

FINAL SUMMARY REPORT OF
MINERAL INDUSTRY PROCESSING WASTES

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FOREWORD

This report was developed and prepared by CDM Federal Programs Corporation, and reviewed by EPA under EPA Contract No. 68-01-6939, Performance of Remedial Responses Activities at Uncontrolled Hazardous Waste Sites (REM II). Just prior to the actual submittal of this report to EPA Office of Solid Waste, CDM's work was shifted from the REM II Contract to the RCRA Implementation Support, EPA Contract No. 68-01-7374.

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EXECUTIVE SUMMARY

This document is a compilation of draft reports on the processes used to recover mineral or metal commodities from ores and concentrates and wastes generated during processing of these commodities. These reports were prepared as a part of the engineering and technical support efforts to EPA's Subtitle D Mining Waste Regulatory Development Programs.

Processing waste summaries were prepared as part of the supporting documentation for the Second Report to Congress on Solid Waste From Selected Metallic Ore Processing Operations (RTC II). These summaries were based on brief reviews of readily available literature, and are the first stage in the scoping of the Third Report to Congress (RTC III) which will address all industries not included in the first two Reports to Congress. Each industry summary discusses production, processing methods, waste generation, and waste management for a commodity or related group of commodities. These summaries include those commodities or stages of production not addressed in RTC I or RTC II. Tables ES1 and ES2 list which commodities are included in each report. Each summary evaluates the potential for the generation of hazardous waste in the production and processing of each commodity.

Based on the commodity evaluation, recommendations are made for further study of those industries that show a potential for hazardous waste generation and potential Subtitle C regulation. Industries that show no potential for hazardous waste generation are not recommended for further study.

A comprehensive list of commodities produced in the U.S. from mineral resources in 1987 was developed based on previous EPA lists, U.S. Bureau of Mines publications, and industry literature. This list was reviewed by the

EPA and U.S. Bureau of Mines and the updated list was divided into nonmetal and metal commodities. Tables ES-1 and ES-2 show in which Report to Congress each of the commodities is addressed.

Processing wastes summary reports were prepared for nonmetal and metal commodities and submitted to the EPA and the Bureau of Mines for comment in 1987. Revisions were made to the processing waste summary reports and the reports were resubmitted to EPA and the Bureau of Mines for further review. One paragraph summaries of these revised reports were prepared for RTC II in August 1987. Further study is recommended for the industries producing 18 nonmetal commodities and 27 metal commodities.

The primary reasons for recommending further study of these industries is a lack of information on waste production and waste characteristics. These are not necessarily recommendations for regulation under Subtitle C, although some waste streams may require such controls. More detailed study is needed before a regulatory recommendation can be made. The recommendations here can be used as a guide to how resources can be best used in developing future regulations.

There are some industries that are not addressed here that are in early stages of development and may become major waste generators in the future. The most notable industry in this class is oil shale. Platinum group metal processing might start in this country in the next 5 to 10 years, and nickel processing could also restart production. Due to the rapid technological changes that can be expected of developing industries, study of current proposals may give little information on future waste generation. Studies on these industries should be deferred until specific processes have been selected and tested, at which time waste characteristics can be accurately determined.

TABLE ES-1
NONMETAL INDUSTRIES

	RTC I E and B ^a	RTC II Process ^b	RTC III E and B ^a	RTC III ^c Process ^b	Comments
Natural Asphalt	-	-	O	O	
Barite	-	-	X	X	
Boron	-	-	X	X	
Bromine	-	-	X	X	
Clay	-	-	X	X	
Coal	-	-	X	X	Note c
Diatomite	-	-	O	O	
Feldspar	-	-	X	X	
Fluorspar	-	-	X	X	
Garnet	-	-	O	O	
Gemstones	-	-	O	O	
Gilsonite	-	-	X	X	
Glaucinite	-	-	O	O	
Gypsum	-	-	O	O	
Iodine	-	-	X	X	
Kyanite	-	-	X	X	
Limestone	-	-	O	O	Note d
Lithium	-	-	O	O	
Mica	-	-	O	O	
Mineral Waxes	-	-	X	X	
Oil Shale	X	-	-	-	Note e
Olivine	-	-	X	X	
Peat	-	-	O	O	
Perlite	-	-	O	O	
Phosphate	X	-	-	X	
Potash	-	-	O	O	
Pyrobitumens	-	-	X	X	
Pyrophyllite	-	-	O	O	
Salt	-	-	O	O	
Sand & Gravel	-	-	O	O	
Silica	-	-	X	X	
Soda Ash	-	-	O	O	
Sodium Sulfate	-	-	O	O	
Staurolite	-	-	O	O	
Stone	-	-	O	O	
Sulfur	-	-	O	O	
Talc	-	-	O	O	
Tripoli	-	-	O	O	
Vermiculite	-	-	O	O	
Wollastonite	-	-	O	O	

O Screened for RTC III but no further study recommended.

X Studied or recommended for study under appropriate RTC.

a Extraction and Beneficiation

b Processing

c Beneficiation, Gasification, Coking

d Cement Processing in Report to Congress for RCRA 8002(o)

e Oil Shale Extraction, Beneficiation, and Processing addressed in RTC I

TABLE ES-2
METAL INDUSTRIES

Commodity	RTC I E and B ^a	RTC II ^b Process	RTC III ^c E and B ^a	RTC III ^b Process	Comments
Aluminum	X	X	-	-	
Antimony	X	-	-	X	
Arsenic	-	-	-	O	Note c
Beryllium	X	-	-	X	
Bismuth	-	-	-	X	Note c
Cadmium	-	-	-	X	Note c
Cesium	-	-	-	X	Note d
Chromium	-	-	-	X	Note d
Cobalt	-	-	-	O	Note d
Columbium & Tantalum	-	-	-	X	Note c
Copper	X	X	-	X	
Gallium	-	-	-	X	Note e
Germanium	-	-	-	X	Note e
Gold & Silver	X	-	-	X	
Indium	-	-	-	X	Note c
Iron	X	-	-	X	
Lead	X	X	-	-	
Magnesium	-	-	-	X	Note f
Manganese	-	-	-	X	Note d
Mercury	X	-	-	O	
Molybdenum	X	-	-	X	
Nickel	X	-	-	O	
Platinum	X	-	-	O	
Rare Earths	X	-	-	X	
Rhenium	-	-	-	X	Note c
Rubidium	-	-	-	X	
Scandium	-	-	-	O	Note c
Selenium	X	-	-	X	
Silicon	-	-	-	X	Note g
Strontium	-	-	-	X	Note d
Tellurium	-	-	-	X	Note c
Tin	-	-	-	X	Note d
Titanium	X	-	-	X	
Tungsten	X	-	-	X	
Vanadium	X	-	-	X	
Zinc	X	X	-	-	
Zinc Oxide	X	X	-	-	
Zirconium & Hafnium	-	-	-	X	Note c

O Screened for RTC III but no further study recommended.

X Studied or recommended for study under appropriate RTC.

a Extraction and Beneficiation

b Processing

c Produced from materials that are by-products of beneficiation or processing of other metals

d Produced from imported ores or concentrates

e Predominantly produced as by-products, one new mine produces Gallium and Germanium as primary products

f Produced from either brines needing no extraction or beneficiation or from dolomite which is covered elsewhere

g Silicon is made from Silica (covered as a nonmetal); Ferrosilicon may use some iron ore in addition to silica sources

1.0 INTRODUCTION

1.1 STATUTORY AND REGULATORY BACKGROUND

Sections 8002(f) and (p) of the Resource, Conservation and Recovery Act (RCRA) (Solid and Hazardous Waste Amendments of 1984), require EPA to conduct a study of mining wastes. Congress prohibited EPA from regulating mining wastes under Subtitle C (hazardous wastes) until at least six months after issuing the mining waste study (RCRA Section 3001(b)(3)(a)(ii)). On December 31, 1985, the Agency submitted its First Report to Congress (RTC I) on wastes generated from the extraction and beneficiation of metallic ores, phosphate rock, asbestos, overburden from uranium mining, and oil shale. Based on RTC I and comments received after issuance of the report, EPA published its "regulatory determination" on July 3, 1986 as required by RCRA 3001(b)(3)(c). EPA's determination stated the Agency's intent to regulate, under Subtitle D (solid waste), the large volumes of waste generated by the mining industry.

The Agency is planning to issue in 1988 a Second Report to Congress (RTC II) on wastes generated by copper, lead, zinc and zinc oxide, bauxite, and aluminum ore processing operations. EPA will issue a regulatory determination on these processing wastes subsequent to receipt of comments on RTC II. A Third Report to Congress (RTC III) on remaining mining and processing sectors has also been proposed but not yet fully funded.

1.2 PURPOSE OF THIS REPORT

The processing waste summaries in Sections 2 and 3 of this report were prepared as part of the supporting documentation for RTC II. These summaries were based on brief reviews of readily available literature, and are the first stage in the scoping of RTC III. Each industry summary discusses production, processing methods, waste generation, and waste management for a commodity or related group of commodities. These

summaries address those commodities or stages of production not addressed in RTC I or RTC II. Tables 1-1 and 1-2 list which commodities are included in each report. Each summary evaluates the potential for the generation of hazardous waste in the production and processing of each commodity.

Based on the commodity evaluation, recommendations are made for further study of those industries that show a potential for hazardous waste generation and potential Subtitle C regulation. Industries that show no potential for hazardous waste generation are not recommended for further study.

1.3 PREPARATION OF THE PROCESSING WASTE SUMMARIES

A comprehensive list of commodities produced in the U.S. from mineral resources in 1987 was developed based on previous EPA lists, U.S. Bureau of Mines publications, and industry literature. This list was reviewed by the EPA and U.S. Bureau of Mines and the updated list was divided into nonmetal and metal commodities. Tables 1-1 and 1-2 show in which Report to Congress each of the commodities is addressed.

Processing wastes summary reports were prepared for nonmetal and metal commodities and submitted to the EPA and the Bureau of Mines for comment in 1987. Revisions were made to the processing waste summary reports and the reports were resubmitted to EPA and the Bureau of Mines for further review. One paragraph summaries of these revised reports were prepared for RTC II in August 1987. The one paragraph summaries are listed in Section 1.5.

1.4 SUMMARY AND CONCLUSIONS

This document contains process descriptions for 74 commodities produced in the U.S. from mineral sources, 42 of which are nonmetals and 32 are metals. Further study for possible regulation under Subtitle C is not recommended for 24 nonmetal commodities and 5 metal commodities. Some of the industries generate no waste, some generate waste with no hazardous

TABLE 1-1
NONMETAL INDUSTRIES

	RTC I E and B ^a	RTC II Process ^b	RTC III E and B ^a	RTC III Process ^b	Comments
Natural Asphalt	-	-	O	O	
Barite	-	-	X	X	
Boron	-	-	X	X	
Bromine	-	-	X	X	
Clay	-	-	X	X	
Coal	-	-	X	X	Note c
Diatomite	-	-	O	O	
Feldspar	-	-	X	X	
Fluorspar	-	-	X	X	
Garnet	-	-	O	O	
Gemstones	-	-	O	O	
Gilsonite	-	-	X	X	
Glauconite	-	-	O	O	
Gypsum	-	-	O	O	
Iodine	-	-	X	X	
Kyanite	-	-	X	X	
Limestone	-	-	O	O	Note d
Lithium	-	-	O	O	
Mica	-	-	O	O	
Mineral Waxes	-	-	X	X	
Oil Shale	X	-	-	-	Note e
Olivine	-	-	X	X	
Peat	-	-	O	O	
Perlite	-	-	O	O	
Phosphate	X	-	-	X	
Potash	-	-	O	O	
Pyrobitumens	-	-	X	X	
Pyrophyllite	-	-	O	O	
Salt	-	-	O	O	
Sand & Gravel	-	-	O	O	
Silica	-	-	X	X	
Soda Ash	-	-	O	O	
Sodium Sulfate	-	-	O	O	
Staurolite	-	-	O	O	
Stone	-	-	O	O	
Sulfur	-	-	O	O	
Talc	-	-	O	O	
Tripoli	-	-	O	O	
Vermiculite	-	-	O	O	
Wollastonite	-	-	O	O	

O Screened for RTC III but no further study recommended.

X Studied or recommended for study under appropriate RTC.

a Extraction and Beneficiation

b Processing

c Beneficiation, Gasification, Coking

d Cement Processing in Report to Congress for RCRA 8002(e)

e Oil Shale Extraction, Beneficiation, and Processing addressed in RTC I

TABLE 1-2
METAL INDUSTRIES

Commodity	RTC I E and B ^a	RTC II ^b Process	RTC III E and B ^a	RTC III ^b Process	Comments
Aluminum	X	X	-	-	
Antimony	X	-	-	X	
Arsenic	-	-	-	O	Note c
Beryllium	X	-	-	X	
Bismuth	-	-	-	X	Note c
Cadmium	-	-	-	X	Note c
Cesium	-	-	-	X	Note d
Chromium	-	-	-	X	Note d
Cobalt	-	-	-	O	Note d
Columbium & Tantalum	-	-	-	X	Note c
Copper	X	X	-	X	
Gallium	-	-	-	X	Note e
Germanium	-	-	-	X	Note e
Gold & Silver	X	-	-	X	
Indium	-	-	-	X	Note c
Iron	X	-	-	X	
Lead	X	X	-	-	
Magnesium	-	-	-	X	Note f
Manganese	-	-	-	X	Note d
Mercury	X	-	-	O	
Molybdenum	X	-	-	X	
Nickel	X	-	-	O	
Platinum	X	-	-	O	
Rare Earths	X	-	-	X	
Rhenium	-	-	-	X	Note c
Rubidium	-	-	-	X	
Scandium	-	-	-	O	Note c
Selenium	X	-	-	X	
Silicon	-	-	-	X	Note g
Strontium	-	-	-	X	Note d
Tellurium	-	-	-	X	Note c
Tin	-	-	-	X	Note d
Titanium	X	-	-	X	
Tungsten	X	-	-	X	
Vanadium	X	-	-	X	
Zinc	X	X	-	-	
Zinc Oxide	X	X	-	-	
Zirconium & Hafnium	-	-	-	X	Note c

O Screened for RTC III but no further study recommended.

X Studied or recommended for study under appropriate RTC.

a Extraction and Beneficiation

b Processing

c Produced from materials that are by-products of beneficiation or processing of other metals

d Produced from imported ores or concentrates

e Predominantly produced as by-products, one new mine produces Gallium and Germanium as primary products

f Produced from either brines needing no extraction or beneficiation or from dolomite which is covered elsewhere

g Silicon is made from Silica (covered as a nonmetal); Ferrosilicon may use some iron ore in addition to silica sources

characteristics, some industries are too small to generate wastes in sufficient volume to require regulation, and other industries have recently shut down permanently.

Further study is recommended for the industries producing 18 nonmetal commodities and 27 metal commodities.

The primary reasons for recommending further study of these industries is a lack of information on waste production and waste characteristics. These are not necessarily recommendations for regulation under Subtitle C, although some waste streams may require such controls. More detailed study is needed before a regulatory recommendation can be made. The recommendations here can be used as a guide to where resources can be best used in developing future regulations.

There are some industries that are not addressed here that are in early stages of development and may become major waste generators in the future. The most notable industry in this class is oil shale. Platinum group metal processing might start in this country in the next 5 to 10 years and nickel processing could also restart production. Due to the rapid technological changes that can be expected of developing industries, study of current proposals may give little information on future waste generation. Studies on these industries should be deferred until specific concrete processes have been selected and tested at which time waste characteristics can be accurately determined.

The following one paragraph summaries are reproduced here from RTC II, Chapter 2.0. They are presented in order that the reader may preview the scope of future investigations in the possible generation of hazardous waste by the mining industry. They are divided into four sections:

- nonmetals not recommended for further study
- nonmetals recommended for further study
- metals not recommended for further study

- metals recommended for further study

The reader should be aware that some commodities that are given separate summaries in this section are combined with closely related commodities in the more detailed reports in Sections 2 and 3. For example, zirconium and hafnium are addressed in Section 3 by the report entitled "Rare Earth Metals" since they are produced from the same feedstocks.

1.4.1 Nonmetals Not Recommended for Further Study

Diatomite - Diatomite is selectively mined to eliminate waste materials. The diatomite is dried and separated into size fractions, which are sold as products. Any material that is too fine for sale is sintered into coarser particles. This processing does not generate hazardous wastes.

Garnet - Garnet materials are quarried and the garnets separated using a variety of techniques, including density separation, magnetic separation, and flotation. Garnet processing uses no hazardous materials, and wastes are not expected to be hazardous.

Gemstones - The gem industry in the U.S. is extremely small as a whole, and each operation producing gemstones is also quite small. Much production will be on hand and as a by-product of printing or quarrying other materials. The gemstone industry therefore is not expected to produce significant quantities of hazardous waste.

Glauconite - Glauconite, also known as green sand, is mined hydraulically and piped to a processing plant where clays and other undesirable materials are washed out. The glauconite is then treated with chemicals such as sodium aluminate, aluminum sulfate, or sodium silicate, to give it ion exchange properties for use in water softening. No hazardous wastes are expected from this processing.

Gypsum - Natural gypsum is selectively mined so that there is little or no waste. Mined gypsum needs no beneficiation. Some gypsum is processed by calcination for use in gypsum board (wallboard), gypsum plaster, and gypsum cement. Calcined gypsum is not hazardous, and all of it can be used in some product. No hazardous wastes are expected from gypsum processing.

Lime, Limestone, and Dolomite - Limestone and dolomite are produced by selective mining which generates a very small amount of non-hazardous waste. Preparation for market is limited to crushing and screening operations, which generate no wastes. There is nothing associated with limestone or dolomite deposits that would be hazardous even if discarded. Lime is produced from limestone or dolomite by heating to high temperature to drive off carbon dioxide, leaving calcium oxide or calcium oxide and magnesium oxide. Since all solids are contained in some product, no solid wastes are normally generated during lime processing.

Lithium - Lithium and lithium compounds are produced from the mineral spodumene and from brines. Spodumene is concentrated from pegmatite ores by froth flotation. The waste materials from froth flotation are non-hazardous silicate minerals. Flotation chemicals that might remain in the wastewaters would not render that water hazardous. Lithium carbonate is produced by acid leaching of heat treated spodumene. Since the acid is neutralized with limestone during the process, the residual calcium sulfate (gypsum) sludge is not expected to be hazardous. Lithium carbonate is precipitated from concentrated brines by the addition of soda ash. No hazardous wastes are expected from this treatment.

Mica - Mica is mined from pegmatite deposits and concentrated primarily by flotation. The silicate minerals in the pegmatite wastes and the flotation reagents in the wastes are not expected to be hazardous.

Peat - Peat is primarily used in agricultural and horticultural applications. Peat is used as mined, and no significant wastes are expected from peat production.

Perlite - Perlite is selectively mined, processed by screening to remove waste rock, and then expanded by heating. The waste rock is not expected to be hazardous.

Potash - Potash is produced by conventional mining, solution mining, and treatment of natural subterranean brines. Conventionally mined ores are treated by froth flotation which generates non-hazardous tailings containing halite (common salt) and some silicate minerals. Potash brines are generally evaporated and selectively precipitated. One operation uses froth flotation to separate the salts precipitated during solar evaporation. The wastes from this process are brine and salts such as sodium chloride, and are not expected to be hazardous.

Pumice - Pumice is a volcanic rock which is selectively mined to eliminate undesirable material, then processed by size reduction and size sorting only. No hazardous wastes are expected from pumice processing.

Pyrophyllite - Pyrophyllite is a talc-like mineral that is produced by selective mining, and is processed by grinding to meet size specifications. No hazardous wastes are expected from pyrophyllite production or processing.

Salt and Rock Salt (Halite) - Rock salt, used for road deicing and other applications where purity is not a prime requirement, is selectively mined, crushed and sorted by size. No hazardous wastes are expected. Some salt is solution mined, yielding a brine from which the salt is precipitated. Solution mining and solar extraction of lake brines and seawater produce waste salts and brines that are discarded. These salts and brines are primarily calcium and magnesium salts and are not expected to be hazardous.

Sand and Gravel and Crushed Stone - Sand and gravel are mined and processed by washing, drying, and sorting by size. The only wastes from processing sand and gravel are fine materials such as clay and silt that are washed

away in processing. These materials are not expected to exhibit hazardous characteristics. Crushed stone production only generates fugitive dust releases with all of the crushed rock being used as product. The fugitive dusts are not expected to be hazardous.

Soda Ash - Soda ash is produced from the mineral trona by conventional underground mining and solution mining, and also from naturally occurring brines. Trona that has been conventionally mined is processed first by calcination, which generates wastes of carbon dioxide and water. The calcined material is then dissolved in water. Insoluble materials such as shale are separated by settling and/or filtration, and are discarded as non-hazardous wastes. the sodium carbonate solution is concentrated by evaporation and crystallized into either the monohydrate or sesquihydrate form. The precipitate can be sold or the sesquihydrate form may be calcined to produce another product. No hazardous wastes are expected from the concentration, crystallization, or calcination steps. Solution mined trona undergoes similar processing and yields similar wastes. Natural brines in California containing sodium carbonate are treated with carbon dioxide to convert the sodium carbonate to bicarbonate, which then precipitates. The bicarbonate is separated from the remaining brine by settling and filtration. The brine is processed further, and the sodium bicarbonate is calcined to convert it back to soda ash, releasing carbon dioxide and water. The only waste from this process would be the final discarded brine, which is not expected to be hazardous.

Sodium Sulfate - Sodium sulfate is produced from brines at Searles Lake, California, Great Salt Lake, Utah, and in West Texas. The West Texas brines are treated by refrigeration to 40°F, precipitating a hydrated form of sodium sulfate which is treated in mechanical vapor recompression crystallizers to drive off the water of hydration and produce anhydrous sodium sulfate. The only waste is the treated brine, which is not expected to be hazardous. Sodium sulfate is produced in a similar manner from lake brines. At the Great Salt Lake, solar evaporation is used to concentrate the brines and to precipitate sodium chloride, which is harvested and sold.

Winter weather is allowed to cool the brine from which Glauber's salt precipitates; the salt is harvested using earth moving equipment. At Searles Lake, California sodium sulfate is extracted from the top layer of brine. Borax is crystallized by cooling and removed as a product. Further cooling to 40°F causes precipitation of Glauber's salt, which is removed by filtration, purified, and dehydrated as above. The only wastes produced are spent brines, which are not expected to be hazardous.

Staurolite - Staurolite is produced as a by-product of beach sand mining for titanium. Staurolite is separated from titanium minerals by high-tension separators, then magnetically separated from other silicate minerals. The silicate minerals are discarded as waste, but they are not hazardous.

Stone (Building) - Building stone is defined, for the purposes of this report, as all stone used in construction exclusive of aggregates used in concrete or asphalt. This includes both structural and ornamental stone. These materials are produced by selective mining or cutting, and are processed by crushing, cutting, and/or polishing. The wastes from any of these operations are negligible in volume and not expected to be hazardous.

Sulfur - The major production of sulfur involves recovery of sulfur from air pollution control systems. This is not a mineral source and will not be addressed in this study. However, 42% of the sulfur in the U.S. is produced by the Frasch process from salt domes. In this process, hot water is injected into the sulfur-bearing layers of the formation. The hot water melts the sulfur, which is pumped to the surface. Waste water is collected from wells at the periphery of the salt dome, treated, and released. This waste water is not expected to be hazardous. Sulfur is also produced by roasting (burning) iron pyrite to produce sulfur dioxide gas and iron oxide solid. The gas can be treated to generate either elemental sulfur or sulfuric acid. Neither treatment produces significant amounts of waste, leaving the iron oxide as the only waste from pyrite processing. It is not expected to be hazardous.

Talc - Talc processing may be as simple as selective mining or involve complex processes such as froth flotation. Wastes are primarily accessory minerals and limestone or dolomite which are not hazardous and accessory minerals which may be asbestiform.

Tripoli - Tripoli is a fine grained form of silica used in abrasives, buffing, and polishing compounds. Mining is by open cut or underground room and pillar methods. The open cut method may produce some mine waste, which is not expected to be hazardous. Processing consists of crushing, drying, and grinding. With the exception of moisture loss, all of the ore is in the product, leaving no wastes.

Vermiculite - Vermiculite is a mica-like mineral that expands when heated. Processing consists of removal of waste rock by screening and expansion. The waste rock is not expected to be hazardous.

Wollastonite - Wollastonite is a calcium silicate used primarily as a filler. Selective mining produces an ore containing few impurities. Any mining waste would not be expected to be hazardous. Processing consists of crushing and screening into product size fractions. One plant uses magnetic separators to recover garnet and diopside by-products which would not be hazardous if discarded.

1.4.2 Nonmetals Recommended for Further Study

Barite - Barium is the element found in barite, and is one of the eight metals for which there are concentration criteria in the specification for the EP-toxicity test, and the test extractant is expected to leach barium from barite. The unavoidable residuals of barite in the processing waste may result in the wastes failing the EP-toxicity test.

Bituminous Materials - The four segments of the bituminous materials industry (natural asphalts, gilsonite, mineral wastes and pyrobitumens) are addressed separately below.

Natural Asphalt - No study is planned because no hazardous wastes are expected to be produced.

Gilsonite - Gilsonite dust generated in handling and processing is potentially ignitable. The amounts and management practices of these wastes are not currently documented in the literature, so further study is recommended.

Mineral Waxes - Solvent extraction is used to produce these materials. The solvents were not identified in the literature reviewed. Since these solvents could be listed substances in 40 CFR 261 Subpart D, the identities, volumes and management practices of spent solvents need characterization.

Pyro-bitumens - These are also processed by solvent extraction and need the same characterization as for mineral waxes.

Boron and Borates - The primary area of concern is the production of boron compounds from desert lake brines. The spent brines may exhibit hazardous characteristics. The nature and management of the brines needs more characterization.

Bromine - Bromine is a reactive material and many bromine compounds will exhibit hazardous characteristics. Chlorine is used in bromine extraction. The nature and management practices of wastes from bromine production are not fully described in available literature.

Clays - Some kaolin clay is subjected to bleaching processes that use hazardous materials such as strong acids combined with reducing agents or oxidizing agents such as chlorine or ozone, which could result in wastes from bleaching exhibiting hazardous characteristics. The nature and management practices of these bleaching wastes are not described in the available literature.

Coal - The coal industry sectors included in the scoping process were beneficiation, liquefaction, gasification, and coking. No further study of coal liquefaction is recommended since there are no commercial operations. Further study of beneficiation is recommended because of the acid generation potential of coal cleaning refuse. Gasification, as performed by American Natural Gas in Beulah, North Dakota, is recommended for study due to the production of reactive (hydrogen sulfide generating) wastes and the possibility of listed solvents as wastes. Coking produces a number of potentially hazardous by-products, such as ignitable materials and organic solvents. While these may be burned in the process or sold for processing, some may end up as wastes.

Feldspar - Potentially hazardous materials are used in the froth flotation processing of feldspar. These materials could result in tailings that exhibit hazardous characteristics.

Fluorspar - Fluorite tailings could exhibit fluoride problems and toxicity due to metals associated with the ore. The nature of and management practices for fluorspar tailings should be further characterized.

Iodine - Iodine is a reactive material and some iodine compounds exhibit hazardous characteristics. Chlorine is used in iodine production. The nature and management practices of iodine production wastes are not fully described in available literature.

Kyanite - Tailings from kyanite processing contain iron sulfides that may generate acid mine drainage when oxidized. The waste may generate hydrogen sulfide if it is exposed to acids, and thus could be reactive. Both situations could result in the tailings exhibiting hazardous characteristics.

Olivine - Lead and chrome bearing minerals are associated with some olivine deposits. There may be enough lead and chrome content to cause tailings to fail the EP-toxicity test. The volumes, nature, and management practices of these wastes need to be defined.

Phosphate Rock, Phosphoric Acid, and Elemental Phosphorous - The large volume of waste generated by this industry (over 400 million tons per year), and the radioactive nature of some wastes (particularly phosphogypsum from phosphoric acid production) are the primary reasons for studying this industry. Other areas of concern include fluorine emissions and the possible generation of corrosive wastes in the phosphoric acid industry.

Silica Sand - The froth flotation process used to upgrade silica sand is carried out at low pH (between 2 and 3) and tailings could exhibit corrosive characteristics (pH <2). The actual pH, volume, and management practices for these wastes need to be determined.

Other commodities are included here that may require further study.

Asbestos is a material that could be hazardous, but is not currently regulated by RCRA and therefore not included in 8002(p) studies. A policy decision by the EPA will determine the probable regulatory status of this industry.

Shale used in making lightweight aggregate is the other commodity needing further clarification. Wastes from lightweight aggregate production are not expected to exhibit hazardous characteristics. However, in some shale popping operations, thermal processing uses listed wastes as fuels. The question to be addressed is whether shale fines from kilns fired with listed wastes are to be considered hazardous under the "waste derived from a listed waste" requirement of 40 CFR 261.

1.4.3 Metals Not Recommended for Further Study

Arsenic - Primary production of arsenic and arsenic compounds has recently ceased in the United States. Demand is being met by imports.

Cobalt - The only primary cobalt refinery in the U.S. closed permanently in 1985. The plant is now reprocessing other materials.

Mercury - Primary mercury production is confined to one mine in Nevada. No hazardous wastes are expected from processing.

Nickel - The only nickel mine in the United States closed in 1986 and the plant was listed for sale by a used equipment dealer in 1987. All other production is a by-product of copper refining, and is not expected to generate wastes with hazardous characteristics.

Platinum Group Metals - There is one mine producing platinum group metals in the United States. This mine went into production in 1987. The ore from the mine is shipped to Belgium for processing. Because the only processing of platinum in the U.S. is from secondary sources, platinum is not recommended for further study.

Scandium - Scandium is produced by only one plant at such a small rate that the wastes produced would probably fall under the small quantity generator limits of Subtitle C.

1.4.4 Metals Recommended for Further Study

Antimony - A large portion of antimony production is a by-product of lead-silver processing. Further study is recommended because of wastes that may be reactive (due to sulfide generation), corrosive, or contain toxic metals.

Beryllium - Beryllium processing uses strong acids and other potentially hazardous materials that may render wastes from such processing corrosive.

Bismuth - All bismuth production is from intermediate metallurgical products such as lead bullion. Most materials generated in bismuth

extraction are products or are recycled. However, acids are used and if some products are discarded they may be toxic.

Cadmium - Cadmium is one of the eight EP-toxic test metals. Residues from processing could contain toxic levels of cadmium and other metals. Corrosive wastes may also be generated. Cadmium is produced as a by-product of zinc processing.

Cesium - Cesium is produced by one firm from imported ore. The processing uses strong acids that could generate corrosive wastes. Contaminant metals could cause wastes to be toxic.

Chromium - All chromium products are made from imported or secondary materials. Wastes, if any, from chromite refractory manufacturing and chromium chemical production may be EP-toxic.

Columbium and Tantalum - These metals are produced together exclusively from imported and secondary materials. Processing to extract columbium and tantalum uses strong acids and solvent extraction. Wastes may be corrosive or contain toxic metals, and waste solvents may be ignitable.

Gallium - Gallium is co-produced as a primary product with germanium at one plant. Another facility produces gallium from imported materials and scrap. Gallium processing uses acid leaching and solvent extraction. Wastes from the leaching may be corrosive and waste solvent may be ignitable.

Germanium - Germanium is co-produced as a primary product with gallium at one plant. Other plants extract germanium from secondary materials and as a by-product of other metal processing. Germanium production uses strong acids which may generate corrosive wastes. Residues from production as a by-product may contain toxic metals.

Gold and Silver - The cause of most health or environmental public concern in gold and silver production is the use of cyanide in leaching, which may generate reactive wastes. Silver is one of the eight EP-toxicity test metals and residual amounts left after processing may cause wastes to be EP-toxic. Strong acids used in precious metal refining may generate corrosive wastes.

Indium - Indium is produced from residues (primarily flue dusts) of zinc and other base metal production. The wastes from this processing may contain toxic metals. Acid leaching is also used, which may cause wastes to be corrosive.

Iron - This industry has undergone and continues to undergo a very large contraction. Despite this, the industry remains one of the largest addressed in these studies. Flue dusts, used refractory materials, and slags may contain toxic metals. Coke-making wastes may be ignitable or contain cyanides and listed organic wastes.

Magnesium - Magnesium is produced from sea water, from brines of the Great Salt Lake, and from dolomite. Processing uses strong acids which may generate corrosive wastes.

Manganese - All manganese raw materials are imported. Manganese dioxide production may generate corrosive wastes. Manganese alloy production may produce flue dusts that contain toxic metals.

Molybdenum - Molybdenum is produced both as a primary product and as a co-product with copper. Flue dusts from molybdenite roasting may contain toxic metals and there may be corrosive wastes from chemical production.

Rare Earth Metals - Some rare earth metals are produced as by-products of titanium and zirconium extraction. Thorium and yttrium are by-products of rare earth metal production. The separation of rare earth metals from each

other uses acid leaching and solvent extraction. The leaching wastes may be corrosive, and waste solvents may be ignitable or listed.

Rhenium - Rhenium is produced as a by-product of the roasting of molybdenum concentrates that come from porphyry copper deposits in the southwestern United States. Rhenium processing uses acid leaching and solvent extraction. Leaching residues may contain toxic metals, wastes may be corrosive, and solvent extraction wastes may be ignitable or listed.

Rubidium - Rubidium is produced by one domestic company from imported ore. Processing uses strong acids and solvents extraction with the possibility of corrosive and ignitable or listed wastes.

Selenium - Selenium is primarily recovered as a by-product of copper electro-refining. Some may be produced from lead electro-refining slimes and flue dusts. Acids are used in processing, possibly generating corrosive wastes. Selenium is one of the eight metals monitored in the EP-toxicity tests. Wastes from selenium processing may be toxic.

Silicon - Most silicon is used for alloying in the steel and aluminum industries. A very small amount of highly purified material is used in electronics. Flue dusts from the electric arc furnace production of silicon metal or ferrosilicon alloy may contain toxic metals.

Strontium - Strontium materials are produced from imported ores. The processing of strontium ores uses strong acids that may generate corrosive wastes. The residues from strontium processing may contain toxic metals.

Tellurium - Tellurium is a by-product from one plant refining copper by electrolysis. Processing to extract tellurium uses strong acids which may generate corrosive wastes. Residual materials from tellurium extraction may contain toxic metals.

Tin - There is one tin smelter in the United States produces tin from mostly imported ore and secondary materials. Previous investigation by EPA identified EP-toxic wastes.

Titanium - The production of titanium uses strong acids which may have some wastes corrosive. Residual materials have been shown to be corrosive, and may contain toxic metals.

Tungsten - Tungsten production uses acid leaching and solvent extraction. Corrosive, ignitable and listed wastes may be generated. The residual materials may contain toxic metals.

Vanadium - Vanadium is produced as a by-product of phosphorous and uranium mined in the western intermountain region of the U.S. Acid leaching and solvent extraction may generate corrosive, ignitable, and listed wastes. Vanadium alloy production may generate residues containing toxic metals.

Zirconium and Hafnium - Zirconium and hafnium are produced from zircon concentrates. These concentrates are co-products of titanium production from beach sand deposits. The processing of zirconium and hafnium uses strong acids which may make wastes corrosive. Residual materials may contain toxic metals.

1.5 REFERENCES

The descriptions in Sections 2.0 and 2.3 all use the following six basic references, and others as noted:

Lefond, Stanley J. 1983. Industrial Minerals and Rocks, 5th edition, published by the Society of Mining Engineers of AIME.

U.S. Bureau of Mines. 1985. Mineral Facts and Problems.

U.S. Bureau of Mines. 1985. Minerals Yearbook 1985, Volume 1, Metals and Minerals.

U.S. Bureau of Mines. 1987. Mineral Commodity Summaries.

Mining Engineering. A journal of the Society of Mining Engineers, Inc.; several issues were used as reference.

E&MJ, Engineering and Mining Journal. A monthly journal published by McGraw-Hill, Inc.; several issues were used as reference.

2.0 NONMETAL INDUSTRIES

INTRODUCTION

This section reviews the processes used to recover 42 nonmetal commodities from ores and concentrates. Of 42 nonmetal commodities, 24 are not recommended for further study for potential regulation under Subtitle C. Several of the commodities not recommended for further study are produced in manners that generate no waste, that is all material mined is sold as product with the exception of some water that is evaporated in drying operations. The rest of the commodities not recommended for further study for potential regulation under Subtitle C are produced by methods that generate wastes that do not have hazardous characteristics.

The 18 commodities for which further studies are recommended are not all expected to require Subtitle C regulation. Many are included in this list because of (1) a lack of readily available information on waste characteristics and (2) evidence that there is some potential for the wastes to be hazardous. Further study will be required to characterize these wastes.

DIATOMITE

Diatomite, also known as diatomaceous earth and kieselguhr, is a sedimentary rock made primarily from the fossilized silica skeletons of the diatom, a one-celled aquatic plant similar to algae whose two walls are overlapping and symmetrical. The tiny hollow skeletons of stable silica give diatomite unusual properties leading to its use as a filter aid (majority of consumption), filler and extender, thermal insulator, and in many other applications. Annual production is estimated to be 640 thousand short tons (1986).

Diatomite occurs in massive deposits and is selectively mined to give a crude product that contains few impurities. The crude is crushed and dried then sorted into size fractions. Some fine material is heated to incipient fusion in a kiln to produce a coarser material with specific properties. All of the sizes of diatomite have some use, so there are no wastes produced by processing. Based on the above analysis, further study for potential regulation under Subtitle C is not recommended.

GARNET

Garnet is a silicate mineral used primarily as an abrasive, although gem quality garnets are produced. The most familiar use of garnet is as the abrasive coating on sandpaper. It is also used to coat non-skid surfaces, for sand blasting, lapping compounds, glass grinding, and as a filter medium. The U.S. produces 70% of the world supply of garnet and 1986 production was approximately 35,000 short tons. No wastes with hazardous characteristics are expected from garnet production.

Based on this analysis, further study of the garnet industry for possible regulation under RCRA Subtitle C is not recommended.

GEMSTONES

There are a wide variety of precious and semi-precious stones produced in the U.S. These include jade, opal, sapphire, tourmaline, turquoise, and many others in small quantities. The total value mined in 1986 was approximately \$8.39 million, according to the U.S. Bureau of Mines "Mineral Commodity Summaries 1987". Some of the semi-precious stones are produced as a by-product of other mining operations. Particularly, turquoise is a copper mineral and the majority of current production is from major open pit copper mines.

The gem industry in the U.S. is extremely small and is unlikely to produce any significant wastes with hazardous characteristics. Therefore, further study of this industry for possible regulation under RCRA Subtitle C is not recommended.

GLAUCONITE

Glaucosite, a hydrous iron, potassium silicate, is a component of greensand which gets its name because of glaucosite's bluish-green to greenish-black color. Greensand also contains quartz and other silicates, and in some cases pyrite. Trace metals such as uranium, beryllium, cobalt, chromium, nickel, molybdenum, vanadium, and titanium also typically occur in glaucosite. The industry is localized in the coastal plain of New Jersey and Delaware. Current annual production is approximately 4,000 tons, from two producers.

Current use of glaucosite are limited to 1) water treatment where it is used to remove iron and manganese salts and 2) soil conditioning as a mulch, top dressing or additive for gardening and potted plants (a "natural" source of potash for organic farmers).

The hydraulicking method is used in mining glaucosite at the Hungerford and Terry's Inversand operation in Sewell, New Jersey. Upper layers of the deposit are removed to reveal ten to fifteen feet of relatively pure glaucosite. The beds are flushed with a high-pressure water jet, and loosened glaucosite is suction-pumped through a complex piping system containing special classifying and washing apparatus. The wastes from this washing contain clays and limonite, a rustlike iron mineral, and would not be expected to exhibit any hazardous characteristics. Lastly, glaucosite is treated with various chemicals, such as aluminum sulfate, sodium silicate, sodium aluminate, caustic soda and phosphoric acid. Little or no waste is expected from this treatment.

Based on this analysis further study of this industry for potential regulation under Subtitle C is not recommended.

GYPSUM

The mineral gypsum, calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and the mineral anhydrite, anhydrous calcium sulfate (CaSO_4) are the major constituents of evaporite deposits. Although anhydrite represents the largest calcium sulfate reserve, it has no commercial value. The evaporite deposits may be near the surface or buried which will dictate whether open pit or underground mining is employed for mineral extraction. Annual domestic production of gypsum is estimated to be 16 million short tons (1986). Major production areas are in California, Iowa, Michigan, Oklahoma, and Texas. Fort Dodge, Iowa represents the largest gypsum mining district in the U.S. where 1979 production was approximately 1.2 million tons. The major use for gypsum is in the production of stucco which is in turn is used to produce plaster and wallboard. Stucco is produced by rehydrating calcined gypsum (otherwise known as plaster of paris, $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) which causes the material to set or harden. Stucco is the hemihydrate $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ resulting from calcining gypsum. Rehydrated it sets by returning to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Gypsum requires little or no beneficiation in that the material mined is relatively pure and adequate for commercial use (85 to 95 percent pure). To avoid beneficiation, care is taken during mining to selectively extract specific grades of gypsum deposits, avoiding mixing in of overburden or other rock or grades of gypsum. Open pit mining utilizes draglines and scrapers to remove overburden, and conventional techniques for mineral extraction, i.e. blasting to loosen the gypsum, and shovels or front end loaders to load the material onto trucks. Underground mining is typically by room and pillar methods where 65 to 80 percent gypsum removal is achieved. Compositions and volumes of wastes generated from the small amount of beneficiation that does occur at some locations are unknown; however these wastes are not expected to exhibit any hazardous characteristics.

Based on this analysis further study of this industry for potential regulation under Subtitle C is not recommended.

LIME, LIMESTONE, AND DOLOMITE

Limestones are sedimentary rocks containing mostly the mineral calcite (calcium carbonate). Dolomites are sedimentary rocks containing mostly the mineral dolomite (calcium-magnesium carbonate). Lime is a calcined (or burned) form of limestone or dolomite that is made up of calcium oxide or calcium and magnesium oxides. Hydrated lime is calcium (or calcium and magnesium) hydroxide produced by adding water to lime. Among mineral commodities, only sand and gravel are produced in larger quantity than limestone and dolomite. In 1981, approximately 644 million tons were produced.

Limestones and dolomites are mined from deposits that meet the specifications for a market. The only processing may be washing to remove clay, which would not be expected to show any hazardous characteristics (Table 2-1), and screening to meet size specifications. Clay washing is necessary only in some operations.

The uses for which limestone or dolomite quality is the most critical are the production of lime and portland cement. In both cases, the feed material is heated to high temperature (between 1,000° and 1150°C for lime production) to produce chemical changes. In lime production, the reaction is called calcination and is the driving off of carbon dioxide from the calcium carbonate, leaving calcium oxide, also called quicklime or hot lime. Calcined dolomite is a mixture of calcium and magnesium oxides. There are several types of calciners used in the U.S. depending on limestone type, fuel availability and other factors. The coarse "lump" products of calcination are usually sold without much further processing. Some is crushed and sized to produce "pebble", "granular", "ground", or "pulverized" lime. The fine material may be compressed into pellets or briquettes or reacted with water to produce calcium hydroxide or "hydrated" or "slaked" lime. Some hydration is done under pressure to ensure the maximum degree of hydration. No wastes are produced by slaking.

Based on this analysis, further study of this industry for potential regulation under Subtitle C is not recommended.

TABLE 2-1

WASTES FROM LIME, LIMESTONE AND DOLOMITE

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Washing of Limestone and Dolomite	1) Clay Waste	N	N	N	N	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

LITHIUM

Lithium is found in the mineral spodumene in pegmatites containing mineral assemblages which are derived from the crystallization of postmagmatic fluids or from metasomatic action by residual pegmatitic fluids. Lithium mineral concentrate, compounds and metal are produced by two companies (one presently inactive) from lithium-bearing pegmatite ores in the tin-spodumene belt of North Carolina. Lithium carbonate is also produced from subsurface brines in Clayton Valley, Nevada. In 1980, the estimated world consumption of lithium was 54.5 million pounds of lithium carbonate equivalent.

Lithium ores and concentrates are consumed by the glass, ceramic, and porcelain enamel industries. Lithium hydroxide is used in the production of lubricating grease. Lithium carbonate is primarily used as an additive in aluminum refining and also in ceramics and glass. Lithium carbonate (in purified form) is used in the chemotherapeutic treatment of manic depression. Lithium chloride and bromide are used in absorption refrigeration systems and dehumidification systems.

The production of spodumene (a lithium aluminum silicate, $\text{LiAlSi}_2\text{O}_6$), begins with the mined ore being crushed, ground, and classified as shown in Figure 2-1. The next step is froth flotation with organic reagents. The froth flotation tailings (waste 1) consists of the pegmatite minerals and would not be expected to exhibit any hazardous characteristics. Extraction of lithium from spodumene is accomplished by the calcination of spodumene to beta-spodumene. Beta-spodumene is then reacted with sulfuric acid to produce lithium sulfate. Soda ash is added to convert to lithium carbonate.

Lithium produced from brines is processed by pumping saline solutions into large solar evaporation ponds (Figure 2-2). During evaporation, halite and sylvite crystallize. Magnesium is precipitated as hydroxide by the addition of lime during the evaporation phase. After final concentration

Figure 2-1
LITHIUM ORE PROCESSING

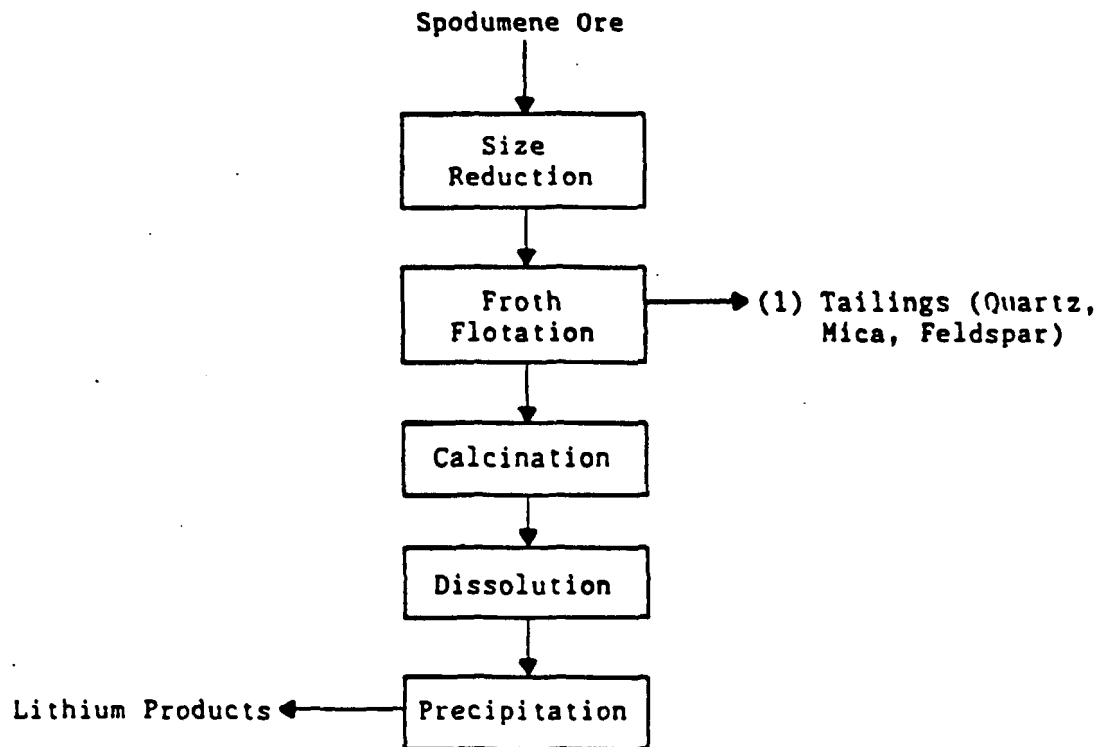
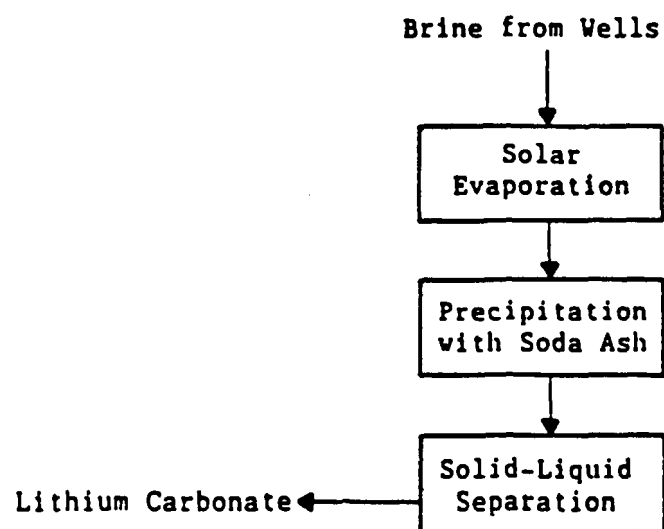


Figure 2-2

LITHIUM FROM BRINES



has been achieved, the brine is purified and lithium carbonate is precipitated by the addition of soda ash. No hazardous wastes are expected from this process.

Table 2-2 summarizes the expected characteristics of the wastes from this industry. Based on this analysis further study of this industry for potential regulation under Subtitle C is not recommended.

Table 2-2

LITHIUM PRODUCTION WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Spodumine Concentration	1. Froth Flotation Tailings (rock)	N	N	N	N	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

MICA

The flake-like mineral mica occurs in differing chemical and physical forms of complex hydrous aluminosilicate. The chemical composition of micas is described by a general formula which is $X_2Y_{4-6}Z_8O_{20}(OH,F)_4$, where X is mainly K, Na, or Ca; Y is mainly Al, Mg, or Fe; Z is mainly Si or Al. Approximately 60% of mica scrap (mica not in sheets) is from North Carolina. The remaining mica comes from Connecticut, Georgia, New Mexico, Pennsylvania, South Carolina and South Dakota. Annual domestic production is estimated at 153,000 tons (1986).

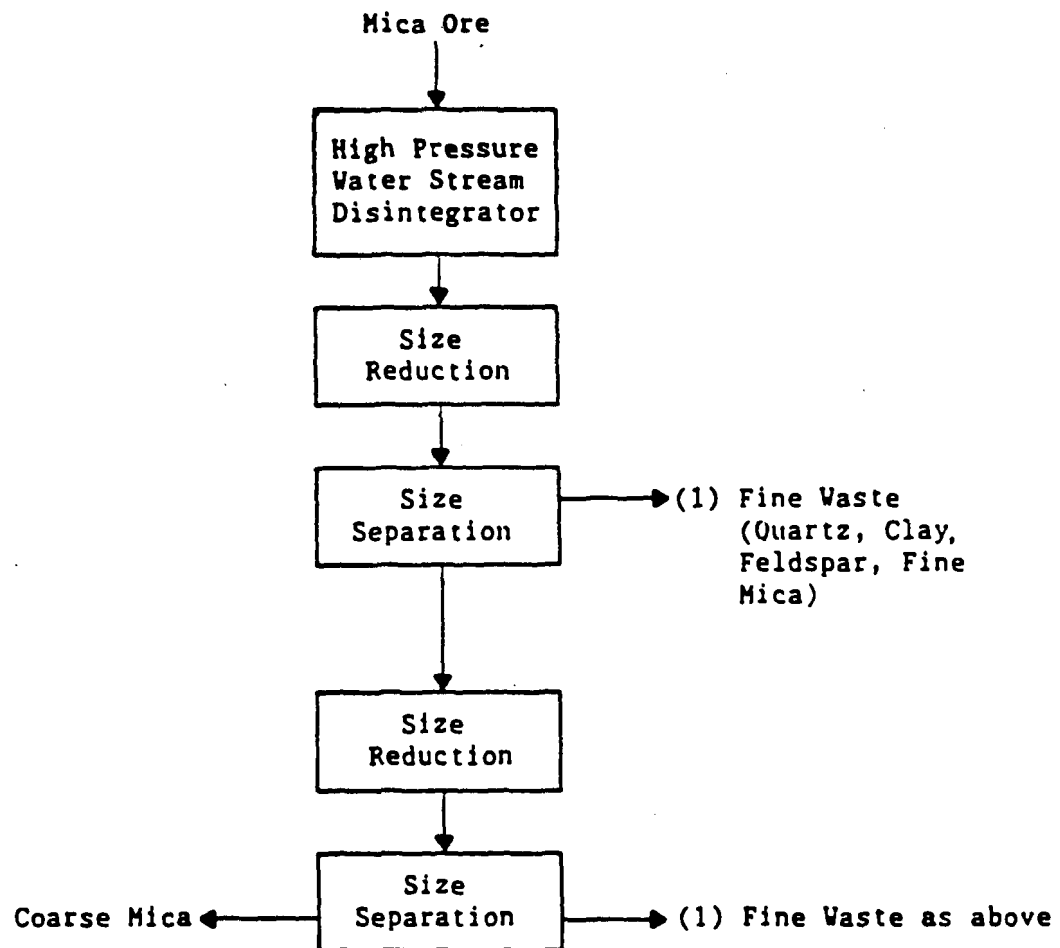
Flake and ground mica made from mica scrap are used in wallpaper, rubber tires, paints, oil well drilling fluids, joint cement, surface coatings, insulation boards, welding electrodes, and plastics.

In the mining of flake mica, conventional equipment removes any overburden to expose the mica ore. Once the mica ore is revealed, it is mined by hydraulic methods, power-driven equipment, or a combination of both.

Recovery of mica can be accomplished utilizing three different methods. Each method will be discussed below.

1. Washer Plant Methods (Figure 2-3): High pressure water streams are first utilized to disintegrate mined ore. It is then crushed and washed through trommel screens and again crushed with roll crushers. The trommel screen removes the fine-sized, non-mica particles. The remaining, coarser particles are crushed numerous times to remove all of the non-mica material. After the crushing is completed, the final coarse mica is stored in bins. None of the wastes are expected to exhibit any hazardous characteristics.
2. Humphrey's Spiral (Figure 2-4): High pressure water washes the mined mica ore into a bowl rake classifier to be deslimed. Classifier sand is sent to a rod mill, then it is discharged to a trommel screen. Larger material is returned and ground again in the rod mill. The smaller material is passed to another bowl-rake classifier for desliming. Humphrey's spirals are utilized for initial concentration of the classifier sand. The rougher concentrate is fed into a cleaner spiral producing a cleaner

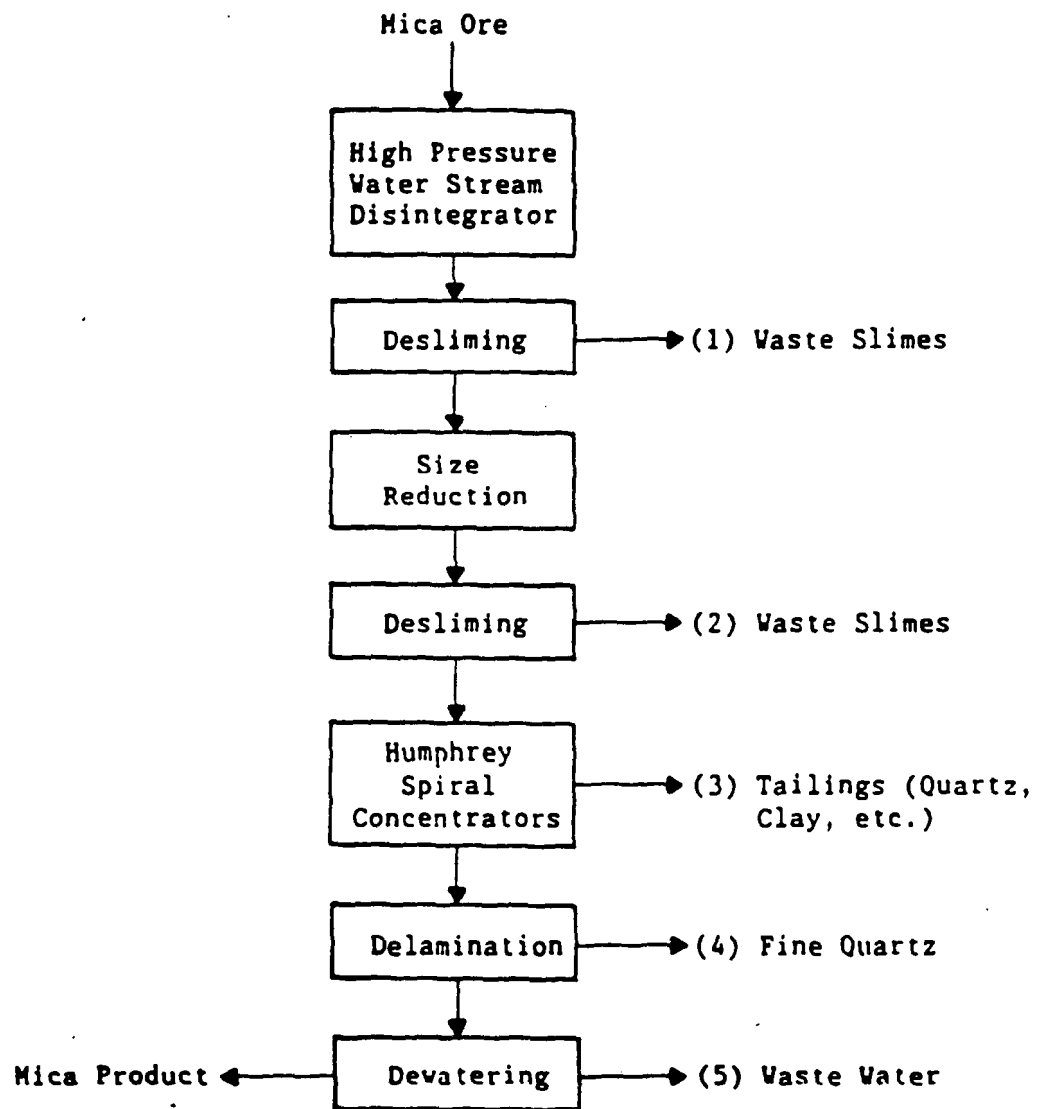
Figure 2-3
MICA PROCESSING BY WASHING



Note: The size reduction and size separation steps are repeated until the maximum amount of undesirable material is removed.

Figure 2-4

MICA PROCESSING BY HUMPHREY SPIRALS



concentrate, also known as middling. This is middling is then passed back through the rougher spirals. Screens are utilized to remove clay and fine-sized minerals from the cleaner concentrate. The oversized materials on the screen are then sent to a hammer mill in order to delaminate the mica and to remove quartz crystals. The final concentrate is once again screened, centrifuged, and stored. The wastes from this process, mostly clays and quartz, are not expected to exhibit any hazardous characteristics.

3. Froth Flotation Methods:

Acid Cationic (Figure 2-5): This froth flotation method recovers mica particles. Sulfuric acid (to a pH of 4) conditions the ground mica ore pulp to allow for the greatest recovery. The floating mica is recovered from the slurry by using a cationic reagent.

Alkaline Anionic-Cationic (Figure 2-6): In the presence of slimes, this method of froth flotation is effective in the recovery of mica. Sodium carbonate and calcium lignin sulfonate are utilized to condition finely ground mica ore. The mica is then floated and recovered with a combination of anionic and cationic collectors. Tailings from either flotation process would not be expected to exhibit any hazardous characteristics.

This analysis has found that wastes from mica processing are unlikely to exhibit hazardous characteristics (Table 2-3) and therefore, further study of this industry for potential regulation under Subtitle C is not recommended.

Figure 2-5
MICA PROCESSING BY
ACID-CATIONIC FROTH FLOTATION

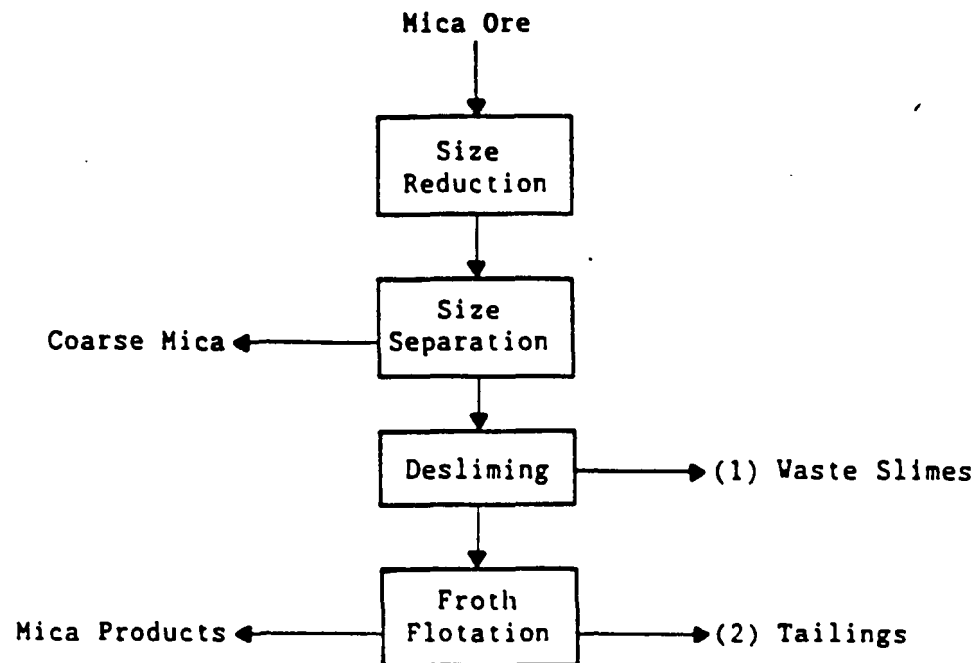


Figure 2-6
MICA PROCESSING BY
ALKALINE ANIONIC - CATIONIC FLOTATION

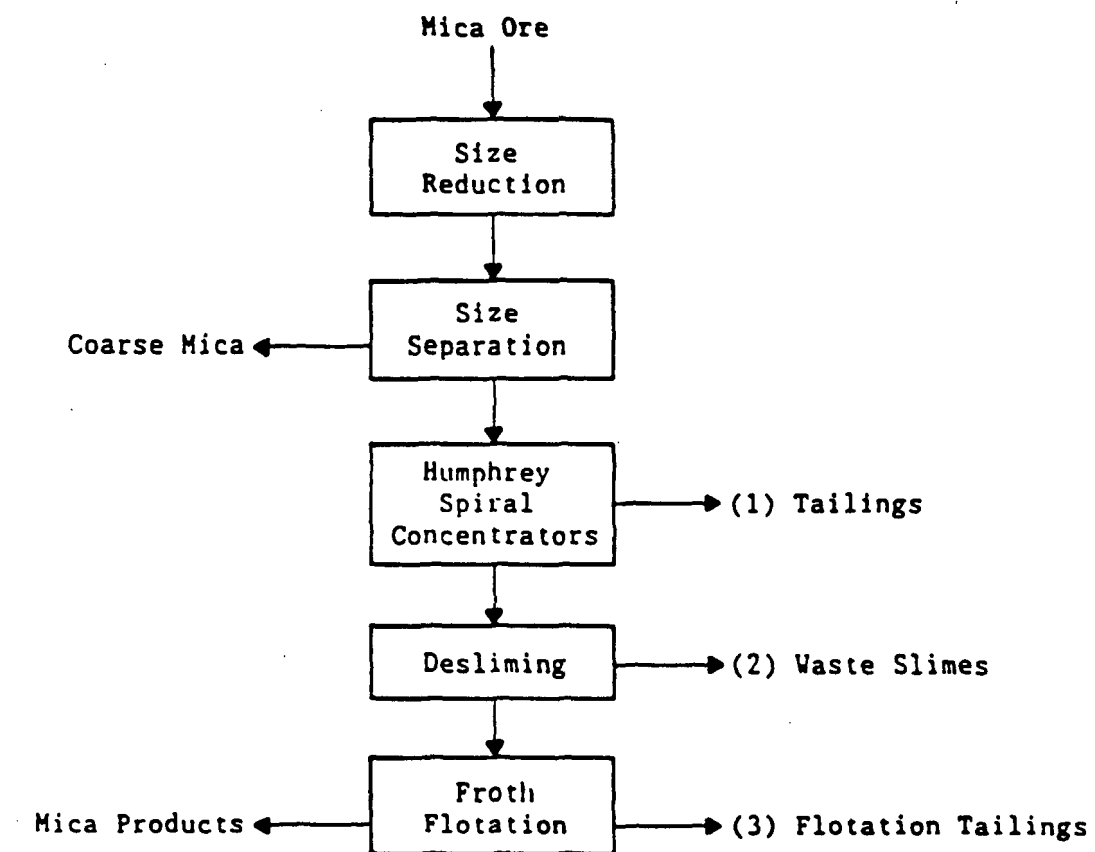


Table 2-3

MICA PROCESSING WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Mica Washing	Washer Tailings (Quartz, Clay, etc.)	N	N	N	N	
Humphrey's Spiral Washing	Waste Slimes (Clay)	N	N	N	N	
	Tailings (Clay, Silicates)	N	N	N	N	
Acid-Cationic Froth Flotation	Slimes (Clays)	N	N	N	N	
	Flotation Tailing	N	N	N	N	
Alkaline Circuit Flotation	Fine Tailings (Clays)	N	N	N	N	
	Flotation Tailings	N	N	N	N	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

PEAT

Peat consists of partially decomposed plant matter occurring in large beds or bogs. Coal beds are thought to be derived from ancient peat bogs that have been heated and compressed over millions of years. Peat is used in the U.S. primarily in agriculture and horticulture and to a very small extent as a fuel. The Bureau of Mines estimated total production at 870,000 short tons in 1986 in the "Mineral Commodity Summaries 1987". Peat is used as mined and there are no significant wastes generated in peat production. For this reason further study of the peat industry for possible regulation under RCRA Subtitle C is not recommended.

PERLITE

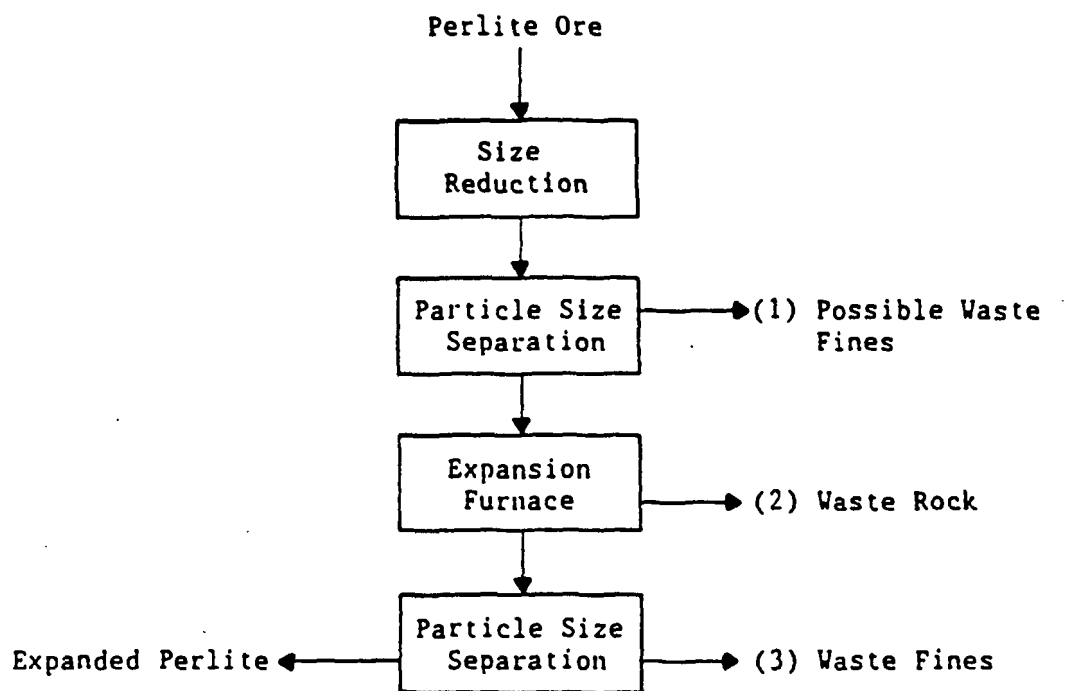
Perlite refers to hydrated volcanic glass that can be expanded through heating to form a lightweight aggregate for use in cryogenics, plaster, concrete, and loose fill insulation. The expanded form is also commonly referred to as perlite. Approximately 475,000 tons were mined in the U.S. in 1986 with most of the mining occurring in New Mexico. Perlite is also mined in Arizona, California, Nevada, Idaho, and Colorado.

Perlite is mined through open pit mining of dome shaped deposits generally hundreds of feet in height. Friable textures of perlite can be extracted by ripping with a dozer and loading the perlite into trucks for transport to a processing plant. Blasting may be required for harder ore, and other techniques are employed to avoid clay seams, obsidian, and other non-perlitic areas.

Figure 2-7 shows a typical general flow sheet for perlite processing. Before expansion, perlite is crushed and screened to attain a specific size range. A jaw crusher is used to reduce the perlite to -3 in., and then a cone crusher and impact mill further reduce the perlite to -5/8 in. and minus 8 mesh, respectively. Various size grades of perlite are produced by vibratory screening and air classification. These size grades are stored and blended to meet demand specifications. As seen in the figure, Waste 1 represents the fines from the screening and classification process. These fines are simply volcanic glass, and would not be expected to exhibit any hazardous characteristics.

Perlite is subsequently heated and expanded to form the final product. Heating is accomplished using either a horizontal or vertical furnace operating at temperatures of 1400°F to 2100°F. In the vertical furnace, the perlite falls through a chute into the hot zone where the particles expand creating a density change allowing the particles to move with an updraft into a cyclone. Waste 2 in Figure 1 represents the fines from the

Figure 2-7
PERLITE PROCESSING



cyclone, and waste 3 represents the non-expansible particles like obsidian and felsite which normally co-occur with perlite. These waste streams would not be expected to exhibit any hazardous characteristics, as summarized in Table 2-4.

Based on this analysis further study of this industry for potential regulation under Subtitle C is not recommended.

Table 2-4

PERLITE PROCESSING WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Screening and Classification	1. Fines (Volcanic Glass)	N	N	N	N	
Expansion	2. Waste Rock	N	N	N	N	
Cyclone Classification	3. Waste Fines (Fine Perlite)	N	N	N	N	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

POTASH

Potash is the generic term for a variety of potassium bearing minerals, ores, and refined products. Potassium is an essential nutrient for plants. Approximately 94% of U.S. potash consumption is used in fertilizers. All commercial potash production is from beds of salts formed by the evaporation of salt lakes or seas. Most potash is processed by one of three processes, 1) froth flotation, 2) selective dissolution (washing) of undesirable minerals or 3) precipitation of potash minerals from natural or artificial brines. Domestic production in 1983 was 1,429,000 metric tons.

Sylvinite ore (potassium chloride-sodium chloride) is commonly beneficiated by the process of froth flotation. As shown in Figure 2-8, the ore is first ground into a slurry with the brine. Grinding releases sylvite and halite particles from their agglomeration. The slurry is then deslimed to remove the fine contaminants (mostly clays and hematite) (Waste 1). The slurry then goes to the froth flotation circuit where the sylvinite is floated from the halite in an aqueous solution saturated with both sodium and potassium chlorides. Halite (rocksalt) is the waste product (Waste 2 in Figure 2-8).

Langbeinite is a mixed potassium sulfate-magnesium sulfate mineral that is relatively insoluble in water. Langbeinite ores are often upgraded by the process of dissolution of the soluble halite and other salts that occur with it. This selective dissolution (Figure 2-9) would have a brine as a waste product.

Some ores are processed by the third process of dissolving the sylvenite and precipitating a pure sylvite product from the clarified brine (Figure 2-10). Natural brines, such as those found at Great Salt Lake, UT or Searles Lake, CA, are also treated to precipitate potassium compounds. At one operation in Utah, an unsuccessful underground mine was flooded and potassium compounds are produced by solar evaporation of the resultant

Figure 2-8

POTASH FROTH FLOTATION PROCESSING

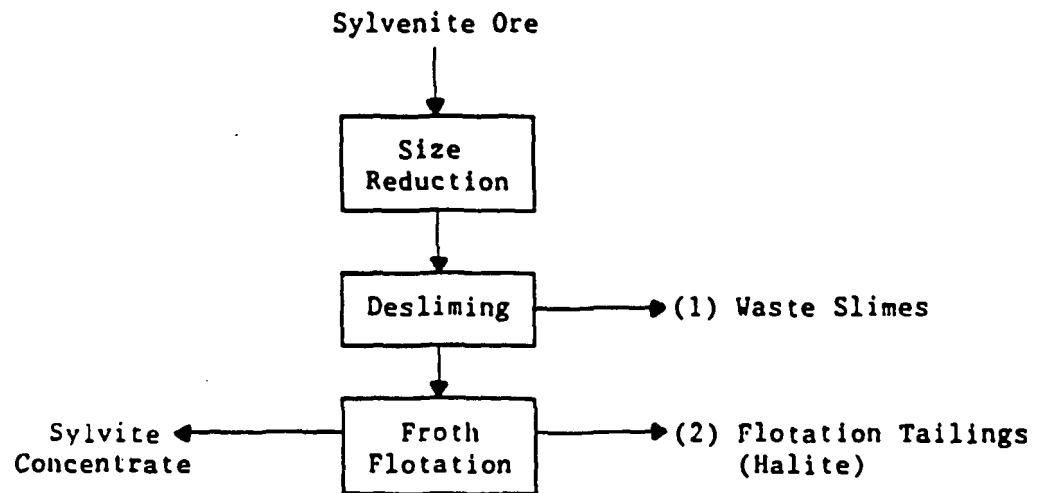


Figure 2-9

POTASH SELECTIVE DISSOLUTION

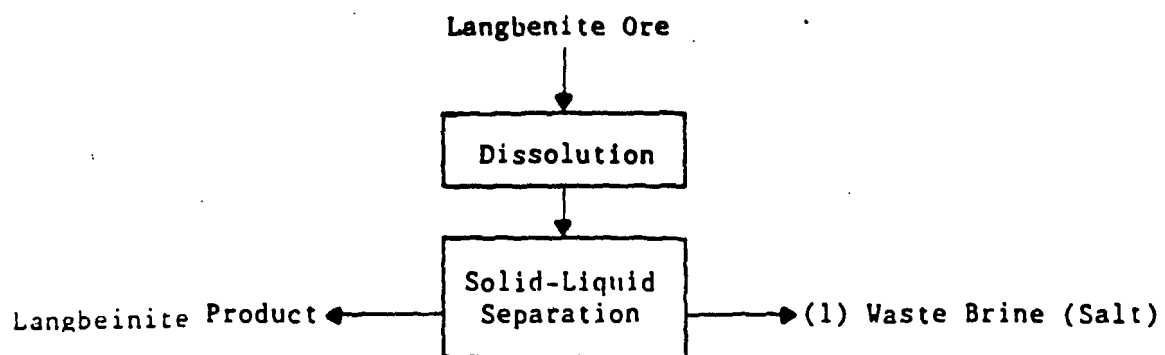
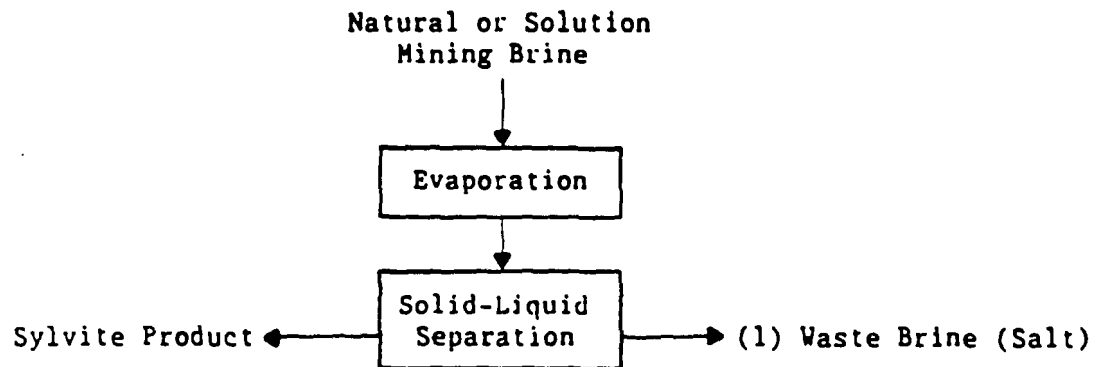


Figure 2-10

POTASH PRECIPITATION



brine. The wastes from these processes would contain considerable amounts of readily soluble salts but they may not contain any hazardous components (Table 2-5).

Based on the above analysis, further study of this industry for potential regulation under Subtitle C is not recommended.

Table 2-5

POTASH PROCESSING WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Froth Flotation	1. Waste Slimes (Clays)	N	N	N	N	
	2. Flotation Tailings (Halite)	N	N	N	N	
Selective Dissolution	1. Waste Brine (Halite)	N	N	N	N	
Potash Precipitation	1. Waste Brine (Halite)	N	N	N	N	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

PUMICE

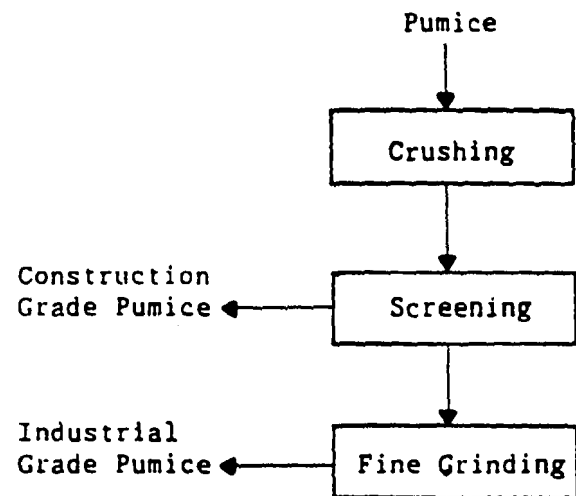
Pumice is the lightweight rock produced from volcanic eruptions. It is produced by the expansion of gases in silicic lava. Pumice deposits are formed in the volcanic regions of the United States, ranging from the State of Washington to California and the Hawaiian Islands.

Pumice has a low density and has very good abrasive properties. The main use of the material is in construction applications, such as road surfacing material and railroad ballast. It also has some industrial applications as an abrasive. Production of pumice in 1986 was estimated to be 415,000 short tons.

Pumice is mined in an open pit. The pumice is transported from the pit to a crushing and screening plant. This is usually the only processing necessary for construction grade material. To be used as abrasives in industry, finer grinding is usually necessary (Figure 2-11). There are no known wastes resulting from this processing.

Based on the above analysis, further study of this industry for potential regulation under Subtitle C is not recommended.

Figure 2-11
PUMICE PRODUCTION



PYROPHYLLITE

The mineral pyrophyllite is a hydrous aluminum silicate. Pyrophyllite was produced domestically in 1983 from 5 sites in North Carolina and two in California. Domestic production in 1983 was 87,000 short tons.

Pyrophyllite is a talc like mineral used primarily in refractory materials, ceramic materials, and insecticides. To a lesser extent pyrophyllite is used in various filler applications much like talc.

Selective mining produces pyrophyllite ores that only need to be ground to meet the size specifications of the market for which it is being prepared. This size reduction produces no waste.

Based on the above analysis, further study of this industry for potential regulation under Subtitle C is not recommended.

SALT AND ROCK SALT (HALITE)

Salt (common name for sodium chloride) is found in nature in sea water, natural brines and as rock salt (halite). Salt is an essential nutrient and flavoring agent for man. Salt is used widely in the chemical industry (over 50% of annual consumption) and rock salt is used as a deicer for roadways and sidewalks. Salt is produced by dry mining, solution mining and by solar evaporation. In 1986, 39 companies operated 68 plants in 14 states to produce an estimated 37 million short tones of salt (USBM, 1987).

Rock salt is mined underground from thick beds of salt at several locations in the U.S. Most rock salt is simply mined, crushed and screened and sold by size. Some is upgraded by the removal of particles of anhydrite (calcium sulfate), shale and dolomite (calcium-magnesium carbonate). These waste rocks would not be expected to show any hazardous characteristics (Table 2-6). Very pure salt is produced by dissolving fine crystal rock salt in hot brine. The high temperature dissolution leaves behind the calcium sulfate and when the salt is recrystallized it may be as pure as 99.99% sodium chloride. The calcium sulfate is not expected to be hazardous (Lefond and Jacoby, 1983).

Another process for extraction of salt from thick beds is solution mining wherein a well is drilled into the bed and the area surrounding the bed is hydraulically fractured. Water is then pumped in and brine pumped out. Approximately 50% of all salt is produced by this method. Much of the brine is used directly in the chemical industry; and a smaller amount is crystallized in evaporators. Some brine purification is done on chemical plant and evaporator feeds, leaving a residue. This residue is not expected to exhibit hazardous characteristics and is reinjected into the formation.

The solar evaporation of naturally occurring salt solutions has been practiced for many years. The main sources of salt solutions are the

Table 2-6
WASTES FROM SALT PRODUCTION

Process	Waste	R	C	I	T	Characteristic Comments
Rock Salt Recrystallization	1) Calcium Sulfate	N	N	N	N	
Brine Purification	2) Brine Purification Residue (Mg, Ca, Fe, SO ₄ , etc.)	N	N	N	N	Recycled to solution Mining
Solar Evaporation	3) Bittern (NaCl, MgCl ₂ , MgSO ₄ , KCl, MgBr ₂)	N	N	N	N	May be processed to recover Magnesium and Potassium.

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

oceans and salt lakes such as the Great Salt Lake, Utah. In this process, the salty brine is pumped into shallow ponds where the water evaporates concentrating the brine. Compounds of calcium, magnesium and iron precipitate at this stage. The brine is transferred to a lime pond to remove calcium sulfate. From the lime pond, brine is transferred to harvesting ponds where approximately 85% of the salt crystallizes and settles out. The remaining solution, called "bitterns" is drained to adjacent ponds for further processing or disposal. Bitterns is a concentrated solution high in magnesium compounds, but still contains sodium chloride. Brine is put into the harvesting ponds for crystallization several times between salt harvesting to build up a sufficient layer of salt for the mechanical harvesters to remove. Prior to mechanical harvesting, the salt is washed with dilute brine to remove residual bitterns and impurities. After harvesting, the salt is transferred to processing facilities where it is washed with fresh water, dried, screened and shipped.

Based on the above analysis, further study of this industry for regulation under Subtitle C is not recommended.

REFERENCES

Lefond and Jacoby, Salt, Industrial Minerals and Rocks, Stanley J. Lefond, ed. Society of Mining Engineers of AIME, 1983.

USBM, Mineral Commodity Summaries 1987.

USBM, Mineral Facts and Problems 1985.

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SAND AND GRAVEL AND CRUSHED STONE

Three mineral commodities that are very closely related in makeup and processing are construction sand and gravel, industrial sand and gravel, and crushed stone. Crushed stone is the largest of these industries in terms of output with 1986 production estimated at 1 billion tons, valued at \$4.2 billion. There were 1,790 companies operating 3,560 quarries in 49 states. The construction sand and gravel industry consists of 4,300 companies with 5,900 operations, in 50 states, that produced 837 million short tons valued at \$2.6 billion. The industrial sand segment produced 29 million short tons from 169 operations owned by 98 companies in 38 states. Crushed stone and construction sand and gravel are used for construction aggregate, fill, metallurgical flux, and many other uses, some of which (such as cement or lime manufacturing) are discussed in other screening studies. Industrial sand and gravel is used for glass making (discussed under Silica Sand), foundry sand, abrasive sand, hydraulic fracturing sand, and many other applications.

Processing of crushed stone is done by simple crushing and screening to provide the size grades desired in the final product. The only waste expected would be fugitive dust which would not be expected to exhibit any hazardous characteristics.

Construction sand and gravel is mined from river beds, glacial moraines, river terraces, alluvial fans, and other such deposits. The primary processes are drying, screening, and blending to meet size specifications. Some coarse materials may be crushed or ground if the deposit does not contain enough fine material to meet specifications. Undesirable materials do occur in some deposits and they must be removed to make the sand and gravel saleable. Clays are removed by washing in water producing a slurry containing the fine material which is sent to waste. This waste is not expected to exhibit any hazardous characteristics. Undesirable dense material is removed by jigging or heavy medium separation. The heavy

medium used in this separation is usually a slurry of finely ground magnetite or ferrosilicon in water. The heavy minerals removed by jigging heavy medium separation are discarded. This waste is not expected to exhibit any hazardous characteristics.

Industrial sand and gravel is processed by the same methods as construction sand and gravel, except for glass sand and other specialty materials discussed separately. The wastes from industrial sand processing are not expected to exhibit any hazardous characteristics.

The industries of crushed stone, construction sand and gravel, and industrial sand and gravel share similarities in product and waste characteristics. None of the waste from these industries are expected to exhibit hazardous characteristics. Therefore, further study for potential regulation under Subtitle C is not recommended.

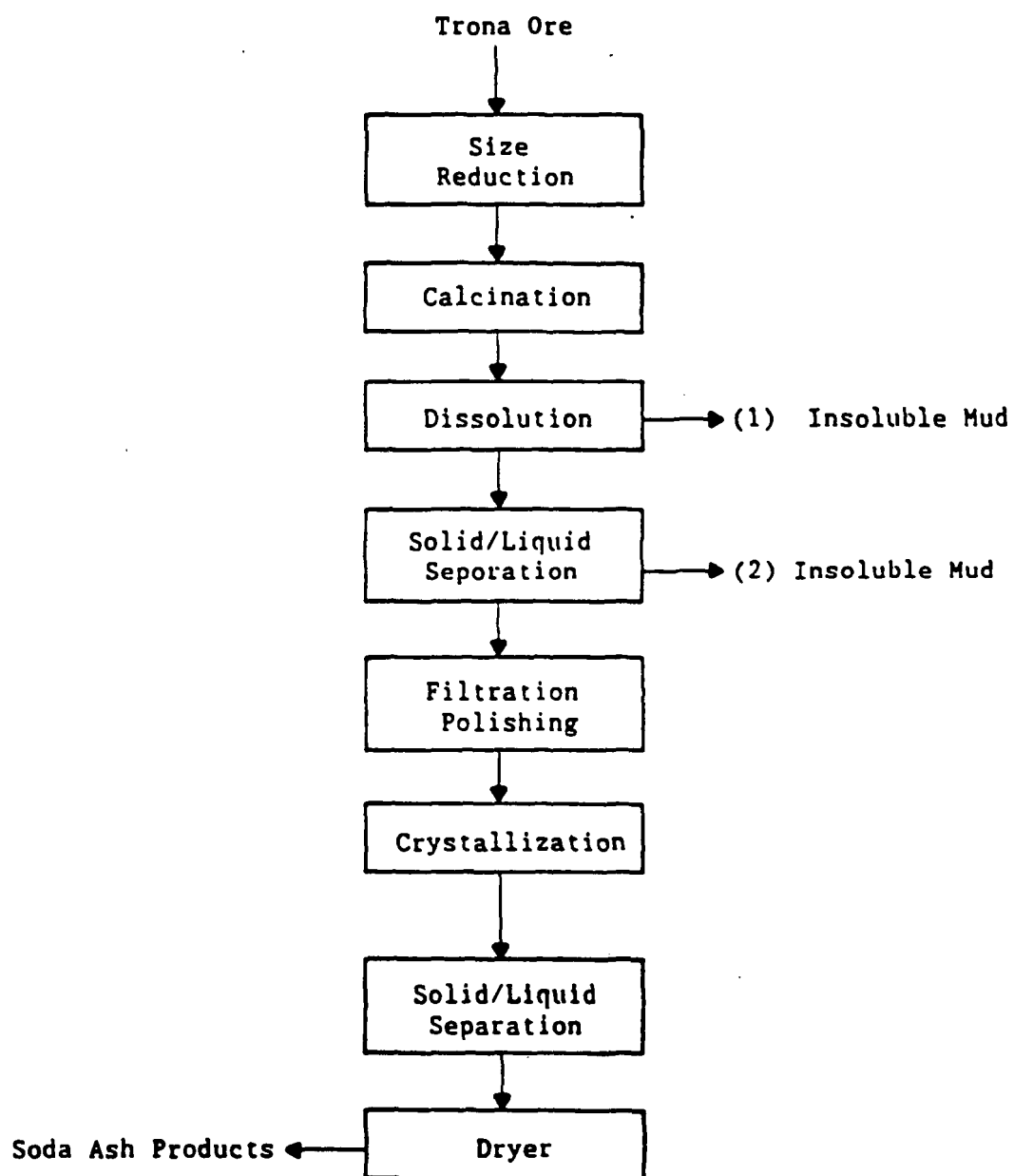
SODA ASH

Soda ash (Na_2CO_3) production in the United States is from the beneficiation and processing of the evaporite mineral, trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$). The most extensive deposits of trona are in the Green River Formation of southwest Wyoming, where trona (typically 70 percent Na_2CO_3) occurs in flat beds of two to six meters thickness at depths from 100 to 1070 meters. The trona resource of 11 such beds is estimated at 52 billion tons. Production of soda ash from Green River, Wyoming, in 1986, was approximately 7 million tons. The other major deposit of soda ash is at Searles Lake, California, where sodium carbonate is a component of brines (5 percent Na_2CO_3) within a series of permeable crystalline saline lenses (primarily halite). Production of soda ash from natural resources has totally replaced principle production of soda ash by the Solvay process in the United States. In the Solvay process, sodium chloride brines are ammoniated, carbonated, and calcined. The higher production cost of the Solvay process, together with the cost for environmental controls was largely responsible for its demise. The soda ash market is dominated by the glass industry (50 percent) and the inorganic chemical industry (30 percent), principally phosphates and silicates.

Extraction of trona is by underground room and pillar mining (Green River, Wyoming) or by brine withdrawal via production wells (Searles Lake, California).

Processing of the Green River trona is one of crushing, calcining (to remove CO_2 and organics), dissolution, removal of extraneous solids by sedimentation and filtration, removal of soluble organics by adsorption on activated carbon, crystallization of the monohydrate by evaporation (multiple effect evaporation), filtration to concentrate the crystals, and lastly drying and cooling to produce soda ash (Figure 2-12). The major waste streams are the muds produced from sedimentation and filtration (waste streams 1 and 2) and waste brine from the vacuum filter (waste

Figure 2-12
TRONA PROCESSING
WYOMING PRACTICE



stream 3)(Table 2-7). The insolubles (shale and shortite) are sent in slurry form to tailings ponds which have a pH of approximately 10.

The Searles Lake brine process is similar to the Wyoming process in that the sodium carbonate precipitate is calcined, dissolved, reprecipitated as the monohydrate, filtered, and dried to remove free water. The brine is initially carbonated using CO_2 from a lime kiln or power plant, the crude monohydrate slurry is separated by sedimentation and subsequently washed and filtered. The solids are then dried, calcined, and bleached, producing a light ash. The light ash is converted to a dense ash by dissolution, reprecipitation as the monohydrate, and filtration and drying to remove free water. The five waste streams represent clarifier overflows or filtrate and have a pH of approximately 10 (Table 2-7). The current industry practice is to reinject these brines back into the formation, dissolving more sodium carbonate.

Based on the above analysis, further study of this industry for potential regulation under Subtitle C is not recommended.

Table 2-7
SODA ASH WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Searles Lake Brines	1. Clarifer Overflow	N	N	N	N	All wastes will show a high pH but they are not expected to be corrosive (pH>12.5)
	2. Washing Filtrate	N	N	N	N	
	3. Seed Crystal Washing Filtrate	N	N	N	N	
	4. Monohydrate Clarifier Overflow	N	N	N	N	
	5. Monohydrate Washing Filtrate	N	N	N	N	
Wyoming Trona	1. Waste mud (clays)	N	N	N	N	
	2. Waste mud (clays)	N	N	N	N	
	3. Monohydrate Washing Filtrate	N	N	N	N	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

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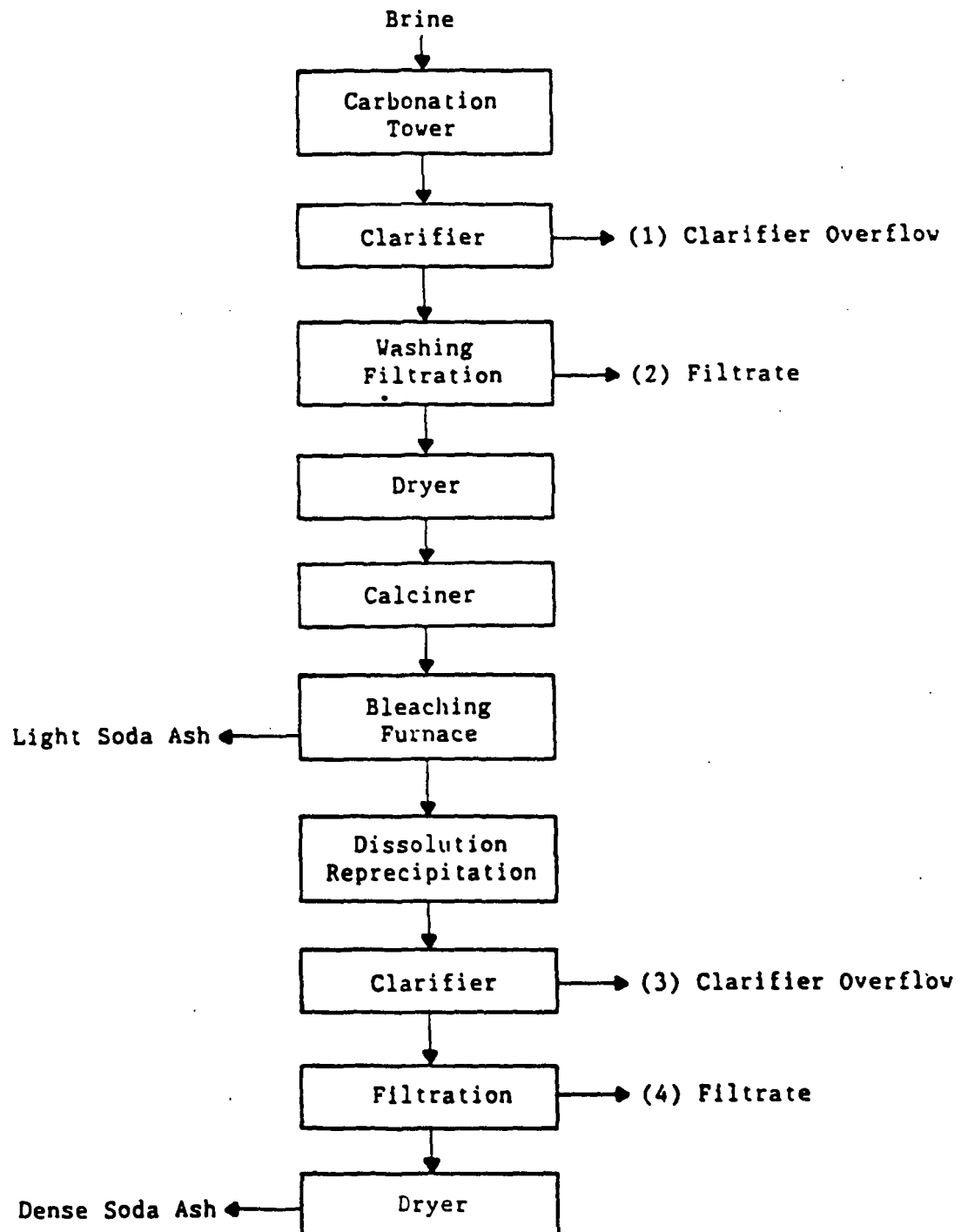
SODIUM SULFATE

Many dried lake beds and natural brines in Arizona, California, Nevada, North Dakota, Texas and Utah contain large quantities of natural sodium sulfate in the form of thenardite and mirabilite. Naturally derived sodium sulfate produced by three companies operating four plants in three states in 1983 produced 435,000 short tons. Sodium sulfate, produced as a byproduct from other industries in 1983, amounted to 665,000 short tons.

Mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), otherwise known as a Glauber's salt, is the most abundant of the sodium sulfate minerals and represents the sodium sulfate deposits of commercial significance. Mirabilite is a large component of evaporites and occurs as crystalline beds within brines or beneath playa lakes. The major use of sodium sulfate is in the detergent industry. Sodium sulfate acts as a filler and diluent. Sodium sulfate is also used in the glass industry where sulfate is used to modify the physical characteristics of the glass and in the production of kraft paper pulp where sulfate is reduced to sulfite, an active component of pulping liquor.

There are three major types of processing of brines in the production of anhydrous sodium sulfate; the Ozark-Mahoning process used in West Texas, Kerr-McGee's process at Searles Lake (Figure 2-13), and the process used by the Great Salt Lake Minerals and Chemicals Corp. in Utah. The Ozark-Mahoning process is shown in Figure 2-14. In this process, brines are refrigerated to selectively precipitate Glauber's salt which is subsequently filtered and washed. Washing produces a saturated solution of Glauber's salt which is converted to the anhydrous form in mechanical vapor recompression crystallizers. The anhydrous salt is separated from solution by centrifugation, and the centrate returned to the combustor. Anhydrous sodium sulfate is lastly dried in a rotary kiln. The only waste that can be identified at this time are those resulting from filtration and washing of the Glauber's salt (Table 2-8). These wastewaters are reinjected into the salt formation in some manner.

Figure 2-13
SODIUM CARBONATE PROCESSING
SEARLES LAKE, CA PROCESS



The Searles Lake process is similar to the above described process, however, in this case other salt products are produced. For instance, sodium carbonate is recovered through precipitation caused by carbonation of the brine. The sodium bicarbonate free brine is refrigerated to selectively crystallize borax and then further cooled to precipitate Glauber's salt. Major impurities are sodium chloride and soda ash.

The process used at the Great Salt Lake relies on solar evaporation and winter cooling of brines for selective precipitation of sodium sulfate. The harvested Glauber's salt is melted and anhydrous sodium sulfate precipitated by the addition of sodium chloride to reduce its solubility through the common ion effect.

Based on the foregoing discussion, further study of this industry for potential regulation under Subtitle C is not recommended.

STAUROLITE

Staurolite is an iron-aluminum silicate mineral that is commonly used as a sandblasting agent. It is also used as a foundry sand and as a source of aluminum in portland cement manufacture, where aluminum is not otherwise available. The only known production of staurolite in the United States occurs in Florida, where E.I. duPont de Nemours coproduces staurolite in association with its titanium mining operation.

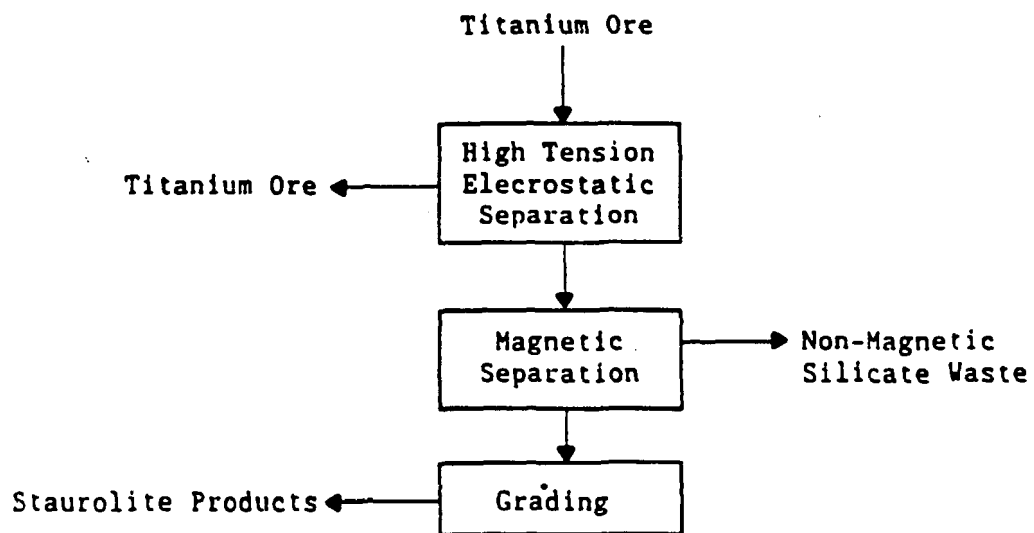
Staurolite and other silicates are separated from titanium ore by high-tension separation. The staurolite is then magnetically separated from the other silicates. The resulting staurolite concentrate contains mainly Al_2O_3 with lesser amounts of Fe_2O_3 , ZrO_2 , TiO_2 , and free silica. The concentrate is graded into fine, medium, and coarse fractions and packages (Figure 2-15).

The only known byproduct from production operations is the silica waste coming from the magnetic separator. The common silicates found in the titanium deposit are zircon (ZrSiO_4), kyanite (Al_2SiO_5), sillimanite (Al_2SiO_5), and tourmaline $(\text{Na}, \text{Ca}) (\text{Li}, \text{Mg}, \text{Al}) - (\text{Al}, \text{Fe}, \text{Mn})_6 (\text{BO}_3)_3 - (\text{Si}_6\text{O}_{18}) (\text{OH})_4$. None of these minerals contain EP Toxic metals.

Based on the above analysis, further study of this industry for potential regulation under Subtitle C is not recommended.

Figure 2-15

STAUROLITE PRODUCTION



BUILDING STONE

For the purposes of this study, building stone will be defined as all stone used as a building material for decorative purposes or as a sole structural material. This includes, but is not limited to, ashlar stone, cut (dimension) stone and rubble and rough construction stone. These are primarily used as facing stone for appearance, and consist of a wide variety of natural types. Stone used for structural purposes is somewhat more limited in type. All such stone is mined in a very selective manner with negligible waste from mining and little if any from finishing. What wastes are produced would not be expected to exhibit any hazardous characteristics.

Based on the above analysis, further study of this industry for potential regulation under Subtitle C is not recommended.

SULFUR

Sulfur is a non-metallic element widely used in industry both as elemental sulfur (brimstone) and in sulfuric acid. Sulfur has three basic sources. Native or elemental sulfur, combined sulfur, and recovered sulfur. Native sulfur is found in salt domes, stratigraphic deposits and volcanic deposits. Combined sulfur occurs in natural compounds such as iron pyrite, copper sulfides and gypsum. Recovered sulfur is produced as a by-product of other processes, such as oil refining or base metal smelting.

In the U.S., the Frasch process for mining elemental sulfur produced about 37% of the total U.S. production of 11 million tons of sulfur in 1986, sulfur from pyrite accounted for 2% and recovered sulfur accounted for the remaining 61%.

The Frasch process uses hot water to melt sulfur trapped in salt domes. The sulfur is then pumped to the surface and is either sold as a liquid or cooled and solidified into a number of forms for market. The water migrates to the edges of the sulfur deposit where it is removed by "bleed water" wells and discharged. This bleed water is not expected to exhibit hazardous characteristics. There has been sporadic production of elemental sulfur from volcanic deposits in the western U.S., but it has been very small and the selective mining used would eliminate wastes.

Sulfur from pyrite (iron sulfide) is produced by roasting (burning) the pyrite to produce sulfur dioxide gas and iron oxide solid. The gas is treated to produce either liquid sulfur dioxide or sulfuric acid and the iron oxide may be sold as feed for iron making. If the iron oxide is not sold, it is not expected to exhibit any hazardous characteristics as a waste.

Recovered sulfur production is not within the scope of this study, except as a part of the study of wastes from primary metal production, and will not be addressed here.

Based on the above analysis, further study of this industry for possible regulation under Subtitle C is not recommended.

TALC

The mineral talc is a soft, hydrous magnesium silicate. There are three talc containing minerals (talc, soapstone and steatite). Talc was produced domestically in 1983 from 26 mines in 12 states. Production in 1983 was 980,000 short tons with 97% produced in Texas, Vermont, Montana, New York and California.

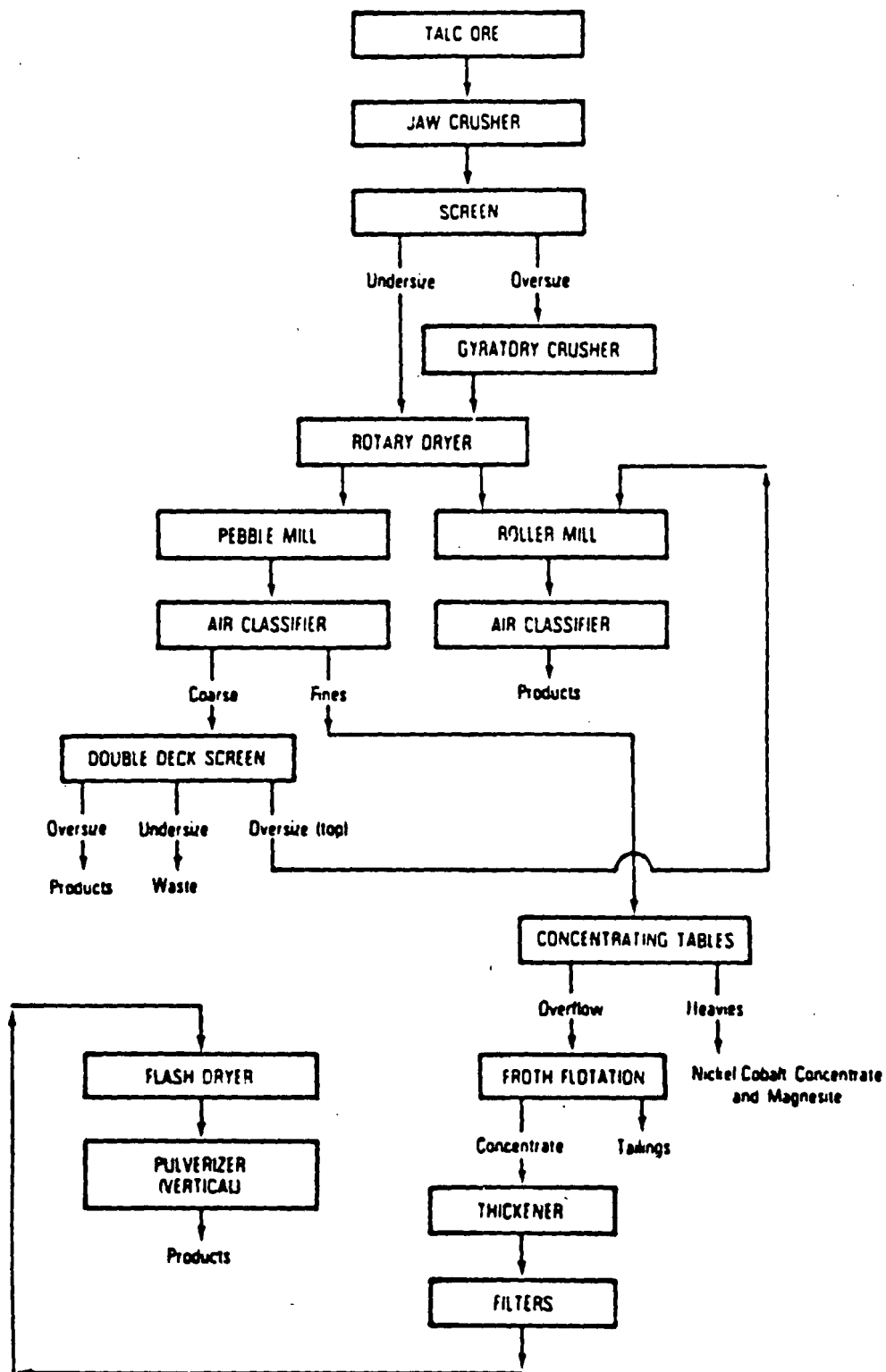
Massive solid talc that is relatively pure is sold as steatite and is suitable for making electronic tube insulators. Less pure solid talc is called soapstone. Soft massive talc is some times called "French Chalk", and is used to make talc crayons. Platy and soft talc is used in a very wide variety of industries, including paint as a filler, paper for coatings, ceramics, cosmetics, plastics as a filler, roofing materials and in the rubber industry, again as a filler.

This wide variety of uses leads to a variety of specifications. Selective mining and hand sorting are the methods most commonly used to improve the quality of the crude talc group minerals. Massive steatite is used as mined, and is just curved to shape. Much soft talc is processed dry, simply being ground to the proper size (generally very fine) in a series of steps. High grade products require more elaborate processing by froth flotation. Figure 2-16 shows a general flotation flowsheet including crushing, drying, flotation, thickening and final drying. The waste products from flotation are sent to a tailings pond. The waste products would typically be carbonates such as limestone or dolomite with some fine talc and other accessory minerals. These wastes would not be expected to be hazardous.

Based on the above analysis, further study of this industry for potential regulation under Subtitle C is not recommended.

Figure 2-16

TALC PROCESSING



TRIPOLI

Tripoli is a finely divided, microcrystalline form of silica that is a recrystallization of siliceous limestone or calcareous chert leachate. Pulverized tripoli is used in abrasives, buffing and polishing compounds, and inert mineral fillers. Silica treated by surface adsorption of organics with organofunctional groups is used in thermoplastic and thermosetting resins for molded engineering plastics, casting compounds, adhesives and coatings. Tripoli is found throughout the southeast United States. The distribution is broken down into districts. These districts are the Missouri-Oklahoma, Southern Illinois, Arkansas, West Tennessee River Valley, and other areas in the southeastern United States. The distribution is broken down into districts. These districts are the Missouri-Oklahoma, Southern Illinois, Arkansas, West Tennessee River Valley, and other areas in the southeastern United States. Approximately 100,000 short tons of tripoli was produced in 1980.

Open cut or underground room and pillar methods are used to mine tripoli. The processing is very simple, the ore is crushed, dried, and ground to produce the final product. None of these stages of processing produces waste (with the exception of moisture loss, all of the mined material ends up as product). Therefore, further study of this industry for potential regulation under subtitle C is not recommended.

VERMICULITE

Vermiculite is the name given to a family of mica-like hydrated ferromagnesian silicate minerals. These minerals expand, when heated, to approximately 30 times their original size. The resulting product is a lightweight insulator that is used in construction and as a lightweight carrier material for fertilizers and pesticides and herbicides. Production of vermiculite in the United States has remained fairly constant over the last decade, at just over 300,000 short tons per year.

Vermiculite deposits in the United States occur mainly in the Piedmont region from Alabama to Pennsylvania and in the Rocky Mountain Range from Montana into New Mexico and Texas. Mining of vermiculite is known to occur in Libby, Montana, Enoree, South Carolina and Louisa County, Virginia.

Processing of vermiculite generally involves separation, sizing, and heating operations (Table 2-9). These operations do not always occur at the milling site. Rough screening may be done at the mining site, and the heating operation may be centrally located to a number of mining sites. The specific processing operations of the two largest mines are discussed below.

The flowsheet for the Libby, Montana, plant is shown in Figure 1. The preliminary screening plant is between the mine and the mill. The preliminary screening plant removes the waste rock from the raw vermiculite ore. The waste rock (waste 1 in Figure 2-17) is disposed of in piles near the mining area and is not expected to exhibit any hazardous characteristics. The raw ore is sent to the mill for rough size fractionation producing Waste 2; then water is added to the ore and further concentration takes place by gravity separation. This process generates tailings (waste 3) which are sent to a tailings pond. The clean water is pumped from the top of the tailings pond to a clean water reservoir and is then reused in the plant. The wet concentrate goes to a drying operation and is sized before being shipped to the exfoliation (heat treating) plant

Table 2-9

VERMICULITE PROCESSING

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Primary Screening	1. Waste Rock	N	N	N	N	
Rough Sizing	2. Waste Rock	N	N	N	N	
Separation	3. Tailings (Waste Rock Fines)	N	N	N	N	
	4. Baghouse Dust					
Exfoliation	5. Baghouse Dust	N	N	N	N	

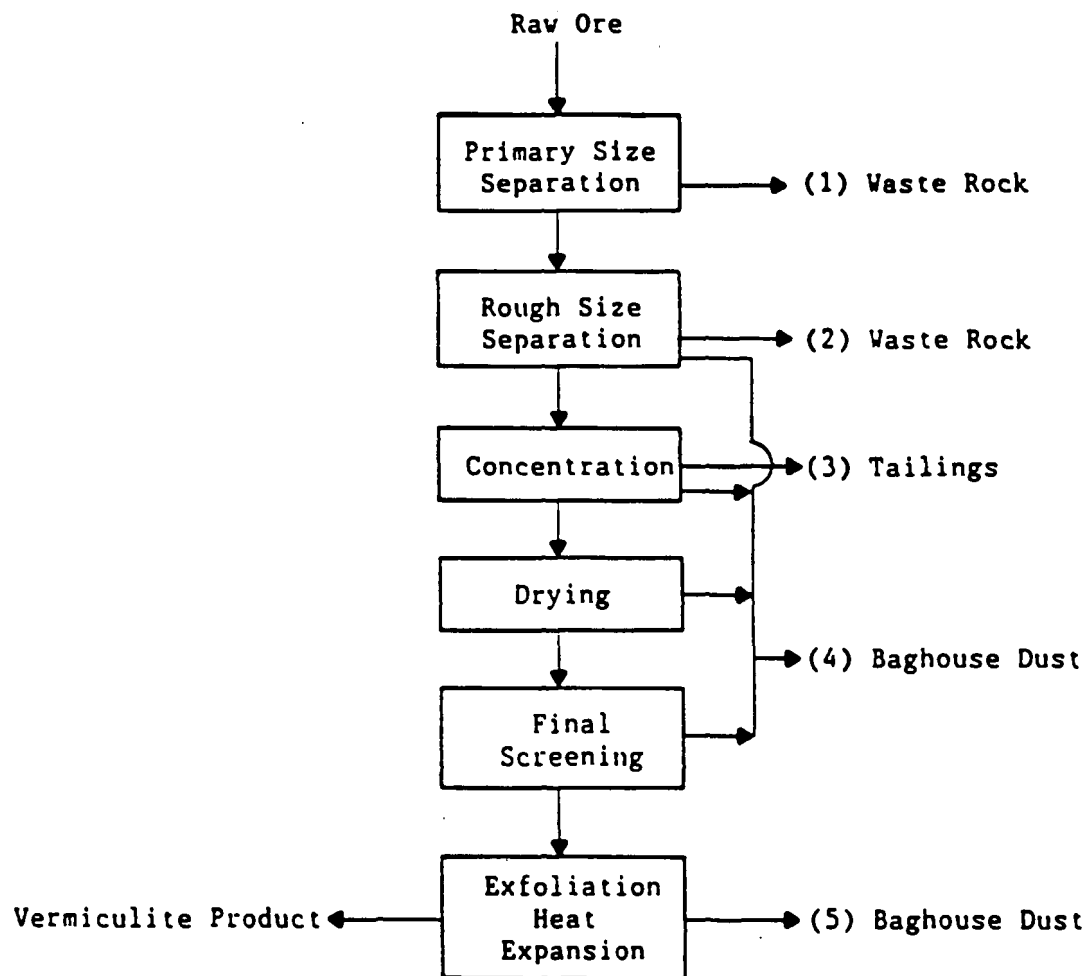
* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

Figure 2-17
VERMICULITE PROCESSING



off-site. The building exhaust system goes to a bag filter which generates a solid waste stream waste 4. The final disposition of this waste is not known, but it is not expected to exhibit any hazardous characteristics.

In the South Carolina operation, the ore is sent to the mill as a wet slurry. The slurry goes through desliming and beneficiation steps, then is dewatered. The dewatered concentrate is dried and screened before being sent to an exfoliation plant off-site. These processes generate a number of aqueous waste streams that are sent to tailings ponds. The clarified water from the ponds is reused in the plant.

Exfoliation involves heating the vermiculite concentrate at high temperatures (2000 - 3600°F) for a short time. After the material leaves the furnace, the rock impurities are removed from the vermiculite. The product is then packaged and shipped. Most furnaces have bag collectors for dust control which produces waste 5 in Figure 2. The waste management methods for the rock impurities and bag collector dust are not known, but they probably will not show any hazardous characteristics.

For these facilities, there is little information available on the quantities or characteristics of the waste streams. Table 1 summarizes what is known. However, the quantities are probably small and it is expected that they would not exhibit any hazardous characteristics. Therefore further study of the vermiculite industry for potential regulation under Subtitle C is not recommended.

WOLLASTONITE

Pure wollastonite is a calcium metasilicate with the composition 48.3 percent CaO and 51.7 percent SiO₂. The United States is the largest producer of wollastonite in the world, with New York and California the two producing states. Production in New York is from an extensive deposit located on the western side of Lake Champlain near Willsboro. In California, wollastonite is produced by Pfizer Incorporated. Wollastonite is also found in the states of Arizona, Nevada, Idaho, Utah, and New Mexico. Production in the United States (California and New York) is considered company proprietary data.

Wollastonite is utilized by the plastics and coatings industries as a filler and extender, and as a partial substitute for fiberglass and for asbestos. Other consumption is for thermal insulation, ceramics, refractories, metal casting plasters, fluxes, matchheads, abrasives, pesticide carriers, and friction papers.

Wollastonite is mined by open pit/open stope methods. At Willsboro, New York, extracted ore is crushed, screened, and concentrated using magnetic separators. The high intensity magnets separate both garnet and diopside which are presumably byproducts that are not wasted and would not be expected to exhibit hazardous characteristics even as waste. The beneficiated wollastonite is further ground in pebble mills or attrition mills to produce grades of granular and fibrous wollastonite, respectively.

The mining and processing of wollastonite does not appear to produce any significant quantities of waste, and any such waste is unlikely to have hazardous characteristics. Therefore, further study of this industry for potential regulation under Subtitle C is not recommended.

BARITE

Barite is the naturally occurring mineral form of Barium Sulfate (BaSO_4), and is produced both from gravel type deposits (residual) and from beds or veins. Most residual production is from Georgia, Missouri and Tennessee while veins and beds are mined in Nevada. Barite is used as a component of petroleum drilling muds (due to its density of 4.5 gm/cc), glass making, paint and to make barium chemicals. Annual domestic production is estimated at 378,000 short tons (1986).

Residual ores are mostly clay with rounded barite and siliceous gravels. Treatment consists of breaking down the residuum, washing out the clay and removing the siliceous gangue by density separation (see Figure 2-18). As shown in the figure, four waste streams are produced in this treatment. Waste stream 1 consists of the cobbles and other large rocks, and waste stream 2 consists of clays and other very fine materials including barite. In Missouri much of the rock waste streams 3 and 4, is used as aggregate in road and dam building.

Bedded and vein deposits often require more treatment using crushers and froth flotation in addition to density separation because of the more complex assemblage of minerals. Figure 2-19 is a flow sheet for this type of treatment. As can be seen from the figure, two waste streams are produced. The tailings products from this type of process would consist of the siliceous components of the mined ore. The first stage (density) tailings would be coarser than those from the second stage. They are most often combined and disposed as a single stream.

There are two possible areas of concern from barite production. The first is that barium is one of the eight EP toxic metals, and because of the nature of the EP toxic test barite tailings may show elevated barium levels. Barium sulfate, however, is not soluble to more than 5 mg/l in

Figure 2-18
BARITE FROM RESIDUUM

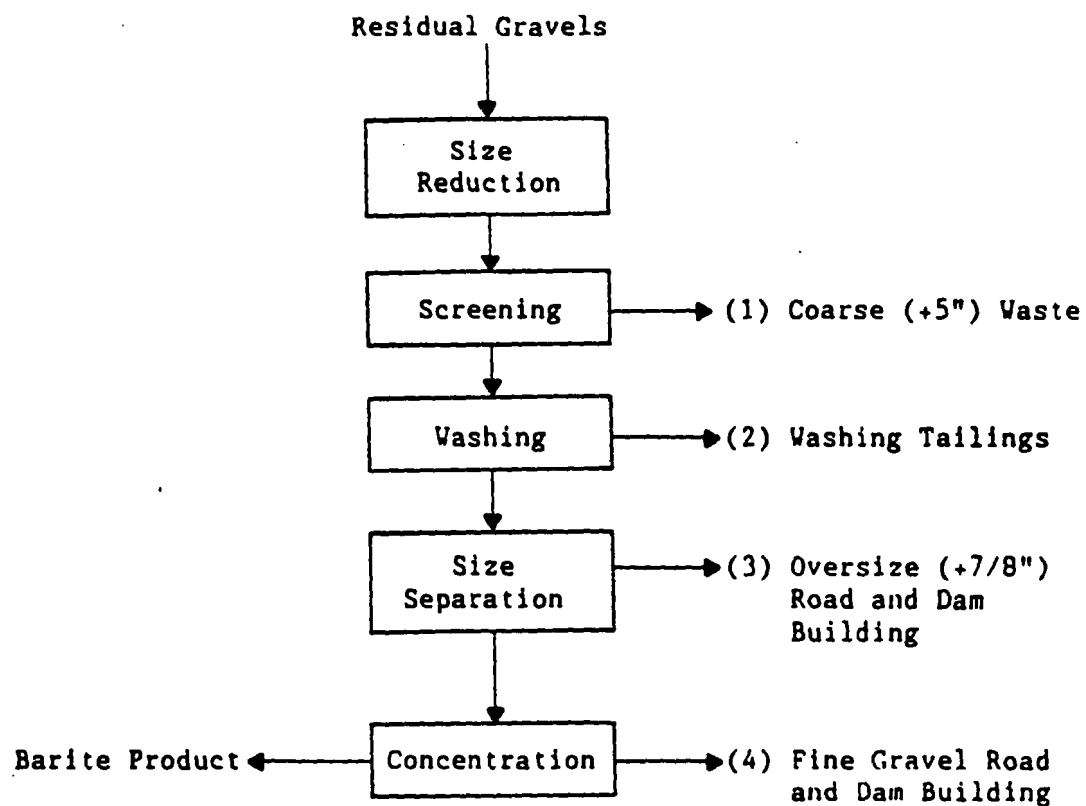
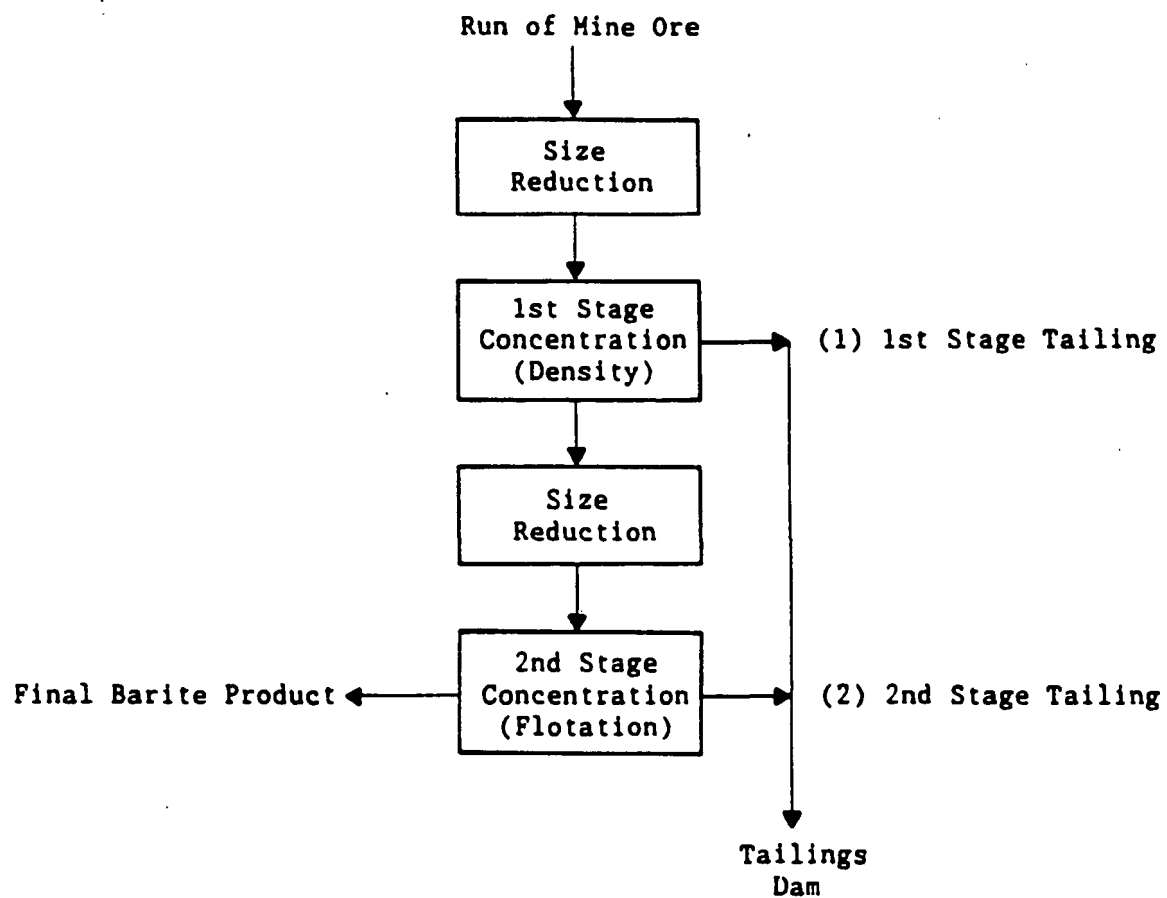


Figure 2-19

BARITE FROM BEDS AND VEINS



water, therefore barite tailings are probably not a major source of barium in the environment. The second concern is that barite is often found with metal sulfides, but there has not been any economic production of metals and barite as coproducts or byproducts from these deposits. If exploitation of these deposits for barite ever commences the waste problems would be essentially the same as found in metal production.

The waste characteristics from this screening study are summarized in Table 2-10. Based on this analysis, further study of this industry for potential regulation under Subtitle C is recommended.

TABLE 2-10
BARITE WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Beneficiation of Residual Ores	1) Coarse Waste (+5")	N	N	N	?	Large rocks
	2) Washing Tailings (Clays)	N	N	N	?	Due to nature of test
	3) Oversize (+ 7/8")	N	N	N	?	Road and dam building
	4) Fine Gravel	N	N	N	?	Road and dam building
Beneficiation of Ores from Beds or Veins	1) 1st Stage Tailing (Fine Barite, Quartz, etc.)	N	N	N	?	Same as 2 above
	2) 2nd Stage Tailing (Quartz, etc.)	N	N	N	?	Same as 2 above

N - Waste not expected to exhibit this characteristic.
Y - Strong indication that waste would exhibit this characteristic.
? - Possibility that waste could exhibit this characteristic.

BITUMINOUS MATERIALS

Bituminous materials consist of a group of hydrocarbon mixtures including asphalts, asphaltites, mineral waxes, and pyrobitumens. Production of asphalts and asphaltites totaled 1.6 million short tons in 1979. Native asphalt is produced by one operation in Texas and asphaltites are produced by three operations in Utah. There is no information on production rates for mineral waxes or pyrobitumens. The four classes of bituminous materials are mined and processed differently and are discussed separately below.

Asphalts

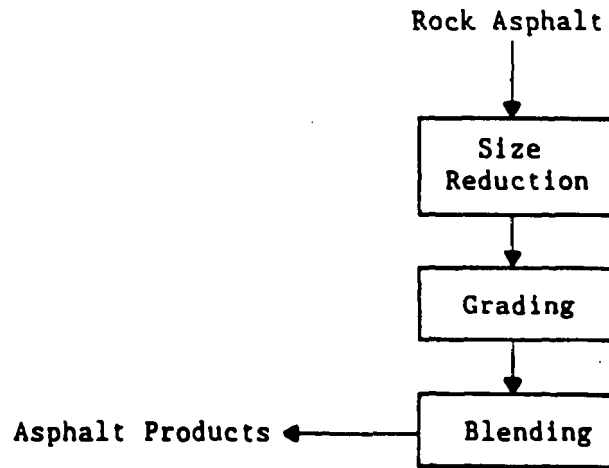
Native asphalts occur in the United States as deposits of bituminous sandstone and limestone. The most extensive deposits are Kentucky, Texas, Oklahoma, Louisiana, Utah, Arkansas, California, and Alabama. Current production is confined to one operation in Texas. Rock asphalt is primarily used for paving, with specialty uses in flooring, roofing, and waterproofing.

Today, native asphalts have largely been replaced by petroleum-refined asphalt. Commercial use of the native product is limited to areas where it is abundant and easily mined. The bitumen content of native rock asphalt ranges from 3 to 15 percent.

Mining of asphalt begins with removal of the overburden. The deposit is blasted, crushed, graded, and blended. Blending assures a bitumen content in the final product of 6.5 to 7.5 percent. The mining operations do not consist of any chemical processes and there are no known wastes generated (Figure 2-20).

Figure 2-20

NATURAL ASPHALT PROCESSING



Asphaltites

Asphaltites are bituminous materials used in specialized markets including automotive sealants, oil well drilling, foundaries, varnishes, paints, inks, coatings, and flooring materials. There are two types of asphaltites occurring in the United States: gilsonite and grahamite. Grahamite is no longer mined and has not been used in many years. Gilsonite is known to occur in one deposit in the United States that extends from 5 miles east of the Colorado border to 60 miles west into Utah.

Asphaltites are hydraulically mined by some producers since they produce an explosive dust when mechanically mined. Water jets or water flooded rotary cutters are used to produce a slurry which is collected and pumped to a surface preparation plant. The material is graded, packaged, and shipped. It is not clear whether dewatering occurs in the surface preparation plant or whether fines are produced during grading operations. The wastes from this processing could be ignitable.

The largest producer of gilsonite, the American Gilsonite Company (AGC) uses air chipping hammers to break up the gilsonite and a vacuum airlift system to transport the broken material to processing on the surface at a central plant. The flow sheet for that plant is shown in Figure 2-21. Processing consists of drying, screening and bagging. Some gilsonite is pulverized prior to shipment. Both pulverized and unpulverized gilsonite is shipped in bulk as well as in bags. The primary waste from this plant is the rock removed by the vibrating screen which is not expected to exhibit any hazardous characteristics.

Mineral Waxes

Mineral waxes do not exist in the United States as a natural substance, and, therefore, must be extracted from lignite or cannel coal. Although coal exists in many parts of the United States, the only known production

Figure 2-21

GILSONITE PROCESSING

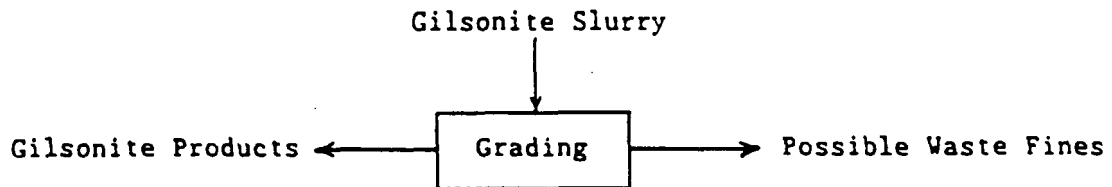
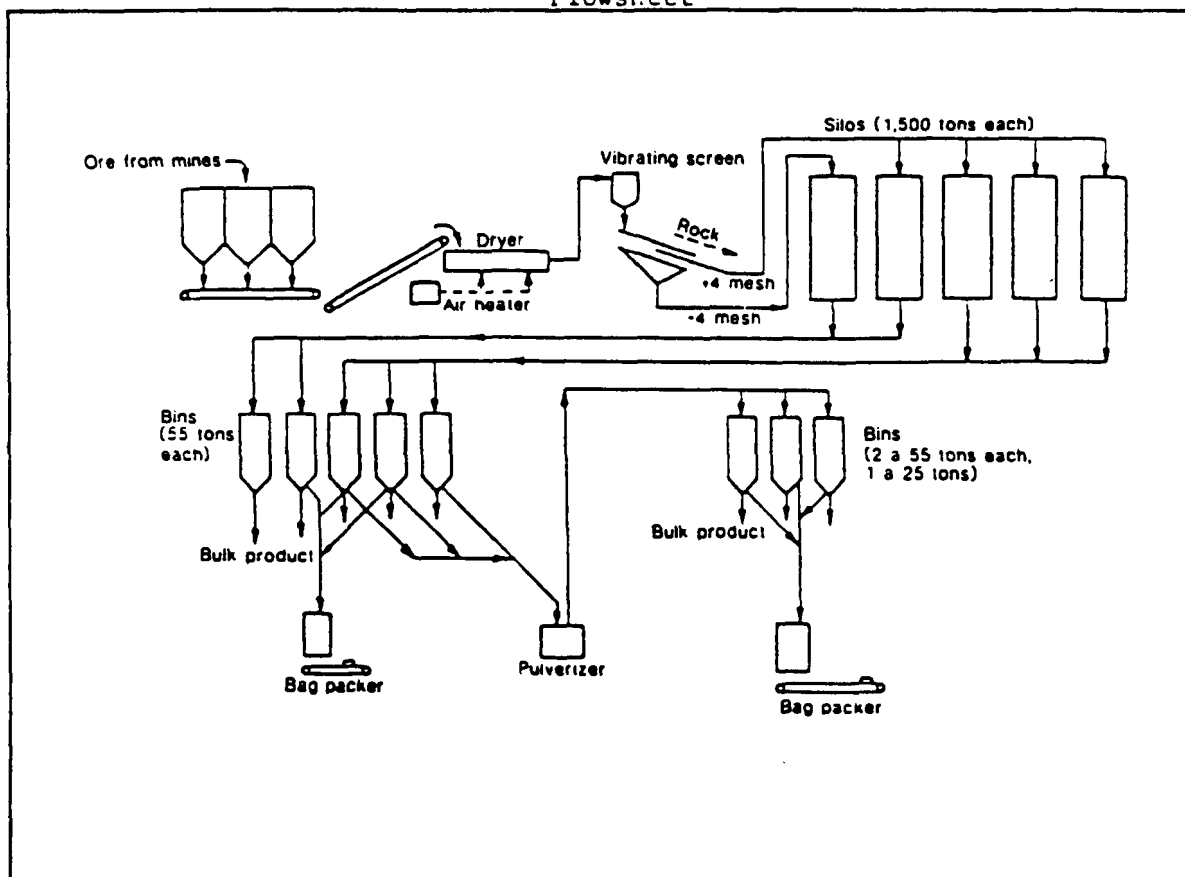


FIGURE 2a

American Gilsonite Company
Flowsheet



E&MJ July 1981

occurs in California. The extraction product, known as Montan Wax, has a very limited use in paints, wood fillers, floor polish, rubber mixtures, and candles.

The processing consists of solvent extraction from coal (Figure 2-22). Probable wastes include spent solvent and spent coal. There is no information available on the quantities or characteristics of these wastes. Waste management methods for this industry are not known.

Pyrobitumens

Pyrobitumens are mined mainly in Utah. They have limited uses in rubber, paints, varnishes, and insulating and waterproofing compounds.

Processing consists of cracking in a still, recondensation and grading. Possible waste products include waste catalyst and still bottoms (Figure 2-23). The management methods, quantities, and properties of these wastes are not known.

Production of naturally occurring bituminous materials is fairly low, due to low cost of petroleum refining substitutes. The volumes of waste materials will be minimal, although some of them may be fairly hazardous.

Based on the above analysis, further study of these industries, with the exception of native asphalt, for regulation under Subtitle C is recommended.

Figure 2-22

MINERAL (MONTAN) WAX PRODUCTION

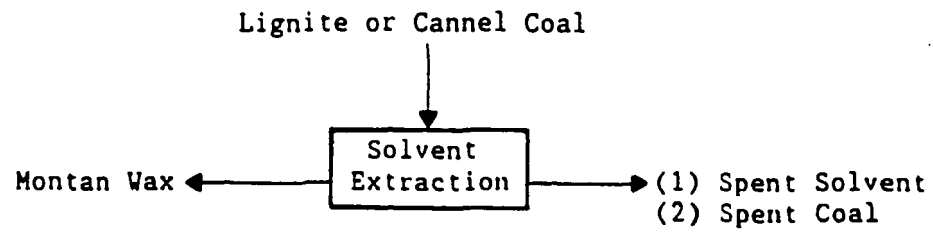
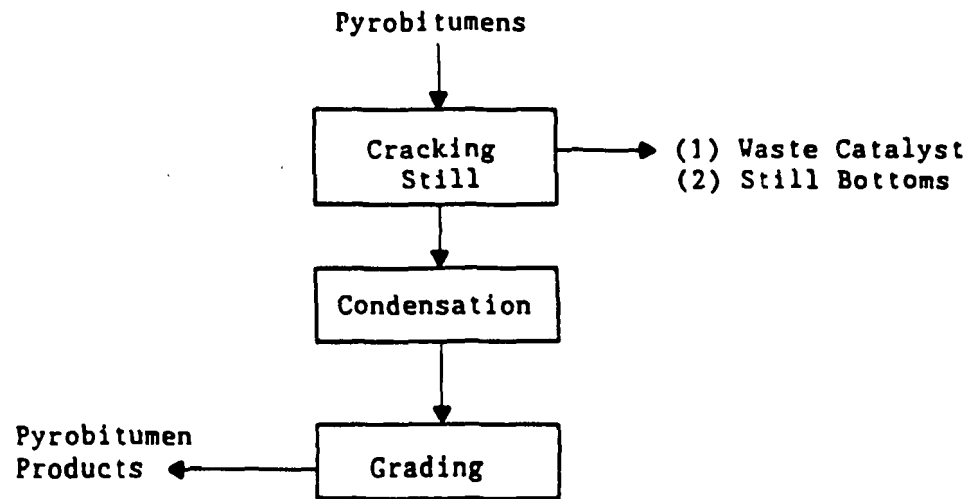


Figure 2-23
PYROBITUMEN PROCESSING



BORON MATERIALS

Boron, commonly found in the mineral tincal, has found many uses in industry. Boron compounds, are used in glass making, textile fibers, enamels, cleaners fertilizers, insulation and many other products. The United States is the largest single producers, with slightly more than 50% of total world production.

Borates are produced both by mining solid minerals and by precipitating the desired compounds from desert lake brines. There are two primary mining areas in the US, Boron, CA and the Death Valley, CA area. Borates are produced from brines at Searles Lake, CA.

Ores at Boron, CA are selectively mined, crushed and stockpiled for processing. The ore is principally tincal (sodium borate), which is easily soluble in water. As shown in the flow sheet, Figure 2-24, the ore is crushed to less than 1" lumps and then the tincal is dissolved in hot, weak, recycled borax solution, leaving some clay and few other insoluble impurities (Waste 1). The insolubles are then separated from the solution and the clarified liquor is fed to crystallizers.

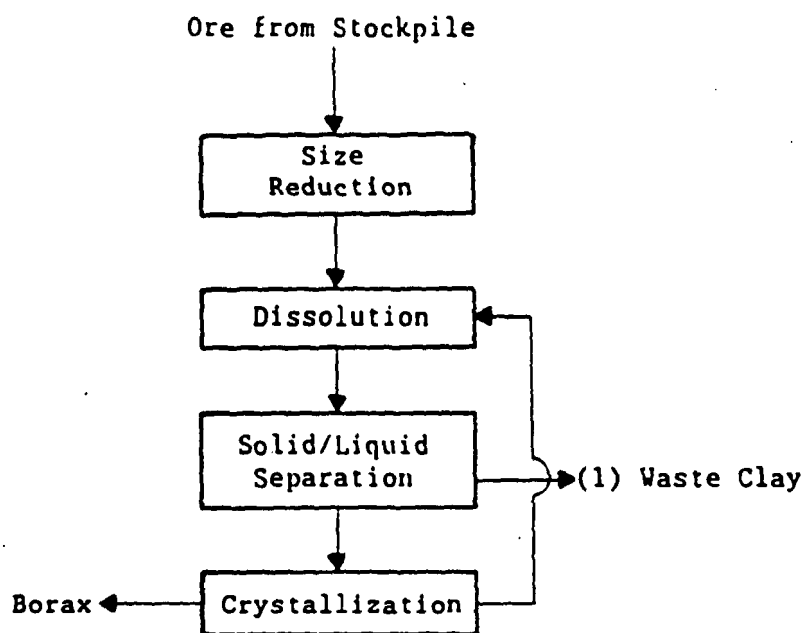
The crystals of sodium borate are separated from the weak solution which is recycled to the dissolution step. The crystals are dried and may be sold as is, as borax, or treated to produce other materials. Some of the ore is reacted with sulfuric acid to produce boric acid and leaves sodium sulfate as a waste, which is not expected to exhibit any hazardous characteristics.

Figure 2-25 shows the flow sheet for processing Death Valley ores containing colemanite (calcium borate) which is insoluble in water. This material is crushed to less than 3/8 in., then washed to remove clay (Waste 1 in Figure 2-25). The clay free material is ground further, and then concentrated by froth flotation producing a saleable product and limestone tailings (Waste 2 in Figure 2-25). This borax product is then dried and a portion bagged for sale. The rest is calcined and the calcine is then

Figure 2-24

BORATE ORE PROCESSING

BORON CALIFORNIA



BORIC ACID PRODUCTION

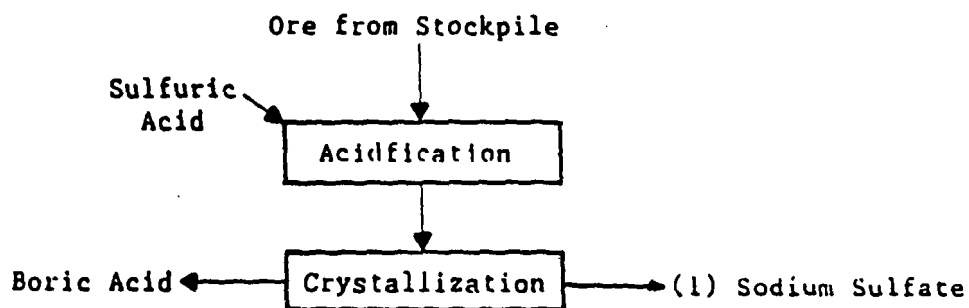
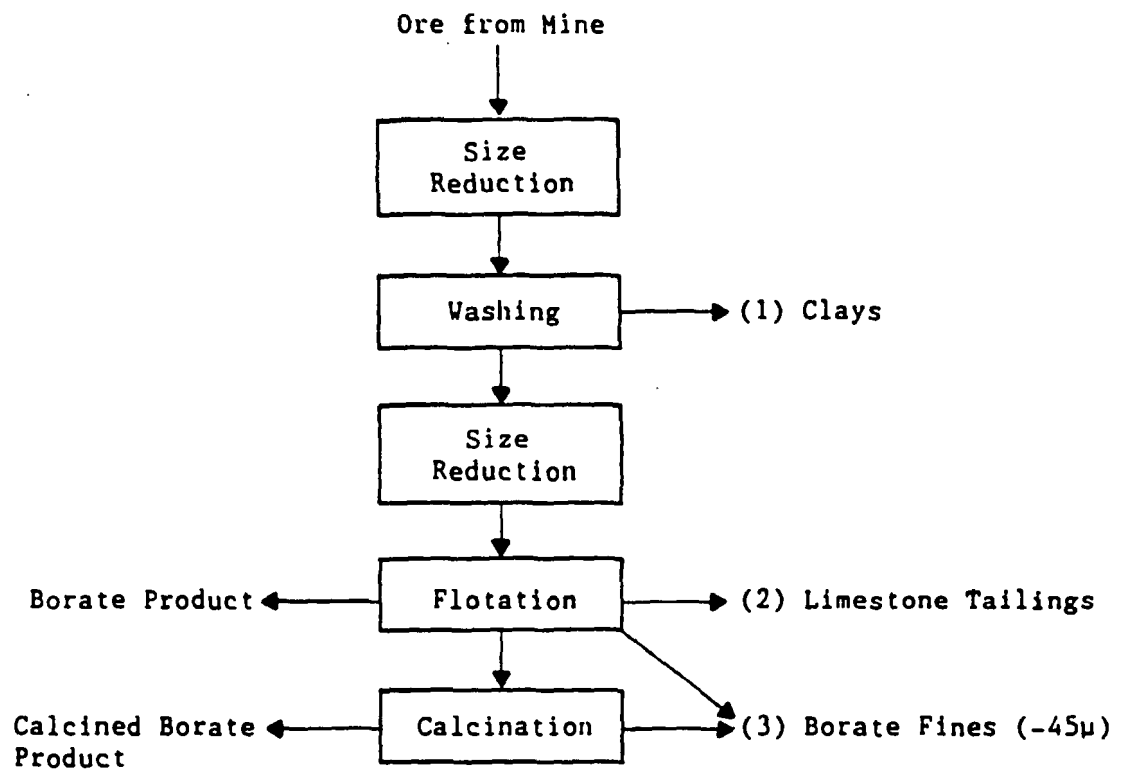


Figure 2-25
BORATE ORE PROCESSING
DEATH VALLEY CALIFORNIA



bagged for sale. Both the drying and calcining processes produce a fine borax dust which is a waste product (Waste 3 in Figure 2-25). This plant is currently inactive.

Borax production from the brines of Searles Lake is carried out by one of two processes (both shown in Figure 2-26). In the first process, carbon dioxide gas from lime kilns or boiler flue gases is bubbled through the brine. Sodium bicarbonate is precipitated. The brine is then neutralized and cooled in vacuum crystallizers producing borax crystals. Further cooling produces sodium sulfate. The borax crystals are dewatered and dried to make borax products. The other process is an evaporation process (Figure 2-27) which first produces crystals of potash (potassium chloride). The remaining solution is then fed into borax crystallization tanks. The borax crystals are then filtered washed redissolved and recrystallized. These crystals are then dried giving the final products.

Boric acid is also made from the brines by a solvent extraction process (Figure 2-28). In this process the brine is mixed with a kerosene solution of a chelating agent which will pull the borate from the brine. The organic solvent is then separated from the brine and mixed with an aqueous (water based) sulfuric acid solution containing no borax. The borates then go into the aqueous phase. After separating the kerosene, the aqueous material is filtered with activated carbon to remove all traces of the organic solvent. The resultant boric acid solution is evaporated and crystallized to produce the final product.

This initial study did not reveal much detailed information about the wastes from these processes. There are no clearly hazardous wastes produced, but the potential does exist (Table 2-11).

Based on the above information, further study of this industry for regulation under Subtitle C is recommended.

Figure 2-26
BORATE BRINE PROCESSING
SEARLES LAKE CALIFORNIA

Carbonation Process

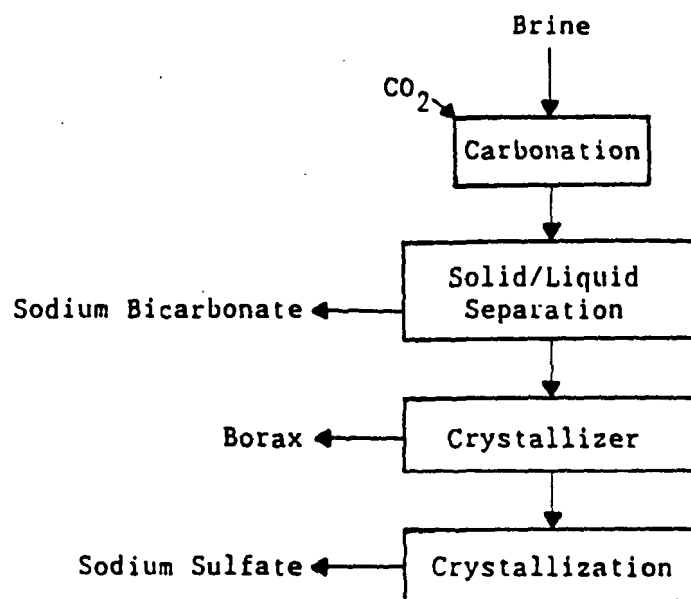


Figure 2-27
BORATE BRINE PROCESSING
SEARLES LAKE CALIFORNIA

Evaporation Process

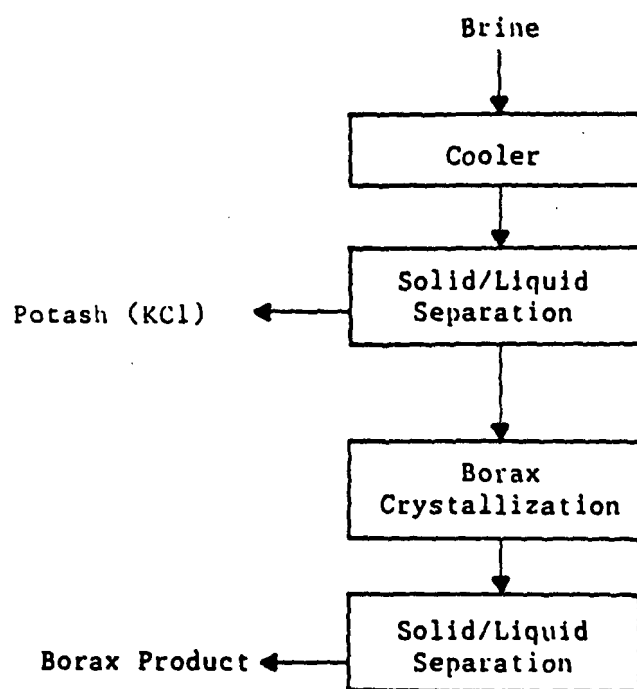


Figure 2-28

BORIC ACID PRODUCTION
SEARLES LAKE CALIFORNIA

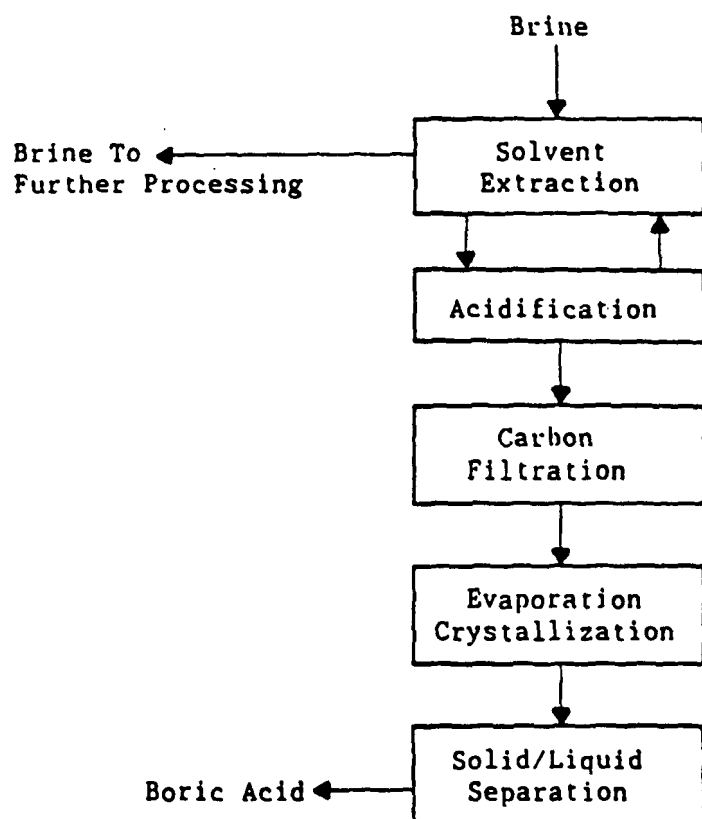


Table 2-11

BORATE WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Boron, CA Milling	1) Waste Clay	N	N	N	N	
Boric Acid	1) Sodium Sulfate	N	N	N	N	
Death Valley, CA Milling	1) Clay Wastes	N	N	N	N	
	2) Tailings (Limestone)	N	N	N	N	
	3) Borate Fines	N	N	N	N	
Searles Lake Brines	1) Waste Brines	?	?	N	?	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

BROMINE

Bromine is a member of the halogen family of elements. Elemental bromine is highly reactive and thus it occurs in nature only as bromide compounds. Bromide compounds are found in sea water, subterranean brines, saline lakes, oil and gas well brines, and evaporate chloride minerals such as halite (NaCl), sylvite (KCl), and carnalite. Five companies in Arkansas and Michigan produced bromine from subterranean brines in 1986.

Bromine has a variety of chemical applications. Ethylene dibromide, an antiknock additive in leaded gasoline, is the single largest compound produced with bromine. Approximately 20 percent of the bromine consumed in the United States is used to produce ring-brominated aromatic compounds, which are used as flame retardants. Other uses include production of methyl bromide, a soil and space fumigant, and the use of bromine in oil field fluids. Total production in 1986 was estimated to be 325 million pounds.

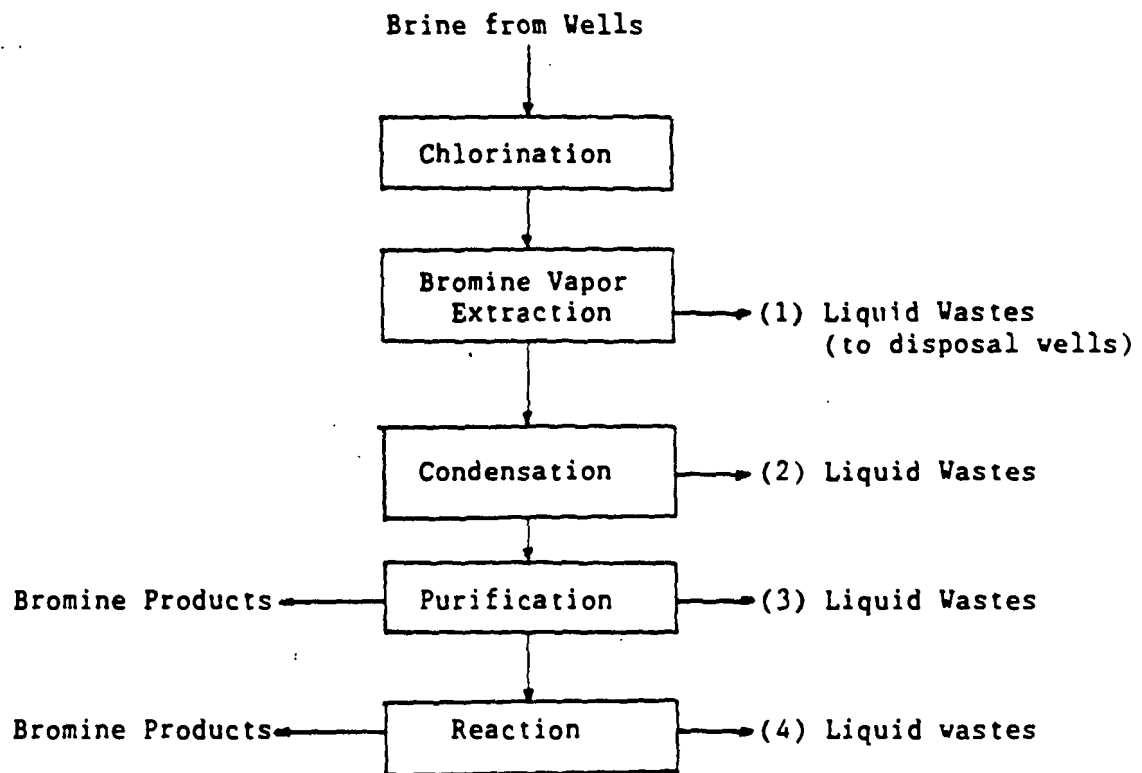
Bromine is extracted from brines by chemical oxidation to bromine gas, followed by air or stream stripping. The essential steps are:

1. Chlorination to oxidize the bromide to bromine;
2. Bromine vapor purging by air or stream stripping;
3. Condensation of bromine vapor or reaction to form a salt or an acid; and,
4. Bromine purification.

Liquid wastes are generated by bromine extraction from brines; however, the exact nature and quantities of wastes are unknown at this time. As shown on Figure 2-29, waste brine is generated by the bromine vapor removal stage of extraction. These are treated with lime to adjust their pH and then are reinjected into Class IV disposal wells. Liquid wastes may also be generated by the salt and/or acid formation and by the bromine purification

Figure 2-29

BROMINE EXTRACTION PROCESSES



processes. There is a possibility that these wastes could be corrosive or reactive due to the nature of the product (Table 2-12).

Based on this analysis, further study of the bromine industry for potential regulation under Subtitle C is recommended.

Table 2-12

BROMINE PRODUCTION WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Bromine Vapor Removal	1. Waste brine	?	?	N	N	Bromine, chlorine
Condensation	2. Process waste	?	?	N	N	Bromine
Bromine Purification	3. Purification waste	?	?	N	N	Bromine
Reaction	4. Liquid Waste	?	?	N	N	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

CLAYS

The clay industry can be broken down into three segments, by general composition. These are (1) bentonite and fuller's earth, (2) kaolin, ball clay and refractory clays, and (3) miscellaneous clays and shale. While these categories are based on clay type, processing and uses are roughly similar within each group. Annual production is estimated to be 5 million short tons for bentonite and fuller's earth, 10 million short tons for kaolin, ball clay and refractory clay and 23 million short tons for miscellaneous clays and shale (1986).

Bentonite is a term based on mineral type and fuller's earth is a term based on use. They are grouped as an industry segment because fuller's earth also consists of non-swelling bentonite. Bentonite is primarily used in drilling muds for oil exploration. This segment of the clay industry also provides materials for absorbent granules, iron-ore pelletizing, and foundry sand binding. The term fuller's earth is applied to clays used in processing oils and fats (oil refining, filtering, clarifying, and decolorizing). There are many other minor uses of these clays. Processing is straight forward. The clay is selectively mined, dried, ground to size, and sometimes blended to give the desired properties. There are no waste products and fugitive dust emission would be the most significant problem.

The second industry segment consists of materials containing Kaolin, a clay that gives the material good forming and firing characteristics needed for making porcelain ware, fire brick, and other such items. Kaolin in the highest grade has a clean white color and is probably the most highly processed. Ball clays are not white but have a light color and are otherwise the same as kaolin. Refractory clays are somewhat cruder, with classification being based on firing and high temperature characteristics with no regard to color.

Kaolin has the most complex processing flowsheet as seen in Figure 2-30. Selective mining is practiced so that little if any waste material is produced at the plant. The clarified clay is used in a host of products. The only area of potential generation of a waste of concern is the leaching (brightening, whitening) step which uses acids, ozone or strong reducing agents (hydrosulfite) to remove the iron compounds that color the clay. If the liquid from this step is discharged it could present a potentially hazardous waste. Ball and refractory clays are not normally processed to this extent.

The final segment of the clay industry is a catch-all for everything that doesn't fall clearly into either of the above categories. Much of the clays in this category are used in low value, high volume applications such as brick, drain tile, vitrified pipe, quarry, flue and roofing tile, pottery, and stoneware. Processing is minimal due to the low value and most is used as mined near the source. There would be little or no waste from this segment of the industry.

Table 2-13 is a summary of the waste characteristics from this screening industry. Based on the analysis above, only the bleached kaolin segment of the clay industry is recommended to be further studied for potential regulation under Subtitle C.

Figure 2-30
KAOLIN PROCESSING FLOWSHEET

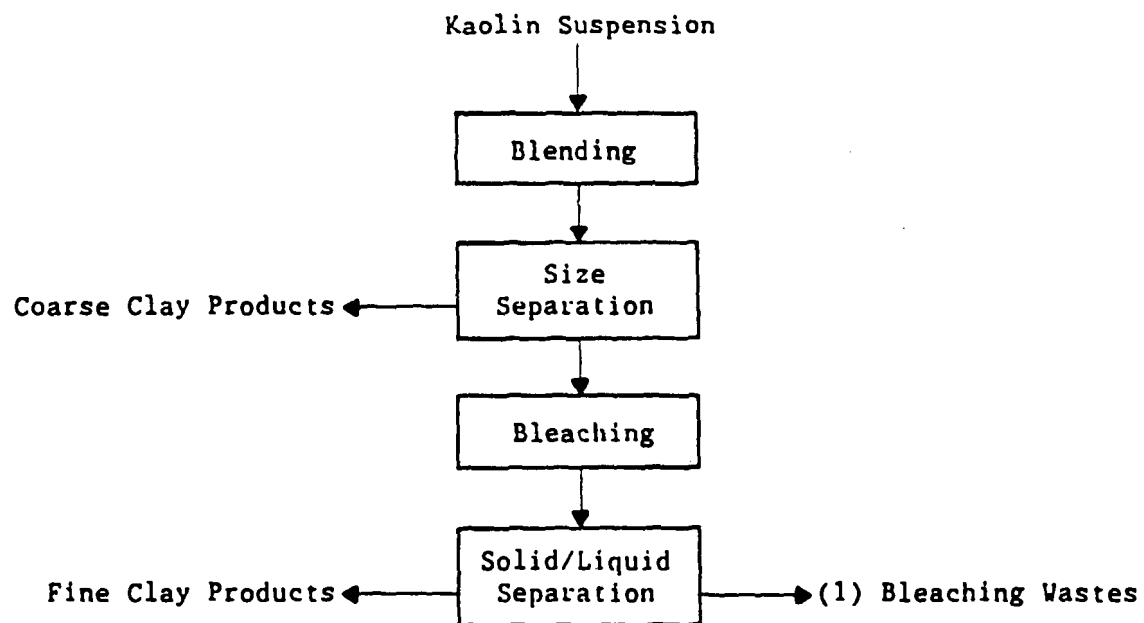


Table 2-13

CLAY WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Kaolin Bleaching	1) Waste Liquor (acid, ozone, reducing agents	N		?	N	N

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

COAL: BENEFICIATION, GASIFICATION, LIQUEFACTION; COKING

Coal Beneficiation

Coal beneficiation (washing or cleaning) is done to remove undesirable materials from a mined coal. The primary goal is to remove ash-forming materials such as silicate shales also called bone or slute. A secondary benefit, which is being actively studied for future improvements, is the removal of sulfur-bearing materials, mainly iron pyrite.

Most coarse coal cleaning uses the difference in density between coal and its contaminants to separate them. Both the ash-forming materials and the iron pyrites are denser than coal. Density separating devices such as jugs, Humprey's spirals, shaking tables, sink-float machines, and dense medium cyclones are used for coarse coal cleaning. The waste from this process, coal refuse, generally retains some fuel value and research has been done to exploit it as a fuel. Most is disposed in piles. The pyrite content causes acid formation when in contact with surface or ground waters. Although coarse coal refuse can be burned and acid can be formed in the refuse piles, it is doubtful that coal refuse will exhibit Subtitle C hazardous characteristics.

Fine coal cleaning has the same objectives as coarse coal cleaning and can use some of the same types of equipment. In addition, fine coal can be cleaned by froth flotation. The characteristics of the wastes from fine coal cleaning are expected to be the same as from coarse coal cleaning.

Coal Liquefaction

Many coal liquefaction processes are currently in various stages of research and development but none have reached commercial production and therefore are not addressed by this study.

Coal Gasification

There is only one commercial coal gasification plant of sufficient size to be addressed by this report. This is the American Natural Gas plant, a Department of Energy facility at Beulah, North Dakota. A complete report on that plant will be written when the necessary information is received from the EPA.

Coke

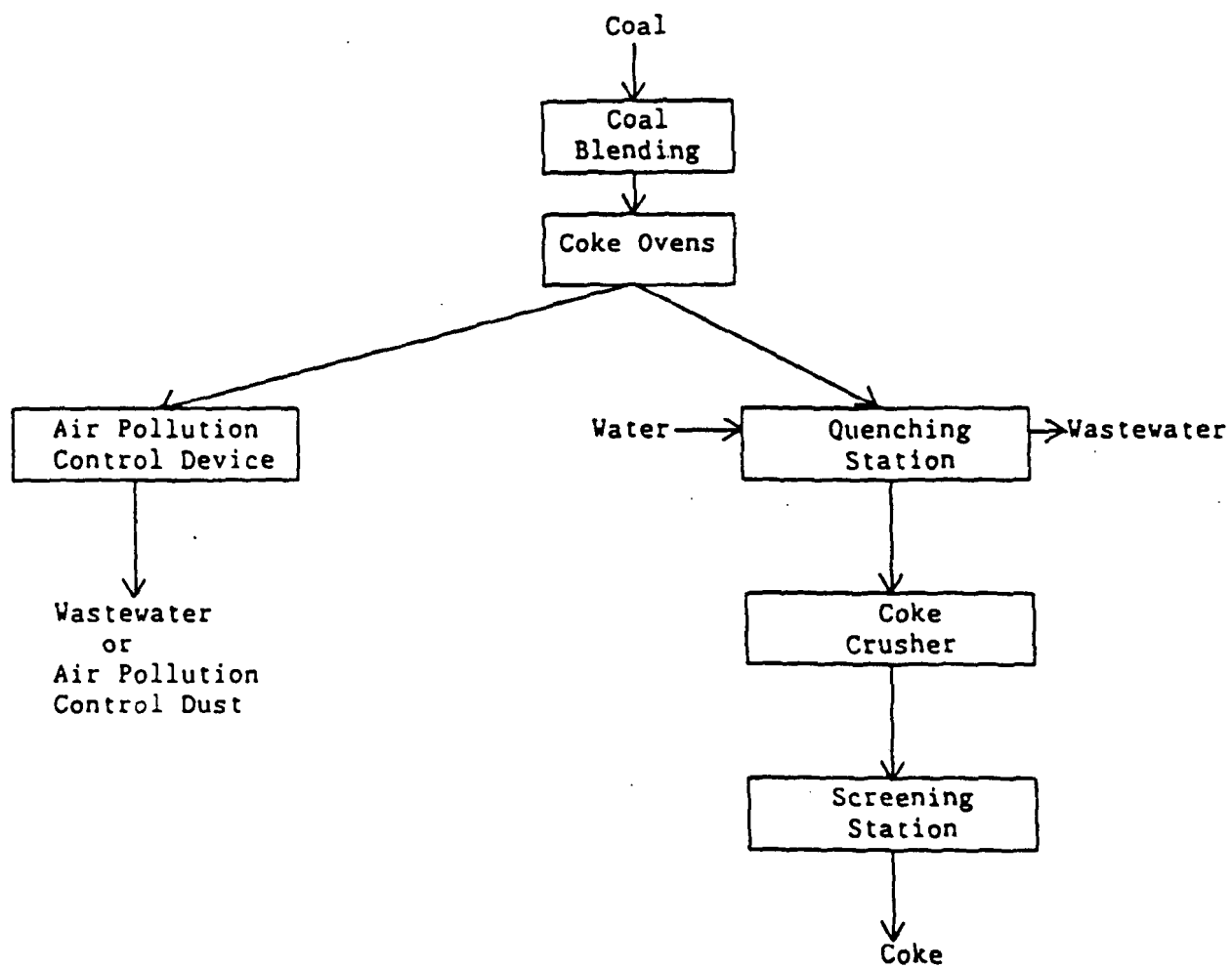
Coke is the solid, porous, carbon product of the destructive distillation of coal. The major use of coke is in blast furnaces used to produce pig iron. It is also used as a fuel in other varied applications.

Two types of processing facilities are operated in the U.S., beehive and byproduct plants. There were only 3 beehive plants operating in the U.S. in 1986, and 46 byproduct plants in 15 states (Nielsen, 1986). Twenty-six of the plants were owned and operated by steel companies. It is estimated that 90% of coke production is for the iron and steel industry. Coking operations are mainly in the eastern U.S., with Alabama, Indiana, Ohio, and Pennsylvania plants numbering over half of the total.

Beehive plants involve a beehive oven that heats blended bituminous coal in the absence of oxygen. Volatile organic compounds are driven off of the coal and released to the atmosphere. The coal is converted to coke in the oven, cooled by quenching with water resulting in a weak ammonia liquor which will contain a mixture high in two classes of toxic compounds, cyanides and phenols, and sent to a crushing, screening, and blending operation. Portions of the quenching water are reused, with the remainder typically treated prior to discharge to surface waters. The fines from screening, or coke breeze, are usually used as feed stock in iron ore sintering or pelletizing, and as "inert" material in foundry coke manufacture, electric smelting, or chemical manufacture. The process flow diagram for the operation is shown in Figure 2-31.

Figure 2-31

BEEHIVE COKING PROCESS



Byproduct plants operate on similar principles, but were developed in the late 1800's to recover some of the organic compounds released to the atmosphere in a beehive operation. The process is illustrated in Figure 2-32. The gases and vapors produced in the coking ovens are treated in a chemical recovery plant. The gas is initially cooled by spraying it with flushing liquor. Tar that is present in the gas condenses and is collected with the liquor. The liquor/tar mixture is sent to a decanter for separation. The liquor is partially recycled to the scrubber, with the rest going to an ammonia recovery unit. Gases from the scrubber flow through the primary cooler where additional tar is removed. Liquid from the primary cooler is sent to the decanter and recycled. An exhauster then sends the gas to an electrostatic precipitator for residual tar removal.

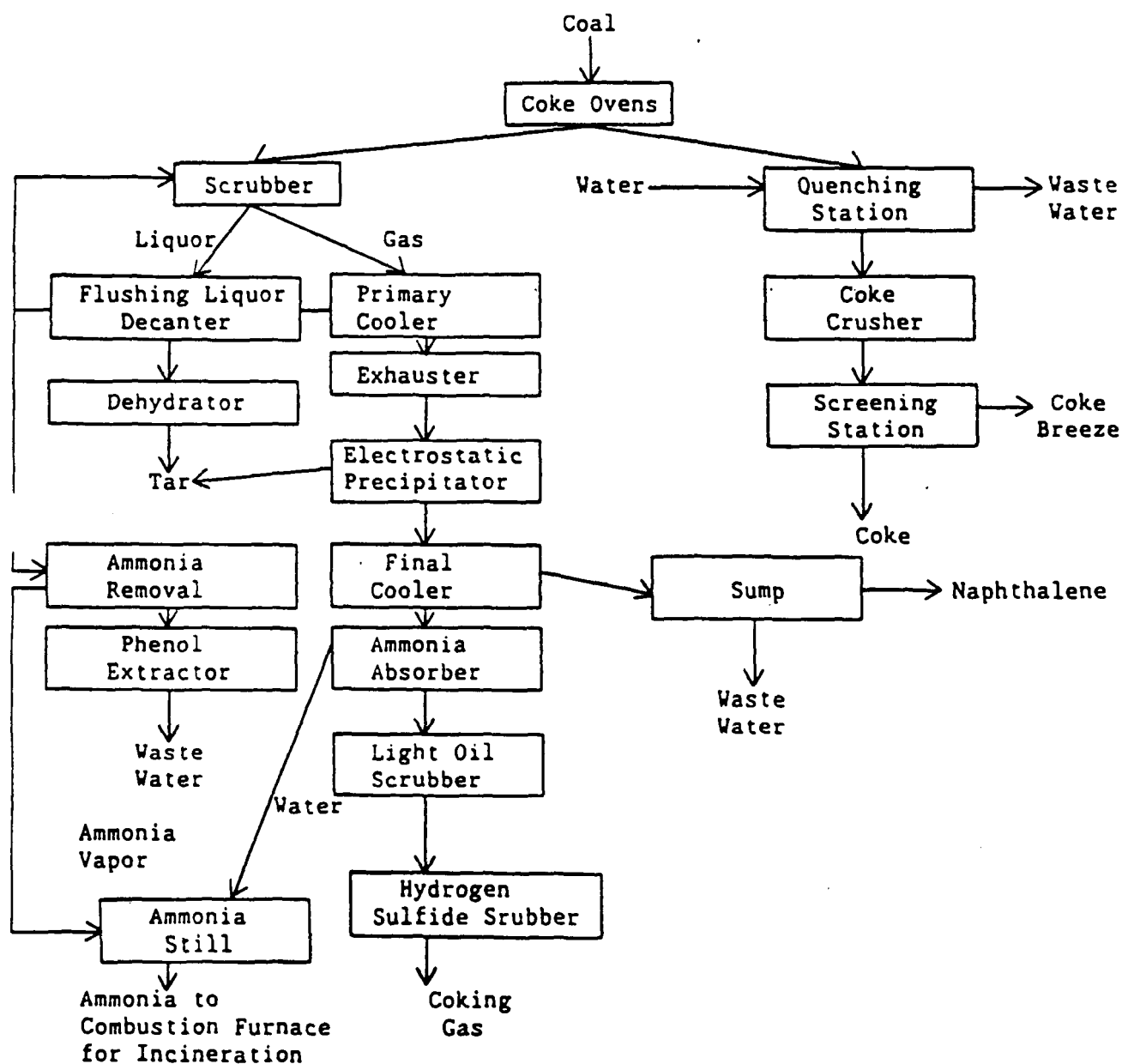
In older plants, the gas flows to an ammonia recovery unit. Ammonium sulfate crystals are separated from solution and dried. The gas is then sent to the final cooler, a direct contact spray system, that condenses naphthalene with the spray water. The naphthalene is then skimmed from the water in a sump. Some plants use an oil in their spray system, then recover the naphthalene from the oil by steam stripping.

Modern plants no longer are designed to recover ammonia. After naphthalene removal, the ammonia is removed from the gas using a recirculating aqueous solution. A still volatilizes the ammonia from solution and the concentrated ammonia vapor is sent to the combustion furnace for incineration.

In either older or more modern operations, the gas is then sent to a light oil scrubber, where aromatic hydrocarbons are recovered. The crude light oil from the scrubber contains approximately 70% benzene, 15% toluene, 8% xylene, and 7% higher homologues, and is usually sold for further processing. The gases still contain hydrogen sulfide. Since the gas is sold as a fuel, hydrogen sulfide must be reduced to prevent formation of sulfur dioxide during combustion. A number of methods are used to separate

Figure 2-32

BYPRODUCT COKING PROCESS



the hydrogen sulfide. Once separated from the coking gas, the hydrogen sulfide is converted either to elemental sulfur or sulfuric acid.

The wastewaters from the various coolers and scrubbers and from coke quenching contain ammonias, phenols, and other organic compounds. Lime or caustic is added to the solution, then the wastewater is fed to an ammonia still. The ammonia vapors are either converted to ammonium sulfate or sent to the combustion furnace for incineration.

Removal of phenols is treated differently in old and modern plants. Older plants remove phenols from the wastewater by solvent extraction and recover them as sodium phenolates by contact with sodium hydroxide. In more modern plants, the wastewater is treated using an activated sludge process to remove organics. After treatment, the wastewater is usually discharged to surface waters.

Wastes produced from beehive coking operations may include waste quenching water, air pollution control dusts, or scrubber water. The wastewaters are usually treated prior to discharge to surface waters as allowed under a discharge permit. The disposition of any air pollution control dusts is unknown.

Byproduct coking plants produce waste waters from coolers, scrubbers, and coke quenching. The waste matters are generally treated prior to permitted discharge to surface waters. The treatment processes may generate solid wastes such as sludge from an activated sludge plant or spent solvent from the extraction of phenols from the wastewater. Waste management methods for these materials are not known.

CONCLUSIONS

The coal washing industry does not generate wastes with hazardous characteristics (Table 2-14). Coal liquefaction is not yet a commercial process and information is needed to develop a report on coal gasification. The coking industry generally reuses many byproduct materials. However,

Table 2-14

COAL WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Coal Washing	Coal Refuse	N	N	N	N	Can burn, Generates Acid
Coking						
Quenching	Coke Quenching Water	N	N	N	?	
Coke Gas Treatment	Flushing Liquors	N	N	N	?	
	Cooling Tower Blowdown	N	N	N	?	
Wastewater Treatment	Sludge	N	N	N	?	Newer Plants Only
Phenol Extraction	Spent Solvent	N	N	?	N	Older Plants Only

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40 CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

due to the size of the coking industry, further study for possible regulation under Subtitle C is recommended.

FELDSPAR

Feldspar are the most abundant minerals of the igneous rocks and are represented by three silicate minerals which, if pure, would be represented as microcline or orthoclase (KAlSi_3O_8); albite ($\text{NaAlSi}_3\text{O}_8$); anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$). Certain terms are utilized to describe the ores of feldspar. Aplite contains titanium and feldspar minerals and is mined and beneficiated in one location in Virginia. Alaskite is a distinctive rock type found near Spruce Pine, North Carolina, and is a major feldspar source. This ore is relatively coarse-grained and granitelike. Graphitic granite is a pegmatite rock predominant in K-spar (KAlSi_3O_8) with quartz as a secondary mineral. Pegmatite is a widely distributed, coarse-grained igneous rock from which potash feldspar is obtained. Perthite is a microscopic intergrowth of plagioclase in K-spar found in graphitic granite and in pegmatites. Feldspathic sand can occur either naturally or can be a processed mixture of feldspar and quartz.

Feldspar is utilized in the glass industry, ceramic industry, and as filler material in paint, urethane, and acrylics.

Annual production is estimated to be with 735,000 short tons (1986). The state of North Carolina accounted for about 70 percent of all domestic feldspar production. The state of Connecticut was second in production, followed by Georgia, California, Oklahoma and South Dakota.

Pegmatite and alaskite feldspar ores are mined by conventional open pit methods. First, the overburden is removed, followed by drilling and blasting on twenty to forty foot benches. Refining of feldspar ores is primarily by froth flotation. This process consist of crushing, grinding, screening, and desliming the raw material. Next, the micaceous minerals are then removed with amine as the collector in an acid environment (pH=3) with pine oil and fuel oil. After dewatering the feed to remove reagents, the pH is lowered to 2 to 3 by sulfuric acid and the feldspar is refloated

with petroleum sulfonate, as a collector, to remove iron-bearing minerals. Water is removed from the flotation concentrate and the feldspar is separated from quartz in flotation cells utilizing hydrofluoric acid and amine as a collector, at a pH of 2-3. This feldspar float concentrate is dewatered using drain bins, vacuum filters, or centrifuges, and lastly dried in rotary dryers.

Although the solid wastes are largely innocuous minerals, these minerals may contain flotation reagents whose characteristics require further investigation (Table 2-15).

Based on this analysis, further study of the feldspar industry, particularly froth flotation tailings, for potential regulation under Subtitle C is recommended.

Table 2-15

FELDSPAR PROCESSING WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Desliming	1. Waste Slimes (Clays)	N	N	N	N	
Froth Flotation	2. Mica Tailings	N	?	N	N	Low operating pH of process (pH = 2 + 03)
	3. Iron Tailings	N	?	N	N	
	4. Quartz Tailings	N	?	N	N	
Dewatering	5. Wastewater	N	N	N	N	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

FLUORSPAR

Fluorspar (calcium fluoride) is the commercial name for the mineral fluorite. The domestic fluorspar industry includes 5 mines and 2 flotation mills. Domestic production in 1983 was 61,000 short tons. Fluorspar is necessary in most steel and aluminum production processes. The chemical and ceramic industries are also significant users of fluorspar. Fluorspar is the most important commercial source of fluorine. It is used as a fluxing agent in metallurgy and ceramics. It is the raw material for hydrofluoric acid which is used to make fluorocarbons, synthetic cryolite and other products. Hydrofluoric acid is also used in the manufacture of electronic devices. Fluorspar is generally sold in three grades, metallurgical (75-85% CaF_2), ceramic (90-96% CaF_2), and acid (97% CaF_2 minimum).

Most fluorspar must be upgraded for marketing. Metspar is often produced by hand sorting of high-grade lump crude ore, followed by crushing and screening to remove most of the fines. In the case of fluorspar ores of lower grade and/or ores with relatively coarse interlocking of minerals, gravity concentration processes are used based on the specific gravity of 3.2 for spar and less than 2.8 for most gangue minerals.

Heavy-media cone and drum separators are particularly effective in the size range of 1 1/2 by 3/16 inch, either for producing metallurgical gravel or for preconcentrating the crude ore for flotation feed. For the finer sizes, the heavy-media cyclone process is frequently used. Ores as low as 14% CaF_2 are being preconcentrated to yield a flotation feed of 40% CaF_2 or more. Lead and zinc sulfides and barite concentrate with the fluorspar to enrich the flotation feed with these valuable minerals. In some cases, washing plants are also used prior to flotation to remove clay or manganese oxides.

Ceramic and acid grades of fluorspar are produced by multistage froth flotation. Ore from the mine is crushed and ground to proper size. If sulfides are present, they are preferentially floated off with a xanthate collector, lead sulfide first then zinc sulfide. Then all the easy floating fluorspar is removed in a quick pass through a flotation circuit and sent on to the cleaner circuit; the tailings are discarded. The middling product is reground to separate the more finely interlocked grains of fluorspar and gangue, and passed through one or more cleaner circuits. The final products generally comprise an acid-grade concentrate and in some cases one or more concentrates of lower grade, which are sold as ceramic grade, or pelletized and sold as metallurgical grade. Fatty acids are used as collectors for the fluorspar. Quebracho or tannin is used to depress calcite and dolomite; sodium silicate to depress iron oxides and silica; and chromates, starch, and dextrin to depress barite. Cyanide is used to depress any remaining sulfides. Lime, caustic, or soda ash can be used for acidity control. Flotation temperatures range from ambient to 80°C.

A typical flowsheet for fluorspar processing, as shown in Figure 2-33, has two main waste streams. The density separation tailings waste stream 1 will be primarily siliceous rocks, but will contain some fluorspar, which is fairly resistant to weathering, but it is soluble enough in water that fluorides could be excessive in run off from piles. The froth flotation tailings waste two would also contain fluorides and in addition could have toxic metals, because lead and zinc sulfides, and barite (barium sulfate) commonly occur with fluorite. While many operations produce these as coproducts, the separation processes would leave some in the tailings.

Hydrofluoric acid (HF) is produced by reacting bone dry fluorspar with concentrated sulfuric acid at high temperature. The HF is removed as a vapor and calcium sulfate is left as a solid. Calcium sulfate itself is not hazardous but there is probably residual fluoride in the residue that should be controlled.

Figure 2-33
FLUORSPAR PROCESSING

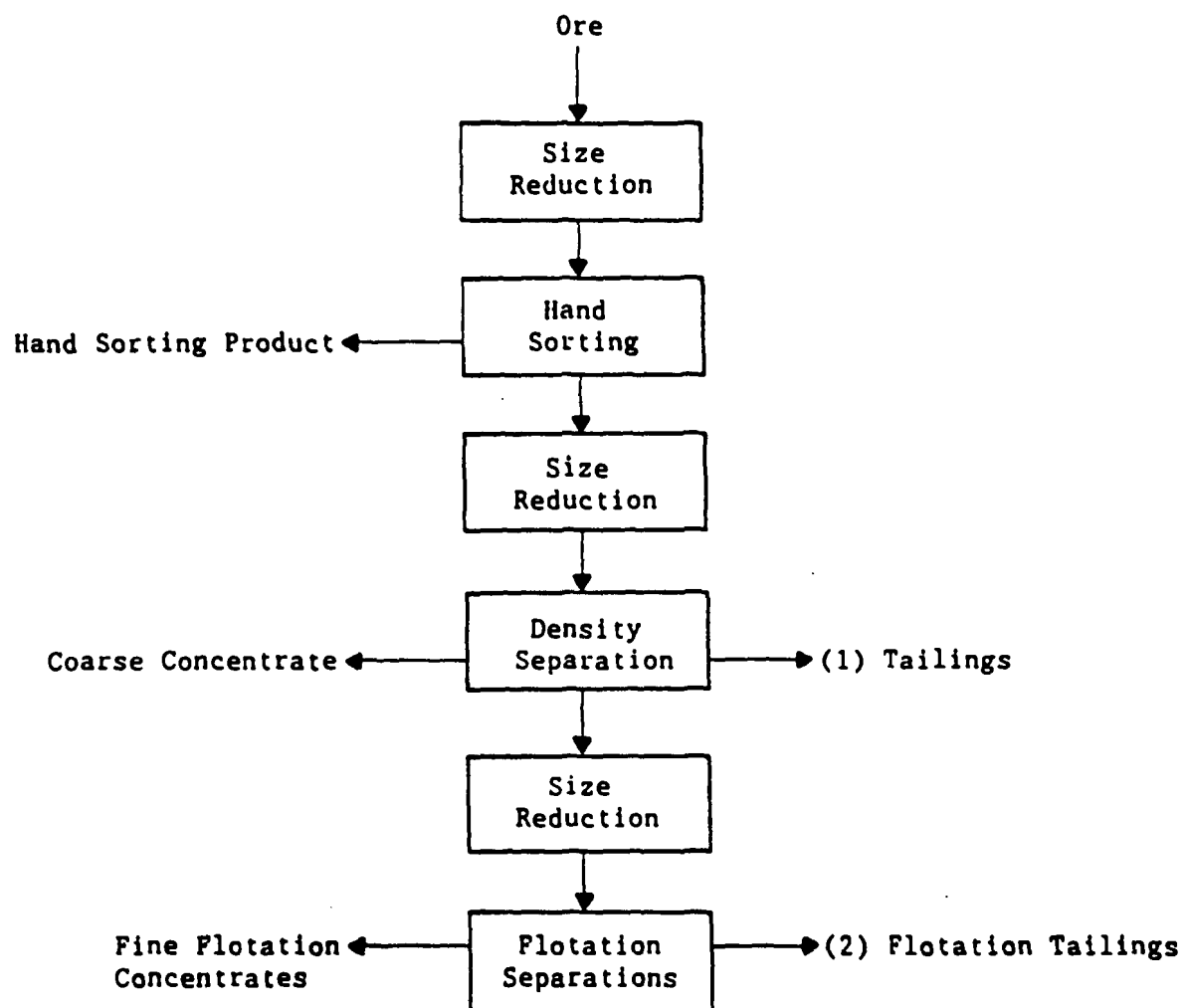


Table 2-16 summarizes waste characteristics from this screening study. Based on this analysis, further study of this industry for potential regulation under Subtitle C is recommended.

Table 2-16
FLUORSPAR WASTES

Process	Waste	R	C	I	T	Comments
Fluorspar Beneficiation	1) Gravity Tailing	N	N	N	?	fluorides
	2) Flotation Tailings	N	N	N	?	fluorides
Hydrofluoric Acid Production	1) Calcium Sulfate Residue	N	N	N	N	fluorides

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

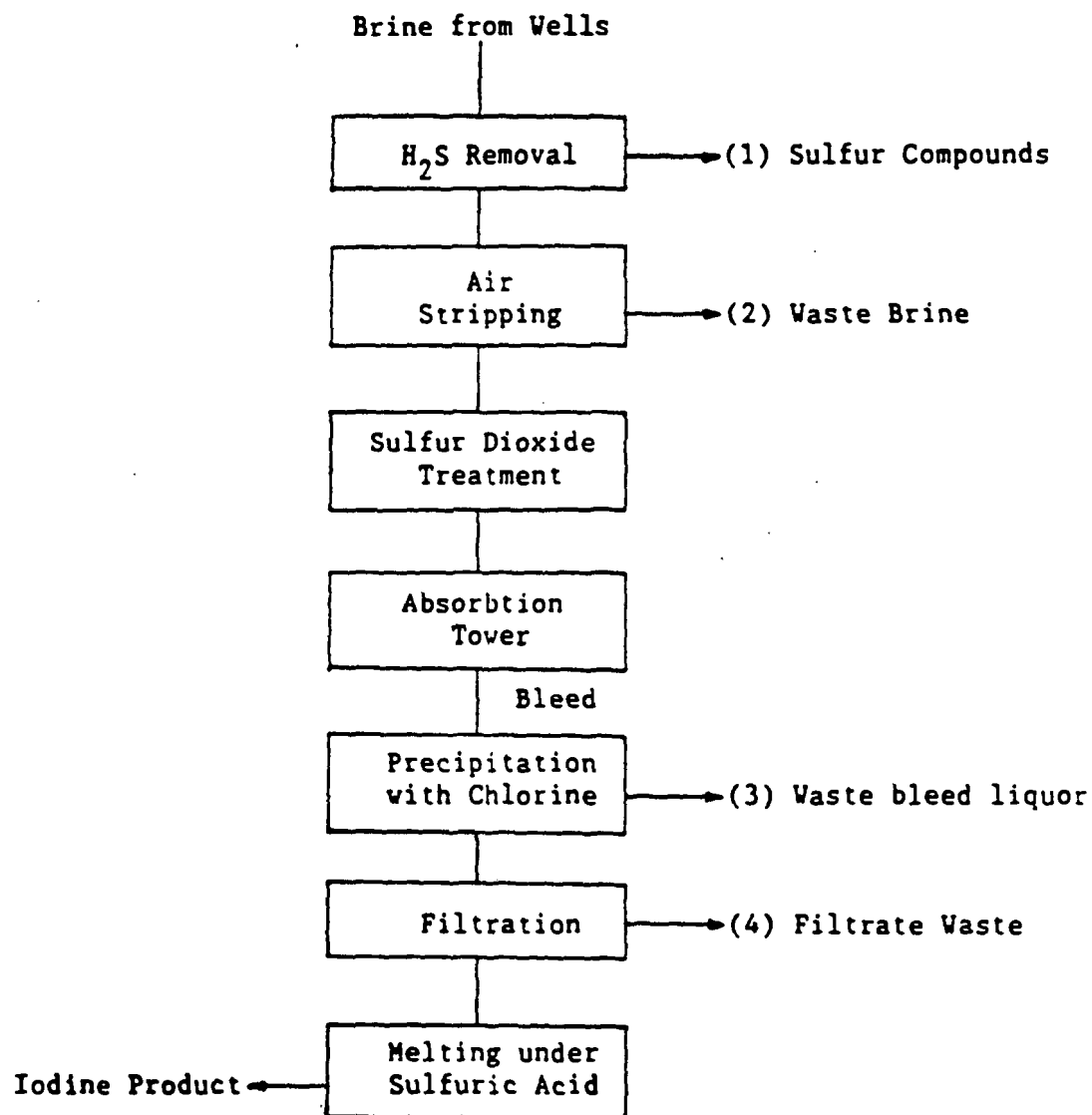
IODINE

Iodine is a member of the halogen family of elements, and because of its reactivity, occurs in nature only as iodates and iodides and other combined forms. Marketed chemical forms of iodine include iodine (crude and resublimed), calcium iodate or iodide, potassium iodide, sodium iodide, and numerous organic compounds. Principal end uses of iodine include photographic chemicals, food supplements (iodized salt), pharmaceutical products, and disinfectants. Two companies produce iodine from subterranean brines in Oklahoma. North American Brine Resources treat brines associated with oil production and Woodward Iodine uses brines extracted for their iodine content.

Production of iodine at Woodward, Oklahoma is by the process shown in Figure 2-34. The first stage of processing removes hydrogen sulfide gas contained in the brine. This gas is reacted to form sulfur compounds which are sent to a hazardous waste disposal facility. The second stage of processing is a chlorine oxidation to convert iodide to iodine. The iodine is then removed from the brine by air vapor stripping (air-blowout). The waste brine is treated with lime to adjust pH and is reinjected into Class IV disposal wells. The iodine vapor is absorbed by a solution of hydroiodic and sulfuric acids. Sulfur dioxide is added to reduce the absorbed iodine to hydroiodic acid. Most of the solution is recirculated to the absorption tower, but a bleed stream is sent to a reactor for iodine recovery. In the reactor, chlorine is added which oxidizes and liberates the iodine which precipitates and settles out of solution. The settled iodine is filtered to remove waste liquor and melted under a layer of concentrated sulfuric acid. The melted iodine is then solidified either as flakes or ingots. The management practice for the waste bleed liquor was not identified.

Iodine recovery from oil production brines probably uses the process described above, with the exception of the hydrogen sulfide removal, which

Figure 2-34
IODINE EXTRACTION
Woodward, OK



may not be necessary. No specific information was readily available. At least one of the wastes from iodine production is presently managed as hazardous, and others have the possibility of exhibiting hazardous characteristics (Table 2-17). Therefore, further study of this industry for possible regulation under subtitle C is recommended.

Table 2-17

IODINE PRODUCTION WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Hydrogen Sulfide Removal	1. Sulfur Compounds	?	?	N	N	Hazardous Waste Disposal Class V disposal wells
Air Stripping of Iodine from Brine	2. Waste Brine	?	?	N	N	Chlorine, Iodine
Iodine Precipitation	3. Liquid Waste	?	?	N	N	Acids, Iodine, Chlorine

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

KYANITE

Kyanite is a member of the sillimanite family of minerals which are anhydrous aluminum silicates ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$). Kyanite is noted for its refractory properties. It represents 10 to 40 percent (balance is refractory clays or coarser grog material) of refractory mortars, cements, castables, and plastic ramming mixes. Kyanite deposits that are currently being exploited are Willis Mountain, and East Ridge, Virginia. Production data is considered company proprietary.

Excavated kyanite ore is crushed, classified, and concentrated as shown in Figure 2-35 to produce a relatively pure kyanite product. After crushing and classifying, the ore is deslimed (producing a slime waste, Waste 1) and then concentrated in froth flotation cells. Tailings from the flotation cells are further separated in scavenger flotation cells and a tailing waste, Waste 2, is ultimately produced. Tailings will contain pyrite and micaeous material. The pyrite content of these tailings may be high enough to exhibit hazardous characteristics.

The flotation concentrate is dewatered, (producing Waste 3), dried and cleaned in a magnetic separator. The magnetic separator will produce an acid soluble iron waste (Waste 4), containing iron oxides which would not be expected to exhibit hazardous characteristics. Kyanite is further ground and classified, and some is calcined to produce final products.

Wastes from the processing of kyanite include tailings, waste slimes, and acid soluble iron as summarized in Table 2-18. This analysis leads to a recommendation for further study of kyanite froth flotation tailings for potential regulation under subtitle C.

Figure 2-35

KYANITE PROCESSING

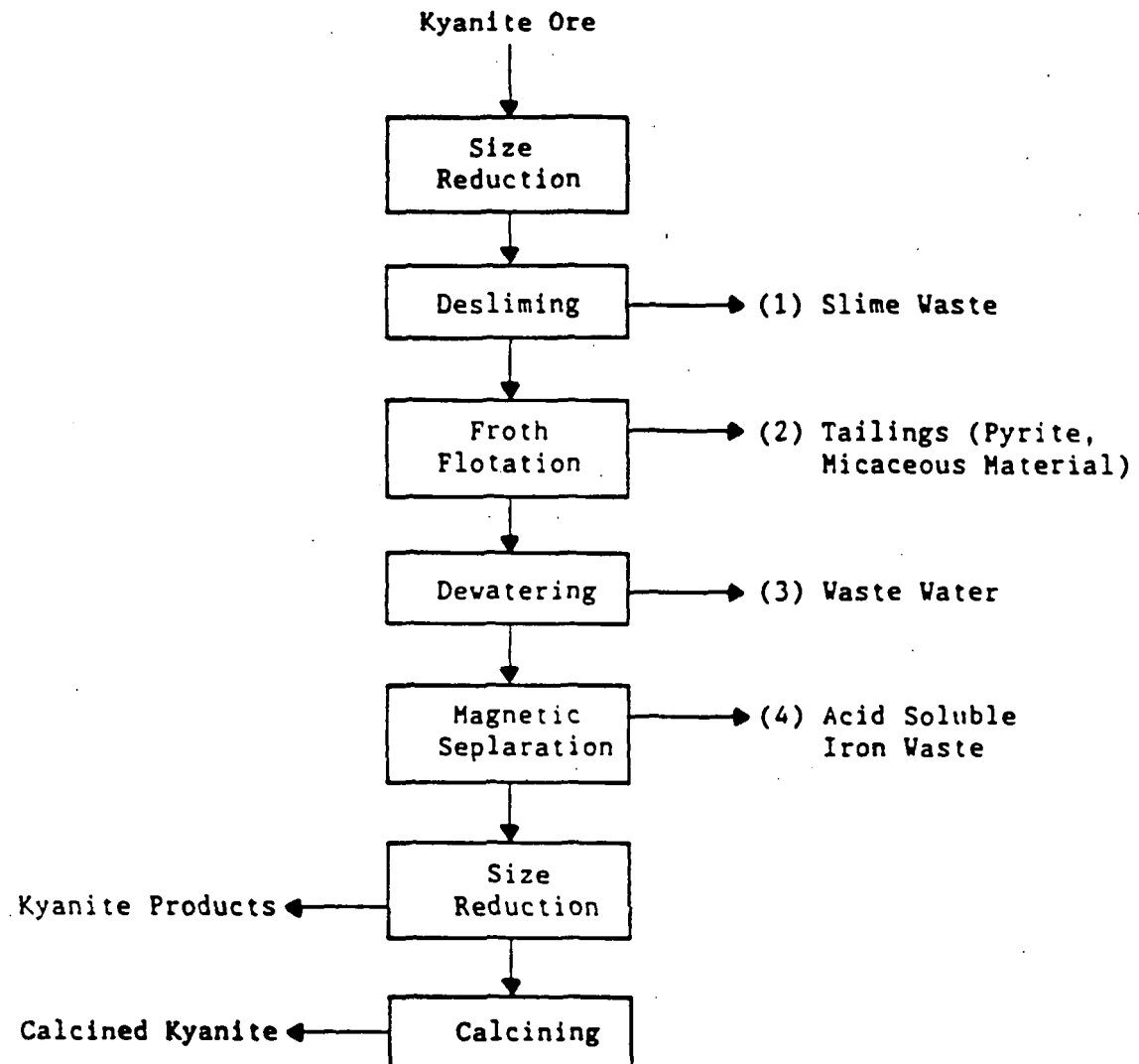


Table 2-18

KYANITE PRODUCTION

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Froth Flotation	1. Slimes (Clay)	N	N	N	N	
	2. Flotation Tailings (Pyrite, Mica)	?	?	N	N	
Dewatering	3. Wastewater	N	N	N	N	
Magnetic Separation	4. Magnetic Tailings (Iron Oxides)	N	N	N	N	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

OLIVINE

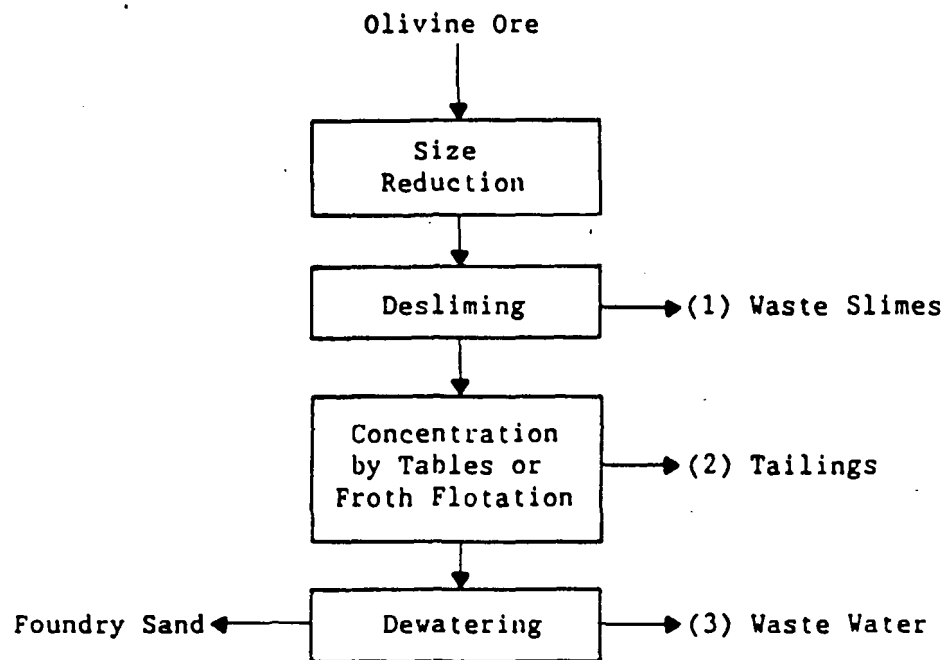
The two primary components of olivine are forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4). The mineral is the principal component of the rock dunite. Dunite deposits exist in the United States in a belt from northeastern Georgia to western North Carolina, in northwestern Washington, and in southeastern Alaska. One company, with mines in North Carolina and Washington, is currently producing olivine in the U.S.

Olivine is a heat resistant material with low expansion qualities. It is used as a slag conditioner in blast furnaces, as a specialty foundry sand, in heat storage blocks, as a refractory (heat resistant) material, and as an abrasive. The use of olivine is closely tied to the hot metal industry. United States production was 240,000 short tons in 1978. This number is probably much lower now due to the decline in the United States steel industry.

Beneficiation of olivine can be done by a wet or a dry process. In the wet process (Figure 2-36), the ore is sent first to crushers to reduce the material to the specified size. North Carolina olivine is relatively impure, and must be further processed to produce foundry sand. After crushing, fines (<20 mesh) are removed, slurried, deslimed, sized, and sent to either concentrating tables or froth flotation. The plus 20 mesh materials is sent to a wet rod mill, deslimed, sized, and then sent to either concentrating tables or froth flotation. Wastes generated include waste slimes from desliming operations, tailings from either concentrating tables or flotation, and wastewater from dewatering operations. The chemicals used in the flotation processes are unknown at this time, but are probably fatty acids or petroleum sulfonates. It is known that olivine ores commonly contain chromite (FeCr_2O_4) and larsenite (PbZnSiO_4), so the tailings may exhibit hazardous characteristics. There is no information on current waste management methods.

Figure 2-36

OLIVINE PROCESSING



The dry process uses crushers to reduce the material to desired sizes, and vibrating screens to separate those sizes. The dry process is used on high grade ores and is not expected to produce wastes with hazardous characteristics. Most olivine is produced by the dry process.

Table 2-19 summarizes the information on the waste characteristics in this industry. Based on this analysis further study of the tailings from the wet froth flotation process for possible regulation under subtitle C is recommended.

Table 2-19

OLIVINE PRODUCTION WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Desliming	1. Waste Slimes (Clays)	N	N	N	N	
Concentration (Froth Flotation) (Tables)	2. Tailings	N	N	N	?	Possible Pb, Zn, Cr
Dewatering	3. Wastewater	N	N	N	N	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

PHOSPHATE ROCK, PHOSPHORIC ACID AND PHOSPHOROUS

There are two primary geographical areas of production of phosphate rock in the United States. The southeast, with mines in North Carolina and Tennessee is lead in production by Florida which is a dominant world producer. Most of the phosphate rock in these areas is in pebble deposit combined with clay and some quartz sand. In the intermountain region, phosphate rock is produced in Idaho, Montana, and Utah. The deposits here are beds often overlain by chert (a form of quartz) or carbonates. Annual domestic production of phosphate rock is estimated to be 40 million short tons (1986).

Pebble deposits in the Southeast do not need the amount of size reduction required for the deposits in the Western States. Washing and recovery of fine phosphate by flotation is generally practiced as shown in Figure 2-37. The clay slimes waste stream (1) (Table 2-20) is the result of a size separation and contains all material finer than about .1 mm (150 mesh) that has come into the plant. The major component is clay with some fine phosphate rock and quartz. It is produced in large volumes and is a water slurry containing 2% to 3% solids by weight, this slurry thickens to 12-15% solids in 2 or 3 years. There are probably no RCRA hazardous characteristics to this waste, but the volume produced may warrant further study. The flotation tailing stream (2) is similar in weight to the dry slime content and consists of quartz sand which is inert. It is usually pumped into mined cuts for disposal and land reclamation.

About 50% of the intermountain phosphates are main bed ore that can be used as mined. Most of the rest is simply washed and screened, and a small amount is upgraded by flotation in Utah and Idaho. Figure 2-38 shows washing flowsheets for low and high grade ores. The coarse waste stream from the low grade ores (stream 5) would consist of overburden and similar materials that were mixed with the phosphate rock. It consists primarily of siliceous rocks which are inert and might even be of use as aggregate.

Figure 2-37

FLORIDA PELLET PHOSPHATE GENERAL FLOWSHEET

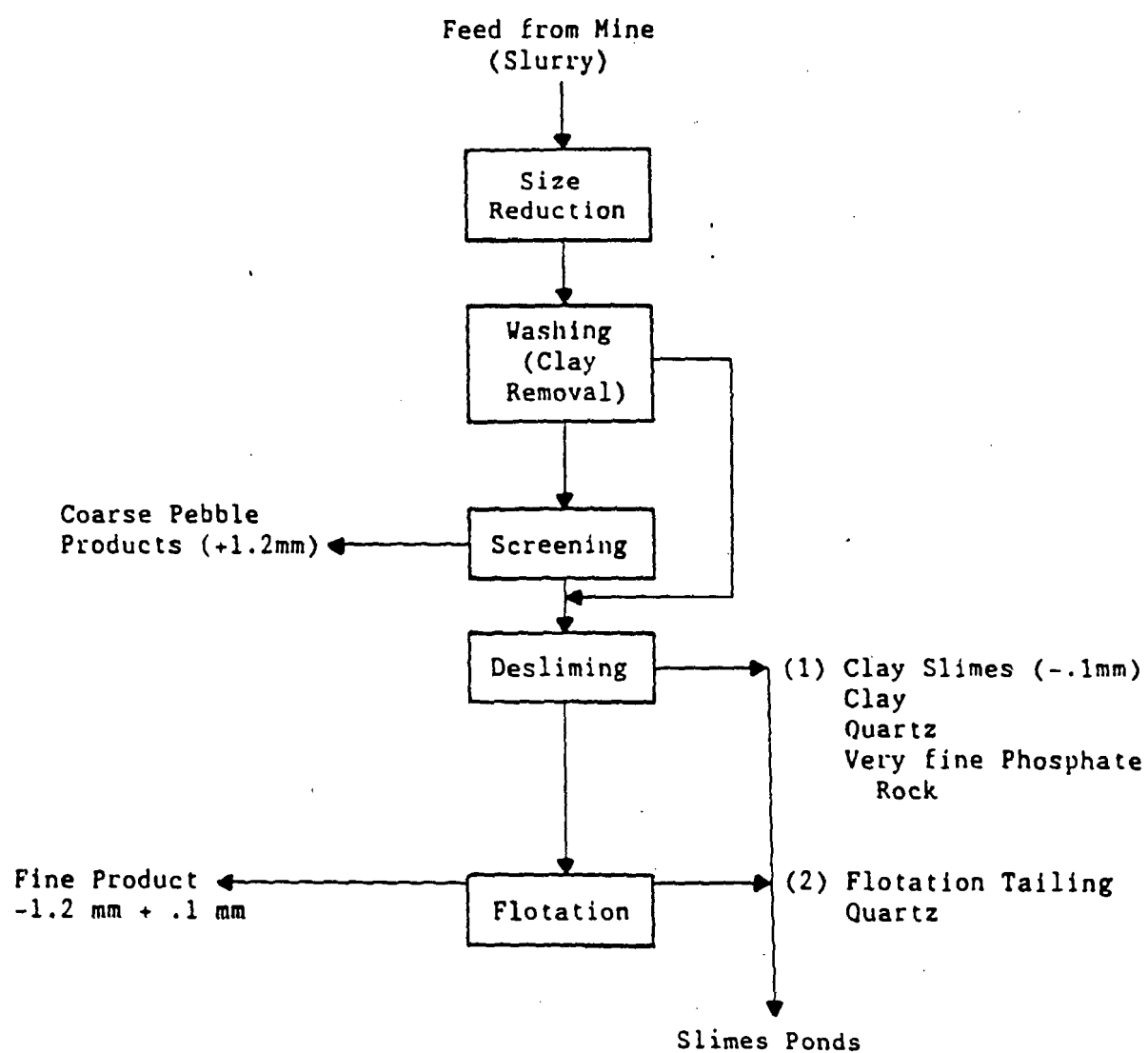


Table 2-20
PHOSPHATE PROCESSING WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Beneficiation	1) Clay Slimes (Clay, Quartz)	N**	N	N	N	Large volume
	2) Flotation Tails (Quartz)	N	N	N	N	
	3) Coarse Waste (Chert, Gravel)	N	N	N	N	
	4) Low Grade Waste Slimes (See 1)	N	N	N	N	
	5) High Grade Waste Slimes (See 1)	N	N	N	N	
Phosphoric Acid	1) Phosphogypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	N	N	N	N	Radioactivity, Large volume
Production	2) Fluosilicic Acid	N	Y	N	N	Potentially saleable product
Elemental Phosphorous Production	1) Calcium Silicate Slag	N	N	N	N	May be radioactive
	2) Dry Particulates (Off-gas Scrubber)	?	?	?	?	May be recycled
	3) Condenser Water	N	Y	N	N	May be recycled

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261

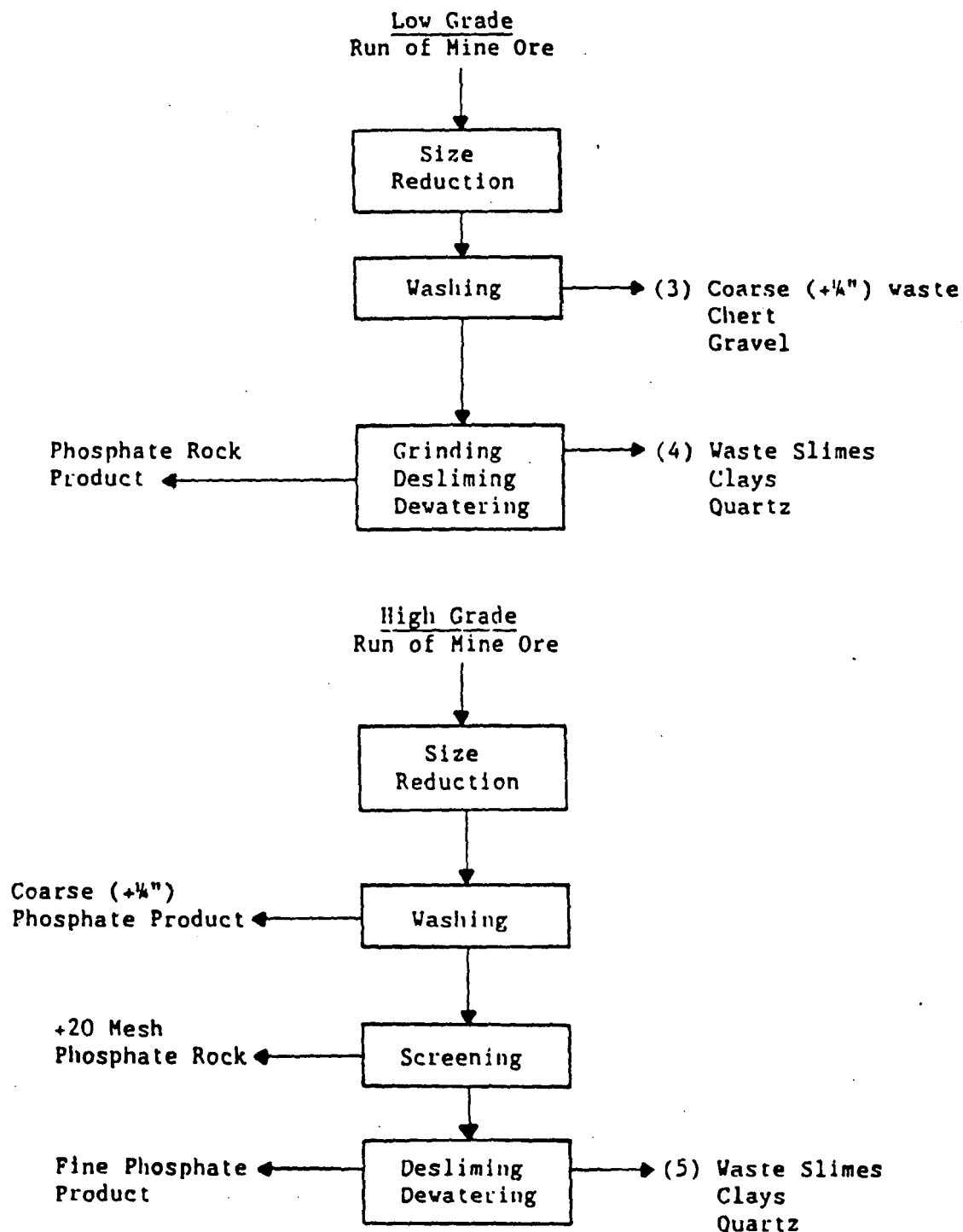
N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

Figure 2-38

INTERMOUNTAIN BEDDED PHOSPHATES GENERAL FLOWSHEETS



The waste slimes (4) would be similar to the clay slimes from Florida deposits but it is a low volume stream. The high grade deposit produces only a waste slime similar to (2) and (4).

Phosphate rock is principally used to make phosphoric acid and only 10% or less is used to produce elemental phosphorous. Some of the phosphate rock in North Carolina is calcined prior to producing phosphoric acid. all phosphate rock in the Western States, if used to manufacture phosphoric acid, is calcined.

Phosphoric acid is produced near the point of phosphate mining in most cases, but may be produced near a cheap source of acid, such as a smelter, or a source of Frasch or recovered sulfur. Figure 2-39 shows the steps of producing phosphoric acid using sulfuric acid, which is the most common acid used in the U.S. to produce phosphoric acid.

A very common mineral in phosphate rock is fluorapatite $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$ which releases hydrofluoric acid when reacted with a strong acid. This reacts with any silicates in the rock to form fluosilicic acid which is volatile and is removed by off-gas scrubbers, creating stream (1). This stream would be corrosive and contain fluorides. Some operations are selling the fluosilicic acid or sodium silicofluoride as a water fluoridation chemical. The solid waste (2) resulting from acidulation is gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) which is not a particularly hazardous material, but it contains uranium that naturally occurs with the phosphate rock. The possibility of radiation hazard is made worse by the large volumes of this waste that are produced. Some attempts have been made to recover uranium from phosphoric acid, but that is not economically profitable at this time unless old contracts, written when U_3O_8 was \$42 per pound, remain in force.

The amount of electricity consumed in producing elemental phosphorous (6 kwh/pound) tends to cause production to be in areas with cheap power. The Tennessee Valley Authority, for an example, was a producer. The process uses coke as a reducing agent and silica fluxes as shown in Figure 2-40.

Figure 2-39

PHOSPHORIC ACID TREATMENT

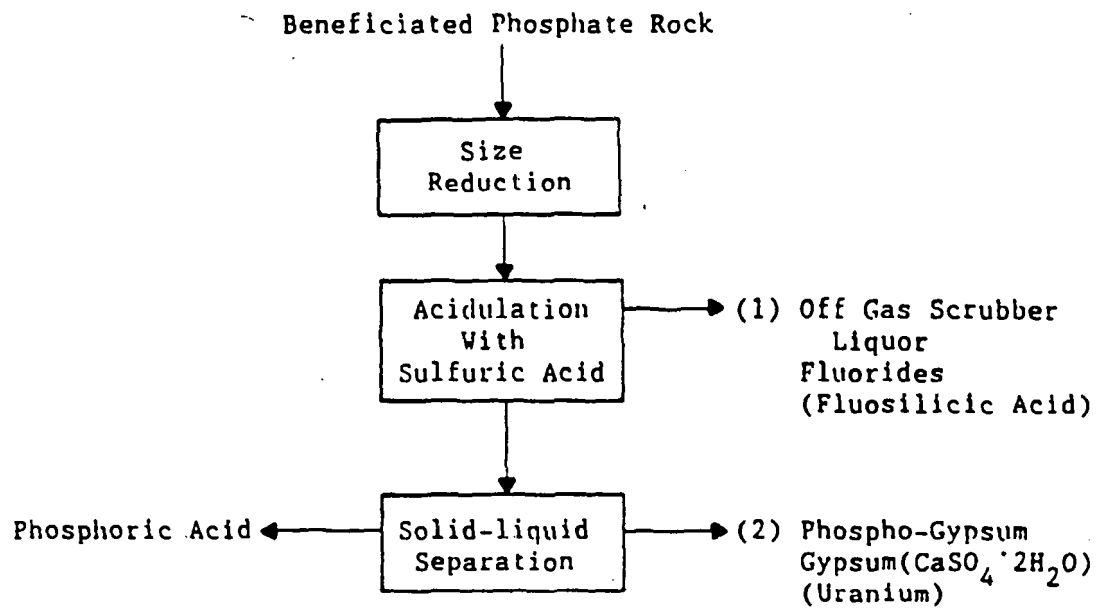
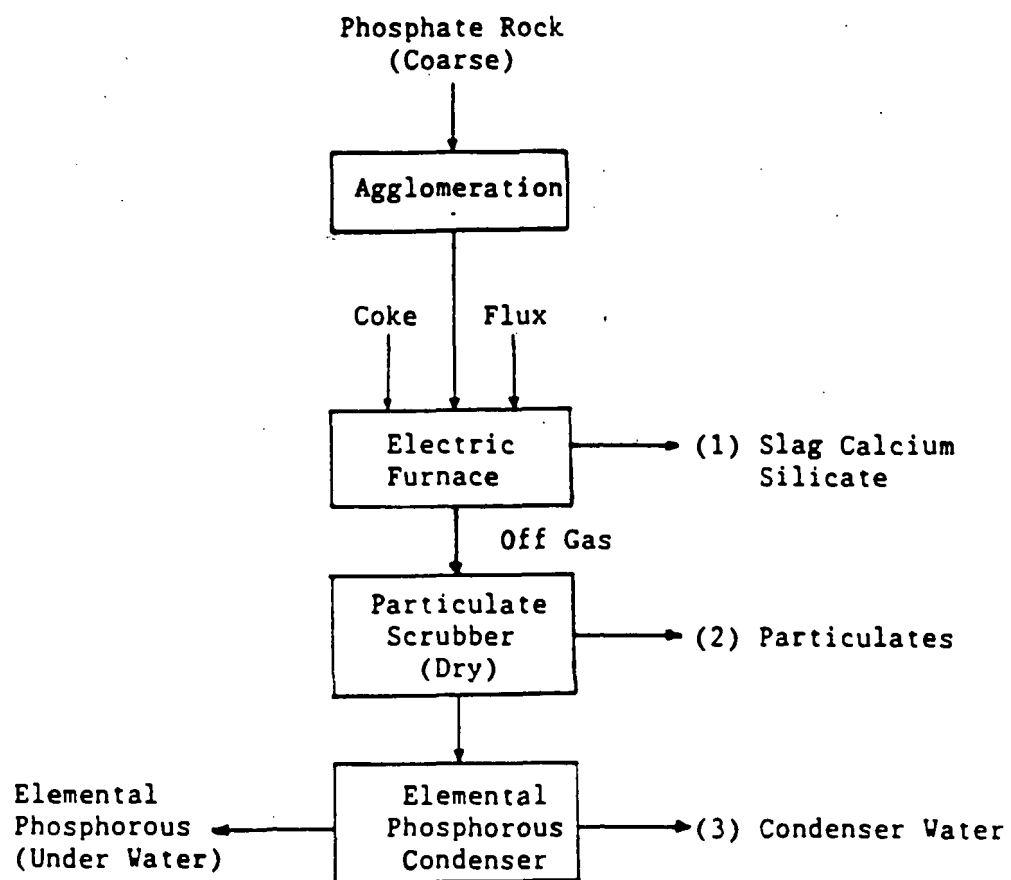


Figure 2-40

ELEMENTAL PHOSPHOROUS



Electric furnace production of elemental phosphorous has three waste products. The calcium silicate slag (1) from the furnace may contain enough uranium to present a radiation hazard, but calcium silicate is similar to the mineral wollastonite and is probably not hazardous itself.

The dry particulates from the off-gas scrubber (stream 2) include fines from the feed materials, (coke, phosphate rock, and silica). These may be recycled to the furnace but further characterization is needed if they are found to be discarded. The phosphorous condenser water (stream 3) could pick up fluorides or other soluble contaminants from the furnace off-gas. This water may be recycled but, again further characterization would be in order if it is not.

Based on the above analysis, further study of this industry for regulation under Subtitle C is recommended.

SILICA

Silica, or quartz, is one of the harder, more abrasive, and chemically resistant minerals found in nature. The mineral is composed of silicon dioxide (SiO_2) which occurs in several crystalline phases imparting different physical properties of and uses for the mineral. Aside from aggregate production (sand and gravel), silica is used largely as a refractory for blasting sands, in the ceramics industry, and in the production of glass (largest non-aggregate use). Foundry and molding sand (refractory) and glassmaking account for 20 million tons/year of silica use. These uses dictate stringent chemical specifications for silica (i.e., specified tolerances for other naturally occurring metals). Silica is generally extracted from sandstone and quartzite formations by open pit or underground mining operations, or by dredging or excavation of sand deposits. Approximately 75 percent of the silica production is east of the Mississippi, near large population centers, where there is the largest demand for the product. In the west, California and Nevada are production leaders for silica.

As shown in Figure 2-41, once extracted, silica is generally subjected to three stages of crushing, followed by washing, concentrating, drying, screening, and possibly pulverization to produce silica flour. The washing/scrubbing stage will produce a liquid waste (waste 1) (Table 2-21) consisting of clay or iron surficial impurities which are unlikely to be RCRA hazardous. Other co-occurring detrital minerals may be removed by separation techniques. If separation is by magnetic or electrostatic means, the waste is not likely to be RCRA hazardous (waste 2); however, the froth flotation process is carried out at a pH between 2 and 3 and the flotation tailings (streams) might be corrosive. After separation, the silica is dried by steam static, rotary kiln, or fluid-bed type incinerators, and is subsequently cooled and screened to produce a product with the required size specification.

Figure 2-41
SILICA PRODUCTION

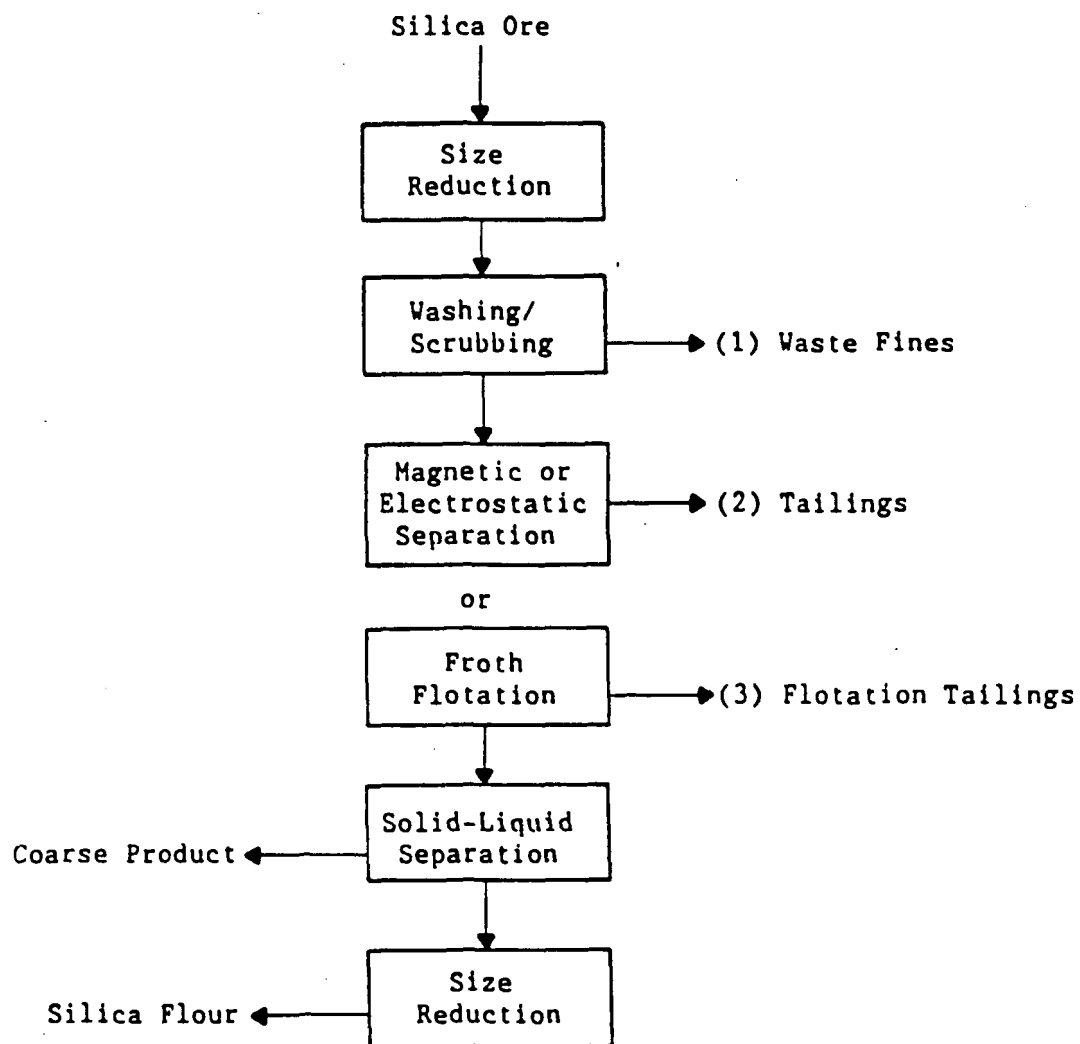


Table 2-21

SILICA

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Silica Preparation	1. Washing/Scrubbing Overflow (Clays)	N	N	N	N	
	2. Magnetic/Electrostatic Tailings	N	N	N	N	
	3. Flotation Tailings	N	?	N	N	
	4. Dryer Stack Losses (fine silica)	N	N	N	N	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

Based on the above analysis, further study of this industry, particularly the flotation separation, is recommended for regulation under Subtitle C.

ASBESTOS

Asbestos is the generic name for a group of fibrous silicate minerals. Chrysotile, the fibrous variety of the mineral serpentine (a magnesium silicate), accounts for about 94% of world asbestos production and all of U.S. production. The amphibole series minerals crocidolite, amosite, anthophyllite, tremolite and actinolite make up the rest of world production. Asbestos is used primarily as a fiber, in various lengths. There are three active asbestos mines in the U.S. Two are in California and one is in Vermont. Total production from all three was estimated by the U.S. Bureau of Mines at 50,000 short tons in 1986.

The lengths of the asbestos fibers are the property for which they are sorted. Most processing is done dry and air is used as a carrying or sorting medium. The general flowsheet (see Figure 2-42), consists of crushing followed by many size separations. As shown in the figure, there are two main waste streams from the processing. Stream 1 is coarse rock from sorting. This would be lumps larger than 2" which show no significant veins of asbestos. This waste would still be contaminated either by dust or very small veins of asbestos fiber. Stream 2 would consist of fine rocks and dust. This stream would also be contaminated with asbestos fiber. One plant in California processes asbestos in water. This plant would have similar waste streams to those found in dry processing plants. The main difference from dry processing would be that the dust control in the plant would be easier, but the final tailings would be a water slurry contaminated with asbestos.

Table 2-22 summarizes the waste characteristics from the preliminary screening study. Asbestos containing materials are not currently listed as hazardous by Subtitle C. The EPA has proposed regulations under the Toxic Substances Control Act that would regulate asbestos under 40 CFR 763 (Federal Register Vol. 51, number 19, Jan. 29, 1986). Due to the hazardous nature of asbestos, wastes containing the fibers may be regulated under subtitle C in the future.

Figure 2-42
ASBESTOS PROCESSING

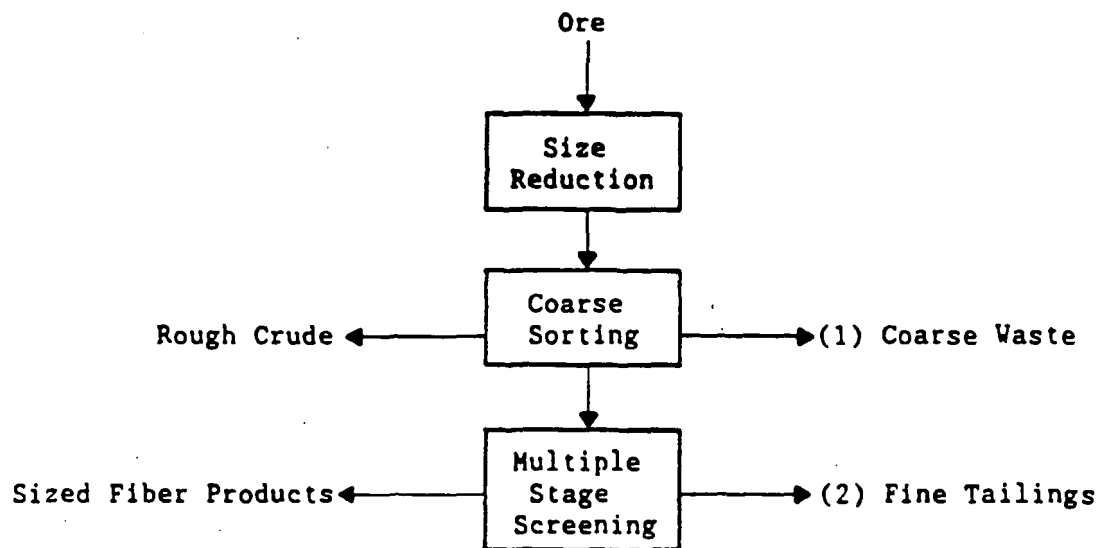


Table 2-22

ASBESTOS WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Beneficiation	1) Coarse Waste Rock	N	N	N	N	Asbestos contamination
	2) Tailings	N	N	N	N	Asbestos contamination

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

SHALE

Shale, for the purpose of this report, is a clay bearing rock that has been indurated into flat plates. It is used for its clay content and to make lightweight aggregate.

When used as a clay source, shale is ground to release the clay and the entire rock is used. It is used in low economic value, high volume applications such as brick, sewer tile, and vitrified pipe. Because of the low economic value the shales are used without any other processing than size reduction and the process produces no waste (Table 2-23).

Shale is also used to make lightweight aggregate for use in concrete. When heated to a suitable temperature, the shale expands or bloats and forms a porous, competent, light weight aggregate. This strong, light aggregate is used to make light weight concrete. Kiln dust is produced by the process, which is the only waste. This waste probably would not exhibit hazardous characteristics by itself. However, some operations are using listed wastes, such as used solvents, for fuel in their kilns. Current regulations would consider the use of listed waste as a fuel to be processing of liquid waste and all wastes from processing of liquid wastes are also listed wastes by definition. The kiln dusts could then be considered hazardous since they are partially derived from the processing of listed wastes.

Table 2-23

SHALE PROCESSING WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Expansion	Kiln Dust	N	N	N	N	May be derived from hazardous waste fuel

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

3.0 METAL INDUSTRIES

INTRODUCTION

This chapter contains reports on 32 metal commodities produced in the U.S. from mineral sources. The quantities of metals produced by these industries range from less than 200 pounds per year to more than 80 million long tons per year.

Further study of the industries producing five metallic commodities is not recommended. These recommendations are based on low volume of production or a recent total shutdown of all production facilities. The 27 metal industries that are recommended for further study may not all require regulation under Subtitle C, but the readily available literature did not contain sufficient information on waste characteristics and disposal practices to determine if such regulation was appropriate.

ARSENIC

The most important sources of arsenic are byproduct materials from the smelting of copper and lead concentrates. Arsenic trioxide is volatilized during smelting and is concentrated in the flue dust. This flue dust can be processed to produce arsenic trioxide as the final product. Arsenic trioxide was produced from flue dust in the United States until 1985. At that time, the last operation in Tacoma, Washington closed. Since then, both arsenic metal and the trioxide have been imported.

It is estimated that over 92% of the arsenic imported in 1986 was in the form of arsenic trioxide. The majority of this arsenic is used in wood preservatives and herbicides. Metallic arsenic is used in nonferrous alloys and as a material for semiconductors in the electronics industry.

The industrial process for production of arsenic trioxide involves roasting flue dust with pyrite or galena to volatilize the arsenic. The vapors are sent to a series of brick cooling chambers called kitchens. The majority of the arsenic trioxide condenses to produce a product of 99-99.9% purity. The arsenic trioxide condensing in the warmest or coolest kitchens is generally less than 90% pure and is pressure leached and recrystallized to produce a more pure product.

At present, arsenic trioxide is not produced in the United States. The majority of the refineries have been closed permanently. For these reasons, further study of arsenic production for possible regulation under RCRA subtitle C is not necessary.

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COBALT

Cobalt and cobalt alloys have several major uses stemming from their ability to maintain high strength and corrosion-resistant properties when heated to high temperatures. Cobalt's principal use is in superalloys used in jet aircraft and industrial turbine engines. In addition, it is used in drying agents in paints, as a catalyst in petroleum refining, and in magnetic alloys.

The large majority of cobalt occurs in mineral forms as arsenides, sulfides, and oxides. Predominant cobalt minerals include linnaeite (Co_3S_4), carrollite (CuCo_2S_4), safflorite (CoAs_2), skutterudite ($(\text{Co,Fe})\text{As}_3$), erythrite ($\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$), and glaucodot ($(\text{Co,Fe})\text{AsS}$).

There has been no mining of cobalt in the United States since 1971 due to unfavorable economics, and no mining is expected in the foreseeable future. However, there are an estimated 1.4 million tons of land-based cobalt deposits in the United States. Most deposits are in Minnesota and the northwest states.

If domestic mining of cobalt resumed at a future date, the lateritic ores found in Idaho and Missouri would be the choice ore for development. Lateritic ore contains 0.06 to 0.25% cobalt.

The U.S. Bureau of Mines has developed a process for the recovery of cobalt from lateritic ores. This process is shown in Figure 3-1. Dried ore is roasted at 525°C in a reducing atmosphere of carbon monoxide for 15 minutes. Cobalt (and nickel) is then extracted from the ore into solution during an ammoniacal leach. The spent ore is thickened before being discarded, resulting in a wastewater stream requiring proper disposal (Table 3-1). The extraction solution is filtered, producing waste solids, and excess ammonia is removed by steam heating. Cobalt is then removed from the solution by organic stripping, and spent cobalt electrolyte is

Figure 3-1

COBALT BENEFICIATION FROM LATERITIC ORE
LATERITIC ORE (0.06 to 0.25% Co)

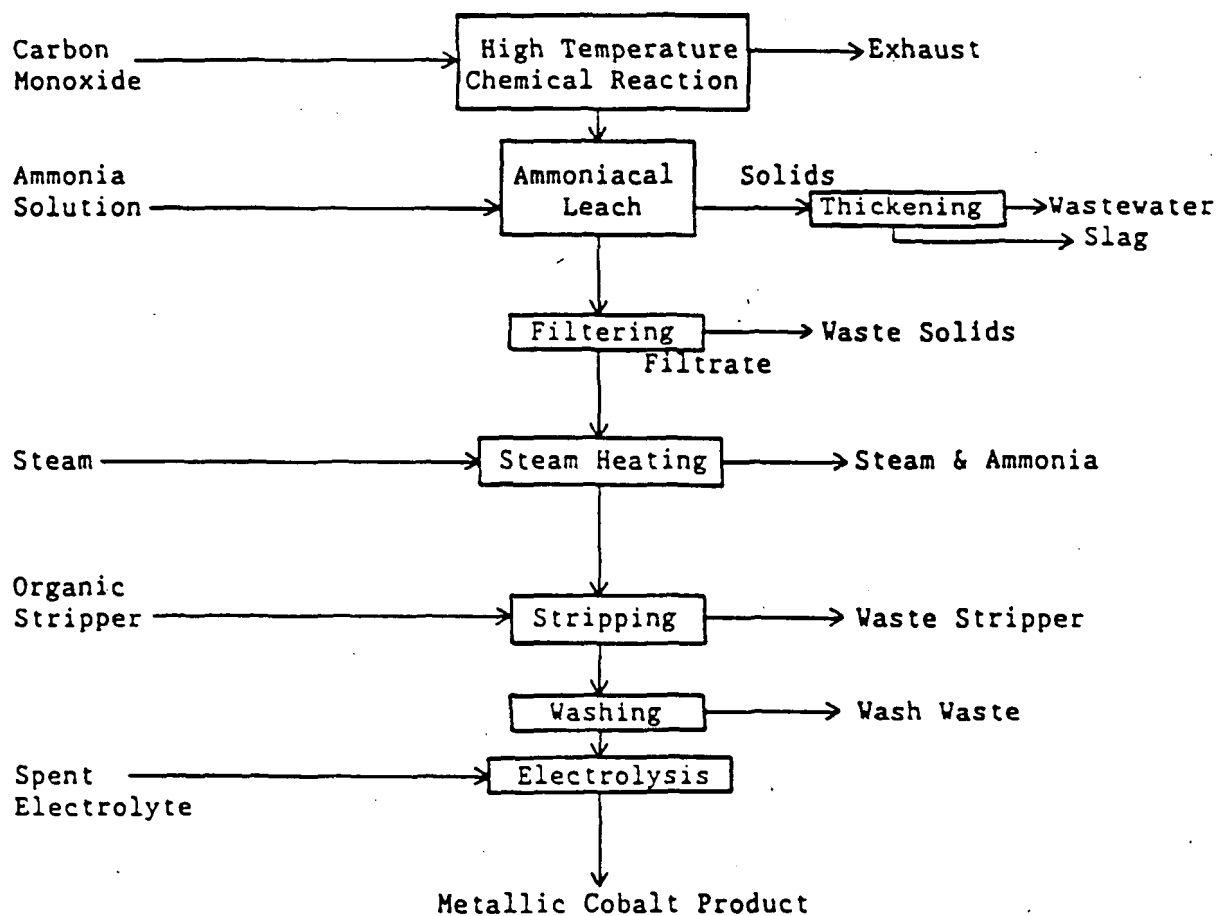


Table 3-1
COBALT BENEFICIATION WASTES

Process	Waste	Possible RCRA Characteristics				Comments
		R	C	I	T	
Ammoniacal Leach	1) Solids	N	?	N	?	
Thickening	1) Wastewater	N	N	N	?	
	2) Slag	N	N	N	?	
Filtering	1) Waste Solids	N	N	N	?	
Stripping	1) Waste Stripper	N	?	N	?	
Washing	2) Washing Waste	N	?	N	?	

* RCRA characteristics are reactivity, corrosivity, ignitability, and EP toxicity as defined in 40 CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

used to separate the cobalt from the stripping solution. The stripping solution is discarded as waste. Electrolysis is used to precipitate the metallic cobalt product. The Bureau of Mines has reported cobalt recoveries of 80 to 90% by this process.

Cobalt is often recovered during the mining and beneficiation of copper and nickel-containing ores. The AMAX Nickel Company, which had the only cobalt refining capacity in the U.S. closed its plant at the Port Nickel, Louisiana plant in 1985. Imported copper-nickel cobalt mattes have been used as the source of cobalt. The cobalt was recovered by atmospheric leaching and hydrogenation which precipitates cobalt from solution. The Port Nickel refinery is now reprocessing petroleum refining catalysts to recover vanadium, molybdenum, and alumina. There are no current plans to reopen the cobalt refinery, but it could be put back into production if the economic conditions become favorable.

As previously mentioned, there is currently no mining in the United States. If mining of the lateritic ore deposits becomes economically practical at a later date, then investigation and characterization of the wastes produced would be needed, since no full-scale operations exist today. However, no development of domestic cobalt deposits is expected in the near future. Therefore, no further investigation of the wastes for potential regulations under Subtitle C associated with the mining, beneficiation, or processing of cobalt is recommended at this time.

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MERCURY

Mercury metal is a silver-white liquid at room temperature and a colorless vapor above its boiling point of 356.9°C. Mercury is an excellent conductor of electricity, is stable in oxygen, carbon dioxide and air, readily combines with halogens and sulfur, and alloys easily with other metals forming amalgams. Mercury exhibits a high surface tension and a uniform volume expansion with respect to temperature.

Mercury's electrical conductivity, uniform expansion over a wide temperature range, and toxicity render it useful in several industries. Batteries comprise the largest use of mercury. Low pressure mercury (fluorescent) and high pressure mercury lamps are used widely for household and industrial lighting. The uniform volume expansion and high surface tension of mercury make it ideal for use in temperature and pressure sensing devices such as thermometers and manometers. In agriculture, mercuric compounds are used primarily as bactericides and disinfectants, and as a pharmaceutical, mercury is used in diuretics, antiseptics, skin preparations, and preservatives. Mercury is also used as a catalyst in the manufacture of anthraquinone derivatives, vinyl chloride monomers and urethane polymers.

Mercury ore is found in over twelve sulfur combined minerals. Cinnabar (HgS) is the most common mercury mineral. Other commercially significant mercury minerals include corderite ($\text{Hg}_3\text{S}_2\text{Cl}_2$), livingstonite (HgSb_4S_7), montroydite (HgO), terlinguaite (Hg_2OCl), calomel (HgCl), and metacinnabar (black cinnabar). Mercury deposits occur in the continental rock formations which are faulted or fractured and have an epithermal character, such as limestone, calcareous shales, sandstones, serpentine, chert, andesite, basalt, and rhyolite. Deposits are found at relatively shallow depths (from 1 to 1,000 meters). Ores typically contain between 4 to 20 kg of mercury per ton.

Mercury ore is mined using open pit and underground methods. Mercury mined underground comprises 90% of overall world production. The open pit mine at McDermitt, Nevada, closed in January, 1987. Until its closing, the McDermitt mine was the only active mine in the United States. Other mines in California may operate intermittently. Mercury can also be extracted as a secondary product in the refining of precious metals.

At the Nevada mine, beneficiation consisted of crushing followed by separation in a flotation cell (Figure 3-2). The flotation concentrate was then heated in a furnace to reduce and vaporize the mercury. The mercury metal is recovered by condensation in a cooling system. The recovered mercury, known as prime virgin mercury, was 99.9% pure and contained less than 1 ppm base metal concentrations. The wastewater produced in both the flotation and cooling processes was impounded in multiple evaporation ponds (Table 3-2). There is no resulting discharge. Other intermittent operations in California and Nevada do not beneficiate the ore and therefore water is only used for cooling. Any cooling water discharges would likely not be hazardous.

The past five years have seen a downward trend in the primary production of mercury. Mercury production is measured by the flask (1 flask = 76 pounds). In 1982, mine production of mercury was reported to be 25,760 flasks, compared to 16,530 flasks in 1985. This downward trend in production was caused by the availability of low-cost foreign material and sales of government stockpiles. Demand for mercury products such as pesticides, fungicides, paints, and antiseptics had dropped due to replacement with other effective but less toxic substances. The fact that mercury is not currently produced in the United States and the zero discharge operation suggest that the mercury production industry need not be studied further for potential regulation under Subtitle C of RCRA.

Figure 3-2

MERCURY

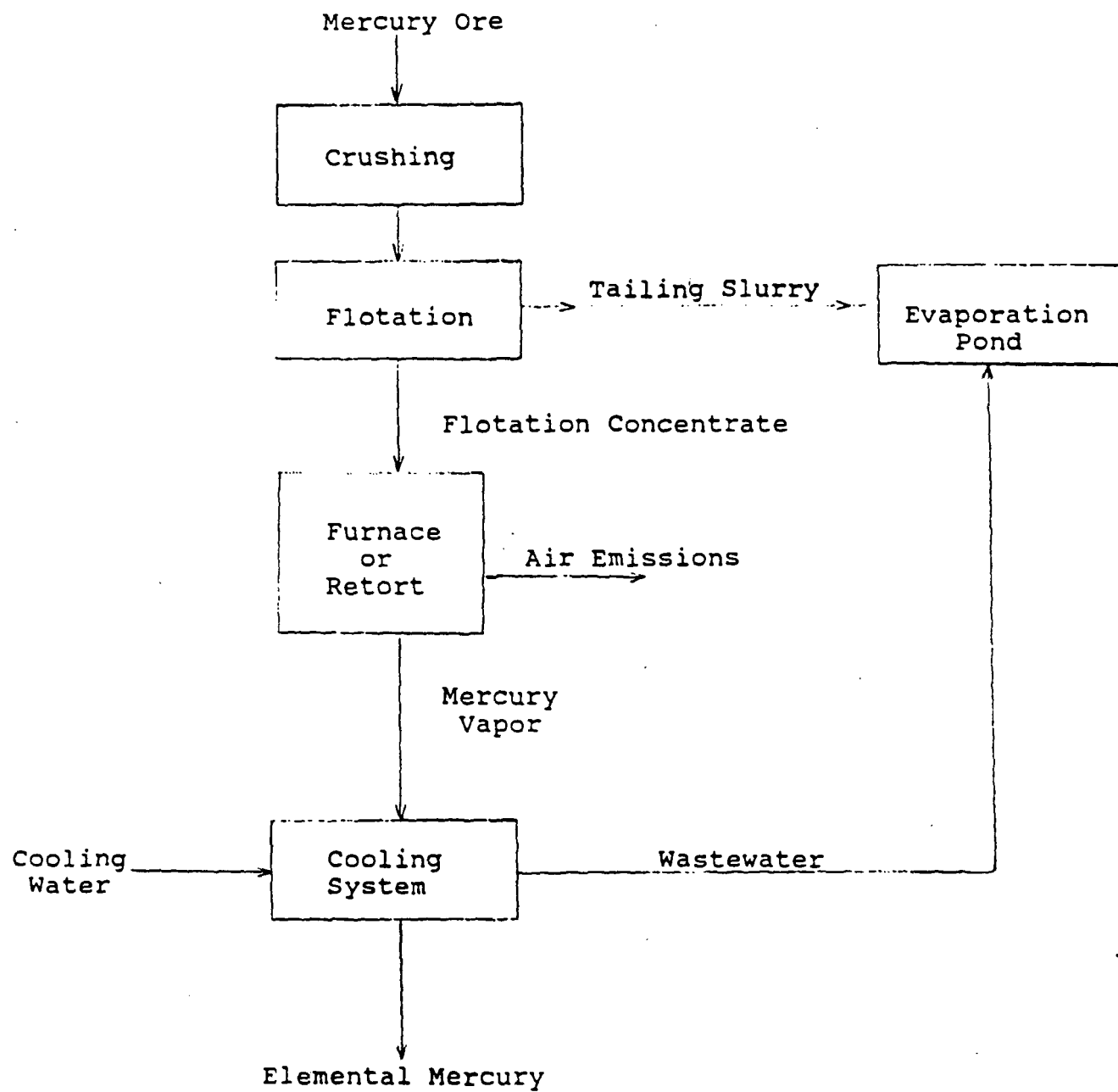


Table 3-2

MERCURY PROCESSING WASTES

Process	Waste	Possible RCRA Characteristics				
		R	C	I	T	Comments
Flotation	1) Flotation Tailings	?	?	N	?	May contain toxic metals or sulfides

* RCRA characteristics are Reactivity, Corrosivity, Ignitability, and EP Toxicity as defined in 40 CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

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NICKEL

Nickel is a silvery-white, hard, malleable, ductile, metal widely used in alloys to impart strength and corrosion resistance. Many of the common stainless steels contain nickel, as do other corrosion resistant alloys such as Inconel, Monel, and the hastelloys. It is also used in high strength steels such as tool and armor alloys. Nickel plating is used as a protective and decorative coating on other metals. It has also found use in electronics, ceramics, magnets, and in catalysts.

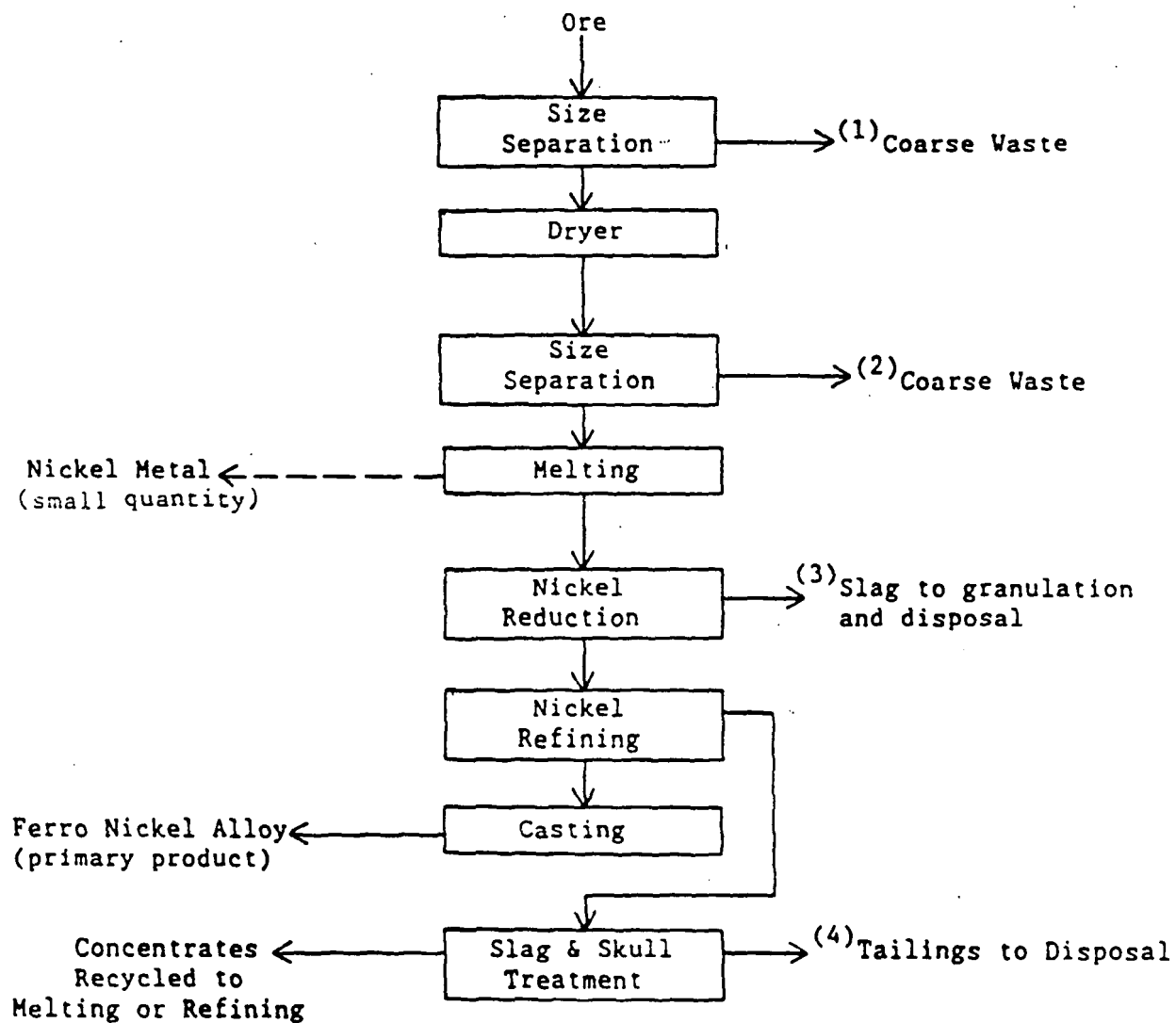
There is no primary producer of nickel in the United States, although the Hanna Mining Company, until recently, produced ferro-nickel used in alloying steel at Riddle, Oregon, by smelting an ore containing nickel oxide. The ore is of a type called a "laterite" which is a weathered deposit in which the nickel is concentrated in soils by the chemical breakdown of the original rock. Fragments of the original rock, called peridotite, remain in the deposit. These fragments have low nickel contents and are much harder than the rest of the ore. The processing, as shown in the flow sheet in Figure 3-3, takes advantage of that hardness to upgrade the ore.

The first stage of processing is a screening step that removes ore fragments that are coarser than 3" producing waste stream 1. These large pieces of rock are almost all peridotite and would not be expected to exhibit any hazardous characteristics. Since the ore contains considerable moisture it is next dried then screened again. The drying tends to break down the softer parts of the ore so that removing particles coarser than 1" will remove peridotite producing waste stream 2 in Figure 3-3, which will have the same characteristics as stream 1.

The dried material smaller than 1" is split into coarse and fine fractions with the coarsest material being crushed to finer than 5/16". The coarse and fine ore fractions are then preheated in separate units. The preheated

Figure 3-3

Nickel Ore Processing
Hanna, Riddle, Oregon



ore is then fed to electric melting furnaces. The primary function of these furnaces is to melt the ore for further processing, but a small amount of metal is produced.

The molten ore is poured into one ladle of a "skip mixer" which has two ladles. The other ladle contains previously made ferro nickel as "seed metal". The ladles are poured back and forth to provide mixing. Ferro silicon is added as a solid reducing agent during the mixing. After seven pours the material is allowed to stand for a time to let the metal and slag separate. The slag is poured off and granulated by high pressure water jets prior to disposal. The cooled slag would not be expected to exhibit any hazardous characteristics.

The ferro-nickel alloy metal from the reduction step then goes to a refining step where phosphorous is removed. The alloy is cast into ingots called "pigs" which are the final product of the process. The slag from refining, along with "skulls" (cooled material coatings) from the reaction vessels and slag kettles and collected spillage are milled and treated by magnetic separation to recover the metal values. The metal concentrates are recycled with fine concentrates returning to the melting stage and coarse concentrates returning to the refining stage. The tailings from this treatment are discarded as waste 4 in Figure 3-3. These tailings are not expected to exhibit any hazardous characteristics (Table 3-3).

Low nickel prices caused the Hanna Mining Co. to suspend operations in May of 1986, for an indefinite period. The plant equipment has recently been offered for sale by a used equipment dealer.

Two copper refineries produce nickel materials as by-products. If nickel is present in a copper ore, some will follow the copper through the preliminary stages of processing and nickel will be found in the impure metal that is cast into anodes for electro-refining. The nickel will dissolve and build up in the electrolyte solution as copper dissolves. The nickel must be kept at a low concentration to prevent contamination of the

refined copper. A portion of the electrolyte from all of the cells in the refinery is removed continuously as a bleed stream and is treated to remove the nickel and other contaminants. The purified stream is returned to the refining cells, which dilutes the contaminants present, keeping their concentrations low enough to prevent interference with the copper refining.

The treatment of the bleed stream is a three-step process. In the first step, part of the copper is plated out of the solution under conditions that give a high purity product essentially the same as the primary refining process. In the second step, the rest of the copper is plated out of the bleed stream along with any arsenic, antimony, and bismuth. The metal from this step is purified to remove the contaminants and returned to the main refining process. The remaining bleed stream solution is then treated by evaporation of the water, which causes the nickel, and any remaining copper, arsenic, antimony, bismuth, iron, and cobalt to precipitate as sulfate. The nickel sulfate is purified and sold for electroplating and other chemical uses. Most of the acid remaining after the precipitation step is returned to the main refining process. A portion is neutralized and discarded to prevent buildup of calcium, magnesium, potassium, and sodium ions in the electrolyte solution. This sludge and the remnants of the nickel sulfate purification could exhibit hazardous characteristics due primarily to leachable metals.

Nickel production in the United States is limited to two producers of nickel materials as a by-product of copper refining. There are wastes from nickel production as a by-product of copper production that could exhibit hazardous characteristics but it appears logical to address those wastes in the context of copper production. Therefore, no further study of the nickel production industry for possible regulation under RCRA Subtitle C is recommended.

Table 3-3
NICKEL PROCESSING WASTES

Process	Waste	Possible RCRA Characteristics*				Comments
		R	C	I	T	
Laterite Smelting						
First Size Separation	1) Coarse peridotite	N	N	N	N	
Second Size Separation	2) Finer peridotite	N	N	N	N	
Reduction	3) Reduction Slag	N	N	N	N	
Skull & Slag Processing	4) Tailings	N	N	N	N	
Copper Refining						
Nickel Purification	1) Residue	N	?	N	?	
Acid Bled Neutralization	2) Sludge	N	N	N	?	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability, and EP Toxicity as defined in 40 CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

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SCANDIUM

Scandium is a soft silver metal which has a slight yellow cast when exposed to air. Scandium readily reacts with acids and is not easily attacked by water. The metal does not tarnish in air, but at high temperatures (500° to 800°C) scandium can be oxidized in air. Scandium is extremely electropositive, and, therefore, its oxide is basic and acid soluble. Scandium exhibits a trivalent state in compounds and has no other observed valences. Scandium is chemically similar to rare earth elements; however, its ion size places it in geochemical equilibria with aluminum, magnesium, hafnium, and zirconium. Therefore, scandium is rarely found in rare earth ores, but has been noted in minor amounts in gadolinite, xenotime, allanite, davidite and others.

Scandium occurs an estimated 7 ppm in the earth's crust, and at about 0.0004 ppm in sea water. One of the scandium-rich ore minerals is thortveitite, $(\text{ScY})_2\text{Si}_2\text{O}_7$, which contains 33 to 42 percent scandium oxide. Thortveitite is found as greyish green, translucent to transparent, prismatic crystals often found in pegmatites. In igneous rocks scandium is concentrated in pyroxenes, amphiboles and biotite with contents up to 0.5 percent scandium oxide. Pegmatite formations are estimated to contain 5 to 20 ppm of scandium. Scandium also occurs in low concentrations in wolframite, euxenite, cassiterite, and some uranium deposits.

There are very few commercial uses for scandium. Demand for scandium is extremely low, causing market prices to be unpredictable. Scandium is principally sold in its oxide form, and in 1985 the total consumption was estimated at 50 kilograms.

Currently, the principal uses for scandium are in high-intensity mercury vapor lamps and lasers. Little is known about scandium, and laboratory research is continuing.

In the United States, scandium was recovered in 1985 as a byproduct from thortveitite-bearing fluorite screenings previously mined at Crystal Mountain, Montana, uranium extracted from copper tailings at the Bingham Canyon copper mine in Utah, and from by-product tungsten concentrate from molybdenum ores mined at Climax, Colorado.

Scandium is extracted from thortveitite by several methods. One method involves dissolution of thortveitite with concentrated hydrochloric or sulfuric acid, yielding a gelatinous residue of scandium-containing silica (Figure 3-4). Another method begins by finely grinding thortveitite with charcoal at 1,800°C, forming scandium carbide (Figure 3-5). This carbide is then further decomposed with hydrochloric acid forming soluble scandium chloride. The third method involves chlorinating thortveitite in the presence of chlorine gas and carbon at 850°C to form scandium chloride (Figure 3-6). The scandium chloride is leached with sulfuric acid. From the residue of any of the three methods, scandium is recovered by adding ammonium oxalate or tartrate to the solution, forming a scandium precipitate. This precipitate is filtered and washed, then decomposed by ignition at 900°C. An impure scandium oxide is formed and dissolved in hydrochloric acid. Scandium can also be extracted from thortveitite using hydrofluoric acid in a similar method. Methods using magnesium or ammonium-hydrogen fluoride have been used. Ion exchange or solvent extraction is used for further purification.

Scandium has been found to closely follow uranium in solvent extraction operations (Figure 3-7). By using dodecyl phosphoric acid in kerosene, scandium does not strip with uranium, but remains in the solvent. The ore is crushed and ground, then leached with dilute sulfuric acid. Oxidant was added to convert uranium metals to soluble form for solvent extraction. Stripped solvent, from the solvent extraction process, contains less than 0.1 ppm scandium. This solution is fed through a two-stage countercurrent solvent extraction system and is treated with hydrofluoric acid. The stream is filtered to yield a cake that is 10 percent scandium oxide (Sc_2O_3) and 20 percent thorium oxide (ThO_2). This cake is digested in a

Figure 3-4
SCANDIUM FROM THORTVEITITE #1

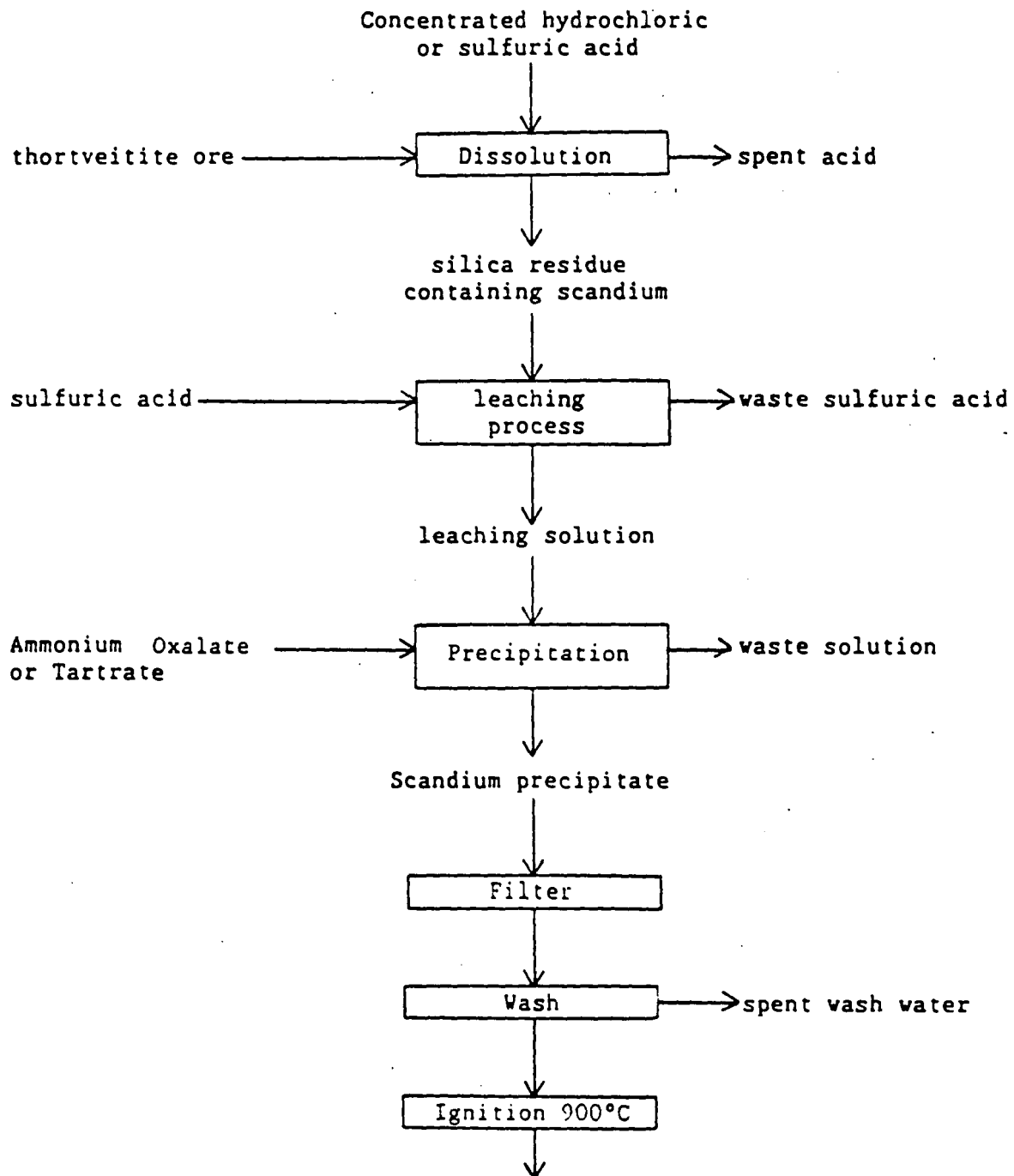


Figure 3-5
SCANDIUM
THORTVEITITE #2

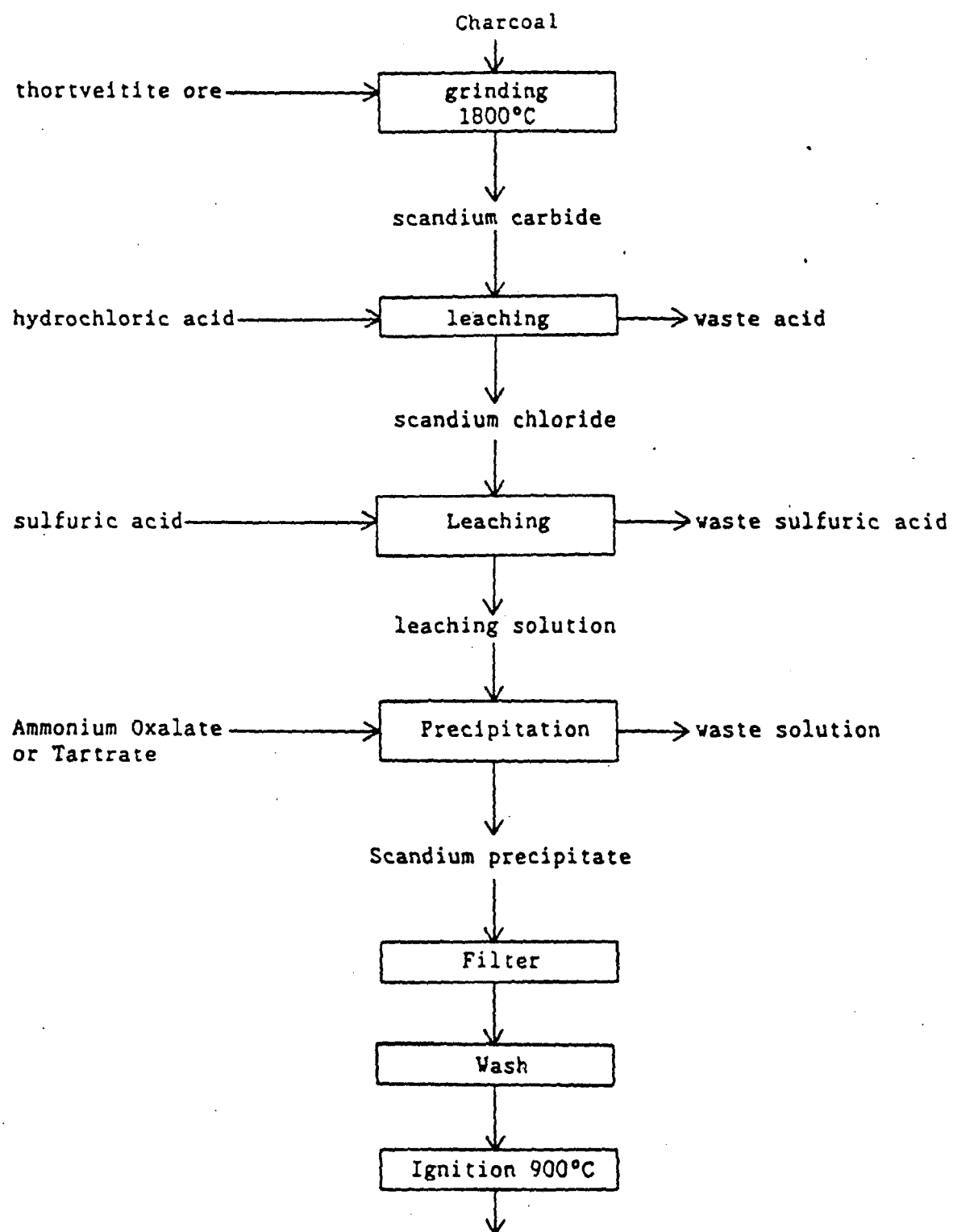


Figure 3-6

SCANDIUM
THORTVEITITE #3

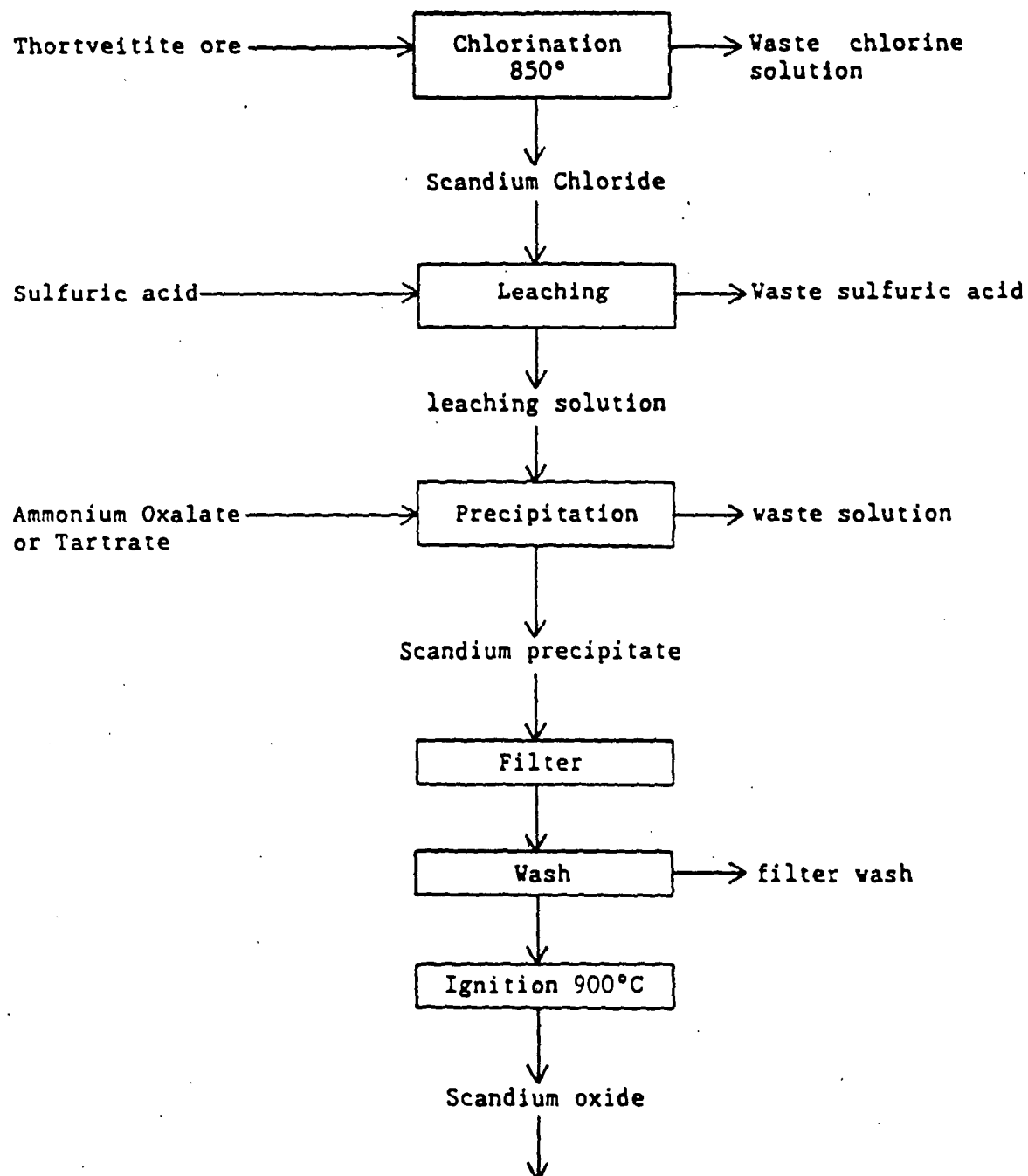
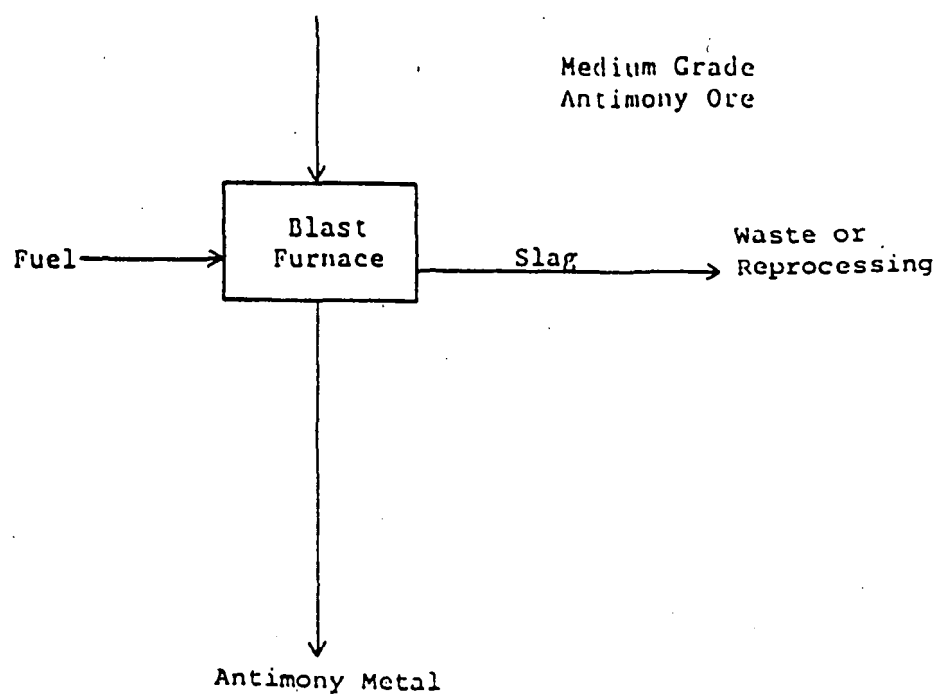


Figure 3-10
ANTIMONY SMELTING



LIQUATION

As shown in Figure 3-11, during liquation high grade ores are heated in either a perforated pot (batch mode) or reverberatory furnace (continuous mode) which allows separation of the melted rich sulfide ore from the slag or residue. It is important to provide a reducing atmosphere to prevent oxidation or volatilization losses. The residue, which generally contains 12-30% antimony is reprocessed by oxide volatilization to recover the antimony. The rich sulfide ore is known as needle antimony, and elemental antimony can be produced using the iron precipitation process, or by conversion to the oxide, with subsequent volatilization and oxide reduction.

IRON PRECIPITATION

The iron precipitation process for conversion of antimony sulfide to elemental antimony is suitable for both high grade ores and needle antimony. As shown in Figure 3-12, the ore is heated with excess iron scrap that serves as a reductant for the antimony. Carbon and sodium sulfate are added to produce excess sulfide to promote iron sulfide production, and salt is added to facilitate formation of an iron sulfide matte that can be skimmed off the molten metal. Because the antimony produced contains unacceptably high concentrations of iron and sulfur, a secondary fusion process is used where needle antimony and salt are heated with the antimony to produce more iron matte and purified antimony metal. The iron matte is either reprocessed by blast furnace smelting, or becomes a waste stream, which might exhibit the RCRA characteristics of reactivity, or EP toxicity.

OXIDE REDUCTION

Antimony trioxide from the oxide volatilization process is reduced to antimony in a reverberatory furnace. As shown in Figure 3-13, charcoal is added to serve as a reductant, and flux agents (soda, potash, sodium sulfate) are added to dissolve sulfides and minimize volatilization.

Figure 3-11

ANTIMONY PROCESSING
LIQUATION PROCESS

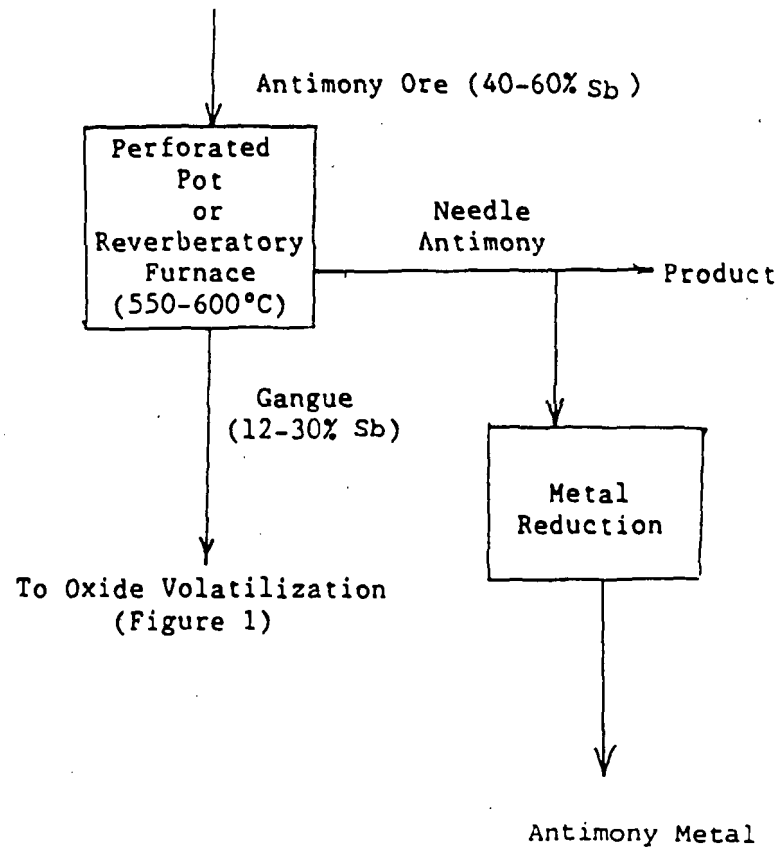


Figure 3-12

ANTIMONY
IRON PRECIPITATION
REDUCTION PROCESS

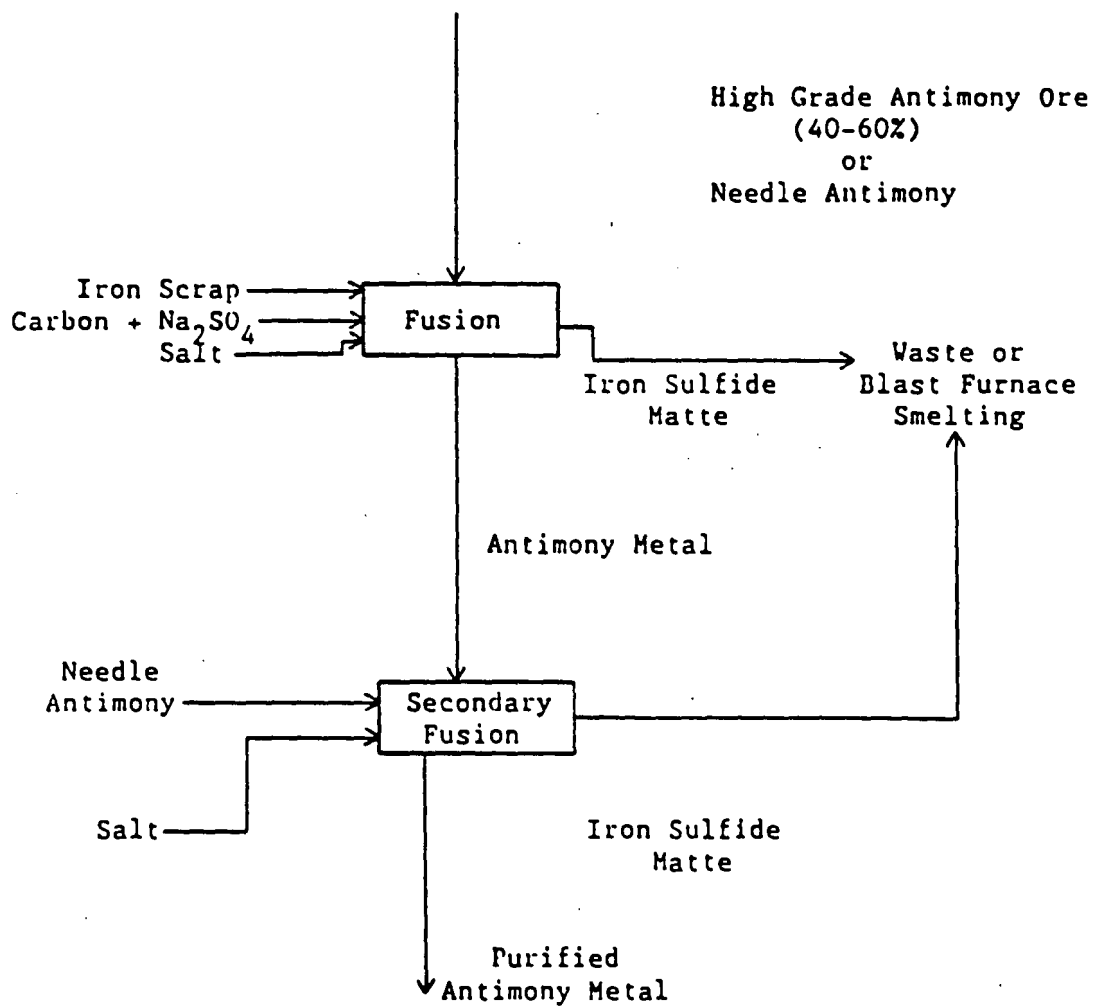
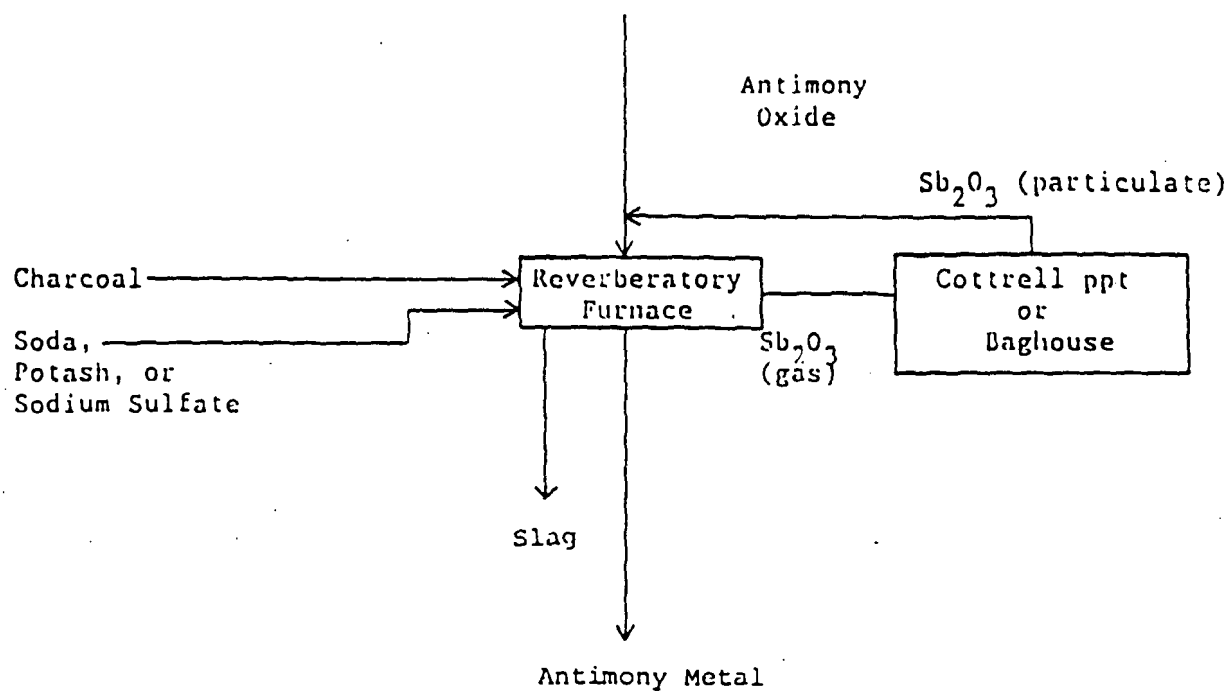


Figure 3-13

ANTIMONY
OXIDE REDUCTION PROCESS



Nevertheless, volatilization of antimony is significant requiring a Cottrell precipitator or baghouse to recover the antimony trioxide for reprocessing. The main waste stream is the slag formed, but, baghouse dust would be a waste if not directly recycled into the process.

LEACHING AND ELECTROLYSIS

The ASARCO plant in El Paso, Texas, and the Sunshine Mining Co., Sunshine, Idaho, each utilize a leaching-electrowinning process for recovery of antimony from complex ores. As shown in Figure 3-14, the ores are first leached with alkali hydroxide or sulfide for extraction of the antimony in the form of sodium thioantimonate (Na_3SbS_4). The sodium thioantimonate is reduced by electrolysis at an iron or mild steel cathode in a diaphragm cell. The leachate remaining after electrolysis is a waste stream generated from this process. The composition of this stream is not detailed in the literature and needs further characterization.

REFINING

Pyrometallurgically produced antimony metal requires further refining to remove arsenic, sulfur, iron, and copper impurities. As shown in Figure 3-15, this is accomplished by heating the antimony with sodium sulfate, charcoal, and stibnite to form an iron matte which is skimmed from the surface. Arsenic and sulfur are removed by heating in an oxidizing environment created by the addition of caustic soda, sodium carbonate, and niter (sodium nitrate). It is assumed that this process necessarily generates an arsenic sulfur waste. Lead is not readily removed. However, if lead was present in the antimony metal undergoing refining, the product is usable for lead base alloy applications. Lead and other, impurities can be partially removed by electrolytic refining.

Figure 3-14

ANTIMONY REDUCTION
BY
LEACHING AND ELECTROLYSIS

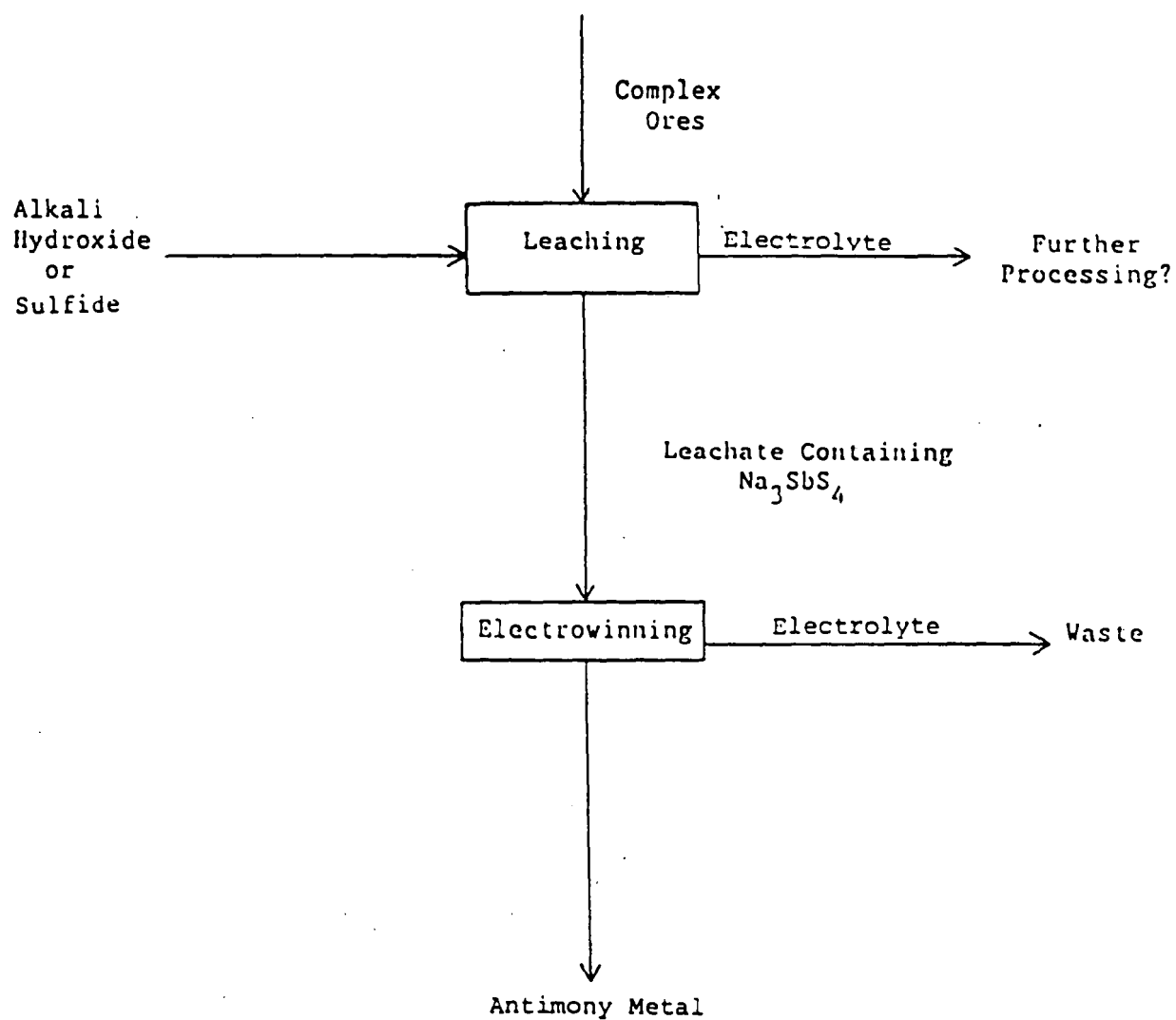
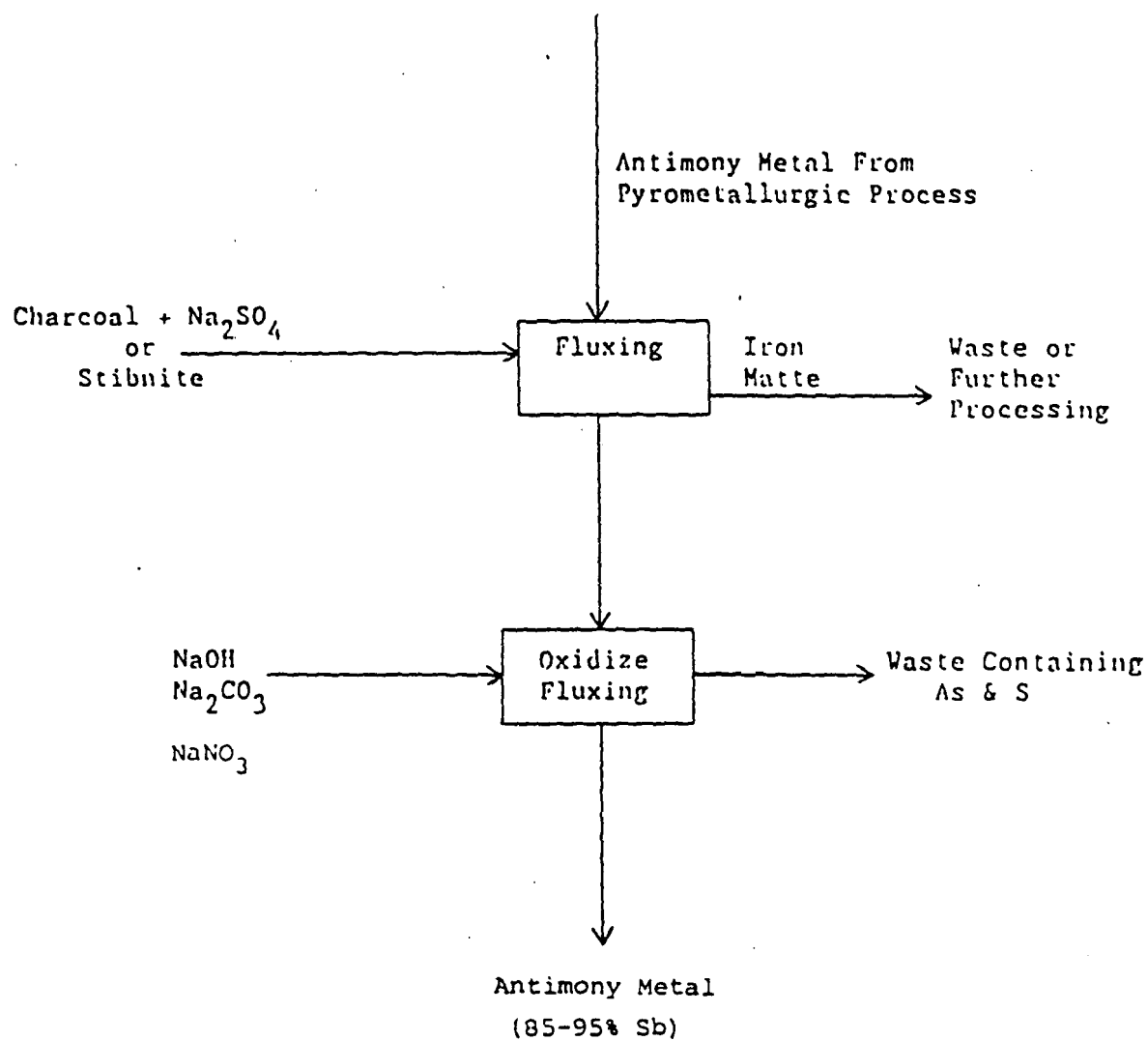


Figure 3-15
ANTIMONY REFINING



CONCLUSION

Gangue and slag are the major wastes produced in the initial processing of various grade antimony ores (Table 3-5). The quantities produced, their chemical characteristics, and their disposition are not available in the literature. The antimony reduction and refining processes produce iron matte, slag, and the sulfur/arsenic waste from oxidizing fluxing. Again the quantities, characteristics, and disposition of these wastes are not available in literature. Although the leaching electrolysis process has current limited use, residue and leachate are produced that may have hazardous characteristics. It is recommended that the antimony production industry be further investigated for possible regulation under Subtitle C of RCRA.

Table 3-5

ANTIMONY PROCESSING WASTES

Process	Waste	Possible RCRA Characteristics				Comments
		R	C	I	T	
Beneficiation by Flotation	Tailings, Thickener Overflow, Filtrate	N	N	N	?	
Oxide Volatilization	Scrubber Sludge	N	N	N	N	
	Gangue	N	N	N	?	
	Bag House Dust	N	N	N	?	May be recycled
Smelting	Slag	N	N	N	?	
Iron Precipitation and Reduction	Iron Sulfide Matte	?	N	N	?	
Oxide Reduction	Slag, Bag House Dust	N	?	N	?	Baghouse dust may be recycled
Antimony Reduction by Leaching/Electrolysis	Leaching Residue	N	?	?	?	
	Waste Leachate	N	?	?	?	
Antimony Refining	Iron Matte	N	N	N	?	
	Oxidized Fluxing Waste	N	?	N	?	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability, and EP Toxicity as defined in 40 CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

REFERENCES

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BERYLLIUM

Beryllium (Be) occurs in a number of minerals, including beryl ($3 \text{ BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6 \text{ SiO}_2$), bertrandite [$\text{Be}_4\text{Si}_2\text{O}_7 (\text{OH})_2$], and chrysoberyl (Al_2BeO_4). The major deposits of beryllium containing materials in the United States are bertrandite deposits in the Spor Mountains of Utah, spodumene pegmatite in the Carolinas, and chrysoberyl in the strongly faulted areas of the Seward Peninsula in Alaska. The bertrandite deposit in Utah is the only area that is actively mined. Estimated production for 1986 was 261 short tons of contained beryllium. Beryl is imported, mainly from Brazil and China, to be processed in the United States. Approximately 60 short tons (contained beryllium) of beryl were imported in 1986.

Beryllium is a light weight, high strength metal with a high thermal conductivity. It also has a low neutron-capture cross section and a high neutron scattering cross section. These properties make the metal useful for application in the nuclear weapons, defense, and aerospace industries. It is used as the metal, as a beryllium-copper alloy, and as beryllium oxide (for ceramic applications).

The Spor Mountain bertrandite deposit is currently being mined by only one company (Brush Willman). A joint venture was recently announced to open a bertrandite mining operation adjacent to the current Spor Mountain operation in Utah. A joint venture between Cabot Corp. and Cyprus Minerals Co. was announced in October, 1986 to develop Cabot's property, Sierra Blanca, near El Paso, Texas. The deposit reportedly contains bertrandite and behoite (BeOH_2). Cyprus planned to complete feasibility studies and mine development within two years.

Processing of bertrandite and imported beryl takes place in the same plant in Delta, Utah. Both processes attempt to extract the beryllium from the respective ores as a solution of beryllium sulfate. Once in solution, the two pregnant liquors cannot only be combined but tend to have a synergistic

impact because of differences in concentration and chemical composition. Once combined, the ore source from which the beryllium was derived loses identity and the combined leach liquor continues through the balance of the process to final product. Thus, the significant differences in the two processes are involved in the procedures required to solubilize the beryllium values from the respective ores.

The bertrandite ore is crushed, wet milled, and sized. The contained beryllium can then be leached or placed in solution under moderate conditions of temperature (95°C) and acid concentration. In contrast, the beryllium values in beryl are tightly bound in the crystal structure of the mineral. To effectively attack the mineral with acid, it is first necessary to destroy the crystal structure. In the Delta process the ore is melted at 1700°C and quenched rapidly in water to fracture and freeze the particles (frit) formed as a solid solution. The frit is heat treated at about 1000°C, ball milled to 325 mesh, reacted with concentrated sulfuric acid at 325°C before the beryllium values can finally be solubilized. This is done by slurrying the sulfated frit in water. The leached or spent solids in both processes are separated from the beryllium sulfate leach liquor using thickeners and washing the solids by counter current decantation (CCD) before discarding the solids to the waste (tailings) pond. Once again, the differences required for processing the two ores are emphasized by the size of the thickeners involved. The beryl system uses five 15-foot diameter thickeners while the bertrandite process requires eight 90-foot diameter units. The leach liquor from the two processes can be combined at this point and proceed through the balance of the process to the final product. In the leaching operations, elements other than beryllium are also solubilized and must be removed in process to prevent product contamination. The solvent extraction system rejects all elements adequately requiring no subsequent treatment except for uranium, iron, aluminum, and fluoride. The solvent extraction process at Delta uses an organic that has good selectivity for the extraction of beryllium. By mixing the beryllium containing leach solution vigorously with the organic, some of the beryllium reacts with the organic. By repeating this process a

number of time in a counter current flow pattern of the aqueous and organic, essentially all of the beryllium can be extracted into the organic phase. A multi-stage mixer settler system is incorporated at the Delta Mill to facilitate this operation.

The most concentrated organic relative to beryllium in the system is referred to as loaded organic. By contacting this stream with ammonium carbonate solution in a two stage mixer-settler system, the extraction process is reversed, stripping the beryllium from the organic into the aqueous stream. The stripped organic is converted to the acid form by contacting it with sulfuric acid in a two stage mixer-settler system. The converted organic can then be recycled to the extraction train to repeat the cycle.

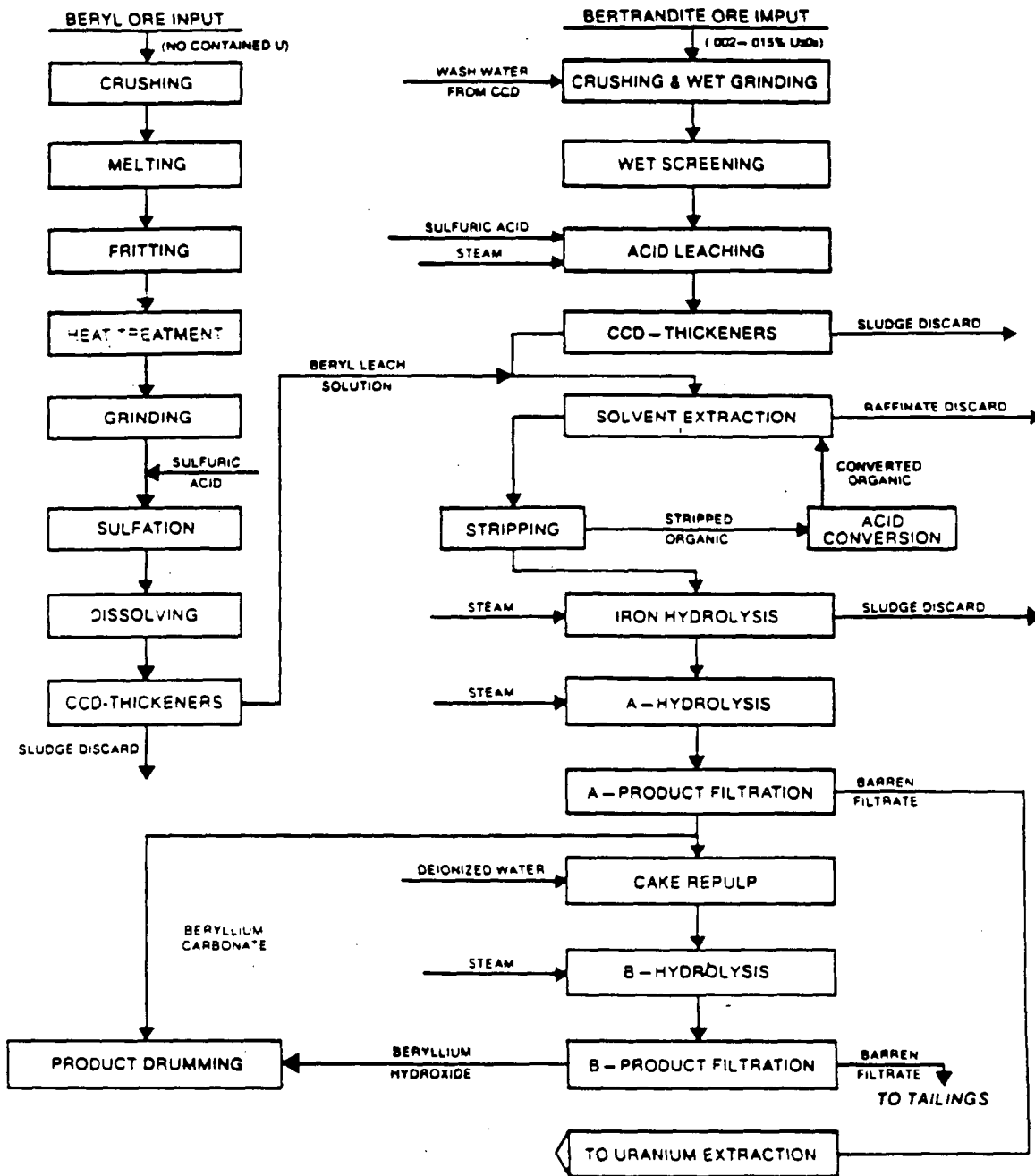
The beryllium containing strip solution is then further treated for the removal of iron and aluminum in preparation for final hydrolysis.

After stripping, the beryllium is present as a solution of ammonium beryllium carbonate. Heating this solution to 91°C liberates part of the ammonia and carbon dioxide and results in the precipitation of beryllium carbonate. This is separated on a rotary vacuum drum filter and may be drummed as a final product or be reslurried in deionized water and processed to beryllium hydroxide. This is accomplished by raising the temperature to 160°C in a pressure vessel and filtering a second time. Both products are packed and stored for future shipment.

The barren filtrate from the first filtration contains the uranium values. This stream is transferred to solar ponds for storage and subsequent processing for uranium recovery.

A flow diagram of the beryl and bertrandite processes is presented in Figure 3-16.

Figure 3-16



BERYLLIUM EXTRACTION PROCESSES
AT
BRUSH WELLMAN
DELTA, UTAH PLANT

Although the beryllium mining and milling industry is small, the wastes produced are potentially toxic (Table 3-6) and the waste management methods are not detailed in the literature. It is therefore recommended that further study be undertaken to determine if the wastes generated by this industry should be potentially regulated under Subtitle C of RCRA.

Table 3-6
BERYLLIUM WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Dissolution	Sludge	N	?	N	?	
Solvent Extraction	Raffinate	N	?	N	?	
	Spent Solvent	N	?	N	?	
Iron Hydrolysis	Sludge	N	?	N	?	
Product Filtration	Barren Filtrate	N	?	N	?	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability, and EP Toxicity as defined in 40 CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

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BISMUTH

Bismuth is a brittle, crystalline, lustrous metal with a pink color. Bismuth exhibits a greater electrical resistance in solid state than in the liquid state. The metal will oxidize only slightly in air, but when heated above melting point, an oxide film is formed. Bismuth is the most diamagnetic of the metals; its thermal conductivity decreases in a magnetic field. It is readily reactive with halogens and sulfur; it is not readily attacked by hydrochloric acid, but is converted to bismuth sulfate by hot sulfuric acid.

Bismuth occurs at an estimated 0.0043 to 1 gram/ton in the earth's crust. The most abundant bismuth-containing minerals are bismite anoxide, bismuthinite, a sulfide; and bismutite, a hydrated carbonate. Bismuth is a chalcophilic element, having been concentrated in the later magmatic stages of crystallization or through deposition from hydrothermal solutions. Bismuth is produced as a byproduct from the treatment of lead, copper, and other metal ores. Domestic sources of bismuth are concentrated in the western United States in lead and lead-zinc ores.

In 1986, 50 percent of the bismuth used was consumed by the pharmaceutical and chemical industry (U.S. Bureau of Mines, 1987). The primary metal industries consumed 25 percent and 23 percent of the bismuth consumption was used to manufacture machine parts. A thin film of bismuth has been patented for microfilming information supplied by a pulsed laser. It is also used as a window material for neutron transparency in medical irradiation devices and in wire form for Hall effect (an electromagnetic effect from current in a piece of metal aligned in a magnetic field used in special motors or sensors) and thermoelectric applications. Due to its low absorption cross-section for thermal neutrons, bismuth has been used in liquid-metal fission reactors as a fuel (^{235}U , ^{233}U) carrier or isolant. Bismuth is used to alloy with other metals for solders, for molding plastics as a heat transfer medium, and other metallurgical uses.

Domestic bismuth can be extracted as a byproduct from copper and tin ores, but is most commonly associated with lead and lead-zinc ores.

In the recovery of bismuth from copper ores, the bismuth will follow the copper into the matte as shown in Figure 3-17. When the matte is converted to blister copper, the bismuth fumes off, and the fumes, along with other elements, are caught in the baghouse. The collected dusts are sent to a lead-smelting process. Bismuth remaining in the blister copper is recovered from electrolytic slimes when the copper is refined. The slimes are handled so that the bismuth is collected in lead bullion. Recovery of bismuth from lead or lead-zinc operations involves one of two processes: Betterton-Kroll Process or Betts Electrolytic Process.

The Betterton-Kroll process used to produce the great majority of bismuth, both domestically and throughout the world, (Figure 3-18) involves the addition of metallic calcium and magnesium to lead bullion in a melt; this creates an inter-metallic compound that melts at a higher temperature than lead, but has a lower density. The melt is cooled to just above the melting point of lead and the inter-metallic compound, high in bismuth content, will solidify and float to the top to be skimmed off as a dross. This dross contains bismuth, calcium, magnesium, and lead. To remove the residual lead, the dross is reheated, to melt the lead which pools beneath the dross float. The lead-free dross is treated with chlorine and/or lead-chloride to remove magnesium and calcium. The result is a bismuth-lead alloy, high in bismuth concentration.

Bismuth-lead alloy created by the Betterton-Kroll process is treated with molten caustic soda to remove acidic elements such as arsenic and tellurium and impurities as shown in Figure 3-19. Then, the mix is desilvered by the Parkes desilverization process. The resultant alloy is then treated with chlorine gas at 500°C to remove zinc and lead (zinc and lead form chlorides faster than bismuth). The chlorination process will continue until the desired amount of lead has been removed. The bismuth is oxidized with air and caustic soda and the final refined product is 99.999 percent pure.

Figure 3-17
BISMUTH
COPPER SOURCES

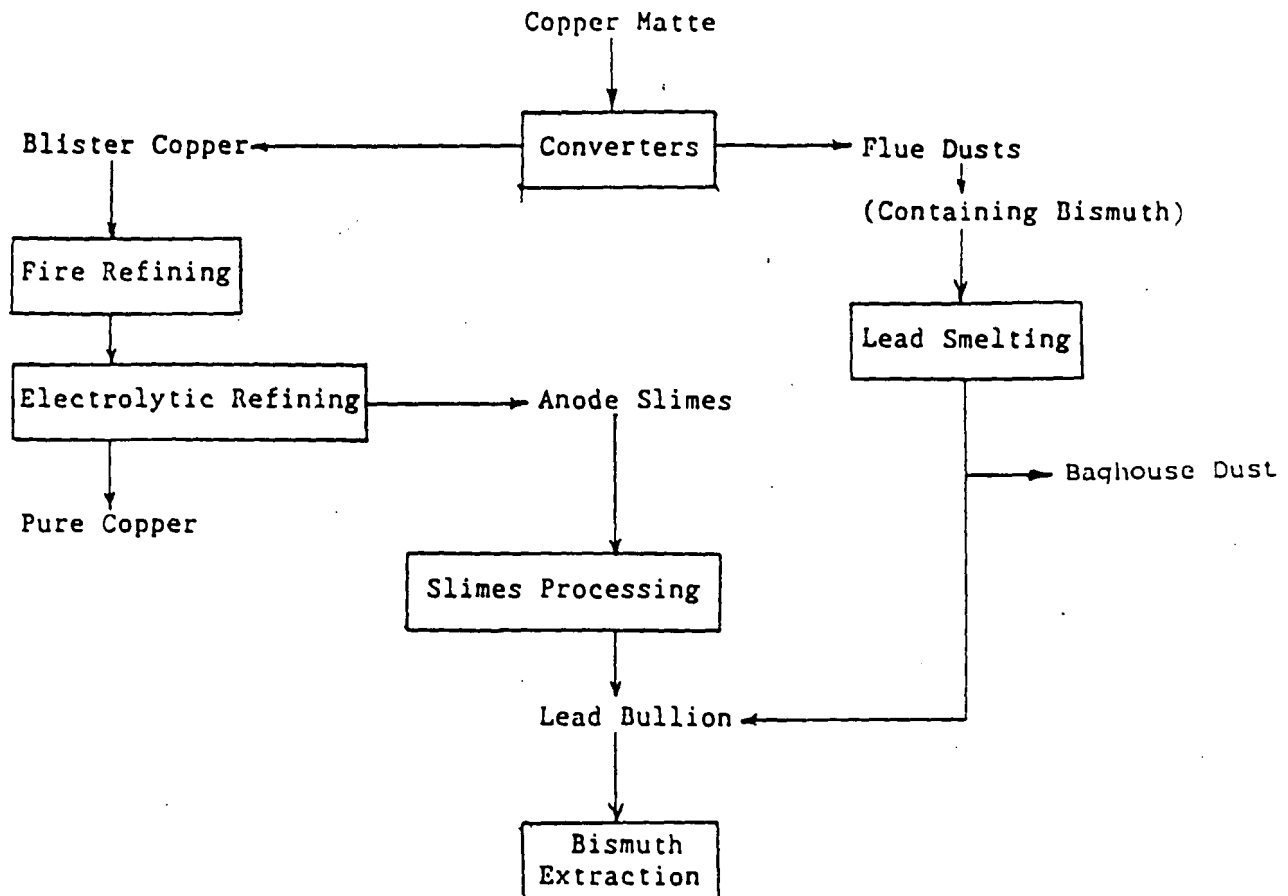


Figure 3-18

BISMUTH
BETTERTON-KROLL PROCESS

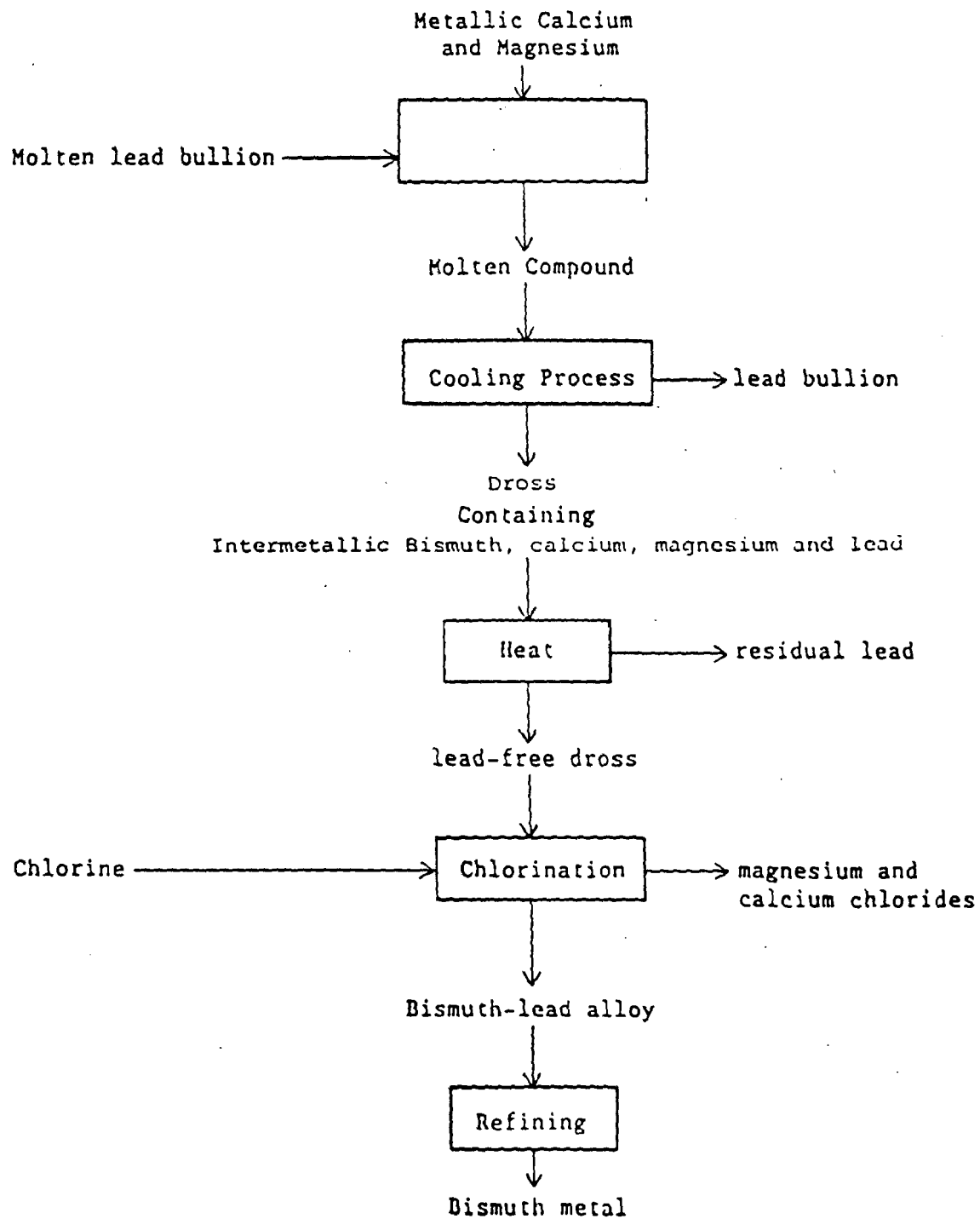
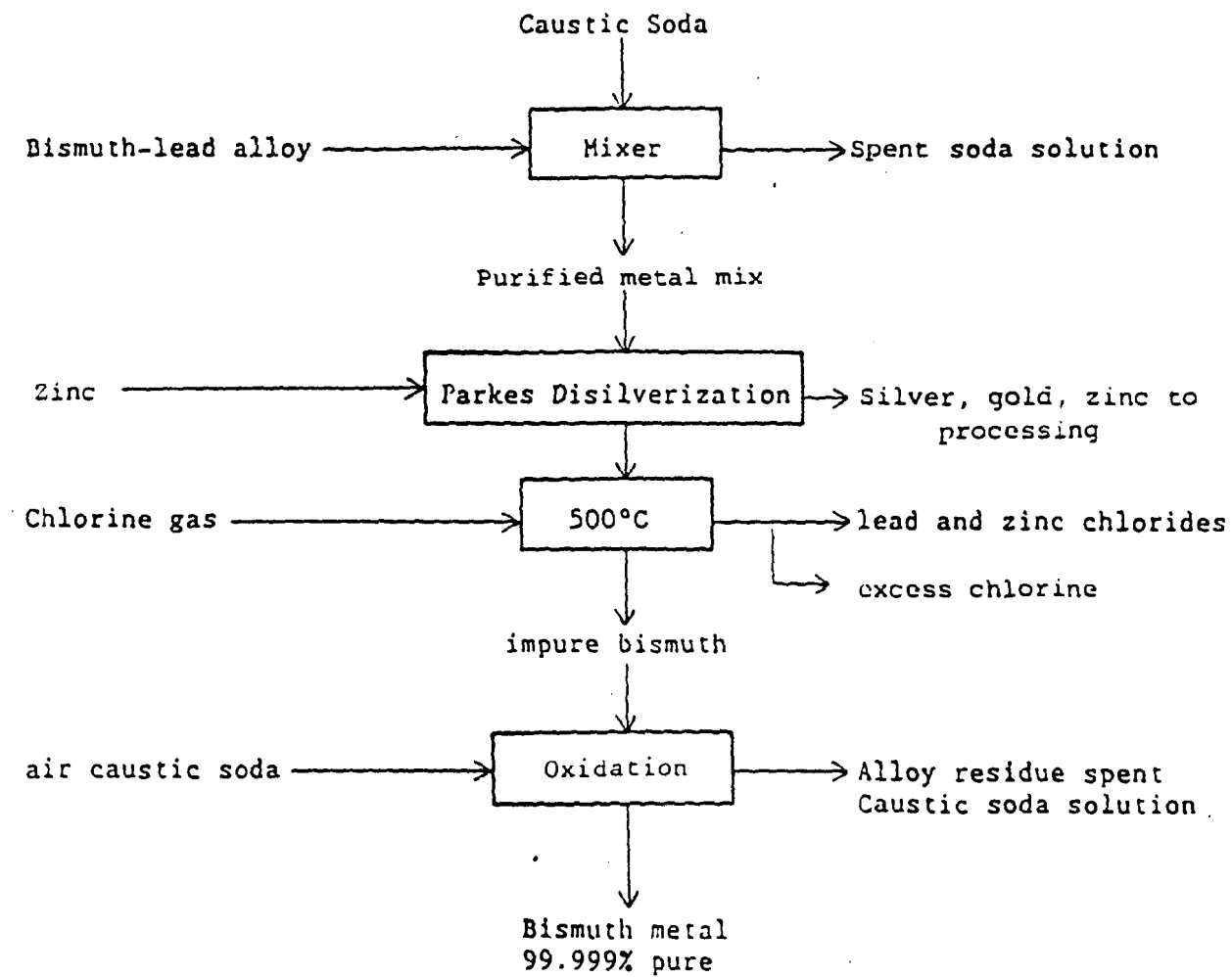


Figure 3-19

BISMUTH
REFINING



The Betts electrolytic process (Figure 3-20) begins with a lead bullion, 90 percent lead, with impurities such as silver, gold, tin, bismuth, copper, etc. The lead bullion is cast into anodes and set in parallel in an electrolytic cell. Thin sheets of pure lead are hung from conductor bars as cathodes. Then several cells are connected electrically in series. The electrolyte solution is a mix of lead fluosilicate and fluosilic acid with glue. A direct current is run through the cells. The lead from the anodes is dissolved and deposited on the cathodes, the impurities are left as a slime on the anodes. The cathodes are removed, washed, dried, and melted to produce slag and metal. The slimes are also washed, dried, and melted. The metal formed is melted and treated by selective oxidation to remove arsenic, antimony, and some lead. The metal is then sent to a cupel furnace to form silver and gold done by further oxidation. The cupel slags, rich in bismuth, are crushed, mixed with sulfur, and reduced with carbon to a copper matte and impure bismuth metal. This impure bismuth is refined in the same way as that from the Betterton-Kroll process.

Extraction of bismuth from roasted tin concentrates and other bismuth containing material is accomplished by leaching with hydrochloric acid as shown in Figure 3-21. The acid leach liquor is clarified, diluted with large volumes of water, and bismuth is precipitated as bismuth oxychloride. For purity, the bismuth oxychloride is redissolved in hydrochloric acid and reprecipitated. Wet bismuth oxychloride can be reduced after drying and mixing with soda ash and carbon, or by way of iron and zinc in the presence of hydrochloric acid.

Since bismuth is produced as a byproduct of copper, tin, and lead-zinc ores, mining wastes are not of consequence here. However, in the extraction methods, electrolysis and leaching, strong acids, and sodas are used which could result in waste caustic sodas, electrolytic slimes, and waste acids (Table 3-7). Therefore, further investigation for possible regulation under Subtitle C is recommended.

Figure 3-20

BISMUTH
BETTS ELECTROLYTIC EXTRACTION

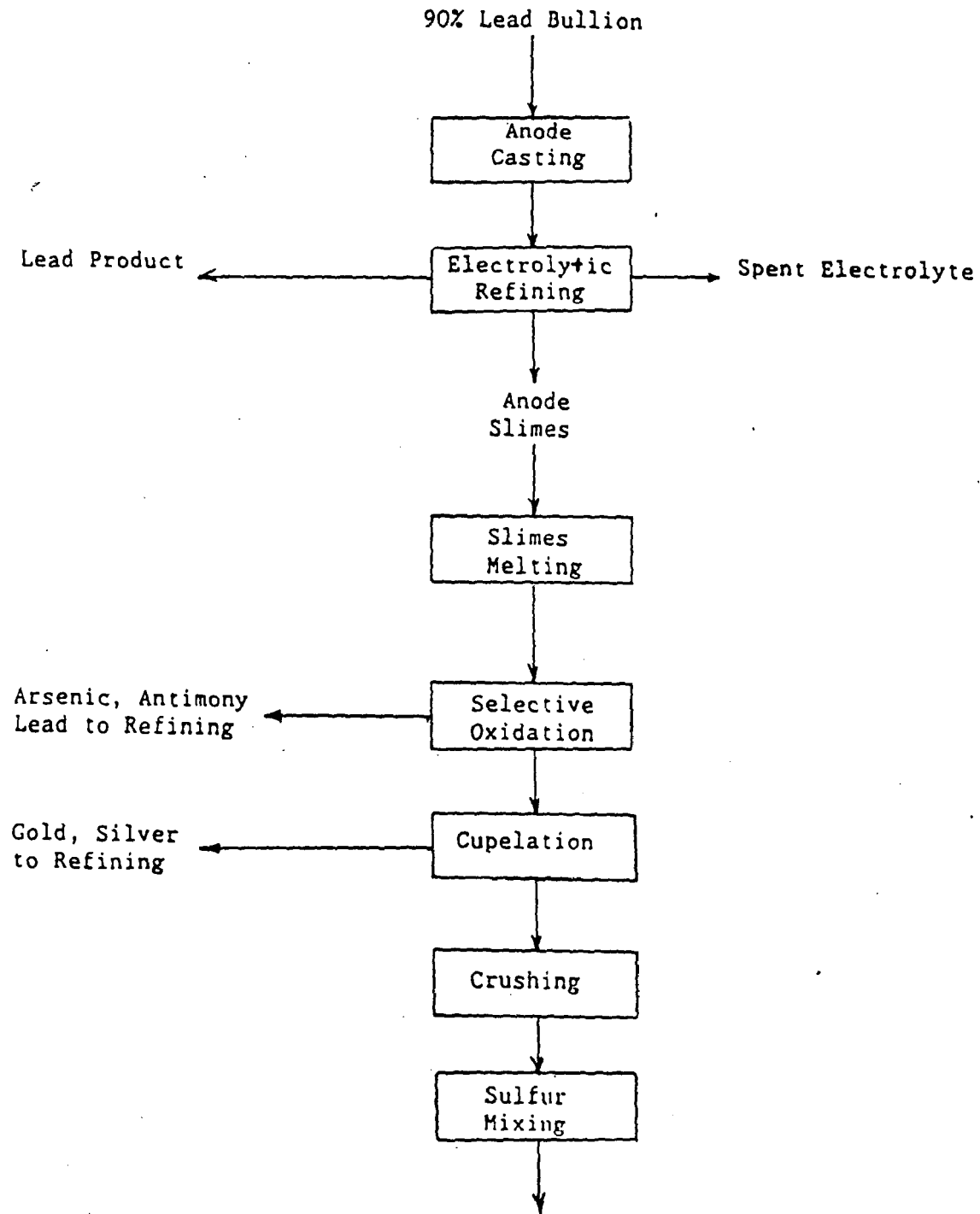


Figure 3-20 (continued)

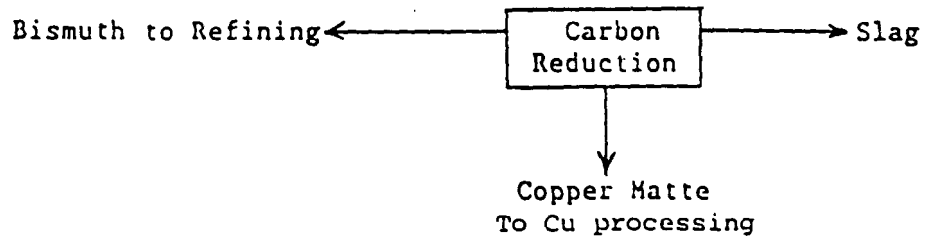
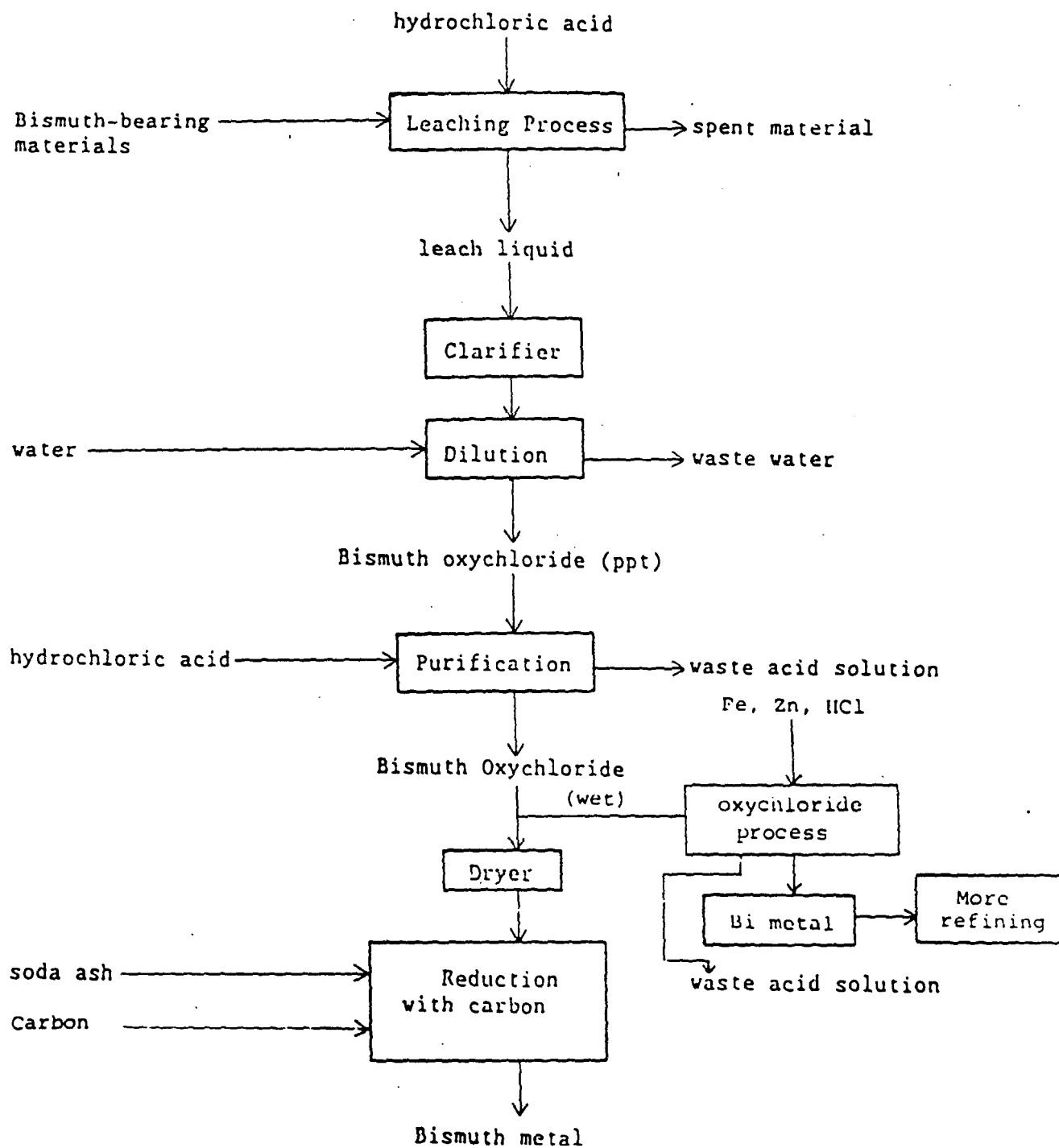


Figure 3-21

BISMUTH
BISMUTH-BEARING MATERIALS



BISMUTH WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
From Copper	--					
Betts Electrolytic Process	1) Spent Electrolytic Solution	N	?	N	?	
	2) Spent Cupel Slag	N	N	N	?	
	3) Spent Soda Solution	N	?	N	?	
	4) Alloy Residue	N	N	N	?	
	5) Caustic Soda Solution	N	?	N	?	
Betterton-Kroll Process	1) Magnesium and Calcium Chlorides	N	N	N	N	
	2) Spent Soda Solutions	N	?	N	?	
	3) Alloy Residue	N	N	N	?	
	4) Caustic Soda Solution	N	?	N	?	
Leaching from Bismuth-bearing Materials	1) Spent Materials	N	N	N	?	
	2) Wastewater (dilution)	N	?	N	?	
	3) Waste Acid Solution (purification)	N	?	N	?	
	4) Waste Acid Solution (reduction)	N	?	N	?	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability, and EP Toxicity as defined in 40 CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

REFERENCES

Bureau of Mines, Mineral Commodities Summary, 1987.

Marks, H.W., Encyclopedia of Chemical Technology, 1978.

CADMIUM

Cadmium is a soft, ductile, silver-white metal, originally discovered as an impurity in zinc carbonate. Cadmium usually occurs in its +2 oxidation state in compounds and there are eight natural isotopes. The metal readily reacts with halogens, phosphorous, selenium, sulfur, and tellurium when heated. Cadmium is resistant to alkali and salt water, is ductile, and has good solderability.

Cadmium is primarily used as an electroplated coating on steel and cast iron parts for corrosion resistance. The metal exhibits an ability to deposit uniformly on intricate objects. Cadmium plate is generally applied from a cyanide bath, but vacuum deposition, dipping, spraying and mechanical (powder) plating are also used.

In the production of rechargeable nickel-cadmium and silver-cadmium batteries, cadmium is the negative electrode. The metal is also used in brazing and fusible alloys. Silver containing cadmium oxide is used in the production of electrical contacts, and cadmium intermetallic compounds with sulfur, selenium or tellurium are used to produce semiconductors.

Cadmium compounds are used as pigments in glass, glazes, paints, inks, plastics, ceramics, and other products. Cadmium is also used as a stabilizer in the production of plastics.

The cadmium concentration in the earth's crust is between 0.1 and 0.5 ppm. Cadmium is found in association with zinc in the form of cadmium sulfide. Minerals containing cadmium are found in zinc-rich basic, basaltic rocks, deposits of zinc-lead-copper sulfides, and coal deposits.

Domestic production of cadmium is dependent upon the processing of zinc ore. Currently U.S. demand for cadmium metal exceeds domestic production.

Cadmium-bearing precipitate, an intermediate from electrolytic zinc ore processing, is dissolved in a mixture of spent electrolyte from the zinc plant, sulfuric acid and spent cadmium electrolyte as shown in Figure 3-22. The cadmium is sponged to zinc by galvanic precipitation. The sponge is dissolved in spent cadmium electrolyte and sulfuric acid. This solution is mixed with electrolyte to form a cell electrolyte. The solution is electrolyzed by silver-lead anodes and aluminum cathodes. Cathode deposits are stripped and are washed, dried and melted under sodium hydroxide, which prevents oxidation and removes waste metals (Zn, As). The metal is then cast into commercial shapes.

Cadmium-bearing flue dust is mixed with concentrated sulfuric acid and the mixture is roasted in a kiln or reverberatory furnace (Figure 3-23). From there it goes to a crusher. The crushed mixture is then leached with water and sulfuric acid to remove volatiles. The resultant mixture is purified to remove heavy metals. It is filtered and purified a second time. In this process, three alternatives of recovery are possible. Alternative 1 (Figure 3-24) is galvanic precipitation with zinc and is taken prior to any purification. Alternatives 2 (Figure 3-24) and 3 (Figure 3-25) are taken after filtering the second purification solution. Alternative 2 is galvanic precipitation with zinc. Alternative 3 is electrolysis, which is the more commonly used method.

Recovery of cadmium results in waste leach and purification solutions, various metal cakes, and electrolytic slimes toxic recharge (Table 3-8). Cadmium itself is a toxic metal and care must be exercised in its handling. Further study of the recovery of cadmium for potential regulation under Subtitle C is recommended.

Figure 3-22

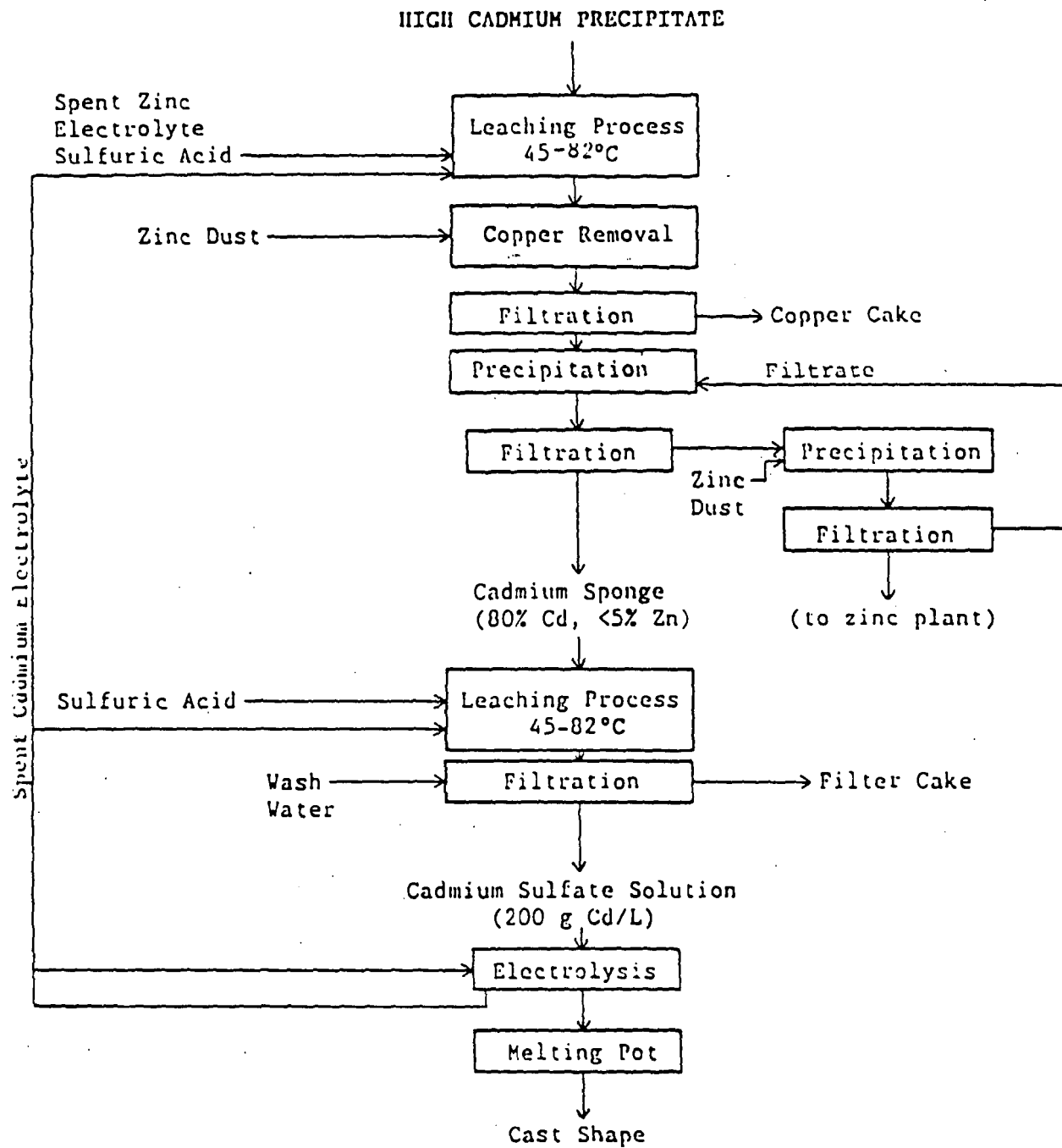


Figure 3-23

CADMIUM-BEARING FLUE DUST

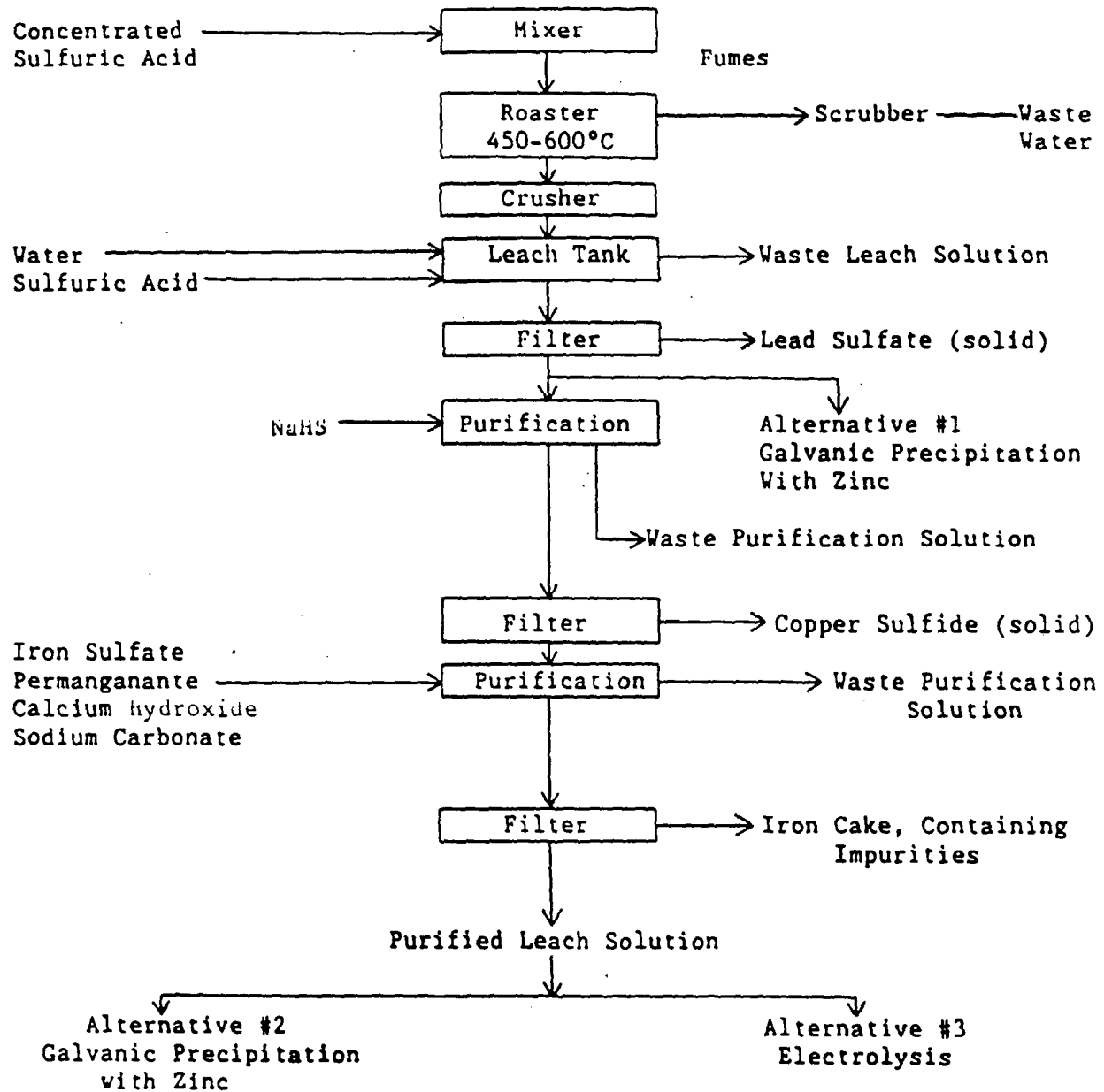


Figure 3-24
CADMIUM PROCESSING
ALTERNATIVES #1 & 2
GALVANIC PRECIPITATION WITH ZINC

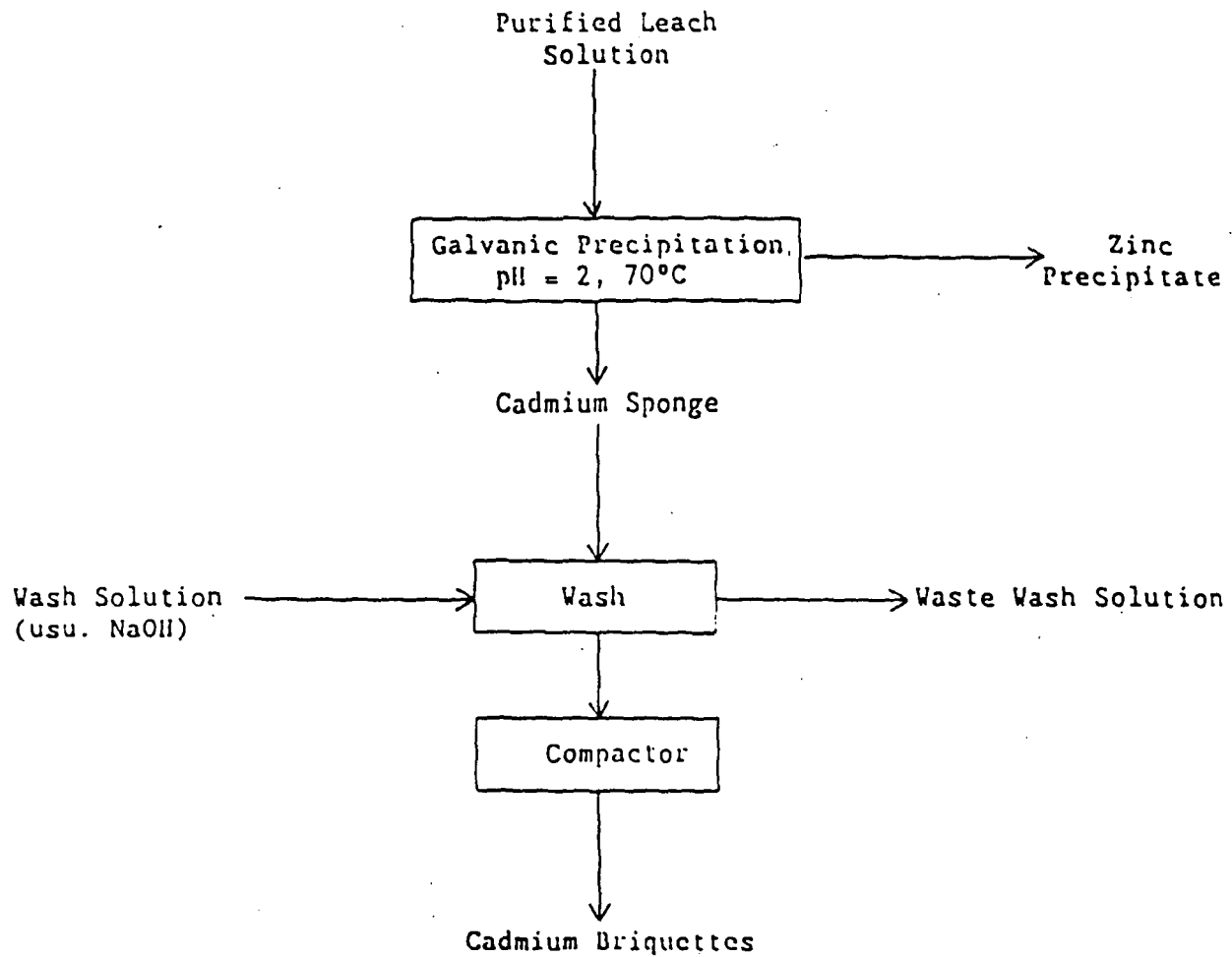


Figure 3-25

CADMIUM PROCESSING
ALTERNATIVE #3
ELECTROLYSIS

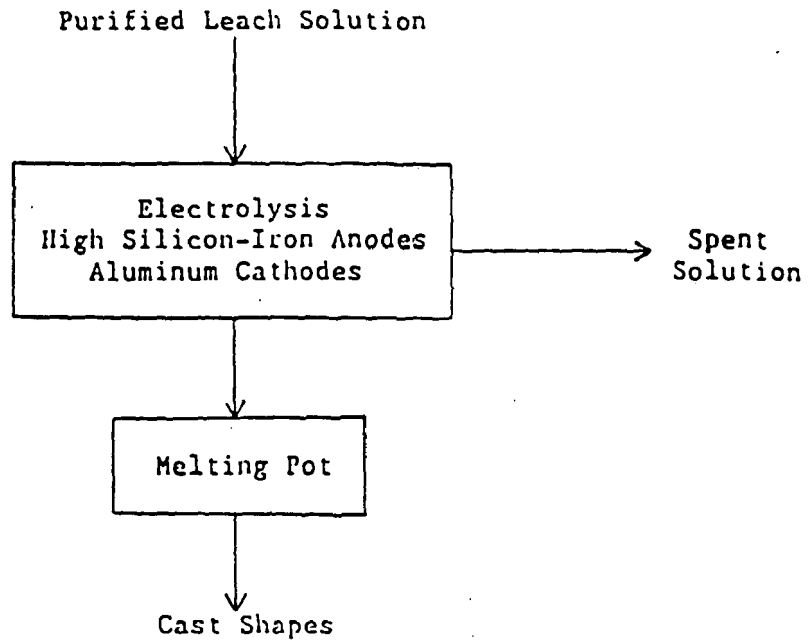


Table 3-8

CADMIUM PROCESSING WASTES

Process	Waste	Possible RCRA Characteristics				Comments
		R	C	I	T	
Cadmium Recovery from Precipitate	Copper Removal Filter Cake	N	N	N	?	
	Post-Leach Filter Cake	N	N	N	?	
Cadmium Recovery from Flue Dust	Scrubber waste water	N	?	N	?	
	Leach Solution	N	?	N	?	
	Lead Sulfate Filter Cake	N	N	N	?	Contains Lead
	1st Purification Solution	N	?	N	?	
	Copper Sulfide Filter Cake	N	N	N	?	
	2nd Purification Solution	N	?	N	?	
	Iron Cake	N	N	N	?	
A. Galvanic Precipitation with Zinc	Precipitate	N	N	N	?	
	Caustic Wash Solution	N	?	N	?	
B. Electrolysis	Spent Electrolyte	N	?	N	?	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability, and EP Toxicity as defined in 40 CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

REFERENCES

Cadmium Association, Cadmium Council, and International Lead Zinc Research Organization; Cadmium 77, Edited Proceedings First International Cadmium Conference San Francisco; Metal Bulletin Limited; London, England; 1977.

Mark, H.F., ed.; Encyclopedia of Chemical Technology, 3rd edition; Wiley-Interscience, New York, New York; 1978.

U.S. Bureau of Mines; Mineral Commodities Summary 1987; U.S. Bureau of Mines; 1987.

CESIUM

Cesium is a ductile alkali metal which melts near room temperature. Its properties are similar to those of other alkalis, particularly potassium and rubidium. The metal oxidizes readily and ignites spontaneously in air. The main use of cesium is as a fluid in several proposed power generation systems, including ion propulsion, and thermionic, turboelectric, and magnetohydrodynamic systems. All of these are strictly in the research and development stage. Cesium is also used in the production of vacuum tubes, photoelectric cells, and in vapor glow lamps.

The only producer of cesium in the United States is Kawecki Berylco Industries, Inc., located in Revere, Pennsylvania. The ore used to obtain cesium is pollucite ($\text{Cs}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$). All of the pollucite used is imported from the Tantalum Mining Corp., Manitoba, Canada.

The primary method of cesium recovery from pollucite is shown in Figure 3-26. Raw ore initially undergoes grinding and is mixed with water to produce a slurry. Froth flotation is then used to produce a concentrate which is acidified with sulfuric acid. Waste gangue from the flotation is discarded. The acidified pump concentrate is treated with hydrofluoric acid, aluminum sulfate, and a cationic reagent such as a cocoamine acetate for conditioning. The conditioned pulp then undergoes another stage of froth flotation, through which relatively pure pollucite is obtained. All of the non-pollucite minerals are separated during the froth flotation and are discarded as waste. The concentrated pollucite is then digested with an acid, producing a cesium salt solution which is evaporated to yield dry cesium salt. Acid digestion produces a solid waste stream containing the metals and other impurities which were generated during final decomposition of the pollucite.

The mining of raw ore for cesium recovery is straightforward and it is unlikely that the wastes produced are hazardous (Table 3-9). The

Figure 3-26

CESIUM RECOVERY FROM POLLUCITE ORE

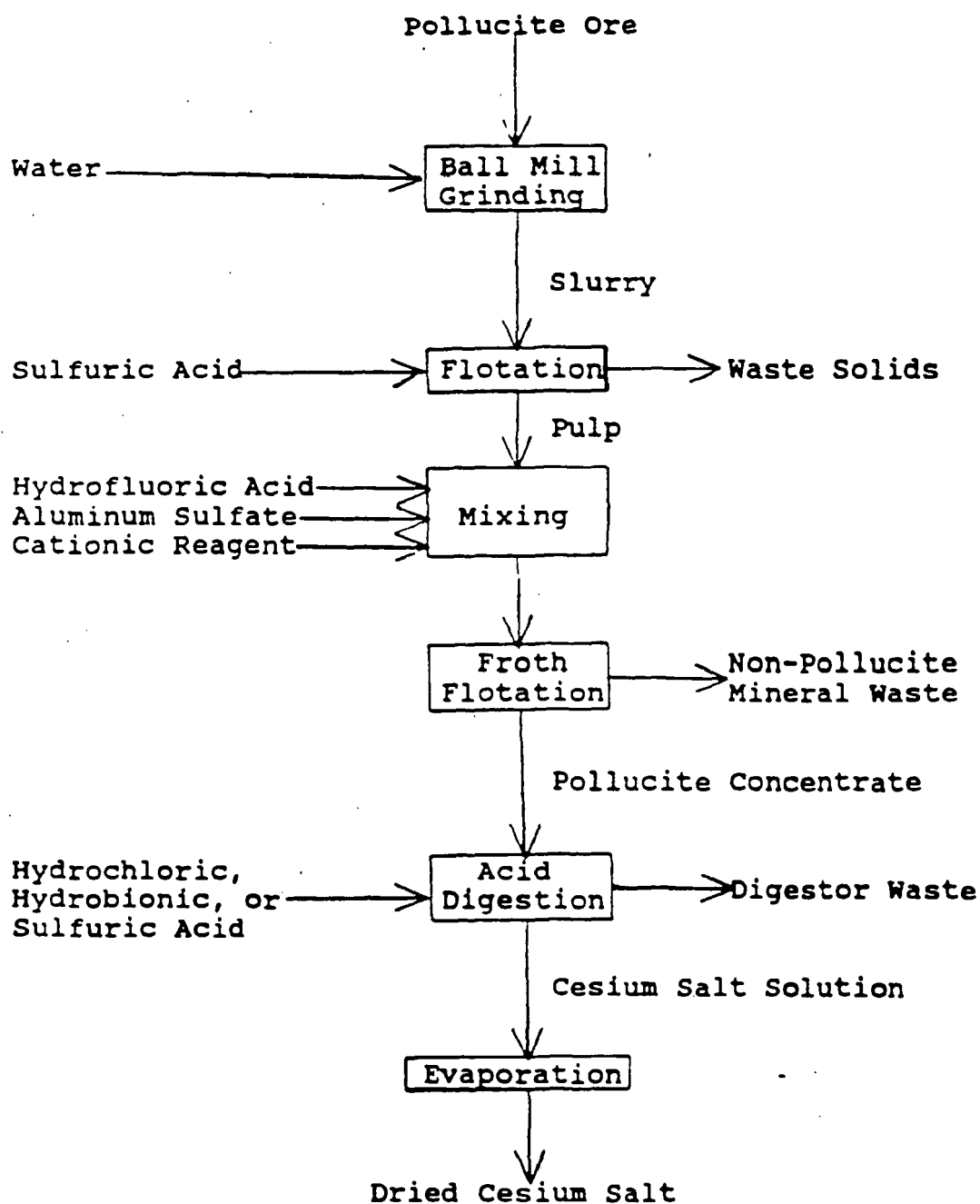


Table 3-9
CESIUM WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Flotation	1) Waste Solids	N	?	N	?	
Froth Flotation	1) Non-Pollucite Mineral Waste	N	?	N	?	
Acid Digestion	1) Digestor Waste	N	?	N	?	
Hydrolysis	1) Wastewater	N	?	N	N	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

processing and refining of cesium from the ore concentrate involves the use of several acids and other chemical reagents. The reagents used, as well as the quantities and characteristics of the wastes produced, were not identified. It is possible that the wastes produced during the final stages of cesium salt refining may have hazardous characteristics. Since only one company processed cesium, production rates and raw material consumption rates were withheld to protect company proprietary data. Thus, it is uncertain whether or not wastes are being produced in quantities large enough to warrant further investigations. Assuming substantial quantities of wastes with potentially hazardous characteristics are being generated, further investigation for possible regulation under Subtitle C is recommended.

REFERENCES

Bureau of Mines, Mineral Commodities Summary; 1987.

Marks, H.F., Encyclopedia of Chemical Technology; 1978.

CHROMIUM

Chromium is a strategic metal used in a number of industrial and commercial applications. Its most important properties are its resistance to heat, abrasion, corrosion, and oxidation in alloys. Approximately 50% of the chromium consumed in the U.S. is used as an alloying metal for stainless and heat-resistant steel. Other uses for the metal are as a constituent in pigments and dyes, in the chemical and photographic industries, in metal plating, as an alloying element in other ferrous and nonferrous alloys and in refractory materials.

Currently, the United States has no chromium ore reserves. The U.S. is dependent on imports for all of its chromium consumption. In 1986, 87,000 short tons of chromium were produced from secondary sources and 436,000 tons were imported. Since the beneficiation and processing of chromium ore has become technically and economically favorable for many of the countries with chromium ore, the U.S. is importing increased amounts of refined materials, such as ferrochromium. The U.S. will continue to import chromite ore for processing domestically, although the trend is to import less ore and more ferrochromium.

Chromite ore imported to the U.S. is used in basic refractories with various mixtures of chromite and magnesia. Roughly 80% of the basic refractories are used in producing steel. They are used in open hearth and in electric arc steelmaking furnaces. The wastes from the manufacturing of these refractory materials are expected to be minimal. There is a possibility that they could exhibit hazardous characteristics, particularly EP toxicity. This is due to leachable chromium from the chromite or from chromic acid, which is used as a binder in some refractory materials. It is possible that there is no waste production, because all materials could be recycled into the main product.

Ferrochromium is produced by the reduction of chromite with coke in an electric arc furnace. Carbon, or silicon is used as the reducing agent, depending on the quality of ferrochromium desired. Slag consisting of aluminum or silicon oxides is the significant waste expected from this process. This slag is not expected to exhibit any hazardous characteristics.

The chromite refractory industry could generate wastes with hazardous characteristics (Table 3-10). Therefore, further study of that industry for potential regulation under Subtitle C is recommended.

Table 3-10

CHROMIUM WASTES

Process	Waste	Possible RCRA Characteristics*				
		R	C	I	T	Comments
Chromite Refractory Manufacturing	Refractory Wastes	N	?	N	?	Chromium and Chromium Acid

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

COLUMBIUM AND TANTALUM

Columbium (Niobium) and tantalum are generally found together in nature as oxides and hydroxides in association with other metals such as tin, titanium, and the rare earth elements. Columbium and niobium are synonyms for the same element. Niobium is the name officially adopted by the International Union of Pure and Applied Chemistry, but the metallurgical industry has persisted in the use of the term columbium, which is used in this report. Ores of commercial significance include pyrochlore $((\text{Na,Ca})_2(\text{Nb,Ti,Ta})_2[\text{OF,OH}]_7)$, and columbite-tantalite $((\text{Fe,Mn})(\text{Nb,Ta})_2\text{O}_6)$, (Marks, 1978). Pyrochlore is the most abundant mineral containing columbium and is found most often in carbonatite and alkalic rocks. Pyrochlore contains very little tantalum. Columbite and tantalite are at the ends of an isomorphous series varying in composition from columbium dominated to tantalum dominated with the name indicating which metal dominates. Columbite-tantalite is obtained as a by-product of other metal mining, mainly tin. Tin slags produced from foreign tin smelting are also an important source of tantalum. The U.S. resources of columbium and tantalum are low grade and are at present uneconomical for mining. Therefore all columbium and tantalum production is from imported raw materials (EPA, 1983). There are currently 7 companies operating 8 columbium and tantalum producing plants in the U.S. These plants are located in the eastern, central, and western United States, and process less than 5 million pounds of columbium and tantalum raw materials annually (Bureau of Mines, 1987).

Columbium is a relatively low density metal exhibiting high strength at high temperatures, retained plasticity at cryogenic temperatures, and corrosion resistance. The principal use of columbium is as an additive in steel making to improve the mechanical properties of the steel alloy. Columbium is also an important alloying element in nickel-, cobalt-, and iron-based superalloys used in gas turbine engine components and other aerospace applications. Columbium/tantalum alloys are used in the chemical

and electrical industries as plating material because of its resistance to corrosion when in contact with strong acids and oxidants.

Tantalum has similar chemical and physical properties to that of columbium, and like columbium it is used in making high temperature alloys (super alloys). Tantalum carbide is used in tools and dies because of its hardness and strength. Tantalum oxide is a component of high grade optical glass. The most wide spread use of tantalum is in the production of electronic components, particularly capacitors. Tantalum also finds use as a construction material in the chemical industry because of its resistance to corrosion and its high thermal conductivity and mechanical strength (Miller, 1959).

Because columbium and tantalum co-occur in ores and slags, they must first be separated. Separation and processing consists of 4 primary operations:

- digestion of the ore (formation of niobium and tantalum salts);
- separation of niobium from tantalum;
- separation of impurities reduction of the salts to the elemental form (metal);
- fabrication (production of ingots, bars, or plates).

Plants in the U.S. will include either the first two operations, the last two operations, or all four operations. The first two operations are shown in Figure 3-27.

Digestion is necessary to release the niobium and tantalum (as salts) from the ores. This is almost universally done by leaching the ores with hydrofluoric acid (HF) to form columbium and tantalum salts. A residual solid waste (gangue) is produced and wet scrubbers used to control acid mists produce a wastewater stream.

Tantalum is separated from columbium by exploiting the varying solubility of each metal in methyl isobutyl ketone (MIBK) as a function of hydrogen ion content of the mother liquor. At low normalities of HF, tantalum is selectively extracted into the MIBK, and subsequently the normality of the solution is increased for extrication of columbium into fresh MIBK. The wasted mother liquor (raffinate) and wastewater from a wet scrubber that controls releases of organic vapors are the two waste streams produced in this operation. Deionized water is used to extract the niobium and tantalum from the MIBK.

Niobium and tantalum are then each precipitated as salts. Niobium is precipitated by addition of ammonia to produce columbium oxide. Tantalum is precipitated by addition of potassium chloride or fluoride to produce potassium fluortantalate (K-Salt, K_2TaF_7) or by the addition of ammonia to produce tantalum oxide. The salts are filtered and the discarded filtrate is a wastewater stream. Drying of the salts produce other wastewater streams, because of the use of wet scrubbers to control dust emissions.

Tantalum metal powder is produced by sodium reduction from K-Salt. Sodium reduction consists of placing alternating layers of the K-Salt and elemental sodium in a reactor, igniting the material to initiate the exothermic reduction process, passing the material through a magnetic separator to remove iron impurities picked up in the reaction vessel, and then leaching with water and acid to produce the purified product. Waste streams are generated from leaching, the magnetic separator, and wet scrubbers on the reactor.

Ferro-columbium, nickel-columbium, and columbium metal are produced by aluminothermic reduction of columbium oxide. The aluminothermic reduction processes are similar to the sodium reduction process with the exception that aluminum is the reductant added to the columbium oxide. In the aluminothermic reaction, potassium chlorate is added to improve the exothermic release of heat and the mixture is ignited with magnesium metal. Ferro-columbium produced from pyrochlore is converted to columbium oxide by

a chlorination process. This oxide is used as a feed to aluminothermic reduction. During carbon reduction, also known as the Balke process, fine carbon is added to the oxides of niobium or tantalum and the mixture is heated to 1,800°C in a vacuum. This produces the metal carbide that is subsequently converted to niobium or tantalum metal by reaction with an excess of the metal oxide. The process releases carbon monoxide. It is assumed that leaching of the metals produced by the aluminothermic and carbon reduction processes is similar to that of the sodium reduction process. This would generate wastewater streams.

Electrolytic reduction is used for tantalum where potassium fluorotantalate is directly reduced to tantalum metal at a carbon cathode. The cathode and plated metal are pulverized and the carbon leached out with acid thus generating a waste stream.

Fabrication generally involves an ultra purification step to maximize the malleability and ductility of columbium and tantalum. The most widely used purification process is electron beam melting. A high voltage, low current electron beam is focused on the metal which causes melting and vaporization of contaminants. The melted metal is cooled in water for resolidification and casting. This water is wasted representing another waste stream.

EPA has extensively studied the niobium and tantalum processing industry in order to propose Clean Water Act effluent guidelines and new source performance standards for direct dischargers, or pretreatment standards for discharge to municipal sewers (EPA, 1983). The following information is based on the information collected by EPA, and refers to the flow sheet in Figure 3-24.

Wastewater 1, in Figure 3-24 which consists of the gangue waste and the wet scrubber wastewater in the digestion stage, is acidic (pH 2), has concentrations of fluoride greater than 10,000 mg/l, contains copper, lead, and zinc at concentrations from 300 to 1,000 mg/l, cadmium at 40 mg/l, and 1,2-dichloroethane and chloroform concentrations at or around 100 ug/l.

There is no data on the specific characteristics of wastewater 2, the solvent extraction wet scrubber waste, because EPA sampled only a mixture of this water and wastewater 1.

Wastewater 3 raffinate waste had chloroform concentrations ranging from 34 to 240 ug/l, chrome at 1,000 mg/l, lead averaging 500 mg/l, selenium 45 mg/l, zinc 433 mg/l, and arsenic 27 mg/l. This wastewater had a pH of approximately 2.

The most notable characteristic of wastewater 4 from niobium precipitation was its high ammonia content (approximately 500 mg/l).

Data exist on the characteristics of a mixture of wastewater 5 and the leaching wastewater from columbium and tantalum reduction. The average chloroform and 1,2-dichloroethane concentrations were 61 and 23 ug/l, respectively. Chrome, nickel, and lead occurred at 1 mg/l, and fluoride concentrations were 3,000 mg/l.

Clearly many of these waste streams have RCRA hazardous waste characteristics, however, all of these streams are presumably regulated under the Clean Water Act. These wastes, once treated, will likely meet the exemption of 40 CFR 261.3(a)(2)(iv) and otherwise not have Subpart C characteristics (Table 3-11). However, the sludges generated from the treatment of these wastes may have hazardous characteristics and therefore further study for potential regulation under Subtitle C of RCRA is recommended.

Table 3-11
COLUMBIUM, TANTALUM WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Digestion	Scrubber, cooling liquor	N	?	N	?	
	Barren solids	N	?	N	?	
Solvent Extraction	Scrubber liquor	N	?	N	?	
	Raffinate	N	?	N	?	
Precipitation	Precipitation Barrens	N	?	N	?	
Calcination	Scrubber liquor	N	?	N	?	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability, and EP Toxicity as defined in 40 CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

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GALLIUM

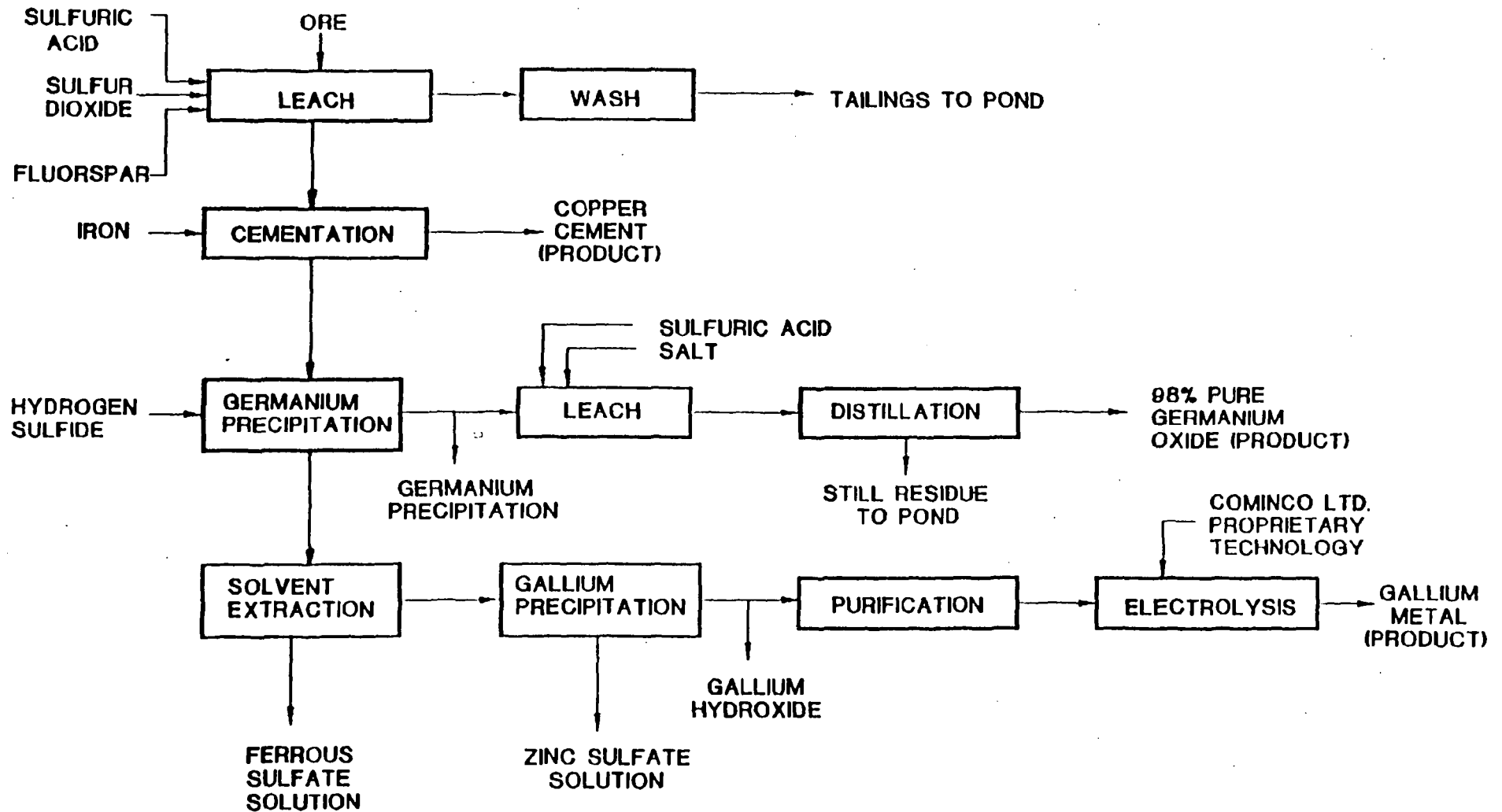
Gallium is one of only four metals which can be a liquid near room temperature, and it has the longest temperature range in which it is a liquid of any element. Roughly 95 percent of the gallium used in the United States is in chemical compounds, mainly gallium arsenide and gallium phosphide. These semiconducting compounds exhibit electroluminescence and are used in semiconductors, light emitting diodes, laser diodes, and in other electronic applications.

There is one producer of gallium from a domestic mine in the United States. Musto Exploration Limited operates a mine and extraction plant for gallium and germanium at St. George, Utah. This is reportedly the only operation in the world producing these metals as primary products. Another company, Eagle-Picher Industries produces gallium from imported and recycled materials in Quapaw, Oklahoma. Actual production figures for these plants were withheld to protect company proprietary data, but the Musto plant has a rated capacity of 9,000 kilograms of gallium per year. Imports of gallium materials in 1986 were estimated at 17,000 kg with reported consumption being 15,000 kg.

The process used by the Musto Co. at St. George, Utah for gallium and germanium recovery is outlined in Figure 3-28. Ore is leached with sulfuric acid, sulfur dioxide and fluorspar. The fluorspar would react with the sulfuric acid to form hydrofluoric acid. The solids that remain after leaching are washed to remove the leach liquor and then are placed in a tailings pond. If the washing is effective, the tailings (waste 1) would not exhibit any hazardous characteristics. Otherwise, acid remaining in the tailings could cause them to exhibit the characteristic of corrosivity (pH less than 2). The leach liquor from the leaching process contains copper which is removed by cementation. In the cementation step, the solution is brought into contact with iron scrap. The copper in solution exchanges with the metallic iron leaving metallic copper precipitate and

Figure 3-28

PROCESS FLOW SHEET FOR GALLIUM AND GERMANIUM PRODUCTION



the iron in ionic form in solution. The cemented copper is removed and sold as a product.

The next step in processing of the leach liquor is to precipitate germanium by reacting the solution with hydrogen sulfide. The germanium is removed and sold or refined and sold. The leach liquor goes onto a solvent extraction step where gallium is extracted from the leach liquor by an organic solvent. The leach liquor is now barren ferrous sulfate solution of low pH which could exhibit hazardous characteristics and could be a problem if disposed. The gallium in the organic solvent is stripped out into another aqueous solution and the organic solvent is recycled. The solvent is typically dissolved in an organic carrier, often kerosene. When any of the solvent in the organic carrier is disposed, it would be ignitable. Ammonia is added to the strip solution, which causes precipitation of gallium hydroxide. As shown in Figure 3-28, the solution left after the gallium hydroxide precipitates is described as a zinc sulfate solution. The exact composition and disposition of this material was not specified in the references.

The gallium hydroxide passes onto purification and proprietary electrolysis stages with the final product being gallium metal. No information was available on the characteristics or disposition of any wastes from those processes.

The plant in Quapaw, Oklahoma processes primarily secondary materials and therefore is not included in this study.

The characteristics of the wastes from gallium production are summarized in Table 3-12. Several of these streams may exhibit hazardous characteristics. Therefore further study of gallium production for possible regulation under subtitle C is recommended.

Table 3-12
GALLIUM WASTES

Process	Waste	Possible RCRA* Characteristics				Comments
		R	C	I	T	
Musto Exploration Leaching	Tailings	N	?	N	N	
Solvent Extraction	1) Ferrous Sulfate Solution	N	?	N	?	May not be waste
	2) Solvent and carrier	N	N	?	N	
Gallium Precipitation	Zinc Sulfate Solution	N	N	N	?	May not be waste

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

REFERENCES

Bureau of Mines, Mineral Commodities Summary, 1987.

Marks, H.W., Encyclopedia of Chemical Technology, 1978.

GERMANIUM

Germanium is a metalloid with highly desirable electrical and optical properties. Its transparency to infrared wavelengths, high refractive index, low dispersion, and moderate strength account for its widespread use in infrared optics and fiber optic systems. It is also used as a semiconducting material in electronics, and as a semiconductor substrate. Small amounts of germanium are also used in catalysts, chemotherapy, and metallurgy.

Germanium is produced by three refineries in New York, Oklahoma, and Pennsylvania. Germanium-bearing residues from zinc ore processing at Clarksville, Tennessee, are sent to Belgium for germanium recovery. At St. George, Utah, germanium is recovered as one of two primary products along with gallium at Musto Exploration's Apex mine. Most coals contain small quantities of germanium, which become concentrated in the ash and dust during coal burning. While the recovery of germanium from coal ash and flue dust is not currently economically practical, it was practiced for several years in the 1950's, and it is considered a possible future source of germanium.

A simplified process flow diagram for the recovery of germanium during zinc ore processing is shown in Figure 3-29. The ore is roasted and sintered (solidified). Sintering fumes, containing oxidized germanium, are collected in a bag house. The sinter fumes are leached with sulfuric acid, producing a leaching solution containing the germanium. The germanium is then selectively precipitated by the addition of zinc dust. The solids remaining after leaching, as well as the wastewater leaving the precipitation process, may contain small amounts of arsenic and other metals. The solids will be recycled to maximize the recovery of germanium.

The germanium recovery process used by Musto Exploration at St. George, Utah is outlined schematically in Figure 3-30. In this process the ore and

Figure 3-29

RECOVERY OF GERMANIUM DURING ZINC ORE PROCESSING

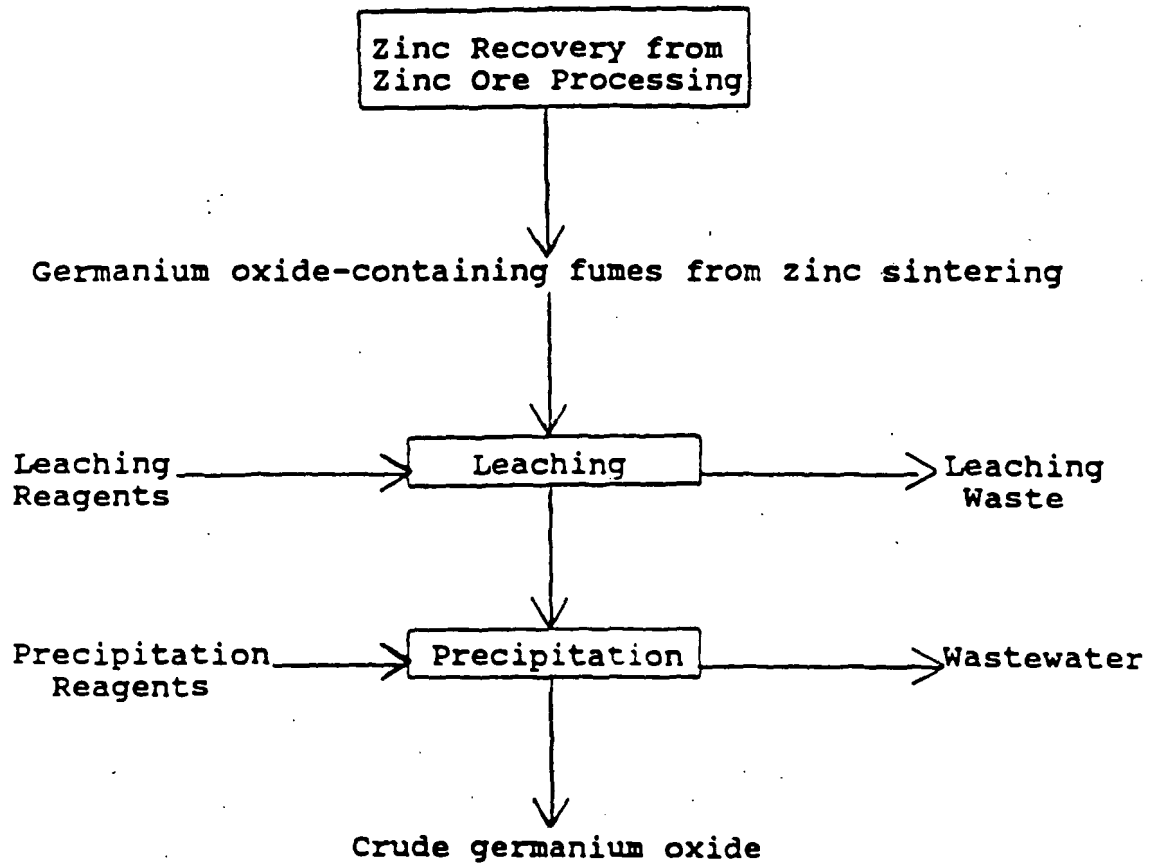
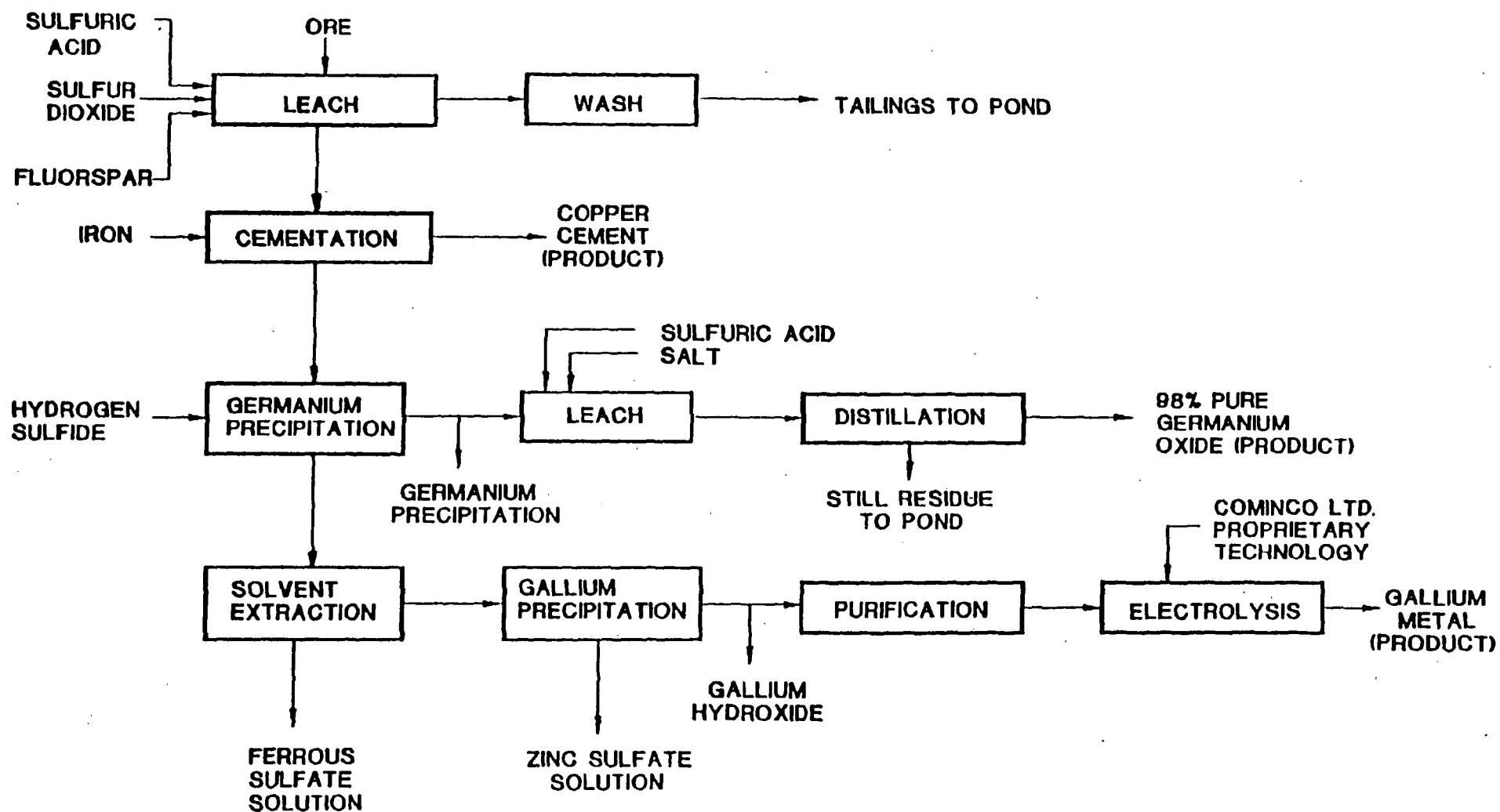


Figure 3-30

PROCESS FLOW SHEET FOR GALLIUM AND GERMANIUM PRODUCTION



fluorspar are leached with sulfuric acid and sulfur dioxide. The fluorspar will form hydrofluoric acid which assists in leaching the germanium and gallium. The residual solids after leaching are washed and disposed in a tailings pond. These tailings could still contain acid if the washing is not adequate. Copper is removed from the leachate by cementation on iron and is sold as a byproduct. Hydrogen sulfide is used to precipitate the germanium. Gallium is recovered from the remaining supernatant liquid. The precipitated germanium is refined by leaching and distillation with a still residue being discarded as waste. The characteristics of the still residue were not described in literature, but it could be acidic.

The recovered germanium oxide precipitate needs to undergo refining to produce the high purity germanium most applications require. As shown in Figure 3-31, crude germanium oxide is chlorinated with concentrated hydrochloric acid to produce germanium tetrachloride in solution. Solid impurities are separated and discarded as waste or further processed. Filtrates and all wash waters are consolidated and sent for further germanium recovery. The relatively pure germanium chloride is then converted to solid germanium dioxide through hydrolysis with deionized water. This process produces wastewater which must be discharged properly. The germanium oxide is reduced to germanium metal with hydrogen at a temperature of roughly 760°C.

The major contaminants of concern in the wastes produced during germanium recovery operations are arsenic and other metals. The arsenic enters the process as a constituent of the sintering fumes recovered during zinc ore processing. In addition, germanium processing uses acids producing wastes which are potentially corrosive. Since the wastes produced during the recovery and processing of germanium may have hazardous characteristics (Table 3-13), further investigation for possible regulation under Subtitle C is recommended.

Figure 3-31

PROCESSING OF CRUDE GERMANIUM

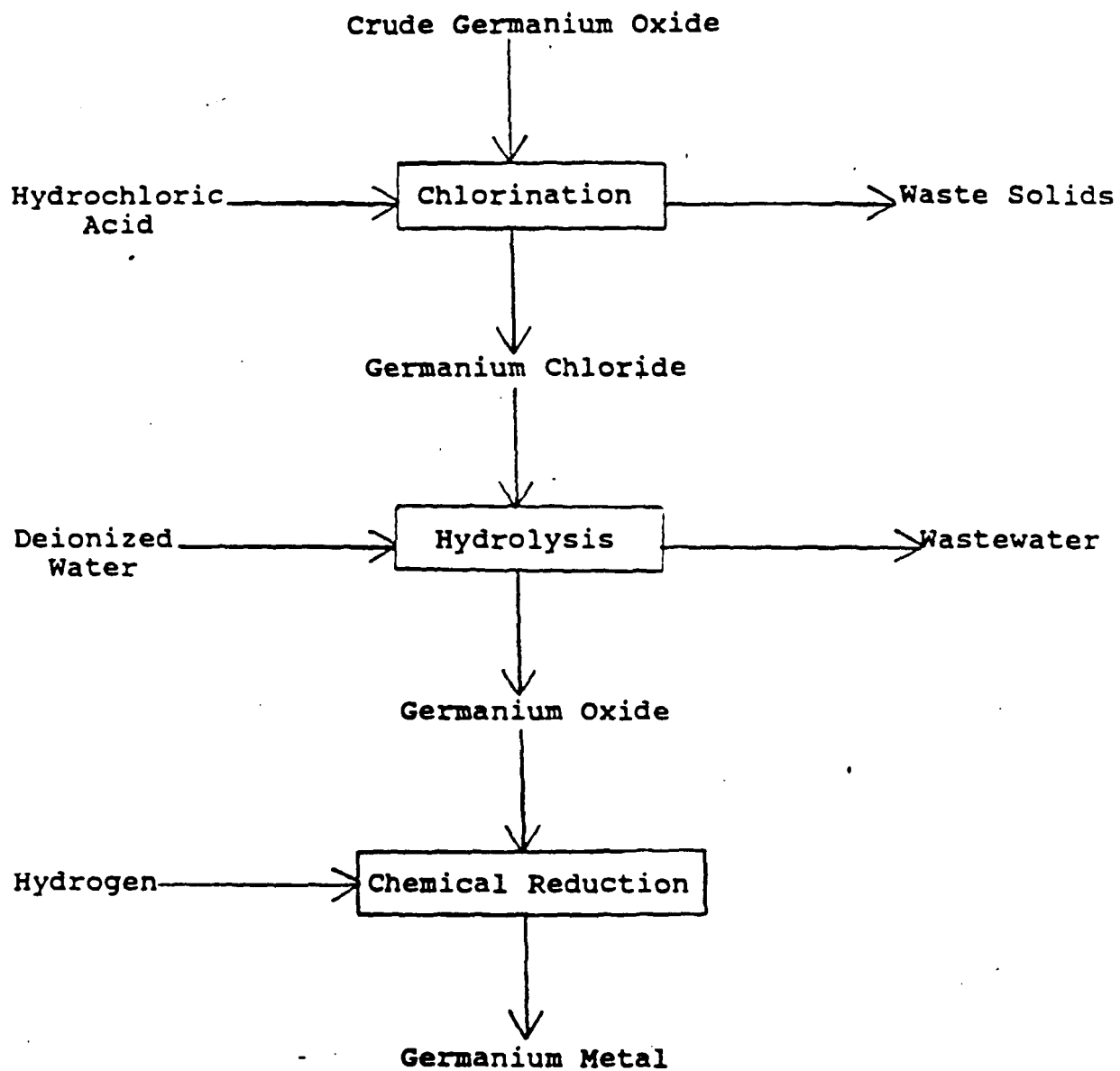


Table 3-13

GERMANIUM WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Germanium from Zinc Residues						
Leaching of zinc sintering fumes	1) Leaching waste	N	?	N	?	May contain arsenic
Precipitation	1) Wastewater	N	?	N	N	
Musto Exploration						
Leaching	Tailings	N	?	N	N	
Refining	Still residue	N	?	N	?	
Chlorination	1) Waste solids	N	?	N	?	
Hydrolysis	1) Wastewater	N	?	N	N	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

REFERENCES

Bureau of Mines, Mineral Commodities Summary, 1987.

Bureau of Mines; Mineral Facts and Problems, 1985.

Mark, H.F., Encyclopedia of Chemical Technology, 1978.

GOLD AND SILVER

Gold and Silver will be described here together since most of the processes to recover one will recover the other. Differences in processing will be discussed when they occur. Also, both metals are often found together in nature, with many mines producing both gold and silver. Whether a mine is classed as a gold or silver mine is usually based on which metal is the greater contributor to the economic value of production.

Gold has been known and used by man since the earliest times. It is most commonly found in nature in its "native" or metallic state. The only minerals containing gold are compounds with tellurium as tellurides. Calaverite (AuTe_2) and Sylvanite ($(\text{Au,Ag})\text{Te}_2$) are examples. Gold may be found as particulate accumulations in some gravels (placer deposits) and in veins (lode deposits), usually with quartz and pyrite. Gold and silver occasionally occur together as a natural alloy known as electrum. Gold is often found in base metal lode deposits and is a common byproduct of copper and lead production. It is prized for its beauty, corrosion resistance, and ductility among other properties. Gold is widely used as a store of value and for other monetary purposes. It is also used in jewelry, industrial (mainly electronics), the arts, and in dental applications. Domestic mine production was estimated at 3.6 million troy ounces for 1986 by the U.S. Bureau of Mines, in the 1987 "Mineral Commodity Summaries". In the USBM "Minerals Yearbook 1985," 93 percent of mine production was estimated to be from precious metal ores, five percent from base metal ores, and two percent from placers. Gold mining is the fastest growing mineral industry in the United States with over 250 mines in operation or in construction. Most gold activity is in the western U.S.

Silver has also been known from ancient times, there is evidence that silver was separated from lead as early as 3,000 B.C. While some native silver is found, it is less noble than gold and many silver compounds are found in nature. It occurs very often in base metal deposits and such

deposits accounted for 70 percent of 1985 production according to the "Minerals Yearbook 1985". The other 30 percent was produced from precious metal ores. Domestic production of silver was estimated at 35 million troy ounces in 1986 by the Bureau of Mines in the "Mineral Commodity Summaries, 1987". Approximately 160 mines produce silver with 70 percent of production coming from five states: Arizona, Idaho, Missouri, Montana, and Nevada. There is little current exploration or development activity for silver due to low prices.

Several processes exist for recovering gold and silver from their ores. These include gravity separation, amalgamation, froth flotation, cyanidation, and smelting. Any given deposit will generally require the use of more than one of the above in combination. In addition there are several methods of cyanidation leaching and recovery of gold and silver from solution. This report will individually discuss various processes and the wastes they produce, with the knowledge that several processes may be combined at any precious metal plant.

Gravity Separation

Gold deposits often contain free gold ranging in size from several microns up to one or more cm (nuggets). If the nuggets are larger than approximately 0.5 mm, they can be separated from the host rock by their density. Gold has a density of 19 g/cm^3 while most rock has a density of 2.7 g/cm^3 . Devices that separate by density range from the simple gold pan to the sluice box, common in the last century, to shaking tables and jigs. The latter two items have been used for many years and are still in common use today. Gravity separation is used at most placer mines and at some "lode" or vein deposits. In the case of the placers, the waste product is gravel which would not be expected to exhibit any hazardous characteristics.

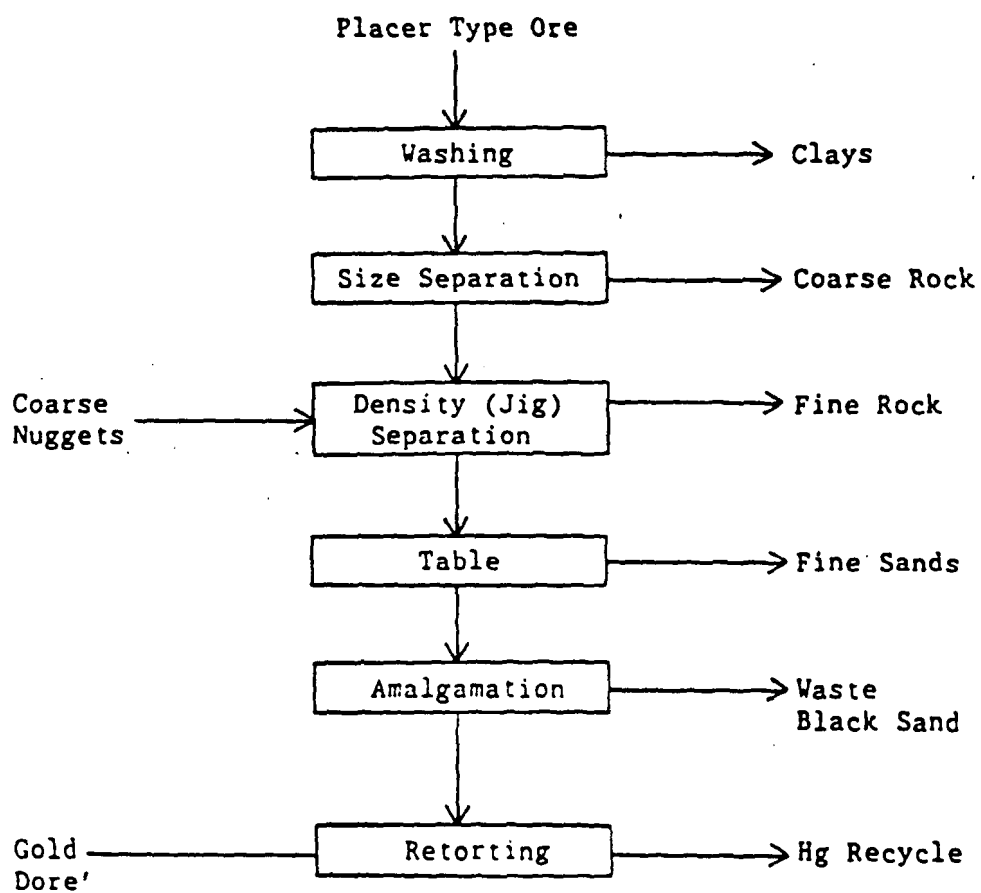
Amalgamation

If the free gold in a placer deposit is finer than approximately 0.55 mm, they often are not cleanly separable from all of the ore minerals by density alone. The fine concentrate stream from a gravity separator often contains several dense minerals as well as fine gold. This product is often called "black sand" because of its color. Many placer operations recover fine gold from such a concentrate by amalgamation. Amalgamation, an ancient process, entails the dissolving of gold or silver in mercury. The resulting alloy, called amalgam is relatively soft and will adhere readily to other pieces of amalgam or to mercury. In the amalgamation process, mercury is added to the ore or black sand and is mixed violently, often in a grinding mill, to assure maximum chance of contact between gold and mercury. After a mixing period, all of the material is placed in a separator that allows the amalgam and any excess mercury to agglomerate and separate from the rest of the ore. The waste black sand is discarded. This waste might contain some excess mercury although the process is operated to minimize such losses. The amalgam is cleared and excess mercury is squeezed out. The amalgam is then retorted to remove the mercury and leave the gold. The mercury is recovered and reused. A general flowsheet is shown in Figure 3-32.

Cyanidation

While density separation can be used to recover coarse gold and amalgamation can recover finer gold from placers, cyanidation leaching is the primary means of recovery of fine gold and silver from vein or "lode" type deposits. In this process, solutions of sodium or potassium cyanide are brought into contact with an ore which may or may not have required extensive preparation prior to leaching. Gold and silver are dissolved by cyanide in solutions of high pH ($\text{pH} > 10$) in the presence of oxygen. There are three general methods of contacting ores with leach solutions, heap leaching, vat leaching, and agitation leaching. These methods are discussed below. After dissolving the metal values the leach solution is

Figure 3-32
GOLD-SILVER
GRAVITY/AMALGAMATION



separated from the ore and the gold and silver is removed from solution. Again several methods exist for doing this and each is described below.

Cyanidation-Ore Preparation

Preparation of an ore for leaching can include size reduction, froth flotation concentration, roasting, agglomeration, and other processes depending on the nature and mineralogical composition of the ore. Of these processes, roasting is the one with the greatest chance of producing a waste which could exhibit hazardous characteristics. In deposits containing sulfide minerals, gold may be trapped in the sulfide grains, often in pyrite. The ore is roasted in an oxidizing atmosphere which converts the sulfide minerals to oxides breaking up their physical structure to allow leaching solutions to penetrate and dissolve the gold. Sulfur, in the form of sulfur dioxide, is removed from the offgas. The offgas will also contain oxides of volatile elements such as arsenic if it is present in the ore. The oxide would be removed from the offgas as a flue dust which could exhibit the characteristic of EP toxicity. However, few operations in the U.S. are roasting gold or silver ores.

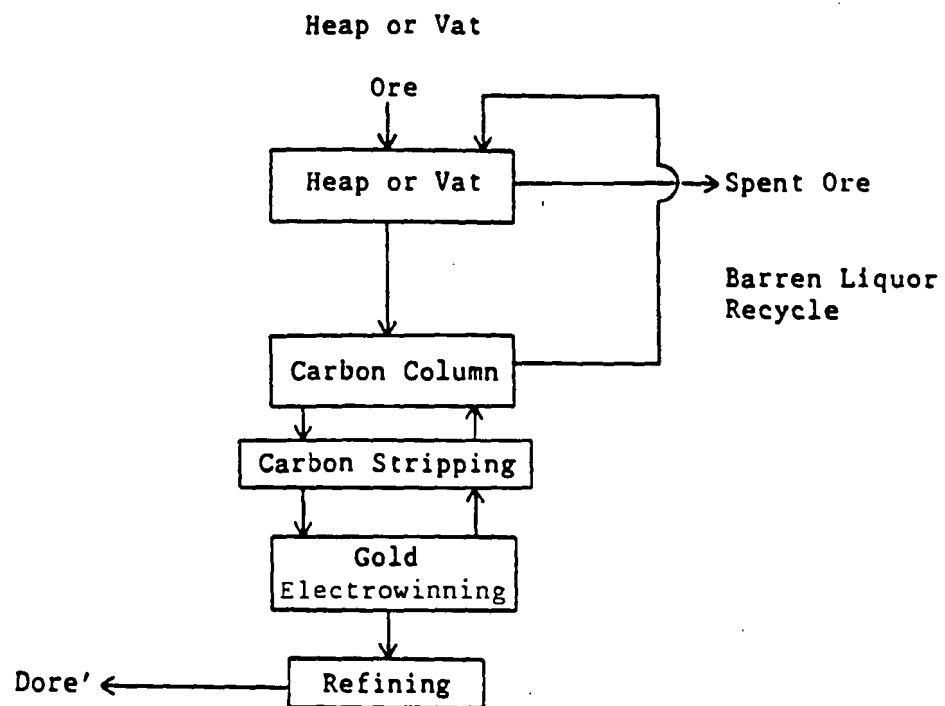
The ores that are leached with cyanide vary widely in metal concentrations and, therefore, value. Low value ores are treated by the lowest cost process, heap leaching, while high value ore are treated by agitation leaching to maximize recovery of metal values.

Cyanidation - Heap Leaching

Heap leaching for gold and silver is very similar to dump leaching for copper. A general flowsheet is shown in Figure 3-33. The ore is piled on a gently sloping impervious leaching pad that has an integral solution collection system. The leaching solution is applied to the top of the pile by sprinklers. The precious metals are dissolved as the solution trickles through the pile. The metal bearing solution (pregnant liquor) is collected on the impervious pad and pumped to a gold and silver recovery

Figure 3-33

GOLD-SILVER
LEACHING



circuit and following rejuvenation returns for reuse after the metals are removed. The leaching process will continue until no more precious metal is extracted. Typical operation will involve leaching for several months on each heap. The process is relatively inexpensive and can be operated for less than two dollars per ton of ore. The disadvantages are that as much as half of the gold and silver may not be extracted either because the leach liquor never contacts the precious metal or because the pregnant liquor is trapped in blind channels in the pile. The waste from this process will be the pile of spent ore and leaching solutions after the completion of the leaching process. The pile may contain residual leach liquor and some operators may attempt to recover this prior to washing the spent ore and transporting it to waste containment sites.

Cyanidation - Vat Leaching

Vat leaching is used when greater solution control than that afforded by heap leaching is necessary. In this system, prepared ore is placed in a vat or tank and flooded with leach liquor. The solution is continuously cycled through draining from the bottom of the vat, then to gold recovery, rejuvenation and return to the top of the vat. The process is more expensive than heap leaching because the material must be removed from the vat at the end of the leaching process. The primary advantage is better solution contact but channelization and stagnant pockets of solution are problems almost as severe as in heap leaching when the solution is drained from the vat. Some of the trapped solution will be recovered when the solids are removed from the vat. Wastes from this process would be the solids and any left over solution.

Cyanidation - Agitation Leaching

High value ores, those containing more than 0.1 troy ounce of gold or equivalent silver, are treated by agitation leaching. The ore will be crushed and ground in water to form a slurry. Cyanide is normally added at the grinding mill to begin the leaching process. More cyanide may be added

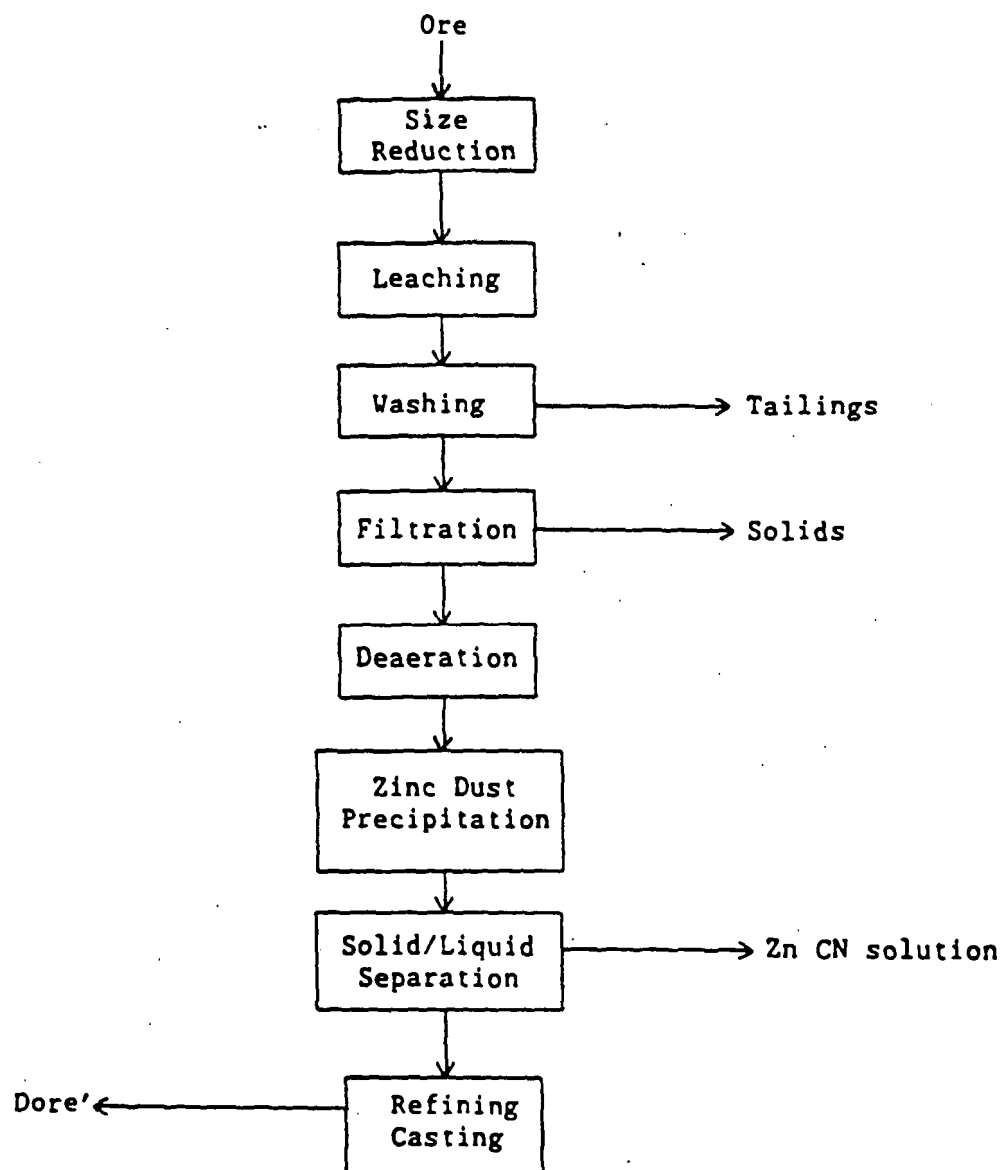
to the leaching tanks. The residence time in leaching is generally greater than 24 hours with some ores being leached for 72 hours or more. Silver ores tend to require longer leaching times. The method of recovering the precious metal from solution determines how the solution is separated from the solids. If the Merrill-Crowe or carbon-in-column metal recovery process are used, the leach liquor will be washed out of the solids usually by a combination of counter-current decantation and filtration washing, with water. This produces a concentrated wash solution and recovers the maximum pregnant liquor from the solids. The resultant slurry will contain very little cyanide or gold and would not be expected to exhibit hazardous characteristics. If carbon-in-leach or carbon-in-pulp metal recovery is practiced, the slurry may be discarded without washing. The carbon should remove all of the precious metals, and the solution is recovered from the tailings treatment and recycled to the process.

Cyanidation - Metal Recovery - Merrill-Crowe

Recovery of precious metals from pregnant leaching solutions is accomplished by several different means. The primary difference is whether the metal is removed by precipitation with zinc or by adsorption on activated carbon. Zinc cyanide is more soluble than gold or silver cyanide and if pregnant liquor is contacted with metallic zinc the zinc will go into solution and the gold and silver will precipitate. Most operations using zinc precipitation in the United States use some variation on the Merrill-Crowe process as shown in Figure 3-34 in which the solution is filtered for clarity then vacuum deaerated to remove oxygen to decrease precious metal solubility. The deaerated solution is then mixed with fine zinc powder to precipitate the precious metals. The solids including the precious metals are removed from the solution by filtration and the solution is sent back to the leaching circuit. The solids are melted and cast into bars. If silver and gold are present the bars are called dore. In most cases, the metal is then sent to an off-site refinery.

Figure 3-34

GOLD-SILVER
AGITATION LEACHING WITH MERRILL-CROWE RECOVERY



Cyanidation - Metal Recovery - Activated Carbon Loading

There are three ways that precious metal leaching solutions are brought into contact with activated carbon. These are carbon-in-column (C-I-C), carbon-in-pulp (C-I-P) and carbon-in-leach (C-I-L). Carbon-in-column systems are used at heap and vat leach operations and in other situations where the leaching solution is separated from the solids being leached prior to precious metal recovery. The leaching solution is then passed through a series of columns containing beds of activated carbon. The gold and silver are adsorbed as cyanide complexes on the surfaces of the carbon. After passing through the columns the solution is returned to the leaching circuit. When the carbon in a column is loaded with precious metals, the column is switched to a stripping circuit as described below.

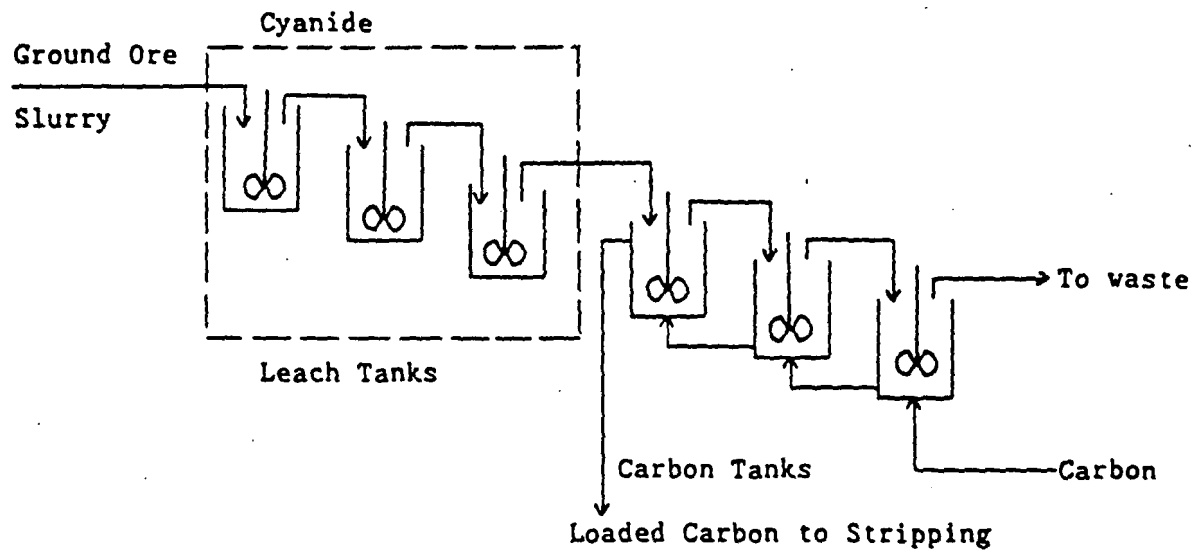
In many agitation leach plants, the gold is recovered from the leached material before the solution is separated from the solids. In the carbon-in-pulp system as shown in Figure 3-35, the leached pulp passes from the last stage of the leaching circuit into another series of agitation tanks. Each tank contains activated carbon granules. The slurry flows from tank to tank in series while the carbon is retained by screens. When the carbon in the first tank is fully loaded with precious metals, it is removed and sent to the stripping and reactivation circuit, the carbon in the other tanks is moved ahead one stage and new carbon is added to the last stage. The carbon therefore moves in a counter current fashion to the leached slurry. The leached slurry is finally sent to the tailings area for dewatering.

Carbon-in-leach is very similar to carbon-in-pulp except that the carbon is in the leaching tanks instead of a separate recovery circuit. One advantage of C-I-L over C-I-P is that some cyanide is released when gold adsorbs on carbon which will be available for more leaching. Another advantage is that fewer agitated tanks are needed since the separate recovery circuit is eliminated. A disadvantage is that the agitation is more aggressive in the leach circuit causing more attrition of the carbon

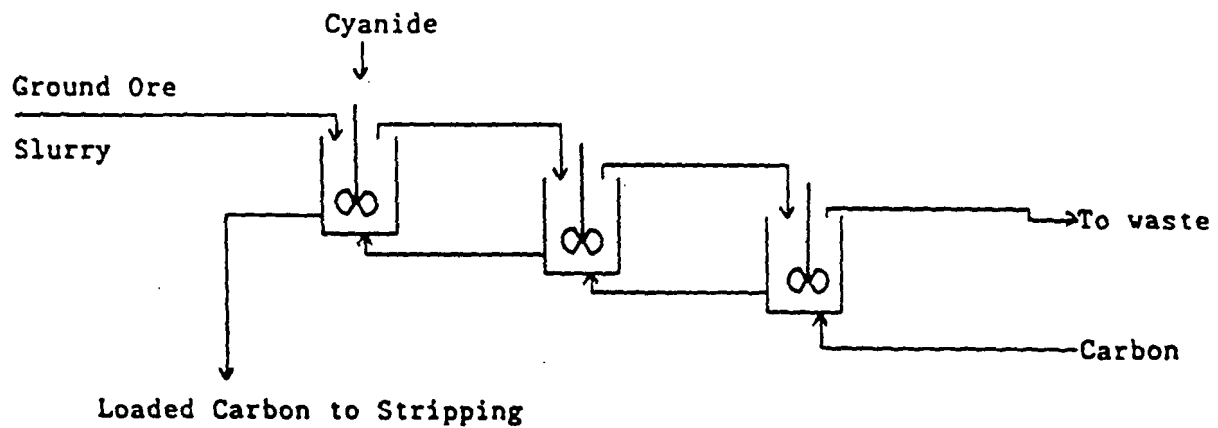
Figure 3-35

GOLD-SILVER - LEACHING
CARBON-IN-PULP VERSUS CARBON-IN LEACHING

Carbon-in-Pulp



Carbon-in-Leach



than in C-I-P, thus, the finely abraded carbon and its load of precious metals may be lost, reducing recovery and increasing costs due to increased carbon replacement. Both C-I-P and C-I-L show this disadvantage when compared to carbon-in-column recovery.

Cyanidation - Metal Recovery - Activated Carbon Stripping

Gold stripping from loaded activated carbon is usually done with a hot, concentrated alkaline cyanide solution, sometimes including alcohol. These conditions favor the desorption of the precious metals into the stripping solution. The solution then goes into an electrowinning cell where the precious metals are plated out, generally on to a steel wool cathode. The solution is recycled to the stripping stage and the cathode is sent on to refining. Some operations refine the steel wool on site to make dore; while others ship it directly to commercial refineries. The primary waste from carbon stripping is the spent stripping solution.

Precious Metals from Base Metal Smelting

Gold and silver are also recovered in the refining processes for base metals, primarily lead and copper. The recovery of precious metals in a lead refinery is a normal part of the operation called "desilverizing". This process takes advantage of the solubility of precious metals in molten zinc which is greater than their solubility in molten lead. Lead from previous stages of refining is brought in contact with a zinc bath either in a continuous operation or in batches. The zinc absorbs the precious metals from the lead and the lead is then passed onto a dezincing operation. The zinc bath is used until it contains 5,000-6,000 troy ounces of precious metal per ton of zinc. The zinc bath is then retorted to recover zinc by distillation. The zinc is returned to the desilverizing process and the "retort metal" left is treated by cupellation to produce dore bullion. In the cupellation step, the base metals in the retort metal are oxidized with air and removed from the precious metals. The oxides are

the precious metals. The oxides are all treated for the recovery of their various metals. The dore is then sent to refining. No wastes are produced by this process.

A major source of precious metals from the copper industry is the cell slimes from the electrolytic refining of copper. The slimes are periodically removed from the cells in the refinery for treatment. The first stage of treatment removes the copper in the slimes by acid leaching, either as is or after roasting. The decopperized slimes are then placed in a furnace and melted with a soda-silica flux. The siliceous slag formed in this melting is removed and air is blown through the molten material. Lime is added and a high lead content slag is formed which is combined with the siliceous slag and returned to the copper anode casting furnace. Fused soda ash is next added to the furnace and air is again blown through the melt forming a soda slag which is removed and treated to recover selenium and tellurium. The remaining dore in the furnace is removed and sent to refining to recovery the precious metals. No wastes are produced by this process.

Precious Metal Refining

There are many different refining operations for gold and silver depending on the composition of the materials in the feed. The most basic operation is "parting" which is the separation of gold and silver. Parting can be done electrolytically or by acid leaching. In either case, the silver is removed from the gold. Further treatments may be necessary to remove other contaminants. These treatments have the potential to produce wastes with hazardous characteristics, primarily corrosivity since strong acids are used.

Summary

In summary, it must be noted that there is considerable controversy about the hazard potential and environmental fate of cyanide in wastes from

data readily available to characterize these wastes as hazardous or non-hazardous. Based upon the study above as summarized in Table 3-14, refining is the only other stage of processing that could be expected to produce wastes with hazardous characteristics. Therefore, it is recommended that further study including data collection, analysis, and evaluation of the gold and silver production industry be limited to cyanide leaching and precious metal refining for potential regulation under Subtitle C.

Table 3-14
GOLD AND SILVER WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Gravity/Amalgamation	Tailings	N	N	N	?	Possible Mercury Contamination
Leaching	Tailings (spent rock)	?	N	N	N	Possible Cyanide Carry Over
	Leach Solution	?	N	N	N	Cyanide
Refining	Wastes	?	?	N	?	Many Acids

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40 CFR 2.61 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

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INDIUM

Indium is a soft, silver-white metal which is highly malleable and ductile. Indium exhibits a highly plastic character and will retain this property at cryogenic temperatures. When heated, indium will react with air to form In_2O_3 . Heated indium will also react readily with halogens, sulfur, phosphorous and metalloids. When in combination with metals and metalloids, intermetallic and semiconducting compounds are formed. Indium is electroplated easily in baths, such as cyanide, sulfate, and sulfamate. Indium can undergo large amounts of deformation by compression, does not work-harden and cold welds easily. Addition of indium to industrial metals increases strength and hardness, improves resistance to corrosion, and will result in a product with increased anti-seizure properties.

In nature, indium is estimated to occur at about the same concentration as silver in the earth's crust, but is usually found to be less than 0.05 ppm. In the copper mining region of Arizona, chalcopyrite contains approximately 35 ppm indium. The highest indium concentrations are found in sulfide cassiterite (tin) deposits. Indium is also associated with zinc, and zinc-lead deposits. Notable concentrations of indium can be found around copper, zinc, and zinc-lead smelters, due to fine dust. Otherwise indium is found as a trace element in other mineral deposits.

In 1986, 40% of the indium produced was used in the electronic, electrical component industry, and another 40% was used in the solders, alloys, and coatings industries.

Indium is used in several metal alloys. Indium additions generally result in lower boiling points, greater strength and hardness, and corrosion resistance. An indium (24%) - gallium (76%) alloy is used in nuclear reactors to circulate gamma activity. Indium is also used in neutron-monitoring badges. An indium (15%) - silver (80%) - cadmium (5%) alloy is used in control rods. When indium is combined with copper, silver and

gold, the alloys formed are used in specialty brazing. Indium is also used in dental alloys. Indium is used in the production of bearings for use in heavy duty, high speed engines. These bearings are in piston-type aircraft engines, high-performance automobile engines and diesel engines. Coatings of indium are used in the electronics industry to increase strength and reduce corrosion. Indium gaskets are used in cryogenic machinery due to their plastic character. Indium gaskets are also used for glass to metal seals. Extensive research and development is being done to explore other applications of indium and its alloys.

The most common sources of commercial indium are zinc, lead, copper and lead-zinc smelter intermediates. In these smelting processes, indium is liberated from the ore to the flue dusts and leaching residues. Recovery of indium from these mediates is accomplished by processes that are different, depending on the source of indium. These processes include chloride slag, residual dross, leaching from cadmium flue dust, hydrochloric acid leaching, and mineral source indium processing.

The most common method of indium recovery is associated with lead-zinc metal production as shown in Figure 3-36. At temperatures between 380°C and 390°C, lead chloride, sodium chloride and zinc chloride are added to the molten lead-zinc. A chloride slag, containing 11% to 14% indium, is skimmed from the kettle. The chloride slag is leached with aqueous sulfuric acid at 70°C to 85°C. This will create a residue containing approximately 500 ppm indium. Zinc dust is added to the solution and an indium sponge is formed. The sponge is digested in sodium hydroxide at 150°C to 190°C. This will leave a crude metal. This crude indium metal, 97.5% pure, is melted at 205°C with pure zinc chloride. This renders an indium that is 99.55% pure. The metal is electrolyzed to give 99.99% pure indium.

Recovery from residual dross from the production of lead or lead alloys, as outlined in Figure 3-37, begins with the addition of sodium hydroxide and sodium sulfide to the residual dross at 590°C to give indium sulfide. This

Figure 3-36
INDIUM FROM LEAD-ZINC SMELTING
LEAD CHLORIDE, SODIUM CHLORIDE, ZINC CHLORIDE

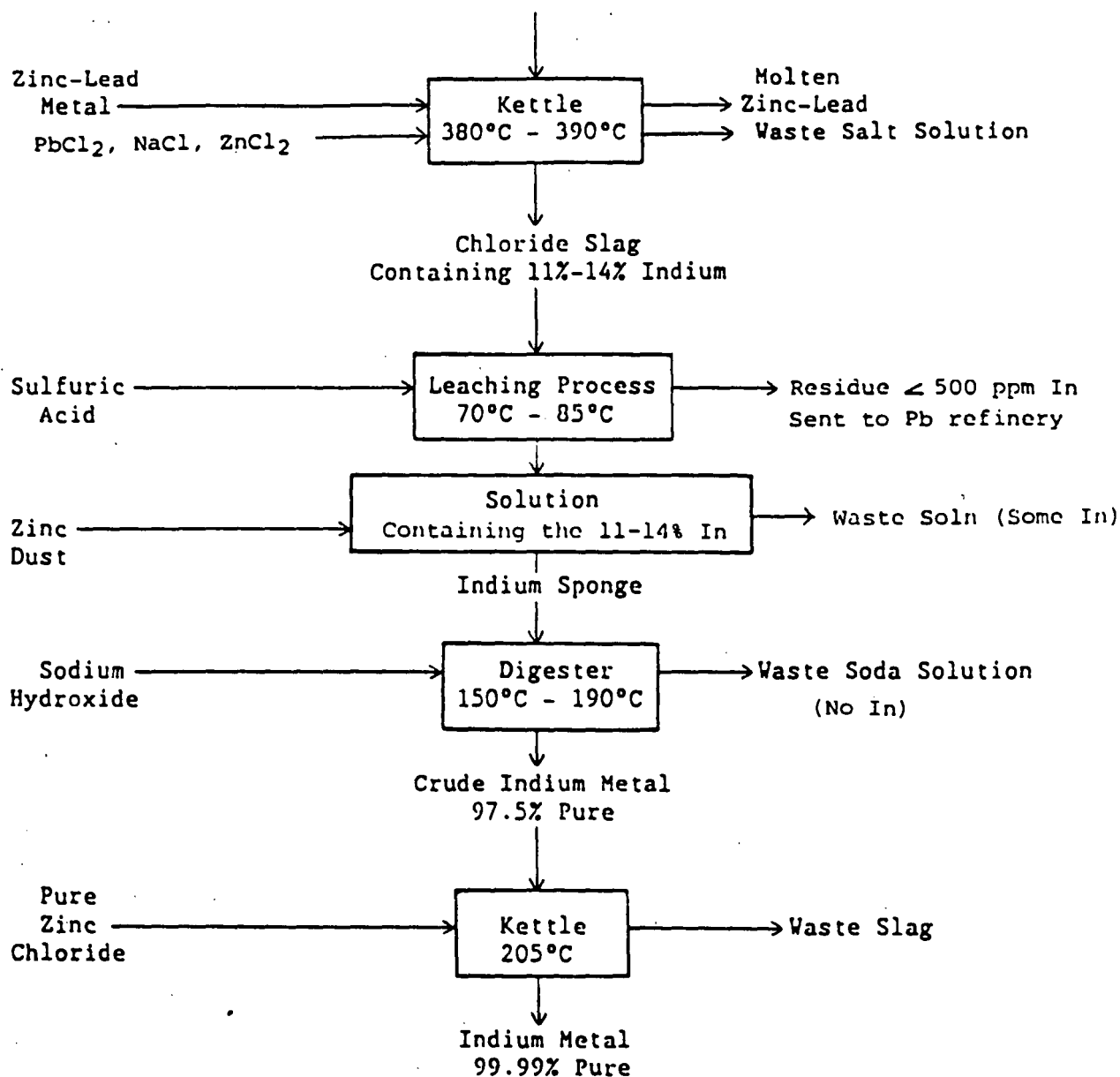
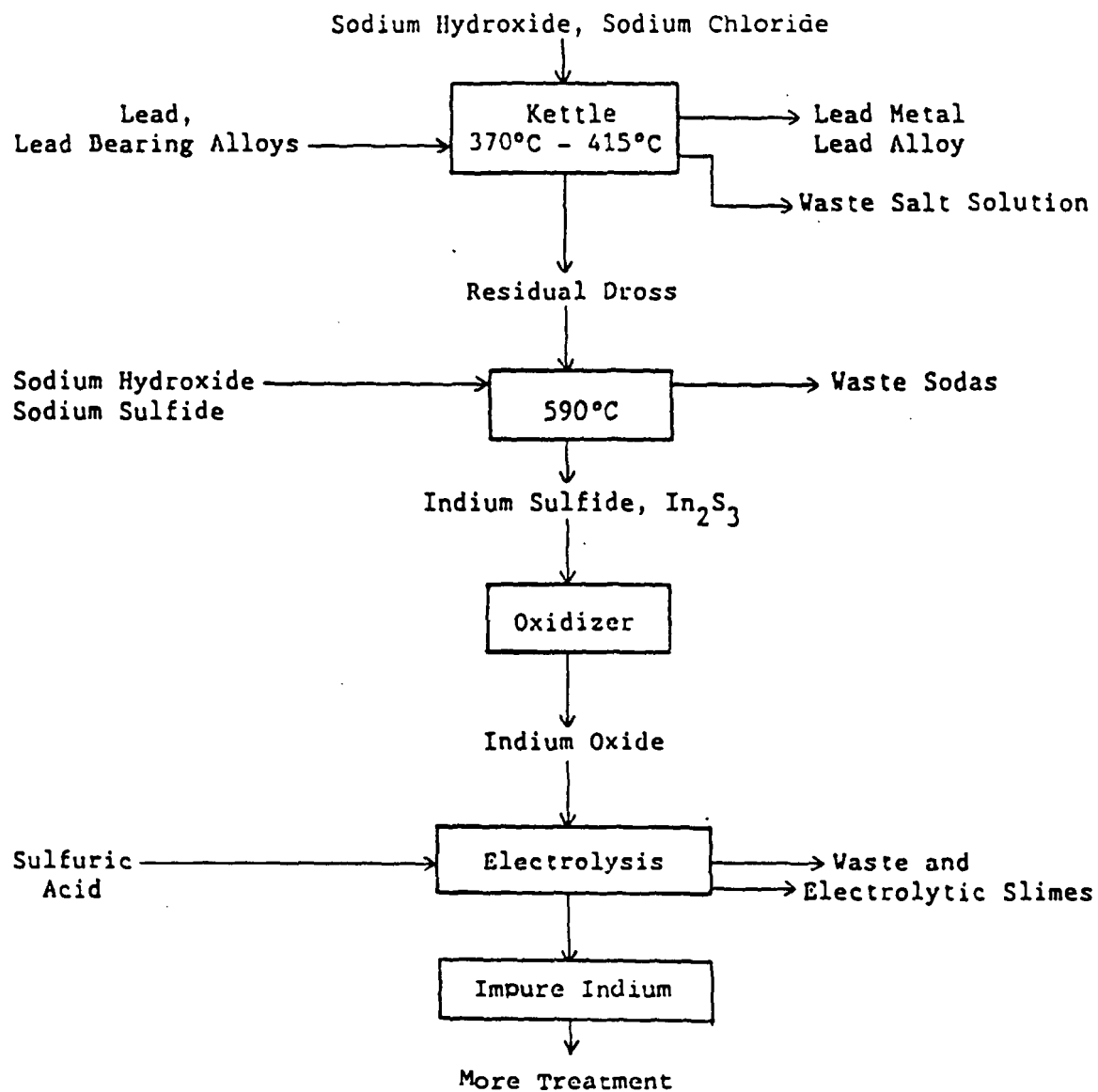


Figure 3-37
LIBERATION OF INDIUM FROM LEAD



indium sulfide is converted to oxide. The oxide is dissolved in sulfuric acid and the solution is electrolyzed to remove impurities, residual metals, and yield pure indium.

Figure 3-38 is a flow sheet for the process by which indium can be recovered from cadmium-bearing flue dusts. The flue dust is leached for cadmium recovery and the residue treated with sulfuric acid. This solution is then treated with sodium sulfate at pH 3.2 to precipitate the indium metal. When the leaching and proceeding steps are repeated approximately 98.7% indium can be recovered. The precipitate is boiled with sodium hydroxide to yield pure indium metal.

Indium recovery by leaching flue dust is achieved by first treating the dust with hydrochloric acid (see Figure 3-39). After this oxidation, iron powder is added with sodium carbonate and the indium is precipitated along with arsenate. Sodium hydroxide is added to dissolve the arsenate and indium hydroxide is precipitated. This process exhibits very good indium recovery.

Indium source material is leached using sulfuric or hydrochloric acid, starting with a reduction bullion, or electrolytic slime. Once in solution, the indium is recovered as a sponge on zinc or aluminum.

Recovery of indium from fumes, flue dusts or residues utilizes strong acids and caustic sodas. Therefore, possible wastes produced are waste acid and soda solutions, spent starting materials, arsenates from flue dust leaching, and electrolytic slimes (Table 3-15). Further investigation should be made into these processes to determine if possible regulation under Subtitle C is necessary.

Figure 3-38
INDIUM RECOVERY FROM
CADMIUM-BEARING FUMES

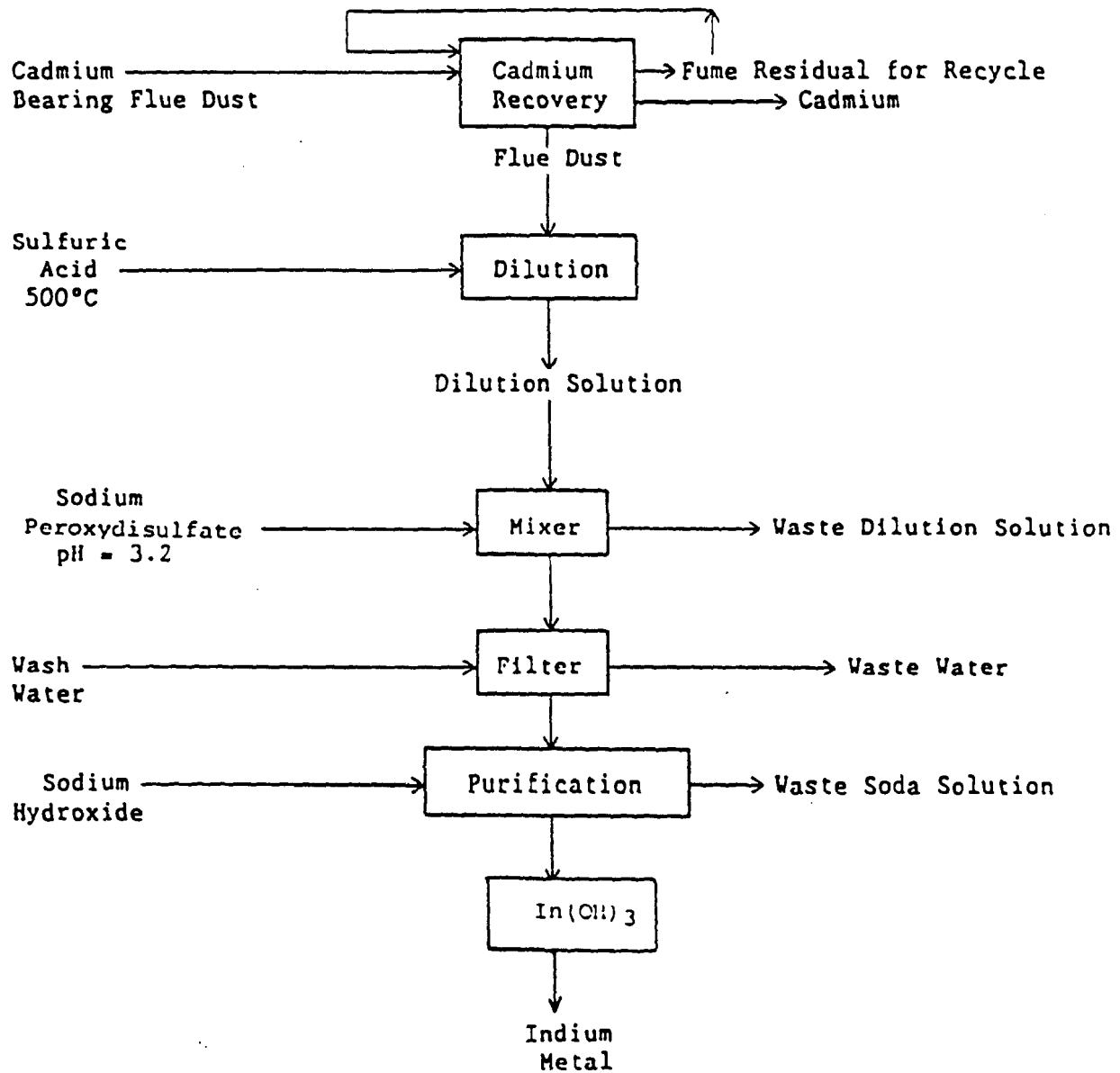


Figure 3-39
INDIUM RECOVERY BY
FLUE DUST LEACHING

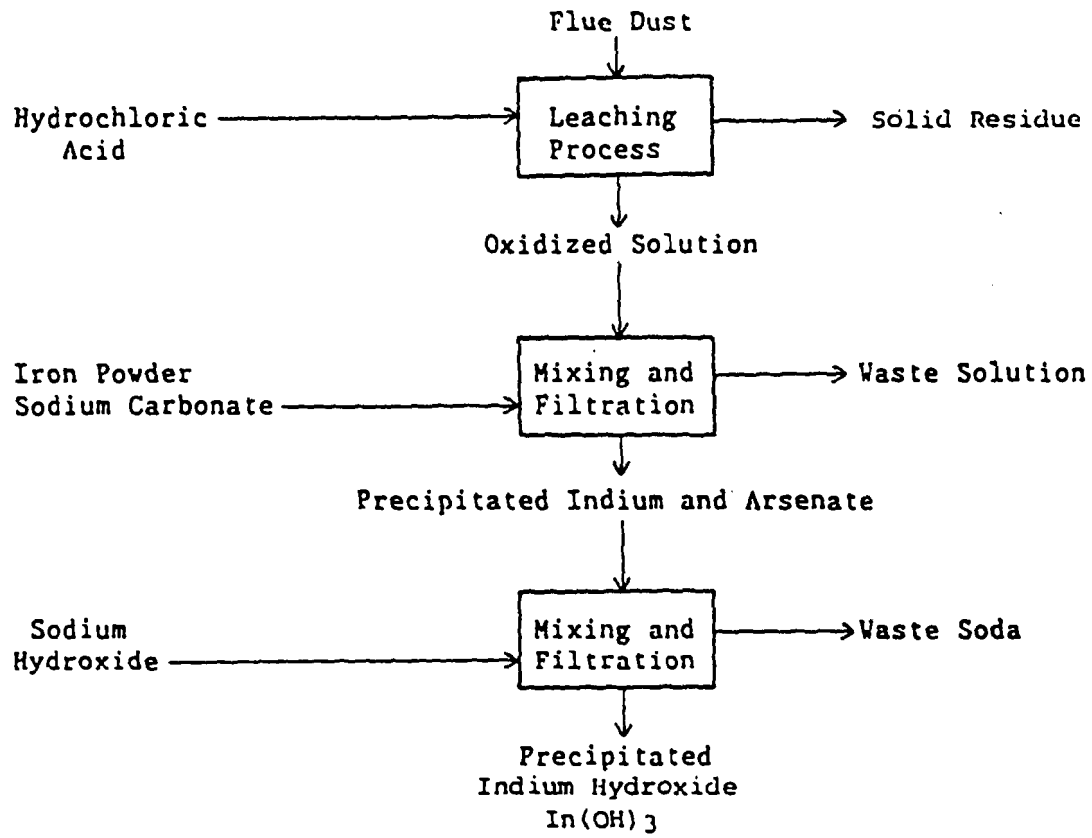


Table 3-15

INDIUM PROCESSING WASTES

Process	Waste	Possible RCRA Characteristics				Comments
		R	C	I	T	
Chloride Slag Processing	1) Solids from Leaching	N	?	N	?	
	2) Soda Solution	N	?	N	?	
	3) Slag	N	N	N	?	
Lead Dross Processing	1) Soda Solution	N	?	N	N	
	2) Electrolytic Acid	N	?	N	?	
	3) Electrolytic Slime	N	N	N	?	May contain lead
Flue Dust Processing in Association with Cadmium Recovery	1) Dilution Solution	N	?	N	?	
	2) Filter Washwater	N	N	N	?	
Flue Dust Leaching Process	1) Leach Residue	N	N	N	?	
	2) Spent Filtrate	N	N	N	?	
	3) Soda Solution	N	?	N	?	May contain arsenic
Leaching of Bullion or Slimes	1) Leached Residue	N	N	N	?	
	2) Kettle Slag	N	N	N	?	
	3) Spent Leachate	N	?	N	?	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability, and EP Toxicity as defined in 40 CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

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IRON AND STEEL

More than 90 percent of the iron ore mined is used to manufacture semifinished steel, which is processed further into a number of steel products. The manufacture of iron and steel involves a number of processes, including mining and beneficiation of iron ore, agglomeration, coking, ironmaking, and steelmaking.

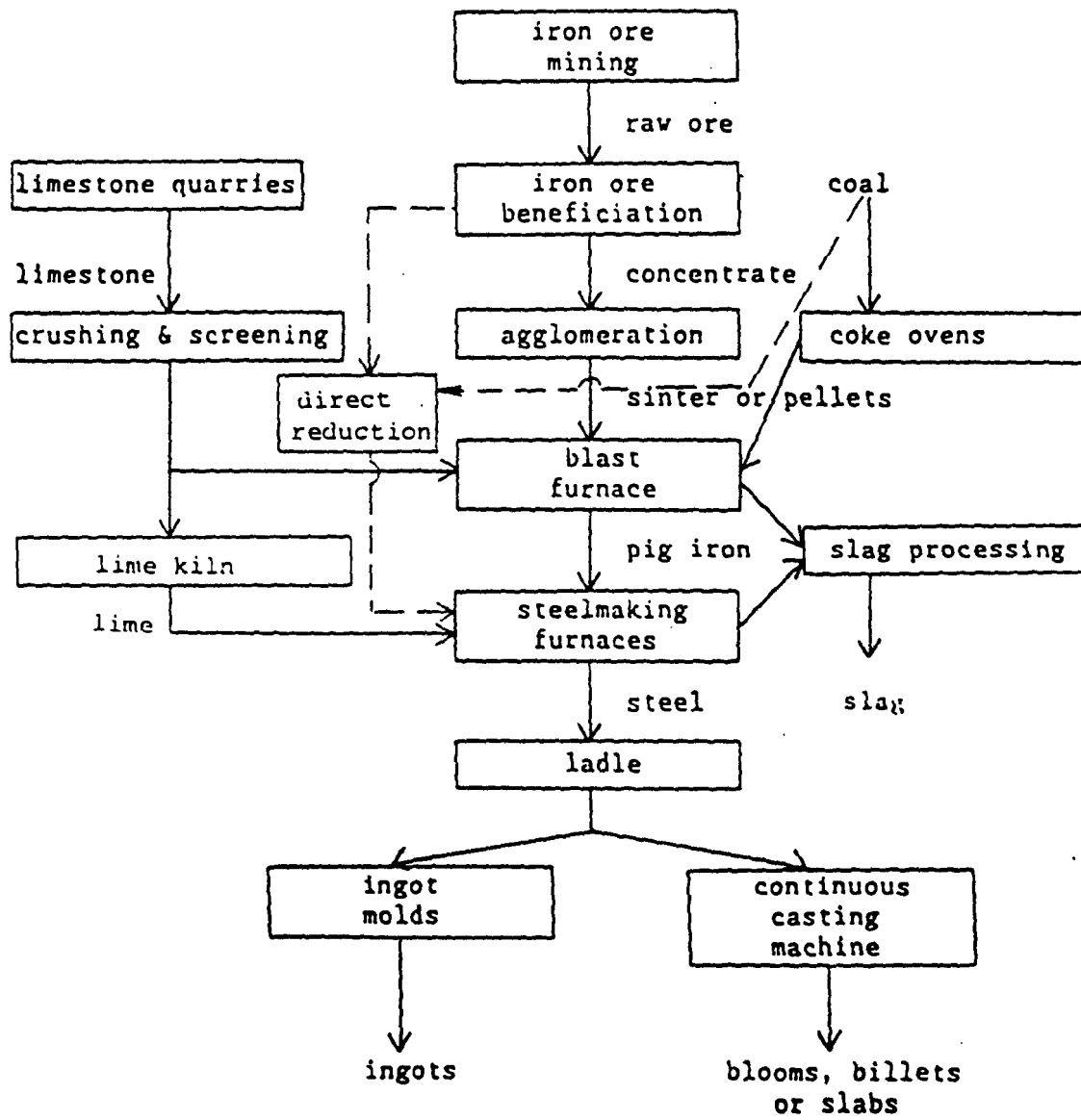
Iron ores have been deposited in a variety of igneous, metamorphic, and sedimentary environments. These ores are oxides, carbonates, silicates, and sulfides, and may be capable of being shipped as mined to ironmaking furnaces. In the U.S., however, most are lower grade ores that must be beneficiated prior to shipping.

The Lake Superior district in Minnesota, Michigan, and Wisconsin is the major source of iron ore in the United States. In 1986, 97 percent of the usable ore produced in the U.S. came from Minnesota and Michigan. The remainder was produced in California, Wyoming, Utah, Missouri, Alabama, New York, and Texas. Relatively little ore from the Lake Superior district is shipped directly to ironmaking facilities. The ore from most areas of the country generally must be concentrated prior to ironmaking. The iron and steel industry is in a depressed state with less than 60 percent of raw ore capacity and less than 75 percent of steel making capacity being used.

A general flow diagram for the production of steel from raw ore is shown in Figure 3-40. There are several stages to this process beginning with beneficiation. The methods of beneficiation for iron ores vary considerably. Some ores are greater than 60 percent iron, and only crushing and blending are necessary to prepare them for further processing. Other operations, such as screening and concentrating, are needed to produce a usable material in some areas. The types of processes used differ with the structure and mineral content of the ore.

Figure 3-40

IRON AND STEEL
GENERAL PROCESS FLOW DIAGRAM



Magnetite is the main iron-bearing mineral in many ore deposits, including those in the Lake Superior district and in the northeastern United States. When magnetite occurs in lower grade deposits, the ore is ground very fine and the concentrate is separated magnetically from the gangue. Magnetic separation is generally done with the ore in a water suspension. The tailings from magnetic separation would consist of mostly silicate rocks and are not expected to exhibit hazardous characteristics.

Hematite and hematite-magnetite mixtures are found in ores in Alabama, the Lake Superior district, and some of the western deposits. The ore can be high in clay and, therefore, may need to be washed to remove the clay and concentrate the iron. The clay wastes are not expected to exhibit any hazardous characteristics.

Lower grade ores containing mineral types other than magnetite may be concentrated by washing, jigging, heavy-media separation, or flotation processes. Jigging involves washing by pulsing water upwards and downwards through the crude ore to stratify the ore. The gangue moves upward and the ore concentrate is removed in the underflow. Wastes include the wastewater used for washing and gangue.

Heavy-media separation utilizes a liquid medium with a specific gravity between the specific gravities of the gangue and the mineral to be concentrated. In the case of iron ore, the medium is non-toxic and consists of a water slurry of finely ground ferro-silicon or magnetite. Generally, the gangue is lighter than the mineral and floats, while the mineral sinks. The only waste from this process would be the tailings.

Froth flotation is commonly used to concentrate low grade iron ores. Fatty acids, soaps, or sulphonates are added to a liquid suspension of finely ground raw ore. The iron minerals are attracted to air bubbles which cause the iron to float to the top of the solution, where it can be collected.

The gangue and flotation solution are usually sent to tailings ponds for settling, and the liquid is discharged to receiving waters.

Ores being sent to blast furnaces for iron making need to be permeable to allow for good gas flow through the system. Concentrates in raw ores that are very fine must be agglomerated prior to being used as feed stock for blast furnaces. The main types of agglomeration used are sintering, pelletizing, and briquetting.

Sintering involves mixing iron-bearing material such as ore fines, flue dust, or concentrate with fuel such as coke breeze or anthracite. The mixture is spread on beds and the surface is ignited by gas burners. The heat fuses the fine ore particles together into lumps, called sinter. The sinter is sized and fines are recycled. Sintering is an operation that commonly recycles wastes from other iron and steel manufacturing processes. Any fines or air pollution control dusts produced are usually recycled back into the sintering process. Air emissions, mostly fugitive dusts, have caused problems at some plants.

Pelletizing involves forming pellets from raw ore or concentrate ("green" pellets) then hardening the pellet by heating. Solid fuel may be added to the concentrate to promote the heating necessary to harden the pellet. Limestone, dolomite, soda ash, bentonite, and organic compounds may be added as binders or to increase pellet strength. The pellets are generally sized and the undersize fraction recycled back into the process.

In briquetting, the ore is heated, then, while hot, pressed into briquettes. The briquettes are cooled, then sent to the blast furnace.

The reducing agent used in blast furnaces is coke. Coke is the hard, vesicular solid product of the destructive distillation of coal. When coal is heated in the absence of oxygen the volatile components of the coal are driven off. The volatile components include water, naphtha, coal tars, and ammonia, among others. The solid left behind is mainly carbon. Good

metallurgical coking coal will form a porous but strong solid that can support the weight of a tall column of material in a blast furnace without crushing. The coal used for coke generally must be prepared at least by the process shown in Figure 3-41 before going to the coke ovens. Over 99 percent of the domestic coking operations use "byproduct" ovens in which the byproducts of coking are collected for use. These plants heat bituminous coal in ovens in the absence of heat to drive off the volatile compounds which are collected as shown in Figure 3-42. The coal is converted to coke in the oven, cooled by quenching, sent to a crushing, screening, and blending operation. The fines from screening are usually used as feed stock in sintering or pelletizing.

The gas from coking operations is sent through a series of coke gas cleaning operations that recover coal tar, ammonia compounds, naphthalene, and light oil. Cleaning of the exhaust gas begins with a liquid scrubber, primary cooler, and electrostatic precipitator. These processes remove coal tars that may disrupt other recovery operations. The gas is processed further to recover ammonia compounds and light oils. The cleaned gas is used as a fuel in the coke ovens or in other locations in the steel plant. The other byproducts are sold as organic chemical feed stocks.

The wastewaters generated from these processes are usually used in coke quenching. Most organic byproducts are combined with the coal tar. Wastes generated include coke quenching solution and may include spent scrubber water and cooling tower blowdown. These wastewaters may contain toxic organic compounds and heavy metals. They are usually treated prior to discharge to receiving waters.

Limestone is prepared prior to being used in blast furnaces for ironmaking. The raw limestone is crushed and screened to produce a prepared limestone that is the appropriate size. The oversize fraction is recycled into the grinder and the undersize fraction is usually used in concentrate agglomeration.

Figure 3-41

IRON AND STEEL
COAL PREPARATION

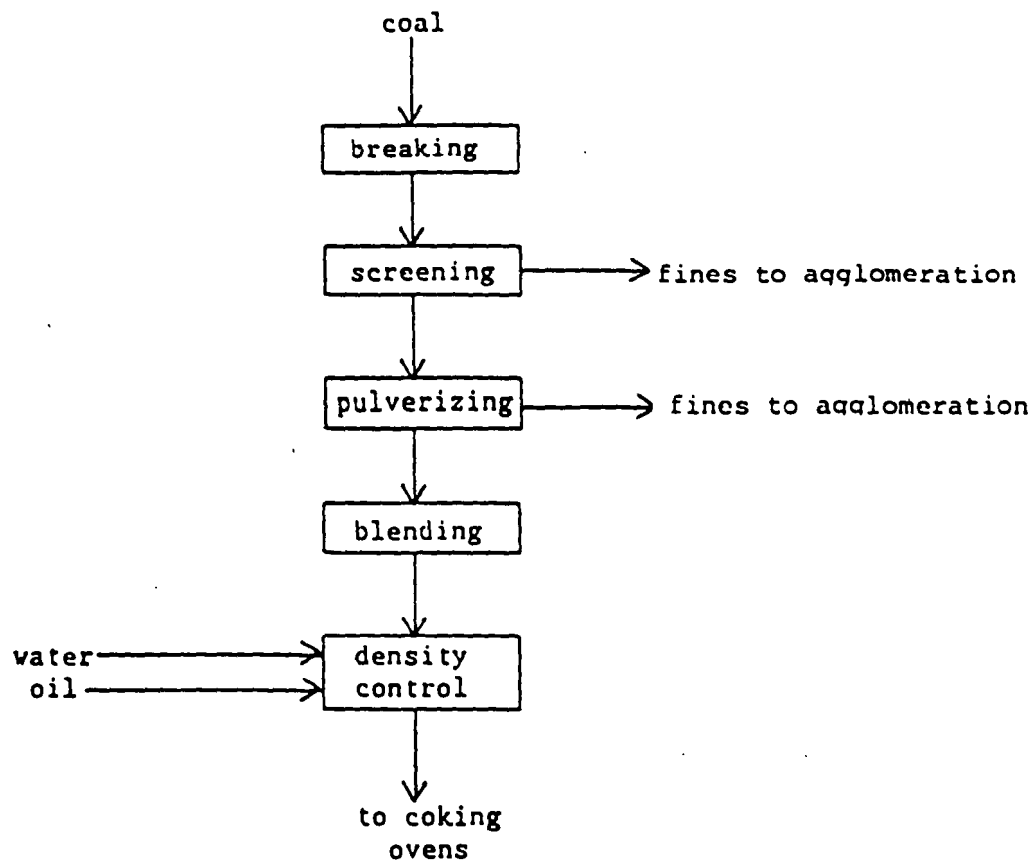
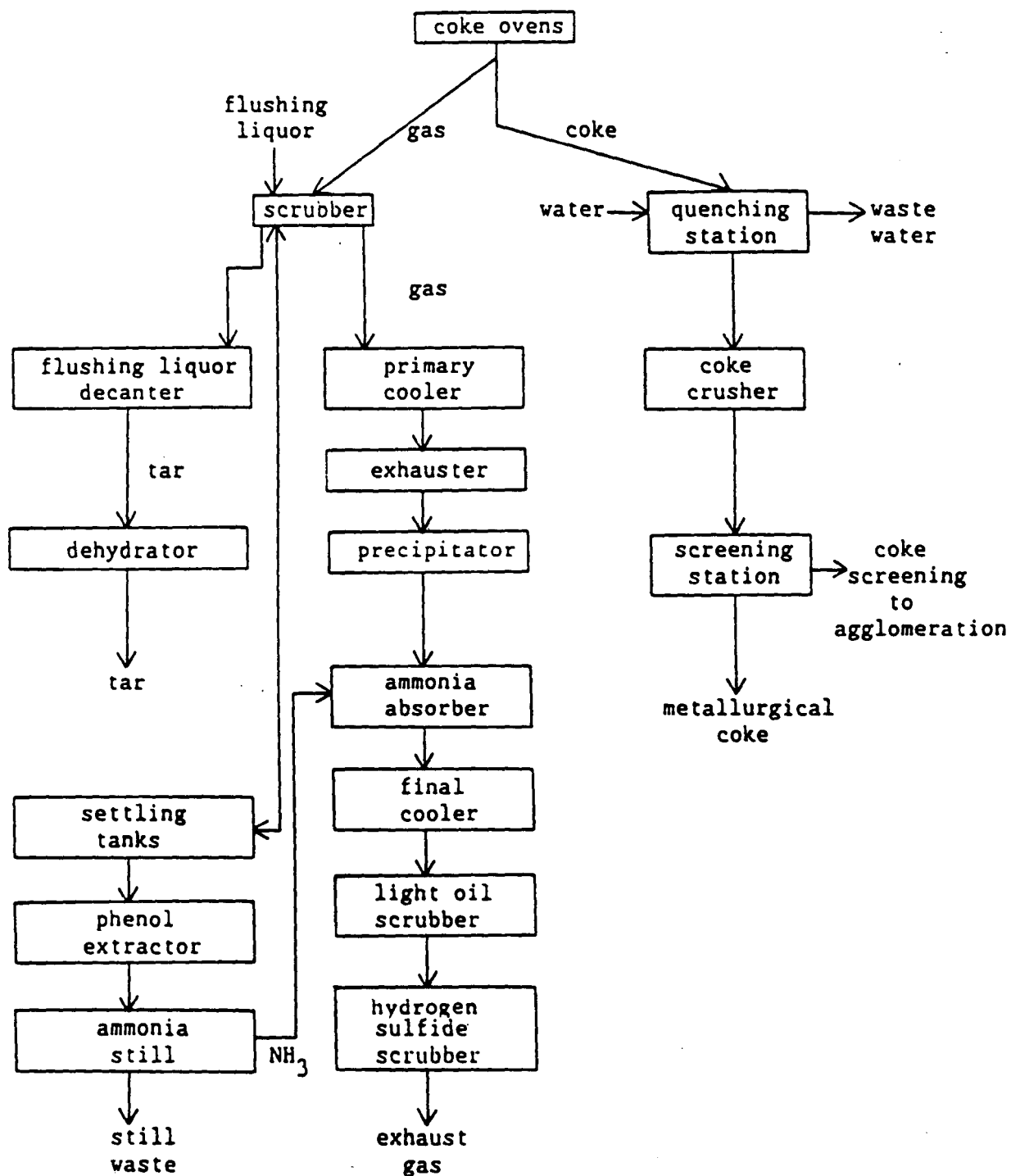


Figure 3-42
IRON AND STEEL
COKING



In ironmaking, agglomerated iron ore, prepared limestone, silica and coke are placed into the blast furnace and heated air is blown into the furnace. The limestone and silica form a fluid slag which combines with other impurities. The slag is separated from the molten iron and sent to a slag reprocessing unit. Most iron from the blast furnace is transferred to the steel making furnaces in the molten state. A small fraction is used to make iron castings or is cast into pigs for re-melting. Fine particles in the exhaust gas are removed and the dust recycled into the process. The exhaust gas has fuel value and is burned to preheat the blast air.

There are three major steelmaking processes: the basic oxygen furnace (BOF), the electric arc furnace, and the open hearth furnace. The different furnaces are better suited to producing different types of steel, and are suited to using particular raw materials. Electric arc furnaces are mostly used for scrap processing, and the open hearth process is being replaced with BOF steel making due to speed and lower costs. The raw materials may include molten iron metal, pig iron, scrap, directly reduced iron, iron ore, or iron bearing material such as pellets or mill scale. Lime, dolomite, fluorospar, or limestone may also be added as fluxing agents. Sometimes other metals, in various forms, are added to produce a steel alloy. More frequently, alloying elements are added in the ladle between steel making furnace and casting. The impurities rise to the top of the molten steel as slag. The slag and molten metal are separated, with the slag sent to a reprocessing unit and the molten steel sent to either ingot molds or to a continuous casting machine producing blooms, billets, or slabs. The exhaust is collected and the flue dust removed. The flue dust is either recycled into the furnace or sinter plant or disposed of as waste. The refractory materials used to line blast furnaces and steel making furnaces must be replaced periodically. Some of these refractories are made with chromium oxide and some use chromic acid as a binder, making used refractories potentially EP toxic wastes.

Much of the slag from iron manufacturing and all of the slag from steel manufacturing is air cooled. The cooling of the slags is occasionally

accelerated by spraying the warm slag with water. This water either evaporates, or is allowed to drain from the slag pit in the same manner as rain water. The air cooled slag is crushed and iron-bearing material is removed magnetically and returned to the furnaces. The crushing of slag may produce fine particles which can escape into the atmosphere. After crushing, the slag is screened and shipped, mainly for use as an aggregate. Some of the hot slag from blast furnaces is poured into water to produce expanded slag, a lightweight aggregate. This cooling water is handled similarly to the water sprayed on air cooled slag, i.e., allowed to drain off. Blast furnace slag is also processed to produce granulated slag, a vitreous product used in cement manufacture and as a soil conditioner. Granulated slag is produced by breaking up the molten slag with jets of water. This process requires larger amounts of water than other slag processing techniques, and, therefore, the water used is recycled. The water in these systems is occasionally chemically cleaned.

Many potential wastes from the manufacture of iron and steel are beneficially used or reused or are actually recycled (Table 3-16). However, due to the size of the industry, the management of the wastes is not clearly defined. Further study for potential regulation under Subtitle C is recommended.

Table -16

IRON AND STEEL WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Ore Beneficiation						
A. Magnetic separation	1) Gangue	N	N	N	?	
	2) Wastewater	N	N	N	?	
B. Washing	1) Wash water	N	N	N	?	
C. Jigging	1) Gangue	N	N	N	?	
	2) Wash water	N	N	N	?	
D. Heavy-Media Separation	1) Gangue	N	N	N	?	
	2) Separation Solution	?	?	N	?	
E. Flotation	1) Tailings	N	N	N	?	
Sintering	Air Emissions	N	N	N	N	
Coking	1) Coke Quenching Solution	N	N	N	?	
	2) Scrubber Water	N	N	N	?	
	3) Cooling Tower Blowdown	N	N	N	?	
Ironmaking	1) Flue Dust	N	N	N	?	May be recycled
	2) Used Refractories	N	N	N	?	
Steelmaking	1) Flue Dust	N	N	N	?	May be recycled
	2) Used Refractories	N	N	N	?	
Slag Processing	1) Cooling Water	N	N	N	?	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability, and EP Toxicity as defined in 40 CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

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MAGNESIUM

The uses of magnesium are tied to its properties. It is a lightweight metal with a relatively high strength which is used in auto parts and hand tools. It is also a constituent in aluminum alloys and is used in explosives and flares as it is pyrophoric in powdered form. Magnesium acts as a reducing agent in the manufacture of titanium and zirconium and is a catalyst in the formation of a number of organic compounds.

Magnesium is fairly abundant in the earth's crust and in the sea. It is currently recovered from dolomite deposits in Washington, from brines from the Great Salt Lake, and from seawater. It is also recovered from titanium processing residues. Four companies produced metallic magnesium in 1987. They were Amax Magnesium Corp. in Rowley, Utah; Dow Chemical Company in Freeport, Texas; Northwest Alloys Inc. in Addy, Washington; and Oregon Metallurgical Corp. in Albany, Oregon. The first two companies used an electrolytic process to recover magnesium from natural brines. The third company processed dolomite by silicothermic reduction. The Oregon Metallurgical Company electrolytically recovered magnesium from magnesium chloride generated in their titanium production process (Bureau of Mines, 1985; Bureau of Mines, 1987). These processes are described below and outlined in Figures 3-43 to 3-45.

There are two basic electrolytic processes in use, the Dow process and the NL process. The Dow process is used at the Dow Chemical Plant in Freeport, Texas, and the NL process is used at the Utah plant in Rowley operated by Amax Magnesium. It is not reported which process is in use in the Oregon facility.

The Dow process involves adding calcium hydroxide to seawater to produce a solid magnesium hydroxide. This solid precipitate is separated from solution, reslurried, and the magnesium hydroxide converted to magnesium chloride by neutralizing the slurry with hydrochloric and sulfuric acid.

Figure 3-43

MAGNESIUM - DOW ELECTROLYTIC PROCESS

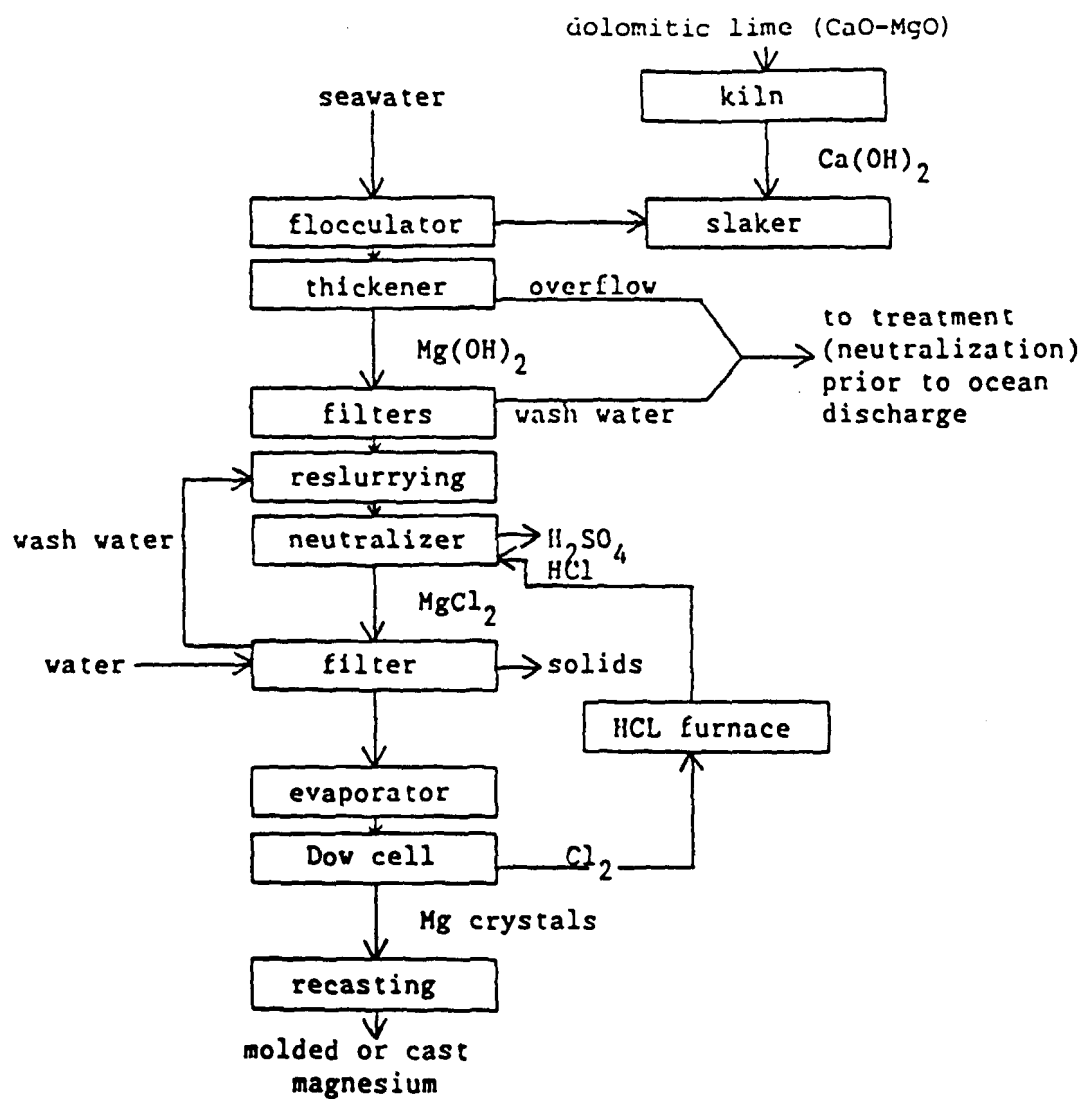


Figure 3-44

MAGNESIUM - AMAX PROCESS

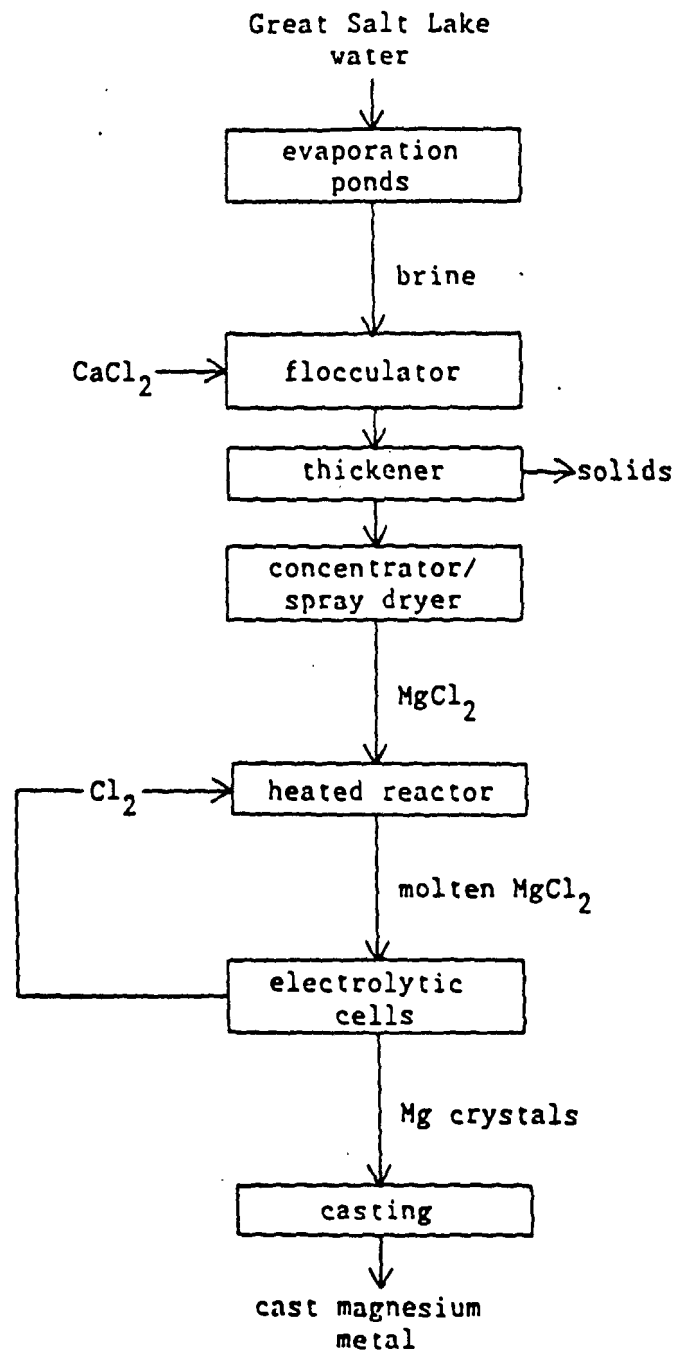
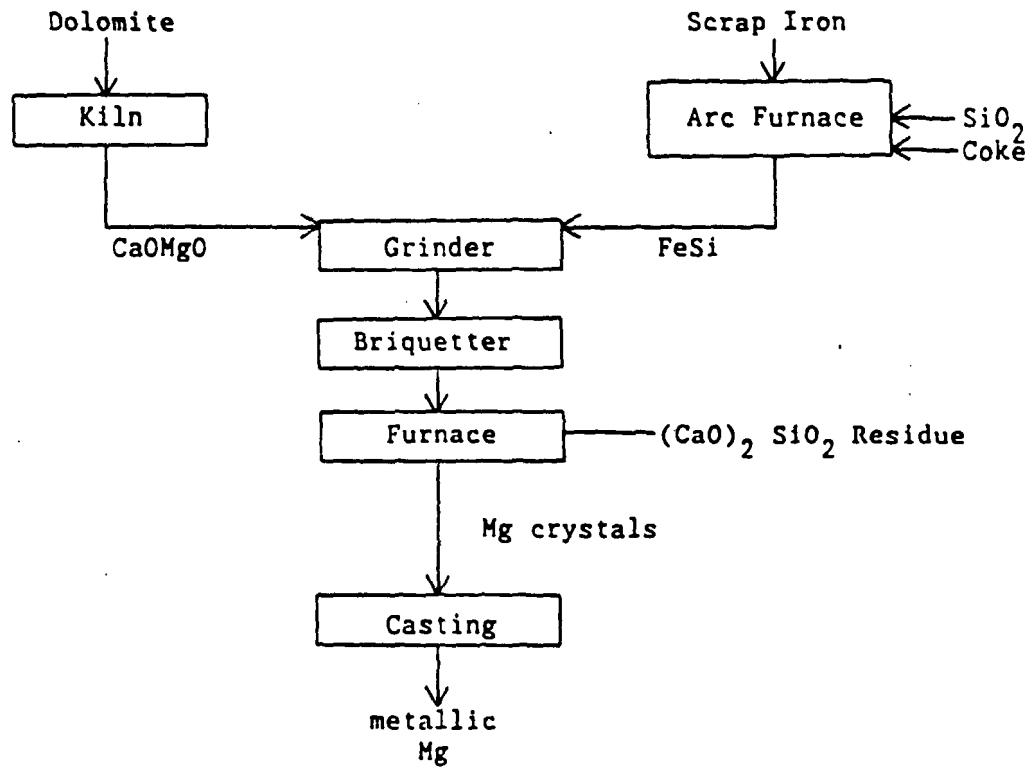


Figure 3-45

MAGNESIUM - SILICOTHERMIC PROCESS



The waste solids are removed and the magnesium chloride solution evaporated. The crystals are placed in a Dow Electrolytic cell, where metallic magnesium crystals and chlorine gas are formed. The chlorine gas is converted to hydrochloric acid and reused in the neutralization step. The magnesium crystals are recast into metallic magnesium ingots or other shapes. Wastes from this process include thickener overflow and filter wash and solids from the second filtration operation. The wastewaters are neutralized prior to ocean discharge. The disposition of the filter solids is unknown.

The NL electrolytic process uses calcium chloride to remove impurities from the feed brine. These solid impurities are removed and the solution concentrated. The concentrated magnesium chloride solution is solidified as magnesium chloride crystals in a spray dryer. The crystals are sent to a heated reactor to which chlorine is fed to remove further impurities. The purified, molten magnesium chloride is sent to the electrolytic cell, where metallic magnesium crystals are formed. The crystals are then recast into ingots. Wastes produced include thickener solids and possible solid residue from the heated reactor vessel. Waste management methods for these wastes are not known.

Dolomite can be processed by the silicothermic process to yield metallic magnesium. The carbonates in dolomite are converted to oxides by calcining, then ground and mixed with ferrosilicon. The mixture is briquetted, then charged into a retort furnace. The resulting magnesium crystals are separated from the slag and recast into ingots. The only identified waste from this process is the furnace slag. The disposition of this slag is unknown.

Although this industry is relatively small, current waste management methods are not clear (Table 3-17). Further study of this industry for possible regulation under Subtitle C is, therefore, recommended.

Table 3-17
MAGNESIUM WASTES

Process	Waste	Possible RCRA Characteristic [*]				Comments
		R	C	I	T	
Dow Electrolytic	1) Thickener Overflow	N	?	N	N	Neutralized and discharged
	2) Filter Wash Water	N	?	N	N	Neutralized and discharged
	3) Filter Solids	N	N	N	?	May contain trace heavy metals
NL Electrolytic	1) Thickener Solids	N	N	N	?	
Silicothermic	1) Furnace Slag	N	N	N	?	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibly that waste could exhibit this characteristic.

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MANGANESE

Manganese is a gray metal which is hard and brittle, and resembles iron. Manganese occurs in three forms, alpha, beta, and gamma. The alpha and beta forms are brittle, yet stable. The gamma form is ductile and unstable, yet can be stabilized by the addition of copper and nickel. The gamma form will convert to the alpha form if not kept at low temperatures. Manganese is capable of forming a series of bivalent and tetravalent salts. The most common salt compounds are permanganates and strong oxidants.

Manganese occurs in over one hundred minerals. Manganese is usually found in metamorphosed deposits such as marbles, slates, quartzites, schists, and gneisses. Manganese ore is widely distributed in the U.S. with the richest deposit found in Franklin, New Jersey and the largest deposit located at Chamberlain, South Dakota.

The diversity and complexity of manganese formations lends them to several types of impurities; metallic (iron, lead, zinc), nonmetallic (sulfur, phosphorous minerals), gangue (silica, alumina, lime), and volatiles (water, carbon dioxide, organics). Primary manganese minerals include pyrolusite, psilomelane, manganite, and hausmannite.

Manganese nodules are found in the ocean. These deep sea nodules are found over wide areas of the ocean floor. Currently, the higher-grade deposits are found in the North Pacific Ocean.

Manganese alone is of little use. Manganese is an essential ingredient for steel making and for that purpose is commonly used as a ferro alloy composed chiefly of manganese and iron. In alloyed or metallic form manganese can be used as a cleansing agent for steel, cast iron, and nonferrous metals. Manganese serves in the steel industry as a control of hot shortness in finishing processes, as a deoxidizer, and as an alloying

agent to improve strength, hardness, abrasion, and wear resistance. Manganese neutralizes sulfur and adds strength to cast iron.

The aluminum industry utilizes manganese in the forms of manganese-aluminum briquettes, master alloys and powdered electrolytic manganese to harden, strengthen, and stiffen aluminum metals.

Manganese dioxide is used in the production of dry cell batteries. Manganese gives colors from bright reddish purple to purple black to ceramics, brick, and tile. In chemical applications, manganese is used as a catalyst, oxidizer and chemical intermediate in the manufacture of both organic and inorganic compounds. Manganese promotes absorption of oxygen in the drying of paints and varnishes.

There is no production of manganese ore containing 35% or more manganese in the United States. In 1987, 390,000 short tons of manganese ore and 430,000 short tons of ferromanganese were imported. The manganese ore was used by about 20 firms mostly located in eastern and mid western states. Much of that utilization was directly as ore.

In the Minerals Yearbook, 1985, the Bureau of Mines surveys found 8 plants owned by 6 companies producing manganese products from ore. Two plants produced ferromanganese alloy, one of those also produced silico manganese alloy and manganese metal. One plant produced manganese metal only, and 5 plants produced manganese dioxide only.

Flow charts for manganese processing are shown in Figures 3-46 through 3-49. The two plants producing ferromanganese use different techniques. One uses submerged arc electric furnaces and the other uses a fused-salt electrolysis method similar to the Hall process for aluminum. Wastes expected from the submerged arc process would be slag and baghouse dust from furnace fume collection. The plant using the submerged arc process for ferromanganese also produces silicomanganese alloys by the same method. The slag from ferromanganese production is fed as part of the charge to the

Figure 3-46
MANGANESE PROCESSING
ANACONDA PROCESS

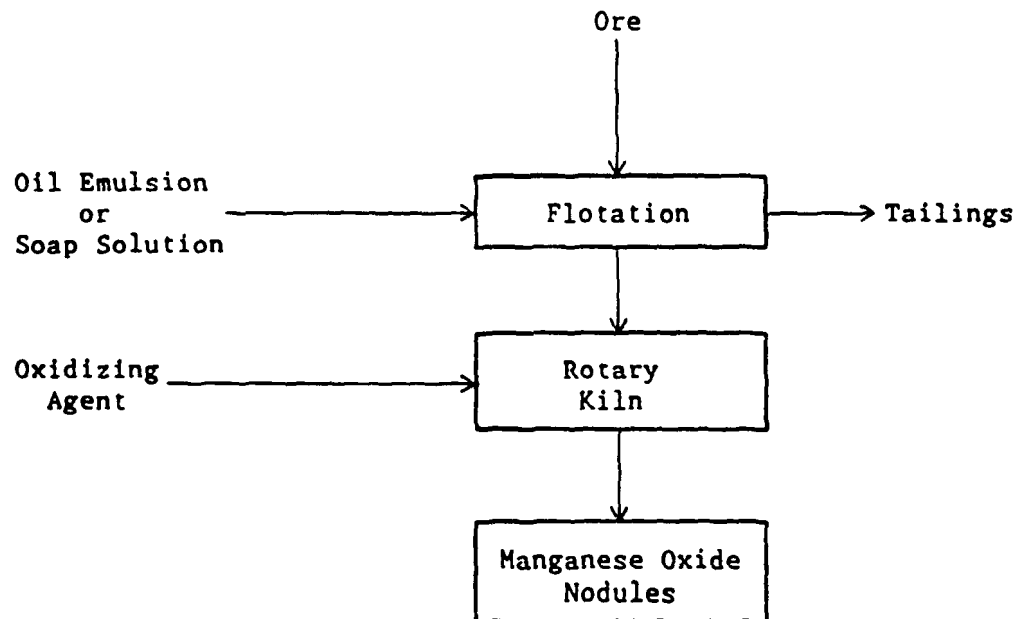


Figure 3-47
MANGANESE PROCESSING
DEAN - LEUTE PROCESS

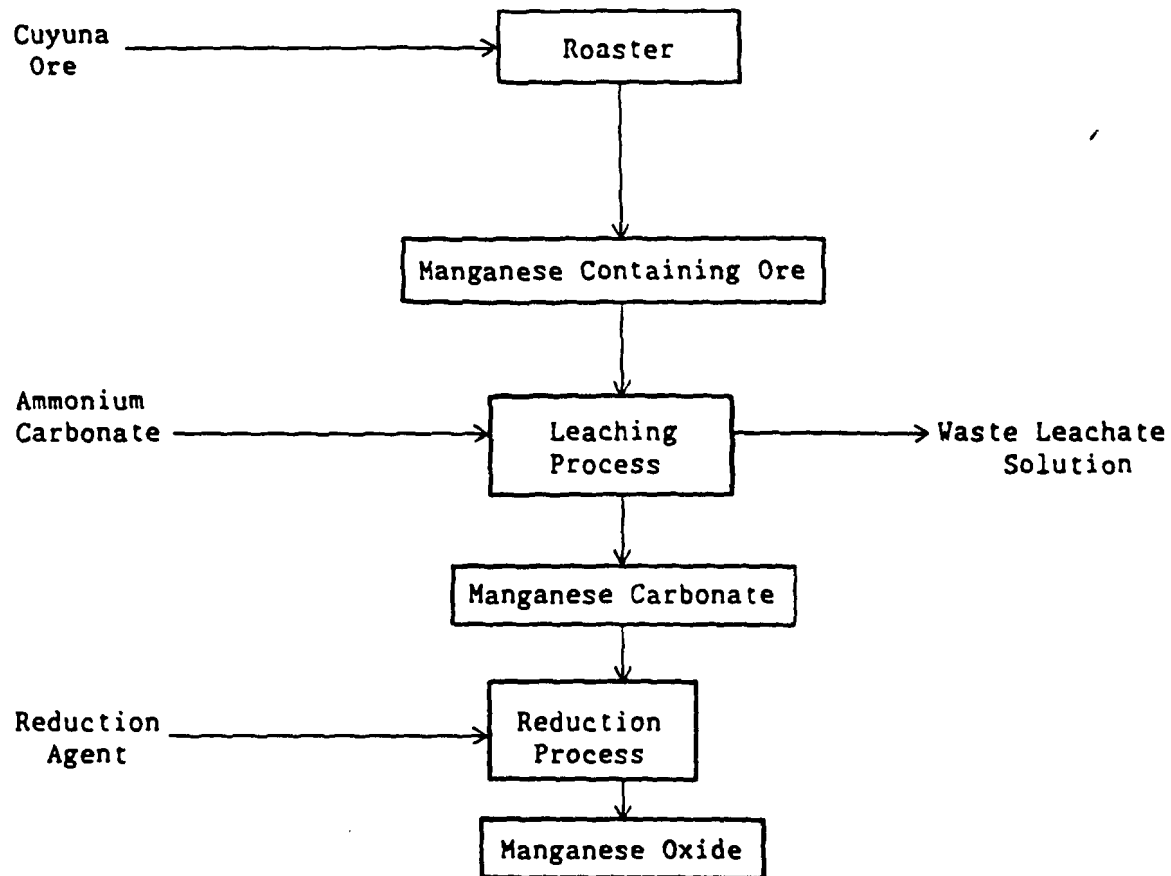


Figure 3-48
MANGANESE PROCESSING
DAUGHERTY PROCESS

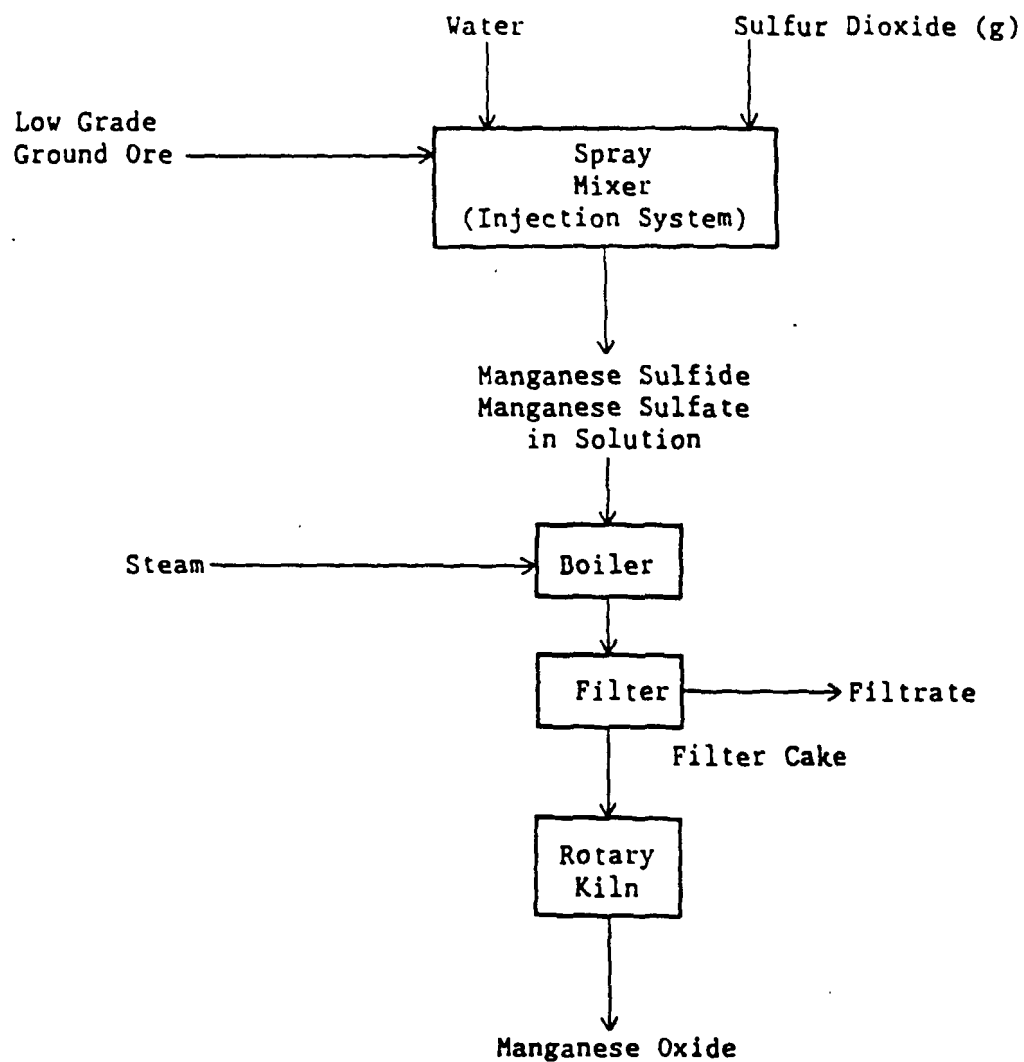
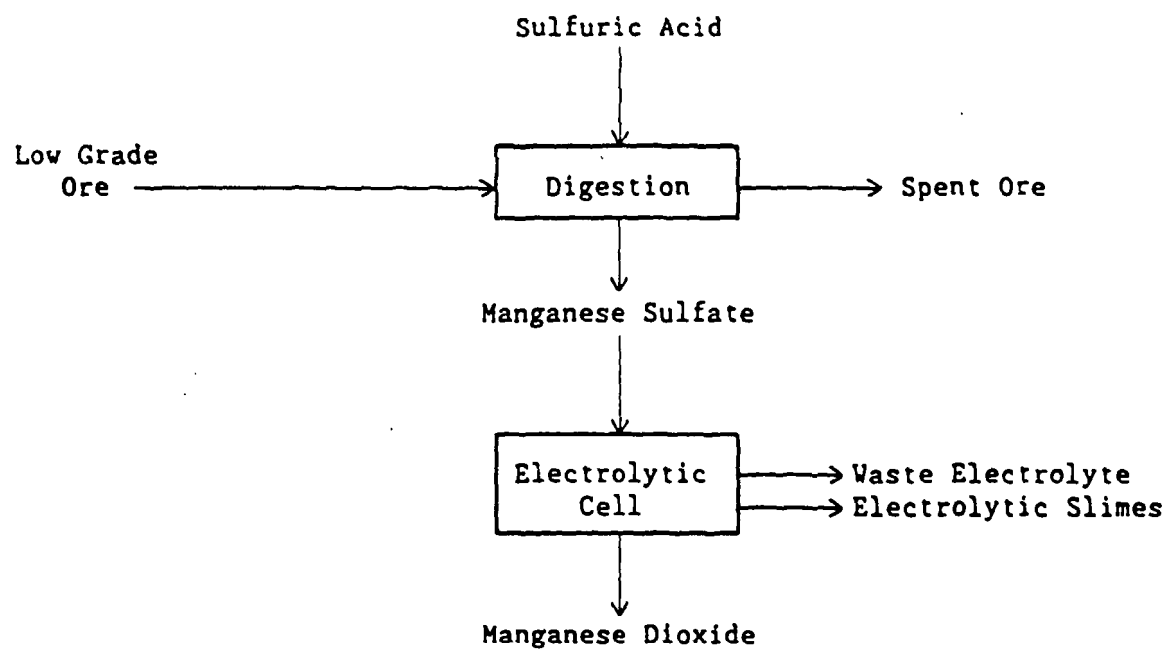


Figure 3-49
MANGANESE PROCESSING
VELCH PROCESS



silicomanganese furnace. Silicomanganese production would also have baghouse dusts and slag as wastes. Both the baghouse dust and slags could contain leachable toxic metals that could cause them to exhibit the RCRA characteristic of EP toxicity. Information on characteristics and quantities of these wastes was not available at the time of this writing.

The fused salt electrolysis method of making ferromanganese would produce wastes similar to those from aluminum production. Specific information was not available at the time of this writing.

Manganese metal and synthetic manganese dioxide can be produced by electrolytic processing (Figure 3-49). In either case, a solution of manganous sulfate is the electrolyte. Electrolytic metal is deposited at the cathode and manganese dioxide at the anode. Both producers of manganese metal and four of the five producers of manganese dioxide use electrolysis. Wastes could include spent electrolyte which would be acidic and possibly EP toxic and electrolyte purification which also could be acidic or toxic. Characteristics and quantities of these wastes were not available at the time of this writing.

The fifth manufacturer of synthetic manganese dioxide uses a chemical approach (Figure 3-47). In this method the manganese feed material is dissolved as a sulfate solution. Manganese carbonate is precipitated and then decomposed to manganese dioxide. The wastes from this process were not described in the literature reviewed for this report.

Producers of manganese materials from imported ore use several different processes and make several types of products. Readily available literature does not contain much information on the characteristics of wastes from these processes (Table 3-18). The information available does indicate that some of these wastes could exhibit hazardous characteristics. Further study of the manganese industry, for possible regulation under Subtitle C, is recommended.

Table 3-18

MANGANESE PROCESSING WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Submerged Arc Electric Furnace (Ferromanganese and silicomanganese)	1) Slag	N	N	N	?	FeMn slag recycled to SiMn production
	2) Baghouse Dust	N	N	N	?	
Fused Salt Electrolysis	1) Wastes	?	?	N	?	
Electrolytic Production of Manganese and MnO ₂	1) Waste Electrolyte	N	?	N	?	
	2) Electrolyte Purification Waste	N	?	N	?	
Chemical Production of MnO ₂	1) Waste	N	?	N	?	

* RCRA characteristics are reactivity, corrosivity, ignitability, and EP toxicity as defined in 40 CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

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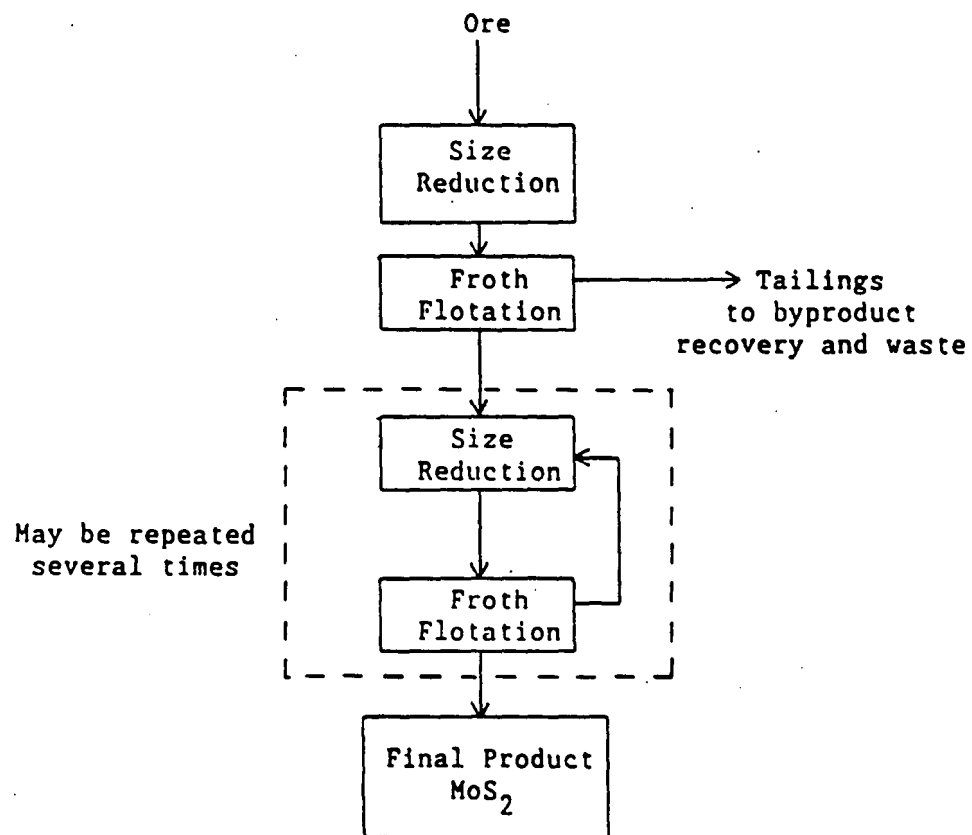
MOLYBDENUM

Molybdenum is a silvery-white, hard metal with a very high melting temperature. The primary use for molybdenum is as an alloying element for steel. Secondary uses generally make use of its corrosion resistance and high temperature properties. Molybdenum disulfide is a lubricant similar to graphite and is used alone and as a component of greases.

There are four mines in the U.S. that produce primarily molybdenum ore. Two are in Colorado, one in Idaho and one in New Mexico. Nine other mines, in Arizona, Nevada, New Mexico, and Utah can produce molybdenum as a byproduct of copper mining. Low prices and large stockpiles have caused considerable fluctuations in molybdenum production in recent years. The U.S. Bureau of Mines records show the following molybdenum production figures: 1982-84.4, 1983-33.6, 1984-103.7, 1985-108.4 million pounds. In 1986, production was estimated at 94 million pounds. This variation is often due to temporary mine closings, and it is unlikely that all of the mines mentioned above are producing at any one time.

The only ore mineral of molybdenum is molybdenite, which is naturally occurring molybdenum disulfide (MoS_2). Molybdenite can be readily recovered from its ores by froth flotation, which is the process used universally in the U.S. At the four primary molybdenum mines, the recovery process is generally as shown in Figure 3-50. The ore goes through a preliminary size reduction then a first stage of froth flotation, which recovers enough of the molybdenite that the tailings are discarded. The molybdenite concentrate contains considerable amounts of impurities, which are removed by several stages of regrinding and froth flotation. The tailings from these stages are recycled and eventually end up in the primary tailings. The primary tailings stream is the only waste stream from this process and is not expected to exhibit any hazardous characteristics, but metal leaching and acid formation are possible.

Figure 3-50
MOLYBDENUM
MOLYBDENITE CONCENTRATION
(Climax Practice)



The recovery of molybdenite from copper-molybdenum deposits is similar to that from primary molybdenum deposits. If the molybdenite content of the ore is high enough, it will be recovered by froth flotation separately from the copper minerals, usually before the copper minerals. The more common situation is that the molybdenite is at a low enough concentration in the ore that direct recovery is not economically feasible. In these cases the molybdenite and copper minerals are recovered in a bulk froth flotation and separated subsequently. Some operations recover the molybdenite first and others the copper first from the bulk froth flotation concentrate. Froth flotation tailings are the only significant waste expected from this recovery and are not expected to show any unusual characteristics different than those of copper tailings, including acid formation and metal leaching.

A small amount of molybdenite is upgraded by froth flotation for use as a lubricant. This process is a continuation of that described above for the production of molybdenite concentrates. Most molybdenite is converted to technical grade molybdic oxide, which is the starting material for a variety of chemical and metallurgical products.

Technical grade molybdic oxide (MoO_3) is made by roasting molybdenite concentrates in an oxidizing atmosphere at temperatures between 1000°F and 1300°F. The overall reaction produces molybdic oxide and sulfur dioxide. The sulfur dioxide is removed from the flue gases along with flue dusts which could contain volatile metals that were contaminants in the concentrates. These might include lead, zinc, tin, and others. The flue dusts and flue gas desulfurization sludges are the only wastes produced by this process, and as stated above, the flue dusts may exhibit toxic characteristics. Four companies produce technical grade molybdic oxide at five plants in Arizona, Iowa, Pennsylvania, and Utah.

Technical grade molybdic oxide is the most widely used form of molybdenum for alloying in steels. It may be used as a powder or formed into briquettes to reduce dust losses. The other form of molybdenum used for alloying is ferromolybdenum, an iron alloy. The molybdenum content varies

widely, but there are only two general processes for producing it. High carbon content ferromolybdenum is made by reducing technical grade molybdc oxide, calcium molybdate or sodium molybdate with carbon in the presence of iron in an electric furnace. The impurities form a slag which is thrown away. This slag is not expected to exhibit any hazardous characteristics.

Low carbon ferromolybdenum produced by the thermite process is more common than the high carbon alloy. In this process technical grade molybdc oxide, aluminum, ferrosilicon, iron oxide, limestone, lime, and fluorspar are mixed and the aluminum ignited. There is a very rapid reaction which produces fumes and dust which are drawn away by fans and collected in a baghouse. These fumes are not expected to exhibit hazardous characteristics. A metal "button" and a slag are also formed which are allowed to solidify and are then separated. The slag, which is not expected to exhibit any hazardous characteristics is discarded.

Other products are made from technical grade molybdc oxide in smaller quantities. These include sublimed molybdc oxide of high purity and ammonium molybdate. The production of sublimed molybdc oxide is not expected to produce significant quantities of waste with hazardous characteristics. Ammonium molybdate is produced by dissolution of technical grade molybdc oxide in ammonium hydroxide. Specific impurities are removed by stages of treatment that may include selective precipitation, ion exchange and solvent extraction. Then the ammonium molybdate is removed by crystallization. The exact procedure is proprietary to each producer. There are hazardous materials used in these processes, but the amounts and characteristics of any wastes are not available in the literature reviewed.

The waste streams and possible hazardous characteristics from the production of molybdenum products are summarized in Table 3-19. There are several waste streams that could exhibit hazardous characteristics. Therefore, further study for possible regulation under Subtitle C is recommended.

Table 3-19
MOLYBDENUM WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Molybdenite Recovery from Ore	Tailings	N	?	N	?	
Technical Grade Molybdic Oxide Production	Flue Dust	N	N	N	?	
Ferromolybdenum Production	High Carbon	N	N	N	N	
	Low Carbon	N	N	N	N	
	Slag	N	N	N	N	
	Flue Dust	N	N	N	N	
Ammonium Molybdate Production	Wastes	N	?	N	N	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability, and EP Toxicity as defined in 40 CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

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PLATINUM GROUP METALS

The platinum group metals (PGM) consist of ruthenium, rhodium, palladium, osmium, iridium, and platinum. The six metals can be classified into three groups of two, with each pair corresponding to a different family on the periodic table. Each metal pair exhibits similar physical and metallurgical properties.

Ruthenium and osmium are the hardest pair and have the strongest rigidity and abrasion resistance of the PGMs. Because of this, osmium alloys are used widely as pen tips and phonograph needles. Ruthenium is used mainly as an electrical contact and in the chemical industry as a titanium anode coating material.

Rhodium and iridium are the least abrasion resistant of the PGMs and have limited ductility at normal temperatures. Both metals are mainly used as alloying elements for platinum. Rhodium is also used as automotive catalyst for NO_x reduction.

Platinum and palladium are the softest and most malleable of the group and are both corrosion resistant. They are often alloyed with other PGMs and are the most widely used. Platinum's major use is as a catalyst in the automotive, petroleum, and chemical industries. Palladium is used most widely in the electrical, medical, and dental industries. It is also used in automotive catalytic converters.

The United States imports approximately 98% of its PGMs. Domestic production has been dropping for several years due to decreases in the mining and processing of copper, from which the PGMs are recovered. Approximately one ounce of PGM is recovered for every 35 short tons of copper produced in the U.S. Currently, domestic PGM production occurs as a by-product at two copper refining plants, in Utah and Texas.

In copper refineries in the U.S., PGM's are typically recovered from slimes that collect in electrolytic refining cells (Figure 3-51). These slimes are the insoluble materials from the impure copper anodes that are dissolved as part of the refining process. The slimes are removed from the cells periodically, and processed for their metal content. The initial treatment is to remove any remaining copper by leaching either without or after roasting. The decopperized slimes are then melted in a reverberatory furnace with a soda-silica flux. The flux helps form a siliceous slag which is removed from the furnace. Air is then blown through the molten metal and a lime flux is added. The air oxidizes any lead in the molten metal and the lead oxide forms a slag with the lime which is removed from the furnace. The siliceous slag and the lead slag are recycled or sent to a lead smelter. Fused soda ash is added to the furnace to form a soda slag. This slag is removed and sent to processing to recover selenium and tellurium. The remaining metal is a dore alloy containing gold, silver and platinum group metals and is processed to separate them.

There are three major sources of PGM ores in the U.S. which could be exploited if the price of platinum were to rise high enough. Since the U.S. imports most of its platinum from the Republic of South Africa, supply cutoffs (and price increases) could possibly occur due to the social instability of that country. The other major supplier of platinum is the Soviet Union. The three potential mining locations are at Stillwater, Montana; Duluth, Minnesota; and Crillion-La Perouse, Alaska. The Stillwater site is the largest, containing approximately 75% of the identified PGM reserve base in the U.S.

Platinum and palladium mining began at the Stillwater, Montana (near Nye, MT) site in March 1987. The platinum and palladium are recovered by bulk froth flotation of sulfide minerals. Wastes expected are listed in Table 3-20. Concentrates are shipped to Antwerp, Belgium, for metal recovery. There are no current plans for mining of the PGM deposits at the Duluth or Crillion-La Perouse locations.

Figure 3-51

PLATINUM GROUP METAL (PGM) RECOVERY FROM COPPER REFINING SLIMES

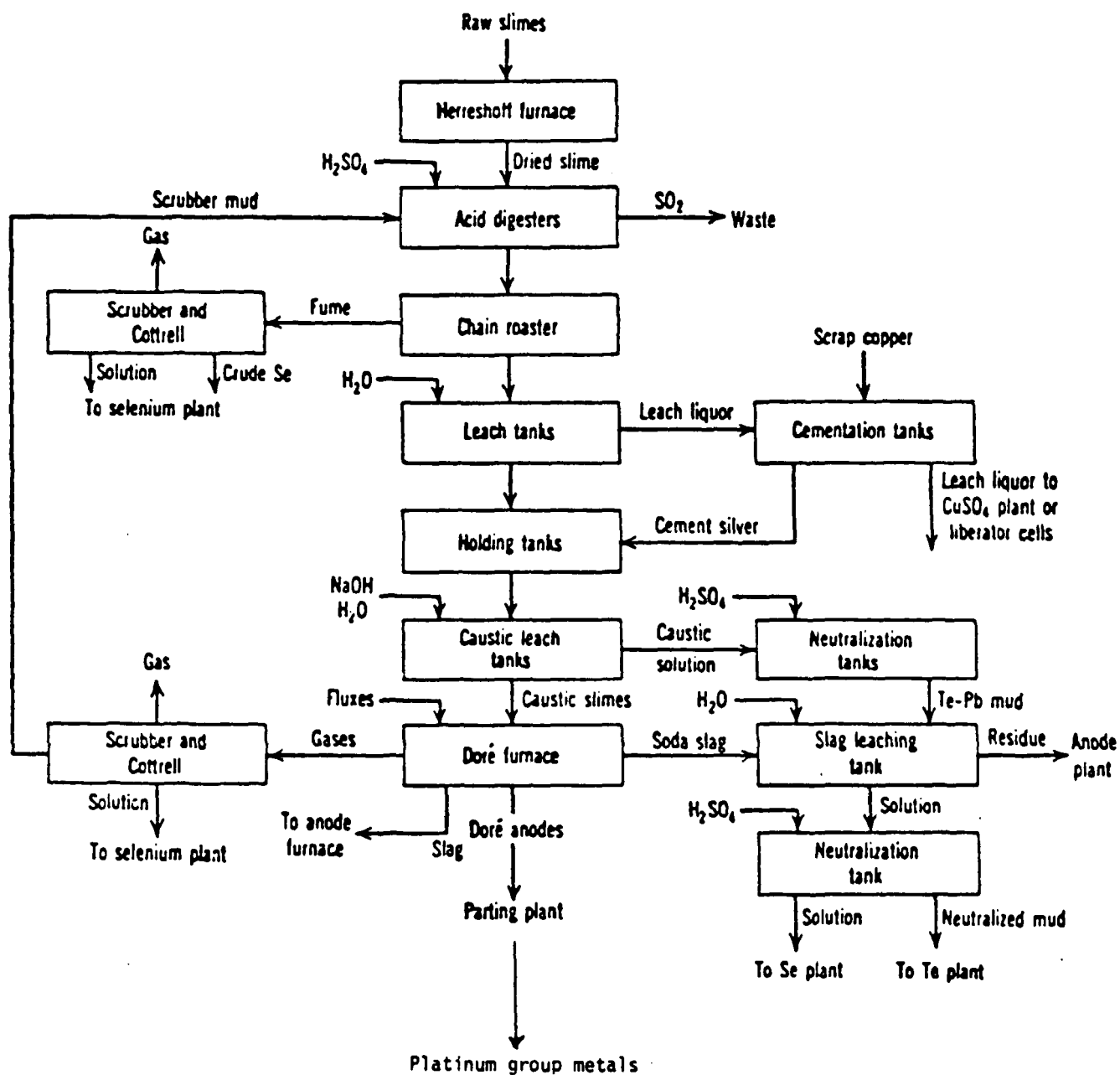


TABLE 3-20

PLATINUM GROUP METAL RECOVERY WASTES

Process	Waste	Possible RCRA Characteristics*				
		R	C	I	T	Comments
<u>Ore Processing</u>						
1. Froth Flotation	Tailing Waste	N	N	N	?	
2. Filtration	Filtrate Waste	N	?	N	?	
3. Thickening	Waste Waters	N	?	N	?	
<u>Production from Copper Refining Slimes</u>	Spent Acids (from parting/refining)		N	?	N	?

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

Many materials containing PGM also contain gold and silver so the refining processes for these materials also recover the other precious metals. There are two processes in use today, selective precipitation and solvent extraction. Solvent extraction is a more recent development that is replacing selective precipitation due to reduced time, capital and operating costs.

In the selective precipitation process, the material to be refined is dissolved in aqua regia (a mixture of hydrochloric and nitric acids). Gold is then precipitated from solution followed by platinum and palladium. The insoluble residue is treated to recover silver and the remaining PGM rhodium, iridium, ruthenium, and osmium. These metals are separated in an elaborate series of stages to yield pure metals. The primary wastes from this process would be spent acids, which might contain residual metals.

In the solvent extraction process the feed material is preleached to remove any base metals. It is then leached with hydrochloric acid and chlorine to dissolve the PGM. A series of solvent extractions remove and recover each of the metals separately. Again, the wastes expected would be spent acids.

The mining, beneficiation, and processing of PGMs can occur in conjunction with the recovery of other metals (such as copper and nickel) or it can be a site's sole activity. There is now a PGM mine in operation, however, no information is yet available about the nature of the wastes from it. The information available concerning PGM refining suggests that it may produce wastes with hazardous characteristics. Therefore, further study of this industry for potential regulation under Subtitle C is recommended.

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RARE EARTH METALS

The rare earth metals include sixteen elements: yttrium (atomic number 39), lanthanum (57), cerium (58), praseodymium (59), neodymium (60), promethium (61), samarium (62), europium (63), gadolinium (64), terbium (65), dysprosium (66), holmium (67), erbium (68), thulium (69), ytterbium (70), and lutetium (71). The elements with atomic weights 57 to 71 are collectively called the lanthanides since they all have properties similar to lanthanum. Scandium (21) is sometimes included as a rare earth metal since it is chemically similar to yttrium and the lanthanides.

The major use of rare earth metals are as catalysts in petroleum refining. They also have many metallurgical applications as pyrophoric alloys. The third major application is the use of lanthanide oxides as a constituent of high quality optical glass.

The two major minerals used as sources of rare earth metals are monazite (Ce-La-Nd-Pr phosphate) and bastnaesite (Ce-La-Nd-Pr fluorcarbonate). Monazite is mined in Australia, India, the United States, and other areas to a lesser degree. Bastnaesite is primarily mined in the United States and China. Several other ores are mined for the rare earths as well, including xenotime, apatite, yttrifluorite, cerite, and gadolinite. Total U.S. production of rare earth metals was approximately 14,000 short tons in 1986. Virtually all of the rare earth metals consumed in the U.S. are mined and processed domestically; reliance on imports is minimal.

Rare earth mineral ores are mined domestically by two companies at mine locations in California (bastnaesite ore) and in Florida (monazite ore). The bastnaesite mining is principally for the recovery of the rare earths. The monazite mining occurs in conjunction with the processing of heavy mineral sands for titanium and zirconium recovery. These ores are processed by four companies with plants in Arizona, California, Colorado, Pennsylvania, Tennessee, and Texas. The processing of monazite ore in the

U.S. is accomplished by sulfuric acid digestion, and bastnaesite ore by hydrochloric acid digestion.

MONAZITE ORE PROCESSING

Rare earth metals are recovered as oxides from monazite ore by an acid digestion process as shown in Figure 3-52. The ore undergoes grinding, spiraling, or other similar operations for the initial coarse purification of the ore. Magnetic separation removes the magnetic ore constituents which can be processed separately or discarded as waste. The refined ore is then digested with sulfuric acid at 200°-220°C. Rare earth sulfates and thorium sulfates are then dissolved and removed from the waste monazite solids by filtration. Rare earth elements are then precipitated as oxalates or sulfates. These precipitates undergo caustic digestion (or roasting) to form rare earth oxides which are finally recovered by filtration. The resulting filtrate is discarded as a waste.

BASTNAESITE ORE PROCESSING

Bastnaesite mining near Mountain Pass in southeastern California is the major source of rare earth metals in the U.S. The recovery process of the rare earths from this ore is shown in Figure 3-53. The ore is initially crushed, ground, classified, and concentrated to increase the rare earth concentrations from 15% to 60%. Tailings produced during these operations are discarded as waste. The concentrated bastnaesite undergoes an acid digestion to produce several rare earth chlorides. Hydrochloric acid is used to digest the bastnaesite. The resulting slurry is filtered, and the filter cake is further digested with sodium hydroxide to produce rare earth hydroxides. This rare earth hydroxide cake is chlorinated, converting the hydroxides to chlorides. Final filtration and evaporation yields the solid rare earth chloride products. The wastes produced include a sodium fluoride filtrate, which is recovered for further processing, and filter cake which is discarded.

Figure 3-52
RARE EARTH RECOVERY FROM MONAZITE BY THE SULFURIC ACID PROCESS

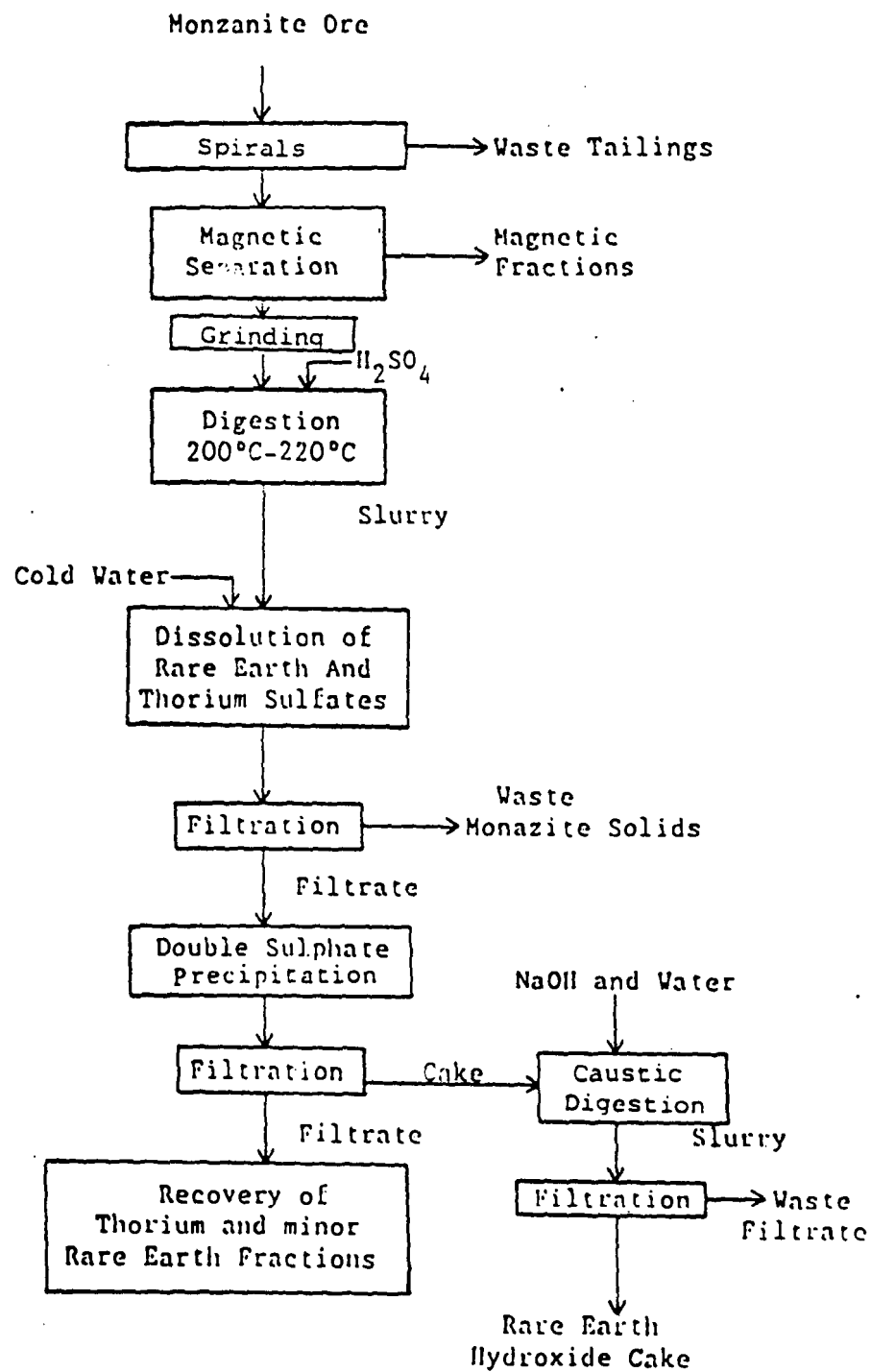
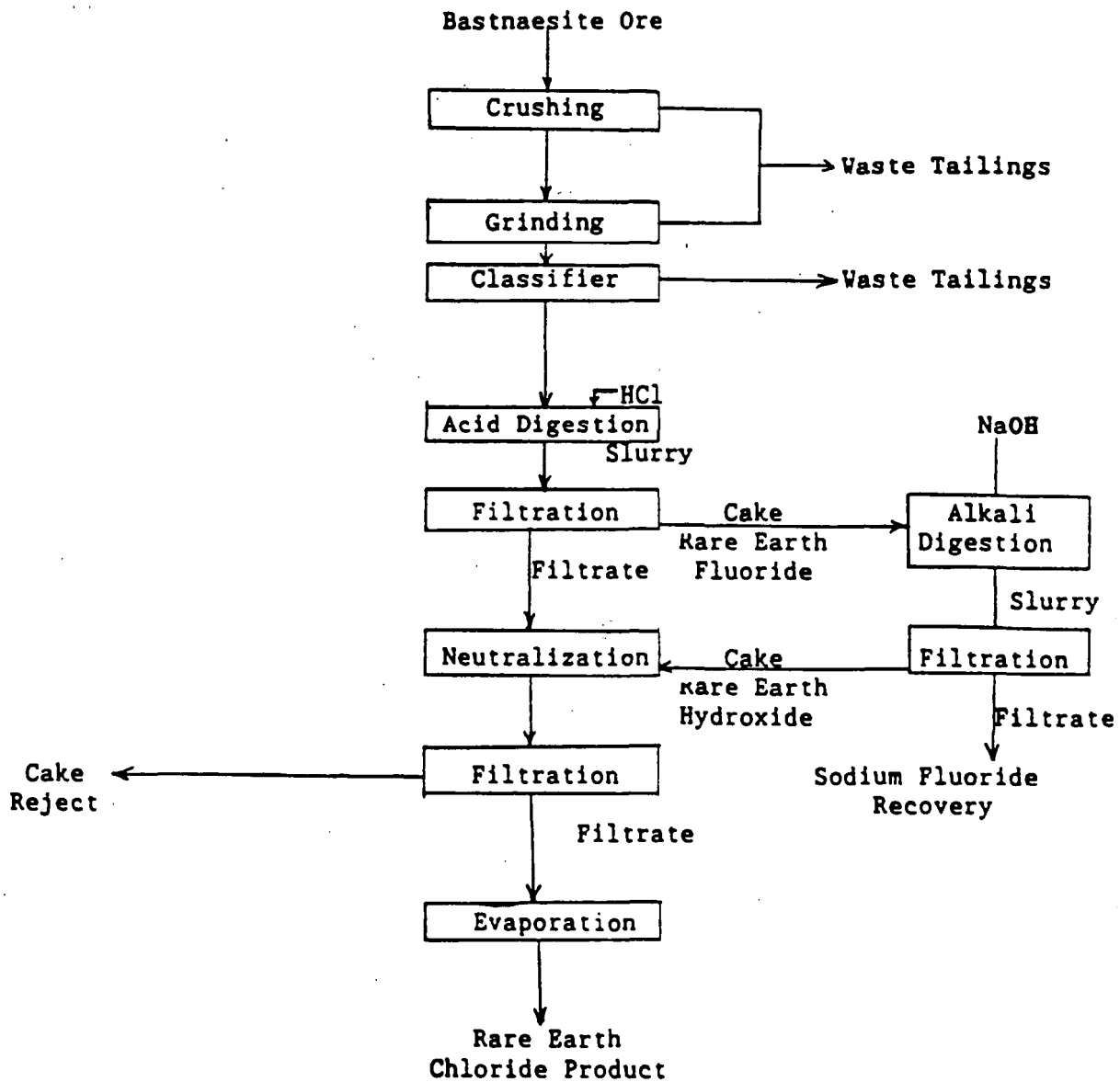


Figure 3-53
 PRODUCTION OF RARE EARTH CHLORIDES FROM BASTNAESITE ORE



The rare earth hydroxides and chlorides which are recovered from monazite and bastnaesite ore, respectively, have no markets or commercial uses. They must undergo further processing to produce and recover individual rare earth metal compounds for a variety of applications. Several processes are used to produce rare earth fluorides, nitrates, carbonates, oxides, and pure metals. Processes used include fractional crystallization, fractional precipitation, solvent extraction, ion exchange, and reduction.

Using fractional crystallization, one or more rare earths in a mixture are precipitated by changing the salt concentrations in solution through evaporation or temperature control. Fractional precipitation involves adding a precipitating agent to selectively remove a metal from solution. A wide variety of processes have been developed to recover specific rare earths by these two techniques, including:

- Separation of lanthanum, praseodymium, and neodymium with ammonium nitrates;
- Separation of yttrium earths by bromate crystallization;
- Cerium salt purification using ammonium nitrate;
- Separation of lanthanum by magnesia basicity precipitation; and
- Separation of yttrium group by sodium sulfate precipitation.

In general, crystallization and precipitation processes produce waste salts and salt solutions requiring proper treatment or disposal. If organic precipitation is used, then organic-containing waste fractions may be produced as well.

Liquid-liquid solvent extractions are often performed to separate a mixture of rare earths from each other. An aqueous solution containing rare earth salts is flowed countercurrent to an immiscible organic stream, i.e., tributyl phosphate, which selectively extracts one rare earth from the others. Several stages of extractions are needed to separate each rare earth metal. Each organic stream is then scrubbed with an aqueous stream

(acid, basic or neutral) to transfer the rare earth element into an aqueous phase. Figure 3-54 shows such a process for the individual recovery of lanthanum, praseodymium, neodymium, and samarium from a nitrate solution containing the four together. Since all of the products are aqueous solutions, the solvents used all leave the process as wastes. These solvents may be discarded as waste or recycled.

Ion exchange is used to produce highly pure rare earths in relatively small quantities. Since ion exchange processes are batch processes; they are not suitable for high volume production; however, few other processes can produce rare earths of such high purity, which are needed for many applications.

Since the rare earths form trivalent cations ($3+$), a cation exchange resin is used. For separating a mixture of lanthanides, the resin is first flushed with a solution such as cupric sulfate to prepare the resin for ion exchange (see Figure 3-55). A solution containing the lanthanides is then passed over the ion exchange resin. The lanthanides displace the cation, in this case cupric, on the resin surface. This step produces an aqueous waste containing the cation which was exchanged, and small amounts of rare earths. At this stage, the lanthanides have been deposited on the resin as a mixture. To separate individual rare earth elements, an element containing a complexing agent, such as ammonium ethylenediamine tetraacetic acid (NH_4^+EDTA), is passed over the resin. The EDTA has a high affinity for rare earths, and the lanthanides are complexed with the EDTA and displaced by NH_4^+ on the resin. Each lanthanide has a different affinity for EDTA, and individual lanthanides can be separated and recovered as a result of these varying affinities. Relative to the amount of product generated, large quantities of waste solutions are generated during the process. The waste solutions may be acidic, basic, or neutral, and will contain the metals displaced from the resin during ion exchange, as well as the complexing agents used.

High purity rare earth metals can be produced by the metallothermic reduction of rare earth halides. This process is used when 99.99% purity

Figure 3-54
RARE EARTH SEPARATION BY SOLVENT EXTRACTION

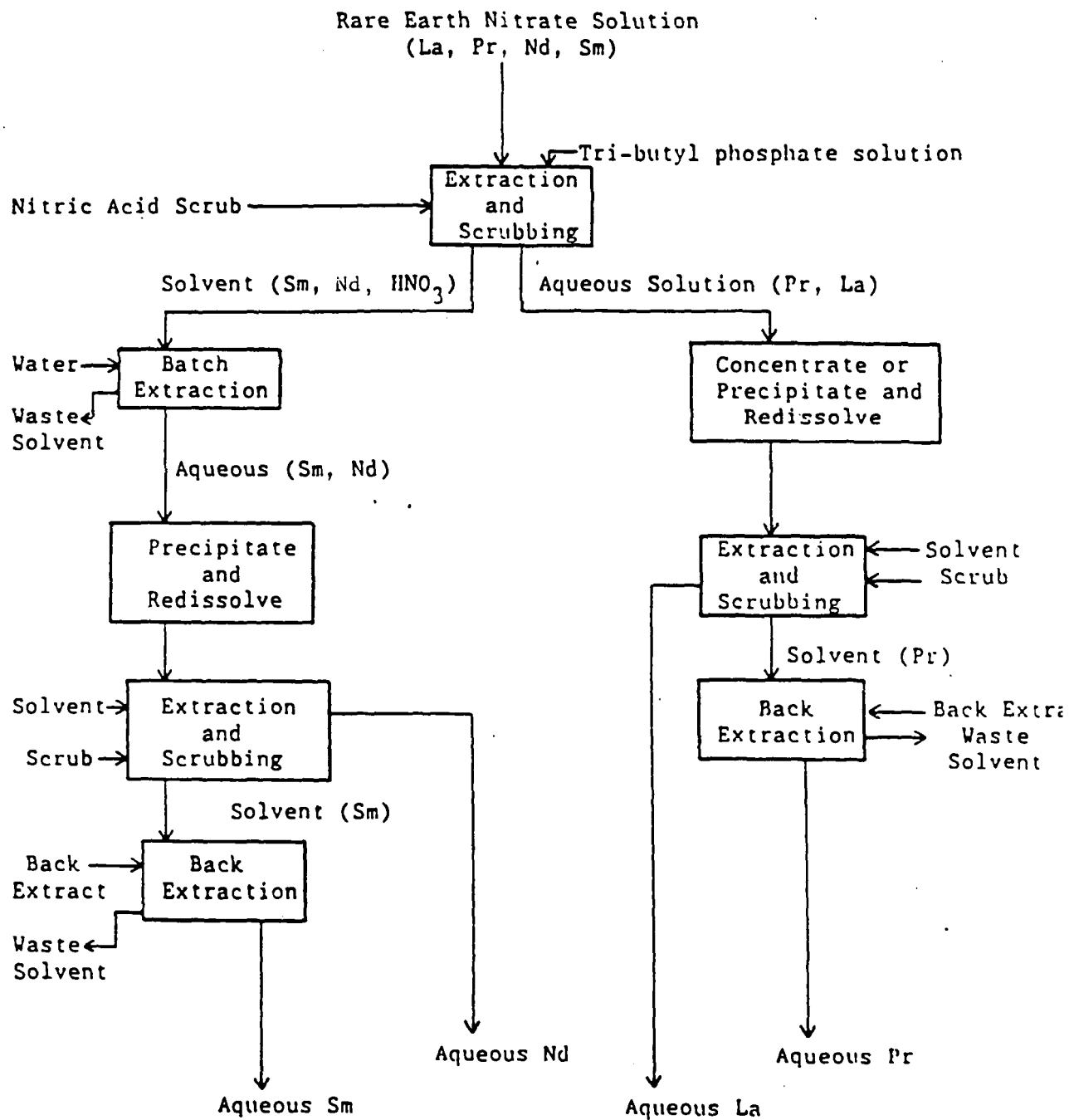
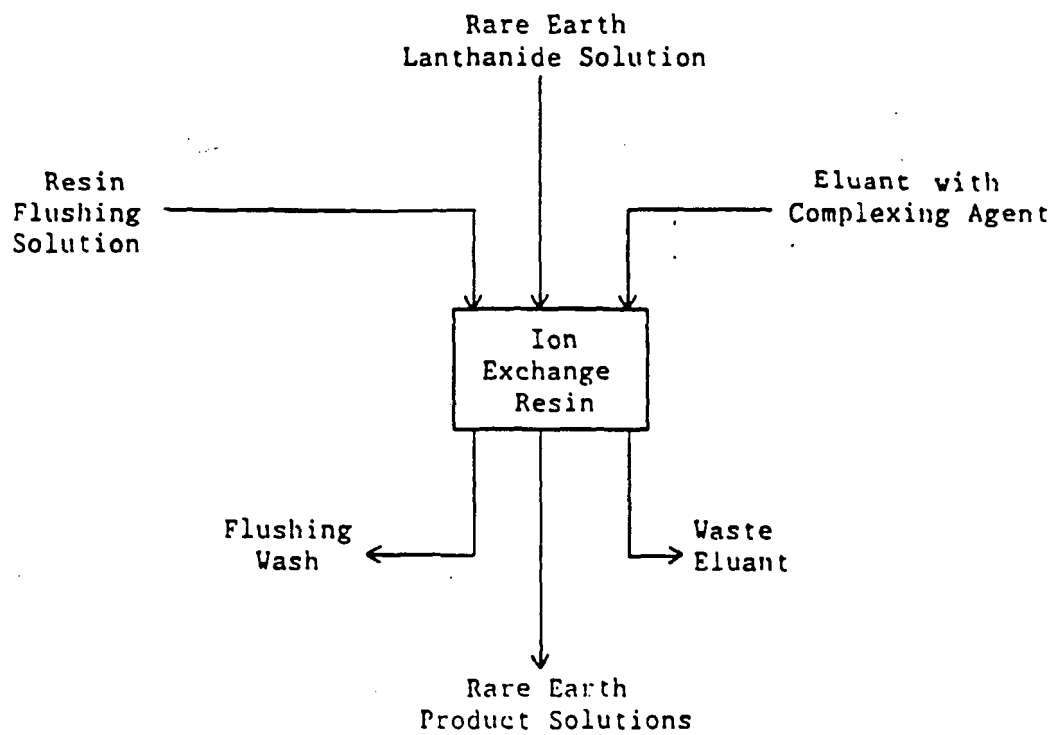


Figure 3-55
LANTHANIDE SEPARATION BY ION EXCHANGE



is required. After converting the rare earths into fluorides, they are reduced to the metallic state through contact with calcium or barium at high temperatures.

A large variety of potentially hazardous wastes are produced during the mining, beneficiation, and processing of rare earth metals Table (3-21). The acid digestions used to treat raw ores may produce corrosive wastes, while refining processes, such as solvent extraction produce waste solvents and the aqueous raffinate often contain quantities of residual product and byproducts which may have hazardous characteristics. Further investigation of the quantities and characteristics of these wastes is recommended for potential regulation under Subtitle C.

Table 3-21

RARE EARTH METAL PROCESSING WASTES

Process	Waste	Possible RCRA Characteristics*				Comments
		R	C	I	T	
Monzanite Ore H_2SO_4 Process	Waste tailings	N	N	N	N	
	Magnetic fractions	N	N	N	N	
	Waste Monazite Solids	N	N	N	?	
	Waste Filtrate	N	?	N	?	
Bastnaesite Ore HCL Process	Waste tailings	N	N	N	N	
	Cake reject	N	?	N	N	
Solvent Extraction	Waste solvent	N	?	?	?	
Ion Exchange	Flushing Waste	N	?	N	?	
	Waste Eluant	N	?	N	?	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

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RHENIUM

Rhenium is a metal with the third highest melting point and fourth highest density of any element. Approximately 90 percent of all rhenium is used in platinum-rhenium catalysts in the production of unleaded and low-lead gasoline. Because of its superior properties at high temperatures, it is also used in thermocouples, heating elements, filaments, and electrical contacts.

There are no ores which are mined for rhenium. The majority of rhenium is recovered from molybdenite concentrates from porphyry copper ores. Porphyry copper ores are mined in Utah, Arizona, Nevada, and New Mexico. Eight companies produced rhenium from these ores in 1986.

During the processing of porphyry copper ores, molybdenite is concentrated in order to recover molybdenum. As a byproduct, the molybdenite concentrate is treated for rhenium recovery, as shown in Figure 3-56. Roasting the molybdenite generates volatile oxides of rhenium, molybdenum, and sulfur. These oxide fumes are collected by scrubbing with a caustic solution, which neutralizes the sulfur oxides. Anion exchange (or solvent extraction) is then used to separate and recover rhenium or perrhenate (ReO_4), which is reduced to ReS_2 under acidic conditions. Oxidation and evaporation then produce a rhenium salt which can either be sold commercially or be reduced to metallic rhenium by reduction with hydrogen. The wastes generated include the roasting slag, anion exchange waste solutions, and acidic wastes generated during reduction with H_2S . If solvent extraction is used, waste solvent will be generated in place of the anion exchange wastes.

The above-mentioned wastes may potentially have hazardous characteristics (Table 3-22). Therefore, further investigation is recommended for potential regulation under Subtitle C.

Figure 3-56
Rhenium Recovery From Molybdenite Concentrate

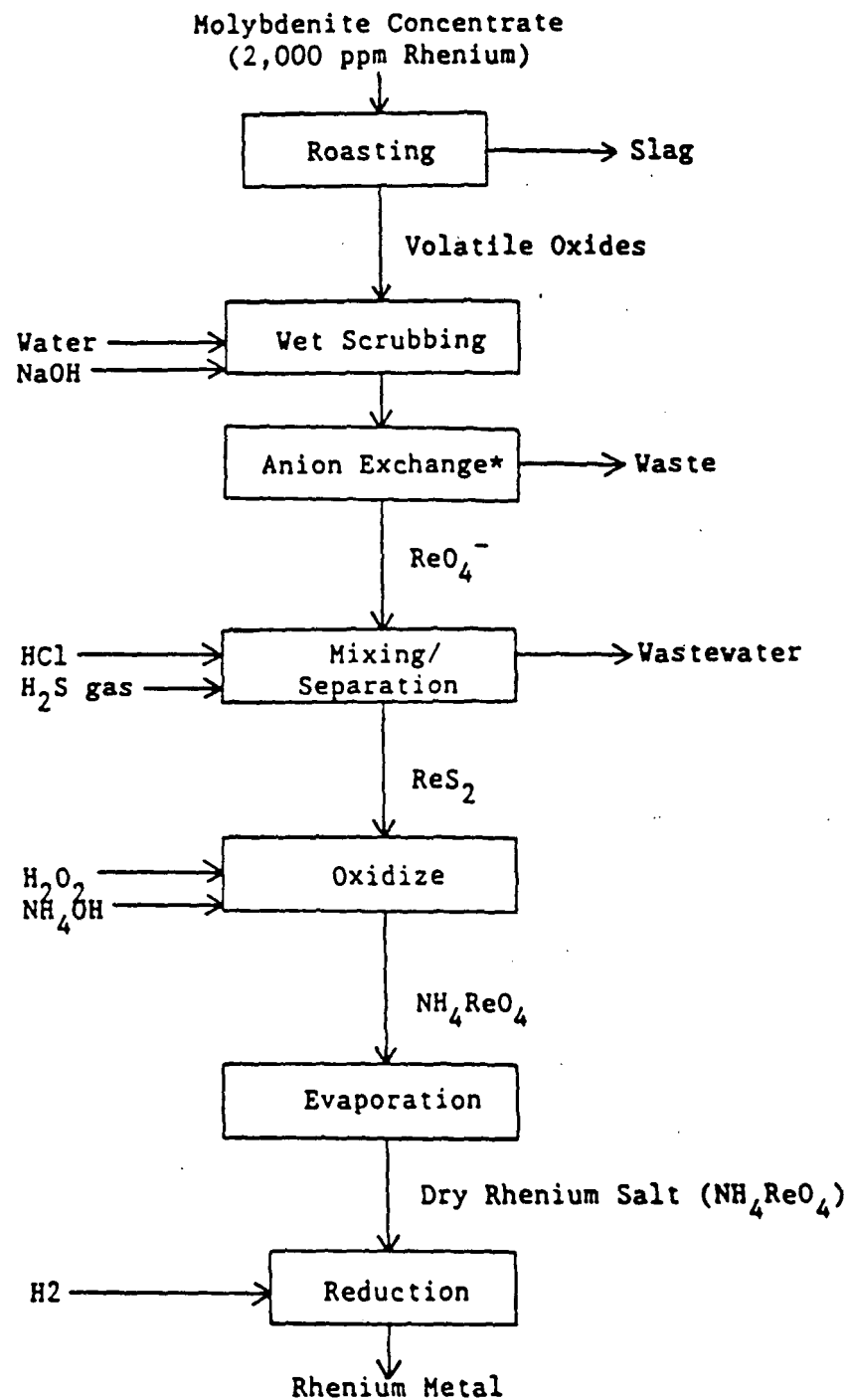


Table 3-22
RHENIUM WASTES

Process	Waste	Possible RCRA* Characteristics				Comments
		R	C	I	T	
Roasting	Slag	N	N	N	?	
Anion Exchange	Waste Solution	N	?	N	N	
Solvent Extraction	Extraction Waste	N	N	?	N	
Mixing/Separation	Wastewater	N	?	N	N	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibly that waste could exhibit this characteristic.

REFERENCES

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Marks, H.W., Encyclopedia of Chemical Technology, 1982.

RUBIDIUM

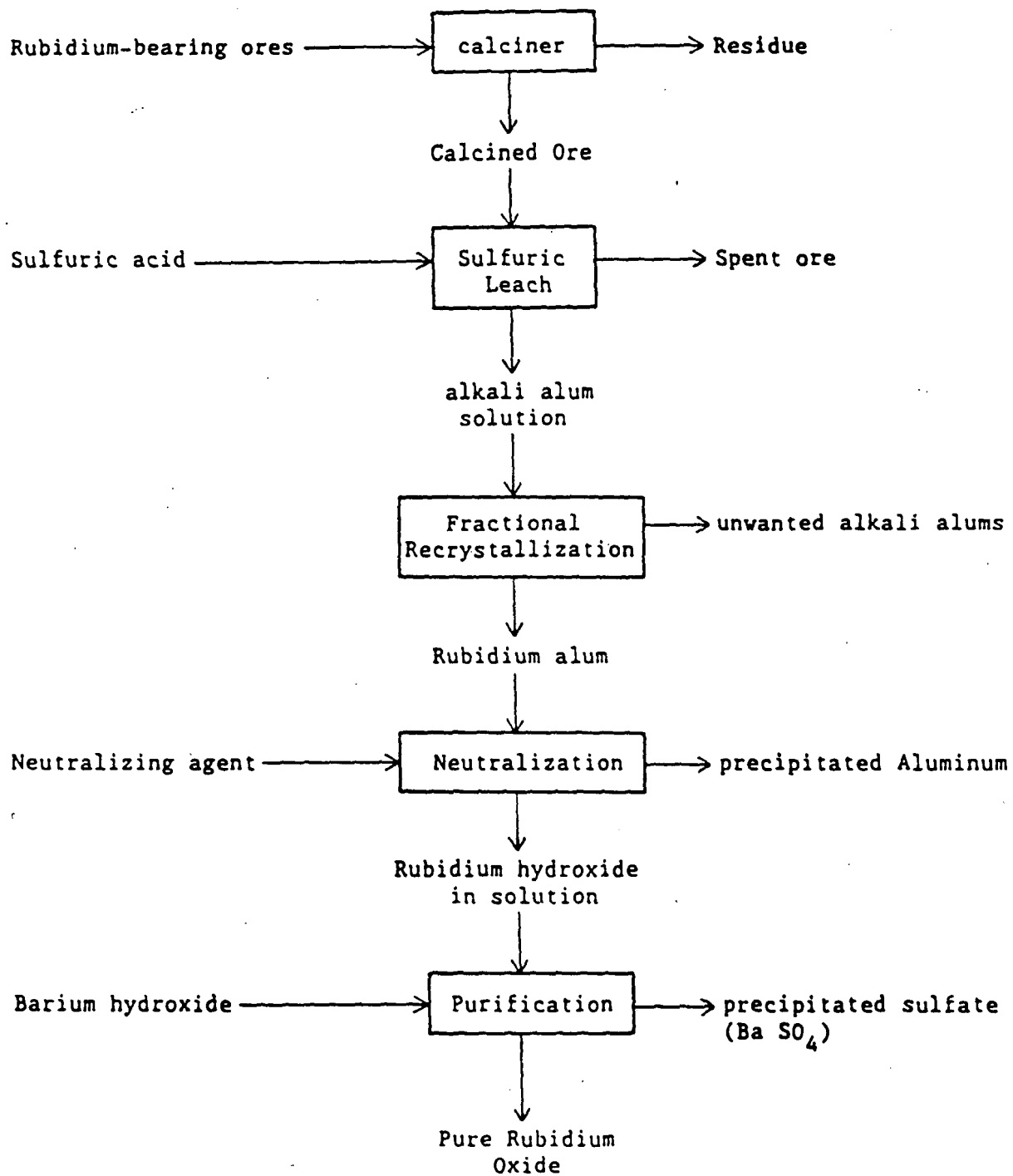
Rubidium is a soft, silver-white, ductile, alkali metal. Rubidium has both chemical and physical properties similar to potassium and cesium. It is one of the most electro-positive and alkaline elements, second only to cesium. Rubidium is the fourth lightest metal. In the presence of air, rubidium reacts violently with water and burns with a violet flame. When oxidized, rubidium will form a mix of four different oxides: yellow monoxide, dark brown peroxide, black trioxide, and dark orange superoxide. Rubidium alloys readily with other alkali metals, alkaline-earth metals, and other metals. The metal will form double halide salts with cadmium, antimony, bismuth, copper, and other metals. The alkaline alloys and double halide salts are water insoluble and nonhygroscopic. Rubidium compounds such as acetate, bromide, hydroxide, and sulfate are water soluble and hygroscopic. In general, rubidium and cesium can be used interchangeably.

Rubidium is the sixteenth most abundant element in the earth's crust. It is widely dispersed and commonly found in association with potassium minerals and salt brines. Lepidolite, a lithium mica, contains approximately 2 to 4 percent rubidium oxide. Pollucite, a cesium-aluminum silicate, contains 1.5 percent rubidium peroxide.

There is little commercial use of rubidium. Rubidium is used on a limited basis in the chemical, medical, and electronic industries. The Bureau of Mines estimated in 1985 the U.S. capacity for producing rubidium was above 6000 pounds per year and forecast that demand would not exceed that figure through the year 2000.

Domestic production in 1986 of rubidium was entirely dependent on the importation of lepidolite ores from Canada. The traditional methods to extract rubidium from ores (Figure 3-57) involve the recovery of mixed alkali alums from the ores. This is achieved by prolonged heating of the

Figure 3-57
RUBIDIUM
ALUMS. EXTRACTION



ores with sulfuric acid. The resulting alum solution is filtered from the residue and washed with water. The alkali alums are separated by fractional recrystallizations, and the rubidium alum is neutralized, forming rubidium hydroxide in solution. Barium hydroxide is added to the solution to remove the sulfate by precipitating barium sulfate.

The alternate chlorostannate method (Figure 3-58) requires the removal of a large percentage of the potassium from the ore. The dissolved carbonates are converted to chlorides, including cesium chlorostannate, which is less soluble than rubidium chlorostannate, and is precipitated out. Rubidium chlorostannate is separated from the chlorides by pyrolysis, electrolysis, or chemical methods. Rubidium may also be removed from alkali metal solutions by solvent extraction and ion exchange (Figure 3-59).

The reduction of pollucite or lepidolite ores with an active metal and vacuum distillation will yield pure rubidium metal (Figure 3-60).

Since domestic rubidium is extracted from lepidolite imported from Canada, no domestic mining waste can be identified. Recovery of rubidium from ores involves leaching with sulfuric acid, separation by stannic chloride, and electrolysis. These processes would result in the following wastes: waste acid, waste slimes, sludges and residues, and spent ore (Table 3-23). Further investigation is recommended for possible regulation under Subtitle C.

Figure 3-58

RUBIDIUM
STANNIC CHLORIDE PRECIPITATION

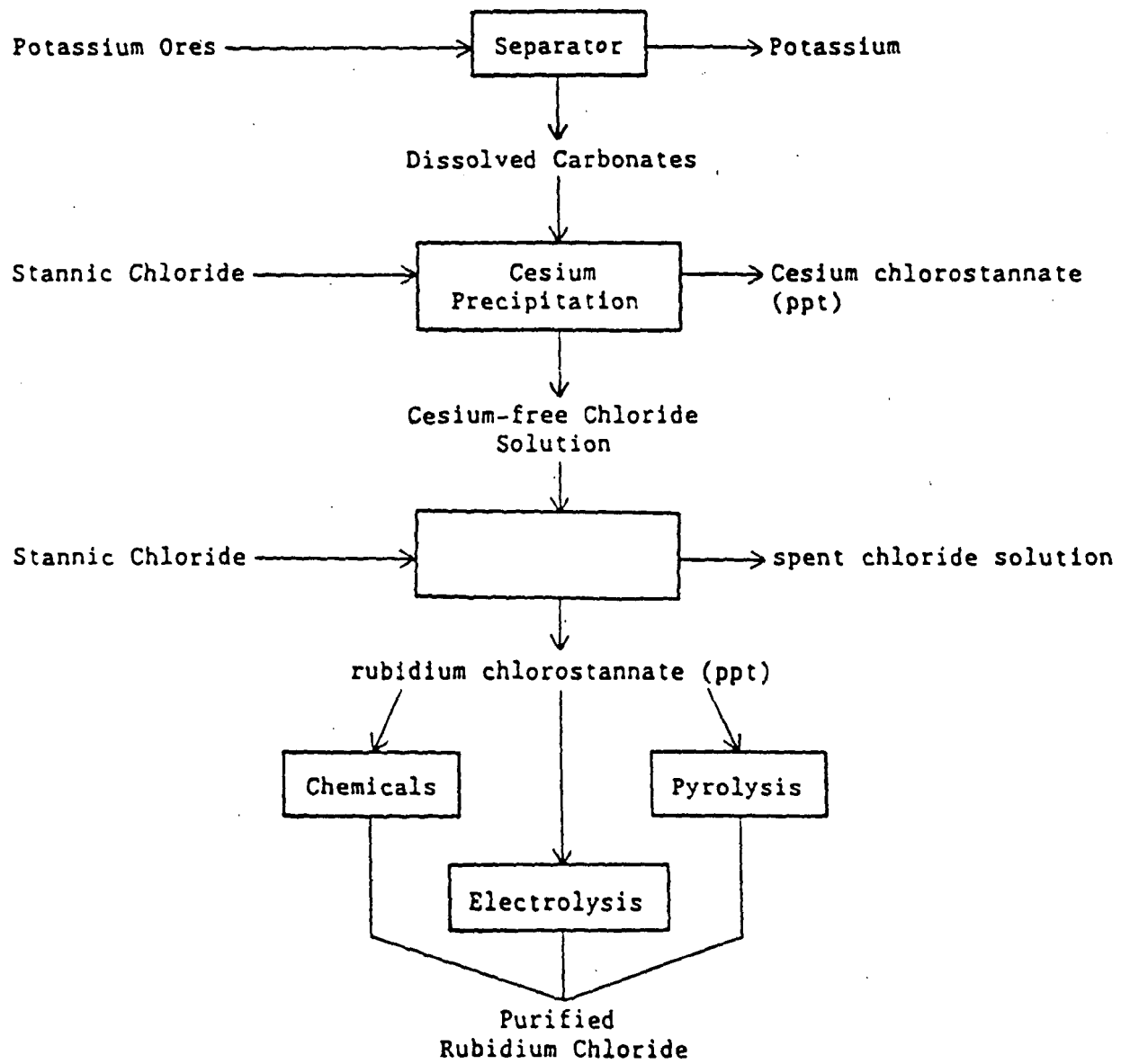


Figure 3-59

RUBIDIUM
FROM ALKALI METALS

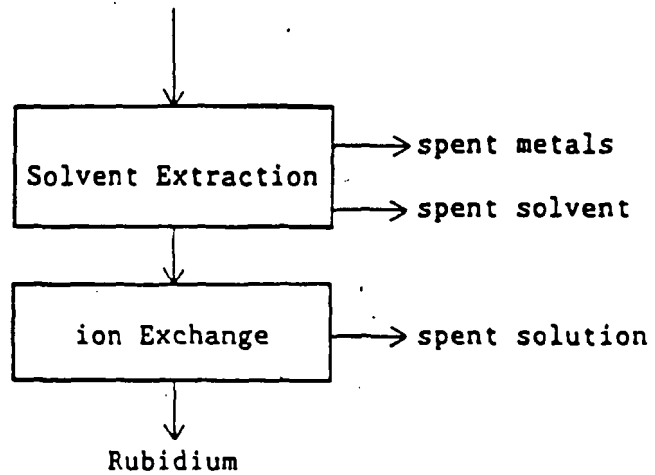


Figure 3-60

RUBIDIUM
REDUCTION

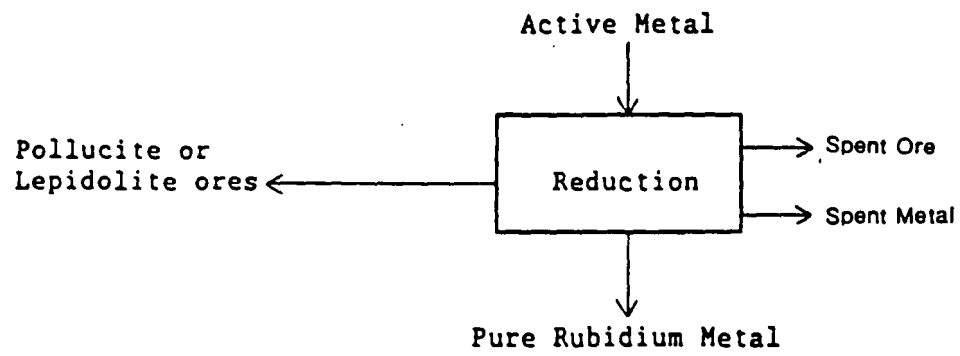


Table 3-23
RUDIBIUM WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Alum Extraction	1) Calciner Residues	N	N	N	?	
	2) Spent Ore	N	N	N	?	
	3) Alkali Alums	N	?	N	?	
	4) Precipitated Aluminum	N	N	N	N	
	5) Precipitated Barium Sulfate	N	N	N	N	
Stannic Chloride Precipitation	1) Cesium Chlorostannate (ppt)	N	N	N	?	
	2) Spent Chloride Solution	N	N	N	?	
	3) Pyrolytic Residue	N	N	N	?	
	4) Electrolytic Slimes	N	N	N	?	
	5) Chemical Residues	?	?	N	?	
Solvent Extraction	1) Spent Metals	N	N	N	?	
	2) Spent Solvent	N	N	?	N	
	3) Spent Ion-exchange Solution	?	?	N	?	
Reduction	1) Slag	N	N	N	?	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibly that waste could exhibit this characteristic.

REFERENCES

Marks, H.F., Encyclopedia of Chemicals Technology, 1978.

U.S. Bureau of Mines, Mineral Commodity Summaries, 1987.

SELENIUM

Selenium is a nonmetal with semimetallic properties. Its electrical conductivity is normally low, but when it is irradiated by light, its conductivity increases up to 200 times. The change in conductivity is proportional to the light intensity, and because of this selenium is used to make light sensing devices. Its major uses are in electronic and photocopier machines, in glass manufacturing, and in chemical pigments.

Selenium is found in 75 different mineral species, although no selenium ores exist. As there are no ores which could be mined only for selenium, it is obtained as a secondary product during the recovery of other metals, primarily as a byproduct of copper refining. Electrolytic copper refinery slimes contain 1.5 to 21 wt percent selenium, depending on the quality of the copper ore used.

The two primary methods of recovery of selenium from copper slimes are smelting with soda ash (Na_2CO_3) and roasting with soda ash. The soda ash smelting process is shown in Figure 3-61. After the copper has been removed from the slime, the slime is mixed with soda ash and silica and smelted in a furnace. Slag containing silica, iron, and several other metal impurities is produced as a waste. The molten charge containing selenium is aerated to oxidize and volatilize the selenium, and the remaining solids are removed for precious metal recovery. The soda ash is leached with water and filtered to separate unwanted solid impurities, which are discarded as waste. The selenium-containing filtrate is neutralized to precipitate out tellurium, and is then acidified to precipitate selenium. The selenium sludge is then boiled, washed, dried, and pulverized to yield the selenium product. Washing produces a relatively clean wastewater stream.

The second major selenium recovery process, soda roasting, is shown in Figure 3-62. Decopperized slime is roasted with soda ash to produce sodium

Figure 3-61

SELENIUM RECOVERY FROM COPPER SLIMES BY SODA SMELTING

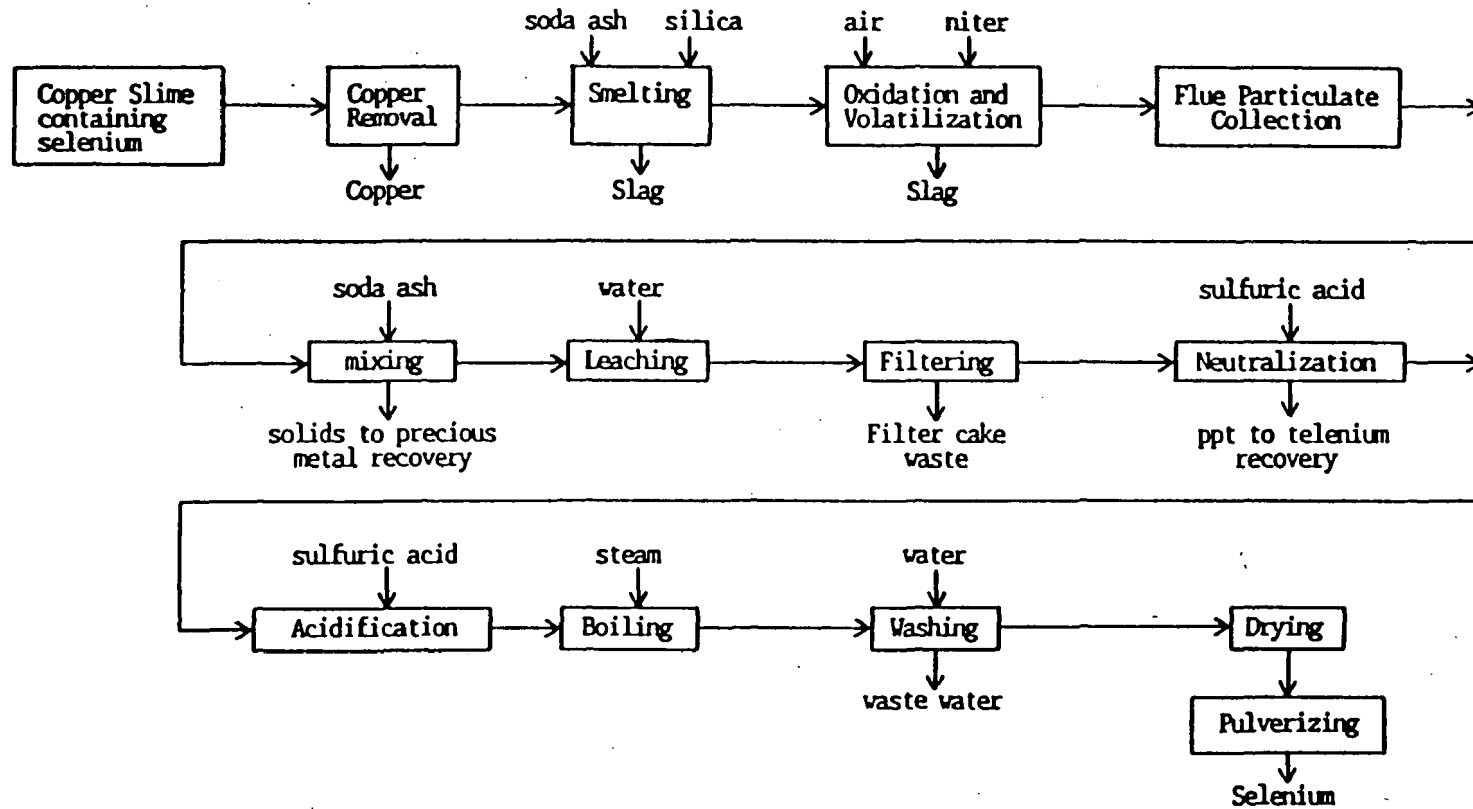
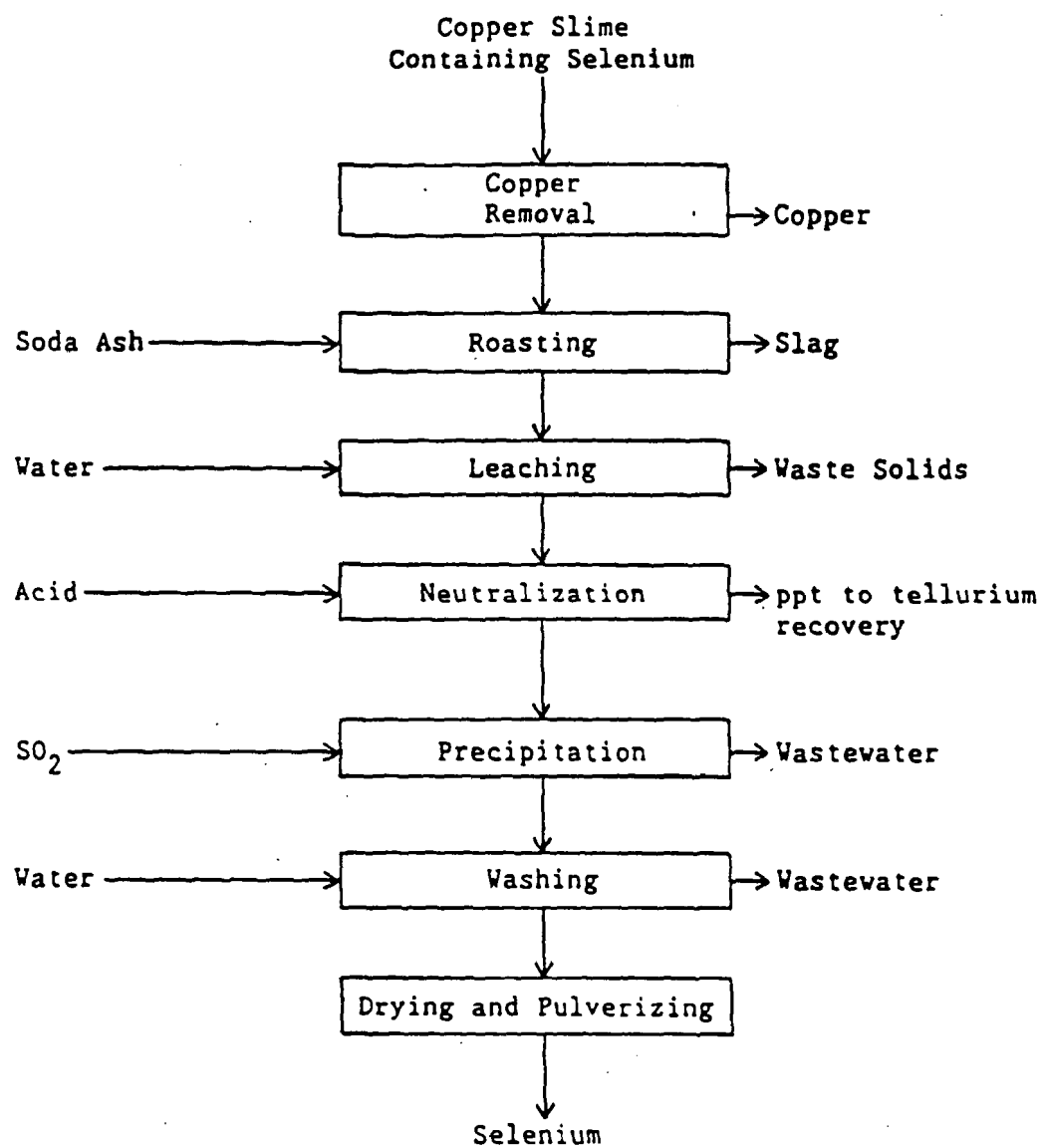


Figure 3-62

SELENIUM RECOVERY FROM COPPER SLIMES BY SODA ROASTING



The selenium is then leached with water, neutralized to precipitate tellurium and then with SO_2 to precipitate selenium. Wastewater produced during the precipitation and final washing operations may be acidic.

The selenium obtained by either the soda smelting or soda roasting process is purified as shown in Figure 3-63. The crude selenium is dissolved in sodium sulfite, and the resulting solution is filtered to remove unwanted solids in the waste filter cake. The filtrate is acidified with sulfuric acid to precipitate the selenium. An acidic wastewater is produced during this precipitation process. The selenium precipitate is distilled to drive off impurities, producing a high purity selenium for commercial/industrial use.

The processes identified for the recovery and purification of selenium include standard unit operations used in the industry. Besides the use of acids, no hazardous substances were identified as being used in the processing. Still, it is possible that the wastewater or slags produced may have hazardous characteristics (Table 3-24). Therefore, further investigation for possible regulation under Subtitle C is recommended.

Figure 3-63
PURIFICATION OF CRUDE SELENIUM

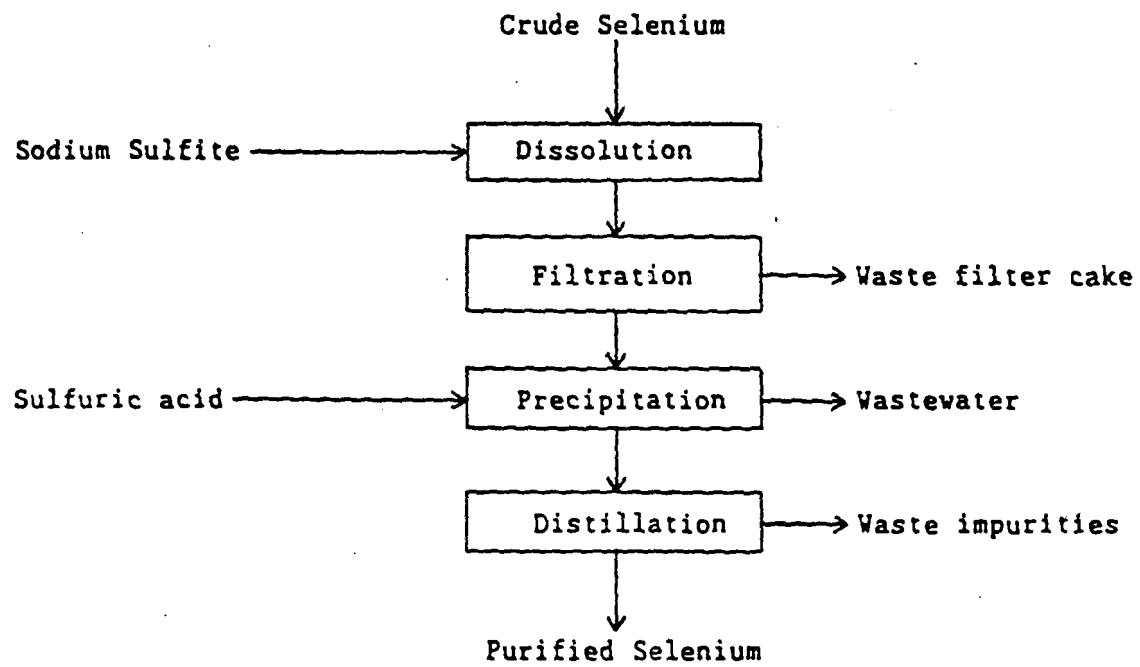


Table 3-24
SELENIUM WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Soda Smelting	1) Smelting Slag	N	?	N	?	
	2) Oxidation Slag	N	?	N	?	
	3) Filter Cake	N	?	N	?	
	4) Wastewater	N	?	N	N	
Soda Roasting	1) Roasting Slags	N	?	N	?	
	2) Leaching Solids	N	?	N	?	
	3) Wastewater	N	?	N	N	
Selenium Purification	1) Filter Cake	N	N	N	N	
	2) Wastewater	N	?	N	N	
	3) Distillation Impurities	N	N	N	N	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibly that waste could exhibit this characteristic.

REFERENCES

Bureau of Mines, Mineral Commodities Summaries, 1987.

Marks, H.W., Encyclopedia of Chemical Technology, 1978.

SILICON AND FERROSILICON

Silicon is a hard, brittle, silver-gray metalloid that is never found free in nature. It is always found in compounds with oxygen or other elements as oxides or silicates. Silicon comprises approximately 26 percent of the earth's crust making it the second most abundant element after oxygen. Almost all of the crust is made of silicate minerals. Silica, silicon dioxide, is used as an industrial material in itself and is discussed elsewhere. Most silicon is used as an alloying element in the steel and aluminum industries, both as silicon metal and as ferrosilicon alloy. Another major use of silicon is in the manufacture of silicones and silanes in the chemical industry. A use that is small in volume (approximately 1 percent of total consumption) but of great economic significance is in the manufacture of solid-state electronic devices. Total domestic production of all forms was estimated at 360 thousand short tons in 1986. Ferrosilicon was produced by 8 companies in 13 plants, primarily for the steel industry. Silicon metal was produced by 6 companies in 7 plants, primarily for the aluminum and chemical industries.

In the U.S., all primary production of silicon metal and ferrosilicon is by reduction in submerged arc electric furnaces. The feed silica materials require little processing other than washing, crushing, and sizing. The silica is mixed with a reducing agent, either coal, coke, or charcoal and fed into the furnace.

Iron and/or steel scrap are added in proper proportions if ferrosilicon is the product. The furnaces typically process 150 to 200 short tons per day. The furnace is tapped periodically and the molten silicon or ferrosilicon is drawn out and cast into ingots. The ingots are allowed to cool, then are crushed to produce the final product. These furnaces are generally equipped with fume collection systems and baghouses to reduce air pollution by capturing emissions from the furnace. The baghouse dust could contain leachable toxic metals, particularly if scrap steel is used to make

ferrosilicon. The references used for this report do not discuss any other waste streams from silicon and ferrosilicon production.

Semiconductor silicon, silicone chemicals, and silicon carbide are all made from silicon metal by secondary processing and, therefore, the production of these materials will not be discussed in this report. The only waste identified for silicon and ferrosilicon production is the baghouse dust from the electric arc furnaces (Table 3-25). This dust may exhibit the characteristic of EP toxicity. Therefore, further study for potential regulation under Subtitle C is recommended.

TABLE 3-25

SILICON AND FERROSILICON

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Submerged Arc Furnace Reduction	Baghouse Dust	N	N	N	?	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability, and EP Toxicity as defined in 40 CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

REFERENCES

- "Silica and Silicon," Industrial Minerals and Rocks, Vol. 2, Stanley J. Lefond, ed. 5th edition, Society of Mining Engineers of AIME, 1983.
- U.S. Bureau of Mines, Mineral Facts and Problems, 1985.
- U.S. Bureau of Mines, Minerals Yearbook 1985.
- U.S. Bureau of Mines, Mineral Commodity Summaries 1987.

STRONTIUM

Strontium is a hard, white, alkaline-earth metal. It is found in natural formations and trace amounts are produced by nuclear fission (strontium-90). Strontium has chemical properties intermediate of barium and calcium. It readily forms compounds with water, oxygen, nitrogen, fluorine, sulfur, and halogens. Strontium metal and salts burn with a bright red flame.

Strontium is estimated to comprise 0.02 to 0.03 percent of the earth's crust. Igneous rocks contain approximately 375 ppm of strontium. Strontium has been found in sedimentary formations such as beds of gypsum, anhydrite, dolomite, limestone, shales, or marls. Strontium is commercially produced from the mineral celestite (Strontium Sulfate), a white to blue-white mineral containing 56.4 wt percent strontium. Strontianite is a naturally occurring strontium carbonate, but is not economically exploited.

The largest volume use of strontium compounds is in the manufacture of glass faceplates for color television picture tubes, where additions of strontium oxide and barium oxide to the glass act as radiation shielding to block secondary x-rays. Strontium compounds are used in the pyrotechnics industry, in ferrite ceramic permanent magnets, and is also used in pigments. Strontium carbonate can be used to remove lead from zinc in electrolysis. In all the above industries, strontium is used in a compound form, not pure strontium metal. Strontium metal is used in aluminum-silicon alloys to improve casting behavior.

In 1986, the United States imported 100 percent of the celestite needed to produce strontium. Celestite was imported from Mexico and Spain. The Celestite imported contained approximately 16,500 short tons of strontium. The one processor of strontium in the United States is located at

Cartersville, Georgia. The producer uses the black ash process to produce strontium carbonate and a number of processes to produce a wide variety of strontium compounds.

The black ash process is shown in Figure 3-64. Celestite ore is crushed, ground, mixed with ground coke, and fed to a rotary kiln. There, the celestite is reduced to strontium sulfide (called black ash). The black ash is then finely ground in a ball mill and the slurry is fed to a leaching circuit. The leaching circuit consists of a series of stirred tanks. The black ash is dissolved with water in a countercurrent decantation system. The final decantation solution is filtered for clarity. The filtrate contains 12 to 13 wt percent strontium sulfide. The filtrate is sent to agitation tank, where soda ash is added, and strontium carbonate crystals are precipitated.

The precipitate slurry is pumped to vacuum drum filters where most of the liquid is removed. Filter cake is 60 wt percent strontium carbonate, which is sent to a carbonate dryer.

Since the United States does not mine celestite for strontium production, no mining or beneficiation wastes are identified. However, process wastes include spent ore, muds, and spent carbon (Table 3-26). Further investigation for potential regulation under Subtitle C is recommended.

Figure 3-64
STRONTIUM
BLACK ASH PROCESS

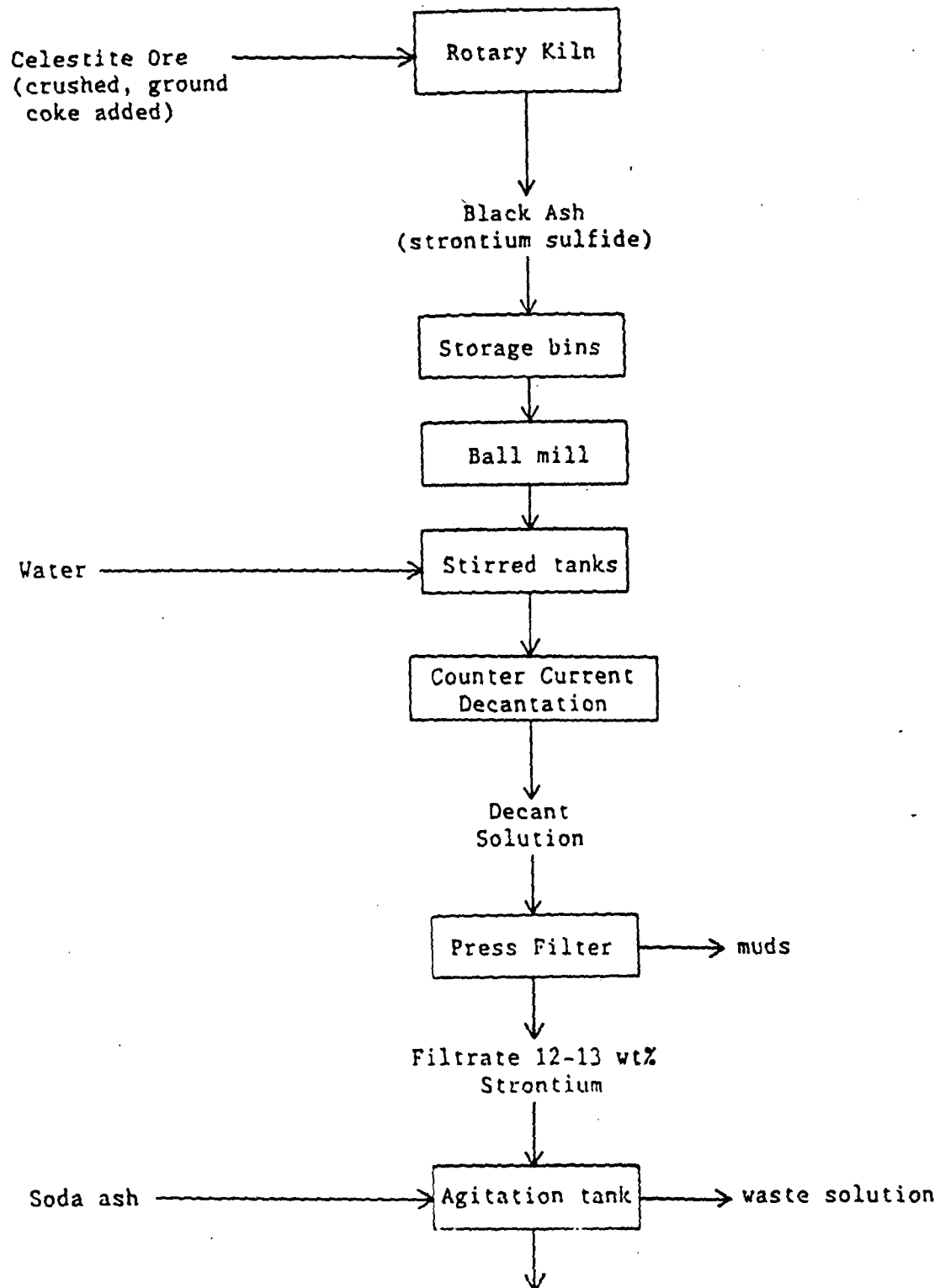


Figure 3-64 (Cont.)

BLACK ASH PROCESS CONTINUED

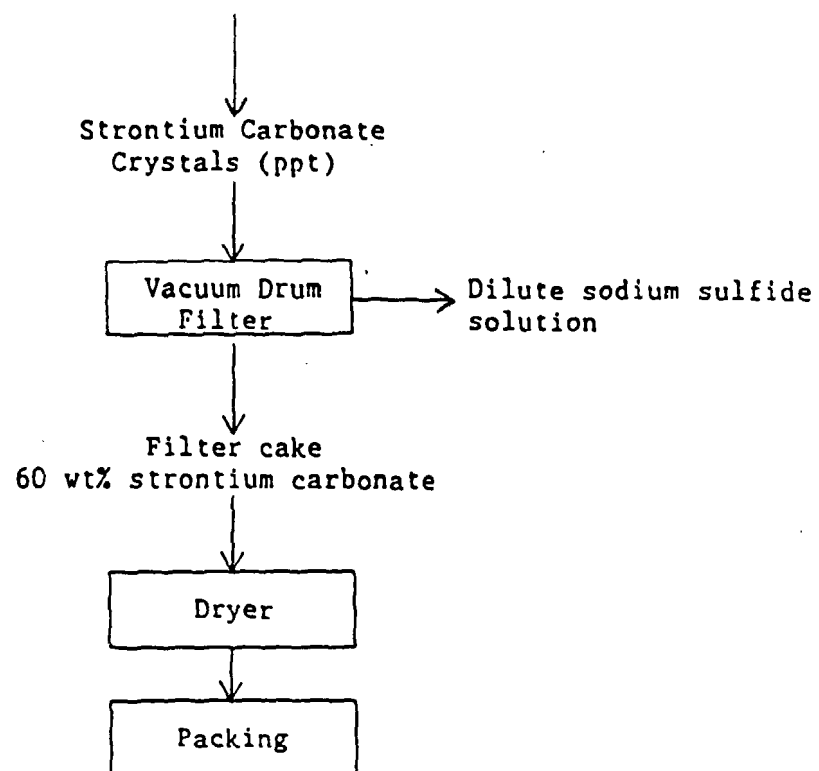


Table 3-26
STRONTIUM WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Black Ash Process	1) Filter Muds	N	N	N	?	
	2) Waste Solution (agitation tank)	N	?	N	?	
	3) Vacuum Drum Filtrate	N	?	N	?	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibly that waste could exhibit this characteristic.

REFERENCES

- Bureau of Mines, Mineral Commodities Summaries, 1987.
- Marks, H.W., Encyclopedia of Chemical Technology, 1978.

TELLURIUM

Tellurium is a nonmetal with a metallic luster, and it is a semiconductor whose conductivity increases with exposure to light. Tellurium's principal use is as an alloying agent in copper and stainless steel. It is also alloyed with lead to improve its strength and hardness. Minor amounts of tellurium are also used in the chemical and semiconducting industries and as catalysts.

Tellurium is present in a large number of minerals, however no tellurium ores exist. Tellurium is obtained only as a secondary product during the recovery of other metals, primarily copper. Commercial grade tellurium is currently produced by only one company in the United States from copper slimes which are byproducts of electrolytic copper refining. These slimes may contain up to 8 percent tellurium, depending on the quality of the copper ore used.

The recovery of tellurium from copper slimes is accomplished as shown in Figure 3-65. The decopperized slime is mixed with soda ash and roasted, producing a soda slime containing tellurium, and waste solids which are discarded. The soda slime is leached with water to extract sodium tellurite. The leached slag may be wasted or returned to a copper anode furnace for further processing. The sodium tellurite solution is neutralized with sulfuric acid to precipitate tellurous acid. After removing the tellurous acid precipitate, the solution is treated for selenium recovery. The tellurous acid is refined by redissolving it in sodium hydroxide solution, followed by fractional precipitation to remove solid impurities, which are discarded as waste.

Tellurium metal can be produced from the crude tellurous acid by one of two methods. As shown in Figure 3-66, the crude solids can be dissolved in a caustic solution, followed by electrolytic reduction of tellurium metal. Washing, drying, and melting of the metal produces the final tellurium

Figure 3-65
TELLURIUM RECOVERY FROM COPPER SLIMES

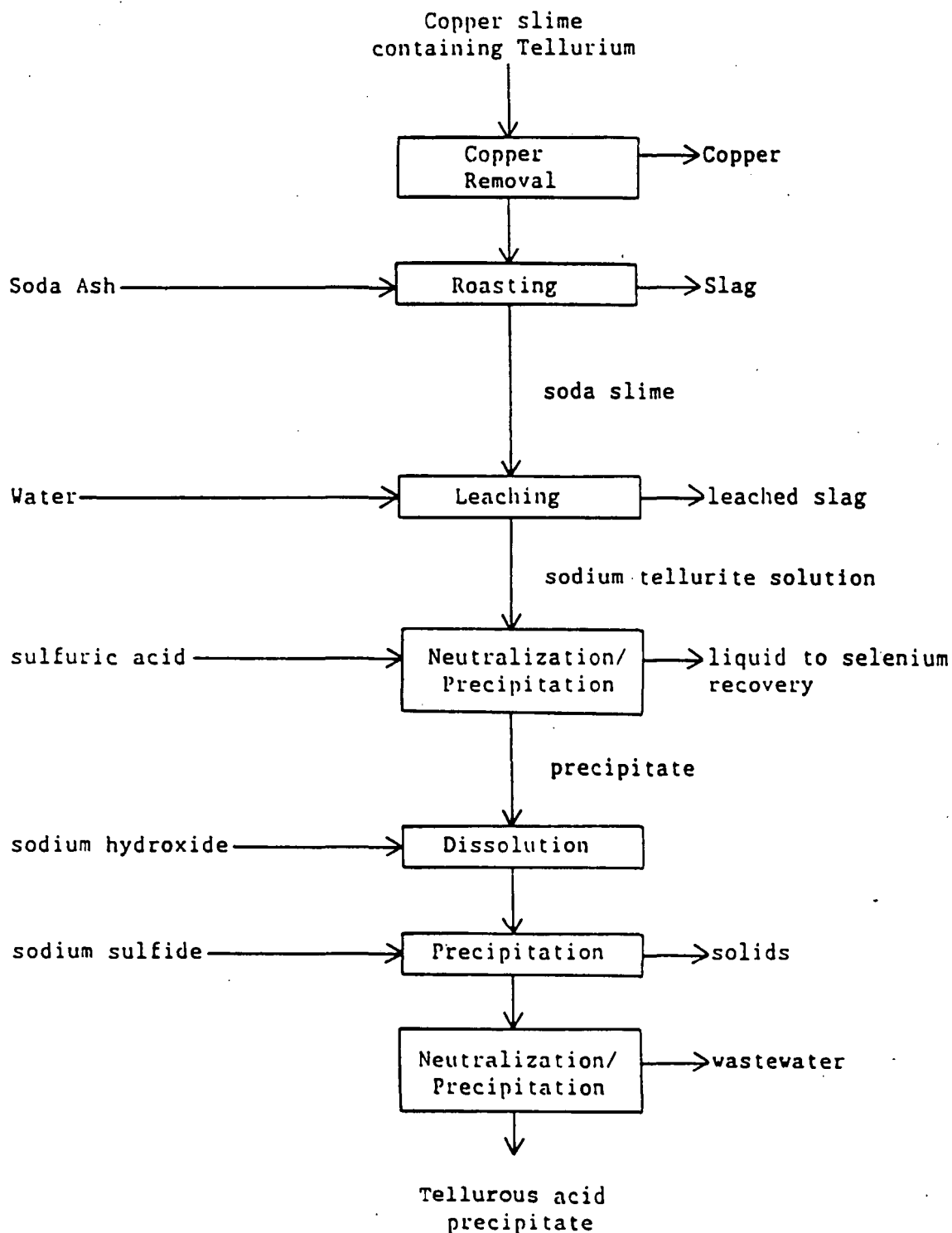
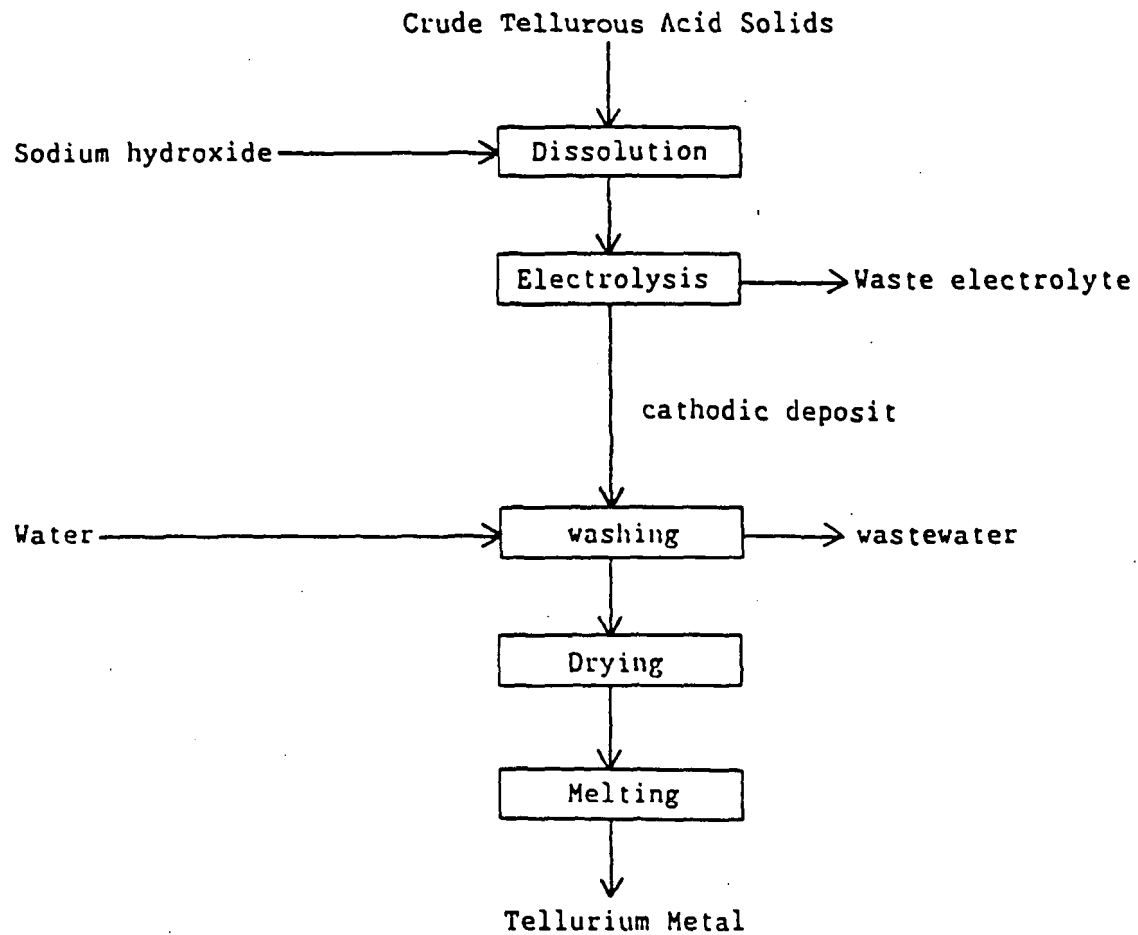


Figure 3-66

ELECTROLYTIC PURIFICATION OF TELLURIUM



metal product. This process produces wastewater as the wastes for which the management practices were not specified.

The second primary method of obtaining tellurium metal from crude tellurous acid is shown in Figure 3-67. In this process, tellurous acid is dissolved in acid and is precipitated from solution with sulfur dioxide. Washing, drying, and melting are used to purify the tellurium metal product. The wastewater produced is disposed of in an unspecified manner.

The processes identified for the recovery and purification of tellurium include standard unit operations used in the industry. Besides the use of acids, no hazardous substances were identified as being used in the processing. Still, it is possible that the wastewater or slags produced may have hazardous characteristics (Table 3-27). Therefore, further investigation for possible regulation under Subtitle C is recommended.

Figure 3-67

PURIFICATION OF TELLURIUM BY ACID PRECIPITATION

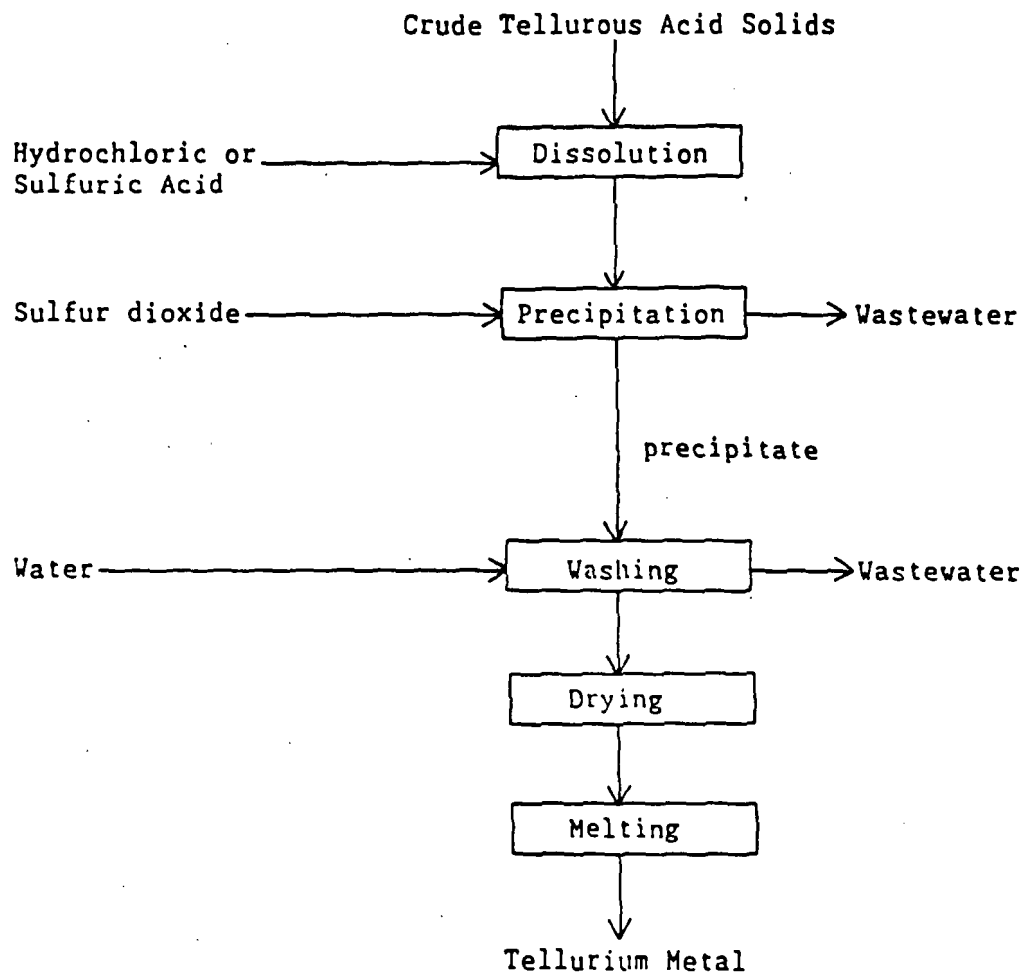


Table 3-27
TELLURIUM WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Copper Slime Processing	1) Roasting Slag	N	N	N	?	
	2) Leaching Slag	N	N	N	?	
	3) Precipitation Solids	N	?	N	?	
	4) Wastewater	N	N	N	N	
Electrolytic Purification	1) Waste Electrolyte	N	?	N	N	
	2) Wastewater	N	?	N	N	
Acid Precipitation Purification	1) Wastewater	N	?	N	N	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibly that waste could exhibit this characteristic.

REFERENCES

Bureau of Mines, Mineral Commodities Summary, 1987.

Marks, H.W., Encyclopedia of Chemical Technology, 1978.

TIN

Cassiterite (SnO_2) is the major mineral used as a source of tin. The mineral occurs in both vein and lode deposits. Metals associated with cassiterite in vein deposits include lead, tungsten, antimony, zinc, copper, silver, arsenic, and iron (Liddell, 1945). The major deposit in the United States exists in the Seward Peninsula in Alaska, with minor deposits in the Rocky Mountain region of the continental United States. Currently, only minor amounts of tin concentrate are being produced from placer mining in Alaska and as a byproduct from molybdenum mining in Colorado. Only one tin smelter is operating in the United States. In 1986, the smelter produced approximately 3,000 short tons of tin from imported and domestic tin concentrates, residues, and secondary tin-containing materials. The majority of the tin used in the United States is either imported as metal or reclaimed from secondary materials.

Tin is relatively resistant to corrosion, and is therefore often used as a protective coating for flat-rolled steel. It also has a low melting point (232°C) and is combined with lead for use as solder (EPA, 1984). The main industries consuming tin include cans and containers, electrical, construction, and transportation.

The cassiterite ore is processed by crushing, grinding, and concentrating. A number of gravity concentration and mechanical separation methods are used. Typical wastes produced from these processes include a slurry of tailings and process water (Table 3-28). The solids are usually settled out in a tailings pond and the liquid either discharged to receiving waters or reused in the process. Any discharge would be regulated under the Clean Water Act.

Tin concentrates are processed in one smelter (Figure 3-68) located in Texas City, Texas. There are a number of factors that complicate the smelting of tin. A high temperature is necessary to reduce tin dioxide

Table 3-28

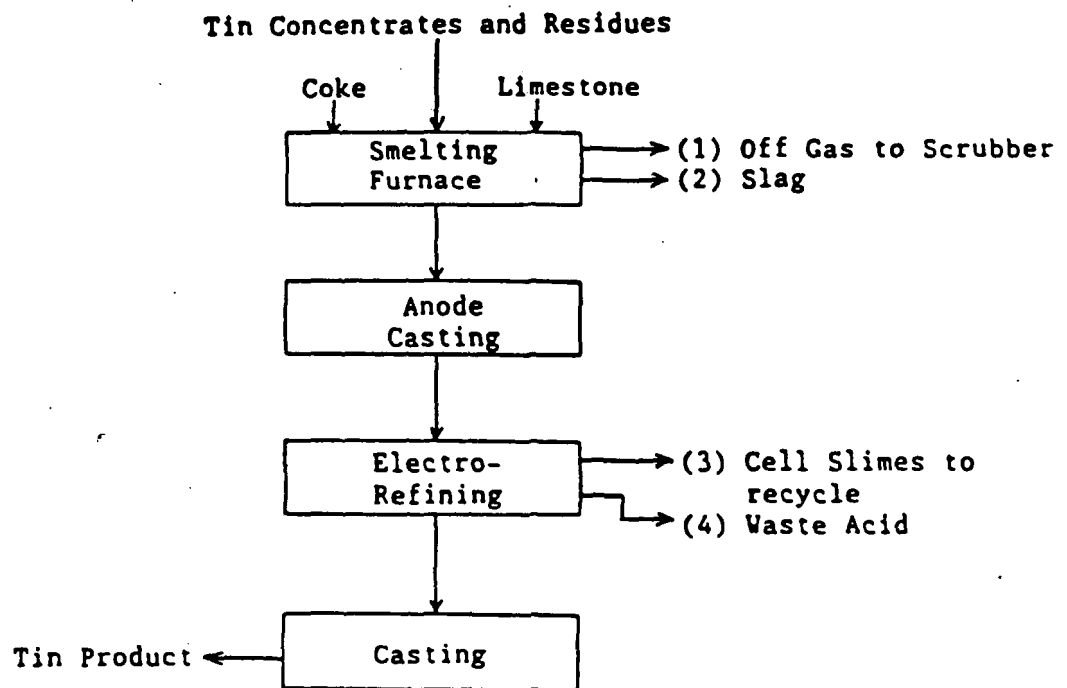
TIN WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Reverberator Furnace	Scrubber Liquor	N	N	N	Y	Arsenic
Electrorefining	Waste Electrolyte	N	?	N	?	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability, and EP Toxicity as defined in 40 CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.
Y - Strong indication that waste would exhibit this characteristic.
? - Possibility that waste could exhibit this characteristic.

Figure 3-68
TIN SMELTING



with carbon. At this temperature, a number of other metal oxides are also reduced. The other metals form compounds with tin that have very high melting points. These compounds are termed "hardhead". At the smelting temperature, tin is also very fluid and soaks into the refractories. These factors decrease the recovery of tin from smelting operations. In an attempt to increase recoveries, tin processing has been divided into two phases. The first phase involves smelting for primary separation. The slag, hardhead, and drosses produced are reprocessed in a second stage of smelting for additional tin recovery.

The reverberatory furnace of the smelter is equipped with a caustic scrubber to control sulfur dioxide emissions. Approximately 50% of the wastewater from the scrubber is recycled in the process. The EPA studied the Texas City smelter in 1984 and reported a production normalized discharge of 21,670 liters of wastewater for every metric ton of tin produced (EPA, 1984). These wastewaters are currently treated by chemical precipitation and sedimentation. PEI Associates found that arsenic exceeded the EP toxicity limits in the scrubber wastes (PEI, 1984).

The tin from the smelter is cast into anodes that are used in an electrorefining process to produce a more pure product. Electrorefining can operate with either an acid or alkaline bath. The acid bath contains stannous sulfate, creosulfonic or phenolsulfonic acids, and free sulfuric acid with beta naphthol and glue added (Grayson, 1978). If the lead content of the anodes is high, slimes collect on the anodes. In this case, the anodes are removed from the bath and scrubbed regularly to remove the slimes. The alkaline bath contains potassium or sodium stanite and free alkali. In this operation, lead plumbite is precipitated and generated as slime. The pure tin generated from electrorefining is recast into ingots and shipped out as product.

The casting processes should generate foundry sands. These sands typically contain some heavy metals, but are not usually hazardous. Electrorefining generates waste slimes and possibly waste baths. Both the slimes and the

electrorefining solutions are probably fairly high in heavy metals. The slimes are packaged and shipped to England for reprocessing. PEI Associates found that no wastes were generated by the refining process (PEI, 1984).

The Texas City tin smelter produces several wastes that either have been shown to be hazardous or have the potential to be hazardous. Therefore, further study of this smelter for potential regulation under Subtitle C is recommended.

REFERENCES

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- PEI Associates, Inc. Overview of Solid Waste Generation, Management and Chemical Characteristics Primary Antimony, Magnesium, Tin and Titanium Smelting and Refining Industries Industrial Environmental Research Laboratory, Office of Research and Development, U.S.E.P.A. Cincinnati, OH, Dec. 1984 (EPA Contract No. 68-031-3197).
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- U.S. EPA; Development Document for Effluent Limitations, Guidelines, and Standards for Nonferrous Metals, Point Source Category, Phase II, Supplemental Development Document for Primary and Secondary Tin; U.S. EPA; Washington, D.C.; 1984 (EPA-440/1-84/019b).
- Wright, P.A.; Extractive Metallurgy of Tin; Elsevier Science Publishing Co., Inc.; New York, New York; 1982.

TITANIUM

Titanium's high strength to weight ratio and its resistance to corrosion make its alloys (principally with aluminum and vanadium) excellent replacements for steel in aircraft and spacecraft applications, and in the chemical and power generation industries. However, its principal use is as a pigment for paints, rubber, paper, plastics, etc. because of titanium dioxide's (TiO_2) whiteness and high refractive index.

The two major mineral forms of titanium are ilmenite ($\text{FeO} \cdot \text{TiO}_2$) and rutile (high temperature polymorph of TiO_2). Ilmenite is generally 43-65% TiO_2 while rutile contains approximately 95% TiO_2 .

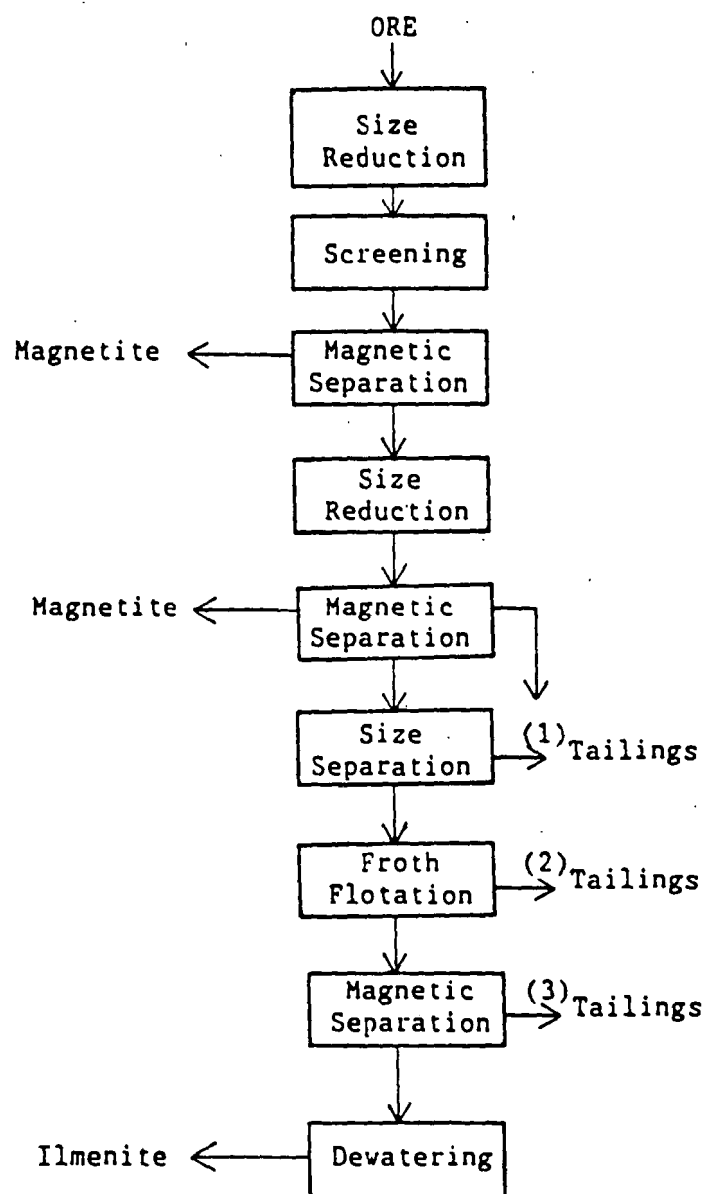
U.S. production of titanium metal and titanium oxide in 1986 is estimated to be 17,400 and 917,000 short tons, respectively. Five companies operating 11 plants in 8 states were producing titanium oxide while 4 companies were producing titanium sponge metal. Titanium sponge metal was derived almost entirely from rutile.

Titanium minerals occur in hard rock deposits or beach/alluvial sands ("black sands"). The major United State's hard rock deposits of ilmenite are the Sanford Lakes deposits in the Adirondack Mountains of New York. Other hard rock deposits of ilmenite and/or rutile occur in Virginia, North Carolina, Arkansas, Wyoming, and California. The MacIntyre Development of NL Industries in New York is the major hard rock mining operation and is currently inactive. The major deposits and mining of titanium minerals from beach/alluvial sands are in the Atlantic and Gulf Coastal Plain geologic provinces.

Hard rock mining and beneficiation consist of open pit mining followed by ore crushing, grinding, classification, magnetic separation, and flotation. As shown in Figure 3-69 (adapted from MacIntyre Development), a main feature of the beneficiation process is the use of magnetic separators to

Figure 3-69

TITANIUM BENEFICIATION
NEW YORK HARDROCK ILMENITE DEPOSITS



remove magnetite. Magnetite has been used as a blast furnace feed, in refractories, and as a component of a heavy medium for coal separation. The tailings from separators and flotation cells are the major waste produced, and are not expected to exhibit any hazardous characteristics.

Figure 3-70 shows a schematic of the beneficiation of the beach deposits. Sands from dragline or front end loader excavation, or from suction dredging are first spiral concentrated to remove low density tails. The ilmenite/rutile rich sand is then dried and subjected to a high tension (electrostatic) separator where the quartz and other nonconducting minerals are thrown off the rotors. These nonconducting materials are processed to produce a zircon and monazite product, and quartz and epidote waste. The conducting fraction undergoes further magnetic separation to separate ilmenite from rutile, and the rutile fraction is screened, and lastly cleaned in a high tension separator. Oversized quartz waste is produced. None of the wastes from beach sand processing are expected to exhibit any hazardous characteristics.

Treatment of the lower grade ilmenite and high grade rutile to produce pigment grade titanium oxide is by the sulfate and chloride processes, respectively. The highest grade rutile concentrates can also be used in the chlorine process, as is done by the largest U.S. pigment producer. The sulfate process generates large, costly, quantities of sulfuric acid waste (2 times the product weight), so sulfate processing of ilmenite has been cut back in recent years producing only about 14% of U.S. titanium dioxide output in 1986. The trend today is production of rutile substitutes by upgrading ilmenite to greater than 90% TiO_2 purity by partial reduction and leaching with sulfuric acid and hydrochloric acid or by electric furnace smelting to produce high TiO_2 slags. The leached product is referred to as synthetic rutile. Kerr-McGee Chemical Corp. has the only synthetic rutile plant in the U.S. at Mobile, Alabama.

The sulfate process for production of titanium dioxide from ilmenite is shown in Figure 3-71. Ilmenite ore or high titanium oxide slag is digested

Figure 3-70
TITANIUM BENEFICIATION
BEACH SAND DEPOSITS

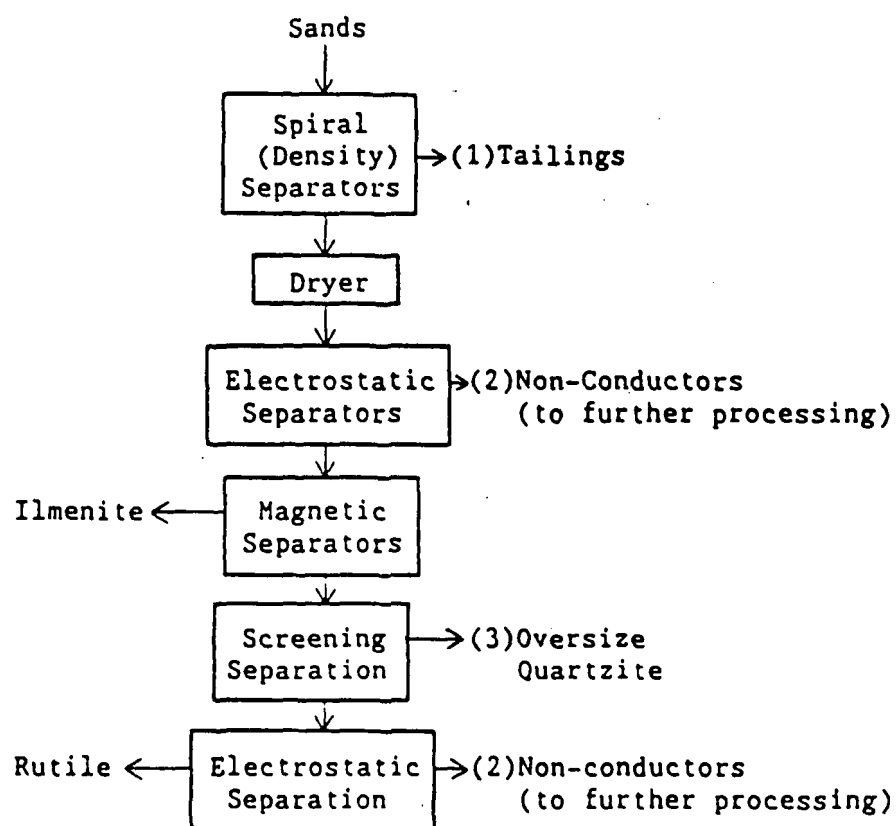
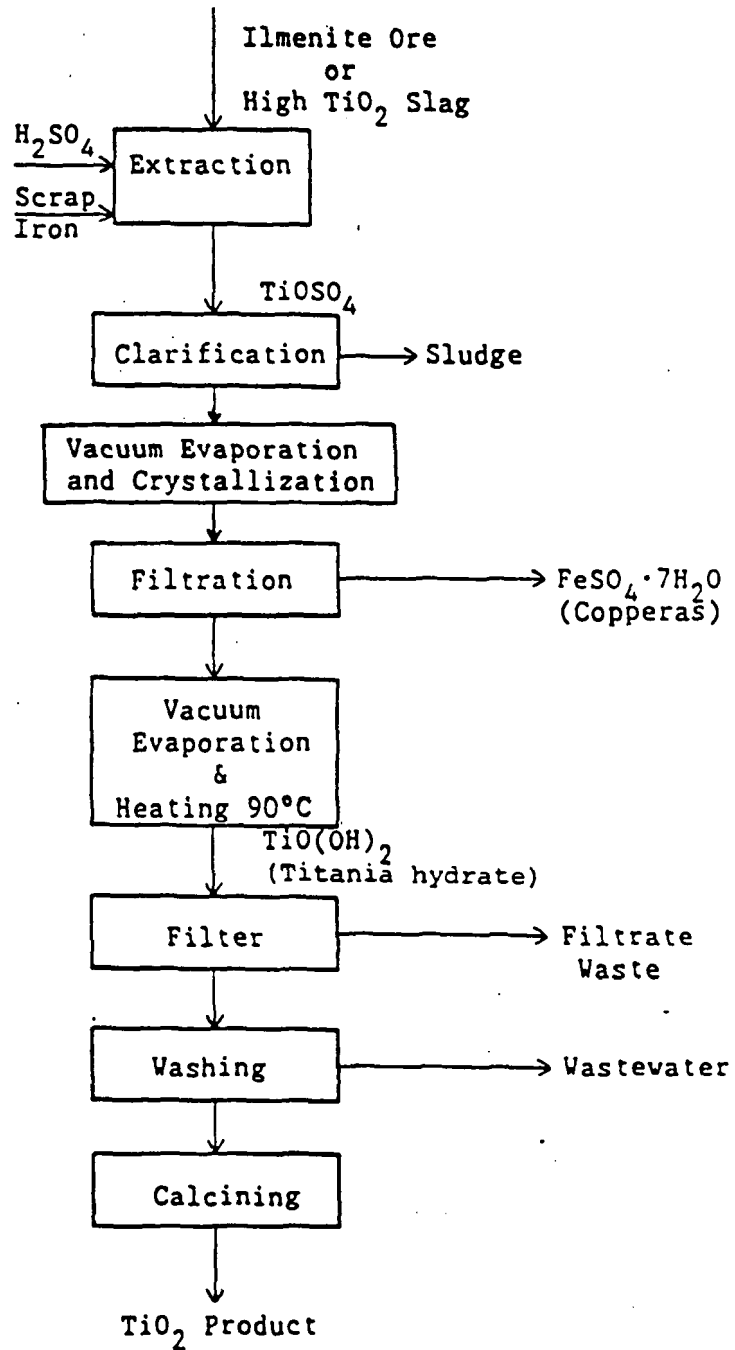


Figure 3-71
TITANIUM PROCESSING
SULFATE PROCESS



with sulfuric acid to form a porous cake that is dissolved in diluted acid to form titanyl sulfate (TiOSO_4). The iron scrap keeps the iron impurities in the ferrous state to facilitate washing of the titanium oxide eventually produced. The titanyl sulfate solution is clarified, concentrated to crystallize copperas, and filtered to remove sludge (waste) and ferrous sulfate heptahydrate (copperas) product, respectively. The filtered titanyl sulfate solution is vacuum evaporated to achieve the desired concentration and hydrolyzed at a temperature of 90°C to cause precipitation of hydrated titania ($\text{TiO}(\text{OH})_2$). The titania hydrate is filtered, washed, and calcined at 1000°C to produce titanium dioxide product. Crystallization of copperas is not required with low-iron feeds such as high- TiO_2 slag.

The chlorine process, shown in Figure 3-72, converts rutile or high grade ilmenite to titanium chloride (TiCl_4). This occurs in a fluid bed chlorinator where petroleum coke is added as a reductant. Volatile titanium chloride and other metal chlorides are separated by fractional condensation, double distillation, or chemical treatment. Chemical treatment is largely to remove vanadium chloride which has a similar boiling point to that of titanium chloride. The vanadium chloride is complexed with mineral oil and reduced to VOCl_2 by H_2S . A major waste product is ferric chloride. The final step is oxidation at 985°C where aluminum chloride facilitates formation of the rutile crystal. The chlorine gas formed during oxidation is recycled to the fluid bed chlorinator.

The Kroll process is the major commercial process for production of titanium sponge metal. As shown in Figure 3-73, titanium chloride is reduced by liquid magnesium in an argon or helium atmosphere. The molten magnesium chloride that forms is drawn off the bottom and is reduced by electrolysis to produce magnesium metal for reuse, and chlorine gas. Magnesium chloride impurities, unreacted titanium chloride, and magnesium residuals of the sponge metal are removed by acid leaching or vacuum

Figure 3-72
TITANIUM PROCESSING
CHLORIDE PROCESS

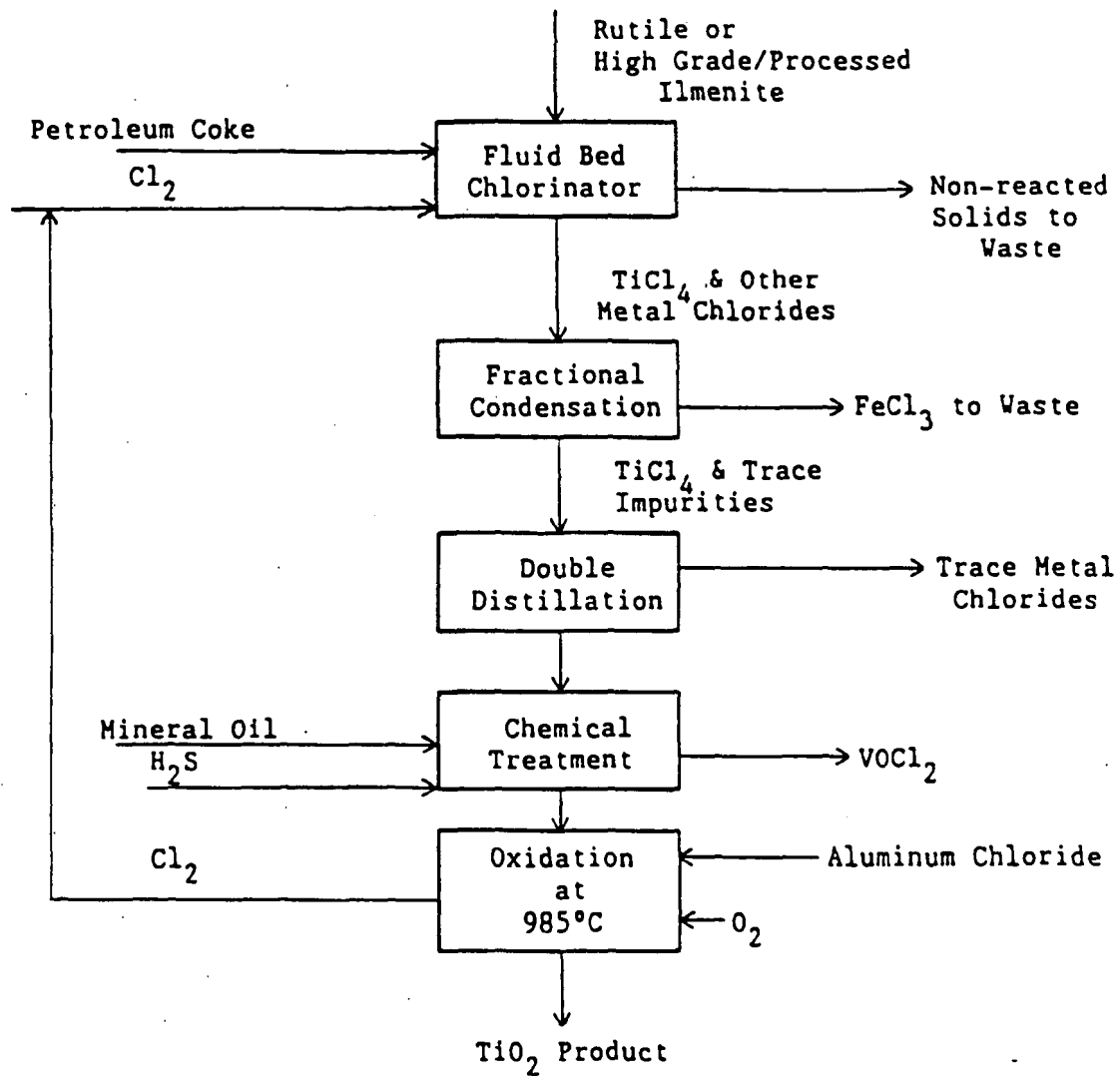
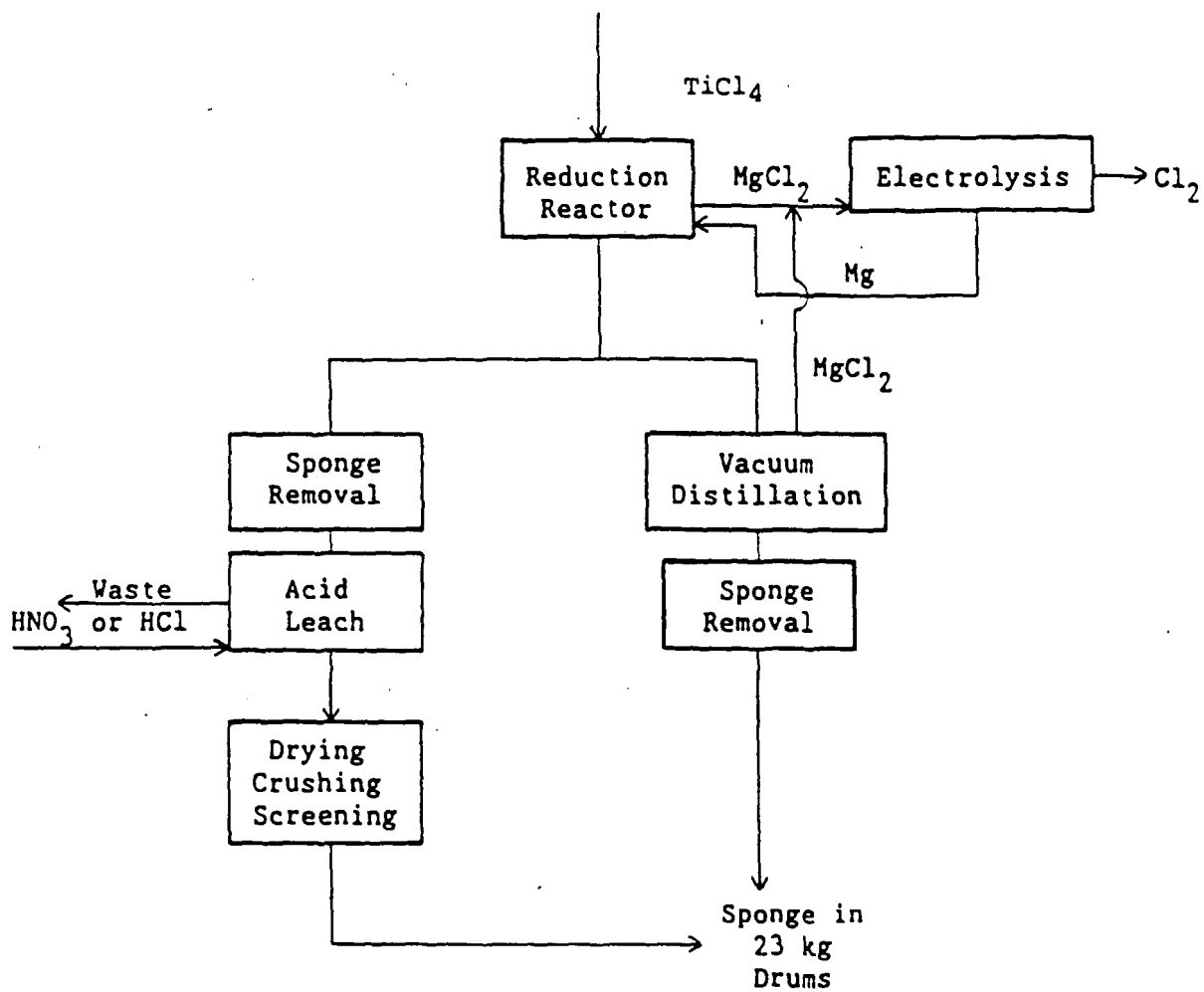


Figure 3-73
TITANIUM PROCESSING
KROLL PROCESS



distillation. The acid leaching produces a waste and the vacuum distillation produces magnesium chloride for recycling.

The sponge metal can be cast into ingots or powdered. Ingots can be milled by forging, hot or cold rolling, and extrusion.

A variety of hazardous and non-hazardous wastes are produced in the mining, beneficiation, and processing of titanium (Table 3-29). The mining/beneficiation of titanium ores produce tailings that are unlikely to have hazardous characteristics. The sulfate process produces large quantities of waste sulfuric acid and ferrous sulfate. It is reported (Lefond, 1983) that the sulfuric acid and ferrous sulfate (copperas), that are not sold as products, are discharged to waterways or the ocean. The chlorine process produces largely ferric chloride which is dumped in the ocean or reused in water treatment as a flocculant. Although the Clean Water Act necessarily regulates all discharges to waterways and the ocean by permits, (necessitating treatment of the wastes), the hazardous characteristics of many of these wastes or sludges produced in the treatment of these wastes should be further investigated to determine if possible regulation under Subtitle C is appropriate.

TABLE 3-29

TITANIUM PROCESSING WASTES

Process	Waste	Possible RCRA Characteristics				Comments
		R	C	I	T	
<u>Hardrock Ilmenite Deposits</u>						
Size Separation	(1) Tailings	N	N	N	?	
Flotation	(2) Tailings	N	N	N	?	
Magnetic Separation	(3) Tailings	N	N	N	?	
<u>Ilmenite/Rutile Beach Deposits</u>						
Spirals	(1) Tailings	N	N	N	N	
Non-Conductor Processing	(2) Quartz Epidote	N	N	N	N	
Vibratory Screen	(3) Oversize Quartzite	N	N	N	N	
<u>Sulfate Process</u>						
Clarification	Sludge	N	?	N	?	
Filtration	Copperas	N	N	N	?	
<u>Chloride Process</u>						
Fluid Bed Chlorinator	Non-Reacted Solids	N	N	N	?	
Fractional Condensation	Ferric Chloride	N	?	N	?	
Double Distillation	Trace Metal Chloride	N	?	N	?	
Chemical Treatment	VOCl ₂	N	?	N	N	
<u>Kroll Process</u>						
Electrolysis	Chlorine Gas	N	N	N	N	
Acid Leach	MgCl ₂ , TiCl ₄ , Mg residuals	N	N	N	N	

* RCRA characteristics are reactivity, corrosivity, ignitability, and EP toxicity as defined in 40 CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic

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TUNGSTEN

Tungsten occurs in over 20 different minerals. The four minerals of commercial importance are ferberite (FeWO_4), huebnerite (MnWO_4), scheelite (CaWO_4), and wolframite ($(\text{Fe,Mn})\text{WO}_4$). These minerals are found in association with metamorphic rocks and granitic igneous rocks..

Tungsten deposits in the United States lie in two north-south bands from Montana and Idaho to southern California and Arizona and from South Dakota to Colorado. United States tungsten reserves amount to approximately 125,000 metric tons of metal (Marks, 1978). Tungsten mines are usually underground and are fairly small, producing less than 2000 metric tons of raw ore per day (Marks, 1978). Production has continued to decrease over the past five years, with only three mines operating in 1986.

The majority of tungsten is used as tungsten carbide for wear resistant applications. Some tungsten is used in metallic form as an alloy additive to steel. Metallic tungsten is also used in lamp filaments, furnace elements, heat shields, and arc-lamp electrodes. The nonmetallurgical uses of tungsten include organo-tungsten dyes and pigments, phosphors, and catalysts in petroleum refining.

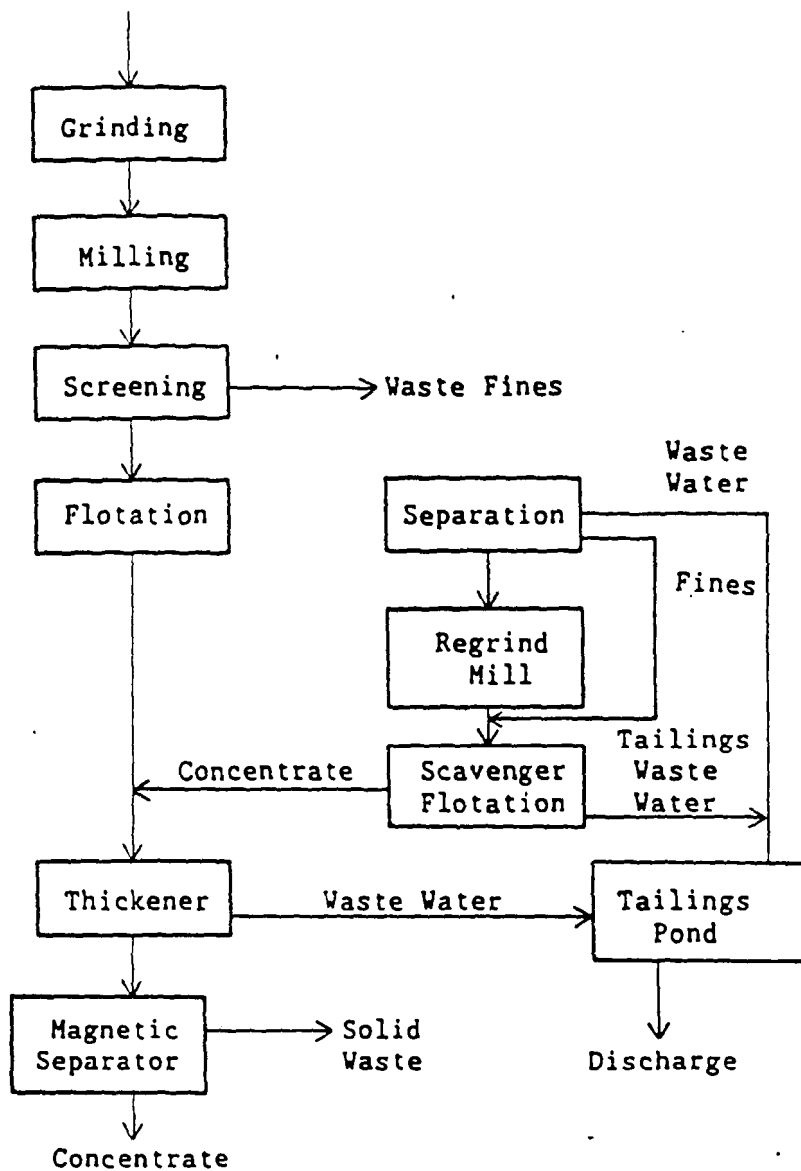
Scheelite and wolframite are the major tungsten containing minerals. Ores containing these minerals are generally very friable and overgrinding can cause sliming problems. Therefore, the ores are generally crushed and ground in stages and waste fines are kept to a minimum. Concentration of the tungsten is usually accomplished by froth flotation, supplemented by leaching, roasting, or magnetic or high tension separation. The choice of separation method depends on ore type as summarized in Table 3-30. The tailings from froth flotation usually are sent through a reprocessing and scavenger froth flotation circuit to maximize tungsten recovery. The beneficiation processes vary with the type of ore being mined. A general flow diagram is shown in Figure 3-74, with ore-specific information

Table 3-30

Common Approaches to Mineral Separation

Ore	Process
Scheelite, simple ore	Gravity, flotation, magnetic
Scheelite, sulfides	Gravity, sulfide flotation, roasting, magnetic
Scheelite-cassiterite concentrate	Electrostatic
Scheelite-calcite-apatite	Flotation, gravity, leaching
Scheelite-powerlite concentrate	Chemical processing
Wolframite, simple ore	Gravity, flotation, magnetic
Wolframite-cassiterite ore	Gravity, flotation, magnetic
Wolframite-scheelite concentrate	Magnetic
Wolframite-sulfides	Sulfide flotation, gravity, magnetic

Figure 3-74
TUNGSTEN PROCESSING
RAW ORE



presented below. The tailings and any wastewaters from thickeners or other separators are sent to tailings ponds. Waters from the tailings ponds are usually discharged to surface waters, with the waste fines remaining in the tailings ponds.

The concentrate may be retreated by roasting (Figure 3-75). Roasting removes impurities such as sulfur, arsenic, and organic residues from flotation. These compounds are oxidized and volatilized. The roaster usually is equipped with a wet scrubber that generates wastewater.

After preparation of the concentrate, the concentrate is processed to ammonium paratungstate (APT) via either sodium tungstate or tungstic acid. The process is dependent on the original ore type.

Scheelite is most commonly processed by acid leaching (Figure 3-76). The concentrate is leached with hydrochloric acid to remove phosphorous, arsenic, and sulfur. The mixture is filtered and the solids washed with dilute hydrochloric acid. The insoluble tungstic acid is then digested with aqueous ammonia to solublize the tungsten as ammonia tungstate. The solution is separated from any remaining solids and magnesium oxide added. Magnesium ammonium phosphates and arsenates are precipitated. Activated carbon is added to purify the solution. The activated carbon and precipitates are removed from the solution by filtration. Ammonium paratungstate (APT) is formed by crystallizing it from solution. The APT crystals are filtered, washed, and dried. The drier is equipped with a scrubber that generates wastewater high in ammonia. This waste water is usually treated and discharged.

Lower grade scheelites are sometimes processed by the high pressure soda process (Figure 3-77). The concentrate is ground and digested in an autoclave with sodium carbonate. This produces a sodium tungstate solution that is filtered and further processed to CaWO_4 or APT.

Figure 3-75
TUNGSTEN PROCESSING

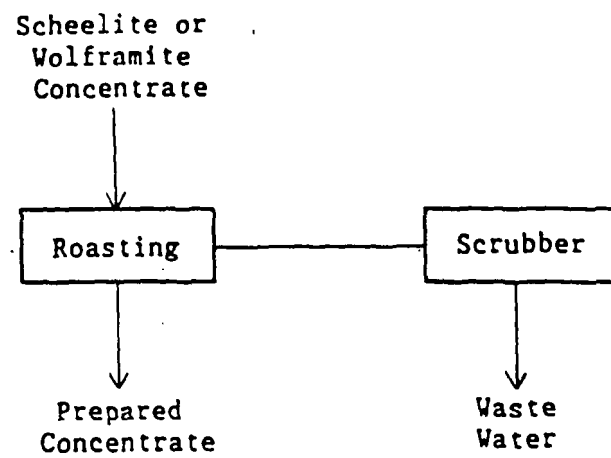


Figure 3-76
TUNGSTEN PROCESSING
SCHEELITE ACID LEACHING

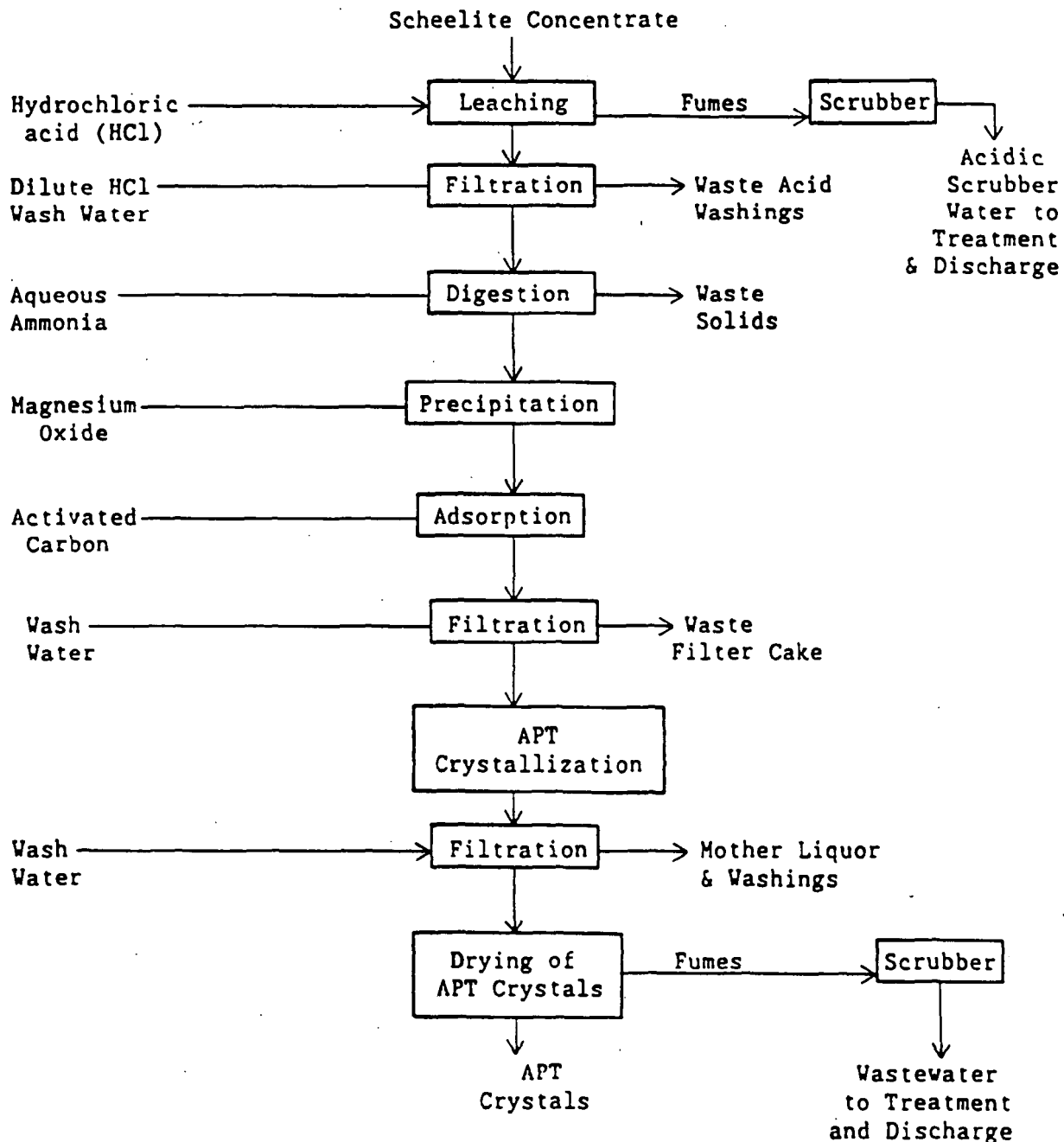
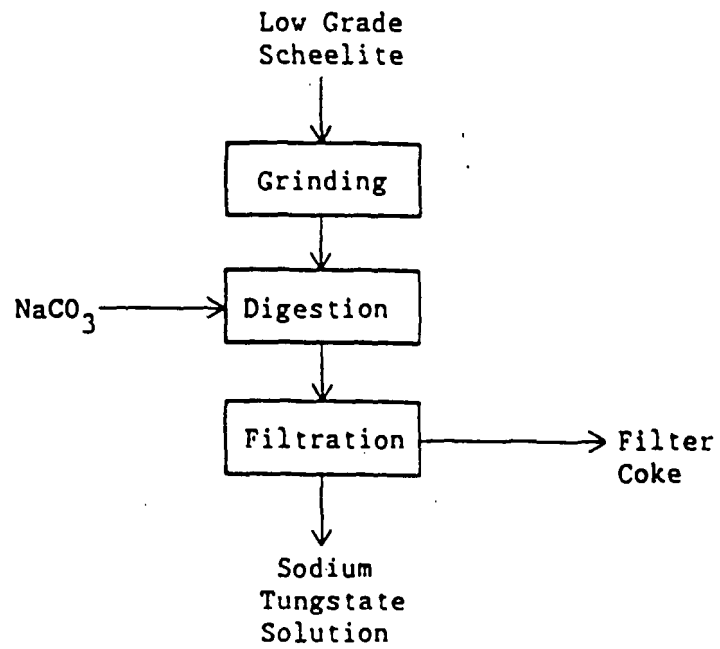


Figure 3-77
TUNGSTEN PROCESSING
HIGH PRESSURE SODA PROCESS



Scheelite or wolframite can be converted to sodium tungstate solution by the alkali roasting process (Figure 3-78). Sodium carbonate is mixed with the concentrate and the mixture heated. The roasted concentrate is then leached with hot water. The leachate, which contains sodium tungstate, is separated from the solids by filtration and sent to other processes for conversion to APT.

Wolframite and scheelite concentrates are commonly processed by the Liquid Ion Exchange (LIX) process (Figure 3-79). The concentrate is digested using a strong base or acid. The digested slurry is filtered and washed. The filtered cake is treated to remove silica and solubilize the tungsten. The solution is filtered to remove solids, then treated to precipitate molybdenum. The molybdenum solids are removed and the pH of the solution adjusted. The tungsten is extracted from solution using a solvent extraction circuit consisting of two stages of extraction, washing, and stripping. APT is crystallized from the resulting solution.

Sodium tungstate solution from the high pressure soda process and from the alkali roasting process is converted to APT by two processes. The first involves using the latter part of the LIX process described above. The second consists of conversion of the sodium tungstate solution to "synthetic" scheelite and processing this to APT by the acid leaching process. This is diagrammed in Figure 3-80.

Dried APT is reduced to tungsten generally by one of two methods (Figure 3-81). The first process is a two stage reduction for metal to be used in lamp filaments. Hydrogen is used in the first reduction and aluminum, potassium, and silicon dopants are added to the second reduction. The metal is washed with hydrochloric acid, then cast into ingots. The second process also consists of a stepwise reduction. The wastes generated are mainly air pollution control dusts and scrubber wastewater.

Figure 3-78
TUNGSTEN PROCESSING
ALKALI ROASTING PROCESS

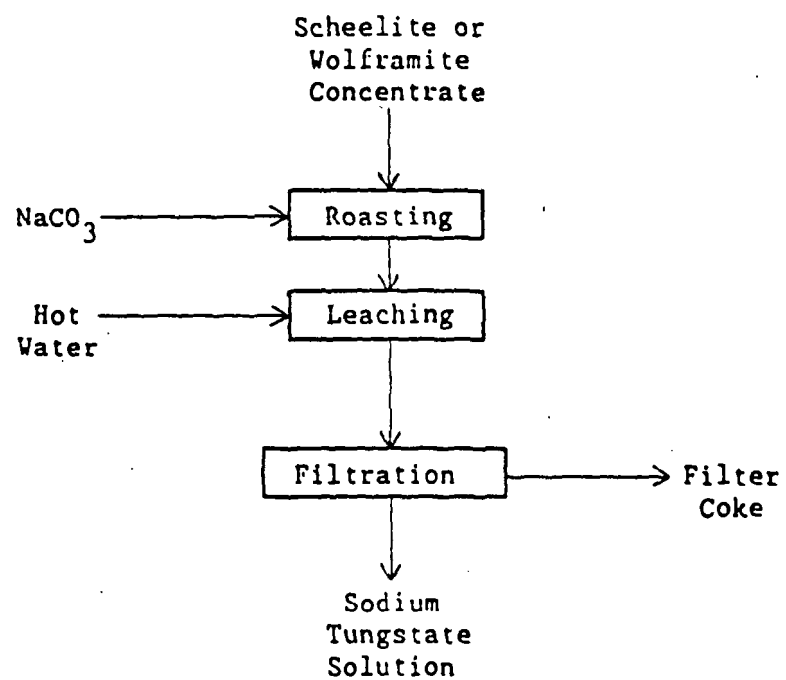


Figure 3-79
TUNGSTEN PROCESSING
LIQUID ION EXCHANGE PROCESS

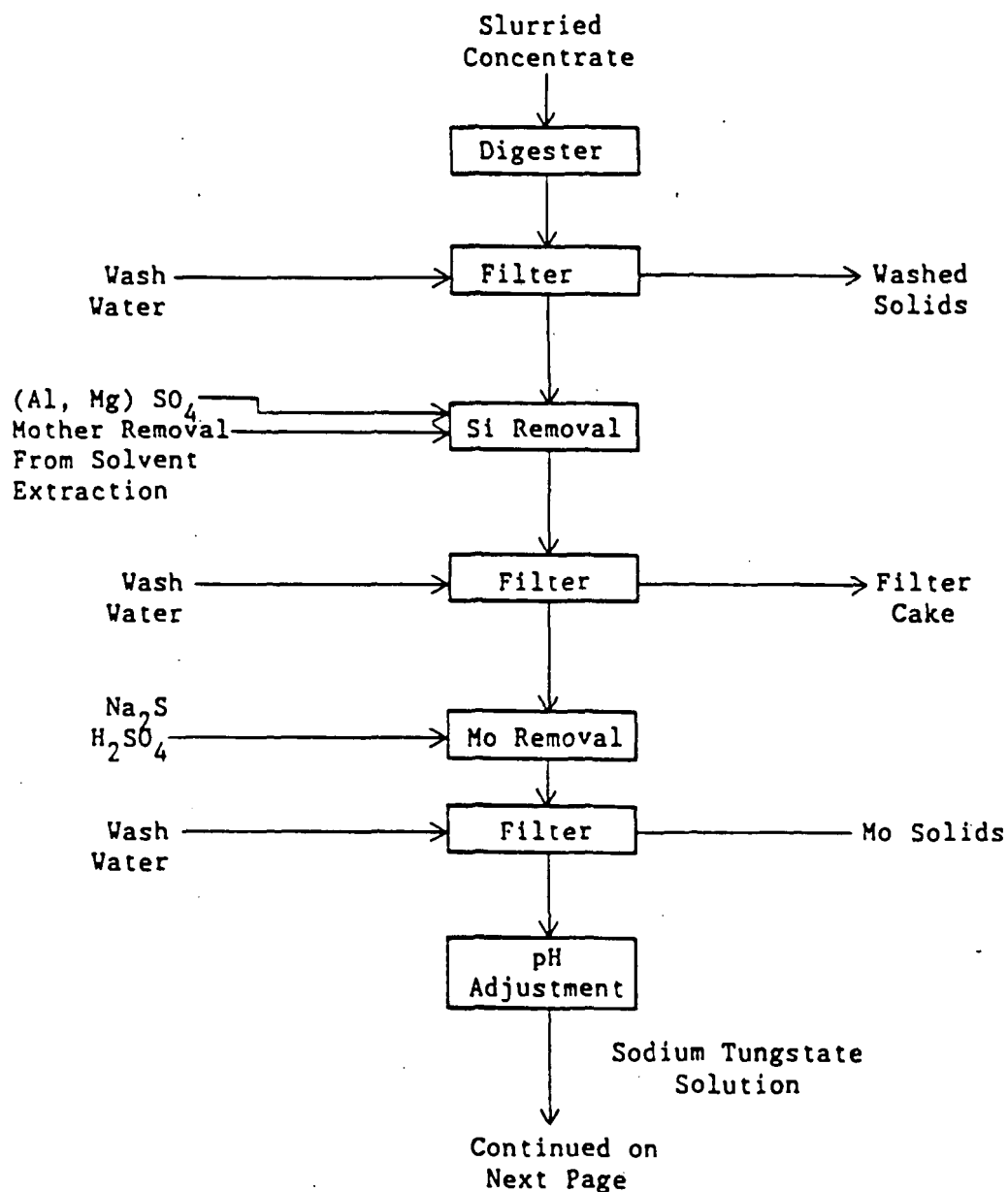


Figure 3-79 (Cont.)
TUNGSTEN PROCESSING
LIQUID ION EXCHANGE PROCESS

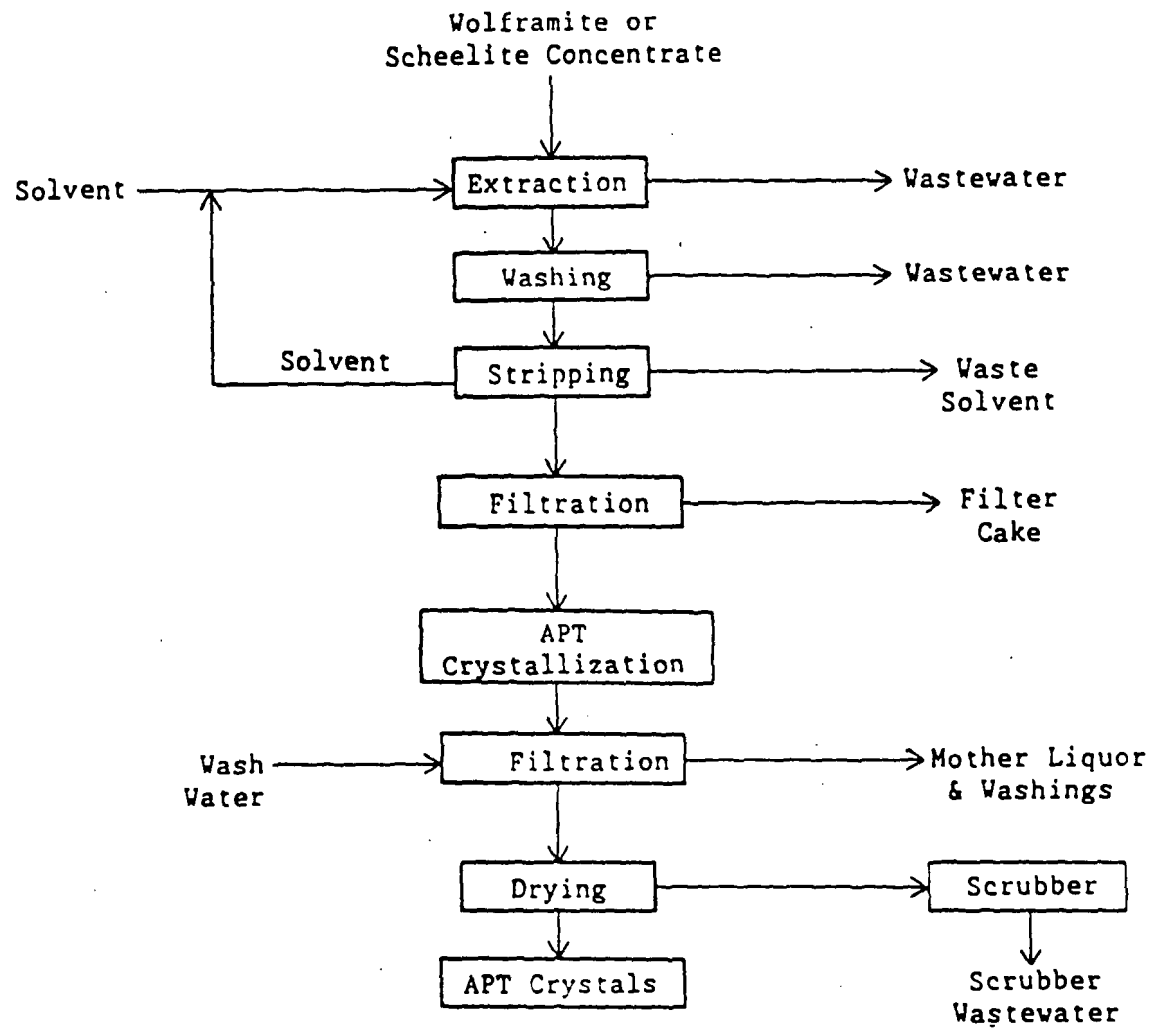


Figure 3-80
TUNGSTEN PROCESSING
SODIUM TUNGSTATE CONVERSION

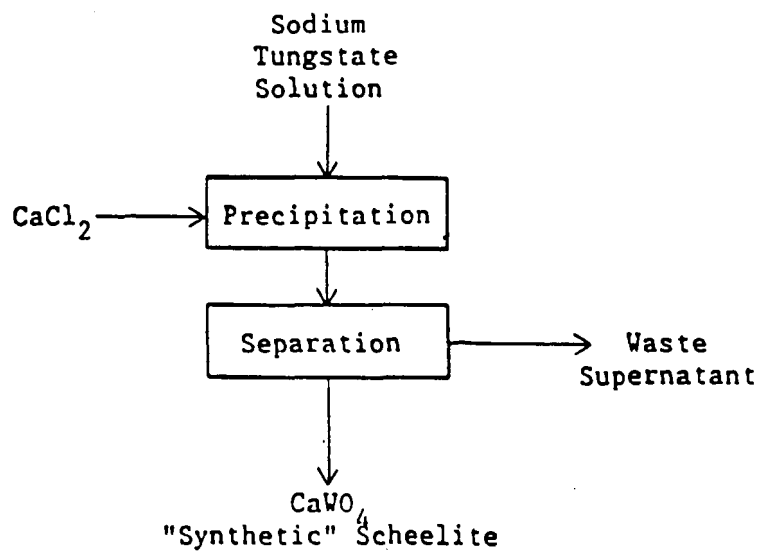
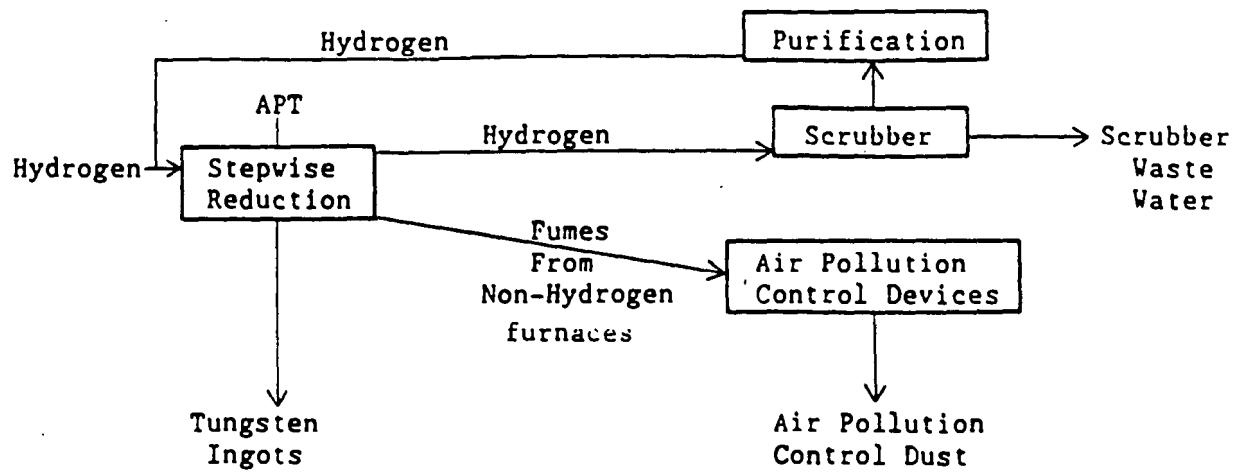


Figure 3-81
TUNGSTEN PROCESSING
REDUCTION TO TUNGSTEN



Although the processes and wastes from the production of tungsten are fairly well documented, waste management practices are not well known (Table 3-31). Further study of this industry is recommended to determine if possible regulation under Subtitle C should be considered.

Table 3-31

TUNGSTEN PROCESSING WASTES

Process	Waste	Possible RCRA Characteristics				Comments
		R	C	I	T	
Raw ore beneficiation	Fines	N	N	N	?	
	Tailings	N	N	N	?	
	Thickener Waste Water	N	N	N	?	
	Solid Waste from the Magnetic Separator	N	N	N	?	
Concentrate Roasting	Scrubber Wastewater	N	?	N	?	
Scheelite Acid Leaching	Acidic Scrubber Water	N	?	N	/	
	Hydrochloric Acid	N	?	N	?	
	Solids from Digestion	N	?	N	?	
	Filter Cake	N	N	N	?	
	Mother Liquor and Washings	N	?	N	?	
	Ammonia Scrubber Water	N	?	N	?	
High Pressure Soda Process	Filter Cake	N	N	N	?	
Alkali Roasting Process	Filter Cake	N	N	N	?	
Liquid Ion Exchange (LIX) Process	Digester Filter Cake	N	N	N	?	
	Silicon Removal Filter Cake	N	N	N	?	
	Molybdenum Solids	N	N	N	?	
	Solvent Extraction Wastewater	N	?	N	?	
	Solvent Washing Wastewater	N	?	N	?	
	Solvent	N	N	?	N	
	Filter Cake	N	N	N	?	
	Mother Liquor and Washings	N	?	N	?	
	Scrubber Water	N	?	N	?	

Table 3-31 (Cont.)
TUNGSTEN PROCESSING WASTES

Process	Waste	Possible RCRA Characteristics				Comments
		R	C	I	T	
Sodium Tungstate Conversion	Supernatant from Separation	N	?	N	?	
Reduction to Metallic Tungsten	Scrubber Water	N	?	N	?	
	Air Pollution Control Dust	N	N	N	?	

* RCRA characteristics are reactivity, corrosivity, ignitability, and EP toxicity as defined in 40 CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.

Y - Strong indication that waste would exhibit this characteristic.

? - Possibility that waste could exhibit this characteristic.

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VANADIUM

Vanadium is a transition metal that is very soft and ductile in its pure form and has a high melting point. It is used mainly as an alloying agent to produce high strength steels. The metal is also used in the production of titanium alloys and as a catalyst in chemical production processes.

There are approximately 65 known minerals that contain vanadium (CSMMF, 1961). However, vanadium is widely distributed, with deposits usually less than 1-2 percent vanadium by weight. Therefore, extraction of vanadium ores is usually associated with the mining of another mineral. In the U.S., vanadium is found in clays in Arkansas, in uranium bearing sandstones in the Colorado Plateau, in titaniferous magnetites distributed throughout the U.S., and with phosphatic shales and phosphate rock in Idaho and Wyoming.

In 1986, the vanadium industry was composed of 14 firms, 8 of which extracted vanadium from raw materials. The remainder were involved in vanadium pentoxide processing. The raw materials used included ferrophosphorous slags produced in Idaho, Arkansas clay, petroleum residues, utility ash, and imported iron slags (Bureau of Mines, 1987). Umetco's Arkansas mine was closed in 1985 and remains closed. The majority of the mines in Colorado and Utah where vanadium was coproduced with uranium were closed due to the low demand for domestic uranium. Some of the phosphate mines in Idaho and Wyoming produced slags from which vanadium was recovered.

Each producer of vanadium materials used a somewhat different process depending on the final product desired and other factors. A generic description of vanadium processing is presented here (Figures 3-82 through 3-85). The first step in the extraction of vanadium from any ore source is the production of an oxide concentrate usually by crushing and screening. The concentrate is mixed with a sodium salt, and roasted to convert the

Figure 3-82

VANADIUM - SODIUM HEXAVANDATE PRODUCTION

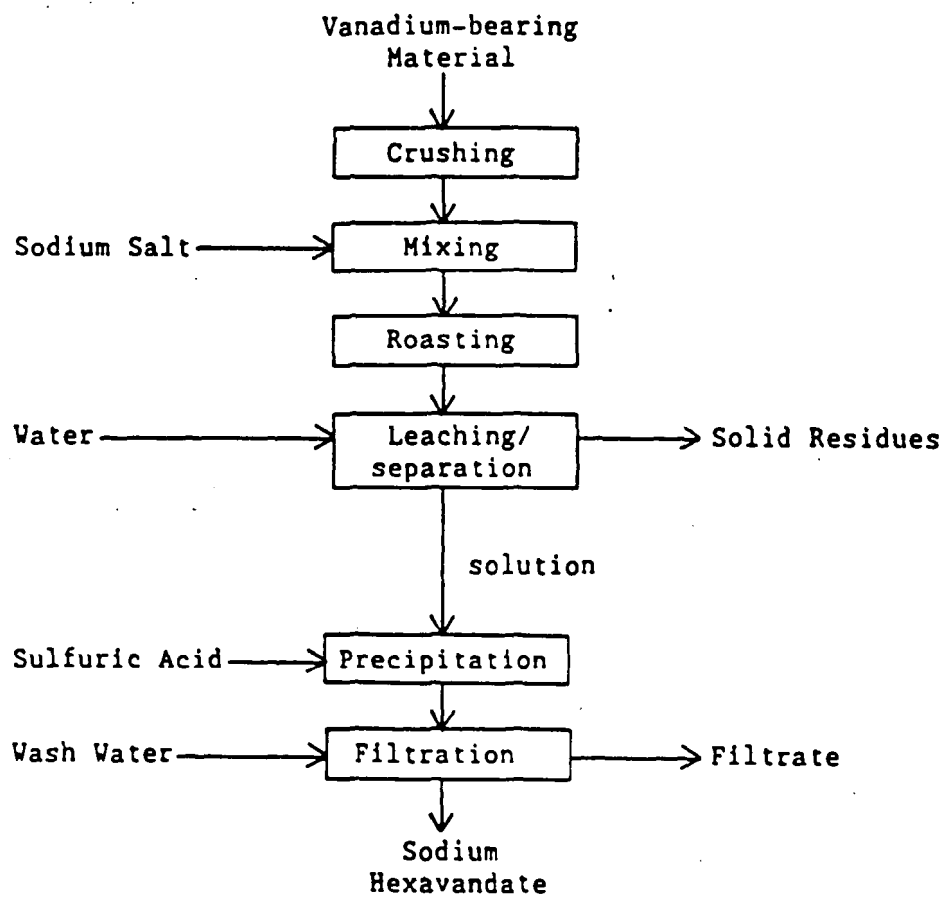
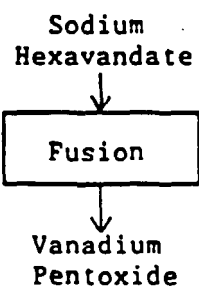


Figure 3-83

VANADIUM - VANADIUM PENTOXIDE PRODUCTS

Option 1



Option 2

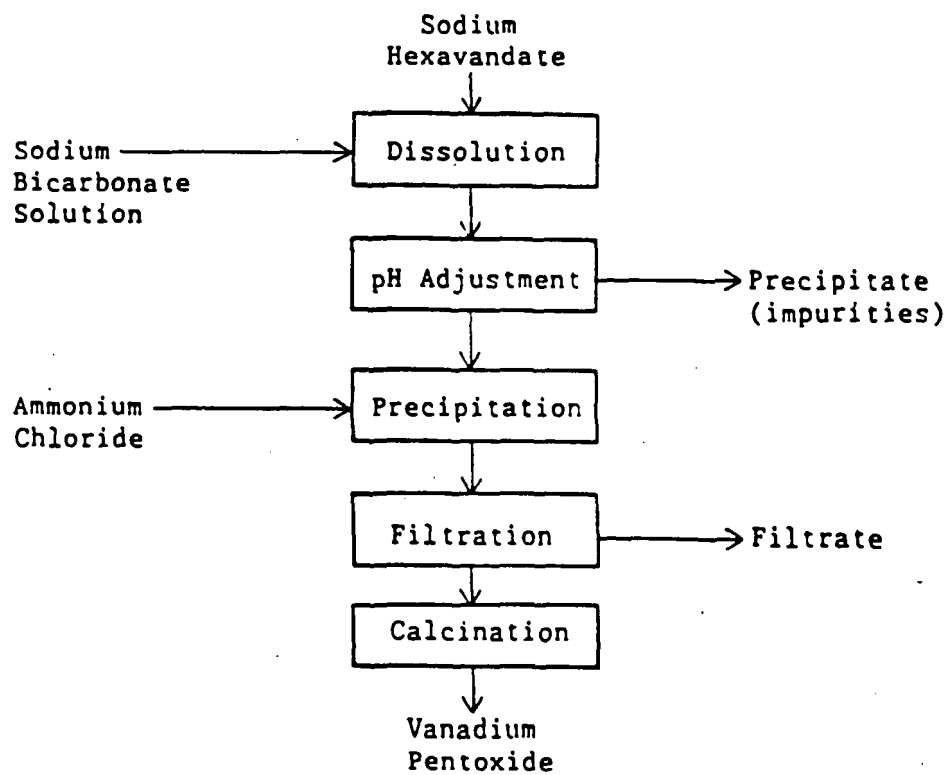


Figure 3-84

VANADIUM - CALCIUM REDUCTION

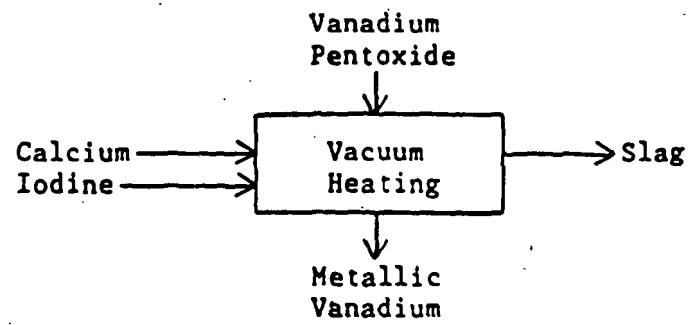
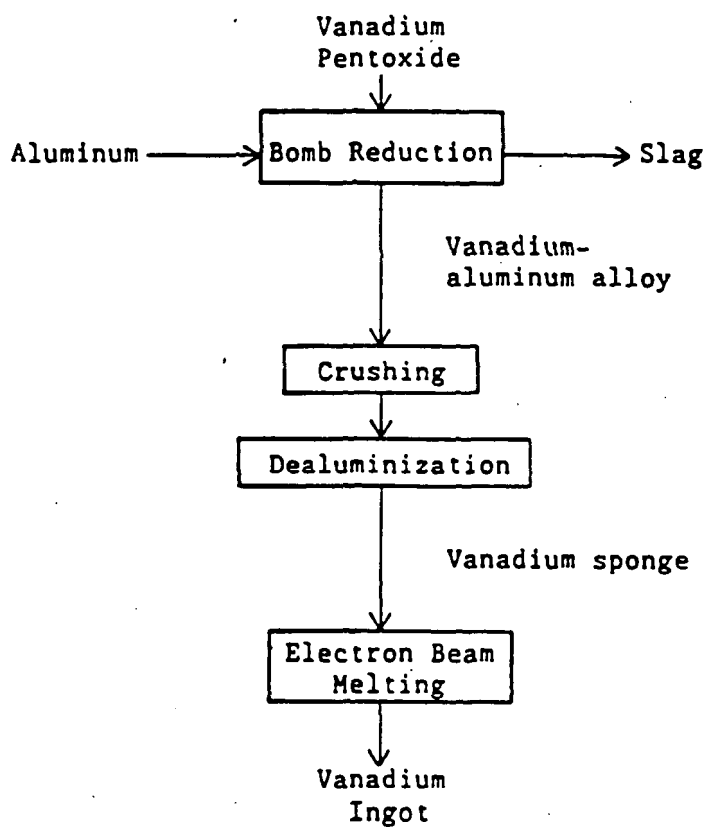


Figure 3-85

VANADIUM - ALUMINOTHERMIC REDUCTION



oxide to sodium metavanadate (NaVO_3). Water is added to dissolve the compound, then sulfuric acid is added to adjust the pH to 2-3 and precipitate sodium hexavanadate ($\text{Na}_4\text{V}_6\text{O}_{17}$). The precipitate is separated from solution and fused at 700°C to produce a technical grade vanadium pentoxide. The precipitate may also be dissolved in a sodium bicarbonate solution. Iron, aluminum, and silicon impurities can then be precipitated by pH adjustment and removed from solution. Ammonium chloride is added to precipitate ammonium metavanadate. This precipitate can be calcined to produce vanadium pentoxide.

Ferrovanadium can be produced by the addition of vanadium ore, slag, or technical grade oxide to iron prior to charging the blast furnace. Vanadium metal can be produced by either calcium reduction or the aluminothermic process. Calcium reduction involves combining vanadium pentoxide with calcium, adding iodine as a flux, and heating the mixture in a vacuum to form metallic vanadium. The aluminothermic process consists of reacting vanadium pentoxide in a bomb to form a vanadium aluminum alloy. The alloyed aluminum and dissolved oxygen are removed in a high temperature vacuum processing step. The resulting vanadium sponge is melted by an electron beam to produce a vanadium ingot. A number of other methods have been used on a trial basis, including iodine-refining, electrolytic refining, and electrotransport, but none are known to be used in full scale processing.

Wastes produced from processing of vanadium-bearing materials include solid and liquid residues from the initial leaching process (Table 3-32). If a more pure vanadium pentoxide is desired, waste precipitate and filtrate are produced from additional processing. The solid residues from leaching of ferrophosphorous slag are returned to the phosphorous recovery process, but the residues from leaching of vanadiferous clays and cannotite ores associated with uranium recovery are not reprocessed. A National Academy of Sciences report in 1974 stated that these residues are "likely to be

Table 3-32
VANADIUM WASTES

Process	Waste	Possible RCRA Characteristic*				Comments
		R	C	I	T	
Sodium Hexavanadate Production						
a. Leaching	Solid Residues	N	N	N	?	May be processed for recovery of other metals
b. Filtration	Filtrate	N	?	N	?	
Vanadium Pentoxide Production						
Option 2	Precipitate (impurities)	N	N	N	?	
	Filtrate	N	?	N	?	
Production of Metallic Vanadium						
a. Calcium Reduction	Slag	N	N	N	?	
b. Aluminothermic Reduction	Slag	N	N	N	?	

* RCRA characteristics are Reactivity, Corrosivity, Ignitability and EP Toxicity as defined in 40 CFR 261 Subpart C.

N - Waste not expected to exhibit this characteristic.
Y - Strong indication that waste would exhibit this characteristic.
? - Possibility that waste could exhibit this characteristic.

heaped on the ground or perhaps used as landfill." The current management practices for solid residues are not reported. It is not clear how liquid wastes from processing are handled.

Although the vanadium industry is currently relatively small, it could become larger if uranium mining on the Colorado Plateau resumes. Further study is recommended for potential regulation under Subtitle C.

MW-MISC/56

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