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STUDY OF AVAILABILITY AND COMPOSITION OF METAL BEARING WASTES

(GENERATED IN TITANIUM EXTRACTION & FABRICATION, ALUMINUM SMELTERS, CHROMITE BEARING REFRACTORY & FOUNDRY SANDS AND MERCURY BATTERY INDUSTRIES.)

Contract No. J0134050

N. H. PARKER, P.E. & ASSOCIATES

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Waste streams generated by mineral, metallurgical, and consumer industries carry in them recoverable metals or minerals of economic or strategic importance. This report summarizes the results of a study identifying the major waste streams, evaluating current practices of waste treatment, and their development requirements. Priorities are identifed for the developmental work by assigning weightage factors from economic, strategic, and environmental importance as well as on the lead time that may be required for process development. The study covers the following industries and wastes in the United States: titanium extraction and fabrication, aluminum smelters, chromite-bearing refractory and foundry sand wastes, and spent and scrapped mercury batteries.

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FOREWORD

This report was prepared by N.H. PARKER, P.E. & ASSOCIATES under USBM Contract No. J0134050. The contract was initiated under the SBIR Program. It is administered under the technical direction of the Division of Materials and Recycling Technology, with Mr. Robert S. Kaplan acting as Technical Project Officer. Ms. Gladys Barrera is the Contract Administrator for the Bureau of Mines. This report is a summary of the work completed under this contract, during the period September 30, 1983 through April 10, 1984. It is submitted by the authors on April 13, 1984.

PREFACE

This is the final report on this study, incorporating observations and recommendations resulting from work undertaken on all the tasks in the study. The quantitative values of waste generation or stockpiled materials are best estimations based on available/published information and are not necessarily accurate within a specified variance. Where reference is made to industry experience, it is the experience that had commonality to several industrial operators and is not specific to any one in particular.

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STUDY OF AVAILABILITY AND COMPOSITION OF METAL BEARING WASTES

by

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ABSTRACT

Waste streams generated by mineral, metallurgical, and consumer industries carry in them recoverable metals or minerals of economic or strategic importance. This report summarizes the results of a study identifying the major waste streams, evaluating current practices of waste treatment, their constraints, and their development requirements. Priorities are identified for the developmental work by assigning weightage factors from economic, strategic, and environmental importance as well as on the lead time that may be required for process development. The study covers the following industries and wastes in the U.S.:

- Titanium extraction and fabrication industry
- Aluminum smelters
- Chromite-bearing refractory and foundry sand wastes
- Spent and scrapped mercury batteries

INTRODUCTION

This study on Availability and Composition of Metal-Bearing Wastes aims at identifying the major operations generating waste streams in the following industries in the United States:

- Titanium extraction and fabrication
- Aluminum smelting
- Chrome-bearing refractory and foundry sand wastes
- Scrapped mercury batteries

The study evaluates the present processes used, as well as the constraints encountered, and recommends developmental research needed for solving problems and for making improvements.

These recommendations are prioritized by assigning weightage factors to the waste streams based on their economic, strategic, and environmental importance. Also included in the weightage factor is the lead time that the developmental work might need.

The U.S. Bureau of Mines has carried out considerable work on the reprocessing of most of the waste streams addressed in this study. This work has been essentially in the form of experimental research and process development. This effort of assessing how the industry as a whole is approaching the reprocessing or recycling concept, aims to evaluate the constraints the industry may be facing that need to be addressed and solved. It is thus complementary to the work already carried out in process development by the Bureau.

Response from the industry to our inquiries has been varied. In general, there is a reluctance to discuss waste streams and currently practiced operations. Quantified data are generally unavailable except through professional or industry associations, which occasionally furnished an industry average or a weighted mean. Information on process constraints experienced is generally not available. The reluctance to share information arises from the fact that such information is in a sensitive area of environmental protection, and industry is very shy of any kind of publicity.

Due to this reluctance, combined with the tight schedule under which this study is conducted, critical evaluation of current practices may be of a generalized nature.

SECTION 1

TITANIUM EXTRACTION INDUSTRY

MAJOR TITANIUM EXTRACTION OPERATIONS

Commercially operated titanium metal production consists of three distinct process stages.

- Upgrading of ilmenite by reduction of iron to the metallic state and recovery of titanium as a molten oxide slag, or by reduction of the iron to the divalent state and leaching with acid to remove it. Alternatively, natural rutile, with high titania content, is used as the starting material, eliminating this stage.

  This upgrading step, when used, is common to both the titanium metal and the titania pigment industries. As a general rule, however, the titanium metal industry favors rutile as the starting point, as its scale of operation is small compared to the pigment industry. On the other hand, the pigment industry, because of its much larger scale of operation, finds it economical to start with ilmenite and upgrade it. In 1982, an estimated 260,000 tons of domestic ilmenite was upgraded and used in the industry, in addition to an estimated 620,000 tons of imported raw and upgraded ilmenite and slag.

- Conversion of the resultant high-grade titanium dioxide, or the natural rutile, to titanium tetrachloride by its chlorination in the presence of carbon, and purifying the titanium tetrachloride so obtained.

- Reduction of purified titanium tetrachloride by metallic sodium or magnesium.

The following are the major titanium extraction operations in the U.S. This includes some ilmenite upgrading operations for the pigment industry.

1. American Cyanamid

   Antioch, California
   Edgemore, Delaware
   Savannah, Georgia
   De Lisle, Mississippi

2. DuPont, E.I., de Nemours

   Wilmington, Delaware

3. SCM Corporation (formerly G&W Natural Resources Group)

   Baltimore, Maryland
   Gloucester City, New Jersey
   Ashtabula, Ohio

4. Kerr-McGee Corporation

   Theodore, Alabama
   Hamilton, Mississippi

5. International Titanium Corporation

   Moses Lake, Washington

6. Oregon Metallurgical Corporation

   Albany, Oregon

7. Reactive Metals, Inc. (RMI)

   Ashtabula, Ohio
   Niles, Ohio

8. Titanium Metals Corporation of America

   Henderson, Nevada

9. Teledyne Wah Chang Albany

   Albany, Oregon

10. Western Zirconium Co.

    Ogden, Utah

Teledyne Wah Chang Albany produces essentially zirconium, but also produces small amounts of titanium on a demand basis, and has experi- ience with waste.

D&H Titanium, a joint venture of Dow Chemical and Howmet Turbine Products Division at Freeport, Texas, operated a titanium pilot plant, which has since been mothballed. Though not a producer, there is considerable experience from that operation available through the president of that venture, Mr. George Cobel, now head of the Inorganic Chemicals Department of Dow Chemicals at Midland, Michigan. The D&H pilot plant was for electrolytic production of titanium. With an improved market, the process will have potential.

OVERVIEW OF TITANIUM EXTRACTION PROCESS

SOURCES OF WASTES AND THEIR GENERATION RATES

As indicated earlier, the titanium extraction process consists of three distinct stages: upgrading of ilmenite (not required with rutile as raw material); titanium tetrachloride production and purification; and metal production. These major stages and waste generated are indicated in Figure 1-1.

The upgrading stage has three alternative processes.

1. Electric Furnace Process

This is known as the Sorel process. The ilmenite is reduced with carbon in an electric furnace, producing metallic iron and an oxide slag containing titanium and all other impurities. The slag may contain up to 8% iron to maintain fluidity.

In cases in which some pyrite occurs along with the ilmenite, it may undergo an oxidizing roast prior to electric furnace reduction.

2. Benelite Process

In this process, the low-grade ilmenite is given a reduction roast at about 900 deg. C with any cheap source of low-ash carbon. The roasted ore is leached with 15 - 30% hydrogen chloride, containing 10 - 15% ferrous chloride, under pressure at about 120 deg. C. The iron is dissolved, leaving titania in the solids. The leached slurry is filtered and the solids are calcined, while the filtrate is spray-hydrolyzed to recover hydrogen chloride and ferric oxide.

Depending upon the source of the ilmenite, the degree of oxidation and leaching it has undergone (weathering) converting it into Leucoxene, and the presence of pyrite, the ilmenite may require an oxidizing roast step before the reduction roast.

3. Sulfate Process

As in the Benelite process, the ilmenite is subjected to a reduction roast and leached with sulfuric acid instead of hydrochloric acid. The iron is leached out preferentially, leaving titania and most of the other metals in the leach residue. The leachant is neutralized and discarded.

4. Other Processes

There are other processes, such as the U.S. Bureau of Mines' borate and carbonate fluxed slag process, and direct chlorination of low-grade ilmenite by the Halomet process developed by Tellus A.G. in Frankfurt. Du Pont probably operates a pilot test unit based on the Halomet process, but there is no information available on commercial operation of any of these.

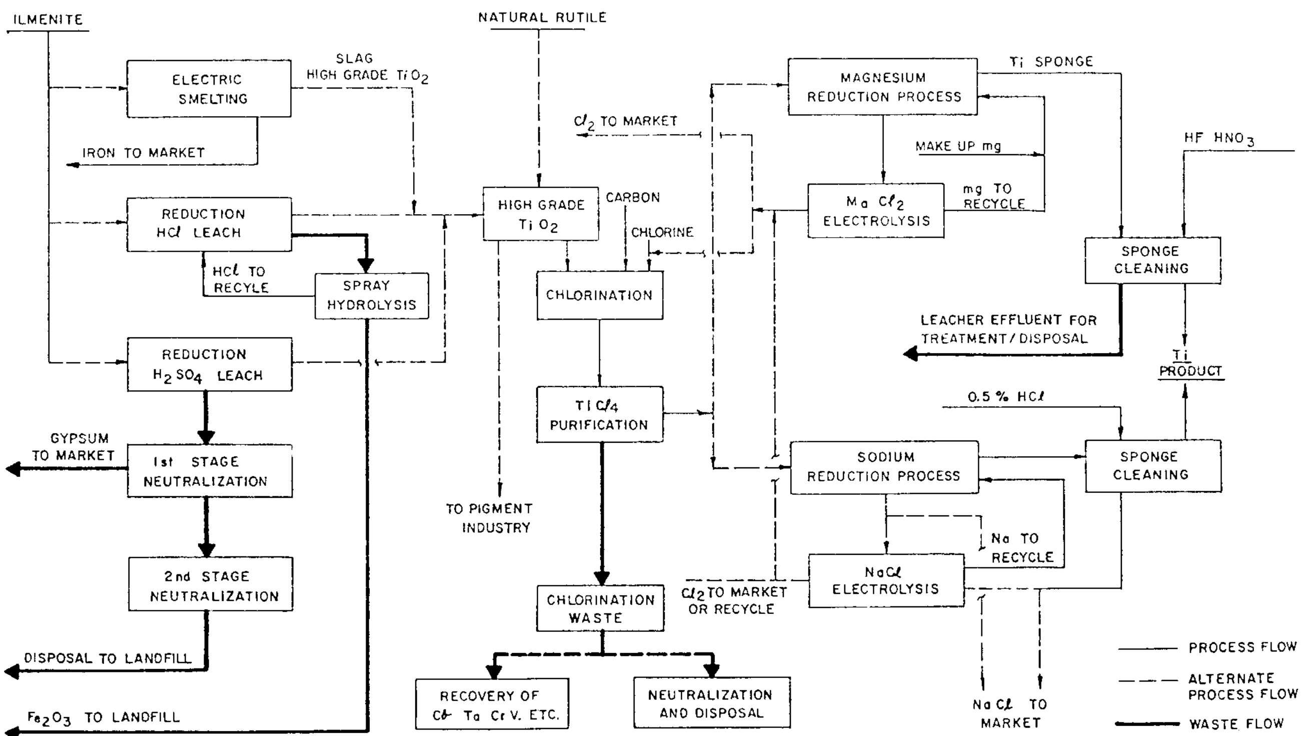

FIG. 1.1

TITANIUM EXTRACTION PROCESS

Generation of Waste

Upgrading

No significant waste is generated in the smelting process of ilmenite upgrading. In this process, the iron is reduced to the metallic state, and the only other product is the titanium-rich slag, carrying with it all the impurities in the feed material. A minor amount of dust may be carried in the vent gases; however, for the purposes of this report, this is not considered a significant waste.

The reduction roast-acid leach process generates some waste streams. As indicated, the leachant may be sulfuric acid or hydrochloric acid. The sulfate process produces a liquid effluent containing the dissolved ferrous sulfate at an acidic pH to prevent its hydrolysis. The separated effluent needs to be neutralized before disposal, which results in a sludge that is bulky and difficult to settle. Environmental problems connected with the disposal of this material have been so great that it has been largely replaced by the chloride process.

Only three plants using the sulfate process are currently in operation in the United States. The capacity of these three plants together is 174,000 tons per year of titanium dioxide, compared to a capacity of 744,000 tons per year for plants using the chloride process. No new sulfate process plant has been built in the U.S. since the mid-60's. The present capacity of sulfate process plants is 19% of the industry total. The industry does not consider there will be any expansion of the present sulfate process plant capacity. Considering these facts, the waste from the sulfate process is not considered in depth in this study.

Two of the operating plants use a two-stage lime-neutralization process, producing salable gypsum in the first stage and a landfill material with all the iron in the second stage. The third operating plant has completed its pilot plant work on a similar neutralization process, which will be put into commercial operation in the near future.

The areas requiring optimization in such a process are:

- The pH to which first-stage neutralization is carried out to precipitate the maximum amount of sulfate ions as gypsum, without contaminants and discoloration.
- Temperature, pulp density, degree of agitation, stages, seeding and gypsum recycle to control gypsum crystal growth, and filterability.

- Final pH in the second stage.

- Temperature, pulp density, degree of agitation, stages, seeding and recycle to control iron precipitation and filterability. Possible precipitation as jarosite.

- Control of post-precipitation. Precipitation, particularly of gypsum, often results in an unstable supersaturated mother liquor that continues to precipitate in pumps, pipelines, etc., where it may meet fresh nuclei or agitation. This "post-precipitation" must be controlled to avoid problems in handling the liquid flows.

- Pulp handling and filtration.

The chloride leach process results in an unreacted leach residue and ferric chloride in solution as the products. The ferric chloride is commonly decomposed to ferric oxide and hydrogen chloride in a spray hydrolyzer. The hydrogen chloride is recovered as hydrochloric acid and recycled, while the ferric oxide is disposed of to landfill. Depending upon the local industrial and consumer infrastructure, the ferric oxide may have some use; commonly, however, it is a landfill material. The unreacted leach residue is the upgraded ilmenite carried over to the next step.

The vent gases, carrying some dust and hydrogen chloride, need to be scrubbed and the effluent treated before disposal. However, none of these are major wastes with recoverable values.

Chlorination

The upgraded ilmenite (or natural rutile) is mixed with a reducing agent, coke, and reacted with chlorine, typically in a fluid-bed reactor. The reaction products go through a hot cyclone, which removes uunreacted solids, and then through a condensation train, where metal chlorides other than that of titanium are condensed and removed in stages, producing the purified titanium tetrachloride product. The stream from the hot cyclones (consisting of the unreacted solids, including the coke and the ash from the coke that is consumed) and the stream from the condensation train (consisting of metal chlorides other than that of titanium) comprise the wastes generated in this process.

Figure 1-2 is a simplified flowsheet of the chlorination process.

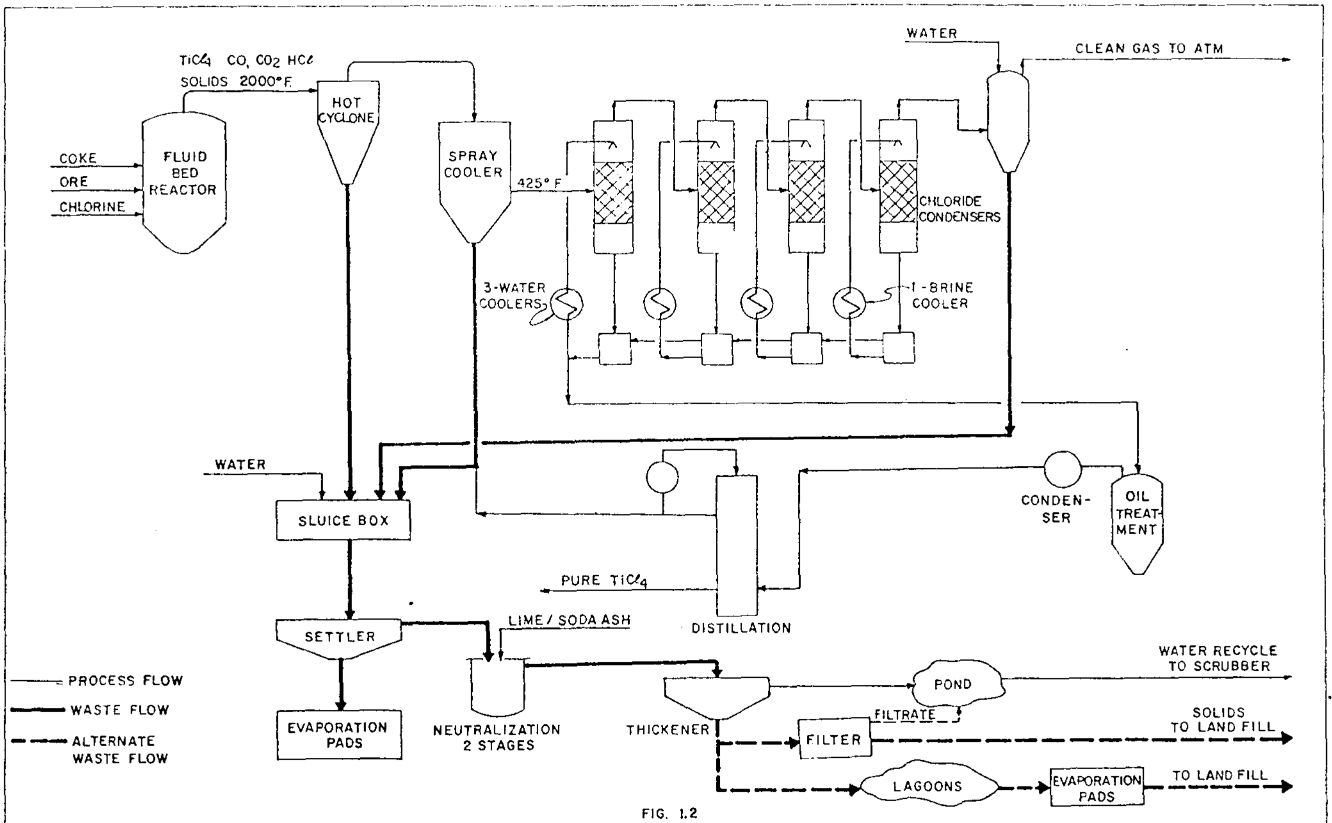

FIG. 1.2

SIMPLIFIED FLOWSHEET

TITANIUM TETRACHLORIDE PLANT AND WASTE TREATMENT

The wastes generated in the process are:

- Unreacted titanium source material (upgraded ilmenite or natural rutile) and coke, with any ash from the coke. This is collected from hot cyclones and such other dust-collection equipment.
- The metal chlorides other than titanium tetrachloride that are condensed out in the purification train.
- The scrubber discharge. The gases leaving the condensation train contain carbon dioxide, small amounts of carbon monoxide, and hydrogen chloride. The scrubber discharge carries essentially some hydrogen chloride in solution.

Some operators treat all three of these together as a single waste stream initially, later separating them into a solid and a liquid waste, which are treated separately. In such an operation, the combined waste may be sluiced with the vent-gas scrubber discharge. The acidity of it prevents the hydrolysis of some of the soluble chlorides, which would make the next step of settling very difficult. The sluiced slurry is allowed to settle. The solid residue, consisting of the unreacted titanium source material and residual carbon, is disposed of separately. The liquid overflow containing the soluble metal chlorides is treated separately. These two streams represent the total waste. These are composites of wastes generated from several point sources, reconstituted into essentially a solid, and a liquid stream.

Other operators do not mix the streams. Disposal, however, is similar and no recovery of values is attempted commercially at the present time.

Titanium Metal Production

Titanium metal is produced from purified titanium tetrachloride by reduction with metallic sodium, or magnesium. Decomposition of titanium tetraiodide, and electrolysis of titanium tetrachloride dissolved in a mixed fused-salt electrolyte, are techniques still in development, and are not commercial.

Kroll Process

The Kroll process uses magnesium to reduce titanium tetrachloride to titanium. The magnesium chloride formed is usually tapped as a melt, and both magnesium and chlorine are recovered by fused-salt electrolysis.

Alternatively, the magnesium chloride vapors may be flushed by helium, condensed, and electrolyzed, as some operators do. If the facility includes a chlorination plant, both magnesium and chlorine are recycled. If the reduction plant purchases the tetrachloride, as some do, the chlorine is sold and the magnesium is recycled.

However, the titanium metal produced by the magnesium reduction process must be cleaned of adherent magnesium chloride and any unreacted metallic magnesium. The cleaning is effected by leaching the titanium sponge with a leachant of dilute hydrochloric and nitric acids. The nitric acid is required to passivate titanium, and the presence of nitrate, makes the leach liquor unsuitable for recycle to the magnesium recovery plant. The leachant also contains a small amount of urea added to suppress the formation of nitric oxides.

This leach liquor, known in the industry as titanium leacher effluent, is a waste stream generated at this stage of the process.

Sodium Process

Purified titanium tetrachloride may be reduced by metallic sodium, the end products being titanium sponge, salt (sodium chloride), and sodium chloride solution resulting from final cleaning of titanium sponge by leaching with 0.5% hydrogen chloride in water. The sodium chloride is electrolyzed to recover sodium and chlorine for recycle to the reduction and chlorination stages of the process. Alternatively, the chlorine may be marketed if the titanium metal production facility does not include a chlorination plant. The waste generated is the acidified sodium chloride resulting from washing of the titanium sponge. This is a minor, non-toxic waste.

Fused-Salt Electrolysis Process

Purified, fused titanium tetrachloride could be electrolyzed to produce titanium metal. There are several cell designs and electrolyte compositions in development. These include:

- The New Jersey Zinc Cell, with an electrolyte consisting of a eutectic mix of lithium chloride, potassium chloride, and sodium chloride with about 4% titanium dissolved in it in the cathode compartment. In the process, the salts adhering to the titanium metal produced are recovered and returned to the cell. No waste stream is reported.

- The U.S. Bureau of Mines Titanium Cell uses a mix of lithium chloride and potassium chloride as electrolyte, to which titanium tetrachloride is added batchwise. No waste streams are reported in the process.

- The Sony Titanium Cell is an experimental unit with a complex electrolyte consisting of chlorides of barium, sodium, magnesium, and calcium. There is no waste stream reported and, to our knowledge, no commercial operation either.

- The Dow Chemical Cell. A pilot plant was operated by D&H Titanium, a joint venture of Dow Chemical and Howmet Turbine Products Division, at Freeport, Texas. By far the best published information is available on this process. There is a waste stream, from the salt reprocessing step, which contains fine titanium, titania, and hydrogen chloride. The process is not commercial and this waste is not studied in depth here.

To summarize, therefore, the titanium extraction industry generates the following waste streams, as shown in Table 1-1.

Table 1-1. Waste Streams in the Titanium Extraction Industry

Process Stage	Waste Stream
Upgrading of ilmenite	None of significance, except vent-gas scrubber discharge, with a small amount of dust. The smelting process produces titanium slag and iron; both are intermediate products for further processing. The chloride process produces ferric chloride as a waste product, which is spray-hydrolyzed, recovering hydrogen chloride for recycle, and a disposable ferric oxide waste. As noted earlier, the sulfate process is not considered in depth in this study.
Chlorination and titanium tetrachloride purification	1. Unreacted solid residue from chlorination, consisting essentially of titanium source material and carbon.
	2. Water-soluble metal chlorides other than titanium tetrachloride derived from the titanium source material, with some titanium and free hydrochloric acid, in a liquid stream.
Titanium metal production	1. Titanium leacher effluent, consisting of magnesium chloride and nitrate, with some nitric and hydrochloric acids and traces of titanium.
	2. Effluents generated in recycling of salts in electrolytic titanium production cells. (Not commercial at present.)

Nature and Generation Rate of Wastes

Chlorination Plant Waste

The feed material to chlorination plants is either upgraded ilmenite or natural rutile, containing from 90 to 95% titanium oxide. The balance, 5 to 10%, is made up of oxides and silicates that normally occur with ilmenite and rutile, which typically include the following elements.

Aluminum
Chromium
Columbium
Iron
Manganese
Silicon
Tantalum
Tin
Vanadium
Zinc

Rare earths, uranium, and thorium may also occur in those cases in which the rutile occurs along with monazite.

The actual composition varies widely, and depends upon the deposit from which the raw material is derived. A large number of these metallic elements are chlorinated along with the titanium, and report to the waste stream as chlorides. Some oxides and silicates, resistant to chlorination, as well as some fine particles of the titanium source mineral, ilmenite or rutile, are found in the solid waste from the process. Table 1-2 gives a typical composition of the solids in the waste material (both the solid waste as well as the water-soluble salts).

The generation of waste varies with the titanium source material. However, an industry average range of total solid content of the waste (both unreacted solids and soluble chlorides) is reported by the industry at around 100 to 140 lb per ton of titanium tetrachloride produced.[1] The total solids in the waste generated in the titanium extraction industry in 1983 would amount to between 3,000 and 4,200 tons. If the waste generated in the pigment industry is included, this amount will work out to 47,000 to 66,000 tons.

Titanium Leacher Effluent

The titanium sponge generated by the magnesium reduction process has some unreacted magnesium and some magnesium chloride physically adhering to the titanium sponge. As previously noted, these are leached out by a leachant consisting of hydrochloric and nitric acids. The resulting leach solution consists essentially of magnesium chloride and magnesium nitrate, with some excess acids. There is also a minor amount

Table 1-2. Typical Composition of Chlorination Wastes

	Percent (approx)
Inerts (coke ash, unreacted titanium source material)	40 - 50
Silica	4
Iron	10 - 15
Aluminum	5
Managanese	2
Vanadium	1
Calcium	1
Columbium	1
Tantalum	1
Chlorine	25 - 30

of titanium, and urea that is added to suppress formation of nitric oxides. Due to the presence of magnesium nitrate and urea, the magnesium chloride cannot be recycled to magnesium chloride electrolysis. This is a value-containing waste at this stage of the process.

A rough estimate of this effluent would place it at about 12,000 tons per year, with possibly 8 to 10% of dissolved salts and acid.

CURRENT AND DEVELOPING WASTE TREATMENT PRACTICES

Current Industry Practice

Chlorination Plant

As mentioned earlier, the wastes from the different point sources typically are collected together and sluiced with the off-gas scrub discharge water. The scrub discharge is acidic, and the acidity prevents hydrolysis of some of the chlorides to oxychlorides and hydroxides. If these are allowed to form, the resultant sludge will be even more difficult to settle and dewater for disposal. After sluicing, the slurry is allowed to separate into a solid and a liquid effluent. The solid, in the form of a thick slurry, is disposed of to a waste dump, and the liquid is neutralized with lime and settled in lagoons. The neutralized material is a difficult sludge to settle because of the presence of hydroxides and oxychlorides. Reclamation of solids from the ponds for disposal is difficult, since the solids do not settle and consolidate easily; hence, this is not attempted. There are large lagoons filled with this material in the industry today. No quantitative data on the stockpiled quantity was available.

Industry reported operational difficulties in recycling the solid waste from the cyclone to the chlorination step. The problems were in the dewatering, drying, and pelletizing of the solid waste when it was recovered after initial washing. In some instances the recycling resulted in severe corrosion of ducting due to the moisture content of the recycled feed, and hydrogen chloride from adsorbed chlorides.

Storage in lagoons/ponds appears to be the common practice in the industry for the chlorination wastes.

Titanium Extraction Plant

The waste in the titanium extraction plant is the titanium leacher effluent. In a typical operation this effluent is neutralized in two stages, first by percolation through a lime bed to neutralize 50% of the acid, and then by neutralization by soda ash to a pH between 8 and 9. The first-stage neutralization reduces cost, and the second-stage neutralization with soda ash ensures that there are no undesirable and difficult-to-handle solid precipitates.

The neutralized liquor now contains chlorides and nitrates of sodium, calcium, and magnesium. This is allowed to evaporate to a density of about 1.4 to 1.5 and is sold as dust depressant and soil stabilizer. The operation that uses this process is actively developing other uses for the liquor.

Other titanium operators neutralize the liquor and dispose of it into lagoons, along with other neutralized effluents. No recovery of contained values is being practiced at the present time.

Processes in Development

The Bureau of Mines conducted test work on the beneficiation of titanium chlorination wastes.[2,3] In one of the test programs, the sludge from the chlorination plant was leached with water and the solids were separated from the leachant, and the solid residue was tested for possible recycle to chlorination. Experimentally, the chlorination was successful. The solid residue was pelletized in the experimental work, by mixing with binders and tray-drying. While the test work establishes the general technical feasibility of the recycling of the unreacted solids to the chlorinator, in-depth study of the process parameters would be required for commercial application. This is discussed under "Recommendations."

In another experimental program, physical beneficiation was tested.[4] Gravity concentration for the recovery of rutile, and flotation for the recovery of carbon, were successful. However, the samples were collected from point sources. Further parametric studies are understood to be under way.

There is merit in collection of some of the solid wastes from different point sources separately, and treating them separately. However, such separate collection would mean a major change in plant configuration and layout, in addition to the process changes in those plants collecting these wastes together. This is also discussed further under "Recommendations."

The Bureau of Mines has conducted test work on the separation of columbium, tantalum, titanium, and zirconium from the wastes from the condensation train.[4] The experimental work employed a liquid-liquid extraction process for the extraction and separation of these metals. The separations were successful. As in the case of solids residue, this establishes the feasibility of separation of columbium and tantalum from zirconium and titanium. It requires further work in optimizing the basic extraction and production of a final, marketable product. At present, none of the processes under development has reached a commercial stage.

The Bureau is at present conducting test work on separation by fractional distillation techniques on wastes collected without dilution by scrubber discharge.

TECHNICAL AND ECONOMIC REQUIREMENTS FOR VIABLE WASTE TREATMENT OPERATION

Chlorination Plant Waste

Chlorination plant wastes are estimated at 100 to 140 lb per ton of titanium tetrachloride produced, of which about 80 to 90 lb is the solid waste and the balance is the dissolved and unsettled solids in the liquid effluent.

Solid Waste

The solid waste, in turn, contains about 30 to 35% titanium source material, 30 to 35% unburned carbon, and about 20% refractory mineral impurities. The balance is absorbed hydrochloric acid and chlorides. At the present market value of rutile, this solid waste represents about \$150 worth of titanium values and about \$15 of carbon value per ton of waste. Recirculation of this solid waste to the chlorinator requires:

- Washing out of the adherent chlorides and adsorbed hydrochloric acid. The hygroscopic nature of the chlorides makes drying difficult, and the moisture makes the agglomeration, which is required for recycle to the fluid-bed chlorinator, also difficult. The hydrochloric acid, along with the moisture, caused corrosion problems when it was tried in one operating plant.
- A process step to remove the refractory mineral impurities. These build up if not removed, and make chlorination inefficient.
- The solids in the residue are extremely fine, and need to be agglomerated before recycle to the chlorinator. The agglomeration must result in a compatible particle size and adequate physical strength and erosion resistance, with good gas-diffusion properties.

All process steps required are standard unit operations, needing only optimization. Considering the contained value, processing of this waste appears to hold economic incentive.

Liquid Effluent

The resulting liquid effluent, after separation of solid residues following sluicing of all the collected wastes with off-gas scrub discharge, contains essentially the soluble chlorides, including those of iron, chromium, vanadium, tantalum, columbium, and manganese, and some titanium, together with minor amounts of free hydrochloric acid. The value of the metals contained in the effluent as chlorides varies widely, depending upon the rutile source. Up to 21 g/l (or 18 lb/100 gal) of these metals have been reported in the liquid effluent.

However, not all of the metals listed are present in all the effluents. The metals content in this effluent varies from plant to plant. It also varies from time to time in the same plant, depending upon the feedstock to chlorination. The concentration of these metals can vary from "trace" up to 21 g/l. Based on the maximum values observed, an average titanium metal extraction plant, with a production capacity of 3,000 tons of titanium per year, may have a potential of 50 to 80 tons each of these metals per year.

Separation and recovery of these metals are as byproducts to the market, and not for recirculation to the titanium plant. As such, a market survey to determine the optimum product mix would be a desirable step before a process design.

Initial recovery steps would be ion exchange and/or solvent extraction. The final recovery of values must be as metal compounds having an optimal combination of price and market potential. This is particularly so since the quantities of these metal values in effluents of individual titanium plants are not large enough by themselves to sustain economical operation of a metal plant.

Metal Extraction Plant Waste

Titanium Leacher Effluent

Titanium leacher effluent is a small waste stream. However, due to its chloride and nitrate content, with free acids, it is an extremely corrosive material. The solvent extraction process developed by the Bureau of Mines[5] has not been commercialized, mainly because the size of this stream does not warrant extensive processing.

The requirement, therefore, is to develop a disposal technique that would be cost-effective. One such development is the controlled neutralization of the free acids, concentration of the dissolved salts, and use of the solution as soil conditioner. Such and similar uses are perhaps the best way to deal with this effluent. Market and applications research in this area are called for to identify new and more cost-effective usage of this material.

RECOMMENDATIONS

Solid Wastes

(Wastes from Chlorinator)

As indicated earlier, some operators collect the solid waste from the chlorinator along with the condensates from the purification train. Since the condensates from the purification train are chlorides, many of which hydrolyze at higher pH, the collected material is sluiced with acidic water and then separated into essentially a solid and a liquid waste stream. Some of the problems arising in the process, particularly due to the acidity of the wash water, could perhaps be avoided if the solid waste from the chlorinator were collected dry, separately from the condensates from the purification train. Since this would be a major change, comparative evaluation will be required of the processes for treating the solid waste collected separately and that resulting from combined collection.

The solid waste from the chlorinator is an extremely fine powder and is contaminated by refractory minerals. This unreacted material is blown out of the reaction zone of the chlorinator, essentially due to its size, since the chlorinator is a fluid-bed reactor. The fineness of size necessitates agglomeration, and presence of refractory minerals necessitates separation of them before recycle.

The first alternative that deserves an in-depth study is reduction of the quantity of the unreacted material generated, or increase of the chlorination efficiency. This could possibly be achieved by one of several ways.

- Introduce a second separate stage of chlorination for the discharge from the hot cyclone. This stage could be a reactor designed as a miniature multi-hearth roaster or a rotary furnace, with low-velocity chlorine through it.
- The fluid-bed reactor could be modified to incorporate a second stage with a low-velocity zone.
- The fluid-bed combustor is a cocurrent reactor. A countercurrent reactor with high chlorine concentration at the solids discharge end could ensure more complete chlorination. A multi-hearth furnace or a rotating tube calciner could possibly achieve this with lower gas velocities reducing the solids carried over. Such a reactor could replace the fluid-bed chlorinator.

Design modification and prototype reactor studies would be worthwhile.

The second alternative is to collect this solid waste from the cyclone, unmixed with the condensed solids from the purification train, and treat it separately. The treatment would be to concentrate the titanium mineral and unburned carbon, rejecting the silicate and other refractory minerals, and to agglomerate the concentrate. The final agglomerate must have reasonable strength, and good permeability to allow diffusion of chlorine into it for efficient chlorination.

A most suitable agglomerate could be produced from a dry mixture of the concentrate (containing both rutile and the carbon) and binder and pelletizing it in a disc or drum pelletizer with water spray that generates a multi-nuclear pellet. This would result in a "cauliflower"-type structure in the pellet, and provide a large surface for unit weight and porosity, compared to a mononuclear pellet with a "cabbage"-type structure. With suitable binder and curing, the final strength could be adjusted to the desired degree.

As a preparation for such a pelletizing procedure, it will be cost-effective to carry out the beneficiation in the dry state, without having to dewater, dry, and delump such concentrate as obtained in a wet process.

Experimental test work in dry tabling and electrostatic separation to obtain a rutile fraction, a carbon fraction, and a reject silicate fraction, would be worthwhile.

If, however, the separate dry collection of the cyclone discharge is not feasible in the industry, the solids settled after sluicing will have to be prepared as a recycle feed. This would involve:

- Washing out the free hydrochloric acid and soluble chlorides absorbed on the surface of the solids.

- Separation and rejection of the refractory silicate minerals.

- Filtering and drying of the concentrates containing rutile and carbon.

- Pelletizing of the concentrates.

The washing of the chlorides and free hydrogen chloride may have to be carried out in two stages -- the first stage at a suitably low pH to prevent any oxychloride formation, which could coat the minerals and reduce efficiency in the next steps; and a second stage with water, to remove the free acid. The acid waste will have to be neutralized, and could be treated along with the liquid effluent.

Wet tabling could yield the rutile as a heavy fraction and the carbon as a light fraction, with reject material as an intermediate fraction. Flotation for carbon may not be necessary. The heavy and light fractions could then be combined together, dewatered, filtered, dried, delumped, and pelletized. Individual unit operations are standard, and require only optimization.

To summarize, therefore, the following developmental work is recommended for the solid waste from the chlorination plant.

1. Design studies in a mini-multihearth and/or rotary tube roaster, as a second-stage chlorinator.

2. Design studies in incorporating a second low-velocity stage in the fluid-bed chlorinator.

3. Design of a suitable countercurrent-type chlorinator, as a substitute for a fluid-bed chlorinator.

4. Prototype equipment construction and testing of Steps 1, 2, and 3.

5. Collection of hot cyclone discharge as dry material and test work on it in:

   (a) Dry tabling separation. The hygroscopic nature of any chloride coating and the fine size of particles could present problems in tabling, requiring innovative solutions.

   (b) Electrostatic separation. As in dry tabling, chloride coating on the solid particulates would tend to diminish discrimination between the mineral phases in electrostatic separation. Innovative solutions will be required in this case also.

6. Collection of currently generated wet solid waste and test work on it in:

   - Attrition wash
   - Wet tabling
   - Flotation for carbon
   - Filtration and drying
   - Delumping and mixing of the rutile and carbon

7. Pelletization studies with concentrate from Step 5, including alternative binders and pelletizing process variables.

8. Pelletization studies with material from Step 6, including alternative binders and pelletizing process variables.

9. Chlorination studies of pellets and the correlation with pellet properties to optimize Steps 7 and 8.

10. Process design and engineering studies for capital and operating costs.

11. Comparative evaluation of the process for dry solid discharge and wet solid waste collection.

Liquid Wastes

(Waste from Titanium Tetrachloride Purification Trains)

As in the case of solid wastes, the liquid waste could be:

- The liquid overflow after all the waste is sluiced with scrubber discharge and settled, as in some plants at present;
- The condensates from the purification train, collected separately and washed with the scrubber discharge; or
- Condensates from the purification train, undiluted by any washwater.

The resultant liquid discharge would be essentially the same in either of the first two cases, and would consist essentially of chlorides of iron, chromium, vanadium, tantalum, columbium, any manganese, some titanium, and free hydrochloric acid. The process for the recovery of valuable metals will have to be developed for each titanium extraction operation separately, since the composition of the liquid discharge varies widely depending upon the source of titanium raw material (rutile or ilmenite).

Solvent extraction appears to be the most versatile process appproach for initial separations. The following systems are known and could be adopted for the liquid effluents.

- Columbium-tantalum separations:

  Methyl isobutyl ketone[6,7,8,9]
  Cyclohexanone[10]
  3-Methyl 2-butanone[10]
  2-Pentanone[10]
  Tertiary amines[11]

- Extraction of vanadium:

  Di- (2-ethyl hexyl) phosphoric acid (D2EHPA)[12,13]
  Tributyl phosphate (TBP)[12]
  Tertiary and quaternary amines[14]

- Extraction of chromium:

  Primary amines[15]
  Quaternary amines[14]
  Alamine 336 and Aliquat 336[16] (trade names of amines from Henkel Corporation)

The predominance of iron influences the initial process steps, since iron extracts easily with most of the organic solvents suggested above. The final products from the process, as has been suggested earlier, must be in the form of compounds of the recovered metals that have the maximum market value. The nature of these compounds as the final products would influence the separation and recovery steps.

The following sequential approach is recommended for process development in this area.

1. Market analysis for identification of compounds of recoverable metals that have the maximum market potential and value. These could be mixtures acceptable to the market.

2. Determination of the solvent extraction system that will most easily lend itself to the recovery of the metals as the end products indicated in item 1.

3. Experimental determination of necessary extraction steps and optimum process parameters.

This approach aims to deal only with newly produced liquid waste in the industry that is not neutralized by lime and disposed of in a hazardous-waste disposal area. A large, unquantified amount of this neutralized material has been generated in the industry in past years of operation. It will be worthwhile examining how this material could be treated, both from economic as well as from environmental points of view. This lime-neutralized material consists of hydroxides, oxychlorides, and chlorides.

No test work appears to have been carried out on this material -- at least, none that has been published. One operator reported executing a sales contract of this dump material with a private firm, which reportedly had a process for the recovery and were planning to put up a plant. However, the contract was broken when the sampling and analysis of the material from the lagoons showed lesser amounts of columbium and tantalum than had been expected. This lower value content was due to the titanium extraction plant switching over to a different rutile source, some time ago. Quantitative information was not available.

In order to develop solutions to the problems connected with the wastes already accumulated and impounded in lagoons, it is recommended that test samples be drawn from these hazardous-waste storage lagoons for analysis; test work be undertaken; and processes be developed as may be indicated by the initial analyses.

Collection of the chloride fractions without dilution by scrubber discharge results in a concentrated mixture of chlorides. A market survey would determine the degree of separation needed. Also, this procedure would still leave a third stream of scrubber discharge requiring handling and disposal. A market survey appears to be the prime need.

Titanium Leacher Effluent

As indicated earlier, an industry approach of controlled neutralization and concentration for sale as soil stabilizer appears to be a simple, cost-effective way of dealing with this material. Some of the newly developing processes indicated in Section 7 of this report may have applicability to this effluent. However, they would be of low priority, considering the fact that the processes are in early stages of development.

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SECTION 2

TITANIUM FABRICATION INDUSTRY

MAJOR TITANIUM FABRICATORS

Military and civil aircraft, space, and missile applications dominate the titanium metal fabrication industry as major consumers, accounting for over 60% of U.S. consumption. The aircraft industry has been volatile in its strength and, of late, demands have been fluctuating. Other uses of titanium are in chemical process plant, marine, and ordnance applications. While the chemical process industry has been depressed, the marine and ordnance applications have brought in newer applications and an upward trend.

The major titanium fabricators in the U.S. are:

1. A. Johnson & Co.

   Lionville, Pennsylvania

2. Armco Steel, Advanced Materials Division

   Middletown, Ohio

3. Astro Metallurgical Corp.

   Wooster, Ohio

4. Cabot Corp.

   Kokomo, Indiana

5. Dynamet Corp.

   Washington, Pennsylvania

6. Howmet Turbine Products Division

   Muskegon, Michigan

7. Martin Marietta Aluminum Co.

   Torrance, California

8. Micron Metals

   Salt Lake City, Utah

9. Nuclear Metals, Inc.

   Concord, Massachusetts

10. Oregon Metallurgical Corp.

    Albany, Oregon

11. Refractory Welding & Fabrication, Inc.

    Houston, Texas

12. Titanium Research & Development Corp.

    Washington, Missouri

13. Titanium Finishing Co.

    East Greenville, Pennsylvania

14. Titech International

    Pomona, California

15. Viking Metallurgical Corp.

    Verdi, Nevada

16. Wymon Gordon

    Grafton, Massachusetts

NATURE AND GENERATION RATE OF FABRICATION WASTE

Titanium is used in the industry both as essentially pure titanium and as titanium alloys. The fabrication of titanium and its alloys can be considered at two levels.

The primary fabrication is the production of mill products, which are essentially standard sections and plates, produced from ingots. The primary fabricators, or mill product producers, usually melt sponge titanium and make their own ingots, from which they roll or extrude the sections.

The secondary fabrication is the production of consumer parts such as jet engine components, airframes, and chemical process equipment parts. These products are made by forging, machining, grinding, welding, and other such machine shop operations.

The scrap generated at these two levels differs considerably in nature and generation rate.

Primary Scrap

The primary scrap consists of edge cuttings and trimmings. Since fabrication at this level is made in batches of metals of the same composition, it is not difficult to keep scrap of like composition isolated. This scrap is easily handled, consisting of larger pieces compared to the scrap produced in the secondary fabrication stage. While occasionally there is oxidized material that causes some problems, this is the scrap that is easily recycled without difficulties in regard either to composition or to contamination.

The rate of generation of this scrap is dependent on the size and shape of the mill product. Exact information is difficult to obtain, both because precise records are not maintained, and also because where there is such information, it is only for the operators' internal use and is not for publication.

A rough estimate made by extrapolation places this in the range of 10 to 40% of the sponge titanium, which is the starting material. The overall average is perhaps about 17%.

Most of this scrap is ultimately remelted by the primary fabricators, who start with titanium sponge. The amount of scrap that can be remelted along with sponge is not unlimited, due to the oxide film on the scrap and constraints arising out of the shape and size. It is estimated that up to 50% of this scrap may not be recycled at times. The total unprocessed primary scrap, however, is estimated at about 15% of the scrap generated. Such material is usually downgraded to produce ferrotitanium for ultimate production of low-titanium alloys.

Table 2-1 shows the reported and estimated production of sponge titanium, and generation of scrap.

Secondary Scrap

The scrap generated by secondary fabricators consists of:

- Scrap cuttings and trimmings.
- Scrap from machining, drilling, and similar shaping operations.
- Sludge produced in chem-milling, cleaning, washing, pickling, and similar operations.

Table 2-1. Estimated Titanium Scrap
Generated in 1982-1983

	1982, ST	1983, ST
Sponge production	18,400[a]	13,000[b]
Primary scrap recycled	3,400[c]	3,210[c]
Primary scrap not recycled	510[c]	332[c]
Secondary scrap recycled	8,600[d]	3,790[d]
Secondary scrap not recycled	3,600[d]	1,010[d]

[a] Reported production, Mineral & Commodity Summaries, 1983, U.S. Bureau of Mines.
[b] Estimated figure, based on data from Minerals & Materials, U.S. Bureau of Mines, June/July 1983.
[c] Estimations based on private communication from industry.
[d] Estimations based on data from Mineral Commodity Summaries, 1983, U.S. Bureau of Mines, ASM Report, System Paper W-72-21-2; and some private communications from industry.

Since the fabricator at this stage processes several parts with materials of varying composition at the same time, it is difficult to keep the scrap isolated with respect to composition. The scrap gets mixed up, particularly in the machine shop.

Also, the machining operations introduce foreign matter such as tool bits, carbide particles, and hard metals into the scrap. These are usually small particles, and are refractory materials that do not melt with the titanium in the scrap.

These two factors make the secondary scrap distinct from the primary, requiring special treatment.

The scrap generation rate is much higher at the secondary fabrication level. Of the mill products shipped to the fabricators manufacturing jet engine components or airframes in a typical aircraft industry, 70 to 75% may end up as scrap. Other industries, such as the chemical process equipment industry, generate less scrap, but percentage-wise at a rate higher than the 17% estimated average for primary scrap. The overall average at the secondary level of fabrication is estimated to be about 45% of the starting material.

It is estimated that 12,200 short tons of secondary scrap was generated in 1982, and that for 1983 could be on the order of 4,800 short tons.

The total scrap recycled, primary and secondary, for 1982 was reported at 12,000 tons[1,2] and that for 1983 is estimated at 7,000 tons.

Some waste material generated in secondary fabrication is such that it cannot be recycled by remelting. The following fall into this category:

- Scrap generated in grinding and brushing. This has heavy contamination, too fine a size, with heavy surface oxidation.
- Pickling and chem-milling sludges. The metal is converted into salts; if these are to be recycled, they need to go to an early-stage metal-extraction process.

The grinding, pickling, and chem-milling waste could not be quantified. Discussions with a few fabricators indicated this could be on the order of 15% of the total secondary scrap generated.

CURRENT WASTE RECLAMATION PROCESSES

Direct Remelting

Direct remelting is applicable to the primary and some of the secondary scrap material. The most common practice is to physically clean the scrap of any foreign matter and weld the large pieces together in a form that can be used as consumable electrodes in an arc-melting furnace, operating in vacuum or under cover of argon. The smaller pieces are cleaned, washed, and compacted into consumable electrodes.

The consumable-electrode arc-melting method was introduced by the U.S. Bureau of Mines.[3,4] Other melting methods in common use prior to introduction of consumable-electrode arc melting included resistance heating, induction heating, and tungsten arc melting.

The process is not applicable if the scrap is likely to contain tool bits or carbide particles, as in the secondary scrap, especially if such particles are small and do not easily settle in the titanium melt. Such inclusions break the continuity of the titanium metal, and are causes for potential failures in titanium parts that contain them.

In the case of secondary scrap of known composition, or smaller batches of primary scrap, recycled by the direct melting process, there is a possibility of adjusting the final composition by suitable additions to the compacted consumable electrode to conform the final metal to desired specifications.

In cases where such adjustments are difficult to make, the material is converted to intermediate alloys such as ferrotitanium, for use in production of alloys with minor amounts of titanium.

Electron-Beam Melting

This is a process developed particularly for recovering the titanium from secondary scrap. The process remelts the scrap and produces pellets or ingots, as required. As a first step, the scrap is sorted out by alloy type, crushed, degreased, and dried. The melting is carried out in an electron beam skull furnace, on a water-cooled copper hearth. The heavier particles sink to the bottom of the titanium melt and the top metal overflows through multiple pouring spouts as droplets over a water-cooled rotating copper drum. The pellets so formed are transferred to a collecting container through a vibrating cooling conveyor.

The pellets are intermediate products, and are sampled, analyzed, blended, compacted with or without sponge titanium, and used as consumable electrodes in arc furnaces for ingot production.

Pellet production by electron beam melting forms an intermediate step in homogenizing the scrap in small batches. The pellets thus produced can be sampled and analyzed for reconstituting to final composition. Sampling of machine shop turnings for analysis and blending is unreliable, if not impossible.

Electron beam melting can produce ingots as well, when the cooling drum is bypassed and the melt is cast into an ingot. This is done when analysis and blending is not required and the starting scrap is of a known and usable quality. The electron beam furnace is particularly suited for melting difficultly compactable scrap, or scrap with contamination requiring removal of heavy foreign substances such as tungsten and tungsten carbide, or where an intermediate stage of pellet for analysis and reconstitution is required. A detailed description of the furnace and process is available in an ASM Report Systems paper.[6]

Other Processes

Theoretically, the scrap could be powdered, analyzed, blended, compacted, and sintered into useful components by powder metallurgy. However, there are two basic constraints that prevent the use of the scrap for powder metallurgical compacts.

1. The scrap (and particularly the machining scrap) has too high a degree of surface oxidation. The oxide film prevents good sinter and is therefore unsuitable for components made by powder metallurgy.

2. The machining scrap is usually contaminated with particles of tools used in machining, including alloys and carbides of tungsten, molybdenum, vanadium, iron, etc. These are not easily separated from the titanium powder. The powdering process itself introduces additional contaminants.

TECHNICAL AND ECONOMIC REQUIREMENTS FOR VIABLE WASTE TREATMENT OPERATIONS

Any process to recover and reuse the titanium from scrap must:

- Purify the scrap of the contaminating metals, alloys, carbides, machining oils, and lubricants. While washing and degreasing removes the machining oils and lubricants, the metallic and carbide contaminations are more difficult to remove.

- Result in a product metal conforming to specified composition. Separate storage of scrap from different types of titanium alloys is difficult, and the secondary scrap usually results in a product of uncertain composition. It becomes necessary either to ensure that the feed to the scrap remelting furnace is of known composition, or to produce an intermediary product that is well-homogenized, which could be sampled, analyzed, and remelted with necessary additions to conform to the composition specifications.

Some scrap materials, particularly machine shop secondaries, fall into the unrecoverable category due to either or both of the above reasons. The scrap generation rate in the production of complex parts, as indicated earlier, could be as much as 75% of the starting material. Scrap generated in grinding, brushing, pickling, and chem-melting also falls in this category.

Sponge titanium was quoted during the second quarter of 1983 at \$5.50 a pound. The scrap value is low -- generally a few cents per pound. The remelting process is carried out under controlled atmosphere or vacuum, and there is very little, if any, melting loss. The scrap remelting and reconstituting process could bear total processing costs of as much as \$3 to \$4 per pound.

The low scrap price compared to the sponge price, combined with the high volume generation of scrap, are good economic incentives for recycle.

RECOMMENDATIONS

The present scrap recycling practice is confined to remelting and reconstituting to the required specification. The scrap that cannot be remelted and reconstituted is either converted to low titanium alloys such as ferrotitanium or dumped as unrecoverable waste material. Pickling and chem-melting scrap requires neutralization before such disposal. This waste deserves developmental work for recovery.

As indicated earlier, the purification of this scrap from the contaminants is impractical by physical means, and restrictive in a melting process. However, chemical and electrochemical methods could possibly be applied for purification and reclamation.

The titanium machining and grinding scrap could be recycled to the chlorination step of the titanium extraction process. The main contaminating metal, tungsten, does not chlorinate as easily as titanium, while chromium, vanadium, molybdenum, and iron do. In chlorination, tungsten could be easily separated as unreacted residue, while iron, chromium, and vanadium would be separated in the purification train.

Virgin metal usually represents a product resulting from a high level of expended energy in extracting it from its ores or its state as a metal compound. Reverting it to the state of a chemical compound for its purification and then reducing it to the elemental state is an energy-intensive process. However, in the case of titanium scrap, with the high rate of its generation, the scrap value, and the value of sponge titanium, it would be worthwhile examining the economics of such a method of reprocessing.

It is estimated that about 15% of the scrap falls into the "unrecoverable" category for the remelting process, due to one or more of the reasons discussed. While it would not be practical to chlorinate the scrap separately for the metal recovery, it may be very worthwhile to recycle it to the chlorination plant, operating with rutile or beneficiated ilmenite.

To establish the feasibility of such a recycle, the following test work would be necessary.

- Chlorination of titanium machining scrap, after cleaning, degreasing, drying, and crushing.
- Chlorination of the scrap as above, but mixed with regular chlorination feed of rutile and coke.

The problems that may be encountered would be due to:

- Relatively different chlorination rates between scrap titanium and rutile.
- Consequent temperature differentials and hot zones in the reactor.
- Any changes in fluidization character.

Experimental work should be able to identify optimal conditions for concurrent chlorination of the scrap and titanium source material.

Electrolytic refining could be another approach. However, an independent plant for the electrolysis of the otherwise unrecyclable scrap may not hold economic incentive. Electrolysis as the main titanium extraction process is not yet commercial,[7] and has a few problems to be solved.[8] Perhaps at a later date, when it becomes commercial, there could be a possibility of using electrolysis as a scrap recycle step.

Chem-melting and pickling scrap could be recycled to liquid effluents in the chlorination process.

Filtration of molten metal through refractory filter blocks is under development in the Avondale experimental station of the Bureau of Mines. The oxide film covering the metal is filtered in this process. Filtration does not occur, due to the size of the solid particulates compared to the apertures in the filter block; rather, this is probably due to the surface properties of the oxide particles. It would appear that the molten titanium scrap could also be filtered from contaminating materials. Since the filter block could form part or all of the bottom of the melting furnace, a high level of superheat may not be necessary for such filtration. This approach is worth further investigation.

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SECTION 3

ALUMINUM SMELTERS

There are 10 primary aluminum producers, of which three contribute a major part of U.S. production. All of the operations have suffered reduction in production in the past few years. At the beginning of 1983, 40% of the installed aluminum production capacity was idle. This was accompanied in some cases by cessation of recycling of wastes generated.

Alcoa, Reynolds, and Kaiser had announced the restart of some of their operations that were shut down in 1981 and 1982. All the restarts were planned to be effective by the end of 1983. This is the first indication of recovery in the past few years.

The major aluminum reduction plants now in operation, or planned to be early in 1984, are listed below.

1. Aluminum Company of America (ALCOA)

   Evansville, Indiana
   Massena, New York
   Badin, North Carolina
   Alcoa, Tennessee
   Rockdale, Texas
   Vancouver, Washington
   Wenatchee, Washington

2. Arco Aluminum

   Sebree, Kentucky
   Columbia Falls, Montana

3. Consolidated Aluminum

   New Johnsonville, Tennessee

4. ALUMAX (Eastalco)

   Fredrick, Maryland
   Mt. Holly, South Carolina
   Ferndale, Washington

5. Kaiser Aluminum & Chemical

   Mead, Washington
   Tacoma, Washington
   Ravenswood, West Virginia

6. Martin Marietta

   The Dalles, Oregon
   Goldendale, Washington

7. National Southwire Aluminum

   Hawesville, Kentucky

8. Noranda

   New Madrid, Missouri

9. Oremet

   Hannibal, Ohio

10. Reynolds Metals

    Sheffield, Alabama
    Arkadelphia, Arkansas
    Jones Mills, Arkansas
    Massena, New York
    Troutdale, Oregon
    Longview, Washington

OVERVIEW OF ALUMINUM REDUCTION PROCESS

SOURCE OF WASTES AND THEIR GENERATION RATES

Reduction Process

Aluminum is produced by electrolysis of alumina, dissolved in a molten bath of fluorides of sodium, aluminum, and calcium.

The bath composition varies. The ratio of sodium fluoride to aluminum fluoride is carefully controlled in each operation, though the control point may vary from one operation to another. These fluorides together usually account for about 75% to 85% by weight of the bath, while calcium fluoride is about 8 to 10%. The balance is made up of alumina. Some operations have special additives, such as lithium fluoride, controlling electrical conductivity.

The electrolytic cell consists of a refractory-lined steel shell called the pot. The inside of the pot is provided with a carbon lining, which serves as the cathode. This carbon lining usually consists of prebaked blocks made up of calcined anthracite and soft pitch, cemented by paste of similar composition. The carbon lining could also be monolithic, made by ramming the anthracite/pitch paste in position and allowing it to bake in during startup. However, prebaked blocks are favored, since the control of fumes generated during baking is better effected in the prebaking step than in the cell.

The anode, composed of petroleum coke and pitch, is suspended into the molten bath.

The cells are arranged in rows called pot lines, and the carbon lining of the cell is called cathode lining, or pot lining.

In the beginning of operation of a new cell, the molten bath materials rapidly penetrate the carbon lining, to its saturation. The collector bar entry is usually not airtight, and the lining absorbs air through this and other access points. Oxygen reacts with the carbon and the nitrogen forms nitrides with the metals penetrating the lining and cyanide with the carbon.

During the life of the lining, which may extend up to five years, the absorbed materials react with the carbon and embedded collector bars, forming carbides, nitrides, and cyanides. Carbon partially graphitizes, and those changes are accompanied by size changes, warping and cracking the lining and causing further penetration. Iron from the embedded collector bars migrates into the molten aluminum, and is an indication of impending lining failure. The operation of the cell is interrupted, the cell is emptied, and the carbon lining is replaced. The used lining removed is known as spent pot lining.

During operation, particulate fluorides and hydrogen fluoride gas are released from the cell, and are swept by vent flow to the gas-cleaning system. The operation is continuous, with periodic addition of alumina and fluorides to make up the bath and maintain the proportionality of the bath components, and periodic siphoning of the molten aluminum from the cell.

Figure 3-1 shows the primary aluminum reduction process in a simplified flowsheet.

Sources of Waste

The vent gases carry with them solid particulates from the cell additions and gases resulting from the cell reactions. This is a waste flow, which is generally treated and collected in the gas-cleaning system and returned to the reduction cell.

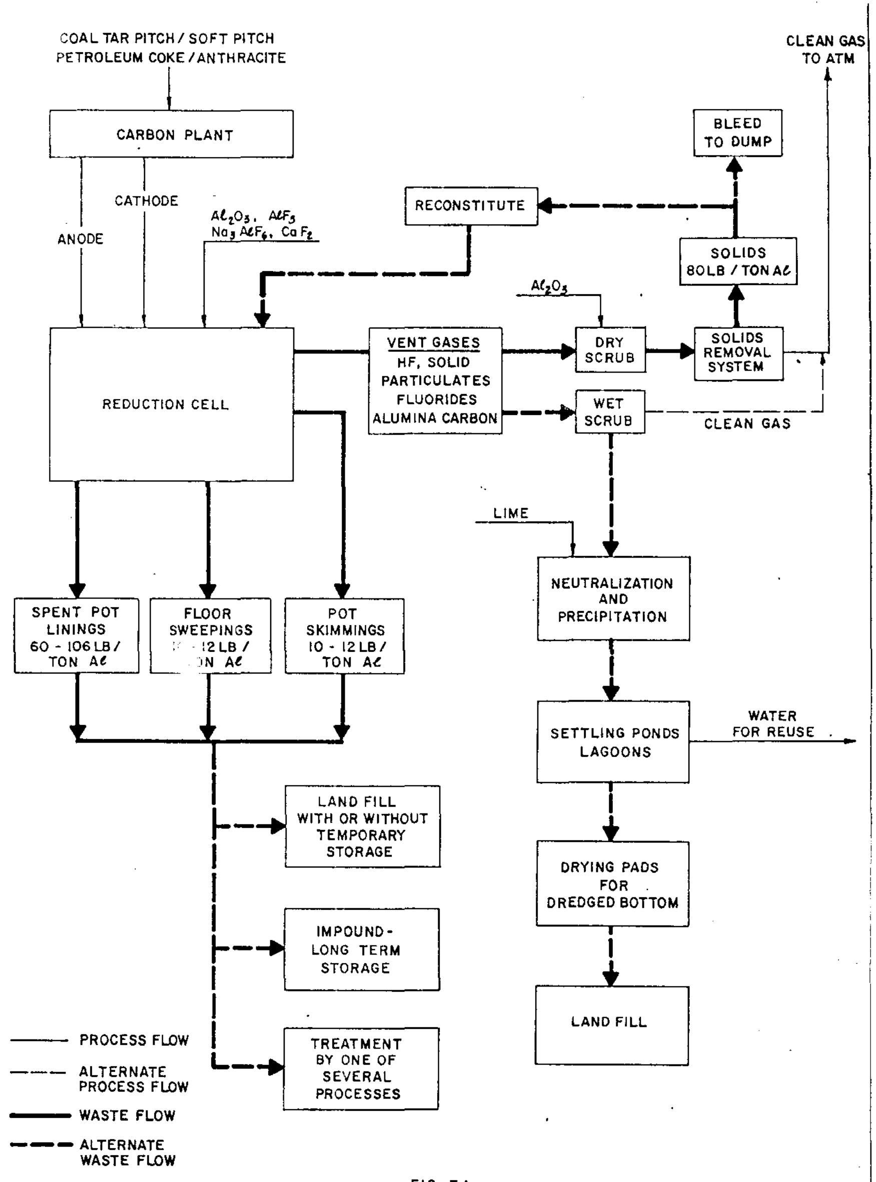

FIG. 3.1

SIMPLIFIED FLOWSHEET

PRIMARY ALUMINUM REDUCTION PROCESS AND WASTE GENERATED

The pot-room sweepings carry values, as does the dross skimmed off the molten aluminum holding furnaces in the casting section of the cell house. These are usually recycled in part. The spent pot liners carry value and are a major waste source.

The wastes generated in the smelter or the reduction plant are, therefore:

- Gaseous and solid particulate effluents from the cell house carried by vent gases and discharged from a wet or dry scrubbing system.
- Solid wastes, consisting of cell house sweepings, pot/furnace skimmings (some of which is recycled), and spent pot liners.

Nature and Generation Rate of Waste

General

The quantity of waste generated varies widely from plant to plant, and depends upon a variety of factors, some of which fall within the range of proprietary process parameters. The waste streams and an industry average of their generation are indicated in Figure 3-1.

Waste materials from vent-gas scrubbing account for approximately 30 to 40% of the total (in plants without dry scrubbers), while the spent pot liners, pot skimmmings, and cell-house/pot-room sweepings account for the balance of 60 to 70%. The main bulk of this 60 to 70% is comprised of the spent pot linings.

These two major categories of waste differ both in the way they are generated and in their composition.

The waste from the vent gas is continuously generated at a fairly uniform rate, and needs to be handled in the plant continuously. All the operating plants have some system for dealing with this waste, by way of wet or dry scrubbing and treatment and disposal of the discharge from the scrubbing systems.

The generation of spent pot linings, on the other hand, is periodic, and produces a good bulk of the waste material in a very short time. Any method of handling this waste has to meet the periodic bulk production of this material. However, the waste could be stored, and treated at a different location, and at a different rate than that of the main aluminum reduction unit.

Scrubber Discharge

The vent gases may contain 50 to 100 lb of solid particulate matter and 20 to 60 lb of gaseous fluorides per ton of aluminum produced. Solid particulate matter contains cryolite, fluorides of aluminum, sodium, and calcium, along with carbon. The gases carry hydrogen fluoride. There are other minor elements, such as lithium, copper, etc., depending upon special cell additives used by some operators.

Dry scrubbing of the vent gases with Bayer alumina, which contains up to 0.6% sodium oxide, results in fixation of hydrogen fluoride in the gas as sodium fluoride and/or cryolite. Some aluminum fluoride could also form. All solid particulates are then collected in cyclones and bag houses, releasing clean gas to the atmosphere. Solids so captured are not always recyclable, depending upon contamination from minor elements, which have a tendency to build up unless some of this is bled and discarded. Also, they need to be balanced with other additives to maintain the overall ratio of sodium/aluminum in the reduction cell, as this ratio is a closely controlled process parameter in cell operation.

Typically, using alumina scrubbing, the dry scrubber discharge may contain impurities as shown in Table 3-1.

The industry trend has been to replace wet scrubbers with dry and return the scrubber discharge to the cell. In the operation of the reduction cell, the sodium fluoride/aluminum fluoride ratio is closely controlled. The recycle increases the sodium with respect to aluminum. Commonly, plants that recycle this material add aluminum fluoride to maintain the balance between sodium and aluminum. This in turn reduces the demand for fresh cryolite to the reduction cell. The other minor impurities also build in the recycle, and would need a bleed that must be discarded. One way to handle the bleed is possibly to treat it with the spent pot linings, if they are process-compatible.

Wet scrubbers generate an acidic discharge containing soluble fluorides. Since these are undesirable to the environment, the scrubber discharge is typically neutralized with lime, precipitating the fluorides as insoluble calcium fluoride for disposal into settling lagoons and later to landfill. As previously noted, the trend is toward use of a dry scrubbing system, as that results in recyclable fluorides and practially no solids for disposal to landfill.

Table 3-1. Typical level of Impurities in Dry Scrubber Discharge

Element	Range, weight %
Fluoride	2 - 3
Carbon	0.5 - 2
Iron	0.05 - 0.1
Silicon	0.05 - 0.2
Copper	0.01
Magnesium	0.01
Vanadium	0.005
Calcium	0.05 - 0.06
Zinc	0.001 - 0.03
Titanium	0.002
Gallium	0.013
Sodium	0.5 - 0.7
Phosphorus pentoxide	0.012

Spent Pot Linings, Pot Furnace Skimmings, and Cell-House/Pot-Room Sweepings

The linings of the pots are broken and collected at the end of cell life. Therefore, production of pot-lining waste is periodic. Since a single cell cathode assembly may weigh up to 80 tons, the total waste generated each time is large.

As indicated earlier, the spent pot linings are the carbon cathode lining of the pots, which have, in operation:

- Absorbed molten cell materials -- aluminum, alumina, metal fluorides, including any special additives, and metallic sodium, which is produced in the cell in small amounts.

- Formed and entrained carbides and nitrides of sodium, aluminum, and calcium, as well as small amounts of sodium cyanide and complex cyanides with iron.

- Graphitized some of the carbon.

Many operators carefully separate the carbon lining by chipping it from the refractory backing as well as the embedded steel bars. However, there is always some contamination from these materials in the separated pot linings. The carbon is known as the first cut, and the refractory as the second cut.

The pot lining is a reactive material due to the presence of metallic sodium, carbides, and nitrides in it. It reacts with moisture and carbon dioxide, generating sodium hydroxide, ammonia, hydrocarbons, and sodium carbonate when it comes in contact with water during the breakup of the cell lining for dismantling, and later with the atmosphere. Typical composition, by weight, of fresh pot lining is shown in Table 3-2.

Some of the cyanides and fluorides are water-soluble and can leach out in open storage and when exposed to moisture and rain.

The major constituents of the pot linings (carbon, fluoride, sodium, and aluminum) are materials of economic value, if they can be recovered at reasonable cost in a reusable form.

The reusability of the carbon is affected by the graphitization it has undergone, affecting the bonding characteristics, and the increased ash content due to the absorbed salts and consequent increase of the resistivity of the carbon lining made with it. The fresh carbon lining is amorphous, and admixing with the partially graphitized carbon tends to disrupt the electrical conductivity pattern. Thermal conductivity increases with graphitization. In general, the carbon of the spent pot lining is not a desirable material for new cathode.

The other constituents are reusable, but they will have to be reformulated to conform to the cell requirements.

The rate of generation of the spent pot lining is a function of cell life, the integrity of the initial lining, its resistance to the infiltration of molten cell charge into the liners, and graphitization. Pot life varies widely from operation to operation, and is held as company-confidential information.

Table 3-2. Typical Weight Percent
Composition of Pot Lining

	Weight Percent Composition		
	Balgord[1]	Aluminum Association[2]	
	Range	Range	Average
Fluoride	10 - 18	7.5 - 22	15.7
Aluminum (total)	13	7.0 - 22.2	15.1
Sodium (total)	12 - 16	8.6 - 22.0	14.2
Carbon (total)	38 - 58	13 - 69	33.1
Aluminum oxide	NR	9.2 - 26.0	
Cyanide	NR	0.04 - 0.6	0.3
Silicon	NR	0.3 - 5.0	1.2
Iron	NR	0.15 - 1.2	0.77
Calcium	NR	0.5 - 6.4	1.8
Sulfur	NR	0.1 - 0.18	0.1
Cryolite	NR	14 - 22	
Sodium fluoride	NR	10 - 13	

NR = Not reported.

Two published reports deal with this subject -- a paper by William D. Balgord[1] and a report by Calspan.[3] There is also a report by the Aluminum Association on a workshop conducted by them in December 1982.[2] The report by Calspan estimates the spent pot liners at 53 kg per metric ton of aluminum produced (or 106 lb per short ton of aluminum), while Balgord uses a figure of 74 lb per short ton of aluminum. An industry average for 1982 is quoted by the Aluminum Association at 60 lb per ton of aluminum produced. To this must be added pot skimmings and cell-house sweepings.

The upper limit of the production of this waste material appears to be about 128 lb, with a minimum of about 60 lb per ton of aluminum produced. Some of the industry sources, however, hold the view that the Calspan report is erroneous in much of its data.

At the present level of annual aluminum production of about 4 million tons, the quantity of spent pot liners generated annually is between 120,000 and 256,000 tons. Balgord estimates a stockpile of 792,000 tons in 1978, and the Aluminum Association estimates 1.19 million tons in storage as of December 1981. At an annual reprocessing rate of 95,000 tons, and an assumed production rate of 227,000 tons, the accumulation rate is about 132,000 tons per year. As of December 1983, there is an estimated 1.45 million tons of spent pot linings in storage.

CURRENT AND DEVELOPING WASTE TREATMENT PROCESSES

Vent Gas Scrubbing (Dry)

Normally, vent gases are subjected to dry scrubbing and dust collection to capture particulate fluorides, other solid particulates, and the neutralized hydrogen fluoride.

The dry scrubber is either a fluid-bed reactor with alumina as the bed, or a cloud chamber with alumina as the absorbant or the gas duct into which alumina is injected. The gases from the reactors pass through solid particulate removal systems consisting of cyclones and bag houses. The recovered solid particulates are normally recycled to the cells. The constraint in the recycle felt by some operators is the buildup of sodium, which is compensated for by addition of aluminum fluoride. There is also a buildup of other minor impurities, the adverse effect of which, if any, depends upon the particular operating conditions.

The dry scrubbing method produces no sludge or landfill material. Any bleed treatment will result in far less landfill material than a with a wet scrubbing process -- which gives dry scrubbing a definite advantage over a wet scrubbing process. Industry did use wet scrubbing some years ago; it has since been replaced by dry scrubbing.

Vent Gas Scrubbing (Wet)

As stated earlier, wet scrubbing is not a favored process; it is included here merely for the sake of completeness. It involves:

1. Capture of water-insoluble solid particulate matter from the vent gas as a suspension in the scrub liquid;
2. Dissolution of soluble salts and gases carried by the vent gas;
3. Neutralization of free acidity and precipitation of soluble fluorides and heavy metals with lime.

All of the above can be achieved in a single stage, or the precipitation and neutralization by lime could follow the water scrubbing. In either case, the resultant sludge needs to be settled in ponds or lagoons, and the settled solids periodically dredged or otherwise collected, dried, and disposed of as landfill.

The water scrub, lime neutralization, and settling in lagoons constitute simple known and proven technologies that do not present technical problems. Since there is no recycle, there is no problem with material balance and critical ratios of materials in the cell house. However, the costs connected with neutralization, lagoons, drying, and landfill have been high enough to warrant a changeover to the dry scrub. The loss of the fluorides, which could be recycled, is a disadvantage. Because of these factors, the industry trend is shifting toward dry scrubbing. The wet scrub, therefore, is not considered in depth in this study.

Pot Linings

A new pot lining is made up of metallurgical coke and/or calcined anthracite, and pitch, either as a monolithic lining inside a refractory-lined shell, or formed into liner blocks, prebaked, and placed inside the refractory-lined cell, with ramming paste of pitch and anthracite mixture. The lining also contains steel bars as electrical conductors.

As has been mentioned earlier, the electrolyte penetrates the lining during operation. Some reacts with the carbon, forming carbides. Some sodium is produced in the cell (which also penetrates the lining), along with some metallic aluminum. Carbon partly graphitizes. All these factors -- the penetration, reaction, and graphitization -- result in expansion of the lining, distorting it. The infiltration of the bath materials, and the changes that occur to the lining itself, contribute to the disruption of the physical and electrical integrity of the linings, and a failure occurs.

The deterioration and failure of the lining is a gradual process and there are a number of operational indications of the deterioration of the lining, notably the increase in iron content in the aluminum. Normally, the pot is taken out of line before rupture, the deteriorated lining is removed, and the cell is relined.

After emptying the cell of its molten charge, the lining is allowed to cool and is sprayed with water. The water reacts with the carbides and nitrides, producing gaseous hydrocarbons and ammonia and fracturing the lining. The gases generated are swept by the vent gas system and treated in the gas scrubbers. While some of the carbides and nitrides are reacted with the spray water, a fair portion of these substances is still left in the lining when it is broken manually and removed for disposal. If the lining is for direct dispatch to a landfill, no special care is exercised to separate the refractory from the carbon. The refractory is usually sent to landfill. Some operators dismantle the lining dry, without water spray.

The carbon lining is handled in one of the following ways.

Disposal as Landfill

Due to possible water leaching and contamination of groundwater, the disposal of spent carbon liner is confined to use of a special hazardous-waste landfill. Typically, the landfill is clay-lined and has a gravel bed, with diversion channels that drain into a plastic-lined evaporation pond. The pond receives only the runoff from the landfill. Diversion ditches constructed around the landfill carry away noncontaminated runoff. Groundwater monitoring systems keep a close watch for any contamination, and the area is fenced. When spent pot liners are used as landfill, such precautions are exercised. Efforts are being made to abandon this practice, and to make the material inert before discarding it.

Storage on a Short or Long Term Basis

The objective of short-term storage is to permit the deterioration of the lining and leaching to take place under controlled conditions, and dispose of the inert material to permanent landfill. Typically, short-term storage may extend from 30 to 90 days. Any effluent from this storage is handled along with the other effluents from the plant, limed, and disposed of in a lagoon. Typically, the storage area is surrounded by drainage ditches to prevent groundwater from surrounding areas from seeping into the storage.

Long-term storage is either for permanent confinement of the potentially undesirable waste or for possible treatment in the future. The present estimate of stored material is well over a million tons.

Typically, the dismantled lining is stored on concrete floors, with provision for collection of washings and leachate with dissolved fluorides in holding tanks. The leachate is periodically treated for recovery of the fluorides as cryolite. One plant uses ion exchange for the cleanup of the leachate before disposal. It is not uncommon to treat the leachate along with the wet vent gas scrubber discharge.

In order to control atmospheric deterioration of the pot linings during storage, it is also a common practice to have a stream of water percolating through the freshly dismantled pot linings for some days until the reaction is complete and no further leaching takes place. The leachant so produced is treated along with the wet scrubber effluent.

Usually, storage is under cover. However, there are a number of storage units in the open as well.

Treatment for Recovery of Valuable Materials

Treatment of pot linings for recovery of valuable materials is one of the highly researched areas in the industry. There are at least 30 U.S. patents on the subject, and several technical research papers, even though there are very few economically successful recycling operations. In general, the industry is dissatisfied with current operating practices and hesitant about newer processes, as yet unestablished though highly researched.

1. Incineration

The spent pot linings are crushed and burned with controlled addition of air and steam. The carbon is burned to carbon dioxide, while carbides and nitrides react with steam to produce hydrocarbons and ammonia. The hydrocarbons also burn, and the ammonia, under controlled incineration conditions, can be burned to nitrogen and water without generating nitrogen oxides. The fluorides remain in the ash, as do all other heavy metal impurities and phosphorus. If the ash is recycled for its fluoride content, the impurities build up to a point at which the ash can no longer be used. A bleed to landfill therefore becomes necessary to keep the impurity level to within limits. Under these conditions, the economics of recovered reusable material could become marginal.

Also, such a plant must be dedicated to a single operation, or to a set of operations that use the same process conditions. If some operations require use of specal additives, the recycle material becomes unsuitable to other contributing operations.

Until very recently, one plant was operating with this process. However, the operation has been shut down, mainly due to the buildup of impurities (particularly phosphorus) in the recycled ash, making it unsuitable for recycle. Without the recycling of the fluorides, the treatment has no economic incentive. This plant is now stockpiling the linings. It has an active program of developmental work, in joint venture with Lurgi of Germany, on a pyrohydrolysis process. There is no definite schedule as to when the new process is likely to become commercial.

Figure 3-2 is a schematic flowsheet of the process.

2. Alcan Process (Steam Hydrolysis)

This is essentially a hydrolysis process. The spent liners are crushed and sized. The fines are either discarded, or agglomerated and returned to the process. The sized material is reacted with steam in a hydrolyzer, at pressures up to 250 psig and temperatures up to 400 deg. F. The gaseous products of hydrolysis -- hydrocarbons, and ammonia resulting from reaction of steam with the carbides and nitrides -- are incinerated. The solid residue contains alumina, carbon, and part of the fluorine as particulate fluorides. All the metallic impurities also remain in the residue.

Carbon has been tried in the past for new pot linings. Published information does not indicate how the impurity buildup is handled. As only gaseous effluents are burned and go out of the system, the solid impurities will build up unless bled and discarded.

The process has been in operation in Canada, and there are a few U.S. licensees for the Alcan patent, but the licensees of the Alcan patent do not appear to be using the process themselves. It is reported that some U.S. operators had satisfactorily used the carbon product from the Alcan process for their anodes. However, it is not in use now, indicating possible problems with such use.

The residual carbon has high resistivity and increases power cost, in addition to introducing impurities. In the U.S., with power costs as they are, the higher resistivity is a strong deterrent for the use of the carbon as electrodes. This would explain the observed reluctance in the U.S. for such use of the recovered carbon.

Figure 3-3 is a simplified flowsheet of the Alcan process.

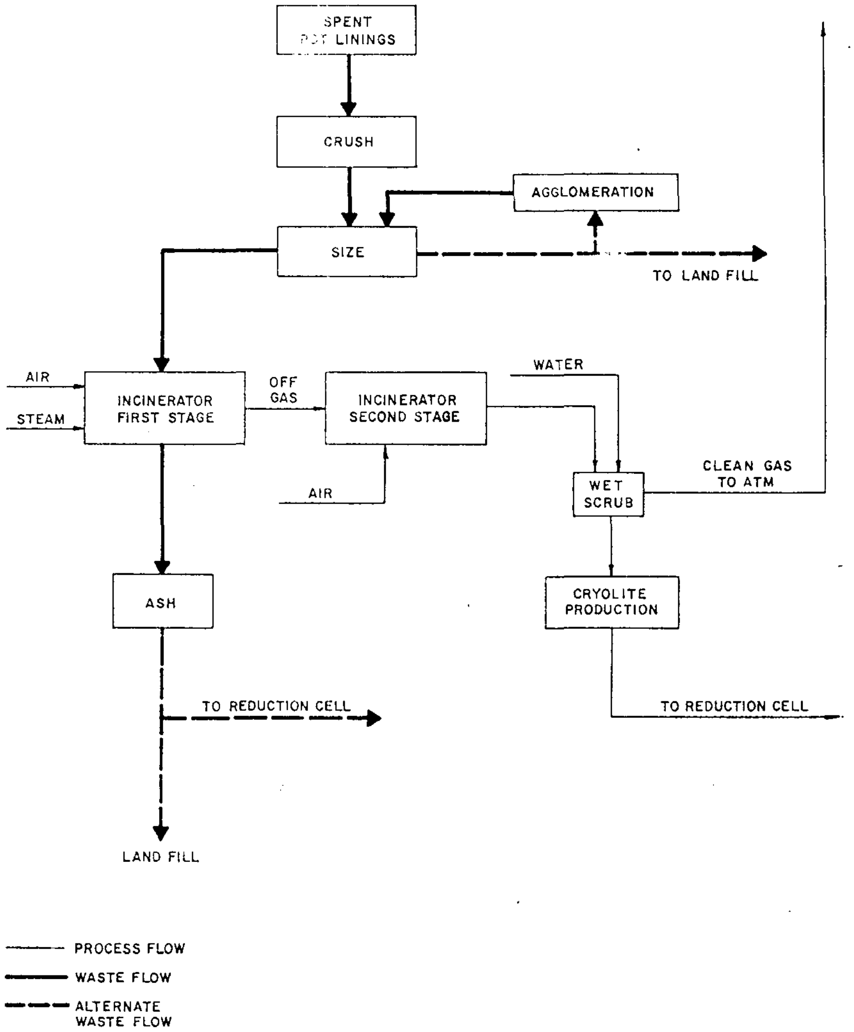

FIG. 3.2

INCINERATION

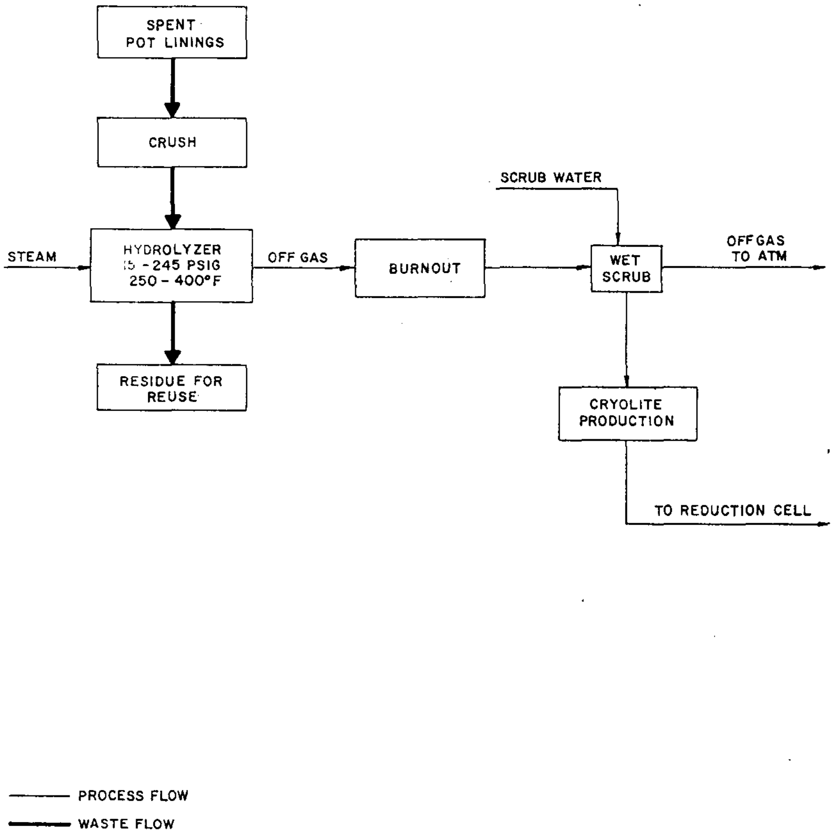

FIG. 3.3

ALCAN PYROLYSIS PROCESS
(STEAM HYDROLYSIS)

3. Caustic Leach

Leaching the pot linings with caustic soda extracts the fluorides, and alumina as sodium aluminate. Nitrides and carbides generate ammonia and hydrocarbons, which are collected and burned. The leachant is then treated with sodium or aluminum fluoride, as the case may be, and the pH is lowered with carbon dioxide, at which time cryolite precipitates. This is filtered and dried for reuse.

The carbon and most other impurities remain in the solid residue from the leaching operation and are allowed to settle in lagoons before disposal. After cryolite recovery, the effluent is limed to precipitate all other impurities still in solution, or recycled to wet vent-gas scrubbers. The resulting sludge is also lagooned for settling and periodically dredged, dried, and used as landfill. Alternatively, when the lagoons are full they are allowed to dry and are then covered with soil.

The process is in operation in the industry. The demand for cryolite has been shrinking since the advent of dry scrubbing systems for vent gases. The solid residue is difficult to settle or dry, due to its alkali content; therefore, the process has not been cost-effective.

Figure 3-4 is a simplified schematic flowsheet of the process.

4. Modified Caustic Leach

This is a modification of the caustic leach described above, patented by National Fluoride and Chemical Corporation[4] (Patent No. 4,113,831). Its main differences from the basic caustic leach process are in the mode of precipitation and the recovery of sodium fluoride and sodium aluminate separately, by use of solubility depressants for the fluoride. The separation of the alumina and the fluoride recovery has merit; however, the main problem of dealing with the sludge produced at the leach step is still unsolved. Because of the demand pattern, the economics are not much better.

Figure 3-5 is a simplified flowsheet of this process.

5. Two-Stage Caustic Leach

In this modification of the basic caustic leach process, a second stage of leach recovers any lithium in the leach residue before it is used as a landfill. This is of use only to those plants using a lithium additive in the reduction cell. In addition to the fact that the process is limited in its application, it has not addressed the solid residue problem and does not particularly contribute to improved overall economics, except for those operations using lithium addition -- and even that is marginal. There does not appear to be any commercial application as yet.

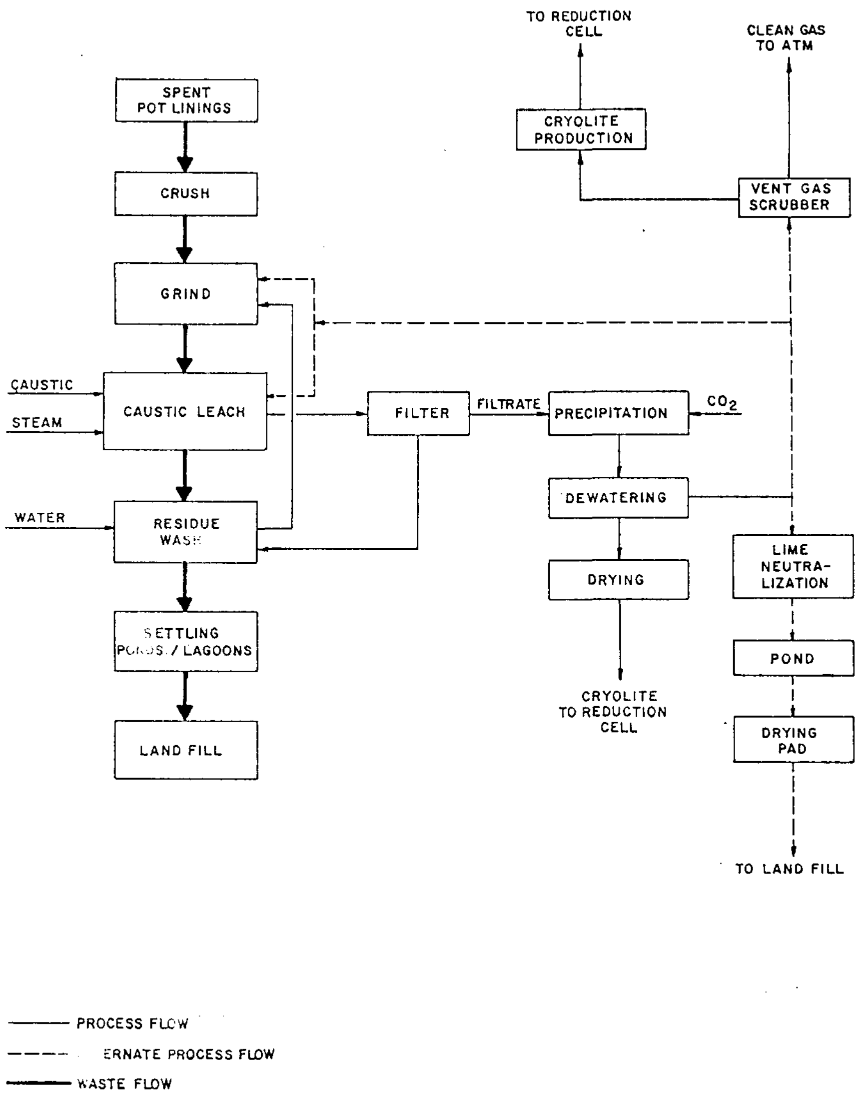

FIG. 3.4

ALCAN CAUSTIC LEACH PROCESS

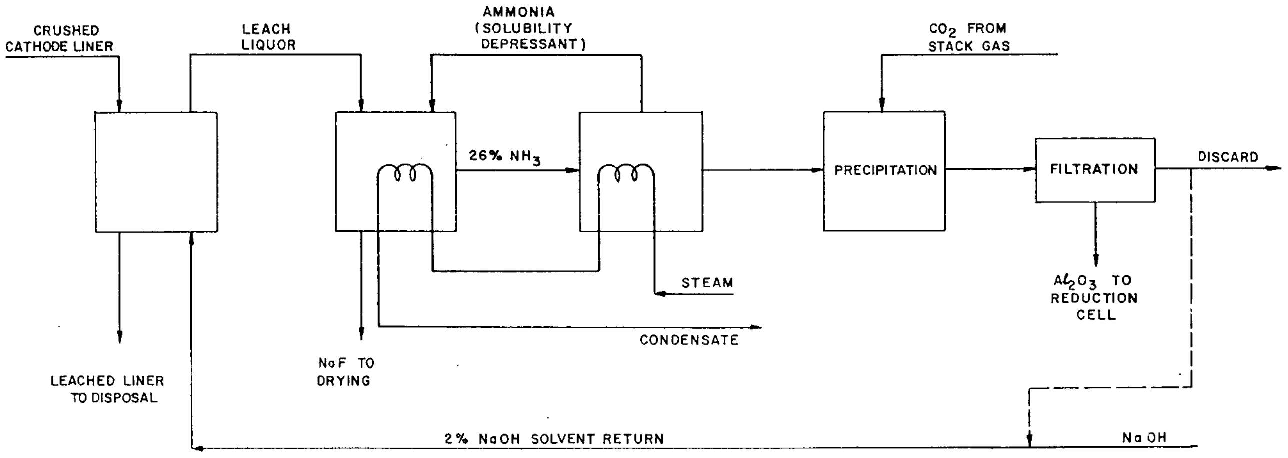

FIG. 3.5

MODIFIED CAUSTIC LEACH

6. Hot-Water Leach

The hot-water hydrolysis process is essentially similar to the Alcan process, except that the hydrolysis reaction is with hot water rather than with steam, thereby reducing energy costs. The process is experimental. While there is an obvious energy saving, the reaction rates would be slower, necessitating a larger-sized plant for the same leach efficiency and throughput. While the atmospheric pressure leach of this process would reduce the cost of the reactor, the size and staging requirements would tend to increase the cost. The relative economics would require an engineering evaluation, which does not appear to have been done (or at least has not been reported publicly.)

7. Modified Pyrohydrolysis

The Alcan pyrohydrolysis process leaves most of the sodium and calcium fluorides in the residual carbon. Hydrolysis of these fluorides is more difficult than that of aluminum fluoride. One patent[5] attempts to solve this problem by introducing sulfur dioxide into the pyrolysis reactor and conducting the pyrolysis at about 850 to 880 deg. C. The reactor may be a fluid-bed unit with provision for multistage controlled reactions, or a multihearth furnace, or a shaft furnace. The major part of the fluorine is recovered as hydrogen fluoride in the gaseous product of the reaction, while the residue contains sodium and calcium sulfates. At that reaction temperature, the aluminum sulfate formed decomposes to alumina, which is also retained in the residue. The carbon is burned in the process, supplying part of the heat.

The patent concentrates on the recovery of fluorine, and the treatment of the residue is not discussed. The recovery of alumina from the residue will involve several steps, as the calcined alumina is difficult to leach by sodium hydroxide.

However, the fluorine recovery, as hydrogen fluoride in the gaseous product, is claimed to be of a high order (85% or more). The hydrogen fluoride in the gases lends itself to possible production of a variety of fluorine compounds, including fluorocarbons. There appears to be an economic incentive to the process, though unquantified. Market assessment would be required to determine the optimum product mix before the economics could be evaluated. It is understood that this process is being tested for commercialization. As yet, no definite opinion appears to have emerged.

Figure 3-6 is a simplified flowsheet of the process.

8. Modified Pyrolysis

This is a modification of the Alcan pyrohydrolysis process.[6] The temperatures used are much higher, on the order of 1000 to 1350 deg. C. The hydrogen fluoride resulting from the hydrolysis of the

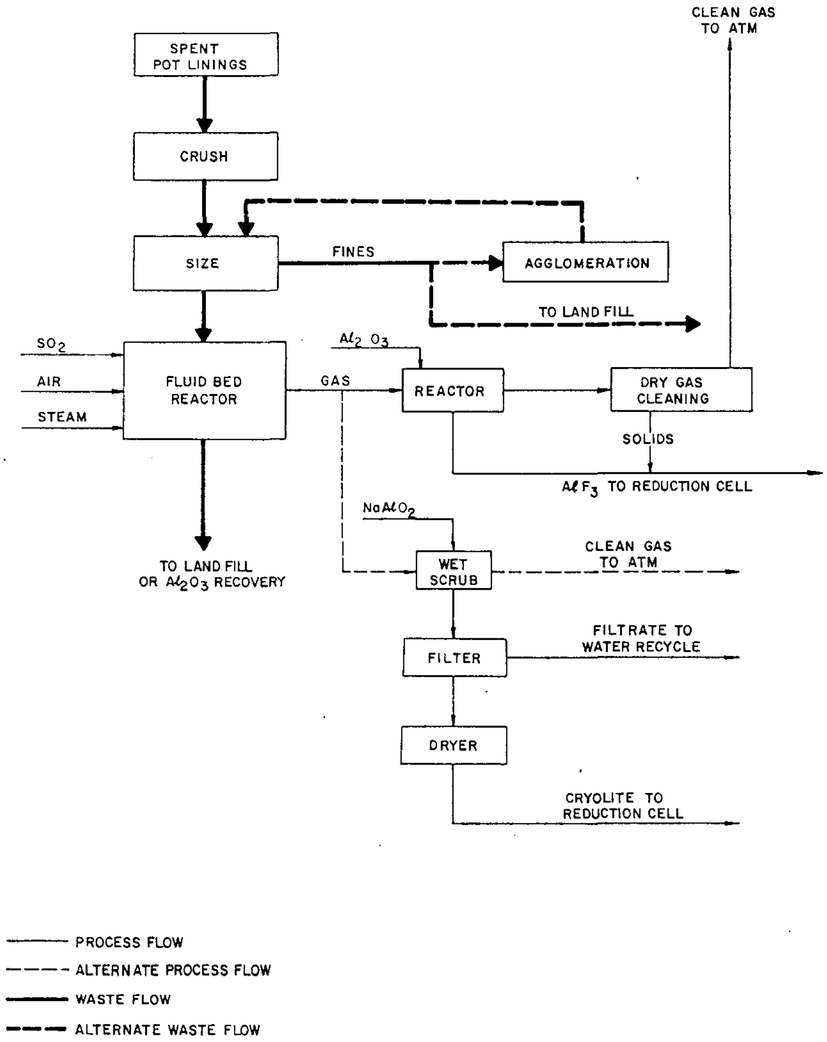

FIG. 3.6

SIMPLIFIED FLOWSHEET

MODIFIED PYRO-HYDROLYSIS

fluorides is recovered from the off-gases by scrubbing with water, sodium hydroxide, alumina, or suitable mix to produce compounds that can be recycled or marketed. The carbon is burned in the process.

The solid clinker resulting from the pyrohydrolysis contains alumina, and sodium as hydroxide, which are leached to form sodium and aluminate. The alumina is recovered separately from it by precipitation or recycled to the Bayer plant. As calcined alumina does not leach easily in alkali or sodium aluminate, alumina recovery may be very poor, despite the patent claim.

It is understood that some developmental research is in progress to determine process economics.

The process is shown in the process flowsheet in Figure 3-7.

9. Acid Leach Process

Reaction of the fluorides in the spent pot linings with sulfuric acid will produce metal sulfates and hydrogen fluoride. The crushed and sized pot linings are mixed with sulfuric acid and the reaction proceeds at moderate temperatures. The hydrogen fluoride in the off-gases is captured by dry scrubbing with alumina. The metals are converted to sulfates and are retained in the residue.

The carbon absorbs a fair amount of sulfuric acid. Part of it is recovered in the next step, wherein the temperature is raised high enough to evaporate most of the absorbed acid, which is then recirculated to the first sulfation reactor. The residue still contains some acid and soluble sulfates. It is necessary to break the residue, by pulping it with water and adding lime to neutralize the free acid and precipitate soluble salts. The resultant sludge is stored in lagoons. The settled solids are periodically dredged, dried, and sent to landfill, or the lagoons are allowed to dry when full and are suitably covered with soil.

The process recovers most of the fluorides efficiently. However, the reaction takes place under adverse conditions and requires special materials of construction and extensive process control for trouble-free operation. Capital costs are likely to be high. The economics of this particular process have not been estimated, and the process is reported as at only an experimental stage.

Figure 3-8 is a simplified flowsheet of this process.

10. Two-Stage Acid Leach Process

This is a variation of the acid process described above. The first stage of the process is similar to the above, in which the crushed, sized, pot liner is reacted with sulfuric acid, producing hydrogen fluoride and metal sulfates. Hydrogen fluoride is recovered as fluorides from the off-gases by dry scrubbing with alumina. The solid

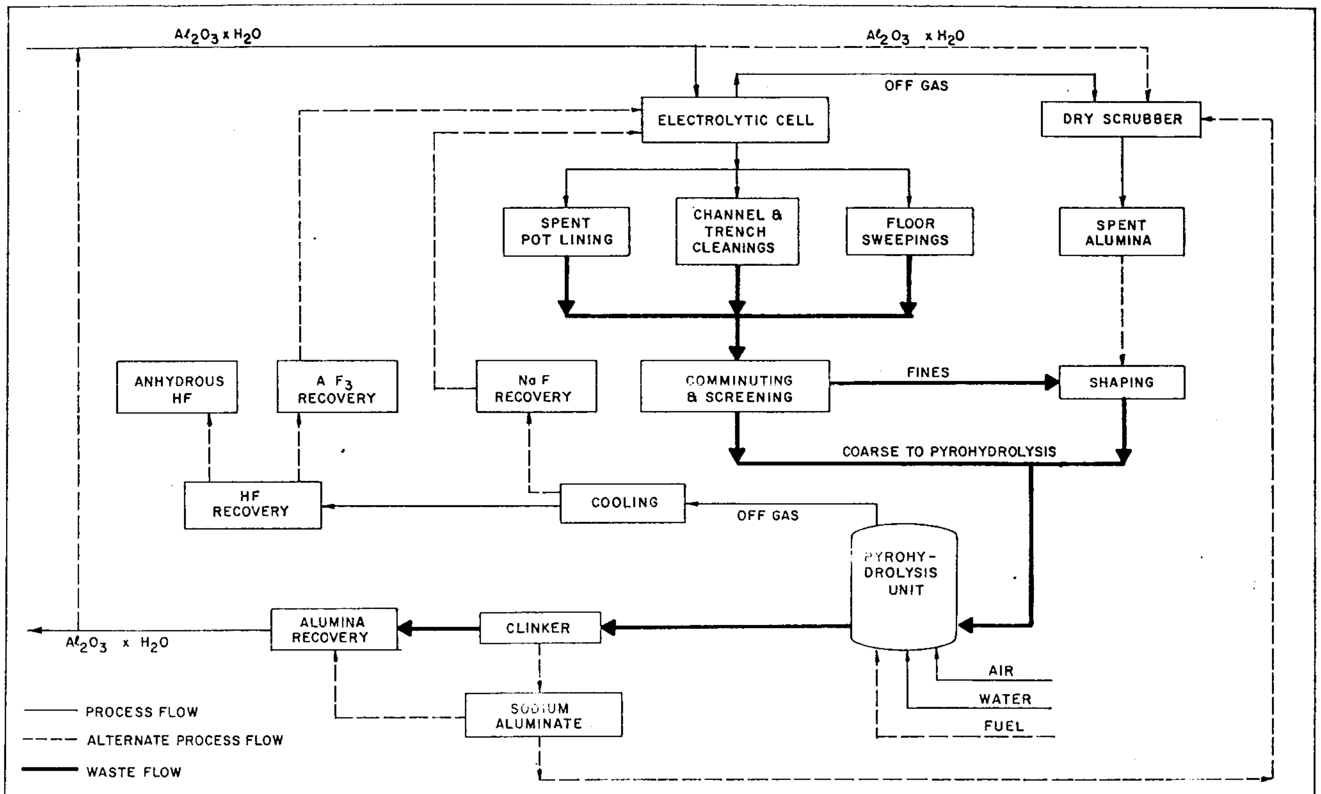

FIG. 3.7

MODIFIED PYROLYSIS

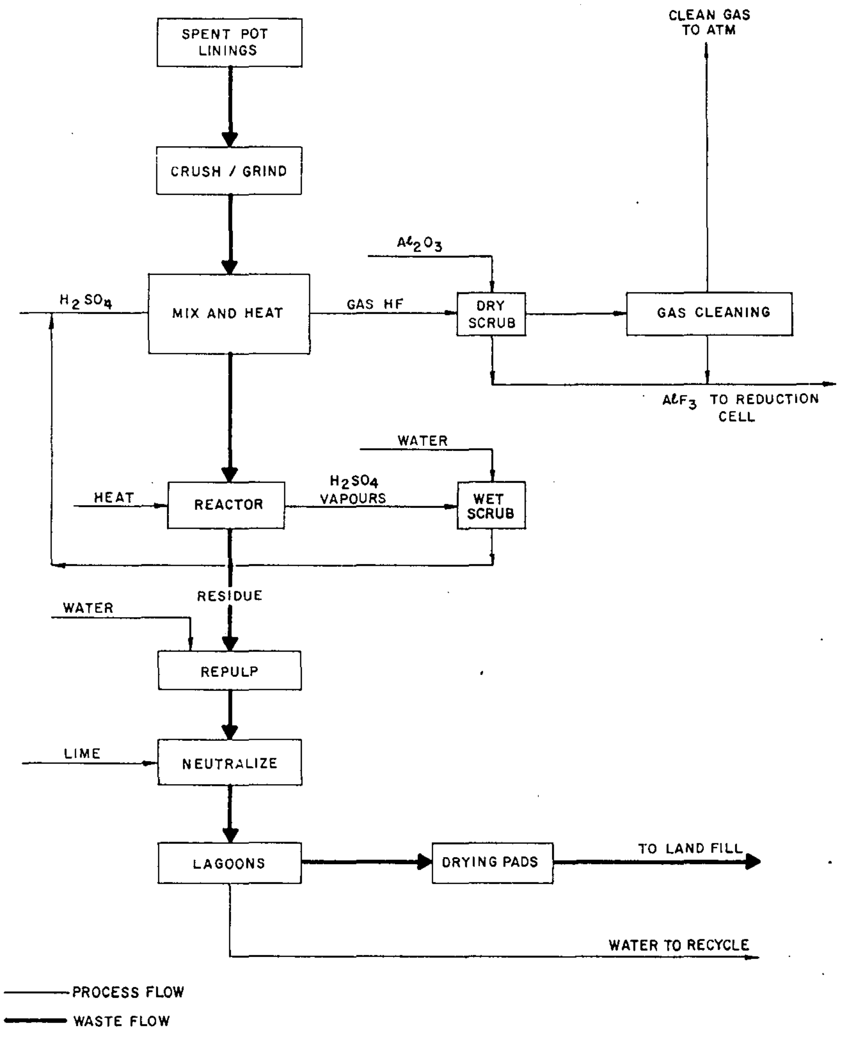

FIG. 3.8

SIMPLIFIED FLOWSHEET

ACID LEACH

residue from the reaction, containing metal sulfates and carbon, is heated in a second reactor, with small amounts of steam (as catalyst) to about 1250 deg. C, producing metal oxides and sulfur dioxide.

The sulfur dioxide from the off-gases of the second reactor is used to make sulfuric acid, which is reused in the first stage of the process. The alumina in the solid residue is either recycled to the Bayer plant or leached with caustic soda/soda ash to produce sodium aluminate and alumina, which are recovered by precipitation with carbon dioxide. As stated earlier, the leaching and recovery of alumina is questionable in the process and requires extensive developmental work.

The process recovers most of the fluorine, and claims to recover alumina in usable form. The majority of the sodium is lost, as well as the carbon. The process is complex, in the sense that there is a mini-Bayer plant to recover alumina and a sulfuric acid plant to recycle the acid. In a large-scale operation, where the alumina recovery could be integrated with the main Bayer plant, this process may have the required economic viability, provided the leachability of alumina is proved. The status of the process is experimental and no pilot work appears to have been carried out so far.

Figure 3-9 shows the process in a schematic flow diagram.

11. Incineration Followed By Carbonate Fusion and Caustic Leach

The U.S. Bureau of Mines developed a process[7] for the recovery of fluorides in the ash resulting from incineration of the pot linings; the ash is sintered with sodium carbonate and the sinter leached with dilute caustic solution. The experimental work did not yield products that could be recycled, as they did not conform to generally accepted specifications. Technological improvements could perhaps be made in this process to bring the products to within the specifications required. However, whether the economics would favor acceptance of the process has yet to be determined.

12. Physical Beneficiation

The Bureau had conducted tests in physical beneficiation of the crushed pot liners, separating the carbon and the fluorides.[8,9] The water-soluble fluorides are lost in the process; the presence of large amounts of water-soluble salts complicates the flotation process. However, these are technical problems for which solutions could be found. Economic viability would depend upon the usability of the recovered carbon, which must be established along with the other technological parameters. With lesser ash and therefore better electrical conductivity, the carbon would have a definite advantage for its reuse in the reduction cell.

Alcan developed a process involving vacuum distillation of the pot liner at 1100 - 1400 deg. C, recovering cryolite and metallic sodium; however, high processing costs prevented commercialization of the process.[10]

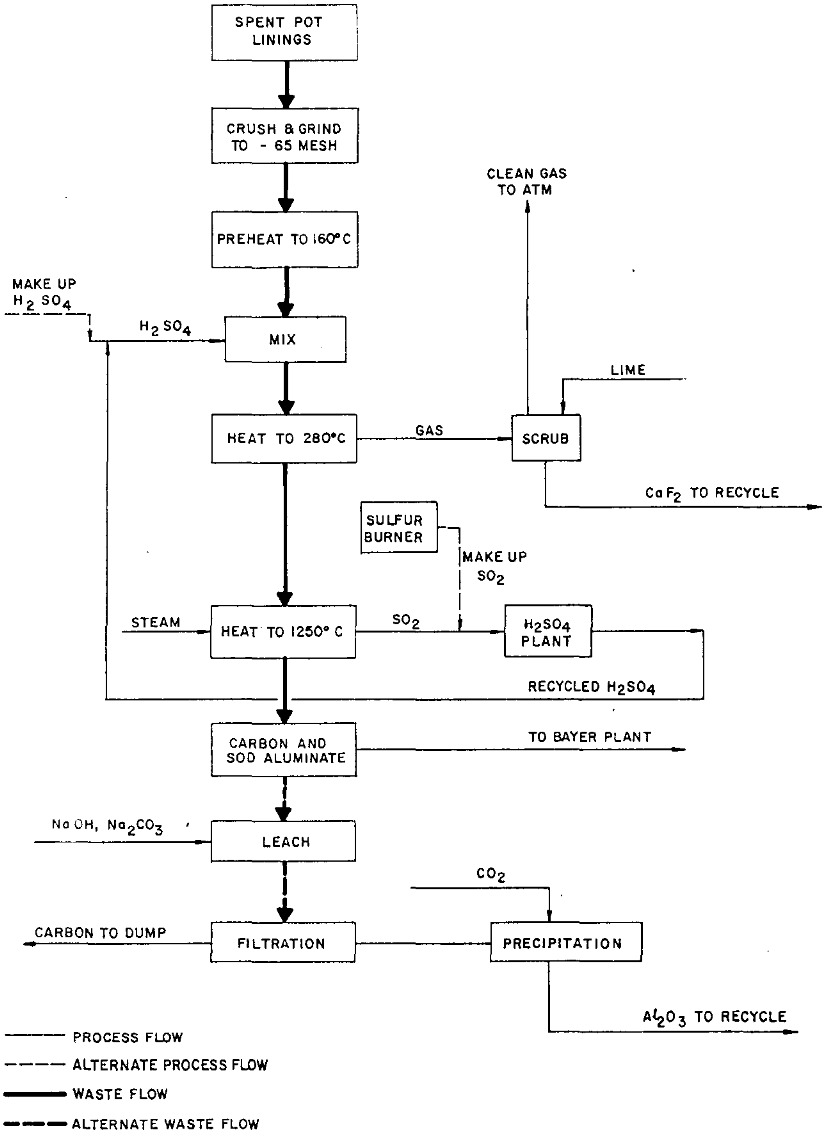

FIG. 3.9

TWO STAGE ACID LEACH

Apart from the recovery and recycling of valuable materials in the pot linings within the aluminium industry, some work has been carried out to investigate possible use of the spent pot liners for their value in other industries.

The Bureau of Mines has conducted experimental work into the use of spent pot liners as a substitute in cupola iron melting[11] and in basic oxygen steelmaking.[12] This work indicates that the pot liners can be used with no adverse effect on either the iron melting or steelmaking processes, or on the refractories in those furnaces. In fact, the consumption of fluorides was found to be less for the same fluidity, due perhaps to the contribution from the sodium content of the spent pot liners toward the fluidity of the slag. The fluorine recovery in the slag and fluorine losses to the scrubber water and solids were also comparable to the use of fluorspar. (In both these cases, carbon burns and contributes to the heat for the process. The carbon of the pot liners is probably reactive enough chemically as well to use as reductant in smelting processes. Though not tested, this application appears possible.)

This would be a good disposal method, provided the logistics and transport costs in present steel industry economics could be justified. Technologically, this appears to be a good solution to the pot liner disposal problem.

Pot liner has also been used with success as fuel in cement kilns.[2,13] As in the case of its use in cupola or steelmaking, the main factor for consideration will be the logistics and economy of transportation.

A summary of current practices in the industry is available from the report on the proceedings of the workshop on storage, disposal, and recovery of spent pot linings conducted by the Aluminum Association in December 1981.[2] Even this is outdated, as some of the plants then in operation have since ceased production and the workshop, while covering the majority of the working plants, did not cover all.

The papers presented at the panel discussion session on "Disposal and/or Recovery of Spent Pot Lining" at the 113th Annual Meeting of TMS-AIME in February 1984 at Los Angeles[10,13-17] updated the results of industry efforts in development of processes to dispose of and/or recover values from pot lining. The following points emerged from the presentations and subsequent discussions:

- Incineration is the basic process that could result in a satisfactory solution to the pot liner disposal problem. Fluid-bed incineration is the most suitable mode.

- The incineration process could be combined with pyrohydrolysis or pyrosulfolysis to fully recover fluoride valuese and make residual solids totally inert. The relative merits are yet to be fully evaluated.

- Fluid-bed incineration does present difficulties due to bed agglomeration. Pyrohydrolysis presents problems of corrosion. However, these problems appear to have been solved (at least in one instance[14]), and a large-scale pilot installation, as a joint U.S./German effort, is being planned in Germany to confirm the results.

- Use of pot liners as supplementary fuel in production of high-alkali cement has been successful. Further tests are under way.

Logistics and transport costs are still problems that need to be solved in the commercialization of any of the successful processes.

Table 3-3 is a summary of the pot liner treatment processes and their present status.

Using the Aluminum Association report as a base and extrapolating with further available information, industry practice (arranged in order of industry preference at present) would be as follows:

- Long-term storage
- Hazardous waste landfill
- Short-term storage and transfer to landfill
- Carbon incineration and fluoride recovery from gases
- Caustic leach processes

Developmental work is in progress in:

- Pyrohydrolysis (with modifications)
- Fluid-bed incineration

A preliminary overview of industry practices, developmental work in progress, and general economics indicates that the developmental work has not as yet produced a process sufficiently attractive economically for adoption by the industry. The fact that most operators prefer to store spent liners indefinitely in protected and monitored facilities indicates that the cost of such storage is economically more attractive than any process presently under development.

Table 3-3. Processes for the Recovery of Values from Spent Pot Liners and Their Status

Process	Status	Remarks
1. Incineration	Commercially operated, but discontinued.	Buildup of impurities in residual ash renders it unsuitable for reuse. The ash is unsuitable as landfill due to presence of water-soluble sodium fluoride. See process under item 11, which is a developmental effort to mitigate this problem.
2. Alcan Process (Steam Hydrolysis)	Commercial in Canada. Not common in the U.S.	Carbon and some fluorides are recovered. Some fluorides remain with recovered carbon, as do minor contaminating metals. Process unsuitable where metal impurities or phosphorus are likely to build up, or as a central processing plant serving several reduction plants, each with its own special bath additives. High electrical resistance of the recovered carbon is a disadvantage in its use in the reduction cell.
3. Caustic Leach	Commercially used.	Only cryolite is recovered, at a low efficiency of about 50%. With dry scrubbing of vent gases, the cryolite demand in the industry has reduced considerably. With the lower cryolite demand, the economics of the process is marginal. The leach residue is a difficult sludge, requiring lagoons, drying ponds, dredging of lagoon floor material, and landfill as the final disposal method.
4. Modified Caustic Leach	Patented; not operational.	Additional recovery of alumina not obtained in straight caustic leach adds to process efficiency, and so to economics. Other problems remain. Further development would be required before economic assessment could be meaningful.
5. Two-Stage Caustic Leach	Patented; not commercial.	The second-stage caustic leach recovers any lithium present in the solid residue after the first leach. Process is of interest to those plants using lithium as an additive to the cell. All other constraints cited for caustic leach and modified caustic leach still exist.

Table 3-3 (contd.)

Process	Status	Remarks
6. Hot-Water Leach	Experimental. Essentially similar to Alcan Steam Hydrolysis.	Claim is made regarding energy saving by use of hot water instead of steam as in the Alcan Process. While this is true, the slower reaction rates, and consequent larger reactors for the same throughput, may neutralize the savings due to non-use of steam. Requires deeper engineering study for economic evaluation.
7. Modified Pyrohydrolysis	Experimental. Some pilot plant scale work is in progress.	Carbon is burned in the process, supplying part of the heat required. Process optimization is required before economic evaluation.
8. Modified pyrolysis with sulfur dioxide addition to the reactors.	Patented. Developmental pilot plant work is progress	Sulfation improves the efficiency of recovery of fluorides.
9. Acid Leach	Experimental. Some mini-plant work is probably in progress.	The process produces aluminum fluoride and sodium fluoride. The other product of the process is a sludge, with all the carbon with high acidity due to free absorbed sulfuric acid, making disposal difficult. Economics is to be proven.
10. Two-Step Acid Leach	Experimental.	The second step of desulfation overcomes the main constraint of the single-stage process. However, the sulfur dioxide produced needs to be handled and the suggested sulfuric acid plant would make the plant complex and highly capital-intensive. Economics will be unfavorable unless the treatment is on a large scale or for a number of reduction plants. In such a case, the logistics and cost of transportation of the pot liners to the central location would be a deterrent factor.

Table 3-3 (contd.)

Process	Status	Remarks
11. Incineration followed by sodium carbonate fusion and caustic leach	Experimental.	The process needs to be refined, as the recovered products did not meet the required specification for recycle. Economics must be established, after process optimization.
12. Physical Beneficiation	Experimental.	The process needs to be refined further with respect to soluble salts before establishment of economic viability.

TECHNICAL AND ECONOMIC REQUIREMENTS FOR VIABLE WASTE TREATMENT OPERATIONS

A process to treat spent pot liners must achieve the following objectives.

- It should be capable of handling the intermittent nature of spent pot lining production.
- Process economics should be favorable for small units serving a single reduction plant, since transport to a central processing plant from several reduction plants is not cost-effective.
- The process must be capable of recovering the valuable materials in a variety of endproducts, since the demand pattern is continuously changing.
- The endproducts must be such that at least some of them could be used outside the aluminum industry, since there does not appear to be a possibility for all the materials to be consumed in recycle only. All the recoverable values would represent surplus of materials required by the aluminum reduction industry, due to the proportionality requirements and physical requirements.
- The final residual waste must be small and manageable.
- All hazardous materials must be made inert.

Converting of hazardous constituents to inert materials is mandatory, while the others are keyed to economics.

The spent pot liners contain several materials that can be reused, if recovered in usable form and purity. On the basis of current prices, they represent monetary values as listed in Table 3-4.

Any treatment process for the recovery of values from pot liners must cost $50 or less per ton treated, in order to be economically viable. The rationale for arriving at the $50 cost is presented later (see pages 67 and 68). In evaluating the capacity of a process to fulfill the concurrent recovery requirements, the following factors need to be considered.

Fluorine is used in the aluminum industry as cryolite, and as fluorides of aluminum, sodium, and calcium. Use of cryolite is restricted to the startup period of new pot liners, until the cathode liners get saturated with it. After that period, the fluorine requirement is generally in the form of aluminum or sodium fluorides to maintain the sodium fluoride/aluminum fluoride ratio in the cell. No fresh cryolite is used.

Table 3-4. Materials of Value in Spent Pot Liners

Material	Pot Liner Average Content (lb/ton)	Market Value ($/ton)		Best Expected Recovery (%)	Value of Recovered Material ($)
		Material	Pot Liner		
Fluorine	314	330	51	85	43
Alumina	400	200	40	70	28
Carbon	660	75	25	100	25
Total		116			96

Note: The estimated value of recovered material at $96 would apply only if the best expected recovery is achieved for all products concurrently. This is unlikely. True value is likely to be much lower.

Recovery of fluorine from the pot liners as sodium or aluminum fluoride requires generation of hydrogen fluoride and scrubbing it with caustic or alumina. Normal hydrolysis, or even pyrohydrolysis, does not release all the fluorine contained in the potliners. Therefore, the fluorine recovery efficiency does not exceed 50%.

Introduction of sulfur dioxide in the hydrolysis process could increase the efficiency to an expected maximum of 85%. Value assigned to recoverable fluorine at $43 is based on this maximum 85% recovery. However, this is not easily attained. If the 85% recovery is obtained by the use of sulfur dioxide, aluminum in the pot liner is converted to aluminum sulfate and alumina recovery drops to zero. Decomposition of the aluminum sulfate and recovery of alumina is theoretically possible, but economically not viable. Thus, process conditions conducive to high fluorine recovery result in low alumina recovery, and vice versa.

Alumina recovered from the pot liners has to be low in silicon and iron to be useful as a recycle material. This is usually not the case. In addition, any impurity (e.g., phosphorus) tends to concentrate along with the alumina, rendering it unfit for recycle.

Calcined alumina is not easily leached by caustic, impeding recovery and purification of alumina to the required level. Whatever alumina is recovered would be more suitable for aluminum alloy producers, rather than pure aluminum metal producers, due to the impurities. Thus, the reusability is restrictive.

After processing, residual carbon contains an average of about 15% ash. The electrical resistivity of the carbon is too high for its use in new monolithic cathode liners, even though it could be used for ramming mix with prebaked block cathodes made of fresh anthracite-pitch mixture. The value assigned for carbon is based on its use in place of anthracite, which does not appear feasible.

Since the recovered carbon cannot replace the anthracite in the cathode liner due to the impurities, and is not a substitute for petroleum coke in the anodes due to its resistivity, a practical use for the carbon is only as a fuel.

To sum up, therefore, the value of $96 for recoverable and reusable materials per ton of spent pot liner must be considered the maximum. A practical value would be of the order of $50 or less. On the basis of 74 lb of spent pot liner production per ton of aluminum, this would work out to $1.85 per ton of aluminum produced.

As reported by the Department of Ecology at Olympia, Washington,[18] spent pot liners generated at individual plants in the State of Washington ranged from 3,000 to 10,600 tons per year, with an average of about 5,000 tons. As previously noted, this is not a continuous generation throughout the year, but is produced periodically. A treatment facility to deal with this generation rate adequately should have a daily rated capacity of about 70 tons. This would enable the facility to handle the total annual production within about three months of temporary storage.

Such a facility will lie idle for nine months a year, unless it receives supplies from other operating reduction plants nearby. In such a case, the transportation of hazardous material from the point of generation to the processing plant represents additional cost, which may range from $5 to $25 per ton, depending upon the distance and mode of available transport. Transportation of the waste pot liner is costly, as railroads can impose a penalty if they deem the material hazardous, and a further penalty if the transportation is for an economic recovery, i.e., a raw material rather than a waste material.

A treatment plant with a capacity of 70 tons per day would not justify auxiliary facilities such as a sulfuric acid plant or an alumina purification plant. Alumina purification cannot be integrated with a primary Bayer plant, since the U.S. imports most of its alumina requirements, and there are only six operating Bayer plants in the U.S., for 27 reduction units.

A hazardous-waste disposal facility -- with necessary linings, covered when the lagoon is full, reasonably dry, and with all the monitoring required to comply with environmental regulations -- was reported by one operator to cost about $67 per ton of liners. A nonhazardous landfill in a dump area near the plant, say within 20 miles, may cost around $12 per ton of dump material, on the average.

The actual cost could go up to several times this amount, depending upon the available landfill area and total inflow to it; however, $12 may be assumed as a reasonable base figure. If the hazardous components of the pot liners are made inert and the pot liners are disposed to a nonhazardous landfill, this cost could work out to less than $0.50 per ton of aluminum produced.

If the potliners are also burned, in addition to making the hazardous components inert, the bulk for disposal could be reduced from about 74 lb per ton of aluminum to about 40 lb. This would reduce the cost of disposal to near $0.25 per ton of aluminum produced. The thermal energy recovered from the burning of the carbon in the liner would be an additional bonus.

It would appear, therefore, that the most economic alternative for disposal of spent pot liners is to make the hazardous components inert, burn the carbon for its fuel value, and dispose of the ash as a landfill material.

The hazardous components are the carbides, nitrides, cyanides, and water-soluble fluorides.

The carbides are easily hydrolyzed to metal hydroxides (mainly calcium and sodium hydroxides) and other hydrocarbons that must be burned off. By burning the dry pot liner, the carbides can also be oxidized to metal oxides and carbon dioxide.

Nitrides, like carbides, can be hydrolyzed, yielding ammonia and metal hydroxides. Alternatively, they can be oxidized to metal oxides and nitrogen. This oxidation needs to be carried out under controlled temperature and stoichiometric conditions, to prevent formation of NOx; alternatively, the NOx formed must be reduced to nitrogen by thermal or catalytic denoxing treatment.

Cyanides can be oxidized at high temperature; the precautions to be taken are similar to those for nitrides. Cyanides can also be oxidized in aqueous solutions.

The water-soluble fluoride in the pot liner is sodium fluoride. It can be hydrolyzed at high temperatures, in a pyrohydrolysis step. Alternatively, the sodium fluoride could first be brought into aqueous solution and then be precipitated as calcium fluoride by treatment with lime.

For making the hazardous materials inert, therefore, the following options are available:

- Room-temperature or hot-water hydrolysis. This step is applicable to carbides and nitrides. Partial hydrolysis of aluminum fluoride is possible, depending upon temperature.
- High-temperature hydrolysis. Applicable to carbides, nitrides, and fluorides, including sodium fluoride, though the hydrolysis of fluorides may be only partial.
- Combustion. Applicable to carbides, nitrides, and cyanides. This would not render the water-soluble fluorides inert; they would remain in the ash.
- Combustion with high-temperature hydrolysis. This is applicable to all materials. The sodium fluoride would be hydrolyzed, resulting in an inert ash. The off-gas would need scrubbing to remove the hydrogen fluoride. Combustion must be controlled to prevent formation of NOx and ensure complete destruction of the cyanides. A combustion process with provision for steam injection would appear to satisfy most of the technical requirements.

Additional provisions, such as sulfur dioxide injection for enhancing the fluorine recovery, may not be cost-effective. Alternative processes, such as acid or alkali leach, do not result in a residue that is manageable, dry, and inert for conventional landfill.

CONSTRAINTS IN CURRENTLY PRACTICED WASTE TREATMENT OPERATIONS

As discussed earlier, the major constraint in the currently pracced and developing processes is the economic viability. Factors that affect the economic viability adversely are:

- Unsatisfactory quality of the recovered materials due to impurities and physical properties such as resistivity.
- Altered proportionality of the recovered materials, rendering some of them surplus for recycle to the main process, particularly due to changing demand patterns in the process.
- Uneconomical scale of operation for a single reduction plant, and unfavorable transport costs and logistics for a centralized plant.

- Unsatisfactory final reject material for simple landfill. The final reject material in the current processes is either in the form of an alkaline or acidic sludge, or a dry ash, but still with soluble fluorides. These types of final rejects are not environmentally acceptable.

DEVELOPMENTS IN PROGRESS

As indicated earlier, the process developments in progress are in the areas of:

- Modifications to the pyrohydrolysis process by introduction of sulfur dioxide. These modifications aim at higher fluorine recoveries. It is not known at present whether the final recovery of fluorine would be as a product mix that will have a high market value, improving the overall economics, and not necessarily confined to the recycle to the main aluminun reduction process.

- Incineration. This aims at producing inert solid residues with as much heat recovery as feasible, by burning the spent pot liners.

RECOMMENDATIONS

As indicated earlier, recovery of fluorine as fluorides for recycle to the aluminum reduction process by itself does not appear to be economically attractive. If fluorine recovery, rather than rendering the fluorides inert, is the primary objective, the process should yield fluorine as a product with much higher market value and potential than aluminum or sodium fluorides, or cryolite. One patent suggests production of fluorocarbons. It is worthwhile conducting a market survey of fluorine chemicals to establish the maximum-value fluorine chemical product mix that could be produced to enhance economy. Process steps could then be optimized for the product mix and the economic viability evaluated.

Incineration, on the other hand, aiming at rendering the hazardous materials inert and maximizing energy recovery, is the minimum treatment that must be undertaken from the environmental point of view. The aim in this approach should be to make the process trouble-free in operation, complete in converting the hazardous materials to inert solids, and high in energy recovery. Developmental work towards each of these objectives is necessary.

Incineration can be carried out by several means: in a grate, in a tube furnace such as a cement kiln, or in a fluid-bed combustor. A fluid-bed combustor offers unique advantages. It ensures complete combustion of the pot liner despite its high ash, due to continuous agitation of the solids in the bed. It also lends itself to close control of process parameters. The fluid-bed combustor, therefore, would be the most viable way of incineration. An engineering evaluation would be required to establish the optimum conditions and controls.

A tube furnace has a definite advantage if combined with such operations as production of cement. In such a case, the combined process needs to be studied, and will be applicable only to specific cases in which the logistics are favorable.

Design of a fluid-bed combustor requires developmental research. Potential problems requiring such developmental work are:

- Incipient fusion of fluorides, agglomeration of bed materials due to this fusion, and scaling on the in-bed steam pipes (if used). Sodium generally reduces the ash softening point, and its presence as fluorides, along with other fluorides with which it could form a low-melting eutectic mixture, enhances this potential. This would result in agglomeration of the bed material, incomplete combustion, and ultimately defluidization of the bed. The fusion will also cause scaling on the furnace walls and on the in-bed steam tubes, if used.

  In fact, both these were reported as occurring "to a minor extent" in the test work under way at the moment, by one company conducting the tests under sponsorship of the Aluminum Association. In this test work, in-bed steam tubes are used with a recirculating bed, with a space velocity of air through the bed of about 15 - 20 feet per second. High space velocity and circulation of the bed material were employed to minimize the scaling and agglomeration. Despite expectations, scaling was observed during short-term runs. In commercial operation, this could present serious problems.

  Control of the magnitude of this problem would demand close control of the bed temperature, well below the initial softening temperature of the high-sodium, high-fluoride ash material. At the same time, burnout of all the cyanides requires as high a temperature as possible. Temperature control, therefore, is critical, and within a narrow range. Bed temperature cannot be controlled merely by the in-bed steam pipes, as these will scale up to an unpredictable extent, reducing the heat transfer also in an unpredictable manner. Alternative or additional temperature-control methods need to be developed to maintain the bed temperature below the initial softening temperature of the residual inerts, at the same time maintaining a temperature high enough to ensure complete combustion of the cyanides.

- The nitrogen compounds, cyanides, and nitrides would tend to generate nitrogen oxides. Controlled incineration in respect to stoichiometry and temperature would minimize NOx formation. Alternatively, the off-gas from the combustor will have to be subjected to thermal or catalytic denox treatment. The NOx formation from the nitrogen of the metal nitrides could possibly be minimized in a two-step process of first forming ammonia by hydrolysis and then oxidizing it to nitrogen and water. Ammonia so formed could assist in a thermal denoxing of any NOx formed in combustion of the cyanides. This is an area requiring developmental research.

- Incineration by itself will leave sodium fluoride in the ash as soluble fluoride, and the ash will not be environmentally inert. This could be solved by one of two methods.

  One would be to hydrolyze the sodium fluoride during incineration at high temperature by steam injection. The process parameters for optimum hydrolysis need to be determined.

  The second way would be to quench the ash from the incinerator in water, leach out the soluble fluorides, lime the leachant to precipitate the fluoride as calcium fluoride, settle the sludge, and dispose of the settled or filtered sludge. While this is a workable scheme, it involves several steps and obviously would cost more than the first alternative of high-temperature hydrolysis.

  The present research work cited earlier uses a circulating fluid bed with space velocites of 15 to 20 feet per second. With the large size of crushed pot liners in the feed at +1/8", these velocities could give rise to erosion problems in long commercial runs. The high velocity does scour the scales that are formed to a certain extent, and by the same token it would also erode the combustor walls, internals, ducts, and cyclones. Optimization between a bubbling column fluid bed and a recirculating bed will have to be carried out for a reliable commercial design.

- Heat recovery from the off-gas and off-gas scrubbing are areas requiring classical parametric and design studies.

It would appear that the most practical approach would be incineration, with the main objective of rendering the hazardous materials inert and obtaining the recoverable energy from the fuel value of the pot liners. This would yield some reusable fluorides as a byproduct. Fluid-bed incineration is perhaps the best way to incinerate the pot liners. However, this will require developmental research in the areas indicated.

Processes aiming at the recovery of all fluorine and aluminum values are not economically attractive, in light of the cost of production, the demand pattern for the products, and the problems of handling the final residue.

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SECTION 4

CHROME-BEARING REFRACTORIES

INDUSTRIES USING CHROMITE-BEARING REFRACTORIES AND INDUSTRY TRENDS IN REFRACTORY USE

Chromite is essentially ferrous chromite with minor amounts of magnesium and aluminum. It is used in the metallurgical extraction and chemical industries as source material for chromium, as refractory material for some furnaces, and in foundry molding sands. Traditionally, the chromite is classified and graded according to the end use. Table 4-1 shows the standard chromite classification.

Traditionally, chromite and magnesite-chrome refractories have been used mainly in basic steelmaking furnaces and copper smelters. Minor amounts are used in rotary kilns in the cement industry and in glassmaking furnaces.

Chromite usage in steelmaking has declined significantly in recent years with the development of oxygen steelmaking. These furnaces use periclase (magnesium oxide) with carbon from pitch, rather than the chromite as was used in the basic open-hearth furnaces.

Chromite usage in electric furnaces has also declined as water-cooled sidewall panels and roofs have replaced the refractory materials in these furnaces. AOD furnaces for producing stainless steels use refractories made from periclase-chrome (magnesium oxide-chrome) or dolomite. Due to the rising cost of synthetic periclase, the trend is toward the use of all-dolomite refractories. There is an upward shift in the consumption of periclase-chrome refractories in ladles, where these refractories are replacing those of fireclay or fireclay-graphite. However, this increase is very small compared to the decline in furnace usage.

The usage rate of chrome refractories in the copper smelting, cement, and glass industries has not suffered similar decline. However, the general slump in copper smelting and the advent of the SX-EW process has had an effect on chrome refractory use.

In general, therefore, chrome refractories are being used less than before and it appears that their use will decline further in the future.

This assessment of the industry trend was the result of discussions with major copper and steel producers and their various operations. These are listed below.

Asarco
Copper Range Co.
Hanna Mining Co.
Kennecott Minerals Co.
Magma Copper
Monsanto Chemicals
Phelps Dodge Corp.
U.S. Metals Refining Co.
Armco, Inc.
Bethlehem Steel Corp.
Cyclops Corp.
Inland Steel Co.
Lone Star Steel Co.
Phoenix Steel Corp.
Republic Steel Corp.
U.S. Steel Corp.
Wheeling Pittsburgh Steel Corp.

Table 4-1. Standard Classification of Chromites

	Metallurgical	Refractory	Chemical
Chromium oxide, percent			
Typical	48	34	44
Range	46 - 56	30 - 40	40 - 46
Chromium/iron ratio			
Typical	3	2.2	1.55
Range	2.0 - 4.2	2.0 - 2.5	1.5 - 2.0
Silica, percent			
Typical	6	5	3
Range	3 - 10	3 - 6	0.5 - 4
Chromic oxide/alumina	--	>60	--

NATURE OF SPENT REFRACTORIES, GENERATION RATE, AND ECONOMIC VALUE

In usage, chrome and chrome magnesite refractories deteriorate due to:

- Penetration of the molten metal.
- Fluxing by components in the molten slag.

Due to both of these causes, the refractory needs to be periodically replaced with new material. The old refractory that is removed represents a waste material that contains:

- Unaltered, usable chromite and other refractory materials.
- Valuable metals that had penetrated the lining during use.
- Undesirable slag and other deleterious material inclusions.

The inclusions may be penetrations through cracks and fissures in the refractory material, or the inclusions may envelop the grains, depending upon the fissure pattern.

GENERATION RATE OF WASTE

The U.S. Bureau of Mines mineral commodity summaries for 1983 reported an estimated consumption of chromite in 1982 of 590,000 short tons, of which 15% was estimated as consumption in the refractory industry. This would place consumption by the refractory industry at 88,500 short tons for 1982. The 115th Annual Survey and Outlook for World Mineral Commodities issued by Engineering & Mining Journal estimated 80,000 tons of chromite used in refractories in 1982.[1]

All of the chromite refractories were most probably installed as replacements of old linings, rather than as new installations. Chrome magnesite refractories average about 16% chromite. The chromite refractories contain up to 95% chromite. Assuming an average chromite content of 40% in all of the chrome-bearing refractories, the total refractory waste generated in 1982 works out to 221,250 tons.

ECONOMIC VALUE OF THE WASTE

The current price of refractory-grade chromite varies from $45 to $60 per ton, depending on the source and on the contaminating impurities. The chromite value in the waste refractories could average $18 to $24 a ton. Refractory waste material also contains metallic inclusions resulting from their infiltration from the molten metal the furnace carried during its life. In the case of refractories in the copper industry, these metallic inclusions could amount to as much as 5%, or up to 100 lb per ton. Steel furnace refractories also have similar metal inclusions; however, the monetary value of the steel inclusions is much lower than that of copper. Overall, the waste refractories hold a minimum of $7 a ton in case of chrome magnesite in the steel industry, to a maximum of $120 for 95%-chromite bricks in the copper industry.

All the chromite used in the U.S. is imported, and as such has a strategic value that must be added to these values.

CURRENT WASTE TREATMENT PRACTICES

Copper Industry

In current practice, industry's main interest in the recycling of the refractory is the recovery of the entrained copper, rather than the recovery of the chromite in the refractory. The industry uses several alternative approaches to the recovery of entrained copper.

- The used refractory is crushed and fed to the copper smelting furnace. In the process, the entrained metal melts and is recovered with the metal in process. The refractory grains are lost in the slag.
- The spent refractory is crushed and used with some fresh refractory to reline the hearth. Such repeated use saturates the hearth with copper, and further penetration of the metal and loss to the refractory is reduced.
- The spent refractory is crushed and metallic copper is recovered by the flotation process. The flotation tailing, consisting of the refractory grains, is discarded as landfill or sold to reclaimers, who mix it with fresh refractory and manufacture ramming mixes.

Steel Industry

The used chrome-bearing refractory from the steel industry also carries inclusions of steel, along with other materials. However, these inclusions of steel are not of economic importance, and the recycling, when carried out, is for the recovery of the refractory material and not for the metallic inclusions, unlike the procedure in the copper industry.

The steel industry trends in dealing with used refractory waste are:

- Disposal of the material in a landfill.
- Sale to reclaimers, who process the waste to produce refractory materials that can be used in other industries, if not recycled to the steel industry.
- Reuse after some cleaning.

Refractory Reprocessing Industry

There are industrial operations devoted solely to the reprocessing of waste refractories. Commonly, the reprocessors tend to confine themselves to the waste from the steel industry. This is due in part to the fact that the copper smelters prefer to recycle the waste internally for the copper content. Also, the copper bearing-refractory is difficult to crush and treat due to the ductility of the entrained copper, requiring specially designed crushers; this is not the case in treating steel plant waste material.

The reprocessing used by the steel industry and the refractory reprocessors consists of several of the following steps:

- Crushing to liberate the refractory, metal inclusions, and retained slag.
- Sieving to separate some of the metal, agglomerated materials, and powdered slag.
- Magnetically separating the metallic inclusions.
- Attrition-scrubbing and washing to remove oxides and other materials coating the refractory grains.
- Reconstituting by mixing with suitable fresh refractory and binding materials.

Generally, the reconstituted refractory is used as a ramming mix, rather than to manufacture baked refractory shapes. This is due partly to incomplete cleaning by the presently operating process, which results in the recovered material being slightly under-specification with regard to composition, and partly to the slightly lower binding characteristics of the reclaimed refractory grains, which still having some slag coatings.

TECHNICAL REQUIREMENTS FOR VIABLE RECYCLE OPERATIONS

As discussed, current operating practices achieve different levels of reclamation of values and disposal.

- Total disposal as landfill, with no recovery.
- Recovery of only the metallic values by crushing and recycling to the melting furnace without any special processing step.
- Recovery of metallic values and refractory grains suitable for a downgraded use other than for new baked refractories.

For full recovery of values, the process must:

- Liberate the refractory grains and the metallic and other inclusions without overgrinding the refractory grains.
- Clean the surface of the liberated refractory grains of any encasing by slag, metal or metal oxides.
- Separate and recover the metallic values.
- Separate the refractory grains from other inclusions of slag and metal oxides.
- Size the recovered refractory grains and reject the off-size material not suitable for molding of the refractory to shape and baking.

Crushing for liberation sometimes presents problems if the metallic inclusions encase the refractory grains and are ductile. In such a case, there are two available choices:

- Concentrate the metal values (including the enclosed refractory grains) and recycle them to the smelter.
- Adopt a chemical leach process to dissolve and recover the metallic values coating the refractory grains.

Cleaning the surface of the liberated refractory of the thin film coating of slag and metal or metal oxides requires a high degree of attrition grind. It is possible that these coatings may not be removed by attrition, in some cases requiring a chemical attack.

Once the liberation and surface cleaning is effected, separation of metallic inclusions or slag is not difficult and can be achieved by standard unit processes.

DEVELOPMENTS IN PROGRESS

The Bureau of Mines has conducted successful tests[2] in:

- Recovery of copper from the refractory derived from the copper industry, by the ammomnia leach solvent-extraction process. The main advantage of the process is the preservation of the size composition of the refractory, making the refractory grains in the tailing suitable for reuse as refractory. The flotation practiced by industry requires a finer grind and the refractory in the tails is discarded.
- Recovery of copper matte and chromite by magnetic separation.

The Bureau of Mines also conducted tests[3] on the recovery of refractory material from steel plant refractory waste. The recommended process consists essentially of crushing, sizing, and magnetic separation.

RECOMMENDATIONS

The unit processes involved in the recovery of refractory grains are standard. However, the actual process for a particular refractory waste will depend upon the type of inclusions -- copper, copper matte, steel, slag, etc. It will also depend upon whether the inclusions are discrete particles that can be easily liberated by crushing, or form a coating on the refractory grains. Consequently, the process steps need to be custom-selected and optimized separately for each of the various industry wastes. Any developmental work therefore becomes industry-specific.

There is, however, one area in which general process developmental work could be of use. The size composition of the reclaimed refractory is important if it is to be used for baked refractory shapes. Crushing for liberation breaks up some of the refractory grains as well, and recovery of shapable refractory falls (though it may still be useful for ramming mix). The severity of the crushing conditions is due to the presence of metallic inclusions of copper and steel. The Bureau of Mines had successfully attacked this problem in the case of copper smelter refractories by ammonia leach of the coarsely crushed refractory not fine enough for full liberation.

This approach can be taken one step further: the metallic values could be leached out by percolation leaching of coarsely broken refractory. If the percolation leach could be optimized for the dissolution of metallic values of copper, copper matte, and steel (if not for value of steel but just for liberation of the refractory), crushing of the leach residue would be easier. In such a case more intergranular (in preference to intragranular) breakage would occur, and the size consistency of the refractory grains would be better preserved. This is worth experimental work. Percolation leach techniques could be applied to steel as well as to copper industry waste.

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SECTION 5

CHROMITE-BEARING FOUNDRY SANDS

SOURCE AND NATURE OF WASTES

Chromite-bearing foundry sands are used in some steel foundries as facings and as molding sands in some cores and other such areas. The sand molds are used once for casting and are destroyed in the shakeout. The sand mold material in its entirety is a recyclable waste. Any organic bonding materials used in the mold char and burn due to the heat of the molten metal in the casting process. The bonding materials also tend to agglomerate the sand grains with a more permanent bond during the casting process. This changes the size composition of the sands.

In the breaking up of the mold, some fines are generated. As the mold needs to have controlled porosity and permeability to gases, close sizing of the sand is important, and the aggglomerated grains as well as the fines produced are contaminants that must be removed before the sand can be reused.

Common binders used are clay and such organics as starches and/or hydrocarbons. The organics, when used, result in carbonaceous vapors and char due to the heat of the molten metal. These vapors and tarry matter permeate the mold and give the sand grains a carbonaceous coating. This coating must be cleaned off before the sands can be recycled, as it reduces the properties of adhesion, which cannot be tolerated beyond certain limits. The clay near the molten metal loses its binding property during baking. Both the altered and the unaltered clay are recovered along with the sands in a normal recycling process. The bonding properties of such recovered clay are diffferent from those of the original.

The casting process also introduces some metal oxides as coatings to the molding sand grains, as well as some metal particles from sparks and spluttering during casting.

Facings, cores, and other parts of the mold with special composition become mixed with the main mold material during the shakeout of the casting. The facings may be chromite, graphite, and several other such special materials.

This waste is a material that requires cleaning of deleterious coatings and contaminants resulting from the casting process, and reconstitution both in size as well as in composition.

GENERATION RATE OF WASTES

Chromite use in foundry sands was reported for 1975 as 70,000 tons.[1] A rough estimate (based on the 1975 estimate and the ratio of chromite used in foundry sands to the weight of castings produced in a number of foundries that appear to typify the industry) places the chromite consumption in 1982 at 82,500 tons.

The waste molding sand generated is not wholly chromite, as it is used mixed with other molding sands in some parts, as wholly chromite in certain facings, and not at all in other parts of the molds.

In a few instances[2] the chromite sand consumption was reported at about 16% of the total molding sands. The industry average of chromite in foundry sands was reported[1] at less than 10%. This would place the minimum generation of waste sand at 515,825 tons per year, with a possible maximum of over 825,000 tons, containing 82,500 tons of chromite. As with the refractories, the foundries also have been using lesser amounts of chromite in the molding sands. Quantitative current data was not available.

CURRENT REPROCESSING PRACTICES

Molding sands are generally recycled. However, processing for recycle is usually a partial cleaning that does not restore the sand fully to its initial composition or purity. When the sands are recycled, the process is usually continuous, with the processed sands blended with fresh material for reuse. However, a bleed becomes necessary when the impurities build up to a high level.

Most commonly, the reprocessing consists of one or more or the following steps.

- A delumping process, which is a mild form of crushing, to break loose agglomerates and free the grains.
- Screening and sizing to remove foreign matter, agglomerates, and fines.
- Magnetic separation to remove metals (steel).
- An attrition scrub to remove adherent oxides and other dele-
- A drying and oxidizing roast or calcination to burn off organic or charred binder material.

Figure 5-1 shows the process steps.

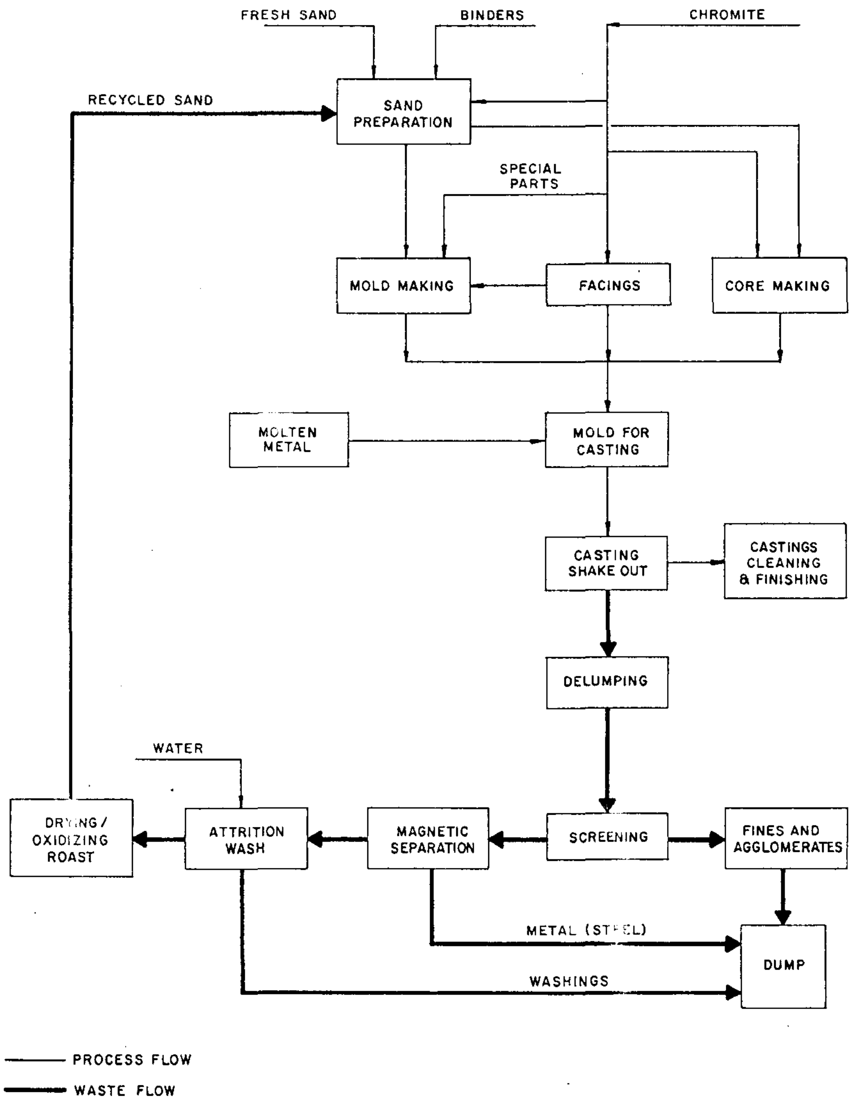

FIG. 5.1

FOUNDRY SAND RECLAMATION

These processes clean and recover usably sized molding sand grains without discriminating or separating the different kinds of sand in the foundry sand mix. Chromite, if used in the molding sand, is mixed and recovered with the balance of the sand. In cases in which chromite is used as a facing material, it becomes mixed with the body of the sand, which increases in overall chromite content. While this may not be harmful in the molding sand up to a limit, it represents a wasted resource. (The limit is due to change of bonding characteristics introduced by the chromite.)

Some foundries report recovering the chromite separately by magnetic separation of the washed sand. Some foundries also report separating the organic and charred materials by a flotation process. However, very few foundries seem to be using these processes.

The U.S. Bureau of Mines has conducted extensive testing[3] on used foundry molding sands for the recovery of chromite. The processes tested include:

- An oxidation roast for burning off carbonaceous matter.
- A heavy media process to separate chromite from silica sands.
- Magnetic separation to separate chromite from silica.

The Bureau concluded that the processes hold economic promise.

TECHNICAL AND ECONOMIC REQUIREMENTS FOR VIABLE RECYCLING OPERATION

As was mentioned earlier, all the components of the waste molding sand (except the binders) are recyclable, once they are cleaned of surface coatings, contaminating chars, and inclusions, and are sized. The economics of recovery could perhaps be improved if components such as silica sand, chromite, graphite, etc., are separated for reconstituting as required. In the presently practiced recycling processes that do not separate the components, the economic edge is lost due to the dilution of more valuable components such as chromite with the silica sand. Such a mixing up also renders the reclaimed sands unusable after a few recycle operations.

The recycling can be continued longer if all the components are separated and reconstituted as required. The separations are achieved by well-established, simple unit operations. These include:

- Delumping.
- Attrition washing.
- Gravity separations such as heavy media and tabling.
- Magnetic separation.

- Flotation.
- Drying and calcination.
- Sizing.

All of the processes are not required in all the cases, and the optimal combination of unit operations that achieve the best separation is easily determined.

The constraints in the industry for such separation processes are:

- Many of the foundries use quantities of chromite too small to warrant installation of a multistep separation process.
- The foundries using chromite may not use it continuously at a steady rate throughout the year.
- Depending upon the type of castings produced, chromite use may vary from time to time.

In addition, it appears that many foundries following the traditional minimal recycling procedure of delumping, washing, and sizing have not evaluated in depth the economics of separate recovery of the components of the waste molding sands. In other words, discussions with many foundries indicated a lack of awareness of what a properly conceived recycling could achieve.

A central custom-processing facility serving several foundries would perhaps be workable, provided an adequate number of foundries are nearby and transportation is not a deterrent factor for the particular location. This is a matter for in-depth study. A campaign to instill awareness would also be of advantage.

RECOMMENDATIONS

A chromite recovery of 90% in the process with a 20% loss due to off-size material generated (an overall recovery of around 72%) could be expected in the recovery process. Assuming 10% chromite in the waste sands, about 144 lb of chromite could be recovered per ton of waste. At $45.00 per ton, this represents a value of $3.24.

Extrapolating operating costs on the basis of the Bureau of Mines' cost estimating systems manual,[4] the operating cost for a 500 ton per day plant, employing delumping, sizing, flotation, magnetic separation, and drying processes, works out to about $1.00 per ton. Allowing for a lower level of utilization and unit processes not utilized in a particular operation, the operating cost is not likely to exceed $2.00 per ton. A definite economic promise exists that needs to be quantified. The waste generated in the process would be inert minerals that can go to landfill.

As pointed out earlier, the unit processes themselves are standard and do not need developmental research. However, it would be worthwhile to develop a design package for a custom mill that can serve a number of foundries, and make it available to interested industries. Such a design package must identify:

- Typical locations with potential volumes of wastes that could be handled.
- Unit processes that would be used for a variety of typical wastes.
- Equipment specifications, sources, and budgetary prices.
- General arrangement, providing flexibility for adaptation to different process schemes.
- Capital costs.
- Typical operating costs and profitability analyses.
- Factors that could be applied for modifying the estimates for other locations and throughput rates.

Such a document would improve industry awareness and provide incentive to serious entrepreneurs.

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SECTION 6

SPENT MERCURY BATTERIES

MAJOR BATTERY PRODUCERS

Mercuric oxide is used as a depolarizer in dry batteries in which both a relatively flat discharge curve and a high energy density are required. Batteries for hearing aids, watches, cameras, and electronic instruments require these special characteristics.

Mercury batteries are produced essentially in two cell structures, the miniature and the cylindrical. The major manufacturers of mercury batteries are:

1. Union Carbide (Eveready Battery Division)
2. Duracell
3. Gould
4. Ray-O-Vac
5. Veterans Administration

Of these, Duracell is perhaps the largest producer of mercuric oxide batteries.

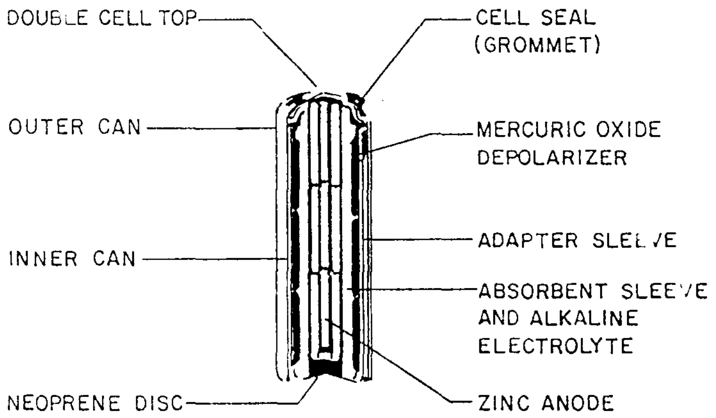
MERCURY BATTERY DESIGN AND GENERATION OF WASTE

The common battery designs using mercuric oxide are shown in Figure 6-1. The mercuric oxide depolarizer is located between the anode and the cathode. The materials of construction of the dry cells include zinc, aluminum, nickel and/or gold platings, neoprene, nylon, polyethlyene and similar plastic materials, and a variety of chemicals, including mercuric oxide, manganese dioxide, potassium or sodium hydroxides, etc.

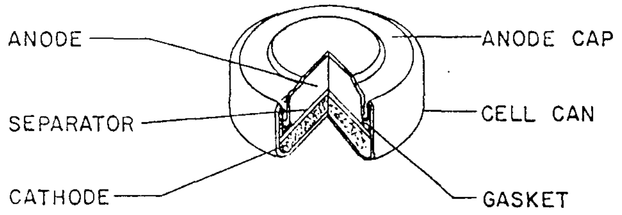
In usage, zinc and aluminum, if present, are partly or fully complexed with the sodium or potassium hydroxide, generating hydrogen, which is oxidized by the mercuric oxide, resulting in metallic mercury.

The physical construction of the cell is designed so as to prevent migration of solids from one part of the cell to another and the physical integrity of the cell is usually retained after the useful life of the battery, if it is not physically damaged in handling.

The used cell, with the cell structure intact but with metallic mercury, is a waste material generated by the battery users and constitutes the major source of waste.



CYLINDRICAL CELL STRUCTURE



MINIATURE CELL STRUCTURE

FIG. 6.1

COMMON MERCURY BATTERY DESIGNS

The battery manufacturers draw representative samples from each production batch and destructively test them for any possible defects (usually internal short circuits).

The test samples are always scrapped. In the case of detection of short circuits, the entire batch of cells is usually scrapped. These scrapped cells constitute a second source of waste.

An Engineering & Mining Journal annual review[1] estimated U.S. consumption of mercury in batteries for the first nine months of 1982 at 18,003 flasks (1,368,228 lb). The U.S. Bureau of Mines estimated[2] the mercury used in batteries in 1982 at 24,880 flasks (1,890,880 lb), of which 17,323 flasks (1,316,548 lb) was primary mercury and the balance was redistilled and secondary mercury. Engineering & Mining Journal[3] revised its estimates of consumption in battery and other electrical products to 28,500 flasks in 1982.

In spent batteries, all the mercury used ends as waste. Assuming that the redistilled and secondary mercury represents the mercury recycled, the primary mercury used will represent the waste generated. Part of the redistilled and secondary mercury could come from sources other than batteries, such as instruments. Therefore, the primary mercury used would indicate a conservative estimate of unrecovered waste. In 1982, this was 17,323 flasks (1,316,548 lb).

Hearing aids and military uses in electronic equipment constitute the major bulk of mercuric oxide battery usage.

CURRENT MERCURY RECLAMATION PRACTICES

Little information is available in published literature on the reclamation of mercury from used and scrapped batteries.

One of the battery manufacturers recycles the factory rejects. One other manufacturer had an experimental reprocessing unit, but has discontinued the operation.

Information regarding the handling of scrapped batteries was not available from other battery manufacturers, who considered such information to be company-confidential.

There are two major operators specializing in the recovery of mercury from spent and scrapped mercury batteries. hey are:

1. Masero Laboratories, Palo Alto, California (Erse Corporation)
2. Mercury Refining, Inc., Albany, New York

Other reprocessors confine themselves mainly to metallic spills such as broken thermometers, and instruments in industries, where they vacuum-clean and collect such spills and refine the mercury.

The process used by operators specializing in the recovery from batteries consists of:

- Retorting the batteries under vacuum.
- Condensing vapors in a water trap.
- Periodically collecting the sludge floating on the top of the water trap, treating it with acetone, in which most of the organics dissolve, and returning the residue to the retort.
- Collecting the metal settled in the bottom of the water trap and returning it to battery manufacturers. This material may at times undergo a second distillation to enhance purity.

The first distillation product is classified as virgin grade.

The present reprocessors consider the process satisfactory. The recovery is a matter of guesswork, since there is no way of checking the material balance. The spent battery input is a mix of different sizes from various manufacturers, with an uncertain amount of mercury input to the process. Also, no analysis is made for mercury content in the acetone wash. It is presumed that the wash would carry only the organics and no mercury under the process conditions.

It is also presumed that the residue in the retort after the completion of distillation would be totally free of mercury due to the temperatures involved. The recovery may or may not be 99.99% as claimed. If the recovery is lower, there could be waste mercury discarded with the solid residue or with the organics.

The economics center around the logistics of collection of used batteries. The reprocessors advertise in such publications as Hearing Aid Journal, and the hearing aid suppliers collect the spent battery when they replace it for a customer. Spent batteries from defense use and scrapped batteries from manufacturers would be easier to collect. The batteries in cameras, watches, etc., are replaced by the consumers themselves, who usually discard the spent battery to domestic waste, which ends up in landfill or occasionally in incinerators.

RECOMMENDATIONS

The main process approach of vacuum distillation presently used is the most direct and suitable technology for the recovery of mercury. However, its processing adequacy cannot be evaluated in the absence of a good system for checking and monitoring the material balance through the process. Developmental work is required in evolving methods of analysis for mercury of the feed material (spent and scrapped batteries and the wastes from the process), the solid residues, organic sludge, and wash.

Once a monitoring method is developed, any inadequacies in the process could be identified and procedures developed to overcome them.

The logistics of spent battery collection would still be a constraint in the treatment and recycling of all the wastes generated. A beginning could be made, however, if the spent batteries from defense and other large consumers of mercury batteries could be routed to reprocessing, with a good monitoring system.

Quantification of available scrap from various sources affording easy collection would be a good starting point, as it would indicate the feasibility of building a facility with a good monitoring system.

If a process monitoring method is developed and the process is optimized, these batteries could be routed to a processor using such an optimized process. Routing the major controllable sources to such an optimized process would in turn act as an incentive for all processors to adopt the process.

At present, the two reprocessing operations mentioned earlier dominate the field. Scrap collectors could be induced to collect the batteries from domestic consumers (similar to the prevailing collection of used aluminum cans), provided there are local processing facilities. This needs development of public awareness, a larger number of processing units located at evenly distributed geographic locations, and a monitoring system for the process.

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SECTION 7

OVERVIEW OF DEVELOPING WASTE TREATMENT PROCESSES

The waste streams in the mineral processing industry need to be processed for:

- Environmentally acceptable disposal, or
- Recovery of value-bearing materials for reuse in the process or for the market.

Environmentally acceptable disposal usually involves:

- Destruction of hazardous materials such as cyanides.
- Neutralization of free acidity.
- Precipitation of dissolved metal salts.
- Dewatering and separation of solids in an acceptable form for landfill.

Of these, the destruction of hazardous materials is usually achieved by oxidation, complexing, and/or precipitation. Neutralization of free acidity very often results in precipitated solids.

But for a few exceptional cases, all these treatments therefore result in a sludge that needs to be dewatered and disposed of as dry landfill. Alternatively, lagoons are allowed to dry and are suitably covered. In effect, this also constitutes another form of landfill.

The precipitated solids are usually hydroxides and sulfates, which are difficult to dewater or dry.

Developmental efforts in this area have been in achieving the dewatering in effective and efficient ways. These include:

1. Control of precipitation to facilitate dewatering, including:

    (a) Temperature control. The crystallinity of a precipitate is affected very markedly by the temperature at which the precipitation is effected. While the optimum range may differ in different cases, a higher temperature usually contributes to better crystallinity.

    (b) Seeding. When a solid forms and separates out of a liquid, it usually builds around any solid nucleus that may already be present. The crystal growth is better if the nucleus is of the same crystal structure as the precipitating solid. Thus, seeding the pregnant liquor with the precipitated solid crystals contributes to crystal growth.

Since freshly precipitated solids act as better nuclei than the same material exposed to air for some time, recirculation of precipitated crystals is a technique that is very useful in the precipitation. Seeding and recirculation of freshly precipitated solids is a known technique in production of intermediaries and final products in many hydrometallurgical operations. Application of the same to waste disposal is comparatively new and has not yet been fully utilized in all instances where it could be of advantage.

2. Control of precipitation to produce marketable product:

Very often the precipitated solids may be of economic value, if they can conform to certain specifications. Gypsum is a prime example of this. If it is precipitated as good crystals, without discoloration (for example, by iron), it has good market potential. This requires staged precipitation and close pH control. This is also a technique that is taking root in treatment of liquid effluents.

3. Flocculation to aid dewatering:

One of the newer innovations in this area is magnetic flocculation. In use in municipal waste and sludge treatment for a much longer time, this is finding application in treating mineral processing waste streams. The otherwise difficult slurry is seeded with finely ground magnetic material such as magnetite, and mixed well. The mixed pulp is passed through a magnetizer, which results in magnetic flocs, formed due to the residual charges in the magnetic seed, which forms a lattice pattern, enclosing and flocculating the difficult-to-settle solids in the effluent. The flocculated pulp is easier to filter. Magnetic flocculation may also be followed by magnetic separation instead of filtration.

Solids in some difficult slurries could be settled by flocculants which form a blanket over the solids, instead of flocs.

4. Filtration:

Pressure filtration, with belts applying pressure to squeeze the liquid out of a slurry by means of rollers, is a technique finding recent application in waste treatment, even though it has been in use for a long period in the chemical and food industries for production of intermediaries or salable products.

Vacuum electric filtration, which combines vacuum filtration with electroporesis, electro-osmosis, and electrophoretic deposition, is probably the latest entrant into the field, and holds high promise. With high dissolved ionizable salts in the waste stream, the filtration would require pretreatment. This process has been used successfully in such filtrations as clay and has high potential for application to dewatering difficult waste slurries.

Recovery of valuable products for reuse or for the market is a wider field, with much larger research activities. These include:

1. Acid recovery:

   Mineral industry waste liquors usually contain free acids. The normal course would be to neutralize the acids and discard the neutralized liquor or the solids resulting from neutralization. New ion-exchange resins are under development that capture mineral acids. The eluted liquor resulting from regeneration of the resin could be too weak for its reuse. Concentration of weak acids could be accomplished by vapor recompression techniques coupled with a simple evaporator.

   Dialysis and modifications of electrolytic concentration techniques also are some of the newer developments. Some of the modifications to dialysis include combination of dialysis with reverse osmosis and ion exchange.

2. Metals recovery:

   (a) Membrane filtration. Membrane filtration is, in effect, separation of metal ions from the anions in an ionized solution. This process uses liquid membranes, which are polymeric materials loaded with ion carriers. The material of the membrane itself, which consists of hollow fibers, as well as the ion carriers that fill the membranes, are subjects for developmental research. While the membrane material would be adaptable to a variety of solutions, the ion carriers must to be specific to each application.

   (b) Bio-accumulation. Microbes have the ability to couple with metal ions in solution. The coupled microbes are easy to harvest from the solution, and incineration of the biomass leaves the metals in the ash as oxides for further treatment. Since the ability to couple, or chelate, is also a function of the shape of the molecules, development of compounds of the appropriate molecular configuration as coupling agents is drawing attention.

(c) Cryogenics. Supercooling of scrap metals by liquid nitrogen, crushing, and sizing has been used to separate one metal from another from mixed scrap. This depends upon the differential embrittlement occurring in different metals when cooled to the same extent, which in turn affects the breaking characteristics.

(d) Metal scrap has also been separated by the use of magnetic fluids. The Bureau of Mines developed "ferrofluid," a colloidal suspension of precipitated and coated magnetic particles. When placed in a magnetic field, objects of different density can be made to move differentially in such suspensions. Potential applications of this appear very high.

(e) Electrolysis of metal compounds held in suspension, where the metal compounds dissolve and undergo electrolysis concurrently, has been used experimentally to recover copper directly from chalcopyrite. A similar process, modified to some extent, can be applied to waste slurries containing metal salts in solution and precipitated metal compounds. "Electroslurry" is a proprietary name for one such modification, and this and similar processes hold good promise.

SECTION 8

OVERALL EVALUATION OF WASTE STREAMS AND THEIR PRIORITIES

The treatment of waste streams is justified or becomes necessary due to:

- o Economic gains the treatment may offer.
- o Strategic importance of such a treatment from a national and mineral economics point of view.
- o The need for such treatment from the environmental pollution point of view.

The effort put into development of waste treatment processes must be guided essentially by these considerations.

An additional, fourth consideration that would influence the development decision is the lead time a technology development is likely to take.

To determine priorities for the developmental work on the various waste streams, weightage factors are assigned to each of the waste streams, for each of the above four basic considerations. The total of these weightage factors for each of the different waste streams then is used to determine their relative priorities.

Of a total of 100 points, the economic gains and need from an environmental point of view are assigned equal weightage of 30 points each. Without an economic gain, there can be no incentive, and without it the industry itself will collapse in the long run, making all other considerations superfluous. At the same time, disregard of environmental requirements may also force an industry to closure. These two deserve equal weightage.

Of the other two considerations, strategic importance is not receiving its deserved weightage at present. Many of the waste streams considered in this report deal with minerals and raw materials that are mainly imported into the U.S. From a national point of view, this factor needs to be given significant weightage, since it could push marginal cases to a positive decision. Twenty-five points are assigned for this consideration.

The lead time required for developmental work, if not considered, could make all other considerations futile. Developmental work with a long lead time needs to be initiated earlier than the work that has a short lead time. Thus the work requiring longer lead time must be given higher priority and is therefore assigned a higher score. A maximum of 15 points is assigned to lead time.

The weightage points assigned to each of the waste streams considered in this report, and the rationale behind their selection, are discussed in the following pages.

UNREACTED SOLID RESIDUE FROM TITANIUM CHLORINATION PLANT MATERIAL

1. Economic: (Weightage - maximum, 30; assigned, 20.)

The economic value of the solid waste was estimated at $150 per ton. Most of it would be recovered with a satisfactory recycle process. The recycling could be costly, due to a number of steps involved and possible major changes in the chlorination reactor as an alternative. The net result could, however, be an economic gain; but not high enough an incentive for extensive capital investment and design development. The alternatives that need to be considered are also many. Weightage assigned is therefore just above the midpoint.

2. Strategic: (Weightage - maximum, 25; assigned, 10.)

Domestic ilmenite production compared to import has been declining for several reasons. However, the potential exists, and therefore ilmenite cannot be considered highly strategic.

Domestic rutile production data is not available. The U.S. does import quite a large amount of rutile. Rutile is a commodity replaceable by upgraded ilmenite.

Despite the large import, therefore, neither of the titanium source materials can be considered scarce from the domestic resource point of view; hence the low weightage from the strategic point of view.

3. Environmental: (Weightage - maximum, 30; assigned, 20.)

By itself, the solid waste is not an environmental hazard, as it is composed of unreacted titanium source materials, refractory minerals, and carbon. However, any chlorides coating the inert solids leach out in water and contaminate the groundwater. If the solid waste is wetted and neutralized, the resulting sludge is difficult to settle and dry. It is stored in lagoons with continuous monitoring and maintenance. The assigned value of 20 is based on the fact that lagooning requires a higher level of monitoring and maintenance than landfill for totally inert material, while at the same time the waste is not toxic and does not represent health hazards.

4. Developmental Lead Time: (Weightage - maximum, 15; assigned, 6.)

The unit processes are not complex and developmental work is essentially that of optimization.

Total: 20 + 10 + 20 + 6 = 56

LIQUID EFFLUENT FROM TITANIUM CHLORINATION PLANT

1. Economic: (Weightage - maximum, 30; assigned, 10.)

The economics of the recovery depend upon the columbium, tantalum, and vanadium content of the effluent and their market value. In the recent past, new titanium source materials have shown lesser columbium and tantalum content. However, this may be only a temporary phase.

While general process steps are known, a marketable final product has not been identified, and the refinery steps to its production have not been developed. Economics at present is a factor that cannot be projected reasonably.

2. Strategic: (Weightage - maximum, 25; assigned, 10.)

The U.S. produced nearly 86% of its consumption of vanadium[1] in 1982. However, it imports all its requirements of columbium and tantalum. From this point of view, this waste deserves a high rating. However, the columbium-tantalum content of this waste appears to be small (on the order of 2% of consumption), compared with the U.S. consumption of 6,100,000 lb of columbium and 950,000 lb of tantalum.[1] A value of 10 is assigned in recognition of the fact that the U.S. produces no columbium or tantalum, while at the same time the quantity of these value metals is low in this waste.

3. Environmental: (Weightage - maximum, 30; assigned, 26.)

The environmental problems are similar to, but more intense than, those connected with the solid wastes, due to its higher volumes, precipitation caused in neutralization, and the character of the sludge.

4. Developmental Lead Time: (Weightage - maximum, 15; assigned, 12.)

Lead time required would be high. Even though main applicable processes are known, the determination of the product mix and optimization of process parameters would require extended research.

Total: 10 + 10 + 26 + 12 = 58

TITANIUM LEACHER EFFLUENT

1. Economic: (Weightage - maximum, 30; assigned, 7.)

The economic potential of recovery of small amounts of magnesium or nitric acid is low.

2. Strategic: (Weightage - maximum, 25; assigned, 0.)

There is no strategic or mineral conservation importance that could be assigned to this waste material.

3. Environmental: (Weightage - maximum, 30; assigned, 10.)

This waste, due to its acidity and combination of chlorides and nitrates in the presence of excess acids, does constitute environmentally unacceptable material. The nitrate ions cannot be precipitated to an inert solid suitable for landfill. However, the excess acids could be neutralized to salts acceptable to the environment, as is done in the manufacture of soil stabilizers.

4. Developmental Lead Time: (Weightage - maximum, 15; assigned, 8.)

The developmental work is two-staged: first, possible usage applications, and second, a process to adopt the waste to the usage. This could be a prolonged process.

Total: 7 + 0 + 10 + 8 = 25

DIFFICULT-TO-HANDLE TITANIUM SECONDARY SCRAP

1. Economic: (Weightage - maximum, 30; assigned, 15.)

If the difficult waste could be recycled to the rutile chlorination stage as suggested, the economic gains would be attractive. Since the total scrap generated forms a good percentage of the primary mill product, recovery at any stage holds economic promise.

However, at this stage the potentiality of the economic promise is only a conjecture. Whether the recycle suggested along with rutile would present problems in the fluid-bed chlorinator (e.g., possible development of hot spots and bed agglomeration) is not known. Considering the theoretical possibility along with practical uncertainty, a rating of 15 out of 30 is assigned to this factor.

2. Strategic: (Weightage - maximum, 25; assigned, 15.)

The scrap generated is a large percentage of the primary mill product, and therefore conservation gains importance. Since the U.S. imports a large bulk of titanium source material, there is also strategic importance.

3. Environmental: (Weightage - maximum, 30; assigned, 5.)

There are no special environmental problems connected with the scrap metal. The pickling and chem-milling is not environmentally acceptable; however, this is a comparatively small stream, and hence a low rating is given here.

4. Developmental Lead Time: (Weightage - maximum, 15; assigned, 8.)

Development would need time, and reorientation in the current process philosophy, if the industry is to accept the recycle suggested.

Total: 15 + 15 + 5 + 8 = 43

SPENT POT LININGS

1. Economic: (Weightage - maximum, 30; assigned, 18.)

Presently this has a low economic potential. In fact, it has an economic disadvantage. However, with full recovery of fuel value and special fluorine chemicals of high value, economics may turn positive.

The upturn in the economics of the process could be sufficient to lower industry resistance to reprocessing. However, currently available data do not indicate a possibility of economic improvement strong enough to warrant a high rating.

2. Strategic: (Weightage - maximum, 25; assigned, 8.)

There is no special importance from a strategic or conservation point of view.

3. Environmental: (Weightage - maximum, 30; assigned, 28.)

Potential hazards are considerable. Even after the fluorides and cyanides are rendered inert, if carbon is not burned out in a controlled the manner, atmospheric oxidation in time would create undesirable environmental effects. The quantities encountered are also very large.

4. Developmental Lead Time: (Weightage - maximum, 15; assigned, 12.)

This is an area of considerable research activity, which has yielded no satisfactory solution as yet. The low economic potential complicates further development, since the process must be cost-effective in an area of low economic return.

Total: 18 + 8 + 28 + 12 = 66

CHROMITE-BEARING REFRACTORIES

1. Economic: (Weightage - maximum, 30; assigned, 20.)

Economic potential is good. Normally, it should rate a higher weightage; however, the industry trend is in decline regarding use of chromite refractories. Therefore the economics, being tied to the declining trend, tend to lower the weightage.

2. Strategic: (Weightage - maximum, 25; assigned, 24.)

All of the chromite is imported. If the usage continues, even at low key, complete dependence on foreign sources raises the weightage of strategic importance considerably.

3. Environmental: (Weightage - maximum, 30; assigned, 0.)

There are no environmental problems, as the waste is an inert solid.

4. Developmental Lead Time: (Weightage - maximum, 15; assigned, 5.)

The technology consists of known unit processes and as such work is only of optimization. Lead time required is low.

Total: 20 + 24 + 0 + 5 = 49

CHROME-BEARING FOUNDRY SANDS

Essentially this would follow the pattern of the refractories. The same total value is assigned: 49.

SCRAPPED MERCURY BATTERIES

1. Economic: (Weightage - maximum, 30, assigned, 10.)

Economic incentive for reprocessing is low, due to problems of collection logistics, but the process itself is simple distillation and has economic potential. A low value is assigned because of the collection problem.

2. Strategic: (Weightage - maximum, 25; assigned, 20.)

Though the U.S. produces a good percentage of its consumption, resources are not unlimited. Moreover, consumption is likely to increase in the future, with the fast developmental activity in the electronics industry.

3. Environmental: (Weightage - maximum, 30; assigned, 25.)

Though not recognized as such, this could lead to environmental problems in the long run.

4. Developmental Lead Time: (Weightage - maximum, 15; assigned, 10.)

The process development itself may not present problems requiring a long lead time; however, the solving of the logistics problem would.

Total: 10 + 20 + 25 + 10 = 65

SUMMARY

Table 8-1 lists waste streams arranged in order of descending priorities as determined.

Table 8-1. Waste Streams Arranged in Order of Priorities

Waste Streams	Priority Weightage
Spent pot linings	66
Scrapped mercury batteries	65
Liquid effluent from chlorination plant	58
Unreacted solid residue in titanium chlorination plant	56
Chrome-bearing refractories and foundry sand wastes	49
Difficult-to-handle titanium secondary scrap	43
Titanium leacher effluent	25

Table 8-2 is a summary of the weightage points assigned to the waste streams for the considerations involved.

Table 8-2. Summary of Weightage Assigned to Waste Streams

	Economic	Strategic	Environmental	Lead Time	Total
Maximum weightage points	30	25	30	15	100
Unreacted solid residue from titanium chlorination plant	20	10	20	6	56
Liquid effluent from titanium chlorination plant	10	10	26	12	58
Titanium leacher effluent	7	0	10	8	25
Difficult-to-handle titanium secondary scrap	15	15	5	8	43
Spent pot linings	18	8	28	12	66
Chromite-bearing refractories	20	24	5	0	49
Chrome-bearing foundry sands	20	24	5	0	49
Scrapped mercury batteries	10	20	25	10	65

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SECTION 9

OVERALL RECOMMENDATIONS

The following overall recommendations are based on the specific recommendations made in each of the sections and are arranged in order of priorities derived for the waste streams in Section 8. The recommendations under each of the priorities are in turn arranged in order of importance and include suggestions regarding the organization of the developmental work.

Priority 1. Spent Pot Linings

1.1 Incineration Program:

(a) Evolve a process design for incineration of pot linings that would incorporate:

- o Reliable temperature control within a narrow range.
- o Effective hydrolysis of all fluorides.
- o Bed agglomeration control.
- o NOx formation control.
- o Effective heat extraction from off-gases.
- o Off-gas cleaning.
- o Recovery of fluorine values from off-gas.

(b) Develop an experimental program to collect adequate data on the effect of variations in process parameters identified in (a) and to carry out sensitivity analyses on the variations.

(c) Run a burn test in accordance with the program developed in Step 1.1(b).

(d) Optimize process parameters, range for control, and modify the process design in Step 1.1(a).

(e) Evaluate and identify the optimal incineration plant size for a typical location serving several aluminum smelters.

(f) Generate a conceptual design for the plant identified in Step 1.1(e).

(g) Evaluate capital and operating costs.

1.2 Product Optimization:

(a) Conduct a market analysis for fluorine compounds that can be made from incinerator off-gas.

(b) Incorporate into the conceptual design generated at Step 1.1(f), production of the highest value compounds identified in Step 1.2(a).

(c) Estimate the additional cost for such plant modifications as called for in Step 1.2(b) and conduct a cost benefit analysis.

1.3 Make final recommendations:

This work is best conducted by an engineering firm in close collaboration with a test facility equipped for the experimental work outlined. The Bureau of Mines could perform the experimental work.

Priority 2. Scrapped Mercury Batteries

The main problem in this area is one of logistics. Considering the possible environmental pollution potential of the waste, development of analysis techniques to monitor process effluent streams and the batteries themselves is recommended. However, if the defense industry and other large bulk users of mercury batteries are encouraged to route their used batteries to a central processing unit, a part of the logistics problem would be solved and a source would be in place for development of analytical techniques and optimal disposal methods, under monitoring by the methods developed. The logistics of collection from other sources and monitoring of reclamation facilities in operation may follow. If the present near-monopoly of reclamation is broken, and the economics are brought to public awareness, there would be encouragement for private industry to collect scrap batteries as is now done with scrapped aluminum cans.

Priority 3. Liquid Effluent from Titanium Chlorination Plant

The Bureau of Mines is already developing process techniques in the separation and recovery of valuable metals from this waste. However, since the products with high economic return from the processing may not be the metals, but rather a metal compound, a market survey is required. The following staged developmental work is suggested.

- Conduct a market analysis to identify the compounds of recoverable metals with high market potential and value.
- Modify or add process steps to the separation processes resulting from the Bureau of Mines program.

- Generate a conceptual design.
- Evaluate capital and operating costs.
- Evaluate the modification required in the process to adopt it to reprocess lime-neutralized effluent.

The market analysis, conceptual design, and cost evaluation could be carried out by an engineering company. The process development work is already under way at the Bureau of Mines. It is therefore best for the Bureau of Mines, doing the developmental work, to spearhead the market assessment and engineering, with whatever help is considered necessary.

Priority 4. Unreacted Solid Residue in Titanium Chlorination Plant

4.1 Experimentally optimize conditions for preparing the solid waste for recycle to chlorination:

(a) Collect samples of solid waste as generated now and determine optimal process conditions for:

- Washing out of free acids and soluble chlorides; separation of inert material other than rutile and carbon by flotation and/or wet tabling.
- Nature and quantity of the binder.
- Drying, delumping, sizing, and mixing the washed and dried waste with the binder.
- Pelletization and curing.

(b) Collect a dry discharge sample of the solid waste before sluicing and determine the optimal process conditions for:

- Dry table separation for rutile and carbon, discarding other inerts.
- Additional electrostatic methods for the above separations.
- Nature and quantity of the binder.
- Pelletization and curing.

(c) Determine the pellet strength and the gas diffusivity in the pellets.

(d) Run chlorination tests on the pellets together with fresh feed. Optimize the pelletizing conditions.

(e) Generate process designs for treating wet solid wastes as generated now and dry solid wastes as proposed, and evaluate the comparative costs.

Step 4.1(e) is engineering, while all other steps are experimental. Steps 4.1(a) through (d) inclusive must be conducted in a facility equipped for the unit processes; Step 4.1(e) could be performed by an engineering firm.

4.2 Evaluate the design modifications of the chlorinator:

(a) Obtain the design and operating conditions for a typical fluid-bed chlorinator.

(b) Identify any available experimental fluid-bed chlorinator test facility capable of process parameters similar to the selected typical unit, or design an experimental unit capable of working under typical chlorinator operating conditions.

(c) Identify, from a design approach, conditions that need to be changed to enhance the chlorination efficiency, and establish the magnitude of the changes.

(d) Generate design modifications in the fluid-bed chlorinator itself, and a second-stage chlorinator facility.

(e) Design and build a pilot prototype incorporating the design modifications to the chlorinator and the second-stage unit.

(f) Carry out experimental runs with material similar to the feed to the selected typical chlorinator.

(g) Evaluate the results and, if satisfactory, design a commercial sized unit for operation for the selected typical chlorination.

(h) Evaluate and conduct a cost benefit analysis.

All of this work is process and equipment design oriented. This could best be achieved under an overall responsibility of an organization with process and equipment design experience in collaboration with a qualified fabricator of fluid-bed reactors.

Priority 5. Chrome-Bearing Refractories and Foundry Sand Wastes

5.1 Refractories:

(a) Conduct tests and determine the optimum percolation leach conditions on waste refractories from copper smelters:

- Obtain typical waste refractory samples from copper smelters.
- Arrange for percolation leach test work with ammonia/ammonium carbonate solutions on refractory broken to 1", 1/2", and 1/4" sizes.
- Delump the residue and concentrate the chromite by standard wet gravity and magnetic separation processes.
- Size the concentrate and determine the waste undersize.
- Crush the refractory to liberation size, concentrate the chromite, and size the concentrate in the same manner as with the percolation leach.
- Evaluate the cost benefit analysis for percolation leach compared to crushing to liberation and concentration.

This is essentially experimental, except for the last step, which is engineering. A test laboratory, such as that of the Bureau of Mines, could undertake this.

(b) Conduct tests as in (a) on waste refractories from steel plants and determine optimum percolation leach conditions. However, sulfuric acid may be used as leachant instead of ammonia/ammonium carbonate.

(c) The primary aim of the leach is to loosen the refractory grains from the bonding due to unfiltered metal. The copper leachate must be treated for recovery of copper, while the iron in the leachate from the steel plant refractory must be precipitated and the liquid neutralized for disposal.

5.2 Foundry Sands:

As indicated in Section 5, the developmental work recommended is a design package for a custom milling operation. The following specific tasks are suggested.

(a) Examine (say) three areas with a high density of foundry operations.

(b) Determine the waste generated in the areas, the willingness of the foundries in the area to cooperate, and a reasonable scale of operation.

(c) Select one of the initially selected three for further work, on the basis of observations in (b).

(d) Design a custom mill capable of several variations of flow schemes, using any or all of the unit processes listed below, as may be appropriate for any given waste sand likely to be generated in the area the mill will serve.

- Closed-cycle delumping with dry screening.
- Calcining.
- Attrition wash.
- Wet tabling.
- Heavy media separation.
- A cyclone as a heavy media separator.
- Magnetic separation.
- Flotation.
- Filtration.
- Drying.
- Sizing.

(e) Design a plant incorporating flexibility for selection among the several process options as may be required. Generate layout, piping, and instrumentation drawings.

(f) Locate suppliers of equipment and develop capital and operating costs.

(g) Generate scaling factors for other sizes and locations.

(h) Prepare a design document incorporating:

- Typical flow schemes to which the plant can configure.
- Equipment list, sources, budget prices.
- General arrangement drawings.
- Piping and instrumentation drawings.
- Capital and operating cost projections.
- Scaling factors to other typical sizes and locations.

This is essentially engineering work and must be carried out in sufficient detail to ensure that the test estimates made from it are realistic. Such a document will include equipment specifications; sufficient engineering details to enable estimation of structural, concrete, piping, electrical, and instrumentation requirements; and estimates of utility requirements. An engineering organization is perhaps best suited to generate this document.

Priority 6. Difficult-to-Handle Titanium Secondary Scrap

The only scrap material on which developmental work is recommended is the scrap produced in machining, grinding, chem-milling, and pickling. Experimental work should include:

- Dewatering (including evaporation, if required) and drying of scrap.
- Compacting powdery material.
- Chlorination, separately and mixed with normal chlorinator feed, rutile and carbon.

Once the feasibility is experimentally determined, the industry may examine the feasibility on a commercial scale. The experimental work is best carried out by the Bureau of Mines.

Priority 7. Titanium Leacher Effluent

The work that would help is application research, considering the size of the effluent and its low priority.

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