as feed. Plants using zinc plant residues are shown in figure 1. One of these plants was the only one indicating that it used Waelz kiln wastes in sinter feed.

Data on weights or assays of sinter products or both were obtained or derived from six plants. Sinter weights were available from three plants; baghouse dust and fume weight or assay data or both were available from six plants.

#### Blast Furnace Operations

Blast furnace feed includes sinter, kiln and flue dusts, calcines, lead residue, lead dross, speiss, lead scale, ingots, scrap, zinc plant products, and reverberatory furnace slag. The only important feed materials, as indicated by data from three plants, were sinter and dusts. One plant (fig. 1) indicated that it also consumed scrap, lead residue, lead dross, speiss, lead scale, and ingots. The high assays on certain metals in copper plant dusts and recycled dusts used by two plants are noted under the individual metals.

Blast furnace products include bullion, dust, fume, and slag. Quantitative information on bullion and slag was available from four plants; assays for some metals are from three of these. One plant showed slag quantities but no assays; a second showed slag weights and assays. A third plant showed assays but no quantitative data for bullion, slag, and dust. Information on quantities of recycled dust and fume and assays were supplied by two plants. Some plants keep no record of the blast furnace fume produced but did supply samples for assay. At three plants about 70 percent of the slag was recycled to sinter or to slag fuming.

#### Drossing Operations

All lead plants have drossing sections in which the blast furnace bullion is treated primarily to remove copper, silver, and several other metals as a dross which is usually transferred to the plant's byproduct (reverberatory) furnace(s) or to another plant for processing. Quantitative data on blast furnace bullion were received from five plants. No quantitative or assay data were received for dross reverb bullion, a material probably introduced into the drossing sections of some plants. One plant estimated it recycled about

40 percent to the dross kettles. Drossing products include drossed bullion and copper (lead) dross. Three plants supplied quantitative and assay data on drossed bullion. Quantitative and assay data on copper dross were procured from two plants and a third supplied only quantitative data. Two of the plants supplied data on both drossed bullion and dross. Dross was said to be about 28.5 percent of weight of original bullion but figures from the plants indicated a wide variation in this (49). Another reference said that dross will usually amount to 10 to 35 percent of the blast furnace bullion (79).

The tenor of some of the minor metals in the drossed bullion is sometimes higher than that in the blast furnace bullion input. This observation is complicated by the limited availability of assays on both blast furnace bullion and drossed bullion within the same plants.

#### General Information About Softening Furnace Feed and Products

Except for the analyses from various plants indicated in the preceding sections on drossing products, no data on drossed bullion feed to the softening furnaces were available. Weights of products from softening furnaces were known, including silver bullion from one plant and various types of refined lead at four plants, including three in southeastern Missouri. Antimonial lead assays were obtained from one plant. No data were available on other products such as decoppered dross, slag, calcium-bismuth dross, and crusts.

#### Reverberatory Byproduct Furnace Feed and Products

Not all lead plants have reverberatory furnaces. Of those that do, feed consists mostly of copper (lead) dross, but can also include decoppered skimmings (also called dross) and dust. Only one plant provided assays but did not provide dross tonnages. Products consist of dust, slag, matte (copper and nickel), speiss, bullion (recycled to drossing), copper dross slag, and copper dross flue dust. Only one plant did not provide any matte data. No lead bullion data were obtained.

#### Slag Fuming in 1971

Processing is discussed in a number of metallurgical texts or articles (24, 49, 69, 72, 83). The feed at four operating plants was mostly new hot slag (over 90 percent); cold slag from other sources was less important. In 1971, 552,727 tons of new hot slag and 50,867 tons of old cold slag were processed (81). Only one plant indicated that it used hot slag exclusively. In addition to cold slag, one lead plant also used some zinc plant residues. Zinc fume weight constituted about 19 percent of the input weight of slag and other materials. The fume from two plants was about 17 and 18.5 percent of the input; two others averaged about 19.8 percent. In 1971 the fume contained about 71 percent recoverable zinc. There were no production data on leaded and delead fume.

### Arsenic in Concentrates to Lead Plant Sintering

A flowsheet for lead processing in 1971 is shown in figure 13. This figure and table 1 are complementary in providing data on arsenic and the other minor metals.

Of the 2,294 tons of arsenic in concentrate feed, 36 percent was in domestic material, with Idaho supplying about 40 percent; Utah, 24 percent; Montana, 15 percent; Colorado, 10 percent; and Missouri (including some New York State concentrates), less than 10 percent. A small amount occurred in concentrates from New Mexico, Washington, Virginia, California, Illinois-Kentucky-Wisconsin, and even less from Arizona, North Carolina, Nevada, Kansas, and Wyoming.

Foreign concentrates accounted for 64 percent of the arsenic with almost 50 percent of that being from Peru, about 38 percent from Canada, about 7 percent from Australia, and the rest from Honduras, Mexico, Argentina, Brazil, and Colombia.

Domestic concentrates, those derived from the complex ores of Montana, Idaho, Utah, and Colorado, were generally higher than those from other domestic sources in arsenic content.

Due to the high content of arsenic in Peruvian materials (some of which assayed more than 2 percent), the average content of arsenic in foreign concentrates was about eight times that in domestic concentrates. The average for all Canadian concentrates was about 0.6 percent arsenic.

### Arsenic in Other Sinter Feed in Lead Plants

The four lead plants using electrolytic zinc plant residues consumed about 219,000 tons of the material. Much of this was used by one plant in the Southwestern United States; two other plants in the Northwest used most of the remainder. The large tonnages to the Northwest plants contained 0.41 and 0.37 percent arsenic; those at the Southwest plant averaged somewhat more. The known total arsenic in these residues, and in a smaller quantity with a lower arsenic percentage used at a Missouri plant, totaled about 1,003 tons.

Slag known to be used as feed by four plants totaled about 200,000 tons. The arsenic content of slag used as feed is estimated at 12 tons, a small quantity when compared with the tonnages in concentrate feed and in zinc plant residues.

Calcines from one plant, which has since closed, were used at two lead plants, Waelz kiln wastes at another, and matte at two others. Two plants fed significant quantities of unrecycled dust to sintering. The calcines averaged 9 percent arsenic; the kiln wastes, from two sources, averaged less than 0.1 percent; and nearly 6,000 tons of matte averaged about 0.9 percent arsenic. The dusts fed to sinter at the two plants averaged 6 percent arsenic. Together, the arsenic content in the known quantities of calcines, Waelz kiln wastes, matte, and dusts consumed was about 923 tons, most being present in the dusts. Total arsenic content of sinter feed, excluding slag, is shown in table 1.

### Arsenic in Dust and Fume

Assays for arsenic in these materials at four plants ranged from 0.014 to 5.68 percent, the lower figure being on total fume and dust, the high percentage being on sinter fume recovered at a Cottrell and recycled to the blast furnace. Although a substantial quantity of arsenic was in the sinter fume recovered from a precipitator at one plant, the figure was only about 8 percent of the 2,090 tons of arsenic known to have entered with the total sinter feed to the plant. Very little arsenic showed in the dust and fume from other plants.

### Arsenic in Blast Furnace Feed and Products

The total known feed of arsenic to blast furnaces is shown in blast furnace input (table 1). The quantities of arsenic in sinter are not available. Sludge, refinery slag, leach cake, dross, matte, and slag were used at one plant and contained various quantities of arsenic.

In some plants, arsenic was not determined in the bullion products. In one case it was extremely low (0.0008 percent), but bullion from one lead plant ran as high as 0.2 percent arsenic. Some published blast furnace bullion assays ranged from 0.01 to 1.1 percent arsenic (49, 79). Recycled fume and dust in this study contained from 0.5 to nearly 6 percent arsenic. The arsenic content of slag, mostly recycled, ranged from about 0.001 to 0.03 percent; an older typical assay for slag showed as much as 0.1 percent arsenic (79). The total known arsenic in all these products (slag, fume, and bullion), about 606 tons, is shown in table 1.

### Arsenic in Dross Feed and Products

Arsenic assays of bullion from two plants are shown above. Another plant estimated it recycled about 40 percent dross reverb bullion to drossing. The arsenic content of the input bullion is shown in table 1. Assays and weight of drossed bullion available from three plants producing about 150,000 tons of bullion annually, also are shown in table 1.

The quantities of dross produced from quantities of blast furnace bullion at three plants varied considerably, being about 13.6, 9.9, and 44.3 percent of blast furnace bullion input. The first two are comparable to ratio data calculated from typical weights of base bullion and dross (79). At another plant, dross was about 46 percent of the total dross and drossed bullion. This compares with a figure of 44 percent at a second plant for which quantities of both dross and drossed bullion are known. The 26,000 tons of dross produced at two of five plants contained the content of arsenic shown in table 1. At another plant, arsenic content of dross has ranged from 2 to 4 percent in recent years.

### Arsenic in Softening Furnace Products

There is little information on these materials shown in table 1. However, a significant amount of arsenic was present in the antimonial lead produced at one plant; the softening furnace dust at this plant contained 1.6 percent arsenic.

### Arsenic in Reverberatory Furnace Feed and Products

The dross feed at one of four plants contained about 8 tons of arsenic (table 1); the arsenic percentage was small. Quantitative data on dross were not available at another plant using concentrates from complex ores, but the arsenic content has ranged from 2 to 4 percent in recent years. Assays of drosses at a large southwestern lead plant in the early 1940's ranged from 6.69 down to 4.3 percent arsenic. No arsenic was detected in byproduct furnace slag from one southeastern Missouri plant; and no other data were available on dust and slag from other plants. Copper matte data are shown in table 1. The assays in the table can be compared with those (1.57 and 2.19 percent) in matte during 1943-44 at a southwestern lead plant (19).

Nickel matte was produced at a Missouri lead plant. Speiss, totaling about 19,200 tons produced at three plants and averaging about 15.8 percent arsenic, was equivalent to 3,034 tons arsenic. This is comparable with the arsenic content of speiss (14.99 and 15.29 percent) in 1943-44 at a southwestern lead plant (19).

A Bureau of Mines assay indicated another type of speiss at another plant contained about 73 tons arsenic.

### Arsenic in Fuming Operations

Arsenic was determined in the new slag at one plant using 34 percent of the hot material and in the cold slag used at another plant. Assays on fume at another plant indicated almost 1 percent arsenic in leaded fume and 0.019 to 0.0044 percent arsenic in delead fume. A high-zinc deleading-kiln product from another plant contained 0.13 percent arsenic.

### Arsenic, Antimony, Bismuth, and Cadmium in Cadmium Roaster Feed

Only two plants showed assays for dusts fed to their cadmium roasters. These assays were: arsenic, 4.65 and 5.01 percent at one plant and 0.54 percent at the second; antimony, 0.20 and 0.33 percent at one plant and 0.55 percent at the second; bismuth, 0.06 and 0.14 percent at the first plant and 0.08 percent at the second; and cadmium, 9.12 and 18.75 percent at the first plant and 4.28 percent at the second. Quantities, particularly cadmium in dust feed, could not be equated with those in output, probably because total quantities of feed materials to the roasters were not available.

### Antimony in Concentrates to Lead Plant Sintering

More than 60 percent of the total antimony from concentrates entered the system as domestic material, with Idaho accounting for 80 percent, Utah 12 percent, and Colorado 4 percent, followed by Montana, Missouri (including New York State), New Mexico, Washington, California, Illinois-Kentucky-Wisconsin, North Carolina, Virginia, and traces from Arizona, Wyoming, and Kansas.

Peru (60 percent) and Canada (25 percent), were the major foreign sources of antimony in lead concentrates, followed by Australia (13 percent), Honduras,

Argentina, Mexico, Colombia, and Brazil. The average antimony content of foreign concentrates was almost four times that of the U.S.-derived material. Peruvian concentrates were the highest of all foreign materials. Idaho and Utah concentrates were the highest of all U.S. material in antimony content.

#### Antimony in Other Sinter Feed in Lead Plants

The antimony contents of the zinc plant residues used by three lead plants were 0.12, 0.13, and 0.17 percent. The antimony in the residues totaled 318 tons. This figure is relatively small when compared with the 3,114 tons of antimony in concentrates. Two plants sintering undisclosed quantities of slag had 0.08 and 0.045 percent antimony in their slags. With assays on recycled slags at four plants ranging from 0.002 to 0.06 percent antimony, as much as 24 tons of antimony could be in this part of their sinter feed.

The calcines used at two lead plants contained about 2 and 3.2 percent antimony, and the matte used at two other plants contained 0.21 and 0.33 percent antimony. The known antimony content in the calcines, kiln wastes, matte, dusts, and zinc residues was about 537 tons; about 59 percent in the residues and 22 percent in the dusts. Cottrell dusts used at two lead plants averaged about 1.3 percent antimony. Total antimony content of the sinter feed, exclusive of slag, is shown in table 1.

#### Antimony in Dust and Fume

Assays for antimony ranged from 0.0033 to 2.31 percent, with the high percentage being on sinter fume recovered at a Cottrell precipitator at one plant. The antimony in the recovered sinter fume constituted only a small part of the 1,870 tons of antimony in the total sinter feed (excluding recycled dust) to the plant.

#### Antimony in Blast Furnace Feed and Products

Assay data available at one lead plant indicated almost 170 tons of antimony in the sinter. The antimony content of other materials consumed in the blast furnace of the same plant totaled about 72 tons, the highest percentages being in lead residue and scale. Purchased dusts at one plant ran from about 2 to nearly 3 percent antimony. Another plant had a significant quantity of antimony in matte, dross, dump slag, leach cake, sludge, and refinery slag fed to the blast furnace.

Excluding antimony in sinter at the plants, the known disclosable quantity of antimony in blast furnace feed is shown in table 1 compared with the larger known total determined in blast furnace products. However, applying a more recent assay to bullion produced at one plant indicated that more than 1,000 tons of antimony was in bullion at that plant. Some plants provided quantities and assays only on blast furnace products. Assays on bullion in this study showed 0.105, 0.054, 0.008, and as much as 0.73 percent antimony. Some blast furnace bullion assays in the literature ranged from 0.16 to 2.9 percent antimony (49).

### Antimony in Dross Feed and Products

Antimony weight and assay data for drossed bullion are shown in table 1. A typical drossed bullion was said to be about 1.75 percent antimony (79). Antimony in dross product at two plants is shown in table 1. Another plant indicated that in recent years the material has contained 1.6 to 2.0 percent antimony.

### Antimony in Softening Furnace Products

At three plants the quantity and assay of antimony in refined lead is shown in table 1. Analyses from the literature showed combined antimony and arsenic of 0.0000 to 0.0001 percent at one southeastern Missouri plant.

### Antimony in Reverberatory Furnace Feed and Products

Dross feed at one of four plants contained about 4 tons of antimony. Compared with the very low antimony content at this plant, dross at another plant was said to contain 1.6 to 2 percent antimony. The antimony contents of dross in the early 1940's at a large southwestern plant ranged from 1.00 to 3.39 percent. Copper matte assays ranged from 0.1 to 0.44 percent antimony; matte, in 1943-44, contained 0.65 and 0.78 percent antimony (19).

Speiss averaged about 7.7 percent antimony. Based on four company assays, another type of speiss contained about 56 tons of antimony. At one lead plant, copper dross slag contained 3 percent antimony, and copper dross flue dust contained 0.6 to 4 percent antimony.

### Antimony in Fuming Operations

The input of antimony in new and old slag and in zinc plant residues is shown in table 1. Leaded fume at the lead plant using zinc plant residues averaged 0.11 percent antimony; delead fume averaged 0.065 percent antimony. A high-zinc deleading-kiln product from another plant contained 0.085 percent antimony. Zinc oxide from slag furnace fume at one plant contained about 0.2 to 0.3 percent antimony.

### Bismuth in Concentrates to Lead Plant Sintering

Analytical data on bismuth in sinter-hearth feed are based on concentrates having assays used by six of seven plants using domestic feed. Bismuth assays were available on foreign concentrates from three plants using such material.

Colorado (about 25 tons), Idaho (about 23 tons), and Utah (about 22 tons) were the main sources of the 99 tons of known domestic bismuth in concentrates. California, Missouri, and New Mexico contributed most of the rest. California concentrate was important because of its high bismuth content, 0.17 percent. The importance of bismuth from Missouri reflects the large quantity of lead concentrate coming from that State.

Peru (55 percent) and Canada (25 percent) were the major foreign sources of bismuth (about 112 tons). Australia also was an important source. The highest bismuth contents were in concentrates from New Brunswick, Canada, and from Colombia (about 0.2 percent).

#### Bismuth in Other Sinter Feed in Lead Plants

Assays on the zinc plant residues used at three plants showed 0.01, 0.018, and 0.031 percent bismuth; at a fourth plant the bismuth content was considerably lower, 0.0018 percent. Known bismuth content of zinc residues feed at lead plants was estimated at 47 tons.

Less than 2 tons of bismuth were present in the slag fed to sintering.

Calcines used by two plants assayed 1.5 and 2.0 percent bismuth; kiln wastes used at another plant assayed 0.0017 percent bismuth; and mattes used at two plants assayed 0.01 percent bismuth. The bismuth content in the foregoing three types of feed was about 58 tons, almost all in the calcines. The Cottrell and other dusts used in two U.S. plants averaged about 0.7 percent bismuth, adding about 66 tons to the total feed. This means that the dust, calcines, kiln residues, and matte contained about 124 tons of bismuth. Total bismuth content of sinter feed, excluding slag, is shown in table 1.

#### Bismuth in Dust and Fume

Recycled sinter fume data are present in table 1. Bismuth was not detected in fume and dust from plants using low-bismuth concentrates and other low-bismuth sinter feed. In a plant that recycled sinter dust, the dust contained about 4 percent of the total bismuth in the sinter feed (excluding recycled dust).

#### Bismuth in Blast Furnace Feed and Products

Bismuth assay data on blast furnace feed are available from three plants. These include data on dust from one plant; sinter, dust, lead scale, and scrap from a second; and dust, dross, sludge, refinery slag, and matte from a third. The sinter fed to the blast furnace at the second plant contained more bismuth than was normal in the sinter feed. The assays on dust ranged from 0.01 percent through 0.24 percent (on recycled material) and from 2.21 percent (on copper plant dust) to about 4 percent. Bismuth contents of the other feed materials at the latter plant were generally not known. Excluding bismuth in sinter at one plant, the known bismuth content of the feed materials at the three plants was 235 tons, about 67 percent of which was in Cottrell dust.

Weight and assay data on bismuth in bullion products are shown in table 1. Blast furnace bullion assays in the literature ranged from 0.008 to 0.20 percent bismuth (49). Bismuth contents of dust were low. In most cases, bismuth was not detected in slag but the bismuth content at two plants where it was detected is shown in table 1.

### Bismuth in Dross Feed and Products

Data on bismuth in blast furnace bullion feed and in drossed bullion product at three plants are shown in table 1. The bismuth tenor of drossed bullion at one plant (0.245 percent) is considerably greater than that (0.033 percent) in blast furnace bullion input. A bismuth content of 0.01 to 0.03 percent was said to be typical of bismuth in blast furnace bullion (79).

Dross produced at the only plant for which data were available contained slightly more than 1 ton of bismuth.

### Bismuth in Softening Furnace Products

The bismuth content of refined lead was known mostly from one of two plants providing quantitative and assay data. Analyses from the literature showed 0.0000 to 0.0001 percent bismuth at another large plant.

### Bismuth in Reverberatory Furnace Feed and Products

Based on assays of 0.004 and 0.01 percent bismuth in copper matte at one plant, the bismuth content of the matte would be less than 1 ton. Nickel matte contained less bismuth than did copper matte. A type of speiss at one plant contained a small percentage of bismuth.

### Bismuth in Fuming Operations

Bismuth in hot slag at two plants accounting for about 42 percent of the total hot slag input totaled about 11 tons. This and the bismuth in cold slag at one plant are seen in table 1. Leaded fume at the latter plant contained about 0.05 percent bismuth; delead fume contained 0.002 and 0.01 percent bismuth.

### Cadmium in Concentrates to Lead Plant Sintering

The average cadmium content of domestic concentrates was 0.045 percent, with the highest content, 0.2 percent, in Utah concentrates. Some Colorado concentrates also were significantly higher than average. Of the 541 tons of cadmium known in concentrates, almost 80 percent was of domestic origin with Missouri contributing 44 percent of the U.S. total, Utah contributing 38 percent, and Idaho and Colorado contributing the rest.

Honduras (with the highest foreign cadmium content), Peru, and Canada were the major sources of cadmium in foreign lead concentrates. Smaller quantities were shipped by Australia, Brazil, Mexico, and Argentina.

### Cadmium in Other Sinter Feed in Lead Plants

Twenty-one assays were available on the cadmium content of the zinc plant residues used by lead plants. At two northwestern plants, assays showed the presence of 0.18 percent cadmium at one plant and 0.2, 0.3, and 0.38 percent cadmium at the second plant. Cadmium in various types of zinc residues used

at a third plant ranged from 0.008 to 0.91 percent. Several assays at a mid-western plant showed 0.09 percent cadmium on about 90 percent of the material used, and much smaller percentages on the smaller tonnage of residues. The cadmium content of the electrolytic zinc plant residues was 433 tons.

Five assays on slag ranged from 0.001 to 0.008 percent cadmium. It was calculated that 4.7 to 9.7 tons of cadmium were present in recycled slag. These quantities are minor when compared with the tonnages of cadmium in lead concentrates and in zinc plant residues.

A cadmium content of 0.9 percent was detected in the calcines used at one plant; no cadmium was shown in similar material used at a second plant. Matte used at two plants assayed 0.104 percent cadmium, totaling about 6 tons of cadmium. The Cottrell dust (0.86 percent cadmium) and a small quantity of other dust contained about 23 tons of cadmium. About 40 tons of cadmium was present in the dust, calcines, kiln wastes, and matte. As shown in table 1, sinter feed, excluding slag, contained 1,014 tons of cadmium.

#### Cadmium in Dust and Fume

The cadmium content of dusts ranged from 0.2 to an average of 13.4 percent. The latter was the average of two dusts from other sources fed to a cadmium roaster at one plant. Another plant fed blast furnace fume containing 4.28 percent cadmium to its cadmium roaster.

Variations in cadmium content of dusts from the New Lead Belt plants indicated that, in general, the lower percentages of cadmium were in unrecirculated dust and the higher percentages were in enriched material.

Some of the cadmium assays were on baghouse dust (recovered from weak sinter gases and blast furnace fumes) and on acid plant baghouse dust. With the plants showing Cottrell sinter dust, the quantities of cadmium in the dust were about 79 percent and about 9 percent of the cadmium in the calculated total sinter feed to each plant.

#### Cadmium in Blast Furnace Feed and Products

Assay data on dusts used at one plant could be applied to the determination of cadmium in these materials. At one plant the input of cadmium in concentrates and other feed is more than 10 times that present in recycled dust at the plant. Assays on a variety of dusts fed to another blast furnace plant averaged 1.6 percent cadmium.

Two plants with cadmium roasters sent dust, averaging 60 percent cadmium, to refineries. Data on bullion product and on blast furnace slag for which both quantities and assays are known are shown in table 1. Cadmium assays for some slags ranged from 0.001 to 0.008 percent, but cadmium was not detected in large quantities of slag produced at two plants.

### Cadmium in Dross Feed and Products

Data on cadmium in blast furnace bullion input, cadmium contents of drossed bullion, and in the dross produced at two plants are shown in table 1. These totals could not be balanced due to lack of data on both blast furnace bullion and drossed bullion from within the individual plants. One plant showed quantities of blast furnace bullion and drossed bullion product.

### Cadmium in Softening Furnace Products

Very small quantities of cadmium were detected in refined lead, the tonnage in table 1 being estimated for two plants. Most was in lead produced at one plant where the average was about 0.005 percent cadmium. Analyses from the literature showed a range of 0.0001 to 0.0005 percent cadmium in the lead product at a large southeastern Missouri plant.

### Cadmium in Reverberatory Furnace Feed and Products

The relatively small amount of dross fed to one Missouri lead plant contained the small quantity of cadmium shown in table 1. Another plant showed no tonnage figures for dross feed which contained 0.02 percent cadmium. Data on cadmium in copper matte, in two types of speiss, and in combined copper dross slag and copper dross flue dust are shown in table 1.

### Cadmium in Fuming Operations

The input of cadmium in hot and cold slag at three of these plants was about 8 tons, as shown in table 1. Cadmium content of slag at two plants was about 0.001 to 0.002 percent; at the third plant it was 0.003 to 0.004 percent. Most of the known cadmium was in zinc plant residues. Deleaded fume produced at one plant contained 0.002 to 0.01 percent cadmium; zinc oxide from slag fuming at another plant contained 0.004 to 0.01 percent cadmium.

### Selenium in Concentrates to Lead Plant Sintering

Information on selenium is based on partial data from three lead smelters. Selenium was not detected in Missouri concentrates, which were about two-thirds of the total domestic lead concentrates used. Apparently, California was the major source of known selenium in domestic lead concentrates because of its relatively high selenium percentage, 0.09 percent. Selenium also occurred in concentrates from Colorado, Idaho, and Utah.

Three plants used foreign concentrates. One showed a small quantity of selenium in a concentrate from British Columbia, Canada. The data indicate that only about 8 percent of the selenium came from sources outside the United States, principally Canada.

### Selenium in Other Sinter Feed in Lead Plants

Selenium assays were available only on the zinc plant residue used at one lead plant, and on most of the material from another plant. Assays showing

0.0005 and 0.006 percent selenium were available on nearly half of these materials. The total selenium based on analyses was slightly over 3 tons. Very little selenium occurred in slag feed.

Only the concentrates and zinc plant residues were important as sources of selenium. The total known input of selenium from all sources is shown in table 1.

#### Selenium, Tellurium, and Thallium in Dust and Fume

Assays of these metals in dusts generated in the plants and collected from all operators were: selenium, 0.002 and 0.001 percent; tellurium, 0.001, 0.0002, and 0.0006 percent; and thallium, 0.0013 and 0.0006 percent.

#### Selenium, Tellurium, and Thallium in Blast Furnace Feed and Products

Except for recycled fume assays, no data are available on these minor metals in blast furnace feed (table 1). Some bullion products contained 0.016 and 0.0015 percent selenium and 0.0006 percent thallium. Blast furnace bullion assays in the literature ranged from 0.01 to 0.036 percent tellurium (49). Dusts generated in blast furnaces contained 0.0015 and 0.035 percent selenium, 0.0007 and 0.075 percent tellurium, and 0.002 and 0.032 percent thallium. Practically all of these dusts are passed through baghouses and then recycled to sintering.

Data on selenium, tellurium, and thallium in slag are shown in table 1.

#### Selenium, Tellurium, and Thallium in Dross Feed and Products

Only two plants showed selenium in their blast furnace bullion feed. About 2 tons of selenium (0.0015 percent) was in the blast furnace bullion fed to the drossing kettles at one plant. Blast furnace bullion assays reported in the literature ranged from 0.01 to 0.036 percent tellurium (79).

No quantitative data on dross reverb bullion recycled to drossing from the reverberatory (byproduct) furnace were available. One plant estimated it recycled 40 percent of its dross reverb bullion. No information was available on tellurium input. At one plant, about 1 ton of thallium was present in the blast furnace bullion.

Assays on drossed bullion at three plants and on dross at one plant indicated the selenium and tellurium contents shown in table 1.

#### Selenium, Tellurium, and Thallium in Softening Furnace Products

The tellurium content of silver bullion and refined lead at one plant was below the detection limit of 0.0002 percent. Thallium in refined lead at this plant amounted to the small quantity shown in figure 1.

### Selenium, Tellurium, and Thallium in Reverberatory Furnaces

Dross fed to a reverberatory furnace at one plant contained less than 0.1 ton each of selenium and tellurium. No assays for selenium, tellurium, or thallium were available on the reverb furnace slag produced at one plant and usually recycled to sinter. Of matte produced, one company indicated that the selenium content was 0.001 percent and the tellurium content was 0.0014 percent. A type of speiss produced at one lead plant contained 1.9 tons of selenium and 0.1 ton of tellurium. Copper dross slag contained 0.1 percent selenium, 0.0075 percent tellurium, and 0.0002 percent thallium; copper dross flue dust contained 0.065 percent selenium, 0.0006 percent tellurium, and 0.0003 percent thallium.

### Selenium, Tellurium, and Thallium in Slag Fuming Operations

Data on these elements in 200,000 tons of material in the lead furnace slag fuming process at one of four plants are presented in table 1. At another plant, a delead fume contained 0.001 percent selenium and 0.001 percent tellurium. Zinc oxide produced from fume at one plant contained 0.001 percent tellurium.

### Tellurium in Concentrates to Lead Plant Sintering

Tellurium data were more complete than those for selenium because some analytical data were available from six of seven plants. The available data showed that more than 99 percent of the 45 tons of known tellurium in lead concentrates was derived from domestic sources; nearly 90 percent of this came from Missouri. These concentrates had an average tellurium content of 0.006 percent.

### Tellurium in Other Sinter Feed in Lead Plants

Limited assays on zinc plant residues used at two plants showed that about 3 tons of tellurium were present in this material.

Available tellurium assays on the recycled blast furnace slags indicated the tellurium content was 6 to 7 tons. Of the other feeds, only the Waelz kiln wastes had a very small percentage of tellurium.

As with selenium, this portion of the feed was unimportant for its tellurium content. Exclusive of the tellurium in slag, the above materials contributed only about 6 percent of the weight of tellurium in sinter feed as shown in figure 1.

### Thallium in Concentrates to Lead Plant Sintering

Domestic thallium data were based mostly on the plants using Missouri concentrates that contained more than 50 percent of about 6 tons of thallium known in domestic concentrates. Most of the rest of the thallium came in concentrates from Idaho and Utah. The highest contents of thallium were found in Idaho, Washington, and Utah concentrates.

Less than 1 percent of the thallium was from foreign sources, apparently Peru.

### Thallium in Other Sinter Feed in Lead Plants

The thallium content of zinc plant residues from one plant was 0.001 percent. Data for blast furnace slag from this plant indicated 0.2 ton of thallium was present. Applying these data to the total slag used would still indicate considerably less than 1 ton of thallium in such material. From available data, it was apparent that the thallium content of sinter feed shown in table 1 was practically all in the concentrates.

### Gold in Concentrates to Lead Plant Sintering

The estimates of 44,000 ounces of gold in domestic concentrates in 1971 are based on assays from those plants using other domestic concentrates. Colorado concentrates supplied about 75 percent of the known gold-bearing domestic lead concentrates.

In 1975, more than 52 percent of the gold in lead concentrates was in domestic material. Of this, more than half was in Colorado concentrates with most of the rest from Washington. Domestic concentrates averaged 0.074 ounce of gold per ton. California assays were 10.2 ounces of gold per ton; Washington assays were 7.31 ounces of gold per ton.

Although three plants used Peruvian concentrates in 1971, only one plant reported both quantitative and assay data for Peruvian concentrates used. The gold content of the concentrates was 0.23 ounce per ton. Using 1968 assays of treated foreign concentrates suggests 1971 Peruvian concentrates contained on the order of 22,000 ounces of gold (48). Countries supplying gold in concentrates, in order of quantity of gold, included Australia, Canada, Peru, Honduras, and Mexico.

In 1975, Australia supplied 49 percent of the gold in foreign lead concentrates, with Canada providing nearly 21 percent; Peru, more than 17 percent; and Nicaragua, nearly 11 percent. The gold in foreign concentrates averaged 0.29 ounce per ton, including 1.41 ounces per ton in Nicaraguan material.

### Gold in Other Sinter Feed in Lead Plants

Assays on zinc plant residues from one plant showed that about 5,600 ounces of gold were present in the material. A considerable quantity of Cottrell dust used at another plant contained about 52 ounces of gold. Using 1968 data would suggest that about 95 percent of the gold in sinter feeds was in the concentrate feed. Total gold in sinter input is shown in table 1.

### Gold in Blast Furnace Feed and Products

Gold in blast furnace input and output materials is shown in table 1. The average of 0.4 ounce of gold per ton in bullion produced at two plants can be compared with some literature assays of 0.08 to 1 ounce of gold per ton (49).

### Gold in Dross Feed and Products

Although as much as 1.07 ounces of gold per ton were determined in blast furnace bullion used at one plant, the probable quantity of gold could not be calculated in the dross feed because the weight of bullion fed to drossing was not available. About 21,000 ounces of gold were present in the blast furnace bullion fed to drossing at one plant which showed both tonnage and gold tenor.

The gold content of drossed bullion produced at one of three plants is shown in table 1. Only one lead plant showed gold content in the dross (0.07 ounce per ton).

### Gold and Silver in Softening Furnace Products

The silver bullion produced at one plant contained a significant quantity of silver. Data on refined lead at three of four plants are shown in table 1.

### Gold in Reverberatory Furnaces

The dross fed to reverberatory furnaces at one lead plant contained about 0.07 to 0.23 ounce of gold per ton. The matte at one plant, accounting for 11 percent of 1971 copper matte production, contained 0.83 ounce of gold per ton. Speiss produced at a plant with less than 2 percent of 1971 speiss output contained about 251 ounces of gold. A similar product produced at another lead plant analyzed 0.14 ounce of gold per ton and contained 313 ounces of gold. Products called copper dross slag and copper dross flue dust at one plant contained about 17 ounces of gold. Gold in output materials is shown in table 1.

### Gold and Silver in Slag Fuming Operations

Data on gold and silver in fuming feed and products are shown in table 1. Silver assays were available on materials from three of the four plants.

The zinc plant residues at one plant contained an average of 19.2 ounces of silver per ton or about 362,200 ounces. Assays on some of the zinc plant secondaries at the plant indicated about 12,200 ounces of silver. Leaded fume at this plant contained 2.24 ounces of silver per ton; delead fume contained only 0.2 ounce per ton. Fire assays on a sample of zinc oxide processed from fume showed 0.2 ounce of silver per ton.

### Silver in Concentrates to Lead Plant Sintering

Information on silver in lead concentrate in 1971 was based primarily on five of seven plants making lead bullion. Assays showed a range of 1.3 to 1.75 ounces of silver per ton in some Missouri lead concentrates.

Approximately 11.5 million ounces of silver (about 94 percent of the total known silver in concentrates) were derived from domestic concentrates. Of these, about 55 percent, averaging about 46 ounces per ton, came from Idaho, and 34 percent, averaging about 36 ounces per ton, came from Utah. Other significant quantities came from Colorado, Missouri, and California. Altogether, the source is known by State for about 98 percent of the total silver in domestic concentrates.

In 1975, Idaho concentrates, with about 102 ounces of silver per ton, contained almost 63 percent of the domestic silver in lead concentrates. Colorado followed with 23 percent. The lowest tenor, 0.54 ounce of silver per ton, was in Virginia concentrate.

Only 6 percent of silver in lead concentrates in 1971 came from foreign sources. This was based on partial assays from one plant which used only 9 percent of the total foreign concentrates consumed. About two-thirds of the foreign concentrates for which silver assays are available came from Canada, the rest came from Peru. Several assays of the Canadian concentrates were about 78 ounces of silver per ton. Applying the average 38.1 ounces of silver per ton from one plant and applying it to the total foreign lead concentrates indicates about 7.98 million ounces of silver in all foreign lead concentrates. This would raise the total of silver in domestic and foreign lead concentrates to about 19.5 million ounces.

In 1975, Canada supplied 46 percent of the silver in foreign lead concentrates, followed by Peru with 27 percent, Honduras with 16 percent, Australia with 10 percent, and then Greenland, Nicaragua, and Colombia. Silver tenors averaged 72 ounces per ton and ranged from 10.4 ounces per ton in Greenland material to 103 ounces per ton in Peruvian concentrate.

#### Silver in Other Sinter Feed in Lead Plants

Silver was detected only in part of the zinc plant residues, in some dusts, and in the Waelz kiln wastes. The residues varied widely in silver content, almost 17 ounces per ton down to about 1 ounce per ton; Waelz kiln wastes contained significant silver. Cottrell and leady kiln dusts used at one plant averaged about 8.05 ounces per ton. The silver known in the materials totaled more than 1,040,000 ounces, about 83 percent of which was in the zinc plant residues. Compared with the total known silver in concentrates, the input of silver in the materials is minor. Using 1971 data, the concentrates would contribute about 92 percent of the silver in sinter feed. Total input of silver in sinter feed is shown in table 1.

#### Silver in Dust and Fume

The fumes and dusts on which assays were available assayed from 0.6 to about 7.6 ounces per ton, the latter on a sinter Cottrell fume.

#### Silver in Blast Furnace Feed and Products

Data on silver in blast furnace feed are shown in table 1. There was a wide range in the silver assay of bullion produced by three plants, from 2.3 to 141.1 ounces per ton. Some blast furnace bullion assays in the literature ranged from 85 to 162.7 ounces of silver per ton (49). As a result of variations in assays, the total known silver from the three plants can be the low and high contents in table 1. Data on silver in fume and in slag at two of six plants are shown in table 1.

### Silver in Dross Feed and Products

Two plants had about 10.5 million ounces of silver in about 285,000 tons of blast furnace bullion feed. Assays at one plant showed 2.3 ounces of silver per ton; at the other they averaged 67.9 ounces per ton. Assays of 32.1 and 141.1 ounces of silver per ton but no quantity data were available at a large lead plant using diversified feed. The silver content of drossed bullion at one lead plant and in dross product at another are shown in table 1. Assays of dross at another plant ranged from 27 to 49 ounces of silver per ton.

### Silver in Reverberatory Furnaces

Except for one plant where dross feed contained 27 to 49 ounces of silver per ton, data on the feed were not available. The matte at the plant mentioned under "Gold in Reverberatory Furnaces" assayed about 30 ounces of silver per ton and contained about 138,000 ounces of silver. Matte at one other plant contained about 6,500 ounces of silver. Speiss produced at the plant, with less than 2 percent speiss production, contained about 20,000 ounces of silver. Another type speiss from one plant contained about 122,000 ounces of silver. As shown in table 1, copper dross slag and copper dross flue dust at one plant contained 17,300 ounces of silver.

### Lack of Assay Data for Byproducts in Lead Metallurgy

There were no analytical data for the following byproducts in the various phases of lead processing: bismuth in copper dross slag and copper dross flue dust from reverberatory furnaces; cadmium in antimonial lead from softening furnaces, and in dusts and slags from reverberatory furnaces; selenium in Cottrell dust, calcines, and matte fed to sintering, in drossed bullion from drossing kettles, and in speiss from reverberatory furnaces; tellurium in blast furnace bullion and in speiss from reverberatory furnaces; thallium in slags at three slag fuming plants, in matte, dross, leach cake, sludge, refinery slag, dust, calcines, and kiln wastes fed to sintering, in dross and drossed bullion from drossing kettles, in speiss from reverberatory furnaces, and in slags; and gold, in most of the feed materials fed to sintering, in dust and fume, and in softening furnace products.

### ZINC PYROMETALLURGY

In 1971 there were six operating domestic pyrometallurgical plants, including the horizontal retorts owned by American Smelting and Refining Co. (ASARCO) in Amarillo, Tex. (closed in 1975); by American Zinc Co. in Dumas, Tex. (closed in 1971); by National Zinc Co. in Bartlesville, Okla. (changed to electrolytic in 1976); and by Blackwell Zinc Co. in Blackwell, Okla. (closed in 1973); the vertical retort owned by New Jersey Zinc Co. in Palmerton, Pa.; and the electrothermic plant owned by St. Joe Minerals Corp. in Monaca, Pa. There were also four electrolytic zinc plants, including those owned by ASARCO in Corpus Christi, Tex.; by Bunker Hill Co. in Kellogg, Idaho; by American Zinc Co. (operated by AMAX since 1973) in Sauget (E. St. Louis), Ill.; and by The Anaconda Co. in Great Falls, Mont. (closed in 1972). Because of the basic differences between the pyrometallurgical and electrolytic processes, recovery of minor metals by each process will be treated separately, beginning with pyrometallurgy.



TABLE 2. - Byproduct minor metals in zinc pyrometallurgy--inputs, outputs, plants, and weights  
(Key to figure 14)

Process	No. of plants <sup>1</sup>	Short tons							Troy ounces	
		As	Sb	Bi	Cd	Ga	Ge	In	Au	Ag
<b>Roasting:</b>										
Input: Concentrates <sup>2</sup> .....	6	378	54	17	2,267	18	6	47	6,200	1,680,400
<b>Output:</b>										
Calcines.....	5	49	9	NA	306	NA	NA	10	NA	45,945
Fume (to baghouse or Cottrell) <sup>2</sup> .....										
<b>Sintering or nodulizing:</b>										
<b>Input:</b>										
Concentrates <sup>2</sup> .....	6	378	54	17	2,267	18	6	47	6,200	1,680,400
<b>Calcines:</b>										
From roasting.....	5	49	9	NA	306	NA	NA	10	NA	45,945
Direct feed.....	3	4	3	3-14	10	.1	NA	.2	NA	34,166
Impure zinc oxide.....	1	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg
Residues.....		NA	NA	NA	NA	NA	NA	NA	NA	NA
Nonmagnetic residues (recycled).....	3	NA	NA	NA	NA	NA	NA	NA	NA	NA
<b>Output:</b>										
Fume (to baghouse or Cottrell) <sup>2</sup> .....	2	<sup>3</sup> 59	<sup>3</sup> 5	<sup>3</sup> 8	<sup>3</sup> 858	NA	<sup>3</sup> .6	<sup>3</sup> 2	<sup>3</sup> 1,263	<sup>3</sup> 693,036
Sinter (to briquetting).....	5	61	75	NA	266	2.3	5.7	59	NA	287,101
Sinter (to recycle).....	1	NA	.2	NA	NA	NA	NA	NA	NA	NA
Ore sinter (to oxide).....	2	NA	NA	NA	( <sup>4</sup> )	NA	( <sup>4</sup> )	( <sup>4</sup> )	NA	NA
Nodules.....	1	( <sup>4</sup> )	NA	NA	( <sup>4</sup> )	NA	NA	NA	NA	NA
<b>Retort furnaces:</b>										
<b>Input:</b>										
Sinter (briquetted).....	5	61	75	NA	266	2.3	5.7	59	NA	287,101
Nodules.....	1	( <sup>4</sup> )	NA	NA	( <sup>4</sup> )	NA	NA	NA	NA	NA
Briquettes.....		NA	NA	NA	NA	NA	NA	NA	NA	NA
Roasted mixed ores.....	1	( <sup>4</sup> )	( <sup>4</sup> )	NA	( <sup>4</sup> )	NA	NA	NA	NA	( <sup>4</sup> )
Calcines.....	1	( <sup>4</sup> )	( <sup>4</sup> )	NA	( <sup>4</sup> )	NA	NA	NA	NA	( <sup>4</sup> )
Willemite.....	1	( <sup>4</sup> )	( <sup>4</sup> )	NA	( <sup>4</sup> )	NA	NA	NA	NA	( <sup>4</sup> )
Skimmings.....	1	.3	NA	NA	.2	NA	NA	NA	NA	3,109
Dross.....	1	NA	NA	NA	NA	NA	NA	NA	NA	NA
Sintered ore.....	1	2	1.4	NA	NA	NA	NA	NA	12	6,275
Waelz sinter.....	1	( <sup>4</sup> )	( <sup>4</sup> )	NA	( <sup>4</sup> )	NA	NA	( <sup>4</sup> )	NA	NA
<b>Output:</b>										
Zinc.....	1	NA	1	NA	75	NA	NA	21.5	NA	NA
Prime western zinc.....	5	NA	<sup>5</sup> 27	NA	<sup>5</sup> 60	NA	NA	<sup>5</sup> 15.4	NA	NA
High-grade zinc.....	2	NA	NA	NA	<sup>6</sup> 10	NA	.2	<sup>6</sup> 4.8	NA	NA
Residues.....	1	124	<sup>7</sup> 50	<sup>7</sup> 7	<sup>7</sup> 2.5	NA	NA	NA	<sup>7</sup> 2,006	<sup>7</sup> 246,659
Retort residues (to magnetic separation)	4	1.3	12	NA	.3	NA	4.3	<.1	<sup>7</sup> 214	<sup>7</sup> 69,532
Retort residues (to Waelzing).....	1	( <sup>4</sup> )	( <sup>4</sup> )	NA	( <sup>4</sup> )	NA	( <sup>4</sup> )	( <sup>4</sup> )	NA	NA
Fume.....		NA	NA	NA	NA	NA	NA	NA	NA	NA
<b>Magnetic separation:</b>										
<b>Input:</b>										
Retort residues.....	4	1.3	12	NA	<sup>8</sup> .3	NA	4.3	<.1	214	<sup>8</sup> 69,532
<b>Output:</b>										
Magnetic residues (shipped or waste)....	3	<sup>8</sup> 86	<sup>8</sup> 16	<sup>8</sup> 7	<sup>8</sup> 3	NA	<sup>10</sup> 4.3	<.1	98	<sup>8</sup> 56,281
Nonmagnetic residues (recycled).....	3	NA	NA	NA	NA	NA	NA	NA	NA	NA
<b>Fume collection (baghouse or Cottrell):</b>										
<b>Input:</b>										
Fume (from sintering).....	5	<sup>3</sup> 59	<sup>3</sup> 5	<sup>3</sup> 8	<sup>3</sup> 858	NA	<sup>3</sup> .6	<sup>3</sup> 2	<sup>3</sup> 1,263	<sup>3</sup> 693,036
Fume (from roasting).....										
<b>Output:</b>										
Dust (recycle).....		NA	NA	NA	NA	NA	NA	NA	NA	NA
Dust (fume leach).....		NA	NA	NA	NA	NA	NA	NA	NA	NA
Dust (other).....	2	24	1.6	3.6	310		<.1	1	364	146,546
<b>Fume leaching:</b>										
<b>Input:</b>										
Fume (from baghouse or Cottrell).....		( <sup>11</sup> )	( <sup>11</sup> )		( <sup>12</sup> )					
Dust (other).....	1	NA	NA	NA	NA	NA	NA	NA	NA	NA
<b>Output:</b>										
Lead sulfate.....	4	<sup>13</sup> 65	<sup>13</sup> 6	<sup>13</sup> 15	<sup>13</sup> 98	<sup>13</sup> <.1	<.1	<sup>13</sup> 6	436	<sup>13</sup> 894,040
<b>Lead and cadmium refining:</b>										
<b>Input:</b>										
Zinc.....	1	NA	( <sup>4</sup> )	NA	( <sup>4</sup> )	NA	NA	( <sup>4</sup> )	NA	NA
<b>Output:</b>										
Refined zinc.....	2	NA	<sup>14</sup> .5	NA	NA	NA	NA	<sup>14</sup> 1	NA	NA
Fume.....		NA	NA	NA	NA	NA	NA	NA	NA	NA

NA Not available. Neg Negligible.

<sup>1</sup>Plants using processes and showing quantities or assays of materials.

<sup>2</sup>Concentrate feed undifferentiated. Figure indicates total quantity to roasting and sintering. For total fume output to baghouse or Cottrell, see sintering output.

<sup>3</sup>Includes 0.3 to 1.18 percent arsenic; 0.015 to 0.1 percent antimony; 0.07 to 0.18 percent bismuth; 7.8 to 11.6 percent cadmium; 0.005 to 0.01 percent germanium at 2 plants; 0.0002 to 0.11 percent indium; 0.06 to 0.18 ounce of gold per ton at 5 plants; 23.7 to 97.4 ounces of silver per ton at 5 plants.

<sup>4</sup>Company confidential.

<sup>5</sup>Includes 0.001 to 0.028 percent antimony; 0.004 to 0.07 percent cadmium; 0.003 percent indium in prime western zinc to 0.002 percent indium in high-grade zinc.

<sup>6</sup>Includes intermediate-grade zinc.

<sup>7</sup>Includes 0.001 to 0.2 percent antimony; 0.03 percent bismuth; 0.0015 to 0.01 percent cadmium; 0.008 and 0.08 ounce of gold per ton at 2 plants; 2.6 and 9.96 ounces of silver per ton.

<sup>8</sup>Includes 0.0015 percent cadmium at 1 plant; 2.6 ounces of silver per ton at 1 plant.

<sup>9</sup>Includes 0.23 percent arsenic (average); 0.04 to 0.07 percent antimony; 0.009 to 0.01 percent bismuth; 0.003 to 0.01 percent cadmium; 2.2 to 4.2 ounces of silver per ton at 1 plant.

<sup>10</sup>Average of 2.5 and 6.2 tons of germanium in retort residues. Probably more than 4.3 tons.

<sup>11</sup>See estimate for fume to leaching under "Arsenic in Fume Leaching"; "Antimony in Fume Leaching."

<sup>12</sup>From 8 to about 10 percent cadmium.

<sup>13</sup>Includes 0.3 to 2.25 percent arsenic; 0.049 percent antimony; 0.125 to 0.3 percent bismuth; 0.5 to 0.7 percent cadmium; 0.0012 percent gallium at 1 plant; 0.02 to 0.21 percent indium at 3 plants; 61.4 to 233.3 ounces of silver per ton.

<sup>14</sup>Includes 0.001 to 0.0027 percent antimony (2 assays); 0.002 percent indium (average).

In 1971, Tennessee supplied about 20 percent of the domestic concentrates; New York, nearly 20 percent; and Pennsylvania, nearly 10 percent. Other minor suppliers were, in order, Virginia, Illinois-Kentucky-Wisconsin, Colorado, Maine, Missouri, New Mexico, and Arizona. In 1975, the principal producing States were New Jersey, New York, Tennessee, Colorado, Missouri, and Idaho.

There is a wide variation in zinc tenors. For example, in 1975 although New Jersey shipped about 23 percent of the total 844,000 tons dry weight of domestic concentrates, they contained only 9 percent of the 397,800 tons of zinc in concentrates received at domestic plants. New York supplied 20 percent of the zinc in concentrate; Tennessee, 14 percent; Colorado, 12 percent; Missouri, 11 percent; and Idaho, nearly 10 percent.

Of foreign concentrates in 1971, Canada supplied more than 60 percent and Mexico most of the rest. Peru supplied about 5 percent of foreign material. In 1975, 25 percent of shipments of zinc in concentrate were from foreign countries with Canada supplying 65 percent; Honduras, 11 percent; Mexico, 8 percent; Thailand, 4 percent; Bolivia, 2 percent; and the rest from Peru and Nicaragua. Undifferentiated various countries supplied 8 percent.

With few exceptions, arsenic, antimony, bismuth, and cadmium were detected in domestic and foreign concentrates; assays on these metals also were available on some concentrates from States, Provinces, and individual deposits. Analytical data for gallium, germanium, and indium were scarce and representative samples of smelter feeds or products often indicated very small quantities or none detected.

#### General Information About Roasting and Sintering Products

Only one company out of five provided quantitative and assay data on calcines from roasting; the gross weight of calcines was about 80 percent of the gross weight of domestic and foreign concentrates used at the plant. Sinter weights were available from all plants; fume weights were received from three plants and calculated for a fourth. One plant that provided calcine data also indicated that it fed 98 percent of calcines, along with purchased material, to the sinter plant. Some plants recycle roasting dust or fume but send sinter fume to Cottrell precipitators or baghouses. The collected dusts are often upgraded and the enriched dusts are sent to leaching plants for further processing; for example, for cadmium removal. Some plants ship the dust elsewhere for processing. Sinter flue dusts are collected in baghouses or Cottrell precipitators, densified in rotary kilns, the oxides sulfated, and processed further to cadmium sponge and refined cadmium (50, 77, 87, 92). Sinter is retorted for its zinc metal content; two metal-producing plants also use sinter to make zinc oxide.

One company showing quantities of calcine produced also provided representative samples in which arsenic, antimony, cadmium, indium, gold, and silver were determined quantitatively by Bureau of Mines analysts.

Arsenic assays were obtained for fume at five plants and for sinter at three plants. Antimony content in fume was reported at four plants and in

sinter at two plants. Bismuth and cadmium contents in fume were available for five plants. Although cadmium was reported in the sinter at five plants, no bismuth was reported in any sinter product. No gallium was detected in any fume; only a trace was detected in some sinter from one plant. Germanium was in fume from two plants and in sinter at two. Indium was present in fume and sinter from three plants and in fume only from another. Gold was in fume at five plants and in sinter at one. Silver was detected in fume at five plants and in sinter at two others.

#### Retort Feed and Products

Because of incomplete data on sinter produced, it is usually impossible to relate minor metals in sinter output and in retort input. Only one plant provided enough data to make estimates on these minor metals for these particular operating phases.

#### Magnetic Separation Feed and Products

Retort residues are screened and then sent to magnetic separation. Products include magnetic and nonmagnetic residues, middlings, ferrosilicon, reclaimed concentrates, and residue fines. The residue over 0.256 inch is discarded, the highly magnetic residue is discarded in part to minimize the iron content, the moderately magnetic residue is mostly returned to mix, the low magnetic residue is mainly returned to sintering, and the nonmagnetic cake is returned to the furnace charge (49). Because of the presence of some minor metals, some magnetic residues were shipped to other plants, including one lead plant, for additional processing.

Data were available on quantities of retort residues fed to magnetic separation only at two plants. This feed was only about 25 percent of the total known retort residue production. Magnetic residue data were available from two plants; another sold the residues and did not disclose the quantity produced.

#### Dust and Fume Collection

Only four firms provided quantitative data on fume and dust collected in baghouses or Cottrell precipitators. Assays also were available from these plants as well as from another that did not show quantities collected. From the available assays, it is evident that the assays were made on upgraded and enriched dusts or fume.

#### Fume Leaching

Two of the four pyrometallurgical zinc plants of the horizontal-retort type also produced cadmium that has been volatilized to fume in the roasting-sintering processes and concentrated in the Cottrell and baghouse dusts. This material is leached with sulfuric acid to take cadmium into solution, the insoluble lead sulfate (lead cake) is removed by filtering, after which the solution is neutralized and the cadmium precipitated with zinc dust. Quantitative fume-to-leaching data were obtained from one of these plants. The other two plants shipped dust to cadmium extraction plants.

### High-Purity Zinc

Plants which produce high-purity zinc provided quantitative and assay data. Assays showed that only very small percentages of antimony, cadmium, germanium, and indium were present. The largest quantity, that for antimony at one plant, was less than 0.003 percent.

### Minor Metals in Cadmium Sponge and Metal

One firm provided analytical data on cadmium sponge production while three others gave data on minor metals in their cadmium metal. Only 0.0001 percent arsenic was present in cadmium metal at one plant. Another plant had 0.0005 percent antimony in metal. One plant had 0.001 percent each of bismuth and indium in its metal. At one plant that showed the quantities of cadmium sponge produced, no gold or silver was detected. Another plant, that did not report the quantity of sponge produced, had nearly 3 ounces of gold per ton in cadmium metal. Three plants provided data on cadmium metal; one plant had about 20 ounces of silver per ton in the cadmium.

### Minor Metals in Waelz Processing

According to a recent review of zinc processing, the Waelz process is used to beneficiate zinc-containing retort residues into an oxide fume product that can be used as a feed in zinc metal, oxide, sulfate, or lithopone production. Residues, mixed with carbonaceous fuel, are processed in a horizontally inclined, rotating kiln at approximately 1,200° C. This reduces and drives off zinc, lead, and other volatile metals such as germanium and oxidizes them to fume products (82).

One plant indicated it fed retort residues, along with other materials, to Waelz processing. Waelz oxide (fume) from this process is fed to a roasting or sintering process and the resulting calcine (called sinter by the plant) is used as feed in oxide and metal production. Samples of Waelz sinter from this plant were assayed but only arsenic, antimony, cadmium, germanium, and indium were detected in the material.

### Arsenic in Concentrates to Roasting and Sintering

Table 2 in conjunction with figure 14 shows the flow of arsenic and other byproducts in zinc pyrometallurgy. In 1971 zinc concentrates to five roasting plants and one sinter plant contained the weight of arsenic shown. Domestic ores contributed 15 percent of the arsenic and foreign concentrates contributed 85 percent. Tennessee supplied about 23 percent of the domestic arsenic, followed by Missouri (19 percent), Colorado (17 percent), and Illinois-Kentucky-Wisconsin, Pennsylvania, New York, New Mexico, Maine, and Arizona supplied the rest. Although Virginia was a large supplier of concentrates to one firm, arsenic was not detected in a representative sample. Of the arsenic in foreign concentrates, about 37 percent was in Peruvian concentrates which, in one instance, had a very high arsenic content. Canadian concentrates supplied about 32 percent of foreign arsenic in concentrates and Mexico supplied 31 percent.

### Arsenic in Sintering Feed and Products

Due to the lack of complete information, only a fraction of total known arsenic in pyrometallurgical plant roaster feed was traceable in sintering feed. The known quantities are shown in table 2.

At one plant, arsenic in sinter products such as fume and sinter is considerably less than in calcines and other sinter input materials, being less than 50 percent of arsenic input. Compared with the arsenic content of concentrates used, the known arsenic content of sinter products at other plants is usually insignificant. In three cases, no data were available for arsenic in sinter that totaled about 200,000 tons. At the plant that sinters concentrates directly, quantitative and assay data on fume and sinter indicate the arsenic in these products is about 55 percent of that in the concentrates fed to sintering.

### Arsenic in Retort Feed and Products

The total known arsenic in retort feed materials may be seen in table 2. Most of the data on arsenic in retort feed was obtained from two plants. Anomalies in retort feed versus retort products result from lack of data. Three companies provided assay data on retort residues. The arsenic content of residues from one of these plants was 96 percent of that in the concentrate feed. Assays at another plant indicated that about 48 percent of the arsenic in the concentrates was in the retort residue.

### Arsenic in Magnetic Separation Feed and Products

Magnetic residues contain the weight of arsenic shown in table 2. One company produced nearly four times as much magnetic residues as nonmagnetic residues. One firm that produced and sold magnetic residues returned nonmagnetic residues to sinter.

### Arsenic in Dust and Fume

Arsenic assays and quantities in sinter fume are presented in table 2. Dust or fume containing 40 percent of the arsenic in such material was shipped to other plants for processing. The total arsenic contrasts considerably with the tonnage of arsenic in feed.

### Arsenic in Fume Leaching

Assays showed 0.3 and 0.5 percent arsenic in fume leached at two plants. The quantity of arsenic in fume-to-leaching calculated for one plant was about 52 percent of that collected at three plants. The quantity of arsenic in lead sulfate from fume leaching was about 53 percent of that in fume feed. Lead sulfate assays and quantities are noted in table 2. Using a 53 percent recovery of arsenic in lead sulfate at one plant and applying it to quantitative and assay data at two other plants would mean that the arsenic in feed to these plants could be about 33 percent greater than the total shown.

### Antimony in Concentrates to Roasting and Sintering

Domestic concentrates supplied about 51 percent of the total antimony content of concentrate feed-to-roasting and sintering plants. Almost 25 percent of antimony in domestic concentrates came from Illinois-Kentucky-Wisconsin, about 18 percent each from New York State and Colorado, about 14 percent from New Mexico, about 10 percent from Virginia, and the rest from Maine, Missouri, Pennsylvania, Tennessee, and Arizona. Of the 26 tons of foreign antimony in concentrates, almost 60 percent came from Canada, about 33 percent from Mexico, and the remainder from Peru.

### Antimony in Sintering Feed and Products

About 25 percent of the known antimony in roaster feed was traceable to sintering feed. At one plant concentrates were fed directly to sintering. One firm reported almost 90 percent of the antimony in concentrate fed to its roasting plant was charged to the sintering hearth, mostly as calcines. Assay data for fume indicated it contained only about 9 percent of the antimony reported in concentrates.

### Antimony in Retort Feed and Products

As with arsenic at one plant, antimony in retort feed was about 50 percent greater than that in sinter products due to the probable presence of antimony in calcines and other retort feed.

Assays and weights for antimony in retort residues and in prime western zinc are presented in table 2.

### Antimony in Magnetic Separation Feed and Products

Only one company reported antimony in retort residues fed to magnetic separation. Two others had magnetic residues.

### Antimony in Dust and Fume

Assays and weights of dust and fume are shown in table 2. About one-third of the dust was shipped by two plants to further processing.

### Antimony in Fume Leaching

Antimony data on fume feed and lead cake product were provided for only one plant. Fume had an antimony tenor of 0.056 percent. The recovery of antimony in lead sulfate at this plant was about 46 percent. Applying this to two other plants for which quantitative and assay data were known for lead sulfate would mean that antimony in fume at these two plants would be about twice that known in fume collected at three plants. Antimony assays and weights in the lead sulfate are presented in table 2.

### Antimony in High-Purity Zinc

Refined zinc data are shown in table 2.

#### Bismuth in Concentrates to Roasting and Sintering

Few data are available on bismuth in domestic concentrates; no assay data were provided by two plants for this element. From available data, it is believed that domestic bismuth in concentrates was only about 20 percent of that of the total bismuth in concentrates. Assay data indicate that nearly 50 percent of the known domestic bismuth in concentrates came from Maine, followed by Colorado, Illinois-Kentucky-Wisconsin, Tennessee, New Mexico, and Arizona. Bismuth was not detected in concentrates from New York, Pennsylvania, and Virginia.

According to analytical data from two plants, Mexico supplied about 53 percent of foreign bismuth in concentrates. Using data from four plants, it is probable that Canada supplied almost 40 percent of foreign bismuth in concentrates. Peru supplied the known remainder from two operations, each supplying one domestic plant.

#### Bismuth in Sintering Feed and Products

The concentrates fed by one plant to sintering contained over 7 tons of bismuth. The only other assay data available for sintering feed indicated the weight of bismuth in purchased calcines.

#### Bismuth in Retort Feed and Products

Data for bismuth in retort residues are seen in table 2.

#### Bismuth in Magnetic Separation Feed and Products

Assays and weights of the magnetic fractions of the retort residues are shown in table 2.

#### Bismuth in Dust and Fume

Assay and weight data on dust and fume at four plants are shown in table 2. Information for another plant provided no tonnage on dust or fume but showed it contained 0.007 percent bismuth. Less than one-half the bismuth in dust was shipped elsewhere for processing.

#### Bismuth in Fume Leaching

Data indicated that the percent of bismuth in the lead sulfate at one plant was about four times that in the fume feed, but the weight of the sulfate was only about half that of the fume. These anomalous data were probably due to different assay methods being used on the two materials. Assay and weight data on lead sulfate are shown in table 2.

### Cadmium in Concentrates to Roasting and Sintering

Cadmium assay data on representative samples on which cadmium assays were made were available from all firms. About 60 percent of the total cadmium in concentrates was from domestic sources, with about 40 percent from Tennessee, 15 percent from New York State, 12 percent from Missouri, 6 percent from Illinois-Kentucky-Wisconsin, and nearly 5 percent from Colorado. The remainder came from Maine, Pennsylvania, Virginia, New Mexico, and Arizona. Canada supplied 49 percent of foreign cadmium in concentrates, followed by Mexico with 47 percent, and Peru.

In the United States, the highest tenor of cadmium in concentrates came from Missouri, the lowest from Virginia and Pennsylvania. Practically no foreign cadmium in concentrates was as high as that from Missouri; Mexican concentrates averaged about 0.33 percent cadmium.

### Cadmium in Sintering Feed and Products

At one plant for which the most complete data were available, cadmium in calcines from roasting appears to be more than that in the concentrates roasted, probably a result of assay differences. Table 2 shows the known quantities of cadmium in feed and products.

At one plant using concentrates as feed to sintering, there appeared to be about 18 times as much cadmium in input concentrates as in output sinter. Depending upon which of two assays on fume was used (8.0 and 9.9 percent cadmium), cadmium in sinter and fume at this plant could range from 68 to 82 percent of that in the concentrate feed. Compared with cadmium in concentrates, calculations on sinter products at four other plants indicated the following: at one plant, cadmium in fume was about 75 percent of that in concentrates and in sinter, about 5 percent; at a second plant, 62 percent as much cadmium in fume as in concentrates; and at two other plants, 7 and 16 percent as much cadmium in sinter as in concentrates.

For all plants, the total cadmium in fume averaged about 38 percent of the cadmium in concentrates; the total cadmium in sinter was about 12 percent of the cadmium in concentrates.

### Cadmium in Retort Feed and Products

Four companies provided some data on cadmium in retort feed and products. The cadmium in retort residues and prime western zinc at the plants was about 46 percent of that in the retort feed. As shown in table 2, the known cadmium in retort feed was about 304 tons, with about 88 percent of it in sinter.

Assay data on retort residues and on prime western zinc are also shown in table 2.

### Cadmium in Magnetic Separation Feed and Products

Some assay and weight data on residues are shown in table 2. Nonmagnetic residues at one plant providing no data on quantities contained 0.008 percent cadmium.

### Cadmium in Dust and Fume

Assay and weight data on dust and fume at four plants are shown in table 2. At another plant with no quantitative data, these materials assayed 8.0 percent cadmium. About 36 percent of the cadmium in dust was sent by two plants for further processing.

### Cadmium in Fume Leaching

Assay on cadmium in fume and assays and weight data on cadmium in lead sulfate are shown in table 2. At one plant with complete data on fume and lead sulfate, the cadmium in the sulfate was about 3 percent of that calculated in the fume. It has been stated that about 5 percent of the cadmium in feed reports to the lead sulfate residues (92).

### Cadmium in High-Purity Zinc

One plant showed 0.001 percent cadmium in high-grade zinc. Prime western zinc shipments from another zinc plant contained from 0.007 to 0.026 percent cadmium. This compares with 0.01 to 0.08 percent (averaging 0.03 percent) from four southwest smelters in assays made a number of years ago (86).

### Gallium in Concentrates to Roasting and Sintering

Domestic sources contributed about 73 percent of total known gallium in concentrates with New York State and Tennessee accounting for more than 80 percent. Assays on New York and Tennessee concentrates showed they contained about 0.005 percent gallium. Lesser amounts of gallium in concentrates came from Illinois-Kentucky-Wisconsin, Maine, and Missouri. No assay data were available on zinc concentrates from Arizona, Colorado, New Mexico, Pennsylvania, and Virginia. Almost all of the foreign known gallium in concentrates (5 tons) came from Canada. Peruvian concentrates averaged only 0.0005 percent gallium.

### Gallium in Sintering Feed and Products

Assays at one plant showed 0.0005 percent gallium in some imported calcine feed and 0.0014 percent gallium in some sinter product. A second plant fed directly about 6 tons of gallium in concentrates to sintering but had no assay data available on sinter.

### Gallium in Retort Feed and Products

Data on retorting input and output are limited; in most cases, gallium was not detected by the methods used. One, perhaps anomalous, assay indicated 0.0013 percent gallium in one retort residue. Another, in a sinter feed to retorting, indicated 0.0014 percent gallium.

### Gallium in Fume Leaching

As shown in table 2, one company had a lead sulfate from leaching of fume which assayed 0.0012 percent gallium.

### Germanium in Concentrates to Roasting and Sintering

Total known germanium in concentrates shown in table 2 was about 83 percent from domestic sources, with about 85 percent of this from the States of Colorado, Illinois-Kentucky-Wisconsin, Missouri, and New Mexico coming from the Fluorspar and Upper Mississippi Valley districts. Germanium was not shown in assays of concentrates or detected in representative samples from Arizona, Maine, New York, Pennsylvania, Tennessee, or Virginia. The Illinois-Kentucky-Wisconsin area had the highest areal average, 0.0067 percent germanium, with some concentrates in the Illinois-Kentucky area (Fluorspar district) as high as 0.035 percent germanium. All known germanium in foreign concentrates came from Canada.

### Germanium in Sintering Feed and Products

Germanium was detected only in the concentrates fed to sinter. The plant using concentrates had about 3 tons of germanium in its feed. Assays on germanium in sinter products were available from three plants. Data are shown in table 2. Sinter at two plants contained 0.002, 0.0011, and 0.0022 percent germanium. The latter two assays were on two types of sinter. At two plants having both quantitative and assay data for germanium in fume and sinter, the weight of germanium in these materials was greater than that calculated in the concentrates to roasting.

### Germanium in Retort Feed and Products

More data were available on germanium input and output than for gallium, particularly on products. The germanium content of sinter was almost as great as that in concentrates. Data on retort residues at one plant indicated that germanium in this material was about 46 percent of that in the feed. As seen in table 2, one plant, with assay data indicating it had about 2.6 tons germanium in sinter fed to retorts, had about 4.3 tons of germanium in its retort residues.

### Germanium in Magnetic Separation Feed and Products

Magnetic residues at one plant contained 0.0205 percent germanium.

### Germanium in Dust and Fume

Of the plants for which quantitative fume data were available, only two provided assays.

### Germanium in Fume Leaching

One company had a lead sulfate which assayed 0.0024 percent germanium. The quantity of germanium in the sulfate was about 13 percent of that in total known fume fed to leaching.

### Germanium in High-Purity Zinc

High-grade zinc at one plant assayed 0.0022 percent germanium.

### Indium in Concentrates to Roasting and Sintering

Reported indium in domestic concentrates (table 2) was about 28 percent of total concentrate input. Indium reported by States totaled about 77 percent of total reported domestic, with about 73 percent of the domestic coming from Tennessee and most of the rest from Colorado. The latter State had the highest assay (about 0.02 percent indium). Small amounts of indium were reported in concentrates from Missouri, Illinois-Kentucky-Wisconsin, Maine, and Arizona. Indium was not detected in concentrates from New Mexico, New York, Pennsylvania, or Virginia.

Canada supplied 30 tons, nearly 90 percent of foreign indium in concentrates. Mexico and Peru supplied small quantities of indium in concentrates.

Tenors of indium in foreign concentrates averaged almost four times those in domestic concentrates, the highest being from Canada which was about the same as the Colorado material.

### Indium in Sintering Feed and Products

Four plants provided information on indium in sintering feed. At the plant using concentrates as feed, there were about 5 tons of indium in the input material. Sinter and fume at this plant constituted about 80 percent of the indium in the concentrate feed, three-fourths being in the sinter. Another plant showed 0.0063 percent indium, for a total of almost 10 tons, in its calcines. This plant also had an oxide feed which contained a small percentage of indium. A third plant used purchased calcines which contained 0.0006 percent indium.

The assay data on indium in fume and the indium content of sinter are shown in table 2. Indium assays on sinter were available from two plants, each of which also provided fume data. Indium in sinter ranged from 0.0004 to 0.03 percent.

### Indium in Retort Feed and Products

Two plants provided data on indium in retort feed and products. Most of the indium in products was in the prime western zinc. Indium content of residues at one plant was 0.0025 percent; that at another plant was 0.0004 percent.

### Indium in Magnetic Separation Feed and Products

Retort residues fed to magnetic separation at one plant contained 0.0004 percent indium. At another plant, the resulting magnetic residues contained 0.0003 percent indium.

### Indium in Dust and Fume, Fume Leaching, and High-Purity Zinc

Data on these materials are shown in figure 2.

### Gold in Concentrates to Roasting and Sintering

Data from one plant indicated Colorado concentrates had about 97 percent of known domestic gold in concentrates in 1971. The only other assays for gold in domestic concentrates were on materials from Missouri, Arizona, and New Mexico. Better data were available on foreign gold in concentrates which indicated that about 78 percent of the known gold was in the foreign material. As shown in table 2, total known gold in concentrates was about 6,200 ounces.

In 1971, Mexico ranked first among foreign sources with about 78 percent. In domestic concentrates, the highest reported assays were of concentrates from Colorado (0.15 ounce per ton) and New Mexico (0.02 ounce per ton).

In 1975, domestic concentrates contained about 66.5 percent of total gold in concentrates received at domestic pyrometallurgical zinc plants. Of these, Colorado supplied 82 percent in concentrate assaying 0.052 ounce of gold per ton.

Canada supplied 69 percent of foreign gold in zinc concentrates, followed by Honduras with 18 percent, and Nicaragua with over 6 percent. Nicaraguan concentrate assayed 0.11 ounce of gold per ton.

### Gold in Sintering Feed and Products

Sintered ore used as feed at one plant contained a low tenor of gold. Concentrates fed to sintering at one plant contained at least 3,600 ounces of gold.

Assays and weights of gold in fume are shown in table 2. Gold assay data on sinter produced at one plant showed only 0.001 ounce of gold per ton, equaling only a little more than 1 percent of known gold in concentrate feed.

### Gold in Retort Feed and Products

Very little data for gold in retort feed were available. About 2,200 ounces of gold were determined in retort residues at two plants.

### Gold in Magnetic Separation Feed and Products

One plant had 0.008 ounce of gold per ton in its retort residues fed to magnetic separation, but assays on its magnetic residues indicated from a trace to 0.02 ounce of gold per ton.

### Gold in Dust and Fume

About 29 percent of the gold in dust was sent by two plants for further processing.

### Gold in Fume Leaching

Gold in lead sulfate calculated at two plants was about 41 percent of that calculated in fume collected at three plants. One plant had as much as 0.14 ounce of gold per ton in its lead sulfate. The quantity of gold in sulfate is shown in table 2.

### Silver in Concentrates to Roasting and Sintering

In 1971, silver assays were available for concentrates from all States except Pennsylvania. However, only about one-third of silver in concentrates was determinable by States because one large user of high silver concentrates (about 7.3 ounces of silver per ton) did not report concentrates consumed by source States. Of known domestic silver in concentrate quantities (858,483 troy ounces), 32 percent came from Missouri, with nearly as much from New York State. Maine provided 11 percent; Colorado, 9 percent; Illinois-Kentucky-Wisconsin, nearly 6 percent; Virginia, 5 percent; and Tennessee, 4 percent. Other suppliers were New Mexico and Arizona.

In 1975, about 62.5 percent of silver in concentrates was of domestic origin. Missouri concentrates contained more than 43 percent of the silver in concentrates and averaged 10.88 ounces of silver per ton. Silver in Nevada concentrates averaged 26.25 ounces per ton.

In 1971, about 49 percent (821,915 troy ounces) of total silver in concentrates came from foreign countries with Canada supplying about 60 percent. Mexico provided about 37 percent of foreign material. In 1975, Honduras produced 45 percent of the silver in zinc concentrates received from foreign countries. Canada and Bolivia supplied 25.8 and 16.7 percent, respectively. Tenors ranged from 1.02 ounces of silver per ton in Nicaraguan concentrate to 34.2 ounces per ton in Bolivian concentrate.

### Silver in Sintering Feed and Products

Sintered ore used at one plant contained silver. At two other plants, calcine fed to sintering contained 0.3 ounce of silver per ton and about 4 ounces of silver per ton, the latter being in imported calcine. One of these plants also used some imported calcines containing about 0.45 ounce of silver per ton. Another plant fed concentrates containing over 900,000 ounces of silver directly to sintering.

Silver assays on sinter product were available from only two plants, with a low of 0.29 ounce per ton and a high of 1.16 ounces per ton at one plant. The other plant showed 0.7 ounce of silver per ton in sinter. The reported quantity of silver in sinter was about 17 percent of that reported in concentrate feed.

### Silver in Retort Feed and Products

Quantitative and assay data for silver in sinter and other feed to retorts were available from four plants; one of these plants showed no assays for silver in sinter but showed some in other feed material. The input of silver in the total known feed materials was about 306,000 ounces. Some of this is in company confidential material in table 2. Quantitative and assay data on retort residues at two plants also are shown in table 2.

### Silver in Magnetic Separation Feed and Products

Data on retort and magnetic residues at one plant are shown in table 2.

### Silver in Dust and Fume

Assays and totals for silver at five plants are shown in table 2. This is about 41 percent of the total silver in concentrate feed known from the plants.

### Silver in Fume Leaching

The assay and weight data on lead sulfate at three plants are shown in table 2. About 66 percent of the silver in lead sulfate was from one plant; one large plant did not report data on the sulfate. Two plants shipped fume collects containing about 146,500 ounces of silver to other processing operations. In one plant for which quantitative and assay data on silver were known for fume and lead sulfate, the quantity of silver in fume collects (527,226 ounces) compared favorably with that in lead sulfate (507,828 ounces).

### Lack of Assay Data for Byproducts in Zinc Pyrometallurgy

There were no analytical data for the following byproducts in the various phases of zinc pyrometallurgical processing: arsenic and bismuth in high-purity zinc; antimony in nonmagnetic residues from magnetic separation; bismuth in retort feed; gallium in Mexican concentrates, in magnetic feed and products, in fume and dust, and in high-purity zinc; germanium in Mexican and Peruvian concentrates, in retort residues fed to magnetic separation, and in prime western zinc from retort furnaces; gold in Peruvian concentrates, in prime western zinc, and in high-purity zinc; and silver in zinc metal and oxide.

### ZINC ELECTROMETALLURGY

The recovery of zinc by electrometallurgical methods is outlined in two Bureau of Mines publications (82, 105). It has been stated that the fume from roasting and sintering contains cadmium while germanium, arsenic, antimony, gold, silver, and some cadmium are in the zinc roast product (106). After the zinc roast product is leached with sulfuric acid, germanium, arsenic, antimony, and cadmium are precipitated. The germanium, arsenic, and antimony are recovered from the precipitates in copper or lead plants. The cadmium in precipitates is usually treated in an electrolytic cadmium plant accompanying the zinc plant. Gold, silver, and gallium occur in residues.

This section deals with minor metals entering and leaving roasting, leaching purification of zinc sulfate, leaching of purification cake, precipitation, and zinc and cadmium electrolysis. Figure 15, along with table 3, is a composite of four electrolytic zinc plants and shows the flow of byproducts in zinc electrometallurgy.

Roasting is carried out at 1,800° F or higher to remove more cadmium and to increase the formation of ferrites. Leaching of calcines and roasted ore with sulfuric acid forms a zinc sulfate solution. Purification of the solution is necessary to remove elements such as arsenic, antimony, copper, germanium, and tellurium which are detrimental to zinc electrolysis (82).

### General Information About Plant Feed

In 1971, about 16 percent of the total domestic zinc in concentrates and about 37 percent of the total foreign zinc concentrates were used in domestic electrolytic plants.

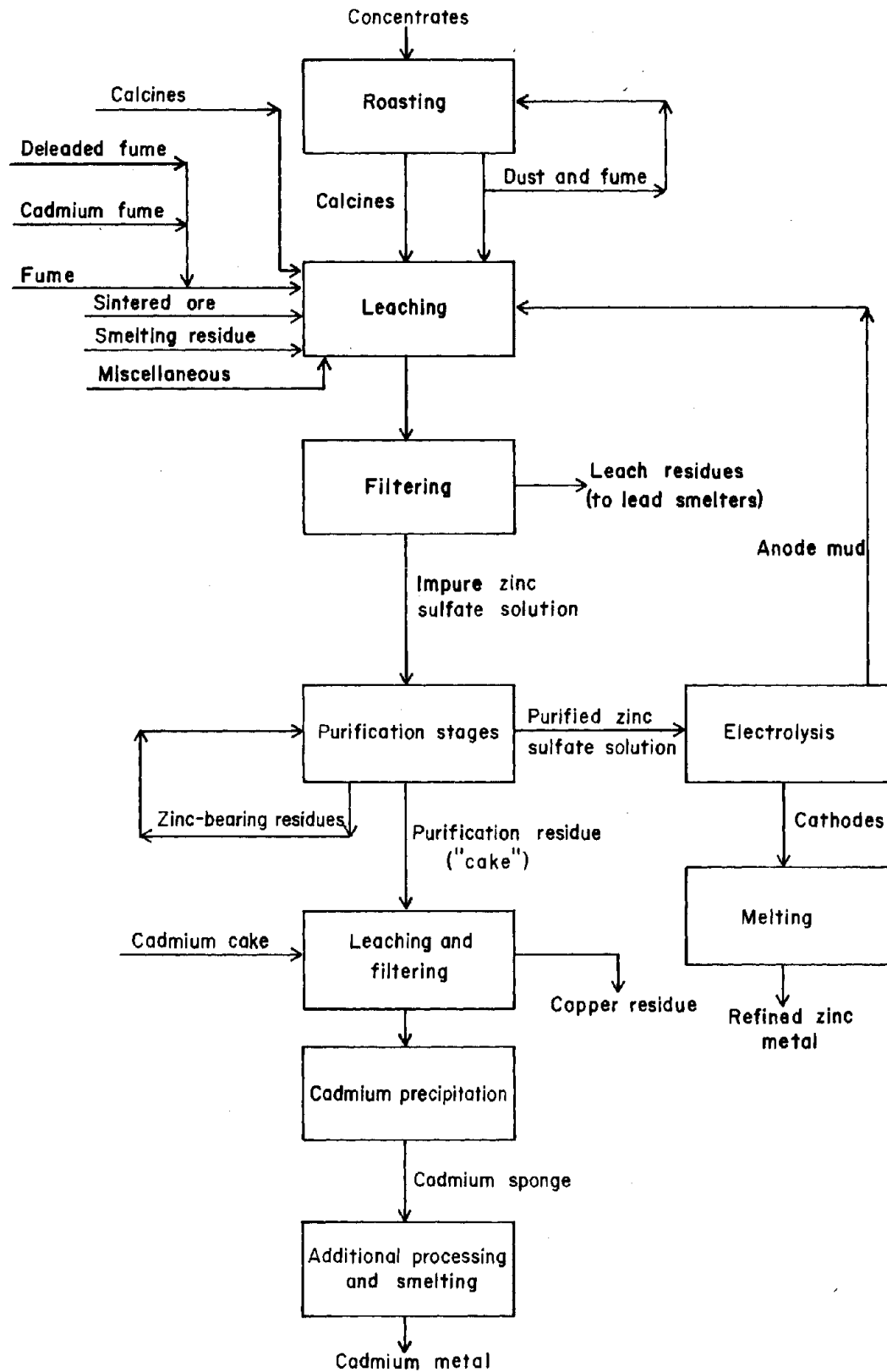


FIGURE 15. - Flowsheet for zinc electrometallurgy.

TABLE 3. - Byproduct minor metals in zinc electrometallurgy--inputs, outputs, plants, and weights

(Key to figure 15)

Process	No. of plants <sup>1</sup>	Short tons							Troy ounces	
		As	Sb	Bi	Cd	Ga	Ge	In	Au	Ag
Roasting:										
Input: Concentrates....	4	<sup>2</sup> 342	<sup>2</sup> 153	8	<sup>2</sup> 1,312	5	5	<sup>2</sup> 14	<sup>2</sup> 4,500	<sup>2</sup> 1,360,000
Output:										
Calcines <sup>3</sup> .....	4	79	14	NA	822	NA	NA	2	1,534	590,959
Dust and fume <sup>3</sup> .....	4	NA	NA	NA	NA	NA	NA	NA	NA	NA
Leaching:										
Input:										
Calcines (from roasting) <sup>3</sup> .....	4	79	14	NA	822	NA	NA	2	1,534	<sup>4</sup> 590,959
Calcines (other, purchased).....	2	41	12	NA	239	NA	<sup>5</sup> 5	NA	2,470	293,932
Dust and fume (from roasting) <sup>3</sup> .....	4	NA	NA	NA	NA	NA	NA	NA	NA	NA
Deleaded fume.....	2	2	8	NA	2	NA	NA	.4	NA	8,871
Cadmium fume.....	1	NA	NA	NA	71	NA	NA	NA	NA	NA
Fume.....	3	78	51	NA	41	NA	<sup>6</sup> 6	NA	NA	<sup>6</sup> 452
Sintered ore.....	1	( <sup>7</sup> )	( <sup>7</sup> )	NA	( <sup>7</sup> )	NA	( <sup>7</sup> )	NA	NA	NA
Smelting residue.....	1	.2	.2	.01	<.01	NA	NA	.02	NA	NA
Anode mud <sup>8</sup> .....	4	NA	NA	NA	NA	NA	NA	NA	NA	NA
Miscellaneous.....	1	NA	NA	NA	NA	NA	NA	NA	NA	NA
Filtering:										
Input.....		NA	NA	NA	NA	NA	NA	NA	NA	NA
Output:										
Leach residues.....	4	<sup>9</sup> 321	<sup>9</sup> 105	<sup>9</sup> 9	<sup>9</sup> 368	NA	<sup>9</sup> 11	<sup>9</sup> 9	<sup>9</sup> 5,090	<sup>9</sup> 1,204,305
Impure zinc sulfate solution.....	4	NA	NA	NA	NA	NA	NA	NA	NA	NA
Purification:										
Output:										
Purified zinc sulfate solution.....	4	NA	NA	NA	NA	NA	NA	NA	NA	NA
Zinc-bearing residues.		NA	NA	NA	NA	NA	NA	NA	NA	NA
Purification residue (cadmium cake).....	4	<sup>10</sup> 116	<sup>10</sup> 7	<sup>10</sup> .2	<sup>10</sup> 22	NA	<sup>10</sup> 4	<sup>10</sup> <.5	<sup>10</sup> 226	<sup>10</sup> 3,075
Leaching and filtering:										
Input:										
Purification residue (cadmium cake).....	4	<sup>10</sup> 116	<sup>10</sup> 7	<sup>10</sup> .2	<sup>10</sup> 22	NA	<sup>10</sup> 4	<sup>10</sup> <.5	<sup>10</sup> 226	<sup>10</sup> 3,075
Other cadmium cake....	1	NA	NA	NA	NA	NA	NA	NA	NA	NA
Output: Copper residue.	2	<sup>11</sup> 22	<sup>11</sup> 2	<sup>11</sup> .04	<sup>11</sup> 19	NA	NA	<sup>11</sup> <.1	<sup>11</sup> 14	<sup>11</sup> 863
Cadmium precipitation:										
Output: Cadmium sponge.	4	<sup>12</sup> NA	<sup>12</sup> NA	NA	NA	NA	<sup>12</sup> NA	<sup>12</sup> Tr	NA	NA

NA Not available. Tr Trace.

<sup>1</sup>Plants using processes and showing quantities or assays of materials.<sup>2</sup>Includes 0.07 percent arsenic (average), 0.03 percent antimony (average); 0.33 percent cadmium in domestic, 0.42 percent in foreign; 0.002 percent indium in domestic; 0.016 to 0.12 ounce of gold per ton; 0.1 to 7.7 ounces of silver per ton in domestic (the latter in Missouri concentrates).<sup>3</sup>One plant combined calcines and dust.<sup>4</sup>Includes 2.38 to 5.65 ounces of silver per ton at 1 plant, 7.32 ounces at another.<sup>5</sup>Includes 0.0016 to 0.004 percent germanium.<sup>6</sup>Includes 0.001 to 0.02 percent germanium; 0.4 to 2.5 ounces of silver per ton at 2 plants.<sup>7</sup>Company confidential.<sup>8</sup>One plant combined anode mud and cake with leach residues and shipped them to a pyrometallurgical smelter. Another plant recycled anode mud.<sup>9</sup>Includes 0.16 to 1.32 percent arsenic at 2 plants; 0.05 to 0.38 percent antimony at 2 plants; 0.01 to 0.018 percent bismuth at 1 plant; weight cadmium at 2 plants with 0.14 to 0.82 percent cadmium at 3 plants; 0.021 to 0.091 percent germanium at 2 plants; indium weight at 1 plant; 0.016 to 0.02 percent indium at 2 plants; gold weight at 1 plant, 0.067 to 0.11 ounce of gold at 2 plants; 8.51 to 30.8 ounces of silver per ton at 3 plants.<sup>10</sup>Arsenic quantity at 2 plants, 0.025 to 4.89 percent arsenic at 3 plants; antimony at 1 plant, 0.026 to 0.2 percent antimony at 2 plants; bismuth at 1 plant, 0.004 percent bismuth on higher assay; 0.2 to 0.6 percent cadmium at 2 plants; 0.0043 to 0.354 percent germanium at 3 plants; indium at 1 plant, 0.003 to 0.0125 percent indium at 2 plants; gold at 1 plant, 0.055 ounce per ton (average); 1.13 to 8 ounces of silver per ton at 2 plants.<sup>11</sup>Three percent arsenic at 1 plant, 0.53 percent at another; 0.23 percent antimony at 1 plant, 0.3 percent at another; 0.006 percent bismuth at 1 plant; 0.75 to 4.0 percent cadmium; 0.046 and 0.002 percent germanium; 0.013 percent indium at 1 plant; 0.02 and 0.026 ounce of gold per ton at 2 plants; 1.2 and 4.07 ounces of silver per ton at 2 plants.<sup>12</sup>Includes 0.06 percent arsenic at 1 plant; 0.106 percent antimony at 1 plant; 0.072 and 0.0016 percent germanium at 2 plants; 0.08 percent indium at 1 plant.

### Arsenic in Concentrates to Roasting

About 32 percent of the reported arsenic in total concentrate feed, shown in table 3, occurs in domestic material. Idaho provided about 70 percent of the reported domestic arsenic in concentrates; New Mexico and Utah ranked second and third nationally. Concentrates from Missouri, Washington, Tennessee, and Colorado contained insignificant quantities of arsenic. One firm supplied no breakdown of domestic concentrates, which were of minor importance at that plant.

There was no breakdown by foreign country at one plant which used about 20 percent by weight of the foreign concentrates used by domestic electrolytic plants. Three other plants consumed about 107 tons of domestic arsenic in concentrate feed, mostly in concentrates to two plants. Peru provided the most arsenic in concentrates, followed by Canada, Honduras, and Mexico.

### Arsenic in Roasting Products

Three plants provided quantitative data on calcines totaling 162,141 tons. One of these plants showed total production of calcines and dust. The content of 0.11 percent arsenic in these indicated the weight shown in table 3.

### Arsenic in Leaching Feed

Leaching feed consists mostly of calcines, produced in-house or obtained elsewhere, with lesser amounts of fume, sintered ores, and certain residues.

Except for the lack of data on bismuth or gallium, assay data were generally available for the minor metals in the leaching feed materials. However, information on minor metals in leaching feed usually could not be compared with information on calcine products due to lack of data on the latter or to additional leaching input (specifically, extra calcines or fume to leaching) compared with roasting products.

Assays at one plant indicated the presence of 0.032 percent arsenic in purchased calcines and 0.019 to 0.15 percent arsenic in two types of purchased fume. At another plant, the amount of arsenic calculated in leaching feed was about 161 tons, about twice as much as that in roasting products, due to the arsenic in purchased sintered ore and fume.

### Arsenic in Filtering Products

Quantities of leach residues products (precipitates) were given for three plants, but weights of impure zinc sulfate products (filtrate) were not available. About 54 percent of the known leach residues were produced at one plant and about 30 percent at another. Quantities and assays for two plants are shown in table 3. Residues at another plant contained 0.17 percent arsenic.

### Arsenic in Purification

Zinc dust and other materials are added to impure zinc sulfate in a purification step. The purified zinc sulfate solution is sent to electrolysis. A purification residue (cadmium cake) is precipitated and sent to cadmium leaching. Sometimes a copper residue is sent to marketing or further processing.

Only two plants provided any quantitative data on purification residue. Assay and weight data are shown in table 3.

### Arsenic in Leaching of Purification and Other Residues

Assays on cadmium cake, the principal feed, are shown in table 3. Copper residue (copper cake) was produced at two plants. Copper-cobalt residue and purchased cadmium cake were fed to leaching at another plant. The cadmium cake fed to leaching at the latter plant contained 0.22 percent arsenic.

### Arsenic in Precipitation Products

Weights were available on cadmium sponge produced at two plants, and on copper residue made at a third. Data are shown in table 3.

### Minor Metals in Cadmium Metal

The only data were for germanium and silver. At one plant, cadmium metal contained 0.0018 percent germanium and 0.14 ounce of silver per ton (a total of 73 ounces of silver).

### Antimony in Concentrates to Roasting

About 25 percent of total reported antimony in concentrates came from domestic materials, with Idaho providing about 67 percent and New Mexico and Utah ranking second and third. Washington, Missouri, Colorado, and Tennessee provided very small amounts.

All four plants used foreign concentrates, but about 97 percent was used at three plants. The chief suppliers of antimony in concentrates were Canada, Honduras, Peru, and Mexico.

### Antimony in Roasting Products

Weight from one plant is shown in table 3.

### Antimony in Leaching Feed

At one plant about 0.009 percent antimony was present in purchased calcines and 0.059 and 0.065 percent antimony was in purchased fume. At another plant, the amount of antimony calculated in leaching feed was about 68 tons, nearly five times that in calcines and dust produced at the plant. Fume in leaching feed at this plant assayed 0.085 percent antimony and sintered ore assayed 0.07 percent antimony.

### Antimony in Filtering, Purification, and Precipitation Products

At two plants, assays and weights of leach and cadmium cake are shown in table 3. Leach residues at another plant contained 0.062 percent antimony. The cadmium cake from purification, fed to leaching at one plant, contained 0.07 percent antimony. Data on copper residue and cadmium sponge also are in table 3.

### Bismuth in Concentrates to Roasting

Few data were available on the bismuth content of domestic concentrates; Utah concentrates averaged 0.003 percent bismuth and those from Colorado averaged 0.007 percent.

As seen in table 3, about 8 tons of bismuth were present in total concentrates. Four times as much bismuth occurred in foreign concentrates as in domestic. Of these, about 70 percent was in Peruvian concentrates (averaging about 0.02 percent bismuth) and lesser quantities came from Canada and Mexico.

### Bismuth in Filtering, Purification, and Precipitation Products

Only one plant had assays on which the tonnage of bismuth in residues was based. These data and those for cadmium cake are shown in table 3.

### Cadmium in Concentrates to Roasting

Of three plants which provided both quantitative and assay data, two consumed about 83 percent of cadmium in concentrates. About 39 percent of total known cadmium in concentrates was in domestic materials, with Idaho supplying about 40 percent of these, followed by Missouri with 22 percent, Utah with 21 percent, and Tennessee with about 7 percent. Lesser quantities came from New Mexico, Washington, California, and Colorado. Some Missouri concentrates contained about 0.8 percent cadmium; materials from Utah averaged about 0.5 percent.

Canadian concentrates at one plant were primarily from Ontario. Three plants used Mexican, one Honduran, and three Peruvian concentrates which provided about 17, 15, and 3 percent, respectively, of the reported tonnage of cadmium in concentrates. High percentages of cadmium (0.91 and 0.95 percent) were in concentrates from Mexico, and Mexican concentrates averaged about 0.72 percent cadmium. Yukon material contained about 0.85 percent cadmium.

### Cadmium in Roasting Products

Data from three plants in table 3 shows the total cadmium in the calcine products. At one of these plants, the calcines were comparable in cadmium content to the content in concentrates feed.

### Cadmium in Leaching Feed

At one plant, 16 percent more calcines was consumed than produced. Different assays for cadmium in roasting products calcines and leaching feed calcines indicated about 38 percent more cadmium was present in the latter than in the former. Altogether, excluding plant-produced calcines, there were about 353 tons of cadmium in leaching feed. Weights of total leaching feed materials, excluding purchased calcines, are shown in table 3. At one plant nearly 275 percent more cadmium was fed to leaching than was reported in calcines due to cadmium in purchased calcines and fumes. Similarly, another plant showed about 10 percent more cadmium in its leaching feed than it did in its calcines and dust products.

### Cadmium in Filtering, Purification, and Precipitation Products

Data on leach, purification, and copper residues are presented in table 3. At one plant, from which no weights of cadmium cake were available, the cadmium tenor was 4.4 percent. Purchased cadmium cake fed to leaching at one plant contained 7.5 percent cadmium.

### Cadmium in Refined Zinc

Refined zinc at one plant contained 0.002 percent cadmium; refined zinc at two plants contained 0.0005 percent cadmium.

### Gallium in Concentrates to Roasting

In domestic concentrates the only meaningful gallium data were obtained from one plant and from Missouri and Tennessee concentrates, which assayed from about 0.006 to 0.01 percent gallium. From the limited data available on both domestic and foreign concentrates, it appeared that about 38 percent of gallium occurred in domestic concentrates.

For foreign concentrates, data were available for two plants. From these it appeared that most gallium was found in Peruvian concentrates for which one assay showed 0.15 percent gallium.

### Germanium in Concentrates to Roasting

From available data it appeared that about 18 percent of germanium in concentrates was in domestic material, with Washington State providing practically all of this. Assays on Washington materials ranged from about 0.006 to 0.009 percent germanium. Foreign germanium in concentrates were about 76 percent from Canada. Peru provided nearly 19 percent, and the rest came from Honduras and Mexico. In some Canadian concentrates, assays ranged up to 0.006 percent germanium.

Germanium in Leaching Feed and in Filtering, Purification,  
and Precipitation Products

Data on germanium in calcines, fume, and sintered ore and in leach residues from two plants are shown in table 3. Data on cadmium cake from three plants, and on cadmium sponge and copper residues at two plants also are presented.

Indium in Concentrates to Roasting

Domestic material provided about 26 percent of the weight of indium in concentrates consumed by two plants. Most of this was from Utah (about 55 percent) and Idaho (about 30 percent). The rest was from Missouri, Colorado, and Washington. Assays ranged from 0.0003 percent to nearly 0.01 percent indium in Utah material.

Canada was the foremost supplier of indium in concentrates, supplying about 85 percent of the foreign material. These concentrates had as much as 0.04 percent indium. Peru supplied most of the remainder, with Peruvian assays averaging about 0.01 percent indium. Few data were available on Mexican concentrates consumed.

Indium in Roasting Products and in Leaching Feed

Only 0.004 percent indium was present in calcines from one plant. Most assay data on indium in leaching feed were available from the plant; two varieties of fume at the plant contained 0.003 and 0.02 percent indium. Smelting residues at another plant contained 0.003 percent indium.

Indium in Filtering, Purification, and Precipitation Products

Data on leach residues and on cadmium cake from two plants and on cadmium sponge and copper residues from one plant are shown in table 3.

Gold in Concentrates to Roasting

Only one plant had any data on domestic gold in concentrates with the highest assay being nearly 0.6 troy ounce of gold per ton in Washington concentrates.

The data indicate that foreign gold in concentrates was more than twice that in domestic concentrates. Canada provided nearly 73 percent of gold in concentrates. Peru and Mexico provided the rest of known foreign gold. Assays on foreign concentrates are shown in table 3.

Some gold assay data were available from 1968 (48). These assays ranged from 0.006 to 0.02 ounce of gold per ton.

### Gold in Roasting Products

One plant that showed indium in calcines also was the only one with assays available for gold (0.036 ounce per ton). However, output quantities of gold could not be compared with the input. Dust at the plant contained from 0.016 to 0.029 ounce of gold per ton.

### Gold in Leaching Feed

Only one plant had any gold assay data, 0.02 and 0.036 ounce of gold per ton in calcines. Traces of gold were detected in fume at the plant.

### Gold in Filtering, Purification, and Precipitation Products

Data on leach residues at two plants, on cadmium cake at one plant, and on copper residue at two plants are shown in table 3.

### Silver in Concentrates to Roasting

Of known silver in concentrates shown in table 3, about 31 percent was of domestic origin and averaged about 2.7 ounces of silver per ton. Missouri provided about 45 percent of domestic silver in concentrates, followed by Utah (about 30 percent), Idaho (about 23 percent), Colorado, and Tennessee.

In 1971 Canada provided about 81 percent of total foreign silver in concentrates. Canadian assays, averaging 6.8 ounces of silver per ton, ranged from 6.04 ounces of silver per ton to as much as 19.4 ounces of silver per ton. Peru and Mexico also provided silver in concentrates.

Assay data for 1968 for silver in zinc concentrates were available for mills in Idaho, Canada, Honduras, Mexico, and Peru (48). Assays ranged from 0.88 ounce of silver per ton (at one Canadian mine-mill) to 26.6 ounces of silver per ton from a mill in Honduras.

### Silver in Roasting Products

Two plants had quantitative and assay data available on calcines; these are shown in table 3. At one plant having both concentrate input and calcine output data, the silver in calcines was 83 percent of that in the concentrates.

### Silver in Leaching Feed

Two plants provided silver assay data. These and weight are shown in table 3. Weight of other calcines and fume feed data also are shown in table 3.

### Silver in Filtering Products

Silver assays on leach residues at three plants and weight of silver known in leach residues at two of the plants are shown in table 3. This is greater than the weight known in concentrate feed at these two plants and is due in part to additional silver-bearing materials such as purchased calcines and fume fed to leaching.

### Silver in Purification and Precipitation Products

Data on cadmium cake at two plants and on copper residue at two plants are shown in table 3.

### Lack of Assay Data for Byproducts in Zinc Electrometallurgy

There were no analytical data for the following byproducts in the various phases of zinc electrometallurgical processing:

1. All byproducts in impure and purified zinc sulfate; arsenic in filtering feed.
2. Arsenic in filtering feed and antimony in zinc electrolysis feed and products (for example, anode mud and cathodes), in refined zinc metal, and in cadmium metal.
3. Bismuth in roasting products and in leaching feed, in leaching of purification and other residues, in precipitation products, in zinc electrolysis, in refined zinc metal, and in cadmium metal.
4. Cadmium in zinc electrolysis.
5. Gallium in roasting products and in leaching feed, in filtering products, in purification, in leaching of purification and other residues, in precipitation products, in zinc electrolysis, in refined zinc metal, and in cadmium metal.
6. Germanium in calcines and other roasting products, in leaching of purification and other residues, in zinc electrolysis, and in refined zinc metal.
7. Indium in Honduran concentrates, in leaching of purification and other residues, in zinc electrolysis, in refined zinc metal, and in cadmium metal.
8. Gold in leaching of purification and other residues, in zinc electrolysis, in refined zinc metal, and in cadmium metal.
9. Silver in leaching of purification and other residues, in zinc electrolysis, and in refined zinc metal.

### MINOR METALS IN ZINC OXIDE PRODUCTION

Five plants were the major domestic producers of zinc oxide (fig. 3). About 5 percent of domestic concentrates was fed to American process producers. Only one plant roasted Tennessee zinc concentrates. Another sintered zinciferous materials, mostly fume, and another furnaced nodules made from Upper Mississippi Valley concentrates. Two major plants, which also produced zinc metal, furnaced sinter that was processed at the plant from domestic and foreign concentrates, and calcines. A smaller producer used decadmiumized calcines for most of the year but then converted to the French process. Figure 3 shows plants using the American process to produce zinc oxide.

The calcine product from roasting concentrates at one plant was estimated at about 85 percent by weight of the concentrate input to roaster. Assuming that all the calcines were sintered, the sinter products were estimated to total about 65 percent of the calcine input, with over 95 percent of the sintering products being decadmiumized calcine and the rest fume. Decadmiumized calcines were furnaced; the resulting products were furnace residue and zinc vapor. The zinc oxide from this plant, all lead-free, constituted about 20 percent of all domestic American process zinc oxide. Arsenic, cadmium, gallium, and silver were detected in concentrates at this plant.

Cadmium determinations were also made on calcines, fume, furnace residues, and refined zinc oxide. The cadmium content of the oxide from one plant was considerably higher than the cadmium content of the oxides from the other operations (0.103 percent compared with 0.029 for highest other plant).

One company had a nodulizing plant which processed zinc nodules from the Upper Mississippi Valley district (fig. 9, location 11). When it was shutdown in early 1971, the plant had enough raw material stockpiled for processing to zinc oxide but in 1972 became dependent on sinter produced at another zinc metal plant.

Two plants produced both zinc metal and oxide. At one of the plants, Waelz sinter feed was higher in arsenic and indium than was ore sinter feed but lower in cadmium. Germanium was detected in the ore sinter but not in the Waelz sinter. No assays were made for gold or silver in either of the sinters. Arsenic, antimony (almost three times as much as arsenic), and indium (about half as much as arsenic) were detected in the American process zinc oxide made at this plant.

At the second of these two plants, high-grade sinter used in zinc oxide processing was greater in arsenic content, lower in cadmium (but having higher cadmium content than the Waelz sinter), but indium was about the same as that in the Waelz sinter, compared with ore sinter at the first plant. In American process zinc oxide, only cadmium was detected and then at about one-third the level of the cadmium in the zinc oxide at the first plant.

#### CONCLUSIONS AND RECOMMENDATIONS

The coverage of lead plants was relatively complete with flue dust samples or assays available from five of seven plants. Most such dust and fume was recycled to sintering. High contents of metals such as arsenic and antimony were noted in concentrates from most of the complex ores. Of the non-concentrate fraction of sintering feed it was noted that slags were relatively high in antimony; some residues, sludges, calcines, and speiss were high in arsenic; calcines were high in bismuth; and certain fumes and dusts were high in cadmium (fig. 13 and table 1).

Weights and assays on sinter products were obtained from six of the seven lead plants. The results of applying these data to sintering and subsequent processes may be seen in the throughput of the various minor metals in figure 13 and table 1.

In zinc electrometallurgy, there is a need to remove arsenic, antimony, germanium, and tellurium from zinc sulfate so that the purified solution can be electrolyzed. Figure 15 and table 3 show the removal of arsenic, antimony, and germanium in leach residues from filtering and in the purification and copper residues. There were no data available on the purified zinc sulfate solution. The data indicate that the arsenic and germanium in input to roasting, leaching, and filtering compare favorably with these metals in the leach residue and purification and copper residues. From available cadmium data, excluding cadmium in leach residues and the small quantities in purification and copper residues, it is probable that over three-fourths of the cadmium input is recovered as cadmium metal.

The relatively simple case of throughputs in zinc electrolysis may be compared with those in zinc pyrometallurgy where there are wide variations in inputs versus outputs in various stages of processing. These can be seen in figure 14 and table 2, which also show the complexity of processing operations. It is apparent that these generalized flowsheets are a reflection of the difficulty of obtaining precise metallurgical balances at individual plants.

In lead and zinc metallurgy, comparing the minor metal content of concentrates and other feed materials to the roasting and sintering steps with the composition of roaster products such as fume and calcines and with the minor metal content of sintering products such as fume and sinter is made difficult by the following factors: The geochemical abundance of some minor metals is so low that assay data on concentrates are not available for either economic or technical reasons. Analysis for certain rare metals such as bismuth, gallium, or indium is usually by atomic absorption, which for these metals is relatively insensitive in the low ranges (1 ppm or lower) in which they may be present in concentrates. Sampling procedures often presented difficulties. Then, too, the data on fume and dust are not entirely dependable because of the recycling and enrichment of such materials and the probability that samples available were not fully representative of the process flow.

It is particularly difficult to measure the interchange of sinter in circuits and to assess the variations of feed to metal and oxide circuits in plants making both zinc metal and oxide.

During this study, much information was assembled and evaluated on the flow of minor metals through lead and zinc processing streams. However, of equal significance, it demonstrated that development of balanced flowsheets would be possible only if much more information were to be made available. Data on both the quantities of material and analyses of the streams are far from complete. Such information would be of inestimable value in guiding research, planning strategic stockpile objectives, improving resource conservation, indicating areas for environment improvement, and increasing the efficiency of plant operations.

National concern over mineral conservation and the environment would justify a detailed study of the materials flow in all base metal concentrators, smelters, and refineries. However, as shown in this report, the magnitude and complexity of such a project indicates that the first step would be to undertake an in-depth study of one operation. Such a study could serve as a guide, first to decide if an industrywide study is justified and practical, and second, to plan the direction of any subsequent studies.

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