ANL/OEPM-79-2

DR. 66

ANL/OEPM-79-2

84

9/20/79

A SURVEY OF METALLURGICAL RECYCLING PROCESSES

Contract No. 31-109-38-4213

by

EIC CORPORATION

MASTER

U of C-AUA-USDOE

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Operated for the U. S. DEPARTMENT OF ENERGY
under Contract W-31-109-Eng-38

DISCLAIMER

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) among the U. S. Department of Energy, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona
Carnegie-Mellon University
Case Western Reserve University
The University of Chicago
University of Cincinnati
Illinois Institute of Technology
University of Illinois
Indiana University
The University of Iowa
Iowa State University
The University of Kansas
Kansas State University
Loyola University of Chicago
Marquette University
The University of Michigan
Michigan State University
University of Minnesota
University of Missouri
Northwestern University
University of Notre Dame
The Ohio State University
Ohio University
The Pennsylvania State University
Purdue University
Saint Louis University
Southern Illinois University
The University of Texas at Austin
Washington University
Wayne State University
The University of Wisconsin-Madison

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights. Mention of commercial products, their manufacturers, or their suppliers in this publication does not imply or connote approval or disapproval of the product by Argonne National Laboratory or the U. S. Department of Energy.

Distribution Category:
Energy Storage-Electrochemic
(UC-94cd)

ANL/OEPM-79-2

FINAL REPORT ON

A SURVEY OF METALLURGICAL RECYCLING PROCESSES

PREPARED FOR

THE OFFICE FOR ELECTROCHEMICAL PROJECT MANAGEMENT
ARGONNE NATIONAL LABORATORY
UNDER CONTRACT NO. 31-109-38-4213

BY

950 3361

EIC CORPORATION
NEWTON, MASSACHUSETTS 02158

MARCH 1979

ACKNOWLEDGEMENT

This survey study of metallurgical recycling processes was carried out during the period from February 1, 1978 to January 31, 1979 under Argonne National Laboratory Contract No. 31-109-38-4213 at EIC Corporation, Newton, Massachusetts 02158.

The contributors to this study were:

✓J. Paul Pemsler, Principal Investigator
F. C. Brown, Senior Process Engineer
L. R. Moschini, Staff Chemical Engineer

This effort was directed by the ANL Office for Electrochemical Project Management, N.P. Yao, Director, with G. M. Cook as Project Manager.

ABSTRACT

In the year 2000, the United States will consume about 3.2×10^{15} BTU to produce the seven major nonferrous metals covered in this study: aluminum, copper, zinc, lead, nickel, magnesium and titanium. Of this amount, 82% will be used in the production of aluminum. It is projected that 0.6×10^{15} BTU will be saved by the recycle of secondary metals. Major opportunities exist for increasing the extent of recycle and thereby increasing the energy savings.

An inherent feature in the energistics of recycle is that physical processes such as magnetic separation, density separations, melting and in some instances vaporization are far less energy intensive than are chemical processes associated with dissolution and electrowinning. It is in the domain of scrap of complex composition and physical form, difficult to handle by existing technology, that opportunities exist for new chemical recycle technology.

Recycle of scrap metal of adequate grade is currently achieved through pyrometallurgical processes. Chemical reactions in reverberatory and blast furnaces are rapid, capable of removing significant impurity contents, and in many cases not very energy intensive. Hydrometallurgical processes when applied to scrap metals, on the other hand, involve chemical dissolution of the metal and its subsequent reduction. This route requires us to pay the energy price of metal reduction which is inherent in the free energy differences between the metal in its oxidized state and the metal in the metallic state. Reduction by electrowinning is particularly capital and energy intensive. The necessity of controlling gaseous pollutants from pyrometallurgical processes may, however, provide additional impetus to the development of hydrometallurgical recycle routes. One can foresee situations where the increased cost and complexity of the process required to reduce emissions to acceptable levels will make the hydrometallurgical alternative more competitive.

Almost all of the aluminum currently recycled, both cast and wrought metal, is reclaimed as cast alloys. At some future date, it will likely be necessary to have technology available to recycle scrap to wrought alloys. Toward that end development of the electrorefining technology of aluminum in the solid phase at low temperature in an aluminum chloride-sodium chloride salt bath appears particularly interesting.

Preliminary flowsheets are presented for the recovery of value metals from batteries considered for use in vehicular propulsion and load leveling applications. The battery types examined are lead/acid, nickel/zinc, nickel/iron, zinc/chlorine, lithium-aluminum/iron sulfide and sodium/sulfur.

A flow sheet has been outlined for an integrated hydrometallurgical process to treat low-grade copper scrap. While this process requires less energy than used for the production of primary metal, the energy and cost requirements are such that there is little incentive to develop this process to replace existing pyrometallurgical technology. However, a significant part of the energy requirement and cost associated with the hydrometallurgical flow sheet is in the electrowinning section. Development of chemical reduction alternatives to the electrowinning of copper are technically feasible and could lead to a more competitive position for hydrometallurgical recycling of copper scrap.

Only a small fraction of obsolete zinc scrap is currently recycled. A major untapped resource exists in metallurgical process dust which are collected in bag houses by the steel, copper, and zinc industries. Both pyrometallurgical and hydrometallurgical routes have been examined for reprocessing the dusts. A fully integrated hydrometallurgical process has been outlined by us, and costs and energy consumption derived, to recover zinc metal from electric furnace flue dusts. Costs and energy are high and the process does not appear to warrant development at this time.

Improvement in the recycle of magnesium is associated primarily with improved recycle in the aluminum industry where magnesium is an important alloy additive. Nickel and titanium recycle are associated with improved collection and sorting of stainless steel and specialty alloys.

TABLE OF CONTENTS

TABLE OF CONTENTS
(continued)

TABLE OF CONTENTS
(continued)

Section Page

TABLE OF CONTENTS
(continued)

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS
(continued)

LIST OF ILLUSTRATIONS
(continued)

LIST OF ILLUSTRATIONS
(continued)

LIST OF ILLUSTRATIONS
(continued)

LIST OF TABLES

LIST OF TABLES
(continued)

LIST OF TABLES
(continued)

1.0 INTRODUCTION

1.1 Purpose of Study

This study was undertaken to identify where new technology, especially that associated with hydrometallurgy and electrochemical technology, can lead to improved recycling of those metals commonly associated with the electrolytic industries.

A second part of the study is a preliminary examination of technology for recycle of metals contained in batteries which are being considered for vehicular propulsion and load leveling applications.

1.2 General Background

The interrelation among materials, energy, environment, and economics is no place better exemplified than in the field of metal recycle. The rationale for the recovery of scrap metals is almost intuitive. We have come to regard metals as a valuable commodity, expensive to mine and produce. In some instances the metals may be in short supply on a world-wide basis. In other cases domestic resources may not be available to use and we must rely upon imported ore or metal. Disposal of old scrap is an environmental problem which, in addition to aesthetic concerns, is quite expensive. Lastly, there is an enormous waste in energy when scrap metal is not reclaimed. It is this latter factor that is the prime motivating force in this study.

Institutional barriers to metal recycle have been well documented. Lack of financial incentive, insensitivity of industry and ignorance of the consumer all contribute to deficiencies in the recycle of metals. Ultimately however, the economics of recycle comes to bear directly on what may be achieved in a free economy. Scrap metal, flue dusts, drosses, etc. all represent ore materials. To the extent that they are concentrated and readily purified they are desirable ores and command a high price which may be a significant fraction of the primary metal price. While price fluctuations of scrap may also reflect the current marketability of a metal, over the long term the ability to economically process a particular scrap will determine whether or not it is recycled.

In recent years the rising costs of energy and the enforcement of even more stringent regulations designed to prevent environmental deterioration have begun to play an important role in metal recycle. The energy saving feature of metal recycle will be documented quantitatively below. As concern for the environment grows and as the standards for safe disposal of toxic materials become more stringent, the disposal cost of waste metals will continue to increase. It is then common sense to attempt to recycle as much secondary metal as is feasible and it is these new forces which impact the economics of metal recycle that will provide increased incentive to improve recycle technology.

While metals can be recycled, energy cannot be recycled, except for the utilization of some waste process heat. Metal recycle can therefore greatly reduce the energy cost associated with a given level of metal usage. In an expanding economy where energy availability will be an increasingly significant factor, the ability to utilize increasing quantities of metal each year will be associated with an energy penalty. The extent to which recycled metal, having a lower energy component, is utilized will determine the extent of this energy penalty. Metal recycle of course has its own limitations in that even total recycle of metal cannot meet the demand in a growth economy where the use of metal is growing at a rate of 2-6% per year and consumer end products may have lifetimes of 10 to 30 years.

Technologically there is a limit to the amount of a metal that can be recycled just as there is a limit to the grade of an ore which can be processed economically. As the scrap material from which the metal is derived becomes more and more dilute, it becomes both more expensive and more energy intensive to reprocess. Furthermore, as metal scrap becomes associated with difficult-to-remove impurities, both the cost and the energy required to effect recycling will increase, although not necessarily in the same proportion. At some point then, a limit is reached where the leanness of the scrap and its impurity content limits its ability to be recycled. It is here that new technology may make a major impact on the ability to reprocess scrap. New, less energy intensive and low cost process technology which can be developed can be of great value in promoting improved recycling of metals.

1.3 Types of Scrap

Scrap is generally divided into two classes: new or prompt industrial scrap, and old or obsolete scrap. New scrap is generated at primary smelters and production facilities. It is the result of the inability to obtain 100% yield during melting and casting and in fabrication operations. This scrap is well characterized and may then be rapidly and efficiently recycled to produce additional metal. While opportunities for improvement in the recycle of prompt industrial scrap may be found, in general, the processes are well managed. Old scrap on the other hand, comes from end products which are no longer useable and must be disposed of. From the point of view of metal recycle, the most significant sources of such scrap are those products which are sold directly to scrap dealers, such as automobile radiators, telephone switch boards, and electronic equipment. Another source of old scrap is dump scrap, which in general is widely distributed geographically. It is difficult to economically separate nonferrous metals from such scrap since these metals are present only in low percentages and are mixed with a wide variety of ferrous and organic material.

The efficiency of recycle of old scrap varies greatly from metal to metal and depends upon the end products for which the metal is used. In some instances uses are considered to be dissipative such as zinc in paints and pigments and magnesium as a protective anode for corrosion prevention. On the other hand, lead in a storage battery is readily reclaimed since all of the lead is contained within a single small package and recycling is a part of the distribution system of the industry.

2.0 SUMMARY AND CONCLUSIONS

1. In the year 2000, the United States will consume about 3.2×10^{15} BTU in the primary production of the seven major nonferrous metals covered in this study: aluminum, copper, zinc, lead, nickel, magnesium and titanium. Of this amount, 82% will be used in the production of aluminum. It is projected that 0.6×10^{15} BTU will be saved by the recycle of secondary metals using current technology. Major opportunities exist for increasing the extent of recycle and thereby increasing the energy savings.

2. An inherent feature in the energetics of recycle, and a common thread which runs throughout this study, is that physical processes such as magnetic separation, density separations, melting and in some instances vaporization are far less energy intensive than are chemical processes associated with dissolution and electrowinning. Improvements in physical separation including hand sorting, spot tests, etc. should be further developed wherever feasible. It is in the domain of scrap of complex composition and physical form, difficult to handle by existing technology, that opportunities exist for new chemical recycle technology.

3. Recycle of scrap metal of adequate grade is currently achieved through pyrometallurgical processes. Chemical reactions in reverberatory and blast furnaces are rapid, capable of removing significant impurity contents, and in many cases not very energy intensive. Also, specific volumes are relatively small and reactions are rapid so that throughput through these furnaces is fast. Hydrometallurgical processes when applied to scrap metals, on the other hand, involve chemical dissolution of the metal and its subsequent reduction. Specific volumes are relatively large and retention times longer so that adequate throughput requires larger facilities. This route also requires us to pay the energy price of metal reduction which is inherent in the free energy difference between the metal in its oxidized state and the metal in the metallic state. Reduction by electrowinning is particularly capital and energy intensive.

The necessity of controlling gaseous pollutants from pyrometallurgical processes may, however, provide additional impetus to the development of hydrometallurgical recycle routes. One can foresee situations where, for example, at a secondary lead smelter, the increased cost and complexity of the process required to reduce emissions to acceptable levels will make the hydrometallurgical alternative more competitive.

4. There is a very large energy incentive to increase the recycle of aluminum. The greatest potential which exists is to improve the collection efficiency and physical separation of the metal from other contaminants.

While the improvements in current recycle technology can be envisaged, there is no incentive to oxidize the metal from the zero valent state and subsequently reduce it electrolytically.

Almost all of the aluminum currently recycled, both cast and wrought metal, is reclaimed as cast alloys. At some future date it will likely be necessary to have technology available to recycle scrap to wrought alloys. Toward that end we recommend development of electrorefining technology to enable removal of impurities such as iron and silicon from aluminum scrap. Efforts should be concentrated on improving electrorefining aluminum in the solid phase at low temperature in an aluminum chloride-sodium chloride salt bath.

5. Recycle of copper scrap is a relatively efficient operation. High-grade scrap is processed with high yield at low energy consumption. Low-grade scrap is also handled by current technology but with lower yields and higher energy requirements.

A flowsheet has been outlined and capital and operating costs generated, for an integrated hydrometallurgical process to treat low-grade copper scrap. While this process requires less energy than used for the production of primary metal, the energy and cost requirements are such that there is little incentive to develop this process to replace existing pyrometallurgical technology. This is especially true since we have not succeeded in identifying a suitably large scrap resource which cannot be treated by current technology.

A significant part of the energy requirement and cost associated with the hydrometallurgical flowsheet is in the electrowinning section. Development of chemical reduction alternatives to the electrowinning of copper are technically feasible and could lead to a more competitive position for hydrometallurgical recycling of copper scrap.

6. Only a small fraction of obsolete zinc scrap is currently recycled. A major untapped resource exists in metallurgical process dusts which are collected in bag houses by the steel, copper, and zinc industries. Recycle of the zinc content of electric furnace steelmaking dusts either as metallic zinc or zinc oxide could lead to energy savings of the order of 5 to 10×10^{12} BTU/yr. Furthermore, the iron oxide residue could be recycled to the steelmaking furnace, thus solving a major environmental problem associated with disposal of the dusts.

Both pyrometallurgical and hydrometallurgical routes have been examined for reprocessing the dusts. A fully integrated hydrometallurgical process has been outlined by us, and costs and energy consumption derived, to recover zinc metal from electric furnace flue dusts. Costs and energy are high and the process does not appear to warrant development at this time.

Processes for treatment of dusts which deserve further consideration are 1) pyrometallurgical processes which combine the dusts with carbon, reduce and vaporize the zinc, and burn it to the oxide which is a readily salable commodity, and 2) a process which selectively leaches and recovers zinc oxide with concentrated ammonium chloride solutions.

7. Recycling of lead will be dominated by its principle use in SLI batteries. There is no incentive at this time to develop a hydrometallurgical process to recover lead from these batteries. Lead/acid batteries for electric vehicle propulsion and utility load leveling are discussed below.

8. Improvement in the recycle of magnesium is associated primarily with improved recycle in the aluminum industry where magnesium is an important alloy additive. Nickel and titanium recycle are associated with improved collection and sorting of stainless steel and specialty alloys.

9. Preliminary flowsheets are presented for the recovery of value metals from batteries considered for use in vehicular propulsion and load leveling applications. The battery types examined are lead/acid, nickel/zinc, nickel/iron, zinc/chlorine, lithium-aluminum/iron sulfide and sodium/sulfur. Physical separation is used where possible and the metals are reclaimed by pyrometallurgical and hydrometallurgical processes.

3.0 ENERGY CONSIDERATIONS

It is desirable to quantitatively assess the energy significance of recycling of the various metals so that we may focus on technological areas which have significant energy incentives. We have therefore collected data on each metal of interest. These data consist of demand, production, and primary and secondary energy content. A major purpose of this study is to identify the potential of new technology to improve metal recycle. Since new process development takes a number of years, we project these data to the years 1985 and 2000. The source of data as well as details of calculations are discussed separately for each metal in Section 4. We here present in Table 1 a summary of information for the year 2000. The metals of interest that have been chosen for study include aluminum, copper, zinc, lead, nickel, magnesium and titanium. All but lead are metals of importance to the electrolytic industry and are used in sufficient quantity to consume significant amounts of energy in their primary production. The metal lead was included in this study because of its significance in the lead/acid battery which is currently a vital part of the automotive industry. In the future the importance of lead may grow as a result of electric vehicular propulsion and the utilization of lead/acid batteries for utility load leveling.

Column 1 of Table 1 lists the metals of interest. In Columns 2 and 3 we give the primary and secondary metal demands. The sum of these two figures is the total demand for metal in the year 2000. The secondary demand is based on an estimate of what the secondary supply level will be in that year. Should the secondary supply of a particular metal be higher than the value listed, the primary demand would be correspondingly reduced. Nickel data in parenthesis reflect the high uncertainty in future domestic nickel production (see 4.5.1). In Column 4 we list primary production figures. In some instances where domestic production will account for all or nearly all of the primary demand, we will be self sufficient and possibly exporters of a particular metal. In other instances, we will have to be net importers of primary metal in order to meet our total demand. In Column 5 we give the primary energy content of the metal in question. This represents the total quantity of energy expended, including mining, milling and reduction, to produce the metal in a form ready for final product fabrication. The primary energy content of the different metals varies widely and depends upon the requisite energy expenditure for various steps required to produce the metal. These again are documented in detail in Section 4. In Column 6 we list the electrolytic energy content of the primary metal which is the quantity of electrolytic energy used in the production of the metal. In this, and all other energy calculations in this report, a conversion factor of 10,500 BTU/kWh is used. For those metals which are produced directly by

Table 1

Demand, Production and Energy Consideration in Metals of Interest in the Year 2000

METAL	Demand, Thousands of Tons		Primary Production Thousands of Tons	Primary Energy Content		Secondary Energy Content 10^6 Btu/Ton	Energy in Primary Production 10^{12} Btu	Energy Saved by Secondary Recycle 10^{12} Btu	Electrolytic Energy Saved by Secondary Recycle 10^{12} Btu
	Primary, as metal	Secondary, reused as metal		Total 10^6 Btu/Ton	Electrolytic 10^6 Btu/Ton				
ALUMINUM	15,800	2,000	12,600	210	134	20	2,650	380	268
COPPER	3,500	1,600	3,150	102	6.9	15	321	139	11.0
ZINC	1,700	200	800	60	38	19	48	8.2	7.6
LEAD	1,470	860	990	27	0	7	27	17.2	0
NICKEL	415	165	(270)	(144)	(20)	(15)	(39)	(21.3)	(3.3)
MAGNESIUM	365	30	365	358	180	20	130	10.1	5.4
TITANIUM	40	22	40	373	287	39	15	7.4	6.3

electrolytic processes such as aluminum, zinc and magnesium the fraction of the total energy content which in electrolytic energy is quite high. Other metals which are electrorefined such as copper and nickel have much lower electrolytic energy fractions of the total energy content. Some of the metals are produced by a number of different primary processes, and in these cases the electrolytic energy component represents a weighted average of the electrolytic energy content of the various processes, taking into account the fraction of metal produced by each process. Column 7 lists the secondary energy content which is the weighted average of the energy used to process secondary metal by the current technological recycle routes. It is immediately apparent that these values are only a small fraction of the energy required for primary production as listed in Column 5. This then is the energy incentive for metal recycle. Column 8 gives the total quantity of energy used in the year 2000 for the production of the primary metal calculated as follows:

Total energy in primary production = primary production

× primary energy content

In Column 9 we list the projected energy saved by secondary metal recycle calculated as follows:

Energy saved = (primary energy content-secondary energy content)

× secondary demand

These data are a quantification of the incentive for secondary metal recycle. The values are based on projections of secondary metal availability in the year 2000. Increased availability of scrap that can be processed by low energy technology will increase the energy savings. In the last column we give values for the quantity of electrolytic energy saved by secondary metal recycle calculated as follows:

Electrolytic energy saved = electrolytic energy content of

primary metal × secondary demand.

Consideration of the values in the last two columns establishes a rank of energy savings for the various metals. Even a small incremental improvement in recycling aluminum will result in a large energy saving. For the other metals we must examine the potential availability of scrap and the state of technology to decide an order of merit for encouraging new technology.

4.0 METALS

4.1 Aluminum

4.1.1 Statistics and Energy Considerations

Aluminum is the most abundant structural metal in the earth's crust and its use exceeds that of any other metal except iron. Aluminum is used extensively in the transportation, construction and electrical industries, and for containers and packaging, durable goods and mechanical equipment.

Aluminum metal is produced in various forms: ingot is a cast form suitable for working and remelting; commercially pure aluminum is of about 99.5% purity and is used primarily for high electrical and thermal conductivity, corrosion resistance and reflectivity. It is also available in the strain-hardened condition of higher strength and reduced ductility; aluminum alloys of over 100 compositions and a wide variety of properties are available either as wrought alloys or castings.

Primary aluminum is produced by the Hall-Héroult process of electrolysis of alumina in a molten bath of natural or synthetic cryolite. The alumina used must be purer than 99.5% Al_2O_3. The alumina is currently obtained by the Bayer process involving a caustic leach of the ore bauxite at elevated temperature and pressure followed by separating the resulting sodium aluminate solution and selectively precipitating the aluminum as the hydrated aluminum oxide ($Al_2O_3 \cdot 3H_2O$). An analysis of the energistics of the production of primary aluminum is given in Fig. 1. The total value of the primary energy content is 244 million BTU/ton of aluminum produced. The electrolytic energy component of production, i.e., the amount of energy used in the electrolysis of aluminum, is 168 million BTU/ton of aluminum.

Forecasts for the U.S. aluminum demand for the years 1985 and 2000 are given in Table 2 along with the data for 1976.

Major contingencies for the low forecast are the possible low growth rate of electrical energy used or changes in the means of transmitting electrical energy, and the substitution for aluminum in machinery, construction and containers. High forecast figures are based on the anticipated low cost of aluminum relative to competing materials such as copper and plastics.

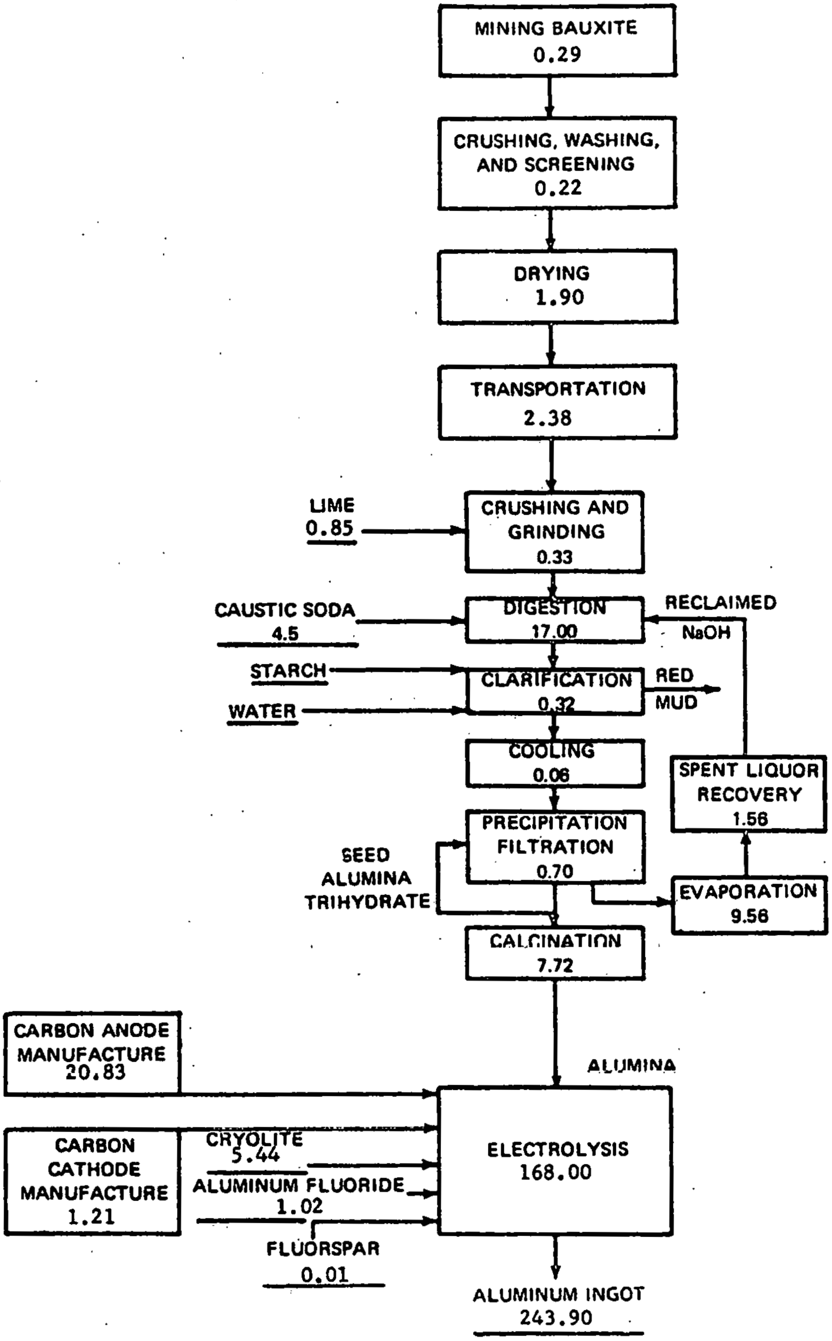


Fig. 1. Production of aluminum from bauxite (1).

Table 2

U.S. Aluminum Demand Forecast (2)
(Thousands of Short Tons)

	Probable			2000 Forecast Range		Average Annual Growth Rate
	1976	1985	2000	Low	High	Growth Rate 1976 - 2000 (%)
Primary	4,709	8,800	15,800	9,500	20,500	5.2
Secondary	409	850	2,000	1,500	2,500	6.8

Primary production in the United States given in Column 2 of Table 3 is estimated to be 85% of the primary demand in the year 1985 and 80% in the year 2000, which indicates we will be net importers of aluminum metal. The quantity of energy which will be used in the primary production of aluminum is given in Column 3 of Table 3. That portion of the energy used in the electrolysis of the metal is given in Column 4. Improvements in the efficiency of the Hall-Héroult cell and/or implementation of a new chloride process by Alcoa leads us to project energy savings in the electrolytic step of the order of 20% by the year 2000. Additional improvements are feasible and savings as high as 30% may be realized. We have conservatively retained the current figures for 1985.

The probable forecast for the year 2000 by end use, along with estimates of product lifetimes is given in Table 4.

A flow diagram for aluminum metal in the United States in 1976 is given in Fig. 2. The quantity of aluminum scrap recycled is estimated at 7.2 million tons. There is an extensive internal recycle loop of aluminum mill scrap within the primary plant. For every pound of sheet sold, the producer must start with about two pounds of molten metal. Since this scrap is in-house, efficient recovery can be achieved, and over 90% of new aluminum scrap generated in the manufacture of aluminum products is directly recycled to the production loop. In the United States it is estimated by the Bureau of Mines that only between 10 and 20% of aluminum that is put into use as industrial or consumer end products is eventually recycled as old scrap.

In the year 1976 consumption of aluminum-base scrap was 1,466,000 tons and a breakdown by category is given in Table 5.

The major recycle technology used for secondary aluminum is reverberatory furnace melting of aluminum scrap to hot metal. Aluminum cans are melted directly to form can sheet stock. The energistics of these processes are shown in Figs 3 and 4. All scrap categories in Table 4 may be assumed to be recycled by the flowsheet in Fig. 3 except for aluminum cans. A weighted average for the energy content of secondary aluminum based on the above is 20×10^6 BTU/ton.

We may now calculate the energy saved in recycling aluminum as (Primary Energy Content-Secondary Energy Content) × (Primary Production). The electrolytic energy saved is equal to (Secondary Demand) × (Electrolytic Primary Energy). Values for the years 1985 and 2000 are given in Table 6.

Table 3

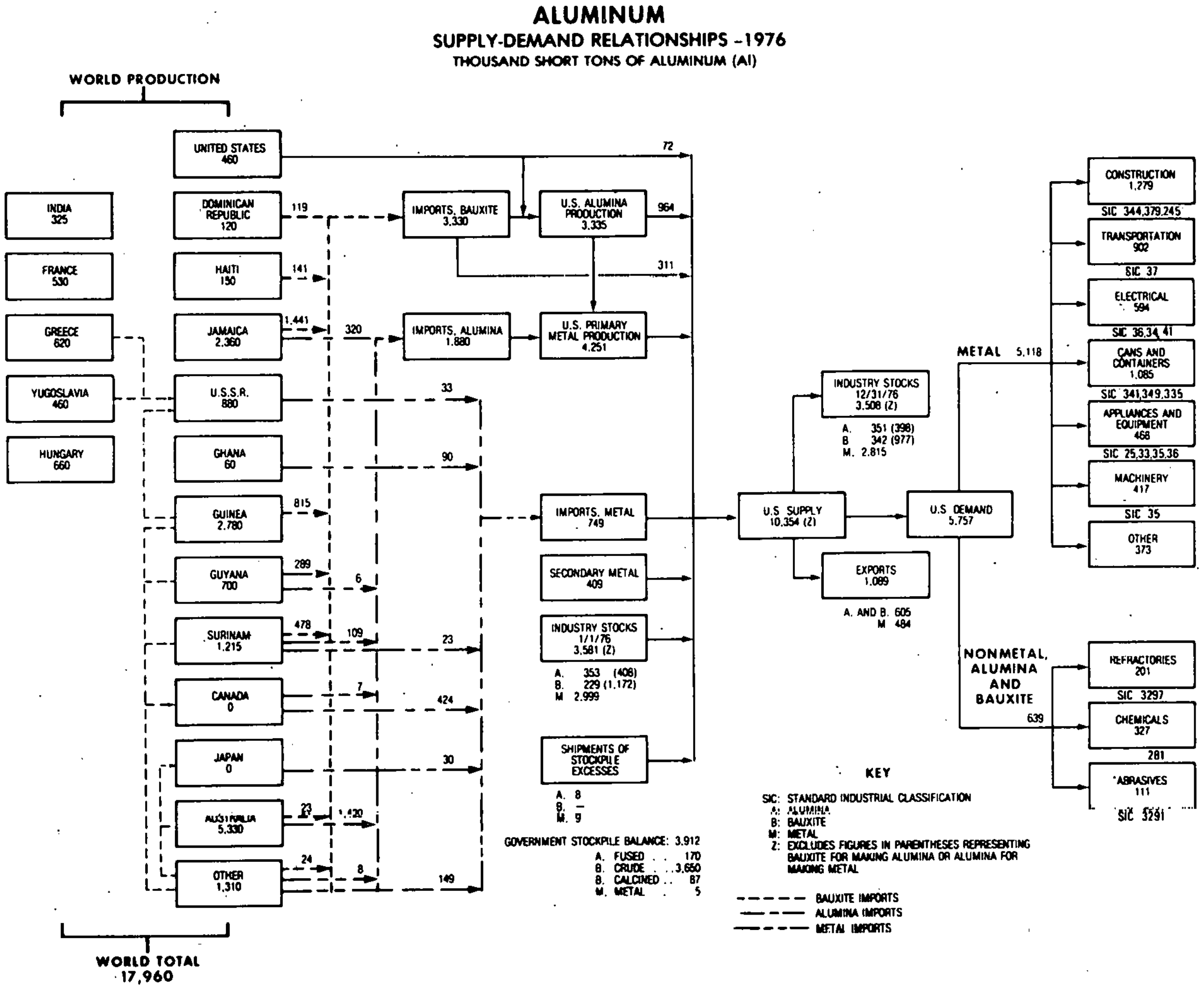
Energy Consumption in the Production of Primary Aluminum in the Years 1985 and 2000

Year	Primary Production (thousands of tons)	Total Energy, 10^{15} BTU	Electrolytic Energy 10^{15} BTU
1985	7,500	1.83	1.26
2000	12,600	2.65	1.69

Table 4

Use and Product Lifetime of Aluminum in the Year 2000 (2)

End Use	Lifetime (years)	Quantity (thousands of short tons)
Construction	40	4,000
Transportation	10	4,000
Electrical	20	2,500
Cans and Containers	2	2,500
Appliances and Equipment	10	1,800
Machinery	20	1,500
Other	20	1,500
	Total	17,800



ALUMINUM

SUPPLY-DEMAND RELATIONSHIPS -1976

THOUSAND SHORT TONS OF ALUMINUM (Al)

Fig. 2. Aluminum metal flow, 1976 (2).

Table 5

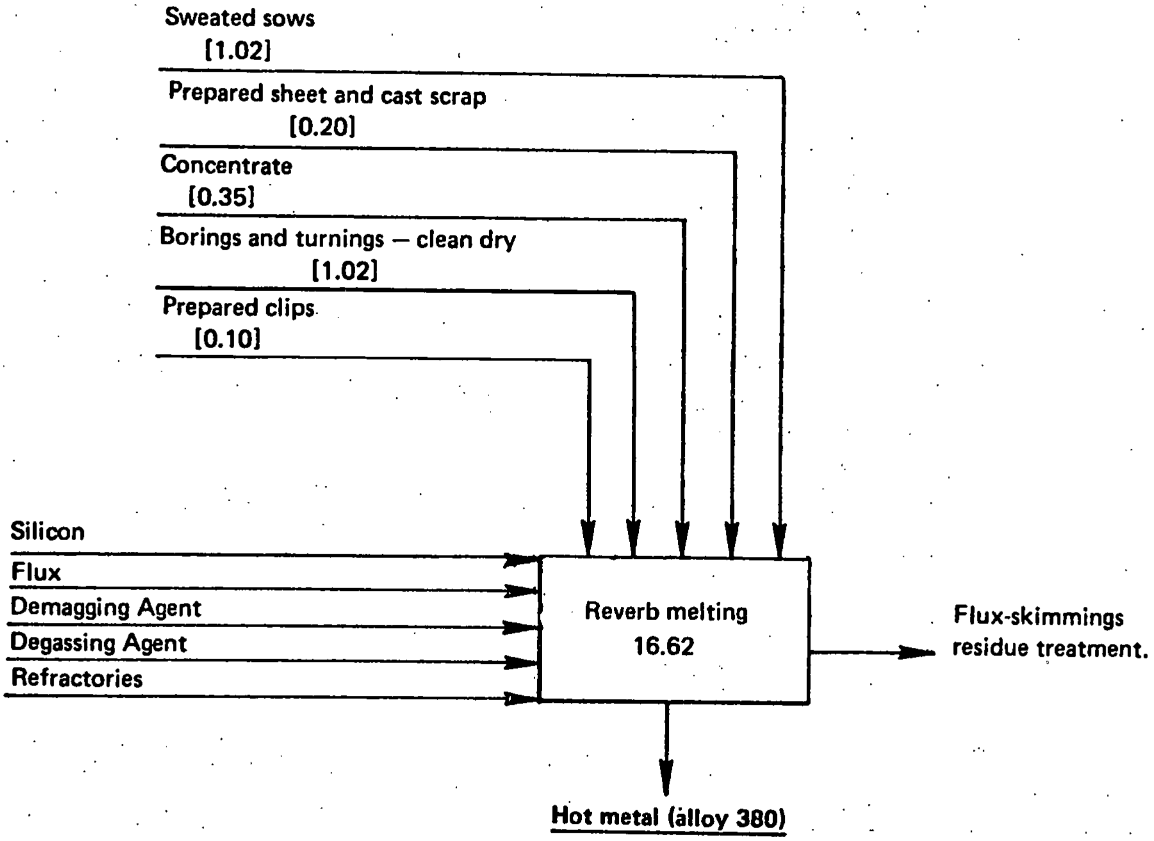
Purchased and Toll-Treated Aluminum-Base Scrap Consumed in 1976 (3)

	Old Scrap (thousands of short tons)	New Scrap (thousands of short tons)
Solids and clippings	-	564
Borings and turnings	-	149
Drosses and skimmings	-	229
Other (includes foil and high-irony scrap)	-	88
Castings, sheet, and chippings	209	-
Aluminum cans	103	-
Other (includes Al-Cu radiators and high-irony scrap)	104	-
	416	1,030

Table 6

Energy Saved by Aluminum Recycle

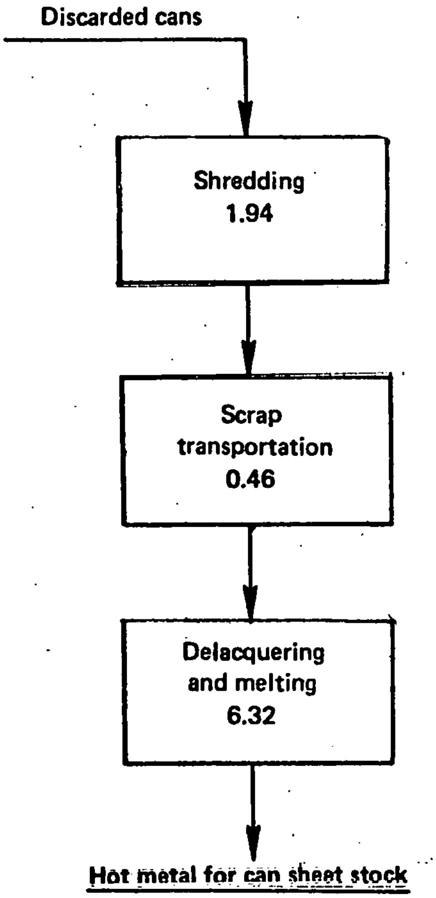
Year	Total Energy Saved, 10^{12} BTU	Electrolytic Energy Saved, 10^{12} BTU
1985	190	143
2000	380	268



SUMMARY

	Million Btu per ton of product
Process energy	19.30
Pollution control energy	0.25
Space heating	0.05
Total energy	19.60

Fig. 3. Reverb furnace melting of aluminum scrap to hot metal (alloy 380) (3).



SUMMARY

	Million Btu per ton of product
Process energy Pollution control energy Space heating	8.72
Total energy	8.72

Fig. 4. Recycling aluminum cans to hot metal for can sheet stock (3).

4.1.2 Sources of Scrap

Approximately 70% of the total aluminum scrap recycled is new scrap, the major categories of which are:

- Clippings, forgings and clean solid scrap from manufacturing operations.
- Borings and turnings from manufacturing operations which constitute, potentially, a highly segregated scrap of known purity but which are contaminated with cutting oils and tool chips.
- Drosses and skimmings from primary production or directly from the secondary operations themselves.

Of the total scrap recycled, 50% is in the first two categories, 15% consists of dross and skimmings, and about 5% consists of the new scrap of other categories.

Old scrap is classified in two main categories:

- Old castings, sheet, and clippings recovered from recycled products. These are typically contaminated with substantial amounts of undesirable material including massive and dispersed irony material, copper, zinc, other metals, and various organic coatings.
- Recycled aluminum cans which constitute a unique resource.

Currently, the ratio of old castings, sheet, and clippings to recycled cans is approximately 2 to 1, but it is anticipated that this ratio may drop to 1 to 1 as more effective collection techniques are developed for recovery of the high value, old can stock.

Only 24% of the total amount of recycled scrap is processed in primary smelters. More than half of the relatively clean clippings, forgings, and other solids are processed in secondary smelters despite the fact that, by the standards of old scrap processing operations, this material constitutes an extraordinary clean and well identified resource. In fact, the bulk of this material, along with the majority of other old and new scrap, amounting to 55% of the total, is processed in secondary smelters while approximately 20% of the total scrap is recycled to smaller remelt shops or is diverted directly to other uses.

It is significant that approximately one quarter of the total scrap processed in primary smelters is recycled can stock. Currently, 90% of the total aluminum cans recycled pass directly to primary smelters and are reconverted to alloys suitable for can body production.

Recent production patterns in the industry have been such that the majority of the casting alloys which are marketed are produced in secondary smelters, with primary smelter production devoted almost exclusively to wrought alloys. In excess of 80% of secondary smelter production, or approximately 60% of the total scrap recycled, is converted to casting alloys. Approximately 10% of the secondary smelter production appears as wrought alloys in billet form, with the balance being converted to deoxidizers, hardeners, and miscellaneous other consumptive uses. Typically, the wrought alloys tend to be low in silicon and iron content and relatively high in magnesium. Casting alloys on the other hand tend to be high in silicon and can tolerate significant iron contents, but must be low in magnesium.

Compositions of selected aluminum alloys and their uses, along with requirements for municipal aluminum scrap are summarized in Table 7. Since it must be anticipated that old scrap in particular, and to a lesser extent, new scrap arising from machining operations (borings and turnings) will be contaminated with irony material which may be too finely dispersed to remove by physical means, it would be difficult to recycle these materials to directly produce additional wrought alloys. On the other hand, as will be shown, it is possible to reduce high magnesium contents of aluminum scrap by a relatively simple refining step so that wrought alloy scrap can be converted to cast alloy material without undue difficulty. Currently, the demand for casting alloys is sufficiently high so that scrap recycle via the casting route is not a problem. Within 5 to 10 years, however, scrap volume and wrought alloy demand may reach the point when it will be necessary to recycle some scrap to wrought products.

Aluminum cans and aluminum lids on steel cans which are not currently recycled represent an enormous potential for future energy savings. By the end of 1978 it is estimated that there will be 100-billion aluminum beverage cans unreclaimed. Further, the number of aluminum cans produced is growing at a faster rate than are can collection projects so that the proportion recycled is diminishing. For example, in 1975 25.2% of the 16-billion cans produced were recycled while in 1977 only 23.6% of the 26-billion cans produced were reclaimed. Also, if the 26-billion steel cans with aluminum lids produced annually were returned for scrap, more than 25-million pounds of aluminum could be recovered.

Table 7

Composition Ranges of Selected Aluminum Alloys and Scrap Purity Requirements

	Wrought Alloys					Casting Alloys			Scrap		
Alloys	2036	3004	5657	6063	7016	380	390	295	No. 1 Municipal	No. 3 Municipal	General Municipal
Composition (%)											
Si	0.5	0.3	0.08	0.2-0.6	0.1	7.5-9.5	16-18	0.7-1.2	0.3	1.0	1.0
Fe	0.5	0.7	0.1	0.35	0.1	1.3-2.0	1.3	0.8	0.7	1.0	1.0
Cu	2.2-3.0	0.25	0.1	0.1	0.6-1.4	3.0-4.0	4.0-5.0	4.0-5.0	0.25	1.0	2.0
Mn	0.1-0.4	1.0-1.5	0.03	0.1	0.03	0.5	0.1	0.3	1.5	1.5	1.5
Mg	0.3-0.6	0.8-1.3	0.6-1.0	0.45-0.9	0.8-1.4	0.1	0.45-0.65	0.003	2.0	2.0	2.0
Cr	0.1			0.1					0.1	0.3	0.3
Ni									0.05	0.3	
Zn	0.25	0.25	0.03	0.1	4.0-5.0	1.0-3.0	0.1	0.3	0.25	1.0	2.0
Ti	0.15		0.1	0.1	0.03		0.2	0.2	0.05	0.05	
Pb									0.02	0.3	0.3
Sn					0.35				0.02	0.3	0.5
Bi									0.02	0.3	
Others											
Each	0.05	0.05	0.02	0.05	0.03		0.1		0.04	0.05	0.04
Total	0.15	0.15	0.05	0.15	0.1	0.5	0.2		0.12	0.15	0.12
Use	Auto Body Sheet	Can Bodies	Bright Auto Trim	Extrusions	Bumpers	Die Castings	Engine Blocks	Crank Cases	To Wrought Alloys		To Cast Alloys

The move toward better fuel economy has led to the increased use of aluminum in automobiles as a weight-saving measure. The 1978 automobiles have average contents of about 35 lbs of wrought aluminum and 75 lbs of castings per automobile. These values will increase by 1985 to about 110 lbs. of wrought and 175 of cast aluminum. A possible estimate for an automobile of the future is given in Table 8.

Many of these automotive alloys can be mixed and recycled but, since melts will contain impurities such as silicon and iron, as documented above, recycling by current practice can be only to casting grade material.

4.1.3 Properties of Aluminum Important in Recycling

The salient chemical and physical properties of aluminum which govern its processing are examined in this section. The key problem in recycling aluminum scrap is the effective and economic separation of undesirable impurities from the material. As a general proposition, separation techniques based on physical separations followed by melting will be less costly both in terms of capital and energy, than separation techniques based on chemical separations and electrolytic reduction. This is especially true in the case of aluminum because of the technology required, i.e., fused salt electrolysis to reduce the oxide.

The physical properties of aluminum are such that relatively inexpensive physical methods can be used to achieve efficient separations from the more common associated contaminants. The low density of aluminum compared with other ferrous and non-ferrous contaminants permits the use of heavy media separation techniques to float the aluminum free of heavier metals. Since it is non-magnetic, it may be separated from ferrous metals effectively by magnetic separation. Under proper conditions, eddy current techniques can be used to levitate aluminum and separate it from other non-ferrous impurities. This is the so-called "aluminum magnet". Finally, its relatively low melting point can be used to preferentially melt aluminum from massive amounts of higher melting impurities where shredding or other size reduction would be impractical and/or ineffective in physically liberating the aluminum from the other metallic contaminant.

The high reactivity of aluminum makes it difficult to conceive of methods for constructing economic, integrated processes for chemically based separation and purification of aluminum scrap. It is unlikely, for example, that a process will be found to preferentially dissolve or oxidize commonly occurring impurities and then to remove them while keeping the massive aluminum in the metallic state. Aluminum itself can often be preferentially dissolved or oxidized but will then have to be re-reduced. This can be done conventionally by the Hall route or by alternate fused salt electroreductions which are likely to have only marginal energy savings.

Table 8

Aluminum Use in Automobiles of the Future

Alloy	Fabrication	Wt, lbs.
390	Casting	100
355, 356	Casting	75
7021, 7046, 7029	Stamping	40
6010 or 2036 Series	Stamping, etc.	40
Clad Materials	Radiators, etc.	30

The ease of chlorination of alumina under reducing conditions and the high volatility of the chloride has served as the basis for several new approaches to primary aluminum production (4). Thus, in the Alcoa process, Al_2O_3 is chlorinated in the presence of coke and the resulting $AlCl_3$ fed to an all-chloride electrolytic bath from which aluminum is electrowon. The Alcan process melts bauxite and coke in an electric furnace to produce a crude alloy of about 50% aluminum which is then reacted with $AlCl_3$ to form aluminum monochloride, AlCl. On cooling the AlCl in a stream of molten aluminum it disproportionates to Al and $AlCl_3$. The Monochloride Process uses $AlCl_3$ passing through a bed of calcined bauxite and coke to form the monochloride which is contacted with sprayed molten lead where the $AlCl_3$ disproportionates to form molten aluminum on top of the lead. The Toth Process chlorinates the oxide feed mixed with coke directly with chlorine and $SiCl_4$. The $AlCl_3$ formed is fractionally condensed to a pure liquid Al_2Cl_6 which is then reacted with metallic manganese particles in a fused salt to give aluminum powder. The manganese is subsequently regenerated.

It is possible that chloride processes which may be adaptations of one of the above processes could be used for scrap metal purification. Of the common alloying elements, only magnesium has a substantially higher free energy of formation of the chloride than does aluminum and can be preferentially removed from molten aluminum by chlorination. However, the selective chlorination of aluminum and the disproportionation reaction discussed above could be used as a basis of purification.

4.1.4 Current Practice in Recycling

The essential feature of all processes presently used to recycle scrap aluminum is the melting furnace into which the treated scrap is charged, and from which the molten product and segregated impurities are withdrawn. Since this operation is central to all scrap treatment, it will be described in some detail, and other processing steps, which are specific to the origin of the scrap, will then be described. A schematic representation of the operations involved in scrap aluminum processing is shown in Fig. 5.

Typically, scrap melting is carried out in a reverberatory furnace of simple design without extensive pollution control or energy recovery facilities, although it is within the current state of technology to improve the operations with little cost penalty. A heel of molten material is kept in the furnace to promote rapid melting of the scrap which is charged. The scrap, which may have been bailed or compressed to increase its density, is charged to the furnace through an external hot well, and

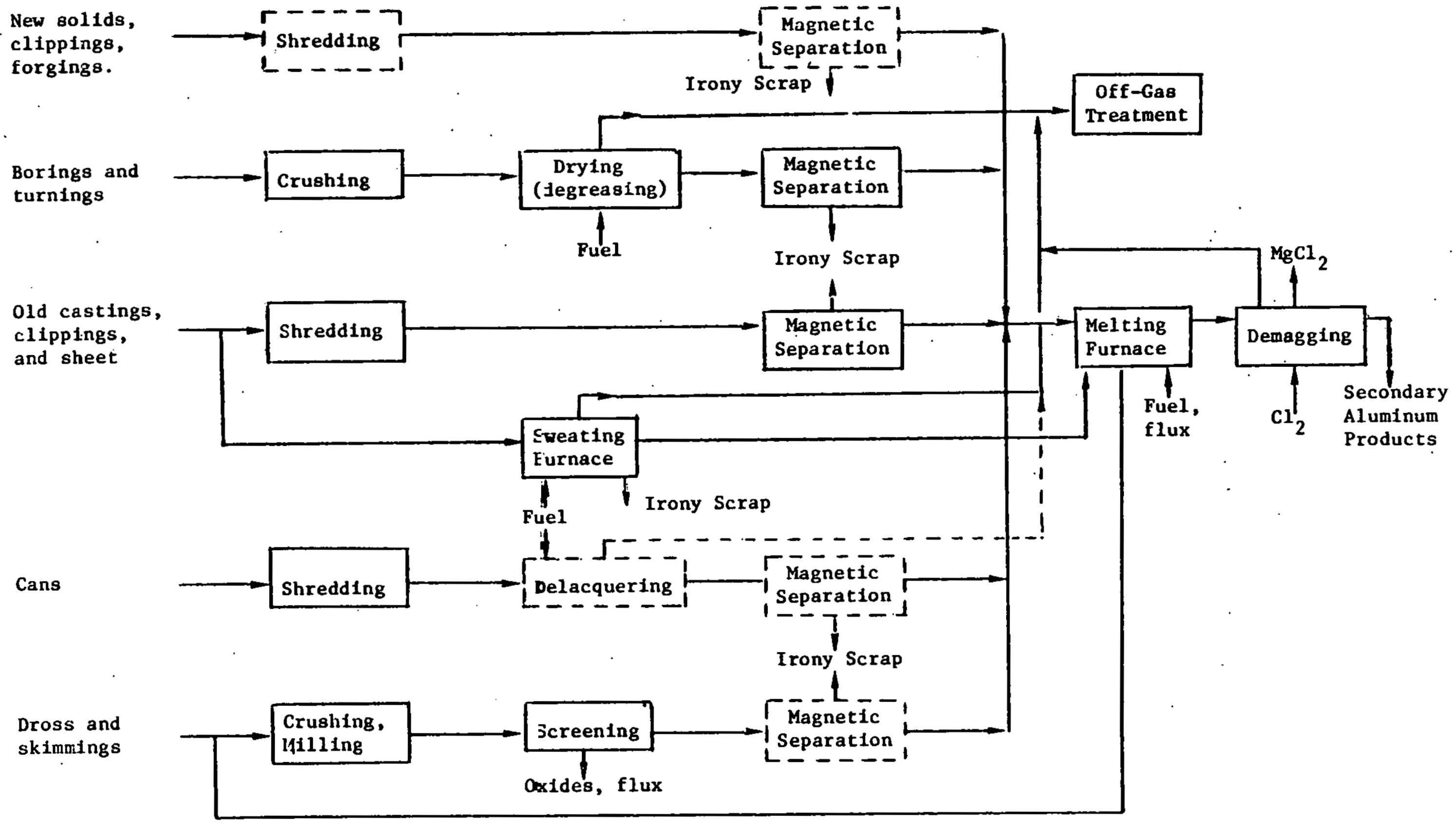


Fig. 5. Scrap treatment processes, material, and energy flows.

energy for melting is supplied by direct combustion of fuel above the internal hearth. Operations are carried out batch-wise, typically on a twenty-four hour cycle, in which the charging and melting time may be of the order of eight hours. Impurities carried into the furnace with the unclean scrap along with oxides which are formed during the melting process are removed by fluxing. The flux material, a mixture of sodium and potassium chlorides, is charged to the furnace in ratios of from 1-50 to 1-5 pounds per pound of scrap, depending upon scrap purity. Up to one pound of impurity per pound of salt is removed from the furnace as a viscous or semi-solid dross. The melt is then sampled to determine its composition and the further purification and/or alloying required. Of the impurities present at this stage, only magnesium can be removed by established means. This is most advantageously carried out by sparging chlorine into the bath under carefully controlled conditions and skimming the magnesium chloride which is formed from the bath. This process is called "demagging". Additional virgin aluminum or very high purity scrap may be added to dilute the remaining impurities to the desired level. The melt is then allowed to settle and the product is tapped from the furnace and cast to billets for further use, or transferred molten as "hot metal" for further processing.

New scrap consisting of clippings, forgings, and other solids may be remelted directly and recycled as wrought products if that is their origin. Metal recovery by this route is over 95%, and energy requirements are low at less than 5 million BTU per ton. Pollution control requirements and waste product formation are negligible and the only processing requirement is to segregate scrap by alloy type if subsequent composition adjustment by dilution is to be minimized.

Borings and turnings, which are inevitably contaminated with cutting oils, must be treated more extensively. Typically, they are crushed or bailed to break stringers and produce a more dense product for shipping or further processing. While solvent degreasing might be used, current industry practice is to degrease the scrap directly with combustion gases under slightly reducing conditions so as to volatilize organic materials. Combustion off-gases are then treated in an after-burner and the degreased scrap may be subjected to magnetic separation for removal of associated iron from cutting tools.

Scrap from aluminum cans may be treated in a similar manner to remove lacquers prior to furnacing, although this need not be done if higher metal losses to dross are accepted.

If old casting scrap is contaminated with massive iron, current practice is to "sweat" the aluminum from the iron by heating the mass of metals under slightly reducing conditions to a temperature above the melting point of aluminum but below that of iron. The resulting molten metal is not of high purity, containing significant amounts of dissolved iron, copper, zinc, and other impurities. Old sheet stock and clippings not containing massive iron are typically shredded and subjected to magnetic separation for iron removal prior to reverberatory melting.

Finally, drosses and skimmings are reworked for recovery of their metallic aluminum content, which is highly variable depending upon operating practice, the extent of fluxing, and the purity of the starting material from which the dross was removed. The dross consists of finely divided metallic aluminum, aluminum oxides, other oxides and inert material, and spent chloride salts. Best current practice in recycling drosses and skimmings is to cool the drosses as rapidly as possible, crush and/or mill the cooled material. Solids are then screened to effect a separation between the finer oxides and salts and the larger metallic aluminum particles, the latter being recycled to the melting furnace.

Historically, little attention was devoted to controlling emissions from secondary aluminum production operations. The main emissions from the various treatments steps are (a) combustion off-gases from the melting, degreasing and sweating furnaces, (b) fugitive smoke and fumes from the furnaces, (c) off-gases from the demagging step, (d) dusts from the material handling operations, and (e) solid residues from the physical separation steps and from dross recovery operations. All of these emissions can be adequately controlled using existing methods to more carefully control the operation, and with conventional equipment to treat effluents. This would, however, add an element of complexity and cost to an industry whose primary efforts have not been directed towards processing technology, but towards scrap material acquisition.

Secondary aluminum processing has evolved in response to classic technical and economic factors. Current practice in primary aluminum production is a capital intensive, mature technology based on the Bayer-Hall process involving the electrolytic reduction of alumina in molten cryolite. The alumina, derived from bauxite, is of extraordinary purity when compared to starting materials for other important primary metal production processes. It has not been technically feasible to recycle even relatively clean, carefully segregated scrap directly to the reduction cell. Operation of primary production facilities has, of necessity, been much more carefully controlled than typical remelt shops.

The electrolytic reduction of aluminum is inherently an energy intensive and therefore costly process, requiring a theoretical energy of approximately 2.6 kilowatt hours per pound, while the theoretical energy requirement for remelting aluminum is of the order of 0.2 kilowatt hours per pound. While practical energy requirements are much higher for both reduction and melting, in current practice the energy cost for remelting amounts to only 5 to 10% of that for fused salt electrolysis. Furthermore, the relatively simple reverbatory melting furnace is inherently less costly than the cells used to reduce alumina in molten cryolite. Recent estimates have put the cost of a scrap remelting facility at approximately $100-200 per annual ton of capacity. Primary aluminum production facilities, on the other hand have been estimated to cost approximately $1500 per annual ton of capacity. Direct operating costs for the production of aluminum from alumina are approximately 35¢/lb, or 3/4 of the total production costs from bauxite. The operating costs of a modest sized remelt shop (6,000 tons per year) on the other hand have been estimated to be less than 4¢/lb. Since, on a weight basis, scrap aluminum is recovered essentially completely in the metallic form, there is no incentive to reoxidize it, attempt to purify the oxide mixture, and then subject it to a costly and energy intensive reduction step.

4.1.5 Alternatives for Scrap Recycle

A factor which will affect scrap recycle technology in a major way is the involvement of the primary producers in secondary recovery. While, in the past, the large primary aluminum producers were content to allow small secondary smelters to account for scrap recycle, in recent years four major factors have converged to force the primaries into the secondary aluminum business:

1) The environmental aspects of the aluminum can.

2) The large energy savings inherent in recycle and the need to conserve energy.

3) Pressure on the price of ore material by the bauxite cartel.

4) A production short-fall is expected in the early 1980's and conventional recycle processes can be built and operated for approximately 10% of the cost of new primary production capacity.

The potential financial reward for improving metal recoveries is significant. Even if incremental recovery costs are double those currently born in scrap processing, i.e., approaching 20% of the cost of primary aluminum reduction, the cost savings are significant and the increased amount of aluminum to be recovered from improved dross, skimmings, and old casting treatment could easily amount to 10% of the current scrap production. While it has been reported that in excess of $65 million has been devoted to research and development efforts for new primary aluminum production processes, no data have been released on the magnitude of efforts which have been devoted to developing new technologies for secondary aluminum recovery.

In the past, with the exception of government sponsored work in physical separation techniques, the work on melting and purification processing has been fragmented, evolutionary in nature and devoted mainly to equipment re-design and operating improvements, for example, to reduce fuel consumption and improve environmental control. With the advent of the major primary aluminum producers entering the secondary recovery market, it is highly likely that significant research and development will be carried out in central industrial research facilities.

The physical separation of impurities from aluminum scrap is a relatively inexpensive and environmentally benign operation compared with most aspects of primary aluminum production. The melting operation with attendant fuming and problems associated with dross removal and disposal are troublesome environmentally by current standards, but the technology involved is old and can be improved upon substantially. Indeed, advantage should be taken of the possibility for improved metal recoveries which will inevitably arise from requirements for tighter process control which will be needed to control emissions. For example, more efficient and less costly demagging operations have been explored in an effort to reduce atmospheric emissions of volatile chlorides. These processes, while requiring the development of some new hardware, by and large have resulted from nothing more than the application of well-known engineering principles, e.g., staged, countercurrent contact, etc. to a new problem area.

The prospects for improved recycling of aluminum scrap may be addressed conveniently by examining the characteristics of each category:

- New, clean scrap consisting of clippings, forgings, and solids are currently recycled in a highly efficient manner. It is unlikely that significant improvements can be obtained except in the area of higher fuel efficiencies and other operating improvements in the melting furnaces, which should be effected by the application of currently available technology.

- Recycle of aluminum cans is also a relatively efficient operation with a high metal recovery and a product of acceptable purity for the intended reuse. The presence of a conversion coating and lacquer and pigments contribute to the formation of dross and can result in losses of aluminum of the order of 3-4% of the charge. Recoveries might be improved even further if more effective delacquering techniques could be developed, or probably alternative lacquering formulations could be derived which would lend themselves to a more easy removal at modest process conditions.

- Borings, turnings, and certain items of old scrap which are heavily contaminated with machine oils and other turnings, might also be recovered at higher yield if more effective cleaning techniques were developed. Successful adoption of physical techniques, such as solvent degreasing, would yield collateral benefits such as the reduction in air pollution problems attending the ineffective treatment of combustion off-gases from conventional oil removal processes.

- Recovery of aluminum by sweating massive old scrap, such as castings, could be improved significantly if more effective physical techniques could be developed for sorting or for the initial size reduction and physical separation than those currently used. This may well require the development of more effective, economic magnetic, eddy current, and heavy media techniques. Some equipment development effort may also be warranted to improve material handling techniques, emission control, and fuel economy.

- Drosses and skimmings, which represent approximately 15% of the scrap currently recycled, present interesting possibilities for improved efficiency since recoveries may be as low as 50% using current techniques. It has been shown that metal recovery from the drosses may be improved by careful control of fluxing conditions, rapid cooling of the skimmed material, and careful crushing and screening of the cooled materials. The soluble salts may then be removed by dissolution and, following evaporation, recycled to the melt furnace for reuse as flux. The residues from dissolution containing aluminum and other oxides and miscellaneous impurities, are currently disposed of or sold as a lower value material for their impure alumina content. However, since the alumina in the residues is already oxidized, it may be justifiable to purify it hydromatallurgically as a feed for electroreduction.

During the next ten to twenty years as more automobiles with higher aluminum contents are junked, it will be increasingly desirable to recycle wrought alloys from auto scrap to their original wrought composition. Efforts are already being made in this direction on several fronts:

1) Wrought alloys which are compatible in recycle have been developed.

2) Wrought alloys are being studied which have higher tolerance for silicon and iron.

3) Automotive designs are being examined to permit dismantling of aluminum components prior to compaction and shredding.

4) Improved physical separations of components such as "chunky" and "fluffy" fractions to separate cast and wrought auto parts are being developed.

As auto recycle increases, chemical separations may eventually be needed to remove such additional impurities as zinc and manganese in order to optimize recycle efficiency. Eventually dump recycle may introduce other unwanted impurities such as tin and lead into the smelter.

4.1.6 Refining of Aluminum

4.1.6.1 Spinning Nozzle Inert Flotation

A recent addition to aluminum refining technology is the spinning-nozzle inert flotation (SNIF) process now in use at Anaconda Aluminum Company's Montana plant (5,6). Inert gas in the form of very tiny discrete bubbles provides a large surface area of contact between the gas and molten aluminum. Hydrogen is rapidly swept from the melt and, reportedly, non-metallic particles such as carbides and nitrides adhere to the bubbles and are floated into the dross. The major advantages of the process are considered to be the elimination of pollution associated with chlorine fluxing and the increase in throughput of the refining furnaces resulting from the elimination of the long holding times required for settling in the conventional process. Costs are reported to be ∿0.1 cent per lb.

4.1.6.2 Solidification Purification

Reynolds metal has a patent (7) on a process in which the purified metal is pulled from the molten state. Ingots in the 12 to 20" range may be produced with upgraded aluminum contents of about 2%, i.e., from 96 to 98% or 98.5 to 99.9%. Yields are only 80% and the reject portion contains appreciable amounts of aluminum. Although the impure fraction could be sold for deoxidation of steel, it is not clear that the overall economics of the process will warrant its utilization.

4.1.6.3 Molten Salt Electrorefining

Aluminum may be electrorefined by the Hoopes process (8) which uses a three-layer cell as shown in Fig. 6. Aluminum is transferred electrolytically from a molten anodic alloy through a mixed chloride-fluoride molten salt electrolyte to a high purity molten cathode at the top of the cell. Current efficiency of the cell is near 100%. The theoretical emf for aluminum transfer is in the millivolt range and overvoltage due to polarization is only about 1.0 to 1.2 volts. The conductivity of the electrolyte is, however, rather poor and since it is necessary to maintain a fairly thick electrolyte layer (about 15 cm), the total cell voltage is about 5 to 7 volts and the power consumption is high at 8 to 10 kWh per pound of aluminum (168 to 210 × 10^6 BTU/ton). Although the process is still used by Alcoa in the United States and is used in several countries abroad, it accounts for only a very small production of high priced pure grade aluminum for use in the electronic industry.

There is extensive literature on the electrodeposition of aluminum in the solid phase from the binary salt system aluminum chloride/sodium chloride. Although most of the work is directed toward electroplating, there are some papers devoted to refining of aluminum. Howie and Macmillan (9) have reviewed the work in this area through 1972 and the discussion below is based on their paper. Collins first succeeded in electroplating aluminum onto steel from an $AlCl_3$/NaCl bath in 1952. He used a current density of 16 mA/cm^2. Midorikama studied the effect of the cathode material, electrolyte composition and bath temperature on the nature of electrodeposited aluminum. Good deposits were obtained on a lead cathode from an $AlCl_3$/NaCl bath at about 90% current efficiency with current densities of 1-3 mA/cm^2 and a temperature of 160°C. The bath was sensitive to iron contents greater than 10 ppm which lowered current efficiencies and roughened the aluminum deposit. Using an $AlCl_3$/NaCl/KCl electrolyte, Midorikama found that superimposing a.c. on the direct current and adding $PbCl_2$ at 10-100 ppm prevented the recurrence of rough deposits of aluminum. Miyate studied the effect of current density on deposition using the $AlCl_3$/NaCl eutectic at 175°C. Satisfactorily smooth plates were obtained at a current density of 20 mA/cm^2 with a current efficiency of 85%.

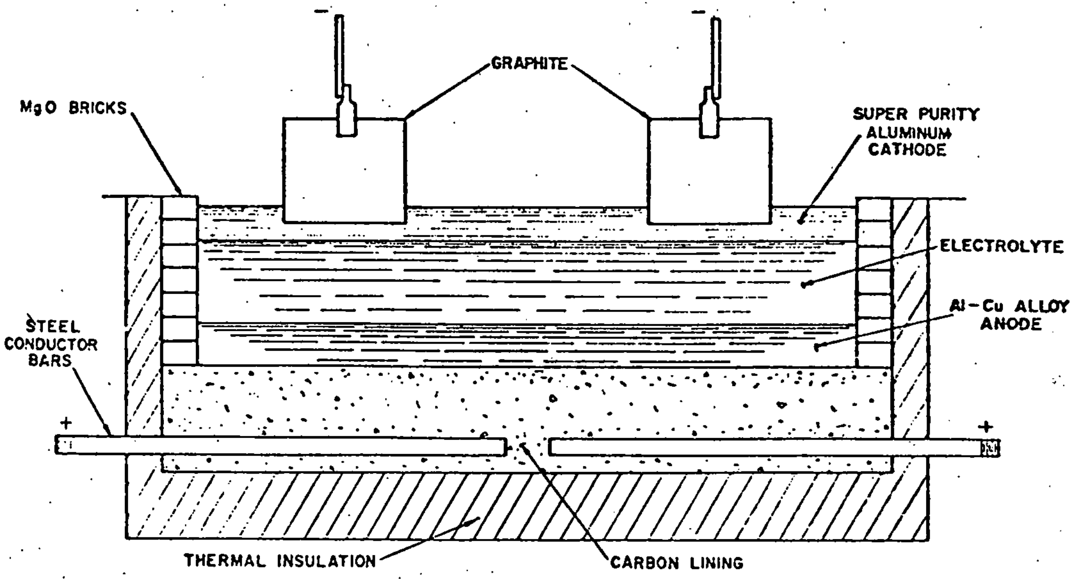


Fig. 6. Three-layer refining cell.

In Howie and Macmillan's own study they demonstrated the value of maintaining hydrogen chloride contents in the bath of not less than 0.07 w/o. They were able to obtain a coherent, dendrite-free plate at current densities up to 16 mA/cm^2 and current efficiencies of 85%. Continued plating consumed the hydrogen chloride which resulted in the current efficiency improving to near 100%, but at the expense of a progressive deterioration of plate quality.

4.1.6.4 Organic Electrolyte Electrorefining

Electrodeposition of aluminum from organic electrolytes offers an alternate to molten salt electrolyte systems. Since high temperature is unnecessary and the possibility exists of using high surface area electrodes, certain benefits might be inherent in such a process. Davenport and Capuano (10) have covered this option in a paper discussing previous literature and their own experimental program. To date, organic based electrolytes have been used only for metal finishing plating in which very small amounts of metal are deposited at low current densities ($\sim$10-20 mA/cm^2). Typical systems have $AlCl_3$ or $AlBr_3$ dissolved in benzene or ethyl bromide, or $AlCl_3$ and LiH dissolved in ether. No organic electrolyte has yet been found which survives under conditions of high current deposition for long periods of time. The authors list three intrinsic problems of organic electrolytes for heavy use: (a) relatively low conductivities ($\sim 10^{-2}$-$10^{-3}\Omega^{-1}cm^{-1}$) which lead to temperature problems in the cells with high current flow; (b) reaction of the gaseous anode product (oxygen or halogen) with the electrolyte; and (c) decomposition of the organic electrolyte under heavy current loads. Cathode efficiencies of the order of 70-80% were observed at current densities of the order of 10 mA/cm^2, but efficiencies decreased rapidly to the order of 30% at cathode current densities of the order of 40 mA/cm^2. $AlBr_3$ in benzene or ethylbenzene gave the best results as plating baths but the authors conclude that for electrowinning aluminum "considerably more work remains before organic electrowinning becomes a reality".

4.1.7 Conclusions

There is a very large energy incentive to increase the recycle of aluminum. The greatest potential which exists is to improve the collection efficiency and physical separation of the metal from other contaminants. While improvements in current recycle technology can be envisaged, there is no incentive to oxidize the metal from the zero valent state and subsequently reduce it electrolytically.

Almost all of the aluminum currently recycled, both cast and wrought metal, is reclaimed as cast alloys. At some future date it will likely be necessary to have technology available to recycle scrap to wrought alloys. In Section 5.2 we consider alternatives and recommend further study.

4.2 Copper

4.2.1 Statistics and Energy Considerations

Copper, known and used in antiquity, became one of the most important metals of the industrial era. Its electrical and thermal conductivity and corrosion resistance have made it almost indispensable in the manufacture of electrical equipment, power distribution systems, air conditioning and plumbing. Only in recent years has substitution become significant and now copper competes with aluminum, plastics and steel for many of its applications.

Copper is produced in three industrial grades: tough-pitch copper has a controlled oxygen content and is cast from electrolytic or fire refined metal; oxygen-free copper is cast without additives from refined copper under deoxidizing atmosphere; and deoxidized copper where the oxygen content of refined copper is tied up metallurgically by additions of deoxidizers such as phosphorus.

Copper-base alloys including brass, bronze, and cupro-nickel are cast into ingots for use by foundries and brass mills where solid, extruded and forged products are produced.

Primary copper is produced mostly from sulfide ores which are concentrated by flotation and smelted with suitable fluxes in reverberatory furnaces where silicates and light impurities are slagged off. A liquid matte of copper, iron and sulfur is then transferred to a converter where air is used to burn off the sulfur as SO_2 and oxidize the iron to the slag phase. The blister copper produced is partially refined in a furnace, cast into anodes, and electrorefined. The refined copper is generally cast into wirebars and other shapes to be shipped to fabricators.

Recently, newer pyrometallurgical processes have been developed to replace the outmoded reverberatory furnace which is wasteful of energy and generates large amounts of off-gases containing low concentrations of SO_2. Foremost among the newer methods are electric-furnace matte smelting, flash smelting, and the Noranda reactor. Currently, electric furnace matte smelting is carried out in the United States at the Anaconda complex in Butte, Montana, and Inspiration Consolidated Copper at Miami, Arizona. Flash smelting is used by Phelps Dodge at Hidalgo, New Mexico, and Kennecott has recently put Norando reactors on stream at Garfield, Utah.

During the mining of copper, large quantities of overburden having a copper content less than the currently acceptable assay are discarded into dumps. Some of these dumps are leached with sulfuric acid generated by the reaction of water with pyrite and other sulfur-bearing minerals in the dump. The resulting dump leach solution is contacted with scrap iron in special reactors and the copper is "cemented" onto the iron as metallic copper. This impure cement copper is added, along with copper concentrate, to the reverberatory furnace as part of the charge. Currently, about 10-15% of pyrometallurgically produced copper comes via the cementation route.

In recent years hydrometallurgy has emerged as an alternate technology for the recovery of copper. This new technology is being developed partly due to environmental constraints at smelters and partly because certain ore bodies lend themselves more readily to this method. In particular, copper carbonates and silicates are not amenable to concentration by floatation and may be leached in heaps or vats with sulfuric acid to produce acidic copper sulfate solution. Copper may be recovered from this solution either by cementation with iron or by direct electrowinning. It has become common practice to purify the copper solution by liquid ion exchange prior to electrowinning. It is only in the past few years that a market has begun to develop for directly electrowon copper.

Although considerable effort has been directed to the development of hydrometallurgical processes for chalcopyrite-containing ores and a number of pilot plants have been successfully run, there is currently no copper produced in the United States from sulfide concentrate by a hydrometallurgical route. It is probable that the decrease in demand since 1973 and the world oversupply has delayed plans for the introduction of these new hydrometallurgical processes.

An analysis of the energistics of production of primary copper is given in Figs. 7 and 8. Figure 7 shows data for cement copper obtained by dump leaching which, in turn, becomes part of the smelter feed. Figure 8 presents a detailed analysis for the conventional mining and smelting process.

Data for the Noranda reactor (including electrorefining) is contained in a report by Development Sciences, Incorporated (DSI) and the energy usage is given as 29.6×10^6 BTU/ton Cu, excluding mining and concentration (11). The DSI estimate for a conventional smelter is 41.4×10^6 BTU/ton Cu, in good agreement with the value from the Battelle study in Fig. 8 of 45.6×10^6 BTU/ton Cu. The large decrease in energy consumption comes from the ability of the newer designs to utilize a portion of the energy inherent in the oxidation of the sulfur content of the concentrate.

The relative energy use in conventional vs. newer smelting is also the subject of a recent paper by Schultz (12). His case is not identical to those above since he does not include precipitate copper in the charge. However, the relative values are in excellent agreement with the Development Science study. Schultz estimates roughly comparable energy values for the

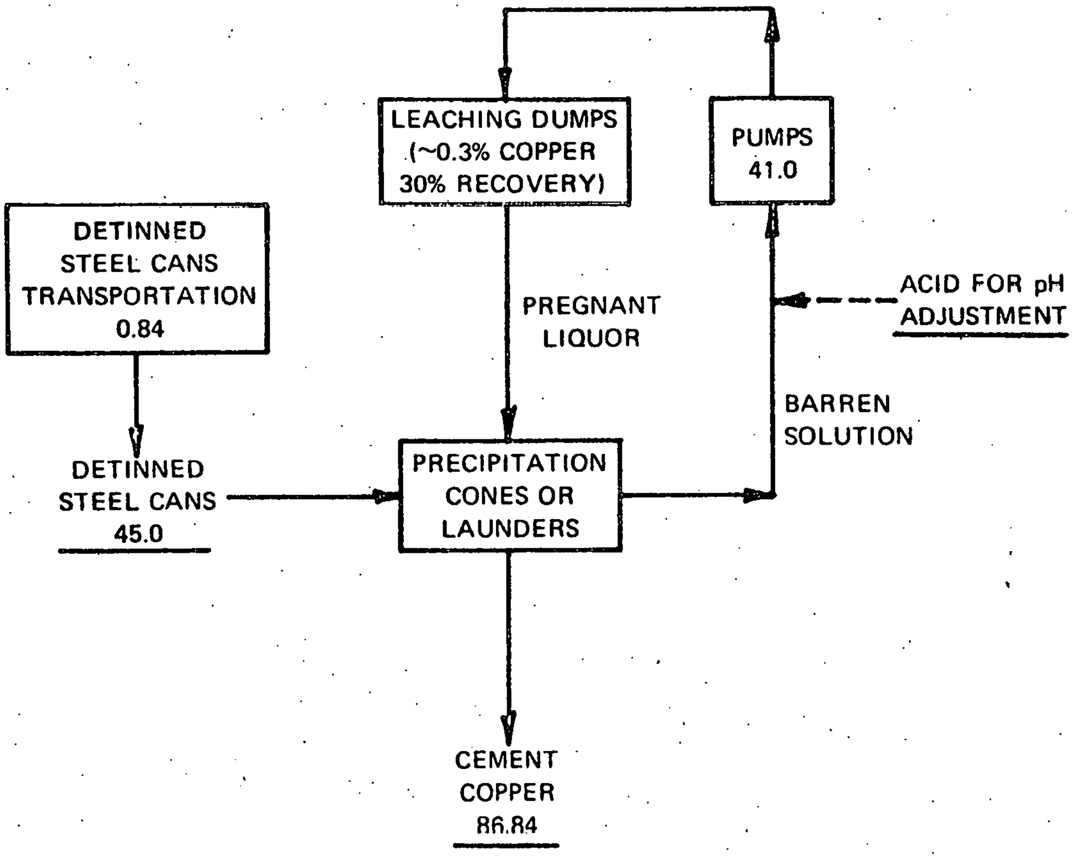


Fig. 7. Dump leaching of sulfide copper ore with dilute sulfuric acid solution (1).

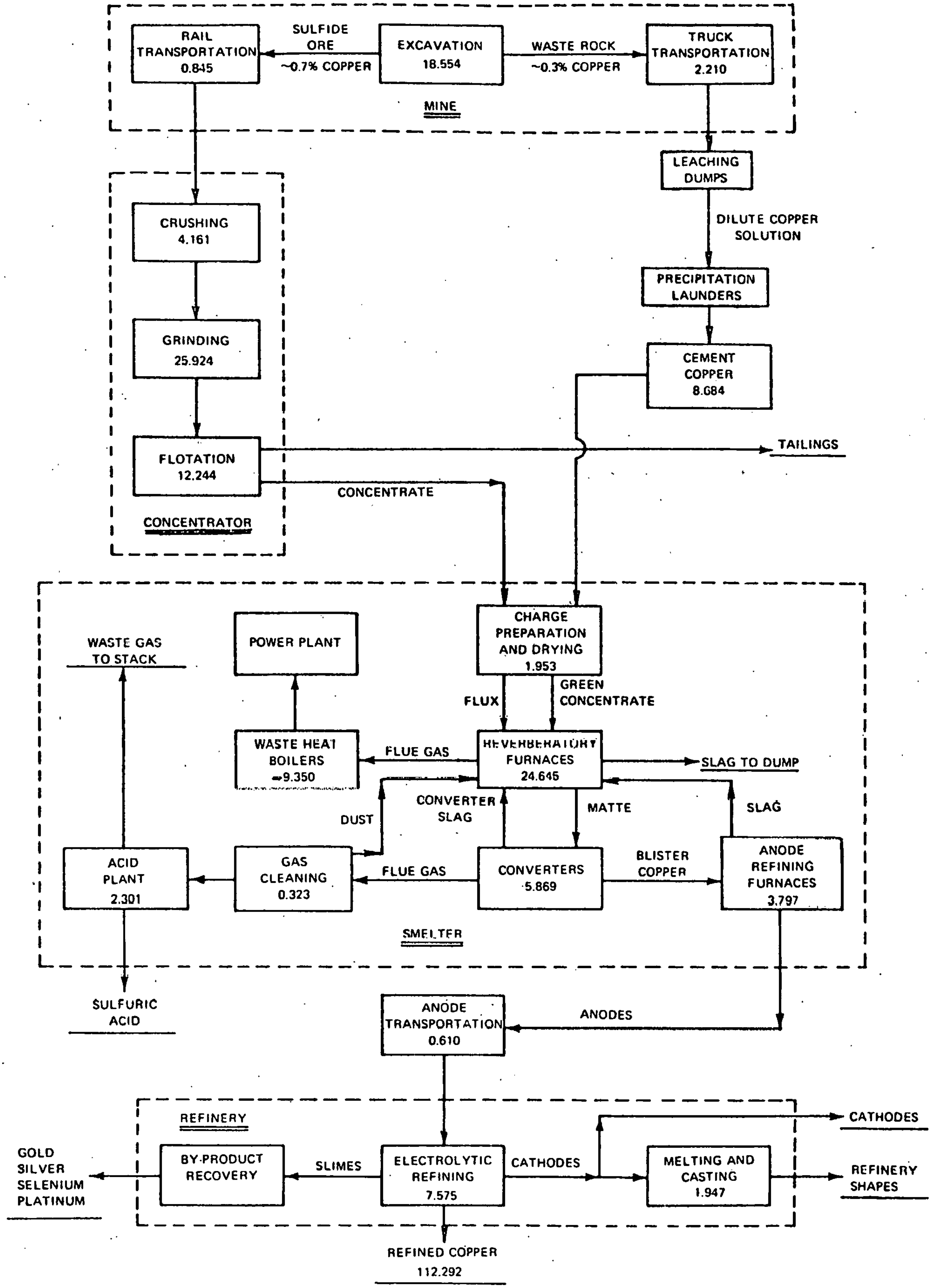


Fig. 8. Production of refined copper by conventional mining and smelting processes (1).

Noranda reactor and the Outokumpu and Inco flash smelters. The energy used in electric furnace matte smelting is assigned a value of about 500 kWhr/ton of feed with copper contents of 20-25% (13). This converts to a value of about 23 × 10^6 BTU/ton Cu for this portion of the flow diagram.

Forecasts for the U.S. copper demand for the years 1985 and 2000 are given in Table 9. The basis year of 1976 is also included.

Major contingencies for the low forecast are substitution by aluminum and copper-clad aluminum, microminiaturization, advanced power systems not requiring generators, and reduced per capita consumption due to substitution of multidwelling homes for single homes and mass transit for individual autos. High side forecasts are based on increased emphasis on recreation, safety, comfort and pollution-free environments and superior performance and ease of fabrication to combat future production and maintenance costs.

Primary production in the United States is forecast to be 2 million tons in 1985 and 3.15 million tons in the year 2000 so that we will be importing about 10% of our primary copper. It is commonly understood in in industry that at present, hydrometallurgy used on sulfide concentrates does not offer an energy advantage over newer smelting technology. Thus, the Bureau of Mines Ferric Chloride Leach (15,16) has been estimated to use 63 × 10^6 BTU/ton Cu (17), excluding mining and milling. Sherritt-Cominco (S-C) reports utility consumption for their sulfate leach process and compares it with data they present for flash smelting (18). We have calculated energy consumptions from these data as 28.9 × 10^6 BTU/ton Cu for flash smelting (in excellent agreement with the Development Science study) and 95.8 × 10^6 BTU/ton Cu for the S-C leach process. It is significant that a large part of the energy (46%) of the S-C process is consumed in electrowinning copper from leach solution. An alternative process for copper recovery proposed by S-C involves the reduction of copper from solution by hydrogen gas. The S-C authors believe that this would reduce energy consumption, but give no quantitative values. Data are not available on energy consumption used in the leaching of oxide and silicate ores.

In summary, energy requirement for primary copper production by pyrometallurgical and hydrometallurgical processes are tabulated in Table 10. The Bureau of Mines estimates that about 10% of primary copper produced in the United States in the year 1977 was electrowon (19). Our estimates and projections of the fraction of primary copper produced by the various relevant processes are given in Table 11.

The electrolytic energy is calculated assuming that 90% of the pyrometallurgical copper produced is electrorefined (the remaining 10% is sold as fire refined) and that all hydrometallurgical copper is electrowon. Electrorefining uses 3.2 × 10^6 BTU/ton Cu (1) and electrowinning requires 23 × 10^6 BTU/ton Cu (20).

Table 9

U.S. Copper Demand Forecast (14)
(Thousands of Short Tons)

	Probable			2000 Forecast Range		Average Annual Growth Rate
	1976	1985	2000	Low	High	Growth Rate 1975 - 2000 (%)
Primary	1,307	2,200	3,500	2,700	4,600	3.0
Secondary	369	800	1,600	1,200	2,000	5.0

Table 10

Energy Consumption for Primary Copper Production

(BTU × 10^6)

	Mining and Concentration	Copper Production	Total
Conventional Smelting and Electrorefining	64	48	112
Electric Furnace Smelting and Electrorefining	64	56	120
Noranda or Flash Smelting and Electrorefining	64	29	93
Ferric Chloride Leach Smelting and Electrorefining	64	63	127
Sherritt-Cominco Smelting and Electrorefining	64	96	160

Table 11

Percentage of Primary Copper Production by Process in the Years 1978, 1985, and 2000

	Percentage		
	1978	1985	2000
Conventional Smelting	60	50	-
Electric Furnace Smelting	16	13	10
Noranda and/or Flash Smelting	14	24	70
Hydrometallurgical Process	10	13	20

The weighted average of the energy content of primary copper may now be calculated from the data in Tables 10 and 11. These values are 110 × 10^6 BTU/ton Cu in the year 1985 and 102 × 10^6 BTU/ton Cu in the year 2000. These data, along with the values of primary production, may be used to calculate the total quantity of energy used in primary production. This information, along with values for the electrolytic energy component, are given in Table 12.

The probable forecast for copper demand in the year 2000 by end use, along with estimates of product lifetimes is given in Table 13.

A flow diagram for copper in the United States is given in Fig. 9. Scrap forms a substantial part of the supply and secondary copper is projected to account for 27% of the U.S. demand in the year 1985 and 31% in the year 2000.

In the year 1976 consumption of copper-bearing scrap was 1,425,000 short tons and a breakdown by category is given in Table 14.

In a detailed study of the flow, product life cycle, and recovery efficiency, Carrillo et al. (21) estimate a weighted average life cycle of all copper products at about 17 years with about 31% of the copper actually being recovered from obsolete products. This percentage is projected to remain about constant to the year 2000 when about 2.2 million short tons of copper products will be unrecovered that year.

Four significant recycle processes for copper, brass and bronze scrap have been identified (3): reverberatory melting of No. 1 copper wire scrap; melting and refining No. 2 copper scrap; cupola melting of low-grade, copper-bearing scrap; and reverberatory melting of brass and bronze scrap. The energistics of these processes are shown in Figs. 10 through 13. If we assign one of these methods to each of the scrap categories in Table 14, we calculate a weighted average for the energy content of secondary copper equal to 15 × 10^6 BTU/ton.

The total energy and electrolytic energy saved in recycling copper in the years 1985 and 2000 may then be calculated and are given in Table 15.

Table 12

Energy Consumption in the Production of Primary Copper in the Years 1985 and 2000

Year	Primary Production (thousands of tons)	Total Energy, 10^{12} BTU	Electrolytic Energy, 10^{12} BTU
1985	2,000	220	5.5
2000	3,150	321	6.9

Table 13

Use and Product Lifetime of Copper in the Year 2000 (14)

End Use	Lifetime (years)	Quantity (thousands of short tons)
Electrical	30	3,500
Construction	30	600
Machinery	20	400
Transformation	10	200
Ordinance	lost	100
Other	20	300
	Total	5,100

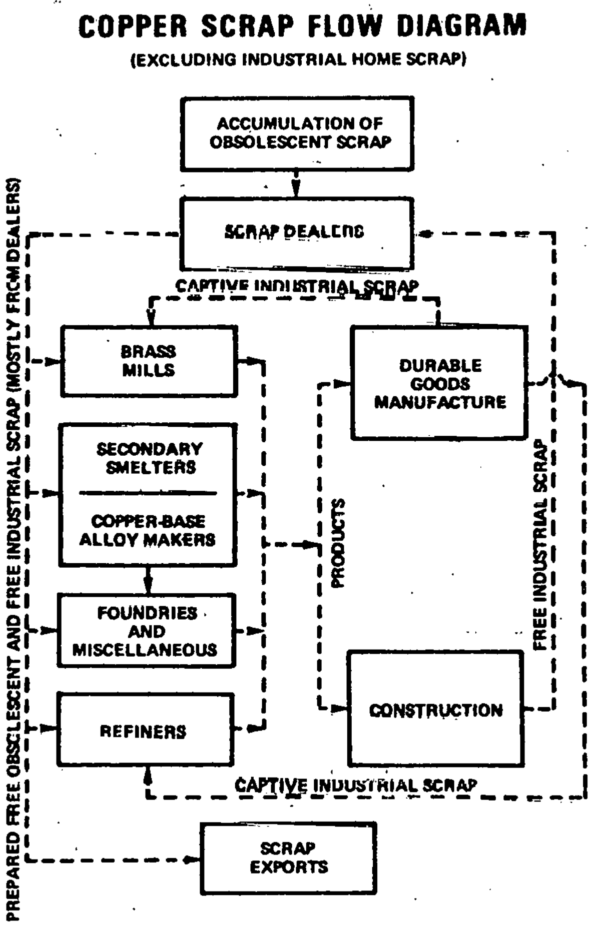


Fig. 9. Copper scrap flow (14).

Table 14

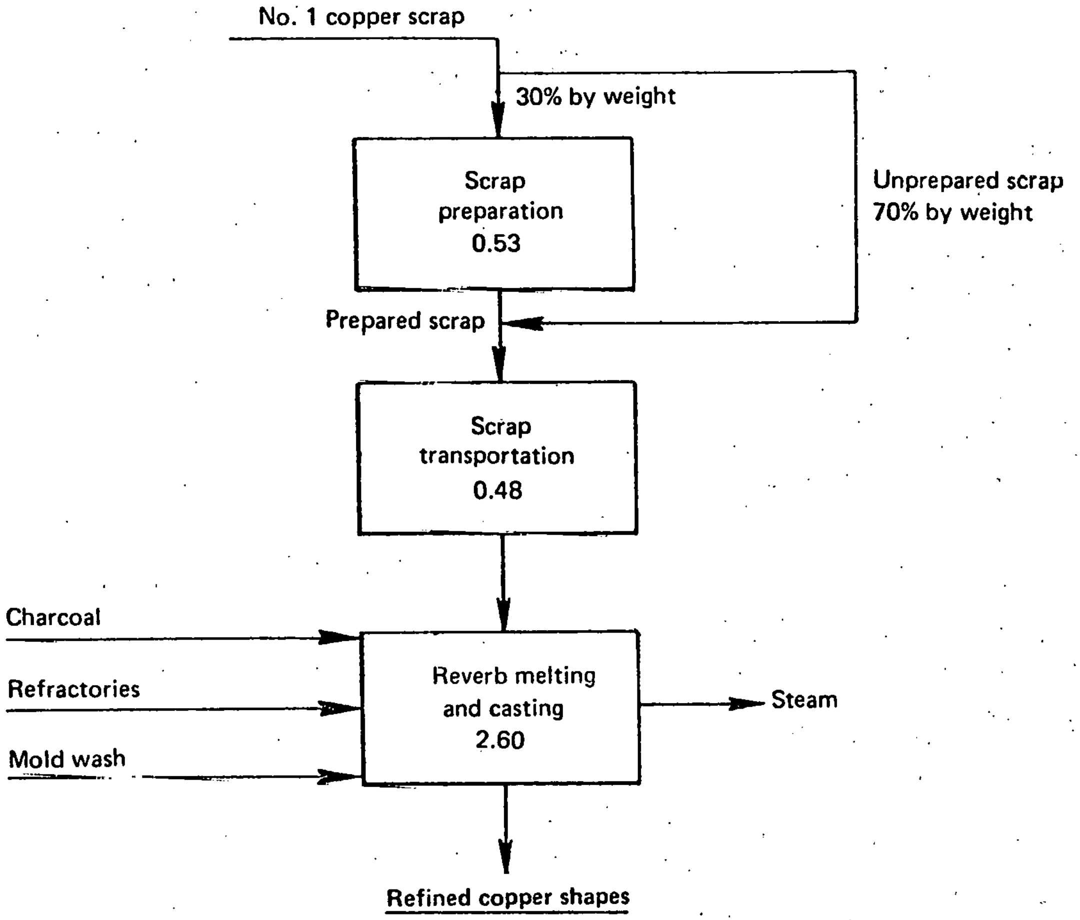
Purchased Copper-Base Scrap Consumed in 1976 (3)

Consumer and Item	Old Scrap (thousands of short tons)	New Scrap (thousands of short tons)
Secondary copper smelters:		
No. 1 wire and heavy	22	3
No. 2 wire, mixed heavy and light	42	16
Composition or soft red brass	45	13
Railroad-car boxes	2	0
Yellow brass	41	5
Auto radiators (unsweated)	49	0
Bronze	17	3
Nickel, silver, and cupronickel	2.5	.5
Low brass	.5	1.5
Low-grade scrap and residues	13	64
	234	106
Primary Producers:		
No. 1 wire and heavy	57	61
No. 2 wire, mixed heavy and light	35	94
Refinery brass	2	2
Low-grade scrap and residues	138	38
	232	195
Brass Mills:		
No. 1 wire and heavy	28	128
No. 2 wire, mixed heavy and light	2	71
Yellow brass	0	272
Cartridge cases and brass	0	78
Bronze	0	4
Nickel, silver and cupronickel	0	29
Low brass	0	46
	30	628
Total	496	1425

Table 15

Energy Saved in Copper Recycle

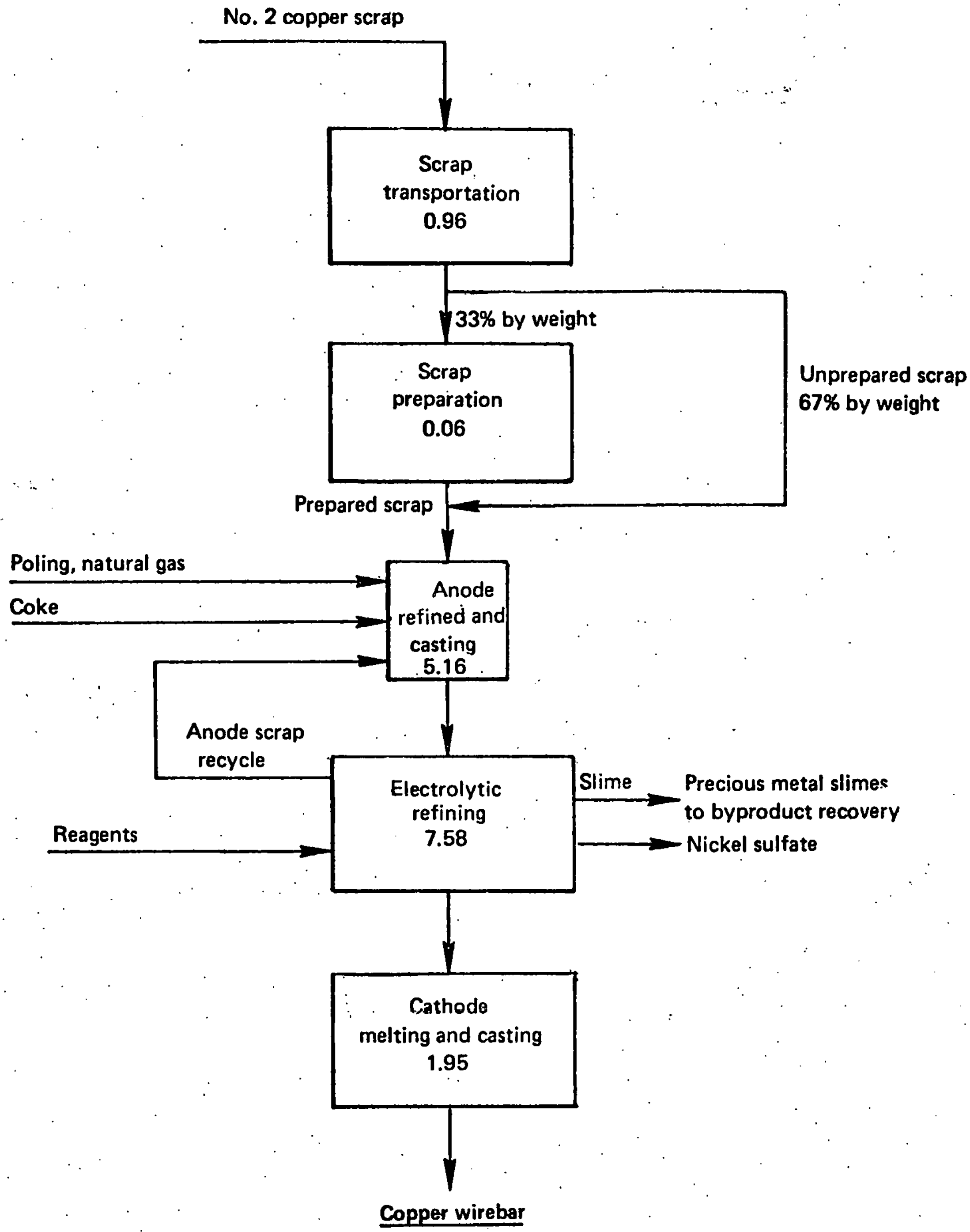
Year	Total Energy Saved, 10^{12} BTU	Electrolytic Energy Saved, 10^{12} BTU
1985	76	4.4
2000	139	11.0



SUMMARY

	Million Btu per ton of product
Process energy	3.61
Pollution control energy	0.05
Space heating	0.15
Total energy	3.81

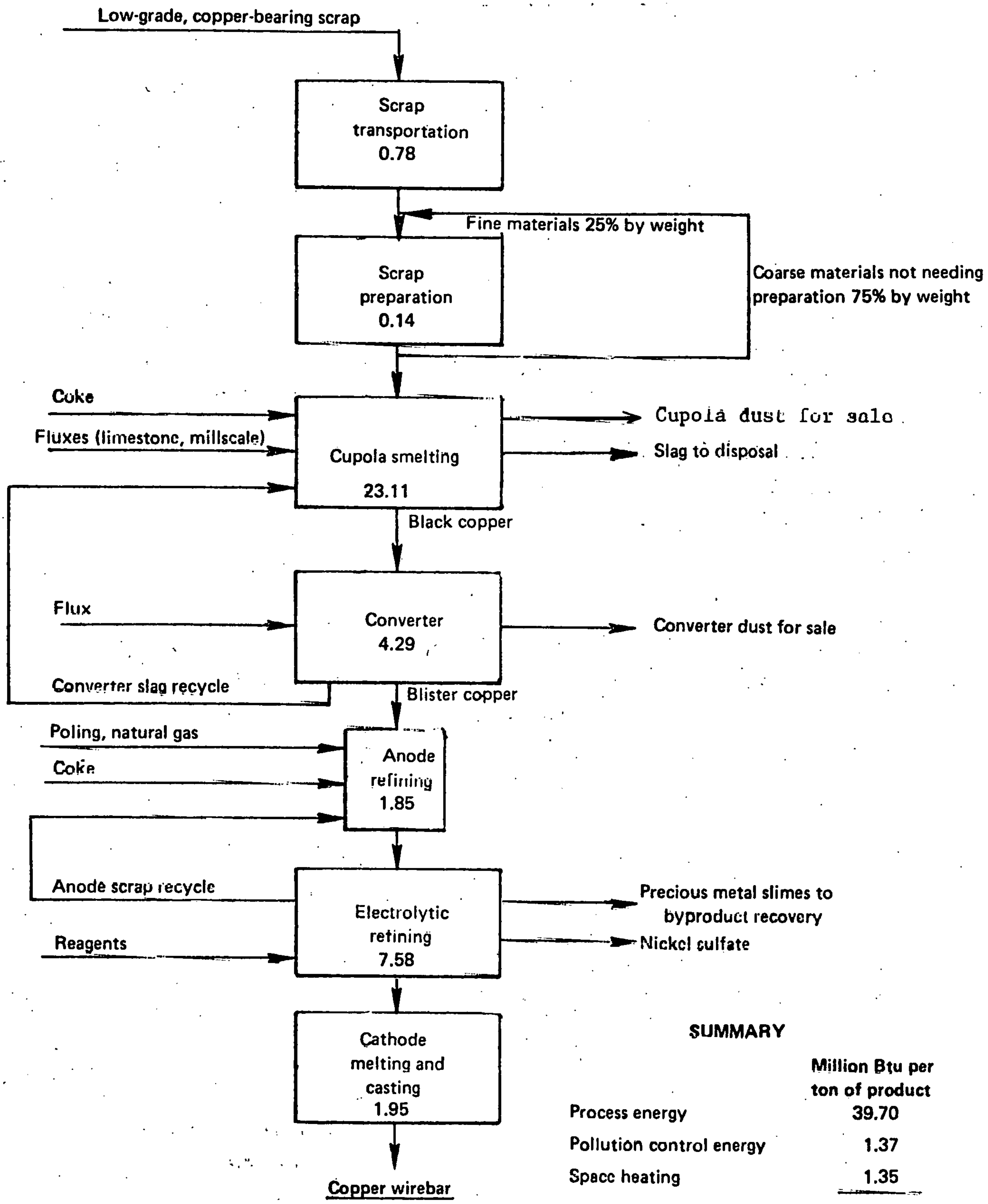
Fig. 10. Copper: Reverb melting of No. 1 copper wire scrap (3).



SUMMARY

	Million Btu per ton of product
Process energy	15.71
Pollution control energy	0.21
Space heating	1.35
Total energy	17.27

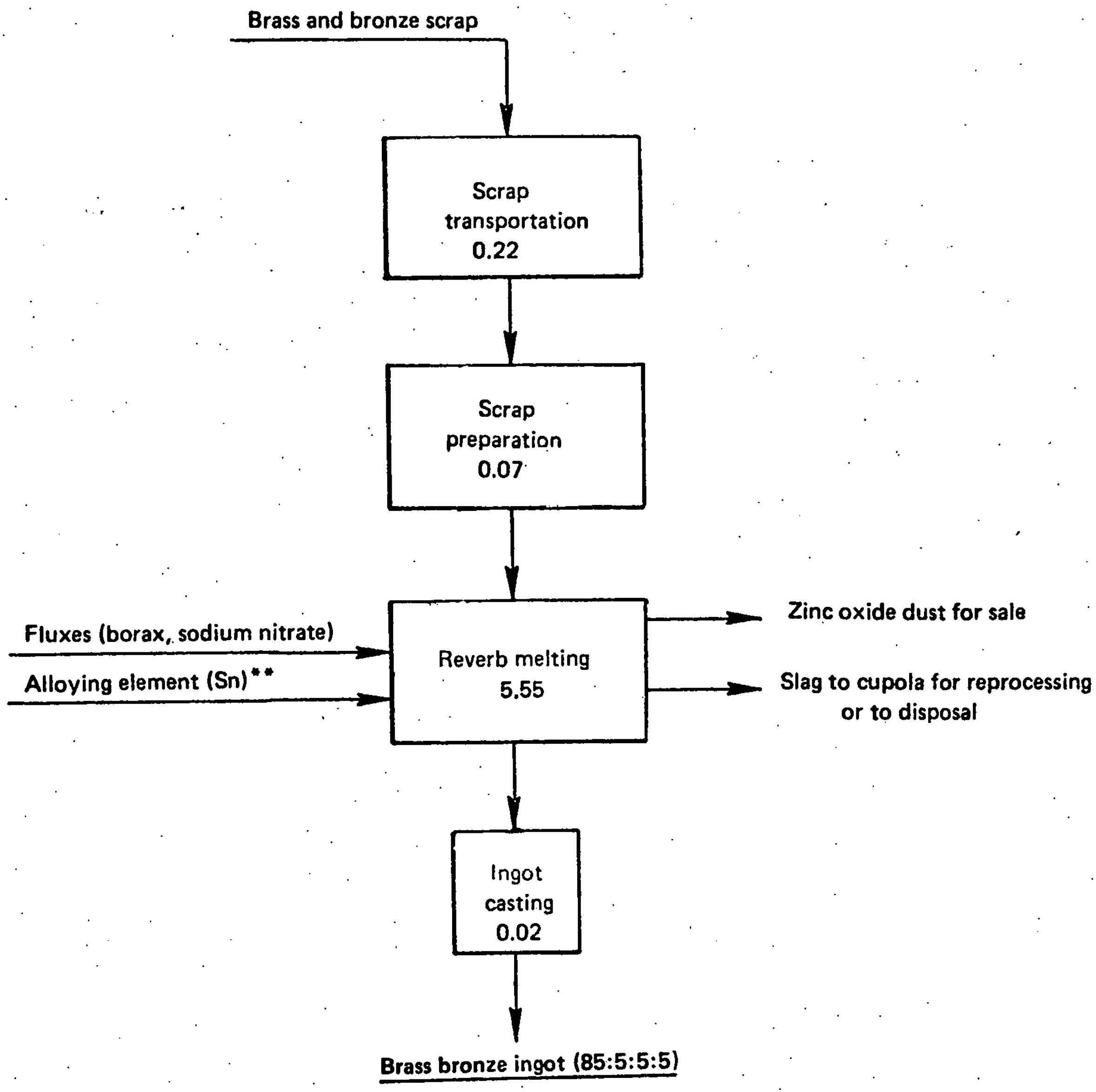
Fig. 11. Copper: Recycling of No. 2 copper scrap (3).



SUMMARY

	Million Btu per ton of product
Process energy	39.70
Pollution control energy	1.37
Space heating	1.35
Total energy	42.42

Fig. 12. Copper: Recycling of low-grade, copper-bearing scrap (3).



SUMMARY

	Million Btu p ton of produc
Process energy	5.86
Pollution control energy	0.91
Space heating	0.32
Total energy	7.09

**Energy content of alloying elements is not included in the total process energy.

Fig. 13. Copper: Recycling of brass and bronze scrap to brass and bronze ingot (85:5:5:5) (3).

4.2.2 Sources of Scrap

The significant extent of copper recycle (∿30%) results from the relatively high cost of the metal, its chemical and physical properties, and the uses to which it is put which permit relatively easy sorting for recovery.

Approximately two-thirds of the total scrap recycled is new or prompt scrap, while one-third is old or obsolete scrap. About one-third of the scrap, of which about half is old and half is new scrap, is recycled in primary smelters. The balance is recycled in secondary smelters. About half of the old scrap is converted to refined copper for recycle, the balance being converted to brass and bronze products. Of the new scrap, only one-third is refined to copper while the majority is converted to brass. These relationships are depicted in Fig. 14.

Major scrap categories are listed below:

- No. 1 scrap consists of unalloyed copper, clean and free of contaminants, >1/16th inch thick or No. 16 BWG wire. Approximately 2/3 of the No. 1 scrap is new or prompt scrap and is carefully sorted.

- No. 2 scrap consists of miscellaneous unalloyed copper materials containing nominally 96% copper. This material is also approximately 2/3 prompt scrap and is carefully sorted in an attempt to minimize the lead and tin content, contamination with brass or bronze, or contamination with oily or ferrous scrap. Light copper, a mixture containing nominally 92% copper, is also processed with No. 2 scrap.

- Brasses and bronzes consist of approximately 90% prompt scrap. Refinery brasses are mixtures containing at least 61% copper with 5% maximum iron content. Other brasses and bronzes are segregated by allow type insofar as possible for recycle to the original alloy.

- Copper bearing scrap, of which the majority is old scrap, consists of miscellaneous copper-bearing materials such as skimmings, grindings, ash, irony brass, slags, burnt wire, auto parts, copper containing electronics and communications equipment, etc.

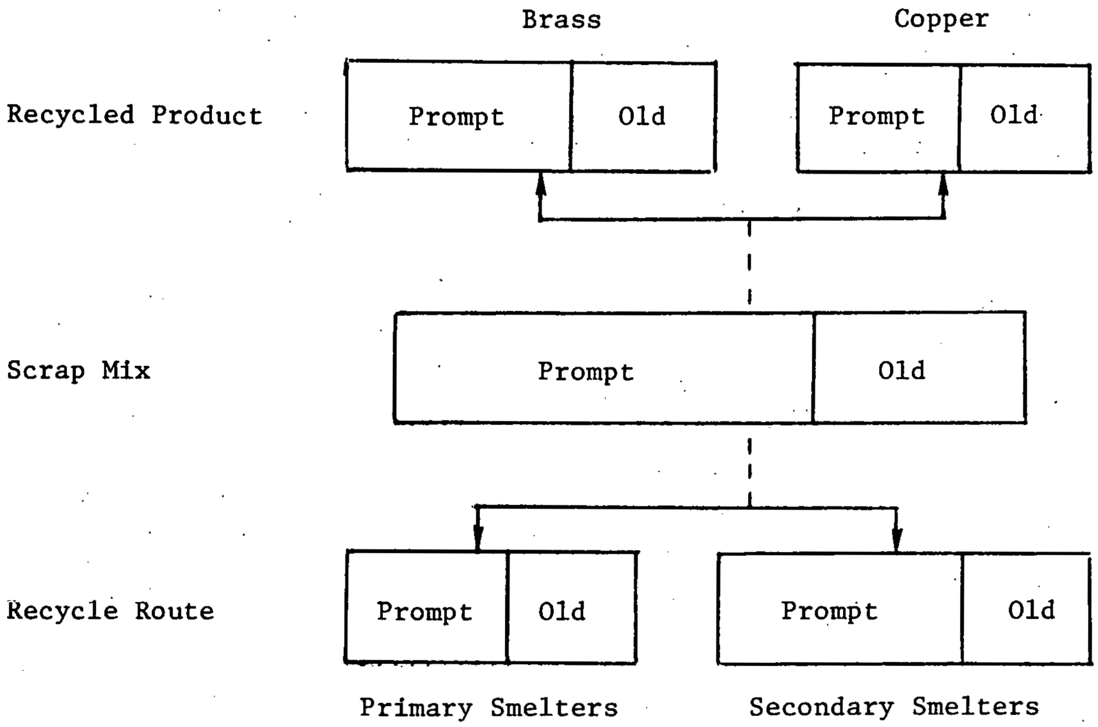


Fig. 14. The partition between (a) prompt and old scrap, (b) recycle in primary and secondary converters, and (c) recycle to brass and copper products. Boxes are drawn approximately to scale.

4.2.3 Properties of Copper Important in Recycling

Copper is a dense, high melting, ductile, easily recognized, nonmagnetic material which does not oxidize readily. These properties permit relatively easy physical separations to be carried out. The scrap may be chopped and separated by gravity from aluminum and light material such as plastic sheeting, separated from ferrous materials magnetically, and then further separated from zinc-rich materials simply by color.

If the scrap material is then melted, it is possible to preferentially oxidize iron, sulfur, and many other common impurities, removing them as vapors or as oxides which report to fluid slags. Copper obtained in this manner has a purity of about 99%.

Copper can be electrorefined to an extraordinarily pure product by well-known technology. Only a few impurities are co-deposited so that control of product purity and process efficiency are easy compared with the stringent purification requirements for zinc electrowinning. In addition, valuable by-products are recovered from tankhouse sludges.

Copper can also be electrowon from solution and, in commercial practice, cupric ions are reduced from acid sulfate solution using insoluble lead anodes. However, energy requirements for electrowinning are high at about 25 million BTU/ton Cu. On the other hand, electrorefining requires only 7.5 million BTU/ton for both electrical and process heating energy since substantially lower voltages are required. Electrowinning cuprous ion from an acid chloride solution requires less electrical energy than does cupric sulfate electrowinning, but is still much more energy intensive than electrorefining since voltages are much higher. Cathode copper of acceptable purity is not produced directly since the dendritic product must be washed, consolidated and then melted. Chloride electrowinning is not widely practiced commercially.

The energy requirements for pyrometallurgical processes to recover copper from No. 1 and No. 2 scrap are only 4 and 17 million BTU/ton respectively. Approximately 40 million BTU/ton is required for the entire process sequence when producing copper from low grade scrap. Therefore, new processes involving electrowinning of copper from solution are not likely to be significantly less energy intensive even for the processing of low grade scrap.

4.2.4 Current Practice in Recycling

The secondary copper industry is highly fragmented consisting of several thousand scrap dealers and collectors and several hundred foundries. Approximately a dozen primary smelters process significant amounts of scrap as well as concentrates, while several major secondary smelters process scrap material only. Generally, attempts are made to segregate the scrap at the collection points to upgrade the material to the type which commands the highest price. Small yards may segregate to only a few types while at larger operations classification is more complete. The material is segregated by color, hardness and the type of article from which the scrap is obtained. Attempts are made to remove bulk impurities by hand if possible. Otherwise physical techniques, such as chopping or crushing, are used to remove insulation or massive irony material and chemical techniques, such as burning, are used to remove combustible insulation. Also, the material may be chopped or crushed to reduce its size and baled or briquetted to increase its density or reduce dusting problems in subsequent processing.

A schematic representation of the operations involved in scrap copper processing is shown in Fig. 15.

No. 1 scrap is refined by a simple melting technique similar to that used in fire refining in primary smelters. The scrap is melted, impurities are oxidized and slagged off, and the melt is "poled" to reduce the cuprous oxide content. The molten copper is then cast into shapes for sale.

No. 2 scrap is treated according to the same procedures as No. 1 scrap except that the deoxidized product is cast into anodes and then electrorefined. The cathodes produced in electrorefining are cast to wire bar or other shapes for sale and the tankhouse purge stream and slimes are treated for precious metal and by-product recovery as required.

Brasses and bronze are most often simply sorted and remelted, usually in a reverberatory furnace, with addition of virgin material as required to achieve the final composition desired for the alloy. A limited amount of purification can be done during these steps to remove iron, cadmium, bismuth, phosphorus aluminum, and other impurities by oxidation and fluxing to the slags. Some copper is lost to the slag in this treatment. Zinc oxide loss to the dust may be significant, although zinc may be recovered from the dusts if justified.

Low grade copper-bearing scrap may be treated according to a variety of procedures. The usual approach is to smelt it in a blast furnace with coke and limestone to produce "black copper". Judicious control of scrap addition and fluxing is required to produce a fluid slag and minimize copper losses. The black copper, which contains approximately 80% copper and significant amounts of iron, lead, tin, and zinc is oxidized in a converter with additional flux to remove impurities. Most metallic impurities and some copper are slagged off and recycled to the blast furnace while

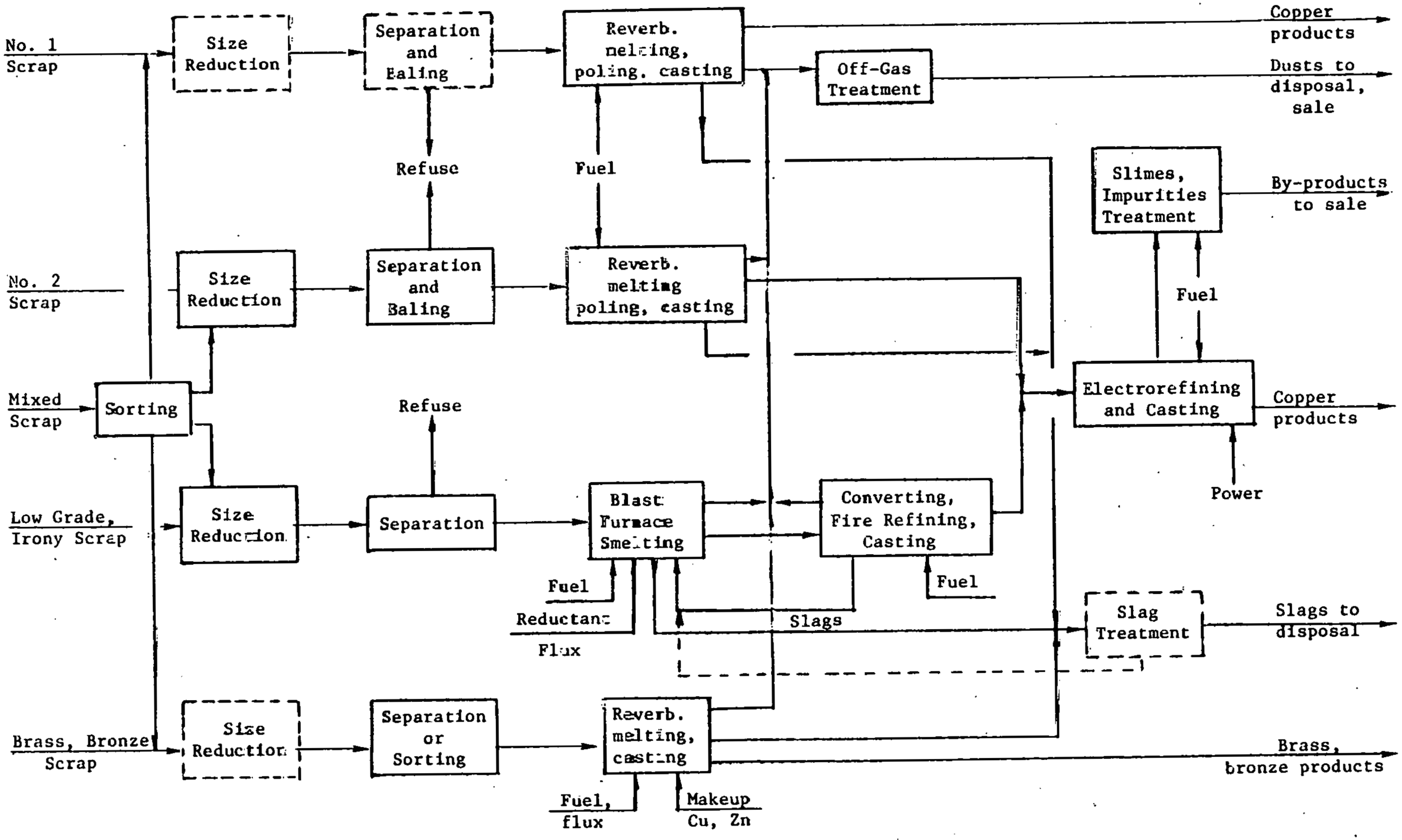


Fig. 15. Copper scrap treatment processes, materials, and energy flows.

significant amounts of zinc and lead are oxidized and report to the converter dusts. The blister copper produced in the converter can be fire refined and electrorefined by the same procedure used for No. 2 scrap. Some smelters treat blast furnace slag further with coke in electric furnaces to remove additional copper while the cleaned slag is granulated and sold. The dusts may be sold for their zinc content or treated on site if justified.

4.2.5 Alternative Processes for Scrap Recycle

Unlike aluminum, the chemical and physical properties of copper permit a wide variety of pyrometallurgical and hydrometallurgical process alternatives for scrap recovery. As shown, current practice in the secondary copper industry is based almost exclusively on pyrometallurgical processes and new process routes will be adopted only if they overcome severe technical, environmental, or economic problems.

No. 1 and No. 2 copper scrap are currently reprocessed with a minimum of operating steps using well established, easily controlled pyrometallurgical processes. Recoveries are relatively high, energy requirements and energy costs relatively low, the amount of waste products produced are small and environmental problems, principally combustion off-gas cleaning, can be solved with currently available technology. Thus, there is little prospect of developing alternative processes which would be more attractive, and changes in technology are apt to be evolutionary.

Brass and bronze scrap are also recovered by simple techniques at relatively low cost and acceptably high recovery. The key to the success of this approach is the careful sorting of the material to be recycled so that the desired alloy composition can be maintained and impurities controlled with a minimum of dilution by new copper or zinc. Control of impurities is the major factor here since relatively little refining can be done pyrometallurgically without major losses of zinc and significant losses of copper. While much of the zinc loss could be recovered from the dusts and sold as oxide, this is not as efficient as retaining the metal in the desired brass or bronze alloy. If, however, a combination of alloy specifications and available scrap compositions required that purification be used which would result in the separation of pure copper and zinc, then hydrometallurgical processes might be advantageously used.

Recycling low grade, irony copper-bearing scrap by conventional pyrometallurgical processes is somewhat more difficult. Recoveries are lower, energy consumption and costs are higher, and wastes are produced which present substantial environmental problems. During the separation of metallic from non-metallic material by pyrometallurgical techniques, the combustion of plastic and rubber generates smoke, and halogens are liberated from coatings which cause corrosion problems in off-gas treatment equipment. Further, multiple processing steps are required to separate metals pyrometallurgically, and some value metals are lost. Hydrometallurgical processes offer the possibility of being more selective in recovering the metal of interest or in recovering all value metals. However, the solution purification techniques required will not necessarily be simple and the electrowinning step is energy intensive.

4.2.6 General Requirements for Hydrometallurgical Scrap Treatment Processes

In general, hydrometallurgical scrap treatment processes will consist of the following steps as illustrated in Fig. 16.

- Pretreatment to obtain the desired physical characteristics for subsequent steps.
- Contacting with lixiviant and oxidant as required to dissolve the metal.
- Separation of undissolved components from metal bearing solutions.
- Treatment of solutions to separate major metals from each other and from deleterious impurities.
- Recovery of the metals.
- Recycling of lixiviant and removal of impurities and waste materials.

Pretreatment will be required to achieve the necessary kinetics and for efficient handling of residues in subsequent steps. Massive scrap must be shredded to a much finer size than that used prior to pyrometallurgical processing in order to permit access of lixiviant and oxidant to the metal. Furthermore, protective coatings must be removed from the metal surface.

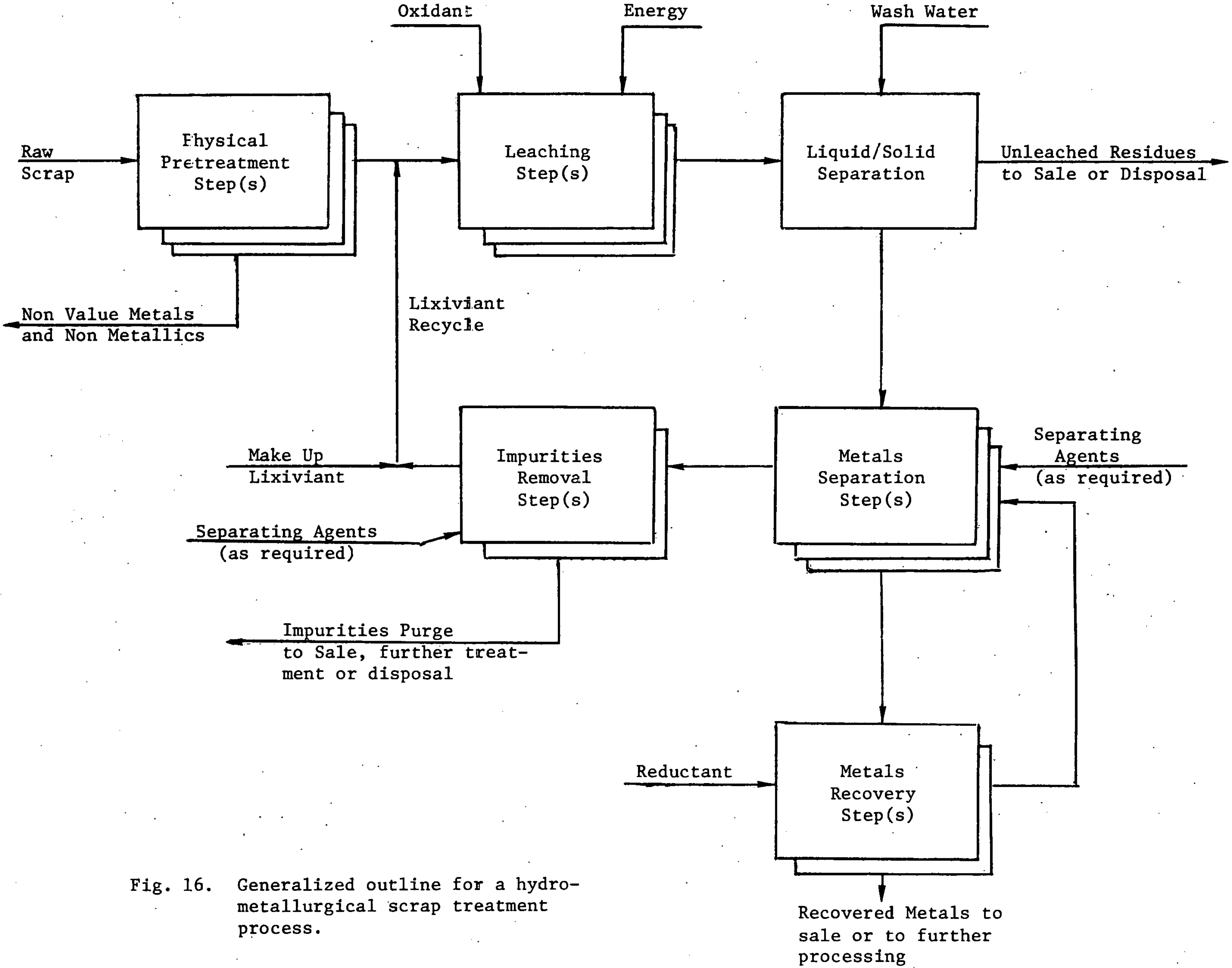


Fig. 16. Generalized outline for a hydrometallurgical scrap treatment process.

A variety of lixiviants and oxidants may be used in hydrometallurgical processes. Sulfuric acid, ammonia/ammonium sulfate, ammonia/ammonium carbonate and acid chloride solutions have been used to dissolve copper-bearing material. Suitable oxidants are air, pressurized air, oxygen, nitric acid, or electricity used directly or indirectly. A major factor in determining the choice of the chemical system used in its selectivity for dissolution. A major metallic impurity in copper-containing scrap is likely to be iron. It is highly desirable to prevent extensive oxidation and dissolution of iron since its subsequent reduction or removal is expensive and troublesome. The lixiviant system must also be compatible with subsequent purification and/or reduction steps. Obviously, the oxidant must be inexpensive, effective, and easily regenerated if required.

Effective separation of dissolved metals from residues is required. For both economic and environmental reasons, one cannot afford to lose either dissolved metals or the lixiviant which ideally would be recycled. Residues cannot be washed copiously since this would have an adverse impact on the process water balance as well as release dissolved heavy metals and acid or alkali solutions to the environment. It is likely that new equipment and operating techniques need to be developed both for scrap preparation and residue washing in order to solve this problem.

A variety of techniques is available to separate and recover metals from solution. Liquid or solid ion exchange may be used to selectively remove metals from leach solutions. Concentration and further selective separation may be achieved during stripping the ion exchangers of their metal values. Metal removal may also be achieved by cementation on more active metals or precipitation by pH adjustment or precipitation reagents.

Reduction may be achieved by a variety of techniques including electrowinning, chemical reduction by hydrogen or carbon monoxide, disproportionation reactions, and chemical reduction using renewable reducing agents.

Unless an unusual situation exists, efficient recovery and recycle of lixiviant will be required on economic grounds alone. Process sequence involving losses of large amounts of reagents in purge streams withdrawn for impurity removal are not likely to be economically viable. Since, in general, it is unlikely that a lixiviant can be completely selective for the desired metal, impurity removal steps will be required. In conventional pyrometallurgical scrap processing, impurities report to the dusts removed from the combustion gases or are tied up in relatively inert slags. In hydrometallurgical processes, however, they are likely to be in the forms of sludges or precipitates requiring careful waste management control to prevent their release to the environment. Economic benefits could be derived, of course, if the waste materials are rich enough in other value metals, such as lead and tin, to be sold to other primary or secondary metal producers for further processing.

Finally, it must be noted that the process sequence outlined above will be entirely new to most firms in the secondary copper industry. Efficient operation of a secondary smelter processing low grade scrap is an art learned over many years. The essential elements are control of the feed to the blast furnace by proper charge selection and rate of raw material addition, and attention to furnace operation using visual clues, simple temperature control, and operator know-how. Operation of a hydrometallurgical processing plant is more akin to the operation of a specialty chemicals plant. Personnel, skills and techniques which are new to the industry would have to be developed to insure a successful operation of these more complex, integrated processes.

4.2.7 Hydrometallurgical Process Alternatives for Scrap Recycle

A variety of hydrometallurgical processes have been proposed for copper scrap treatment, and design data have been obtained in tests ranging from laboratory to pilot scale. None is currently in commercial operation and very few cost data are available.

Cupric chloride dissolved in concentrated brine has been used to leach brass scrap in the absence of air to produce a solution of cuprous chloride and zinc chloride (22). Curpous ions are normally insoluble in aqueous solution but, due to the formation of complex ions such as $CuCl_3^{2-}$ and $CuCl_4^{3-}$, are quite soluble in high chloride concentrations. A flow chart for the process is shown in Fig. 17. The proposed process sequence requires zinc removal by precipitation with caustic or soda ash followed by copper recovery electrolytically in a diaphragm cell. The anolyte would be recycled to leach additional metal values. No method was proposed for removal of other impurities and obviously the zinc precipitate could require extensive additional treatment. It was not shown that the copper produced in this process is of cathode grade. If additional copper purification were required it is unlikely that the process would be economically viable.

Several scrap recovery processes have been proposed based on the use of an ammonia/ammonium carbonate lixiviant. The flow sheet of a patented process directed towards processing automobile scrap (23) is shown in Fig. 18. The scrap material is first freed of organics by burning in a rotary kiln. The temperature is then raised sufficiently to sweat off as much of the zinc content as possible. The cooled residues are leached to recovery both copper and zinc. Copper is removed from the pregnant solution by liquid ion exchange and the purge stream is evaporated to dryness for zinc recovery. It is not apparent, however, what is to be gained in this case by combining pyrometallurgical and hydrometallurgical techniques since the zinc must be recovered in two separate steps.

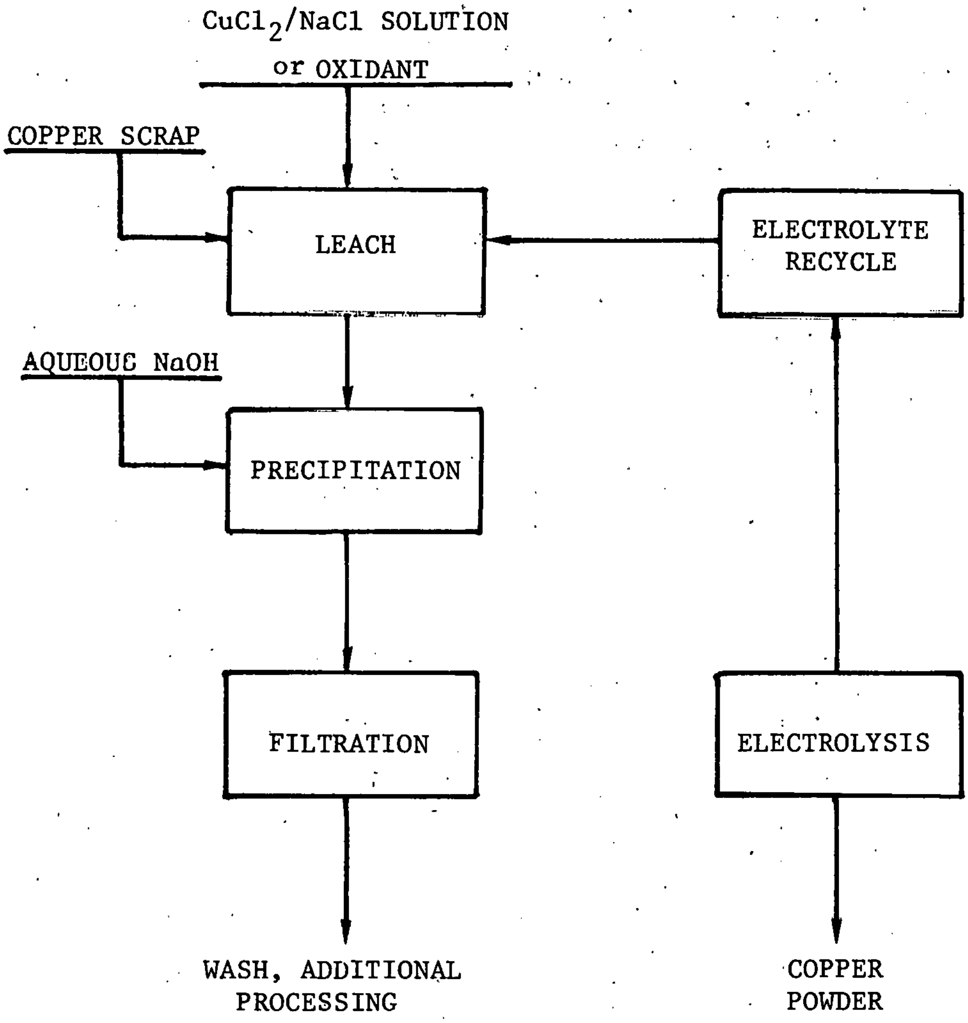


Fig. 17. Flow chart for the recovery of copper by the cupric chloride/sodium chloride process (22).

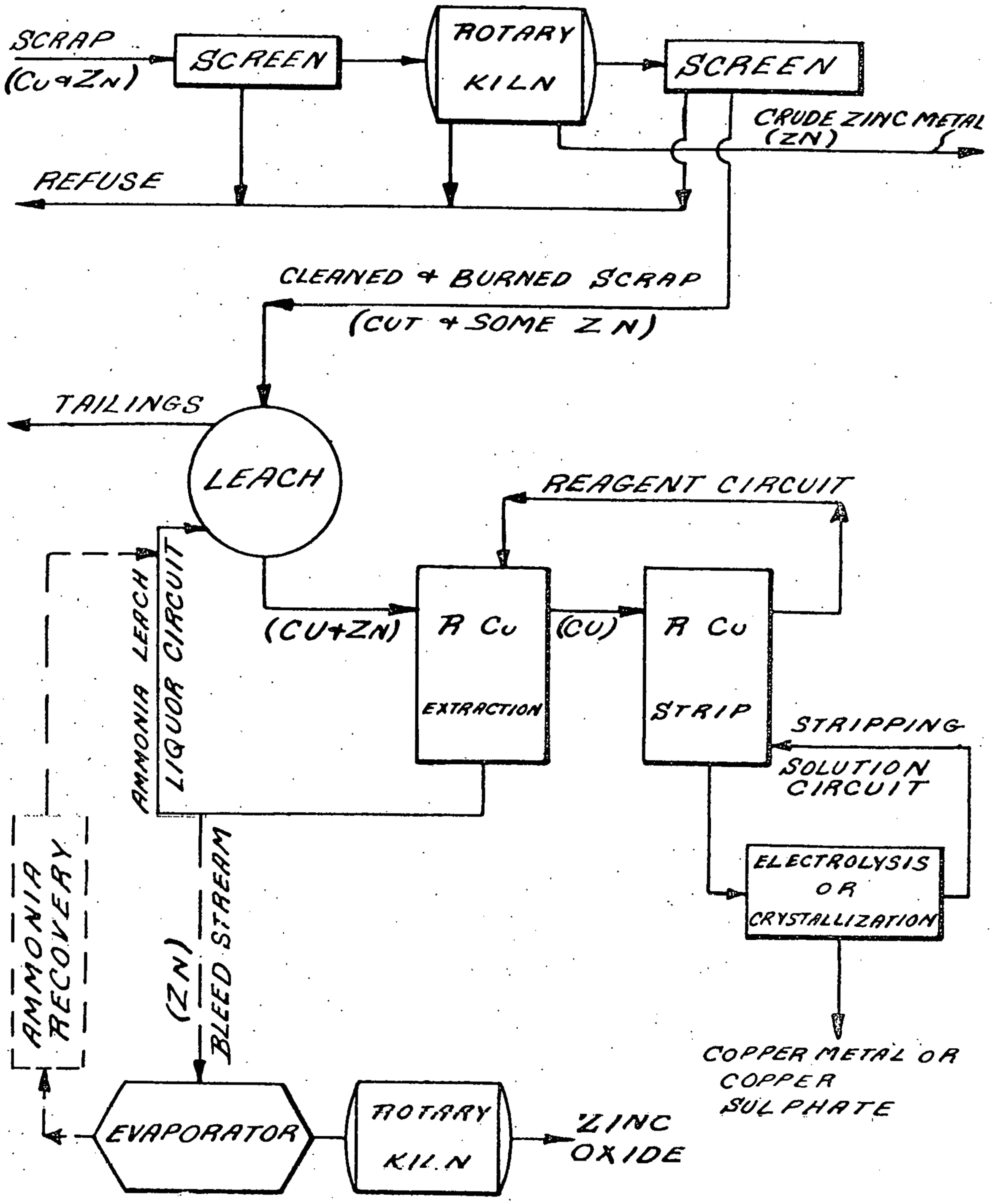


Fig. 18. Recovery of copper and zinc from automobile scrap (23).

A process sequence based on the selective leaching of copper from bearing scrap and clad material has also been reported (24). The technique is based on the fact that iron is insoluble in the ammonia/ammonium carbonate leach solution so that copper recovery from an otherwise very low-grade scrap may be economically feasible. During leaching, the scrap must be continuously agitated to abraid the surface to remove a tin-lead sludge which would otherwise decrease the leach rate. The sludge is filtered from the electrolyte and sold while copper is recovered by liquid ion exchange and electrowinning. Capital costs have been estimated at about \$650/annual ton of copper for a plant to recover approximately 2 tons/day. In contrast, the capital cost of a new plant for primary copper production is of the order of \$2000/annual ton for a much larger size plant. Direct operating costs for this process are estimated at approximately 12¢/pound, which is about half of the cost of recovering primary copper from concentrate. This cost is such that it would be possible to pay about 75% of the price of recovered copper for the scrap material and still obtain a return on investment sufficient to justify use of the process.

A patent has been granted on the use of chelated ferric ion to increase the rate of oxidation of metallic copper (25). While this may overcome a key process problem of low dissolution rates, there is no indication of how an integrated flow sheet can be constructed to take advantage of the more rapid leach.

Processes based on sulfuric acid as the lixiviant may find wider acceptance because elements of such processes exist in commercial primary production processes. A patent has been granted for processing high purity, low iron, lead-containing brass scrap by dissolution in sulfuric acid (26). A flow sheet is shown in Fig. 19. After dissolution of the copper and zinc, the lead residue is removed by filtration and copper is recovered by electrowinning. A purge stream is treated with zinc dust to remove residual copper, and the zinc is then electrowon. The barren solution is recycled to the leach step. The patent claims are restricted to use on high purity scrap, but a lower grade material could be treated if more elaborate solution purification steps were employed.

A combined pyro- and hydrometallurgical process has been tested in a Russian scrap reprocessing plant (27), Fig. 20. Low grade scrap is smelted to blister copper so that the bulk of the iron and other impurities are removed with the slag. The impure copper is reduced in size, leached, and recovered from solution by reduction with hydrogen. Since the copper would have to be further refined to be of cathode grade, it is not likely that this process would be economical.

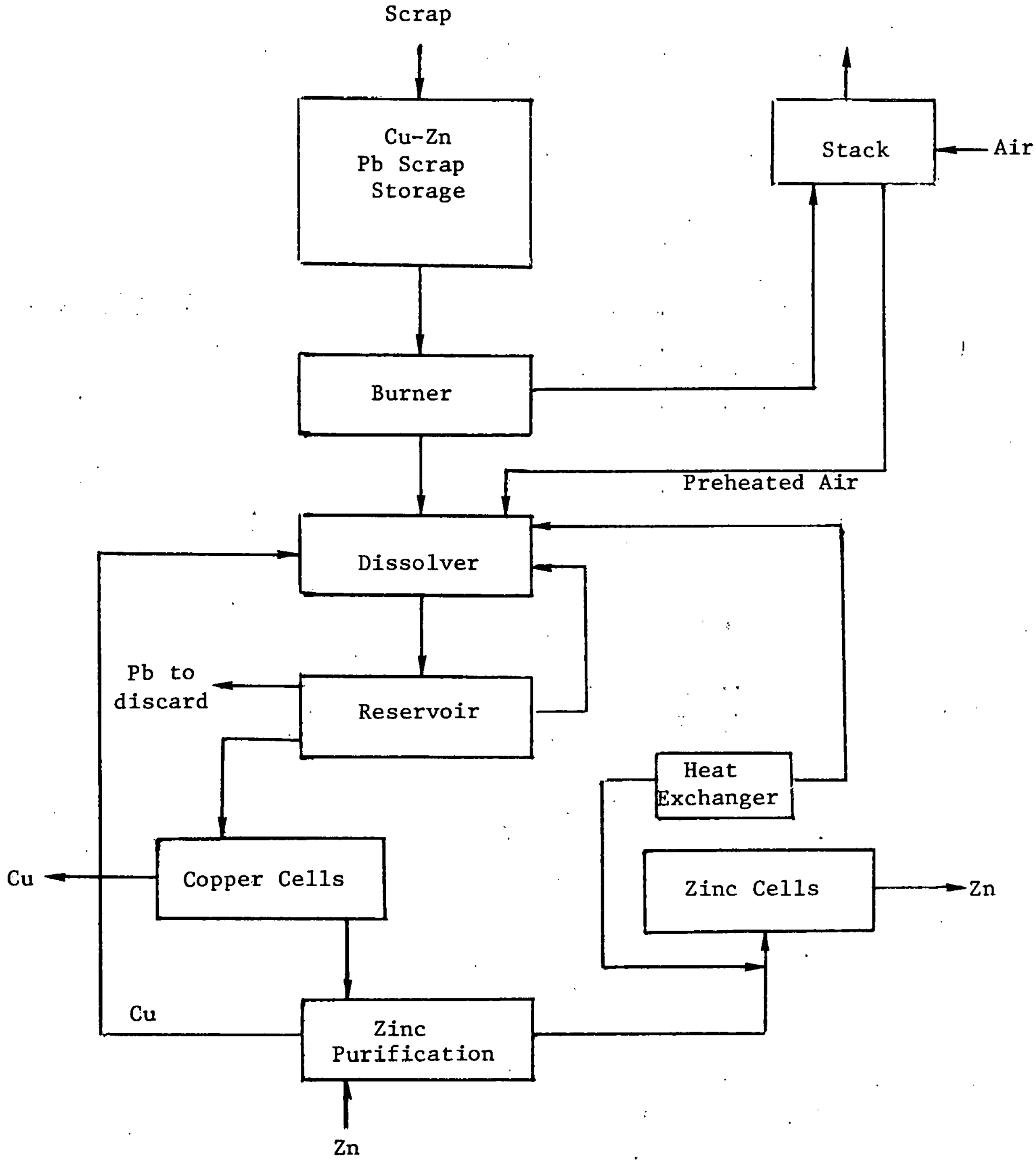


Fig. 19. Sulfuric acid dissolution process for the recovery of copper and zinc from scrap (26).

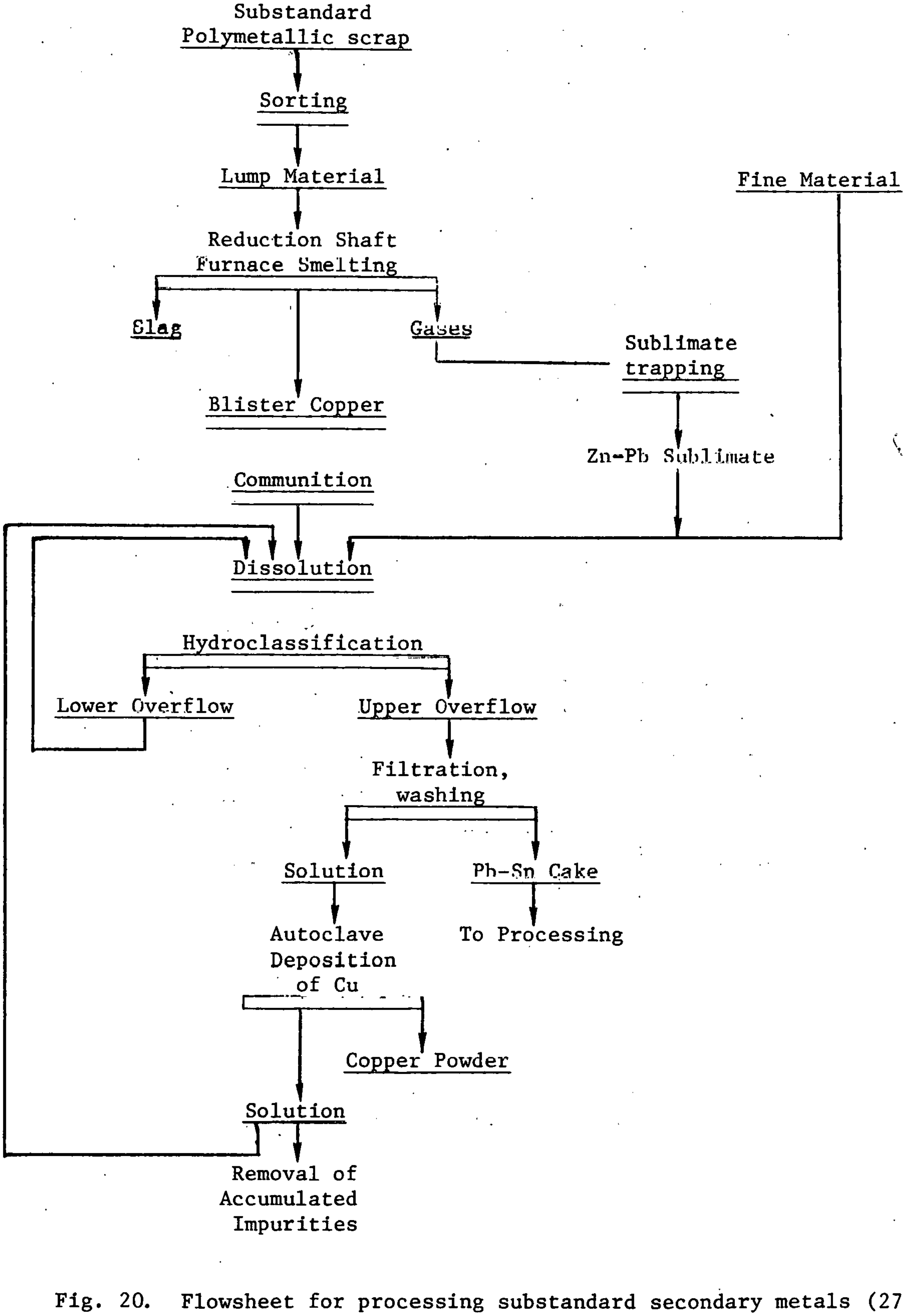


Fig. 20. Flowsheet for processing substandard secondary metals (27).

In a process currently being piloted by Air Products and Chemicals (28), scrap or cement copper is dissolved in a cupric sulfate-sulfuric acid-acetonitrile solution (see Fig. 21). Acetonitrile acts as a stabilizing ligand for the cuprous ion so that the dissolution reaction may be written as

$$Cu^{\circ} + Cu^{++} + 4CH_3CN \rightarrow 2Cu(CH_3CN)_2^{+}$$

Insoluble impurities are filtered from the solution. When the acetonitrile is steam-stripped from the solution, the remaining cuprous sulfate solution is unstable and the copper disproportionates, one-half going to copper powder and the other half remaining as cupric sulfate solution. Soluble impurities remain in the solution. The copper powder is washed and dried prior to consolidation for melting. The acidified cupric sulfate solution is recombined with the condensed acetonitrile and returned to the leach reactor. A high purity copper product is claimed. An energy expenditure of only 10×10^6 BTU/ton Cu is claimed for the process from solution to melted copper product (29). In an alternate recovery scheme a one-electron process is described where copper is directly electrowon from cuprous nitrile solutions (30). The cells were operated at $\sim$15 mA/cm^2. Deposition rates are twice that of a cupric sulfate bath at a similar current density, but cell voltages are only slightly higher. Current efficiencies are >95% and good cathode quality is reported. The electrolyte must be covered with kerosene to avoid oxidation of the cuprous ion, and problems may exist with nitrile stability.

Sulfuric acid leaching is used commercially in Japan to recover copper, cadmium and zinc from flash furnace dusts (31). All metals in the dust except lead are dissolved and the latter is filtered and sold to a lead smelter for subsequent reduction. Hydrogen sulfide is used to precipitate most of the copper from the sulfate solution, the pH is then raised to approximately 2, and the balance of the copper is removed by cementation on iron. The cement copper and the copper sulfide are sold to a smelter for purification. The decopperized solution is further neutralized by air sparging to precipitate iron and arsenic, which are disposed of. Cadmium is removed by cementation on zinc dust, the zinc precipitated as a hydroxide by addition of ammonia, and the cadmium and zinc precipitates sold to a zinc smelter for purification. Thus, a waste material has been effectively reprocessed to recover value metals which are then processed in existing primary or secondary plants. It is probable that the economics of this process are environmentally driven and that the revenues from the toll-treated metals offset the cost of disposing of the dust in an acceptable manner.

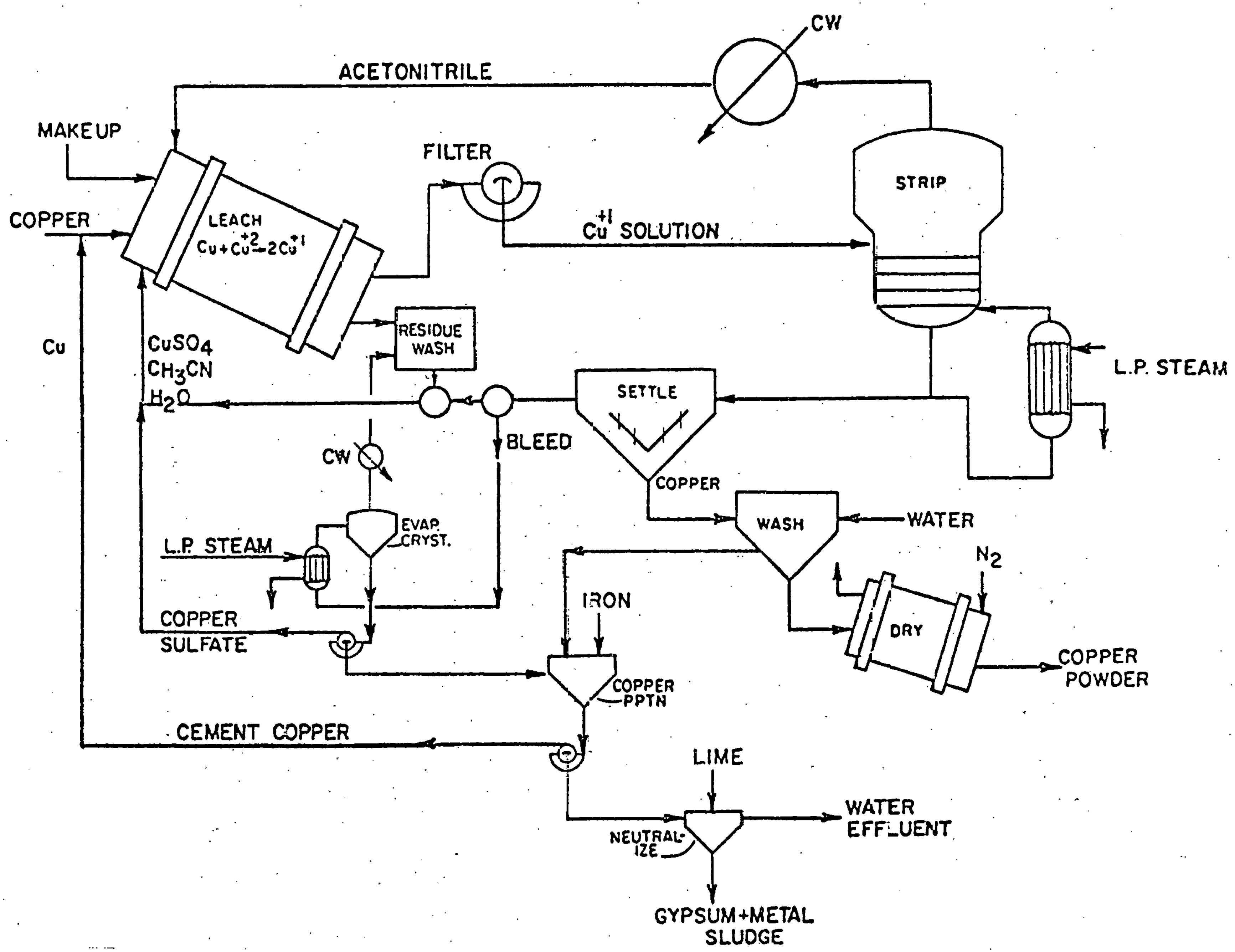


Fig. 21 . Acetonitrile leach - disproportionating process for scrap copper refining (28).

A process has been devised which is capable of recovering copper and zinc separately from scrap brass while also accepting feeds of copper machining scrap and zinc oxide dust (32). A flowsheet for the process is given in Fig. 22. The brass is cast into anodes and the copper content is electrorefined. However, the copper cathodes produced are not of wire bar quality, being high in tin and lead, and the anode slime production is ten times that encountered in conventional practice. The electrorefinery impurities bleed stream has a very high acid content and is neutralized by dissolving the required amount of zinc oxide scrap. Solution purification follows techniques currently employed in electrolytic zinc production although nickel recovery is troublesome, requiring a four to five fold excess of the precipitating reagent, dimethylglyoxime. Zinc is recovered from the purified solution by electrowinning and the acid electrolyte from the zinc tankhouse is used to redissolve metallic copper scrap for recycle to electrorefining thereby maintaining the required concentration of cupric ions in solution. The process is interesting because it combines pyro- and hydrometallurgical techniques and treats three distinctly different types of scrap. However, the process material balance will severely restrict the amount of each metal which may be used and could cause control or raw material supply problems. The relatively high copper electrorefining power required, caused by slime adherence to the anode, and the impure product produced limit the attractiveness of the method. In addition, process complexity would be increased substantially if significant amounts of iron entered the circuit with the scrap feed material.

4.2.8 Conclusions

Recycle of copper scrap is a relatively efficient operation. High-grade scrap is processed with high yield at low energy consumption. Low-grade scrap is also handled by current technology but with lower yield and higher energy requirements. We have not identified a large scrap source of copper which cannot be treated by current pyrometallurgical technology followed by electrorefining.

In Section 5.3 we consider the energy and cost of a hydrometallurgical alternative, which includes electrowinning, for the recovery of copper from low-grade scrap.

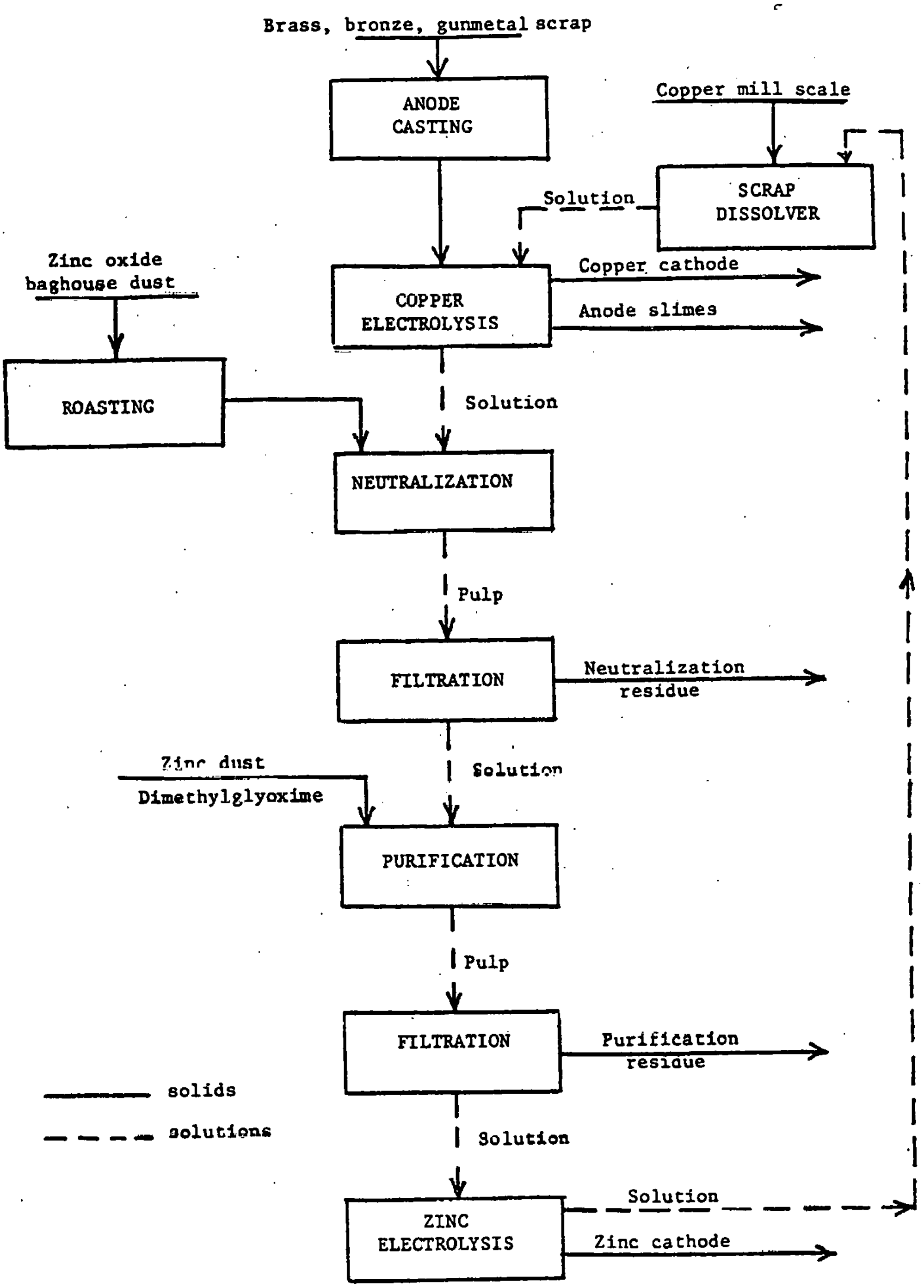


Fig. 22. Flowsheet of copper alloy scrap treatment pilot plant (32).

4.3 Zinc

4.3.1 Statistics and Energy Considerations

The versatility of zinc, both as the metal and as an alloy addition, has made it fourth among metals in demand both in the United States and throughout the world, being surpassed only by steel, aluminum and copper. Zinc is produced in several grades such as Prime Western for hot-dip galvanizing as a protective coating for steel, High Grade zinc with aluminum additions for die castings for automotive and other uses, and Brass Special and Intermediate Zinc for alloying with copper. In addition, large quantities of zinc dust and zinc oxide are used in paints and coatings.

Primary zinc is obtained largely from the sulfide ores sphalerite and wurtzite which often occur together with other minerals such as lead and copper sulfides. Concentration and separation of lead and copper fractions are achieved by a differential flotation process. Significant oxidized ores exist in the United States where zinc is present as the carbonate or silicate. Beneficiation of these ores may be achieved by addition of sodium sulfide to sulfidize the mineral surface prior to flotation.

Zinc is produced in the United States by three processes, two pyrometallurgical and one hydrometallurgical. The high temperature processes take advantage of the volatility of zinc by using a reduction - volatilization - condensation sequence. The electrothermic process roasts the concentrate in fluid and flash roasters. The calcine is mixed with coke and other materials to produce a sintered pellet which is then reduced in an electrothermic retort and the zinc vapor condensed. In the vertical retort process, the concentrate is pelletized before roasting and the calcine mixed with coal and briquetted. The reduction products, zinc vapor and CO, flow upward and out of the retort where the zinc is condensed. In the electrolytic process the concentrate is roasted to the oxide, and the oxide leached by spent sulfuric acid electrolyte. After filtration, the leachate is purified by the addition of zinc metal and the purified solution is then electrowon.

Energistics for the three processes are given in Figs. 23, 24 and 25. The electrolytic process is somewhat less energy intensive than the distillation processes.

In addition to these processes practiced in the United States, Imperial Smelting Corp. has developed a process which burns coke in intimate association with ore in a blast furnace. Again, in this process zinc vapor is released and condensed. This process is used extensively in many countries in Europe and Asia as well as in Australia. The Kivcet-CS process, developed in the USSR, combines sintering, blast furnace and slag fuming into a single autogenous unit.

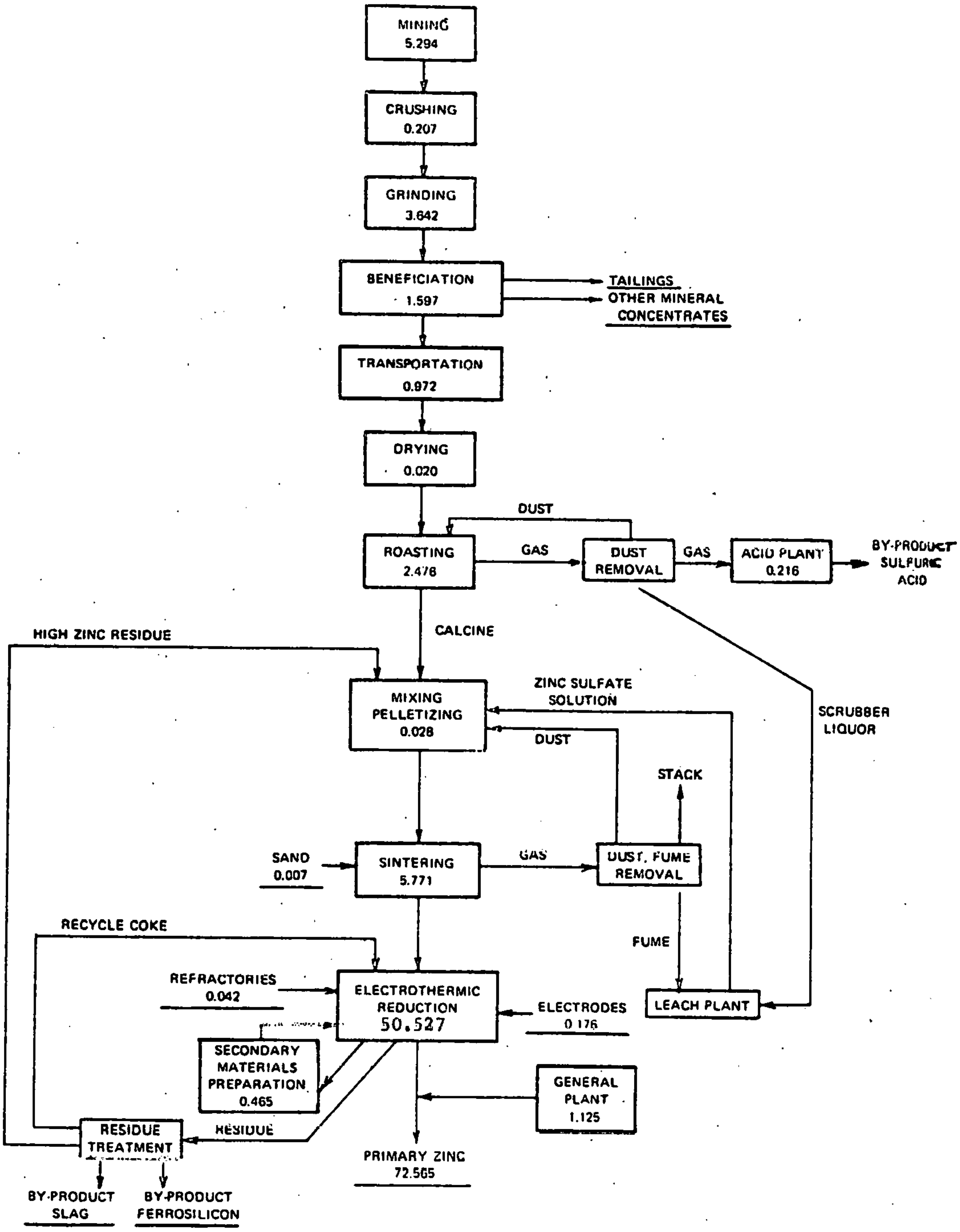


Fig. 23. Production of zinc by the electrothermic process (1).

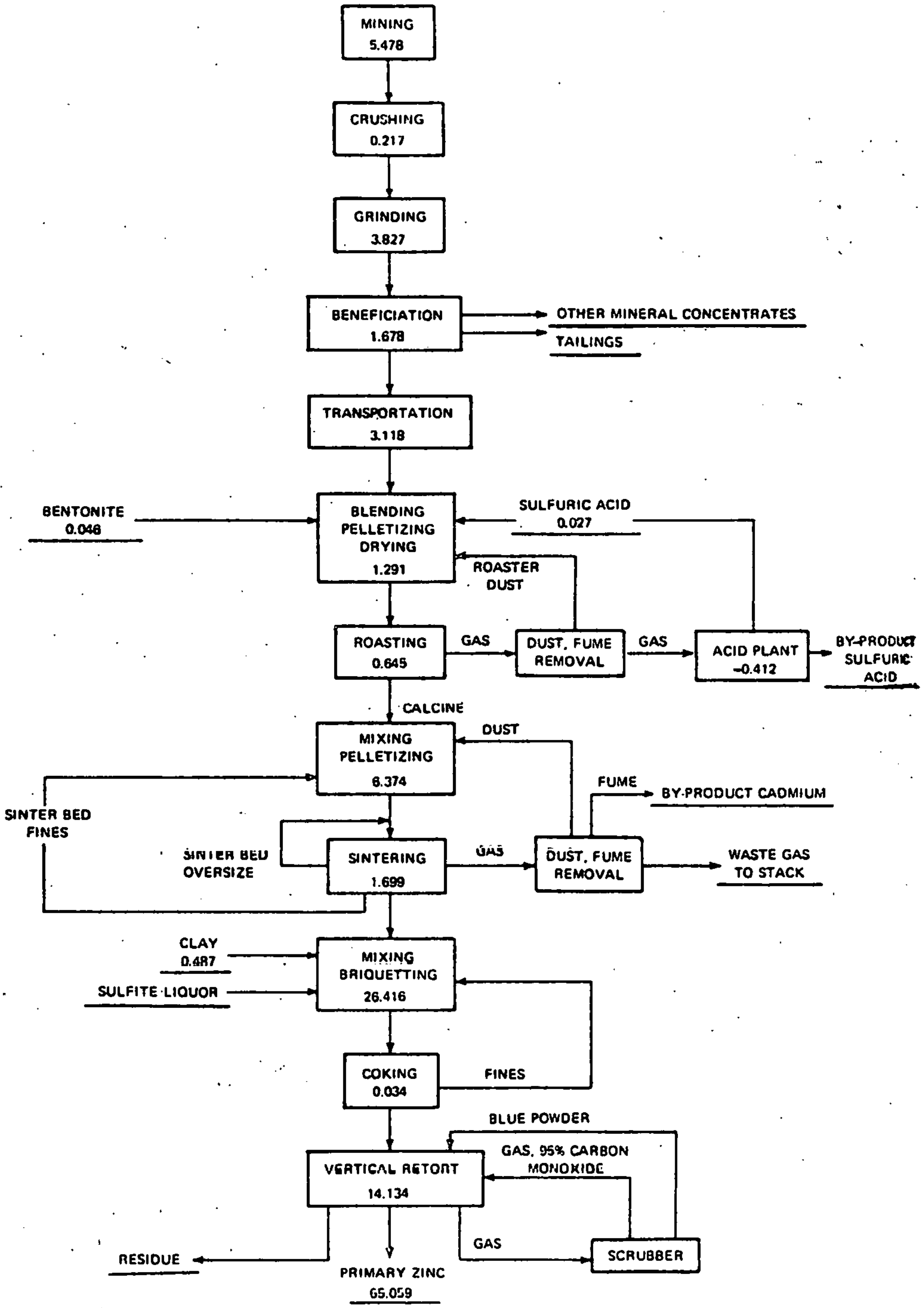


Fig. 24. Production of zinc by the vertical retort process (1).

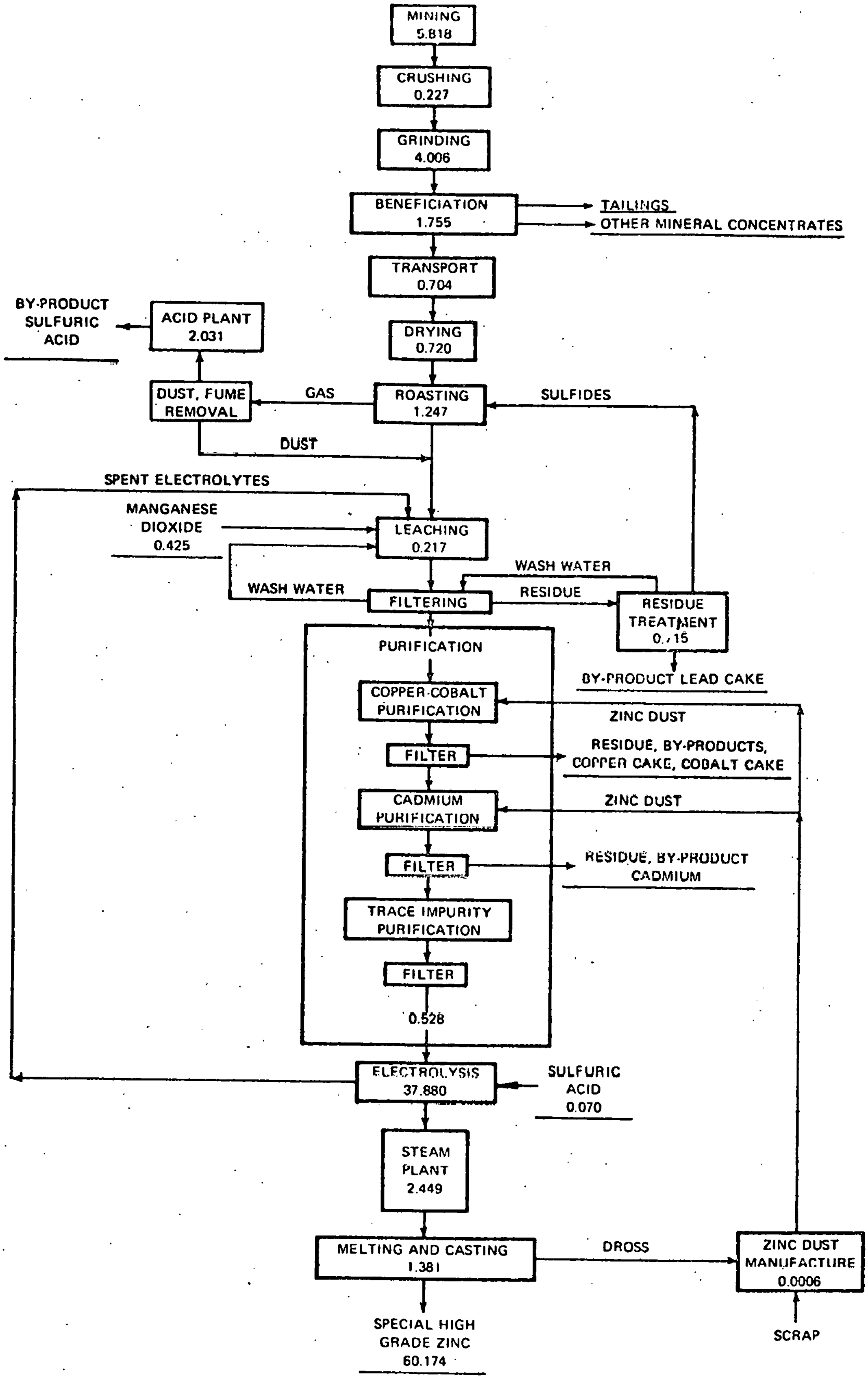


Fig. 25. Production of zinc by the electrolytic process (1).

4.3.2 Zinc Oxide

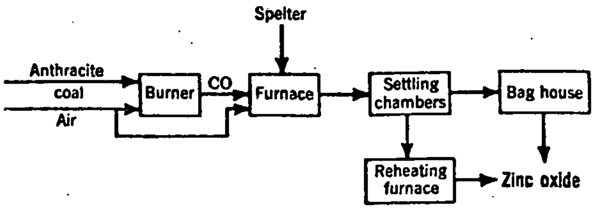
Zinc oxide is produced from zinc metal by the French (or Indirect) Process, from zinc oxide ore by the American (or Direct) Process, and from secondary metal by distillation. Flowsheets and energy inputs for the French and American processes are given in Figs. 26 and 27. Energy requirements are 69 × 10^6 and 115 × 10^6 BTU/ton zinc oxide respectively. We may assume that the energy needed for zinc oxide production from secondary metal is equivalent to that required for zinc dust production as shown below and has an average value of 20 × 10^6 BTU/ton zinc oxide. The energy for zinc oxide production from secondary material is only about one quarter of that required for production from primary sources.

Forecasts for the United States demand for zinc metal and non-metal in the years 1985 and 2000 along with data for 1976 are presented in Table 16.

The average annual growth rates for the primary metal and non-metal are quite low at about 2%. For the metal, major contingencies in the low forecast include elimination in major industrial fields due to substitution and changes in automobile types. High forecast data comprehend increases in galvanized sheet use in construction and automotive industries and expansion of use of die cast and brass products. For the non-metal, major contingencies on the low side are replacement in residential latex paint market by competitive pigments (although the maintenance and industrial paint market is expected to continue to use zinc-based pigments) and low automobile output with the attendent decrease in tire production. High side contingencies are a result of high growth rates in the paper and automotive tire industries.

Primary production of metallic zinc in the United States accounted for only 38% of the demand in 1976 and is expected to remain at about this figure through the year 2000. We will therefore remain large net importers of zinc. Primary production of zinc oxide accounted for about 92% of demand and we should remain self-sufficient in this commodity.

In the year 1973 about 35% of the primary zinc was produced by the electrothermic process, 20% by the vertical retort and 45% by the electrolytic process. This gave a weighted average of 65 x 10^6 BTU/ton of zinc for the energy content of the primary product. By 1978 there was only one electrothermic plant and one vertical retort in operation in the United States as the newer, more efficient electrolytic plants take over the primary production. The last vertical retort is expected to phase out within the next few years and by 1985 all zinc production capacity is likely to be electrolytic. The quantity of energy used in primary production projected for the years 1985 and 2000, is given in Table 17. The electrolytic component is also given and refers to the quantity of energy used during electrolysis of the leached calcine solution.



Reaction

$$Zn + \frac{1}{2}O_2 \rightarrow ZnO$$

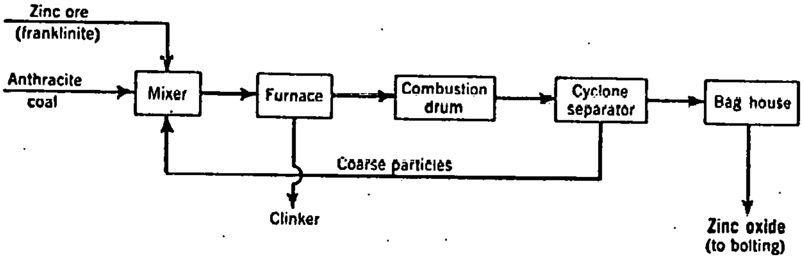
95–96% yield

Material and Utility Requirements

Basis—1 ton zinc oxide (all grades)

Spelter (metallic zinc)	1,740 lb
Coal (anthracite)	1,300 lb
Electricity	35 kwhr

Fig. 26. Production of zinc oxide by the French process (33).



Reaction

$$\underset{\text{(In ore)}}{ZnO} + CO \rightarrow Zn + CO_2$$

$$Zn + \frac{1}{2}O_2 \rightarrow ZnO$$

92–93% yield (recovery from ore)

Material and Utility Requirements

Basis—1 ton zinc oxide

Franklinite ore (20% ZnO)	5.25 tons
Coal	3 to 5 tons
Electricity	360 kwhr

Fig. 27. Production of zinc oxide by the American process (33).

Table 16

U.S. Zinc Demand Forecast (34)

(thousands of short tons)

	Probable			2000 Forecast Range		Average Annual Growth Rate
	1976	1985	2000	Low	High	Growth Rate 1976-2000 (%)
Metal:						
Primary	1,096	1,290	1,700	1,280	2,880	1.8
Secondary	95	130	200	120	220	3.2
Nonmetal:						
Primary	180	210	300	200	400	2.2

Table 17

Energy Consumption in the Production of Primary Zinc in the Years 1985 and 2000

Year	Primary Production (thousands of short tons)	Total Energy 10^{12} BTU	Electrolytic Energy, 10^{12} BTU
1985	600	36	23
2000	800	48	40

The probable forecast for zinc metal demand for the year 2000 by end use is given in Table 18.

A flow diagram for zinc scrap, including non-metallic zinc is given in Fig. 28. Secondary zinc accounted for only about 7% of the primary demand in 1976 and is projected to increase to only 9% in the year 2000.

In the year 1976 zinc scrap consumption, including zinc oxide, was estimated to be about 180,000 short tons, and a breakdown by category is given in Table 10.

An analysis of the product life cycle and recoverability of zinc (21) indicates that at present over 90% of all zinc products which become obsolete are not recovered. Over 50% of this amount is used in capacities which are considered as dissipative such as galvanized steel and oxide products. The potentially recoverable products are found primarily in brass, zinc-base alloy and rolled zinc products. In 1970 only 109,000 short tons of zinc were recovered compared with 1,158,000 tons unrecovered. Of the unrecovered fraction, 636,000 tons were considered as dissipative, leaving 522,000 as recoverable.

Three principle methods have been identified for recycling scrap zinc metal: retort distillation, muffle furnace distillation and pot melting. The energistic flow sheets are shown for these processes in Figs. 29, 30 and 31. Pot melting is used primarily for pure scrap such as new clippings, remelt zinc and die casting. The weighted average for the enegy content of recycled zinc is 19 × 10^6 BTU/ton Zn.

The total energy and electrolytic energy saved by recycling zinc in the years 1985 and 2000 are given in Table 20.

4.3.3 Sources of Scrap

The major categories of zinc scrap are listed below:

- Galvanizers' dross, amounting to approximately 1/4 of the total scrap processed, are zinc rich mixtures of zinc oxide, iron and small amounts of sal salts.

- Ashes and skimmings, also amounting to approximately 1/4 of the total, are mixtures containing relatively less zinc, more zinc oxide, and in the case of sal skimmings, significant amounts of chloride fluxes.

- Die cast scrap, new and old, amount to another 1/4 of the total. New die cast scrap is usually relatively clean, while old scrap is contaminated with other metals derived from the article of use from which the zinc scrap was recovered.

Table 18

End Use of Zinc Metal in the Year 2000 (34)

End Use	Quantity (thousands of short tons)
Construction	700
Transportation	500
Electrical	400
Machinery	150
Other	150
Total	1,900

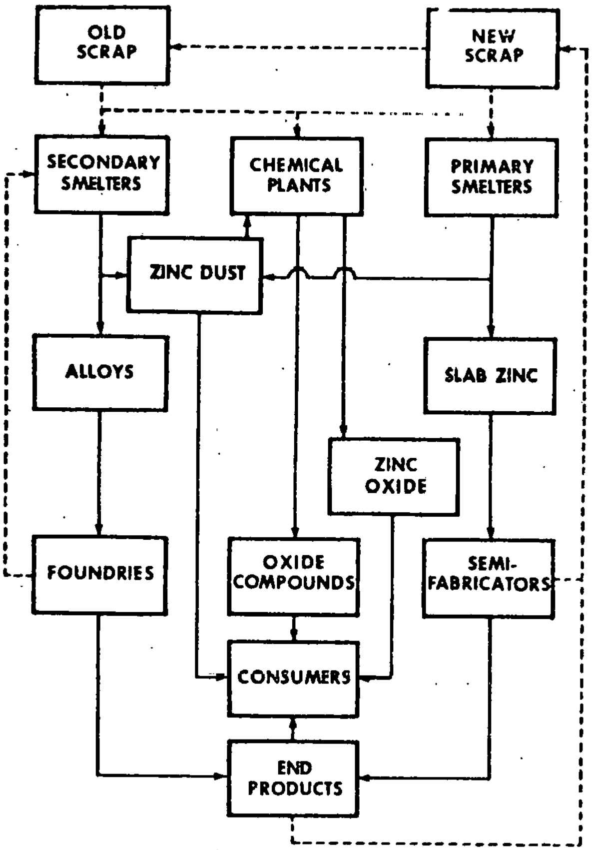


Fig. 28. Zinc scrap flow diagram (34).

Table 19

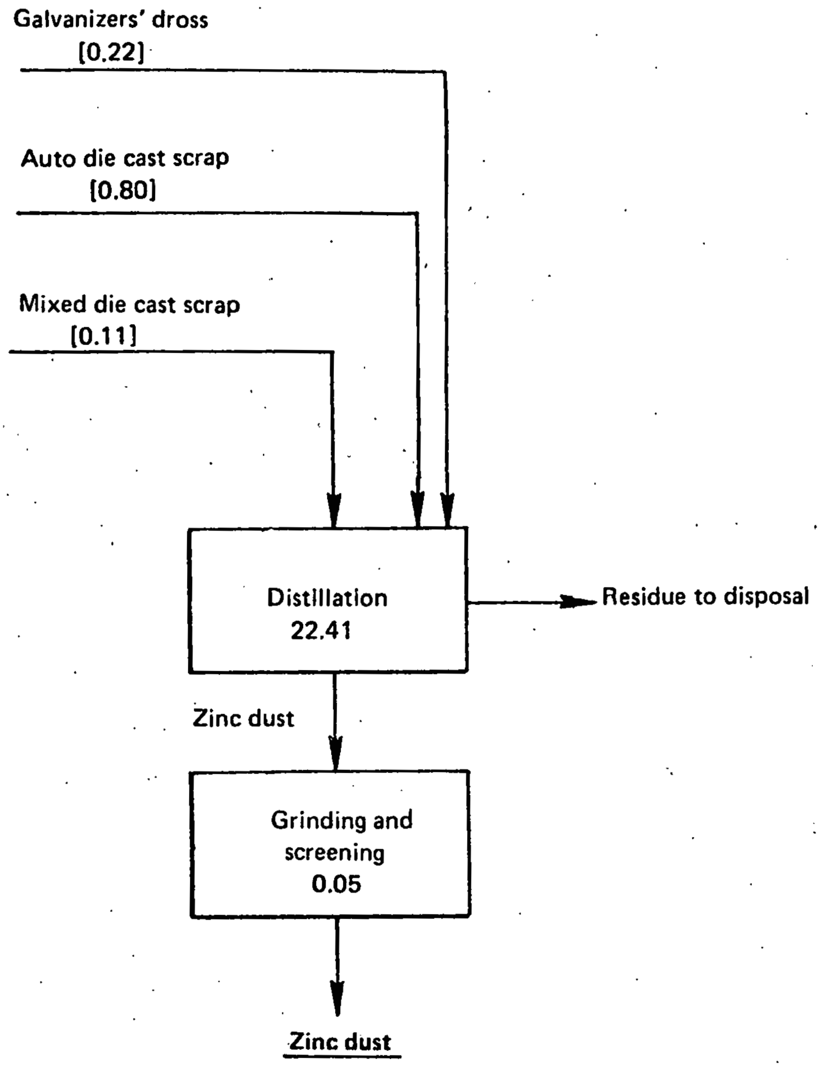
Zinc Scrap Consumed in 1976, Including Oxide (3)

	Obsolete Scrap (thousands of short tons)	Prompt Industrial Scrap (thousands of short tons)
Smelters and Distillers:		
New clippings	-	721
Old zinc	8,948	-
Remelt zinc	-	3,248
Engravers plates	801	-
Rod and die scrap	5,334	-
Die castings	10,881	-
Fragmentized die casting	14,918	-
Remelt die cast slab	7,882	-
Skimmings and ashes	-	49,397
Sal skimmings	-	6,614
Die cast skimmings	-	4,504
Galvanizers' dross	-	46,369
Flue dust	-	5,995
Chemical residue	-	13,837
Other	-	97
Total	48,764	130,782

Table 20

Energy Saved in Zinc Metal Recycle

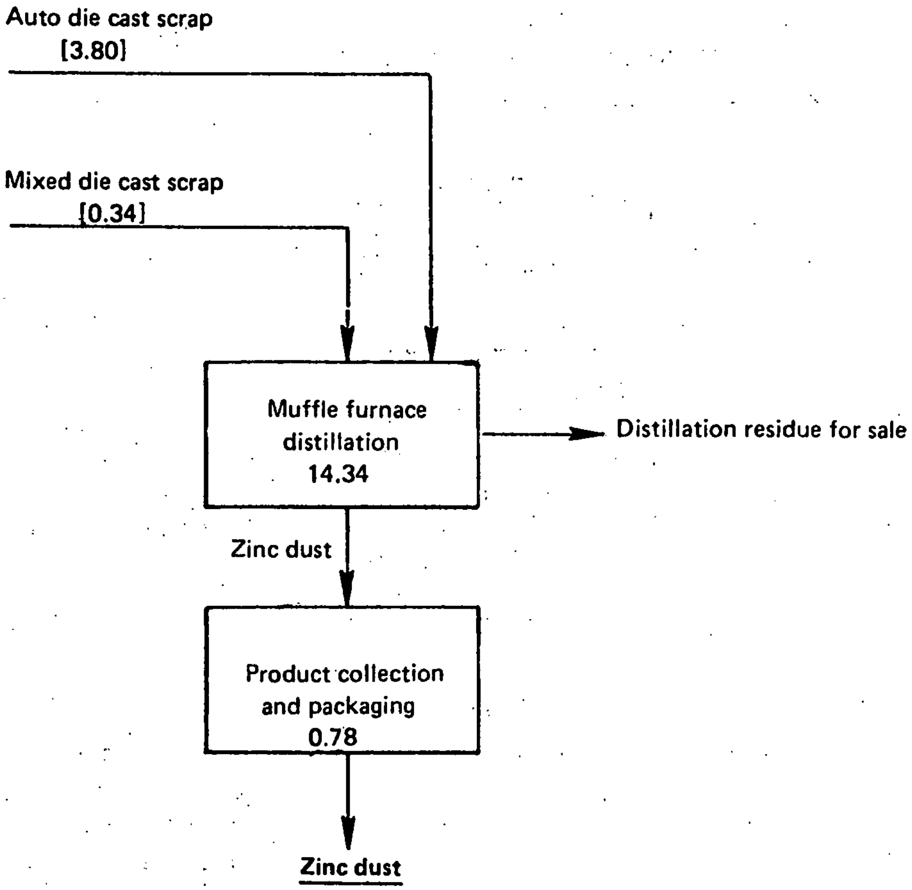
Year	Total Energy, 10^{12} BTU	Electrolytic Energy 10^{12}, BTU
1985	5.3	4.9
2000	8.2	7.6



SUMMARY

	Million Btu per ton of product
Process energy	23.59
Pollution control energy	0.29
Space heating	0.13
Total energy	24.01

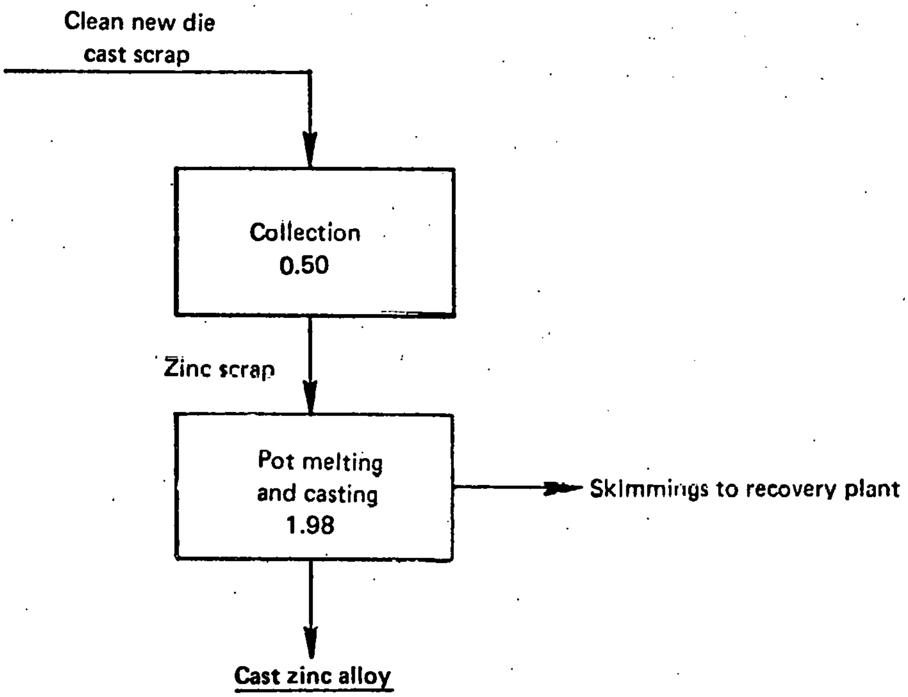
Fig. 29. Zinc: Production of zinc dust from scrap in distillation retorts (3).



SUMMARY

	Million Btu per ton of product
Process energy	19.26
Pollution control energy	0.32
Space heating	0.13
Total energy	19.71

Fig. 30. Zinc: Production of zinc dust from scrap in muffle furnace (3).



SUMMARY

	Million Btu per ton of product
Process energy	2.48
Pollution control energy	0.00
Space heating	0.10
Total energy	2.58

Fig. 31. Zinc: Recycling of clean zinc die casting scrap by pot melting (3).

In addition, large amounts of zinc-rich dusts are generated in the ferrous and nonferrous processing industries from which zinc and other metals might be recovered. Although these dusts are not currently processed in the United States, technology exists to do so and recovery is currently practiced in both Europe and Japan.

Almost one half of the secondary zinc is recovered as various grades of slab zinc which are used largely in galvanizing operations. The majority of the remainder is recycled as zinc dust and oxides of zinc which are used in the rubber industry, in pigments, and for production of the various zinc chemicals used for agricultural and miscellaneous purposes. A small amount, derived from new scrap, is remelted to die cast material.

4.3.4 Properties of Zinc Important in Recycling

Conventional zinc recycling practice is based on the fact that the scrap material consist largely of metallic zinc and that the element has both a low melting point and high vapor pressure. Of the common metallic impurities associated with zinc, only cadmium, tin and lead have lower melting points and only cadmium has a higher vapor pressure. The next most volatile impurity, lead, has a vapor pressure 0.1% that of zinc at normal operating temperatures used in zinc distillation. Since the heats of melting and vaporization for zinc are low, 0.5 and 2 million Btu/ton respectively, relatively simple and energy efficient processes based on melting and vaporization can be used to recover the metal.

Zinc oxide, derived either from calcined ores or from scrap material, can be reduced with carbonaceous materials and the metal distilled. This serves as the basis for the classic Waelz process where reduction takes place in a rotary kiln and the resulting zinc is condensed from combustion gases containing carbon monoxide in an external condenser. Other relatively easily reducible metal oxides, and especially lead, may also be volatized and carried over, condensing with the zinc and reducing the product purity. The theoretical energy requirements for this reduction is only 3 million BTU/ton but, as in the case of distillation, practical energy requirements are substantially higher.

Zinc can also be reduced from aqueous solution electrochemically but the voltage required is sufficiently high so that, for the process to operate, it is necessary to take advantage of the hydrogen overvoltage on the cathode surface to prevent water dissociation. Contaminants such as arsenic, antimony, copper and tin, which permit liberation of hydrogen more readily than zinc, cause a fall in current efficiency for zinc deposition. Other common impurities such as cadmium and lead are co-deposited with zinc and adversely affect its properties. Iron, cobalt and nickel are detrimental since they lead to re-solution of the cathode with attendant losses in current efficiency.

The success of an electrolytic zinc recovery process from ore or scrap is, then, critically dependent upon solution purification. This becomes particularly important when lower grade scraps or alternative sources, such as dust of complex composition, are considered. An advantage of electrolytic zinc production, however, is that the product is produced directly at a high purity suitable for use in die cast applications. The energy penalty paid to achieve this is significant, however, since electrowinning requires about 30 million Btu/ton, significantly higher than is needed for distillation processes even at conventionally low efficiencies.

4.3.5 Current Practices in Recycling

Technology for the recovery of zinc from these scrap materials is mature, relatively simple, and not highly sensitive to the grade of the scrap processed. A schematic representation of the operations involved in zinc scrap recovery is shown in Fig. 32. Some scrap, ashes, and particularly skimmings, may be crushed, ground, and classified to remove salts and oxides prior to further treatment. Low grade, irony die cast scrap may be "sweated" by direct heating in rotary furnaces to separate a relatively impure zinc from other residues.

These upgraded materials, drosses, and some die cast scrap are treated in retorts or muffle furnaces where indirect heating supplied by the combustion of fuels is used to melt and vaporize the zinc. The vapors are collected in external condensers where liquid zinc of 99% purity can be produced. Alternatively, the vapors may be oxidized in air to produce zinc oxide directly. Overall zinc recoveries approach 90%, but operating problems and equipment degradation are experienced in removing residues from the stills.

New die cast scrap of high purity may be remelted in pot furnaces and recast. This operation is simple and metal recoveries are high, but the thermal efficiency of the process is rather low.

Zinc produced by distillation may be further purified, if required, by redistillation in multi-stage contactors to significantly reduce the lead and cadmium contents.

These relatively simple techniques are effective because of the normally high purity of the new scrap which is processed, and because of the relatively high volatility of zinc as discussed above. While these methods are applicable to scrap material containing preponderantly metallic zinc, they would not be as efficient in processing low grade, oxidic, or zinc alloy materials. Here, hydrometallurgical techniques could offer a more attractive route to the recovery of zinc. A collateral benefit to hydrometallurgical processing would result from the high purity of zinc produced which would be suitable for die casting or alloying to brass rather than being generally restricted to use in galvanizing.

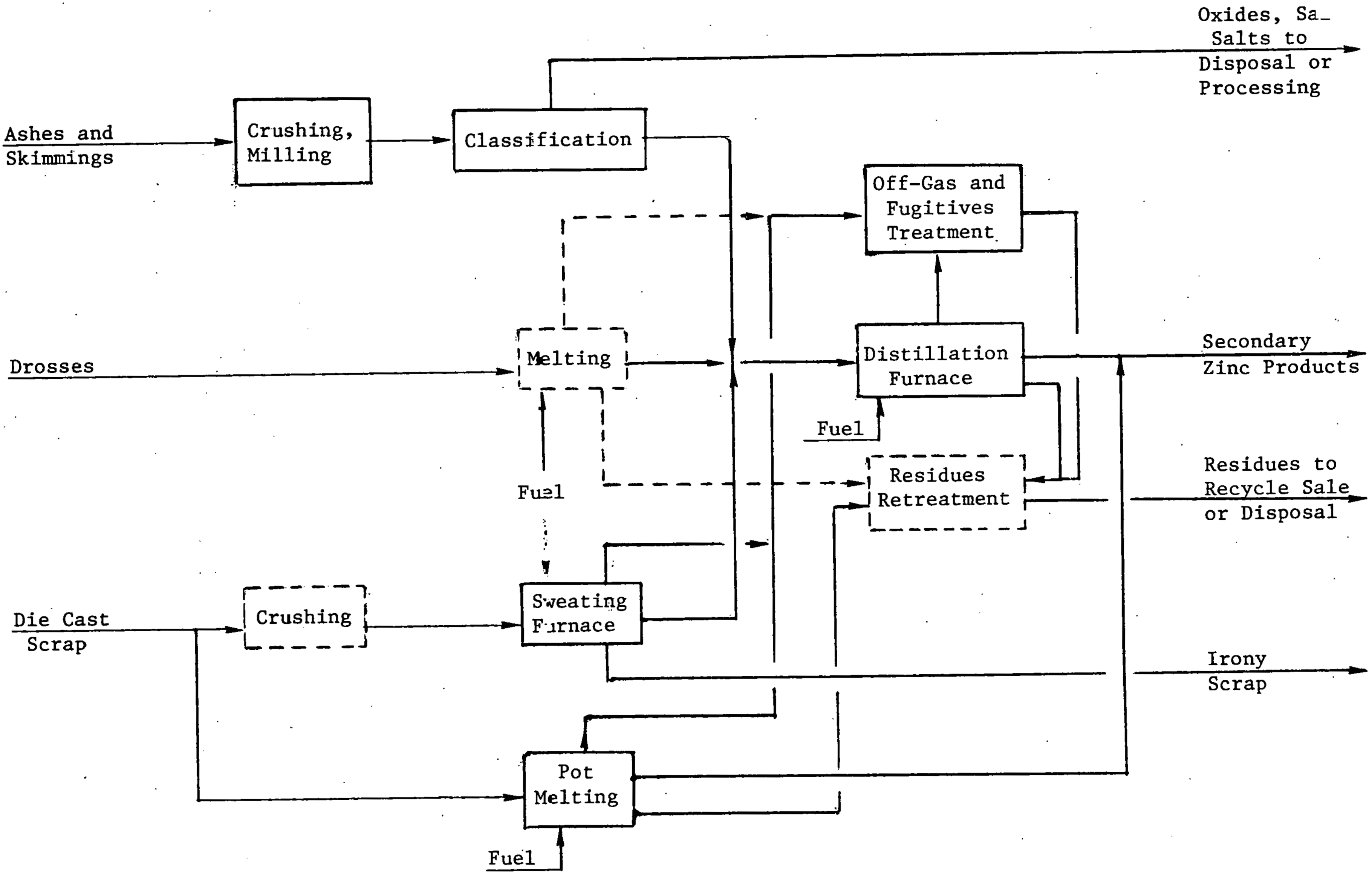


Fig. 32. Zinc scrap treatment processes materials and energy flows.

4.3.6 Alternative Processes for Scrap Recycle

Recovery of slab zinc from drosses and skimmings is currently carried out by techniques and equipment which have been used for many years. Clearly, there is substantial room for improvement in the thermal efficiency obtained in current processes, which have historically been rather low. Closer control of the distillation operation, including more careful selection of the charge material, may reduce both energy requirements and maintenance problems while increasing the recovery of the material charged. It is not likely that the hydrometallurgical process, with complex solution purification requirements, could displace even moderately improved distillation techniques. The thermal efficiency of pot melting might also be improved, and little incentive exists to oxidize and re-reduce electrohydrometallurgically an already relatively pure die cast material. Improved control of these pyrometallurgical operations would also decrease environmental problems, particularly control of fugitives from fuming in zinc oxide production operations. Improved control could be managed with currently existing technology.

A significant portion of the so-called dissipative zinc scrap is contained in flue dusts derived from steel mills, secondary smelters, brass mills, remelters, galvanizers, etc. The Bureau of Mines (19) estimates that, during the early 1970's, about 220,000 tons of zinc was potentially available annually from stack dusts. About half of the zinc content of these dusts originates as emissions from steelmaking operations. Open hearth and BOF processes generally contain 3-5% Zn, while electric furnace discharges are rich in zinc, usually containing more than 20% Zn. Twenty percent of steel production in the United States is by electric furnace, and the total zinc in the dust generated is estimated to be about 65,000 tons annually.

In addition to their value as a source of zinc oxide, the dusts are also potential sources of iron oxide which could be recycled were it not for its zinc and lead content. In high concentrations these metals are capable of rapidly attacking refractory furnace linings, but dusts with up to 2 percent combined zinc and lead can be pelletized and recycled. Generally, however, steelmaking wastes are disposed of in solid waste dumps with no regard to future reclamation.

A number of studies have been conducted in the United States to devise processes for recycle of the zinc, lead and iron contents of steelmaking dusts. Since none is practiced industrially, they apparently are not economically viable. The extent to which environmental factors have been taken into account in deciding the feasibility of these processes is not known. It is possible that some wastes are not disposed of in an environmentally acceptable manner, especially those containing lead.

Barnard et al. (35) mixed flue dust with sulfuric acid and rabble roasted the slurry to oxidize the iron sulfate and then leached the copper, zinc and other soluble sulfates. The residue was reduced with carbon monoxide at elevated temperature, reducing the iron to metal and vaporizing the lead. The iron product, however, contained about 2 percent sulfur which is undesirable for iron recycle.

Holley and Weidner (36) heated pelletized dusts in a rotating hearth furnace to reduce the zinc content from 2.7 to .07 percent. Thom and Schuldt (37) added anthracite and dolomite to open hearth dust in a kiln and achieved 95% reduction of zinc and lead contents. Higley and Fukubayaski (38) pelletized and reduction roasted electric furnace dusts in a shaft furnace to recover about 90 percent of the zinc in a grade equivalent to Prime Western zinc. The iron residue, however, contained about 2.5 percent lead and could not be recycled to an electric furnace. The authors suggested that the feed should be adequate for basic oxygen steelmaking. Holowaty (39) at Inland Steel reports a pilot plant study where dusts containing up to 12% Zn were roasted with coke breeze to produce metallized iron pellets containing only 0.1 to 0.3 percent zinc. The principal objective here was to obtain iron oxide suitable for steelmaking, and the zinc oxide product was highly contaminated with iron fines. The Krupp Company in Rheinshausen, Germany, further tested Inland Steel dusts using a modified Waelz process. Following the Krupp tests a regional plant design flowsheet was prepared for the Chicago area with a nominal intake capacity of 400,000 tons of dust per year. This program is currently inactive.

A similar process is described by Allen (40) who briquettes the dust with a pitch binder and sufficient carbon to reduce the lead and zinc oxides present. Briquettes are hardened at temperatures between 175° and 320°C and then heated to 1000° to 1400°C to reduce the oxides to metal, volatize the lead and zinc and subsequently re-oxidize them to PbO and ZnO. The zinc and lead oxides are recovered from exhaust gases and the iron-bearing briquettes are reported to be suitable for charge to iron or steelmaking processes.

Japan is the only industrialized nation to treat high zinc-containing dusts commercially. Several plants which recycle steelmaking wastes are operated or supported by the steel industry. The Japanese government also supplied a considerable subsidy to these operations. Inazaki (41) uses the Waelz process in a rotary kiln at 1200°C with coke as the reductant. Leaded zinc oxide at 12,000 tons per year is produced along with metallized iron pellets. The Sohetsu Metal Company (42) announced a project with a 25-company consortium to process 60,000 tons per year of flue dust, also in a Waelz kiln, to produce metallized iron pellets and a crude zinc oxide. Kawasaki Steel Corp. (43) operates three plants which have a capacity of 840,000 tons per year of dusts and sludges to produce 500,000 tons per year of pre-reduced iron pellets.

The complex oxides from flue dusts may lend themselves more readily to processing by hydrometallurgical techniques where recovery and separation of other value metals in addition to zinc are possible. The higher revenues obtained by sale of all the various metal values could offset higher operating costs.

4.3.7 General Requirements for Hydrometallurgical Scrap Treating Processes

The general process and requirements for zinc recovery are the same as for copper recovery processes previously outlined in Fig. 16. If copper-containing dusts or low grade brasses or bronzes are to be treated, the conceptual flowsheet would also be quite similar. Major difference would occur in the solution purification steps. If it is required to remove small amounts of zinc prior to copper recovery, then even an inefficient zinc purification step could be used since copper electrowinning can take place in the presence of substantial concentrations of zinc. The converse is not true, however, and copper and other impurities must be removed to very low levels, as previously stated, if zinc is to be recovered.

4.3.8 Hydrometallurgical Process Alternatives for Scrap Recycle

A significant literature exists dealing with zinc recovery incidental to processes for treating copper scrap, but there is little evidence that a comparable effort has been devoted to hydrometallurgical process development for bulk zinc scrap even though the same general techniques apply. A patent has been granted for a continuous countercurrent sulfuric acid leach at controlled pH to remove the galvanized coatings from scrap iron (44). It would appear that a combination of material handling problems (the raw material is very low grade) and iron removal requirements would result in the cost of an integrated process being unacceptably high.

No fully hydrometallurgical scrap process is known to be in commercial use, but several had been proposed, all based on the use of sulfuric acid as a lixiviant (45-49). Experimental data which have been reported from these various sources are internally consistent; zinc recoveries range from 70-90%, increasing with a decreasing pH in the leaching step. Unfortunately, the dissolution of iron also increases substantially, to as high as 90% at lower pH, rendering the process uneconomical due to increased acid consumption and the size and cost of the iron removal steps. Lead and tin are not dissolved from the dusts. It is claimed that they could be sold to smelters for further processing, although it is not clear how they would be removed from the undissolved iron. Copper recovery is also high, 80-90%, and if enough were present in the dust, its recovery would be easily justified. Most of the data which are reported deal with leach results only, although in some cases, details of the solution purification steps are given. While integrated laboratory or pilot data would be necessary to comprehend fully the effects of trace elements and impurities, it does not appear that there are technical impediments to the development of a process if the economics can be shown to be favorable.

Lixiviants other than sulfuric acid, for example, sulphite solutions, can be used to dissolve zinc oxide (50). Zinc can be extracted and purified from such solutions by liquid ion exchange, and an integrated flowsheet for the process can be constructed. A source of SO_2 such as from the roasting of sulfide concentrates would be required since scrap zinc, including dusts, is low in sulfur.

A patent has been granted (51) for a process which makes use of the solubility of zinc oxide in concentrated ammonium chloride solutions. Electric furnace dust is leached with hot ammonium chloride solution to dissolve zinc, copper and lead. Copper and lead are cemented out with zinc dust and separated from the solution. When the solution is cooled, zinc oxide crystallizes and can be removed. The solid contains some ammonium chloride which must be washed out to obtain the final product. Only bench scale results are available, but the process appears to be simple and low in energy consumption and may warrant further attention.

The flowsheet for the Bureau of Mines hydrometallurgical process (46) for metal recovery from brass smelter flue dusts is shown in Fig. 33. Dissolution in sulfuric acid solubilizes the copper and zinc fraction. After removal of the bulk of the lead and tin by filtration, the small amount of copper in the leach liquor is removed by cementation on zinc. After filtration to remove the cement copper, the solution may be electrolyzed to recover zinc. Current efficiencies of the order of 85-90% were achieved when low chloride levels were present. However, at 2 g/ℓ Cl^-, arising from the presence of flux in the dust, the current efficiency dropped to 50%.

4.3.9 Conclusions

Only a small fraction of obsolete zinc is currently recycled. A major untapped resource exists in metallurgical process dusts which are collected in bag houses by the steel, copper, and zinc industries. Recycle of the zinc content by electric furnace steelmaking dusts either as metallic zinc or zinc oxide could lead to energy savings of the order of 5 to 10 × 10^{12} BTU/yr. Furthermore, the iron oxide residue could be recycled to the steelmaking furnace, thus solving a major environmental problem associated with disposal of the dusts.

Pyrometallurgical processes which combine the dusts with carbon and reduce and vaporize the zinc appear promising. Selective leaching of the zinc oxide with ammonium chloride solutions is also an interesting approach.

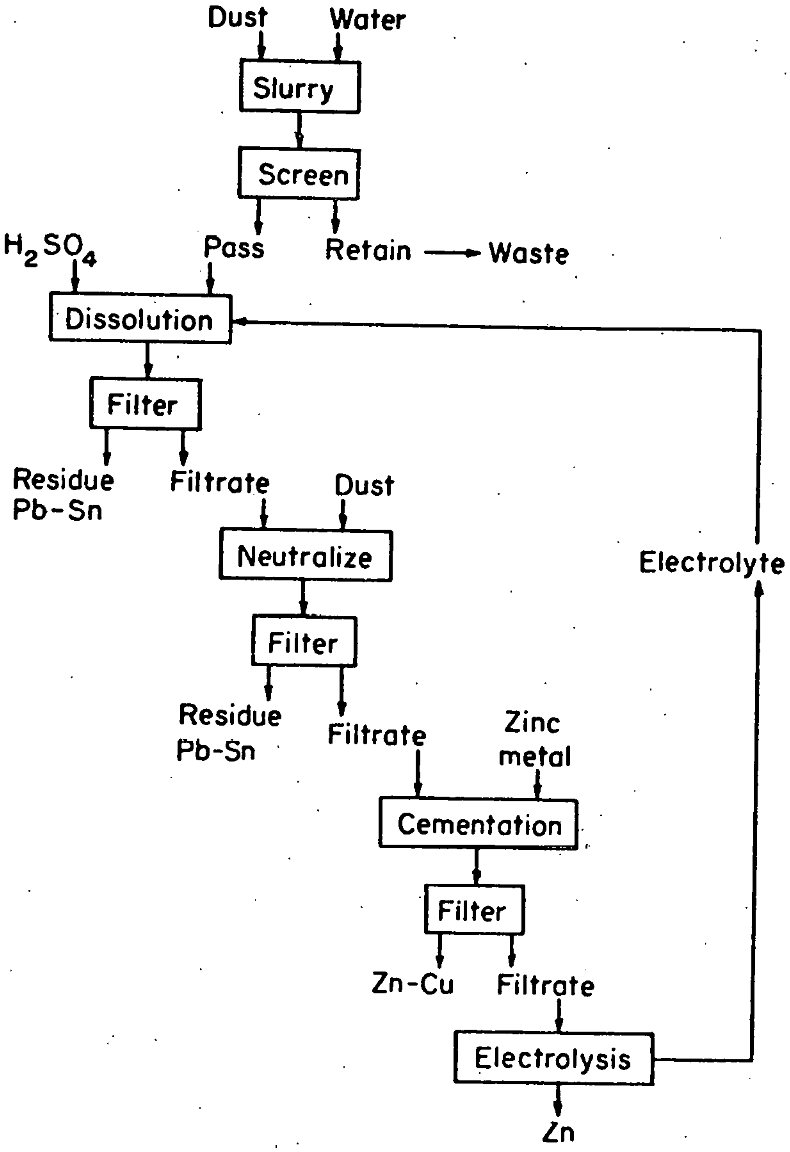


Fig. 33. Flowsheet for electrolytic zinc recovery from brass smelter flue dusts (46).

In Section 5.4 we consider the energy and cost of a hydrometallurgical alternative, which includes electrowinning, for the recovery of zinc from metallurgical process dusts.

4.4 Lead

4.4.1 Statistics and Energy Considerations

Lead is one of the oldest metals in use by man, and it has retained its utility throughout the ages. In tonnage produced, it ranks behind the other nonferrous metals aluminum, copper, and zinc. The lead/acid storage battery for automobiles and battery powered vehicles represents an increasingly important use for lead. If advanced lead/acid batteries come into wide use in vehicular propulsion or in load leveling applications, a major increase in use of the metal will result. Other uses of lead in cable sheathing and in paint pigments have decreased in recent years and will probably continue to do so due to replacement by other materials.

Refined lead has a minimum purity of 99.85% and is produced by a metallurgical refining process. Lead is obtainable in many forms such as ingots, pigs, sheet, foil, powder, shot, etc. and is available in four grades: corroding lead of very high purity, chemical lead which retains the silver content of the ore, acid-copper lead made by copper addition to refined lead, and common desilverized lead which has had the silver content removed. Lead is available in alloy form as antimonial (hard) lead, calcium lead, white metals, fusible alloys and soft solders.

Primary lead is produced mostly from the sulfide ore galena (PbS) which commonly occurs mixed with zinc, copper, and iron sulfides. Ground ore is concentrated by flotation to produce a feed for smelting. Lead smelting is practiced in the United States by sintering or roasting the concentrate to remove most of the sulfur as sulfur dioxide. The sinter is combined with coke and fluxes and smelted in a blast furnace. Impure lead bullion from the blast furnace is further treated in a drossing kettle to reduce impurities and to remove copper as a dross. Zinc dust is added to remove silver which is separately recovered. Traces of zinc are removed from the lead by vacuum distillation and a product of better than 99.9 percent lead is obtained.

An electrolytic process, the Betts process, is used in Canada and Peru. Here, anodes of lead bullion are refined to cathodes by electrolysis in a solution of lead flurosilicate and flurosilicic acid.

The Imperial Smelting process is in common use abroad and is used to process a mixed lead-zinc concentrate. Blast furnace production produces zinc, lead bullion and matte. Secondary metal can be included in the feed to this process.

An analysis of the energistics for the production of primary lead is given in Fig. 34. The total quantity of energy required for production of refined lead is about 27 × 10^6 BTU/ton lead.

Forecasts for U.S. lead demand for the years 1985 and 2000 are given in Table 21 along with the values for 1976.

The probable average annual growth rate for the primary and secondary metals through the year 2000 are only 1.9 and 1.7 percent respectively. The major contingency in the forecast is the demand for lead/acid batteries. Widespread use of electrically powered vehicles could result in a major new demand while alternate advanced battery concepts or fuel cells and increasing battery life could lower demand.

Primary production of lead in the United States accounted for about two-thirds of the primary demand, and this figure is expected to remain constant through the year 2000. The total energy required in primary lead production in the years 1985 and 2000 is given in Table 22. No electrolytic energy is involved. The probable forecast for lead demand in the year 2000 by end use is given in Table 23. The Bureau of Mines study did not include the possibility of lead/acid batteries being used for utility load leveling.

A flow diagram for lead scrap is given in Fig. 35. Secondary lead accounted for 38% of the total lead demand in 1976 and is projected to increase to 58% by the year 2000.

In the year 1976 lead scrap consumption was estimated to be 670,000 short tons, of which 78% is from obsolete scrap. A breakdown of consumption by category is given in Table 24. Should lead/acid batteries come into general use for utility load leveling, then by the year 2000 as much as 3.6 million tons of scrap could be generated per year (see Table 45). Presumably this scrap would be efficiently recycled.

A product-life cycle analysis of lead scrap for the year 1969 is shown in Table 25. While collection efficiencies are good relative to other metals, significant improvement is still available. If half of the unrecovered lead from batteries were recovered, the total quantity of secondary lead would increase by twelve percent.

Three methods have been identified for recycling scrap lead: simple pot melting of prompt industrial scrap, blast furnace recovery of hard lead, and a combination reverberatory/blast furnace process to produce both soft and hard lead. The energistics of these processes are shown in Figs. 36, 37 and 38. The weighted average for the energy content of recycled lead is 7 × 10^6 BTU/ton Pb.

The total energy saved by recycling lead in the years 1985 and 2000 is given in Table 26.

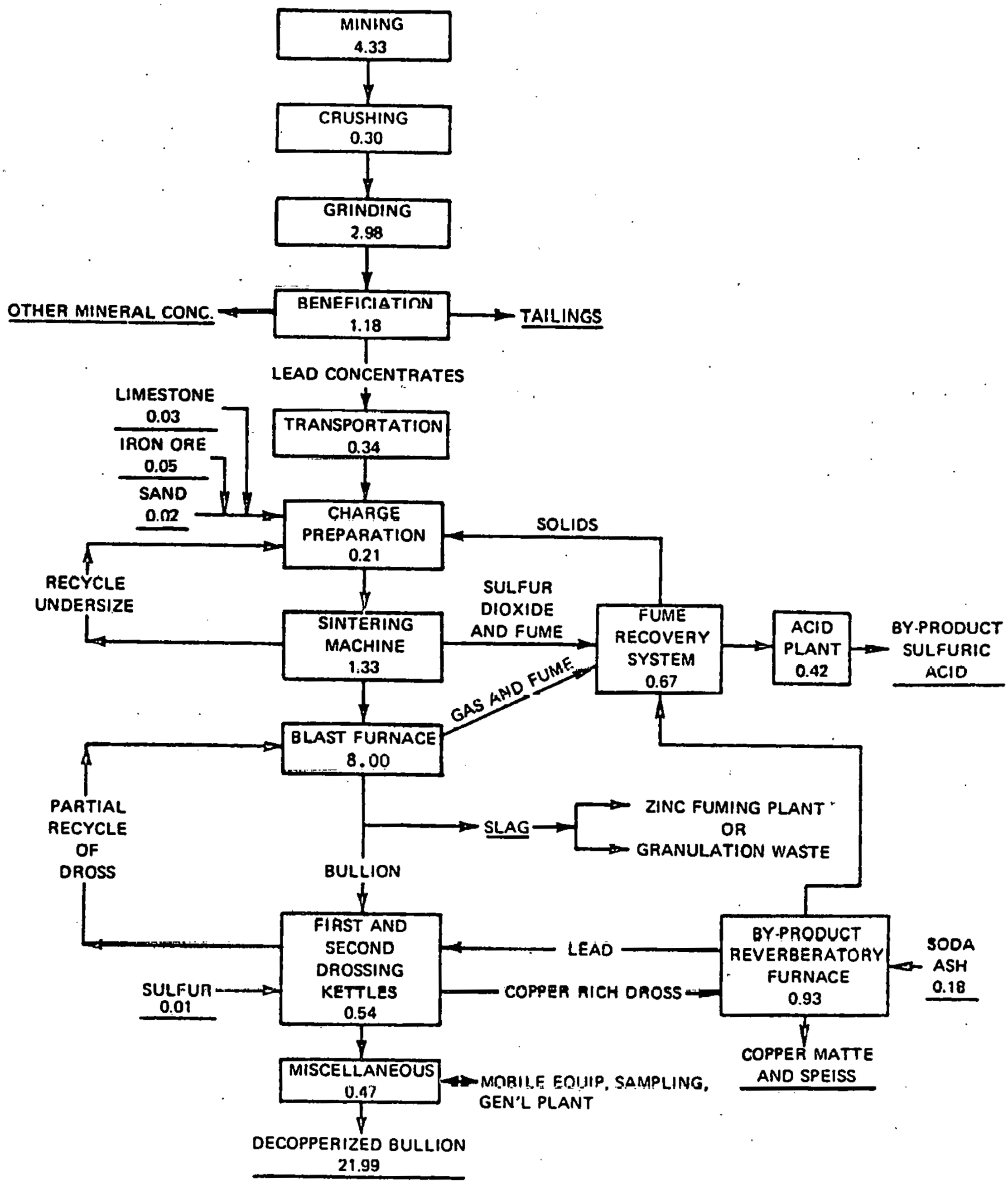


Fig. 34a. Production of refined lead (1).

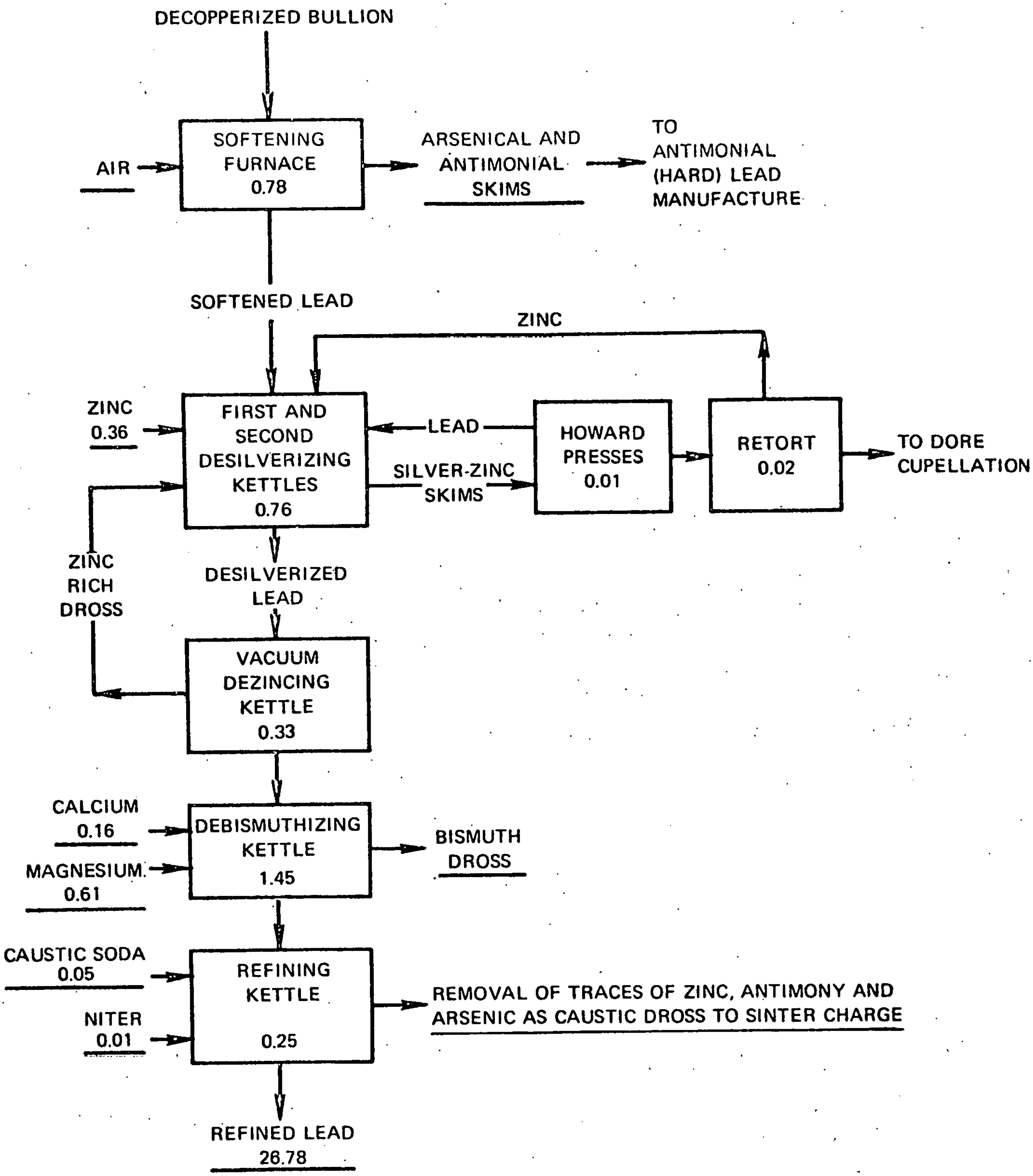


Fig. 34b. Production of refined lead (continued) (1).

Table 21

U.S. Lead Demand Forecast (52)

(thousands of short tons)

	Probable			Year 2000 Forecast Range		Average Annual Growth Rate
	1976	1985	1970	Low	High	Growth Rate 1976-2000 (%)
Primary	930	1100	1470	1030	2340	1.9
Secondary	580	680	860	600	1380	1.7

Table 22

Energy Consumption in the Production of Primary Lead in the Years 1985 and 2000

Year	Primary Production (thousands of short tons)	Total Energy 10^{12} BTU
1985	780	21
2000	990	27

Table 23

End Use of Lead in the Year 2000 (52)

End Use		Quantity (thousands of short tons)
Gasoline additives		80
Transportation		1,670
Construction		70
Paints		130
Ammunition		150
Other		140
	Total	2,240

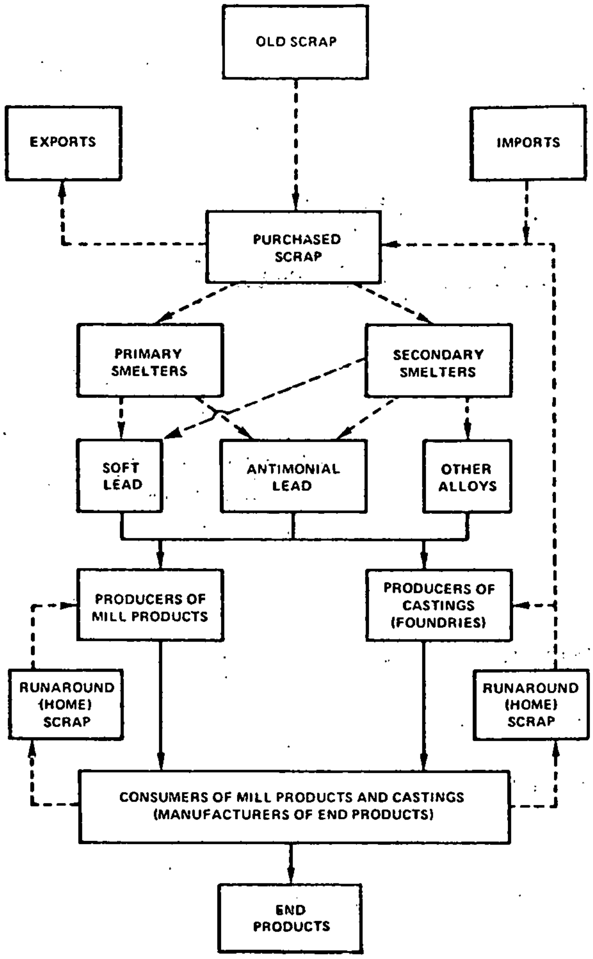


Fig.35. Lead scrap flow diagram (52).

Table 24

Lead Scrap Consumption in 1976 (3)

	Obsolete Scrap (thousands of short tons)	Prompt Industrial Scrap (thousands of short tons)
Smelters and Refiners		
Battery Plate and Operator Scrap	400	45
Prompt Industrial Scrap		
● Drosses and residues	-	105
Other Scrap		
● Cable covering	45	
● Antimonial lead	27	-
● Soft lead	28	-
● Type metals	11	-
● Common babbit	6	-
● Solder	3	-
Total	520	150

Table 25

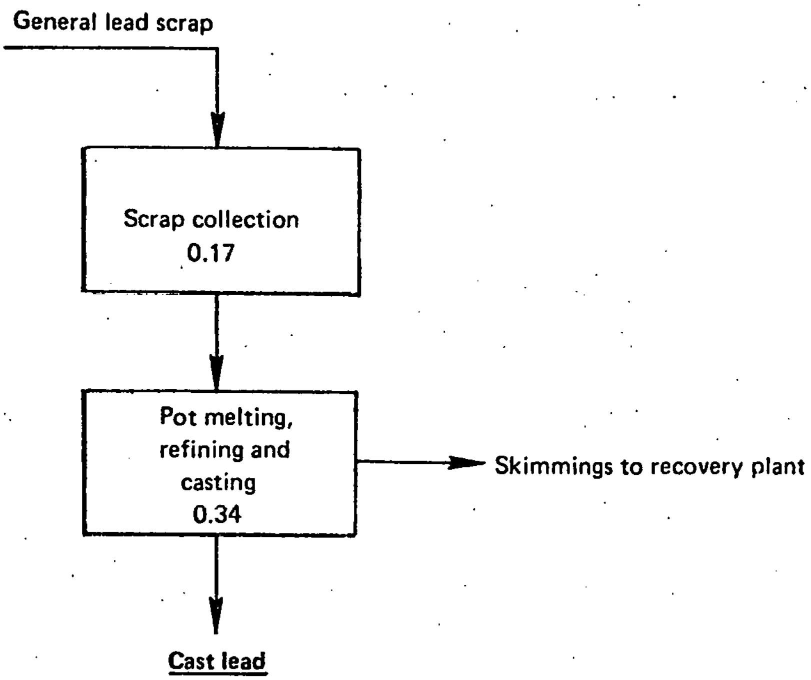
Product-Life Cycle Analysis of Lead Recovery (53)

	Life Cycle (years)	Percent of Available Lead Recycled
Batteries	2.3	72
Drosses and Residues	0.1	100
Lead Alloys		
Type metal	2.0	100
Bearing metal	20.0	30
Solder	20.0	14
Cable Sheathing	40.0	25
Ammunition	0.5	6
Miscellaneous Obsolete Scrap	30.0	62

Table 26

Energy Saved in Lead Recycle

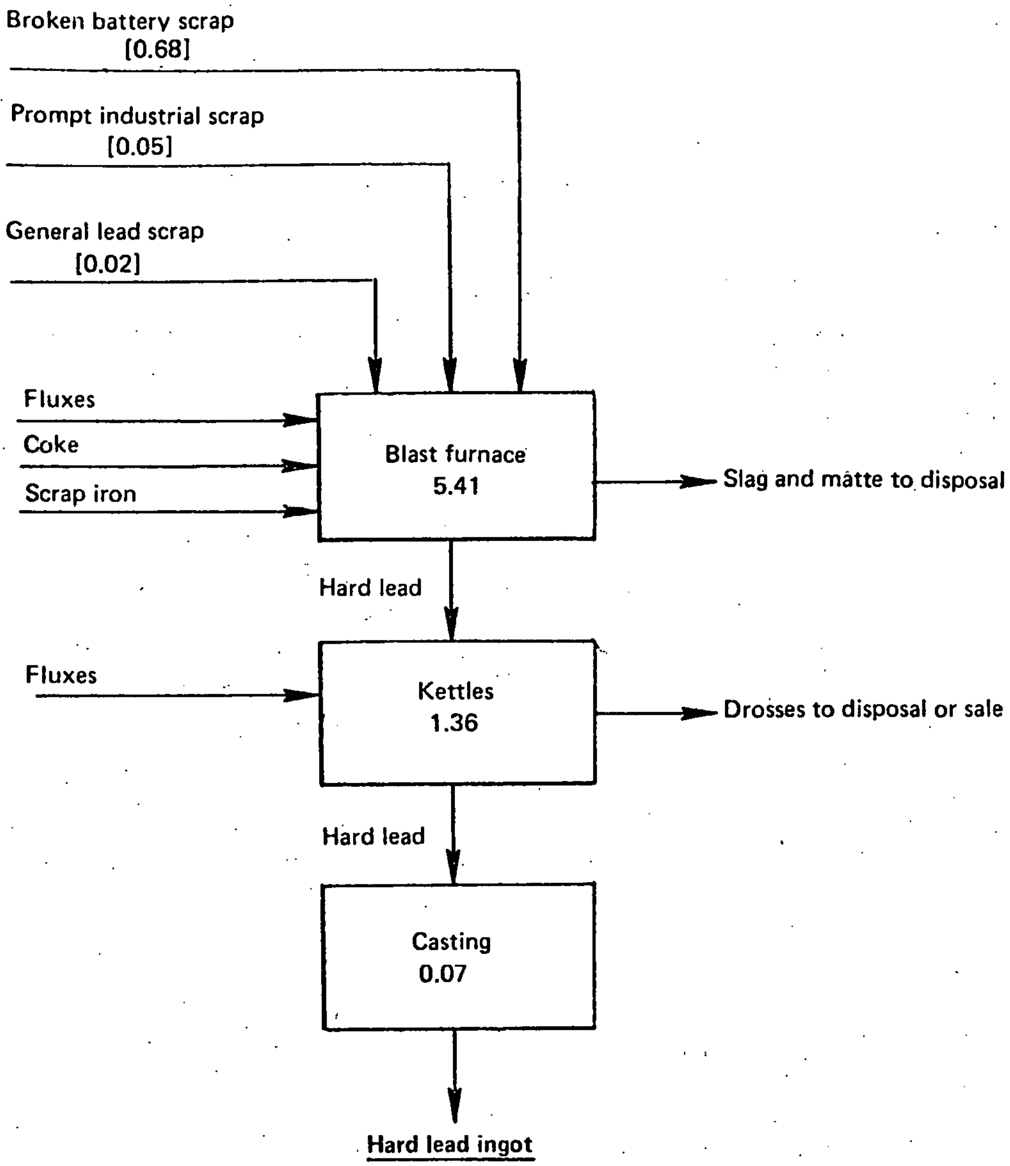
Year	Energy, 10^{12} BTU
1985	14
2000	17



SUMMARY

	Million Btu per ton of product
Process energy	0.51
Pollution control energy	0.00
Space heating	0.10
Total energy	0.61

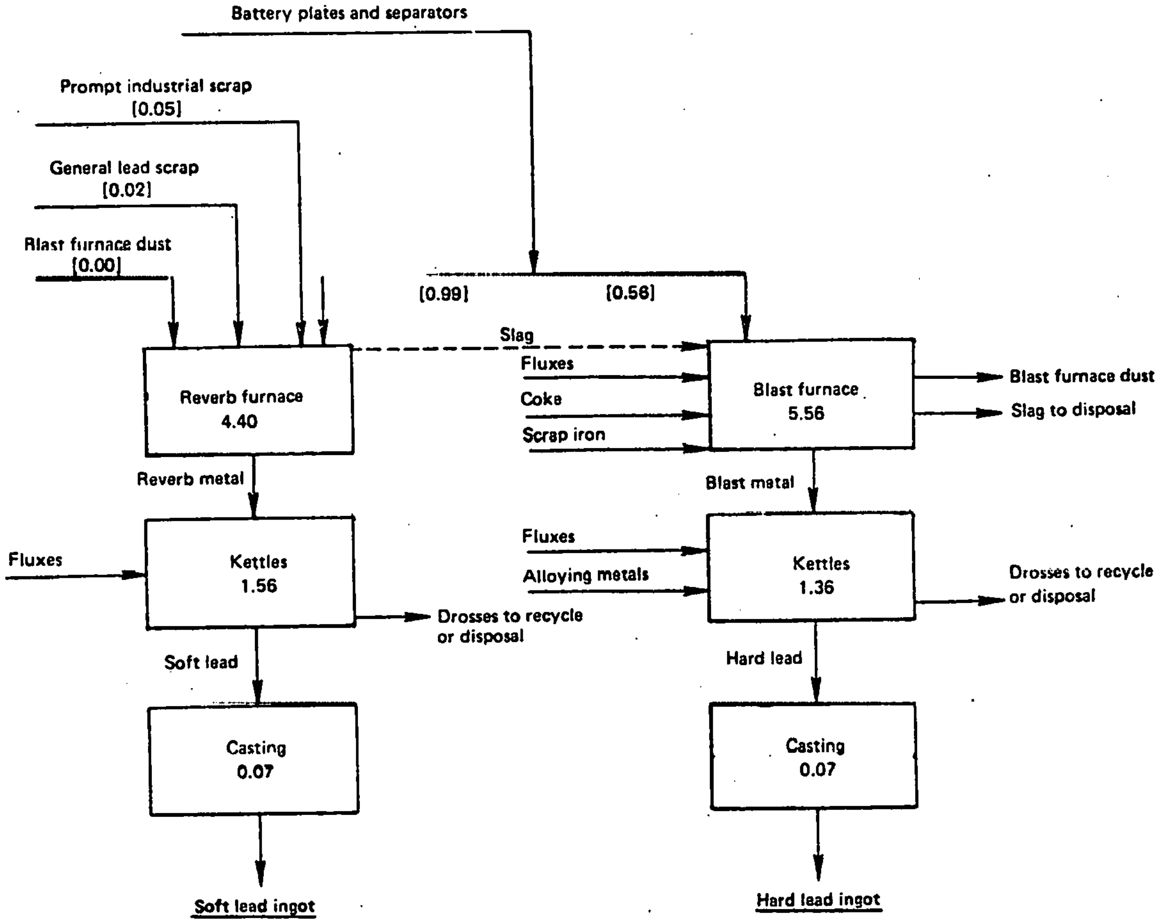
Fig. 36. Lead: production of cast lead by pot melting process (3).



SUMMARY

	Million Btu per ton of product
Process energy	7.59
Pollution control energy	1.99
Space heating	0.07
Total energy	9.65

Fig. 37. Lead: production of hard lead by the blast furnace process (3).



SUMMARY

	Million Btu per ton of product
Process energy	7.09
Pollution control energy	0.89
Space heating	0.07
Total energy	8.05

SUMMARY

	Million Btu per ton of product
Process energy	7.55
Pollution control energy	1.99
Space heating	0.07
Total energy	9.61

Fig. 38. Lead: production of secondary lead by reverb/ blast furnace process (3).

4.4.2 Sources of Scrap

Approximately one half of the total lead currently consumed is derived from secondary production. This extraordinarily high percentage of metal recycled is a result of the properties of the material and its major end use market, starting, lighting and ignition (SLI) batteries for automotive use. Evaluations of current secondary lead processing technology, or projections concerning future technology for lead, must be fully consistent with the evolving technology in the major end use market.

Lead scrap processed in secondary smelters may be classified in three major categories:

- Battery plate and separator scrap, arising both from reclamation of used SLI batteries and from the battery manufacturing process, is by far the most important raw material, accounting for approximately 60% of the secondary industry's feed stock.
- Drosses and skimmings from both primary and secondary lead smelters constitutes approximately 1/6 of the total lead recycled, and is prompt industrial scrap.
- General lead scrap, recovered from a variety of sources, constitutes the remaining major category of material which is reprocessed.

It has been estimated that as much as 80% of the lead consumed in the manufacture of SLI batteries is eventually recovered and recycled. This is possible because the discarded battery is compact, can be easily identified and removed, and is easily broken down into the component parts from which a high percentage of the lead can readily be recovered. Furthermore, an organized system for recovery of these items exists as an integral part of the automobile reclamation industry and through the trade-in normally offered at new battery sales outlets. Drosses and skimmings, which constitute the prompt industrial scrap, are of course identified and managed as a consequence of the main production processes which generate them. The balance of material processed in secondary smelters, general lead scrap, is recovered from obsolete articles. Much of this material arises from products with relatively long use lives, and recovery from these sources is substantially lower than for battery and prompt scrap.

The product mix produced by the secondary lead industry is dominated by requirements for the manufacture of lead/acid batteries. Thus, half of the output of secondary smelters is in the form of lead alloys, particularly lead-antimony alloys with 2 to 7% antimony which are recycled almost exclusively to battery manufacturers for use in grids, posts, and lugs. Minor quantities of calcium lead, white metals, or other alloys are also produced. About 1/3 of secondary smelter output is in the form of various grades of refined lead, including corroding, chemical and acid-copper lead from which the antimony, tin, arsenic, and other impurities and alloying elements have been removed. In contrast, the product of the primary lead industry is almost exclusively these various refined leads. Finally, a minor amount of secondary lead is produced simply by remelting general scrap to produce a lower grade product, containing 96-99% lead, for general use.

4.4.3 Current Practice in Recycling

The secondary lead industry relies exclusively on pyrometallurgical processes for the production of all grades of material which are marketed. The basic technology is venerable, and, except for purification steps and environmental control considerations, relatively simple. The chemical and physical properties of lead, including its low melting point, relatively high vapor pressure, high density, and ease of reduction of oxides or sulfate, dictate the approaches which have historically been used.

A schematic representation of the operations involved in processing lead scrap is shown in Fig. 39.

Used batteries are subjected to a variety of hand and mechanical techniques to remove the lead for reprocessing. The cases may be split or broken and the acid then drained. Broken pieces are washed and the liquid effluent filtered to recover particulate lead and then neutralized for disposal of waste acid. In some instances, attempts are made to further segregate the posts, lugs, grids, paste and separators and case parts one from another to improve the efficiency of the lead recovery process. Drosses, lead-bearing scrap, and general scrap can be charged to the lead recovery processes without additional treatment, except for necessary size reduction and/or agglomeration or sintering for dusty materials. The majority of lead scrap is reprocessed in reverberatory or blast furnaces, although use has been made of other types of equipment, including long rotary furnaces, to accomplish the same results. Lead processed in a reverberatory furnace is melted under neutral or slightly oxidizing conditions, where the antimony is preferentially oxidized and reports to the slag. Antimony removal is not complete, however, and the lead product from a reverberatory furnace still contains about 1% antimony. This material may be sold directly as semi-soft lead or further refined. The slag from a reverberatory furnace contains substantial amounts of lead, up to 60-80%, as well as antimony, and must be processed to recover its lead values. Reprocessing, along with treatment of other lead-bearing scrap, is customarily accomplished in a blast furnace. The charge to the blast furnace includes coke or other reductants, fluxes including limestone and irony scrap, and dusts and other revert material from the blast furnace. The air-to-reductant ratio is controlled so that the lead oxides and

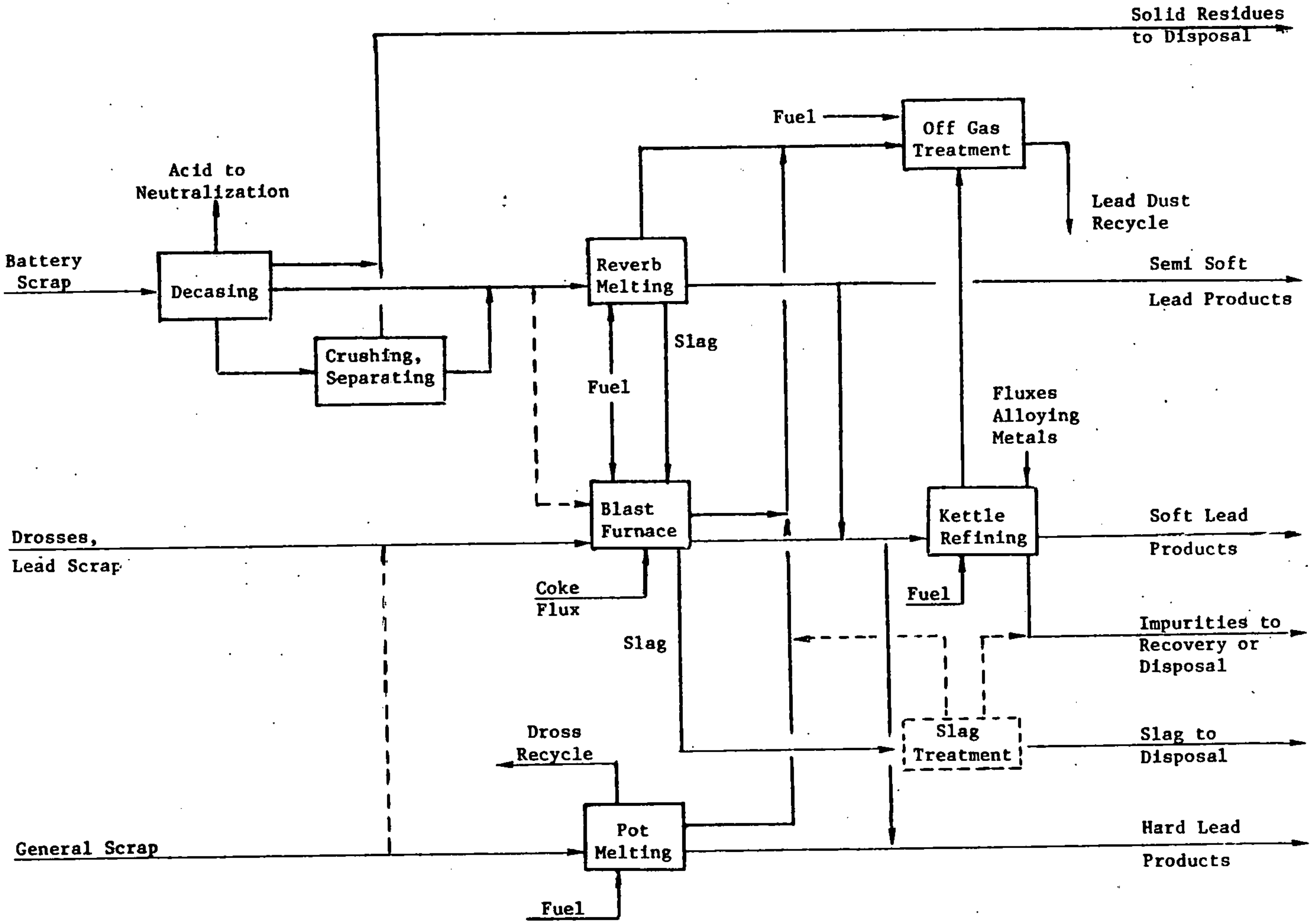


Fig. 39. Lead scrap treatment processes, materials, and energy flows.

sulfates are reduced while major impurities report to the slag or matte phases. Lead and alloying agents, particularly antimony, are tapped from the furnace. The amount of matte produced is usually small, less than 5% of the lead production, and it may be treated further for copper and lead recovery if justified. The slag may be fumed for zinc recovery and treated for removal of other by-products before disposal.

The majority of the lead produced in blast furnaces is recycled to battery manufacture with little additional processing. The production of soft lead, however, requires a series of purification steps with process conditions adjusted to selectively remove the undesired impurities. Copper is removed by thermal drossing, which involves cooling the mixture to a temperature just above the freezing point of lead where copper is thrown out of solution and removed by hand or mechanically. Copper, as well as zinc, bismuth and cadmium, may also be removed by mechanically agitating sulfur into the lead held in kettles at 400°C and then allowing the resulting sulfides to disengage and be skimmed for further purification. The remaining impurities, including antimony and tin, are removed by fluxing the molten material with caustic or sodium nitrate and blowing air through the mixture to selectively oxidize the impurities. The slags and drosses produced in these operations are sufficiently concentrated in impurities in some cases to permit their recovery. This may represent a significant source of income for the refiner who buys material at the price of lead and sells impurity metals at the higher prices which they command. The soft lead obtained by these purification steps may then be alloyed as required.

The energy consumption in the reverberatory furnace-blast furnace-kettle refining process for lead recycling is of the order of 8-10 million BTU/ton. A significant amount of this energy is consumed in off-gas treatment, and technology exists to decrease waste heat to further improve the savings in energy vis-a-vis primary lead production. Overall lead recoveries by this route are reasonably high at 90-95%, although any emission of lead in a processing sequence is of concern because of its toxicity.

Key technical problems in secondary lead processing by pyrometallurgical techniques are the control of gaseous emissions and the development of a simple purification technique. Off-gases from the blast furnace are mildly reducing and contain particles of unburned carbon and lead-containing dusts which are pyrophoric. Additional fuel and air must be added to remove the unburned carbon, and the gases must then be quenched below the melting point of lead prior to particulate removal, which leaves little opportunity for energy saving. Obviously, particulate removal from reverberatory and blast furnace off-gases must be highly efficient in order to meet environmental standards. Further, large volumes of air used to control fugitive emissions must also be treated to remove particulates and materials fumed off in the purification steps.

Off-gas treatment is further complicated by the nature of the battery scrap charged to the processes: the material of choice for separators is PVC and the chlorine liberated during its combustion can react with lead and other nonferrous materials to form volatile chlorides. These corrosive, soluble chlorides tend to concentrate in the dusts removed in the gas cleaning steps and cannot be recycled indefinitely without providing for some purge.

While it is possible to envision solutions to the off-gas treatment problems involving the use of available technology, the use of such techniques as slaging boilers and combined dry and wet scrubbing would increase the complexity of the lead refining process. It would also involve the creation of other waste streams to be treated and add significantly to the capital and operating costs of the processing sequence which could not be fully recovered through either decreased fuel costs or additional revenues from by-products. In addition, a significant shift in the manufacture of SLI batteries to the "maintenance free" type would impose changes on the operations of a secondary smelter. Unless physical separation techniques can be developed to segregate the low antimony, calcium-lead alloys from the conventional hard lead material used in posts and lugs, a larger portion of the secondary smelters' output will have to be fully refined than is currently the case. Thus, incentive exists to explore the development of alternative techniques for the treatment of scrap lead.

4.4.4. Hydrometallurgical Process Alternatives

A significant development effort on the hydrometallurgy of lead has been carried out, but it has focused on primary processing routes. No fully hydrometallurgical process has been developed or tested beyond the laboratory or pilot scale for either primary or secondary lead production.

The chemistry and electrochemistry of lead are well known; it can be dissolved in acid chloride, ammoniacal ammonium sulfate or strong caustic lixiviants. It is possible then to conceive of a variety of schemes for selectively removing lead from solution, purifying it, and reducing it to metallic lead. As is the case with aluminum, copper, and zinc,however, it is unlikely that economically viable processes can be developed which involve oxidation of metallic lead and subsequently reducing it electrochemically because of the inherently higher energy requirements. However, battery scrap, which constitutes the majority of secondary smelter feed, consists of both metallic and oxidized (lead oxide-lead sulfate) materials. Thus, if it were feasible to mechanically or physically separate the oxidized materials from metallic lead it would be possible to replace pyrometallurgical processing with hydrometallurgical purification and reduction of the oxidized lead, while simply remelting and purifying the separated metallic components. The metallics might be purified by a relatively simple sequence of pot melting and kettle refining which would avoid the more troublesome off-gas cleaning problems associated with the reverberatory and blast furnaces. Alternatively, the purification might be carried out using the well known Betts process for electrorefining lead. The latter process,however, is not itself without environmental problems, mainly involving emission of fluorides and the treatment of slimes. A second alternative would involve purification by distillation at extremely low pressure, but the yields reported for one such approach are so low as to be economically unattractive (54).

Unfortunately, it does not appear likely that mechanical or physical techniques can be developed which would separate metallic from oxide materials with sufficient selectivity and efficiency to make such an approach viable on conventional SLI batteries. It may be possible, however, with proper battery and equipment design to develop such a process for the larger load leveling lead/acid batteries which may be developed in the near future.

The acid chloride system has served as the basis for a substantial process development effort in the hydrometallurgy of lead (55-57). The Bureau of Mines has explored a variety of process options for recovering lead from sulfide concentrates,and a proposed flow sheet is shown in Fig. 40. It has been found that the sulfide ore can be leached with ferric chloride to recover lead chloride in high yield. The lead salt is removed from solution by crystallization as a high purity product. Lead sulfate, if present, also must be removed since it would contaminate the chloride product. This would have significant consequences in processing battery scrap since the presence of sulfate

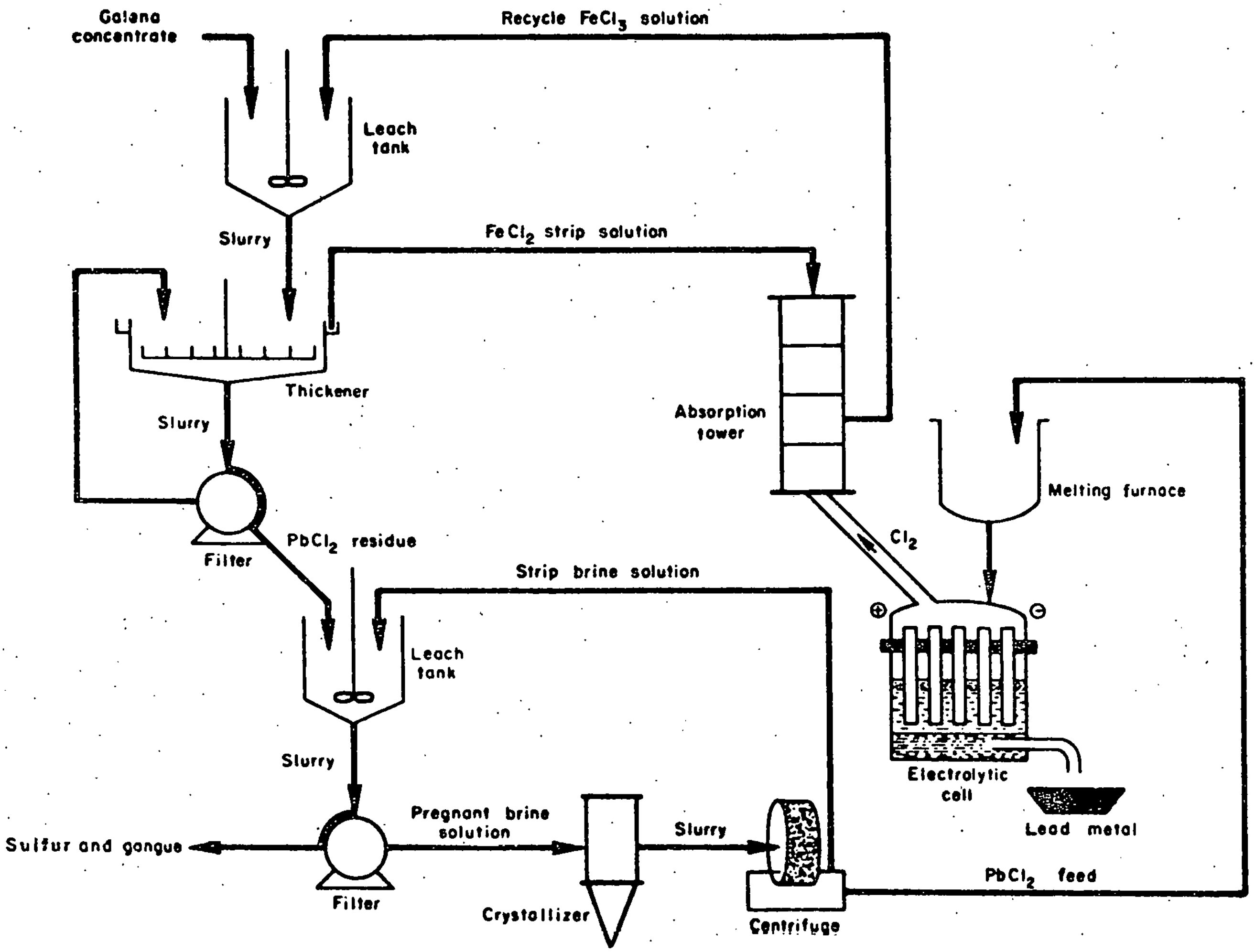


Fig. 40. Flow diagram for preparing lead metal from galena concentrate (55).

is unavoidable. Both aqueous and molten salt electrolysis of the crystallized lead chloride have been demonstrated, but only the molten salt approach is likely to be amenable to large-scale use. Unfortunately, the power requirement for this step is at least .5 kWh/lb (11 million BTU/ton), which is itself higher than the total energy requirement for conventional recycling of lead, and the energy cost of leaching, crystallization and chlorine recycling, will add significantly to the total.

Lead oxides or sulfates may also be dissolved in strong ammoniacal ammonium sulfate lixiviants (58), and a possible processing sequence is shown in Fig. 41. Lead can be removed from the pregnant liquor by hydrolysis or by precipitation as the basic salt when the pH is reduced by stripping free ammonia from the solution. The lead could then be reduced pyrometallurgically to produce the desired product, but it is not clear why this approach would be preferred to direct pyrometallurgical reduction. Alternatively, it was shown that lead could be reduced directly from solution with a modest power requirement (.12 kWh/lb total lead) using rotating cathodes. However, for each mole of lead reduced, another mole of lead is oxidized to lead dioxide which is formed as a powder. This, in turn, would have to be re-reduced pyrometallurgically or recycled to the leaching step, thereby doubling the power requirement per pound of metallic product.

It is also known that lead can be dissolved in strong caustic and recovered by electrowinning from the aqueous solution using rotating electrodes (59, 60). However, cathode lead of acceptable purity is not produced directly since the material is deposited as powder or dendrites. At the least, remelting would be required and a means would have to be found to cope with purification of the depleted electrolyte prior to recycle to purge impurities from the system. No integrated process has been proposed based on the use of a caustic lixiviant.

It has also been shown that it is possible to dissolve the paste from used SLI batteries in a mixture of an alkyl amine and sulfuric acid (61). The lead can be recovered subsequently by precipitation as lead carbonate if carbon dioxide is bubbled into the solution. The carbonate, in turn, may be calcined to oxide or reduced pyrometallurgically to produce metallic lead. Again, no details are available on the fate of impurities of such a scheme or whether the oxide produced by this sequence would have properties suitable for direct reuse in battery manufacture.

4.4.5 Conclusions

No data have been reported to indicate that a fully integrated, economically viable hydrometallurgical process can be developed for recovery of lead from general secondary smelter scrap. It is possible that such a process could be developed for recovery of lead from paste material removed from grids, but it is not currently possible to carry out such an operation on conventional automotive batteries.

In Section 6.4 we present preliminary flow sheets for the recovery of lead from electric vehicle and load leveling batteries.

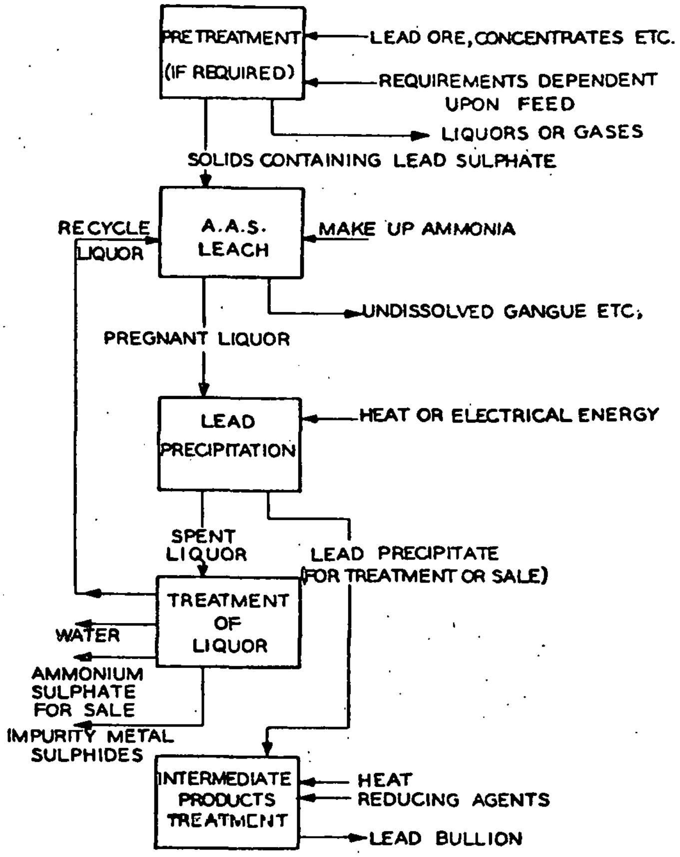


Fig. 41. Basic flow sheet for a lead production process based on ammoniacal ammonium sulfate (AAS) leaching (58).

4.5 Nickel

4.5.1 Statistics and Energy Considerations

Nickel plays an important role in the iron and steel and the aerospace industries. Its greatest value is as an alloy addition to promote both corrosion resistance and higher strength. The use of nickel is expected to grow, especially in the petrochemical and electrical industries, as the United States seeks to satisfy the increasing demand for energy. The metal is marketed as cathodes, powder, briquetts, ingots, shot, nickel oxide sinter, and ferronickel.

Nickel is mined primarily as the sulfide and concentrated by flotation. High grade concentrates may be roasted to the oxide and smelted with a coke reductant to form anodes which are then electrorefined. Lower grade concentrates are smelted to an impure copper-nickel-iron matte and then converted to a copper-nickel matte with the iron reporting to the slag. The cooled matte may be crushed and the sulfides removed by flotation. The impure metal phase is refined electrolytically. Nickel sulfide may also be cast directly to anodes for electrolysis, or dead roasted and reduced to metal which is then further refined either electrolytically or by the carbonyl method. Sulfide concentrates can also be leached with ammonia and, after purification, both nickel and cobalt can be obtained by hydrogen reduction.

The energistics of the production of electrolytic nickel from a nickel-copper concentrate was studied (62) and details are given in Fig. 42.

Forecasts for the United States demand for nickel in the years 1985 and 2000 along with data for 1975 are given in Table 27. The average annual growth rate for the metal is slightly above three percent.

The United States produces only a small part of its nickel requirement, about nine percent in 1976, although some nickel is also produced using imported ore. A projection of the 20 year trend would indicate that we will be mining and smelting only about six percent of our primary demand in the year 2000. However, the Bureau of Mines projects that new mining and extraction technology will be developed for one or more new sources: the Duluth, Minnesota gabbro ore, laterites in Oregon and California, and deep seabed manganese nodules. Projections based on the exploitation of these new resources leads to an estimate of a production of 65% of our primary demand by the year 2000.

Only one of the many possible production routes for nickel has been analyzed for energy consumption (see Fig. 42). If we do exploit additional resources such as laterites or nodules, new technology will undoubtedly be developed for the extraction process, and hydrometallurgy is likely to play a major role in such new technology. Uncertainties in the amount of metal produced and the nature of the new processes make it very difficult to

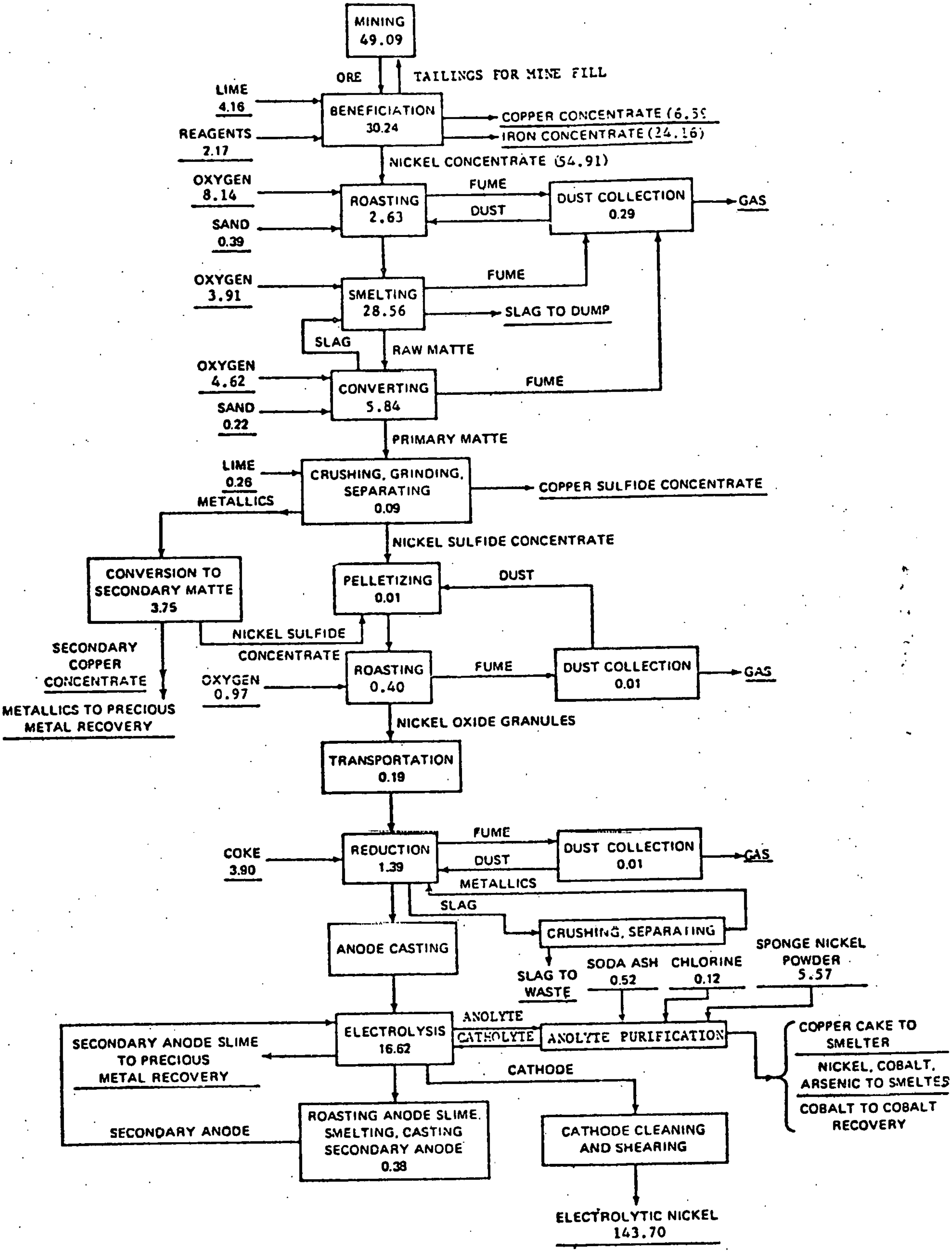


Fig. 42. Production of electrolytic nickel (62).

estimate the quantity of energy used in the production of nickel in the future. It is also hard to project the fraction of this energy which will be used in electrowinning or electrorefining. Accepting the optimistic Bureau of Mines figure of 100,000 tons per year in 1985 and 270,000 tons per year in 2000, and an estimated energy content of 144 × 10^6 BTU/ton Ni, we derive the values in Table 28. We will further assume that 90% of the primary nickel produced in 1985 in the United States is electrorefined and 5% is electrowon, and that 75% of the primary nickel produced in the year 2000 is electrorefined, while 20% is electrowon. Using data from Ettel (20) we calculate that nickel electrorefining requires 18 × 10^6 BTU/ton Ni and nickel electrowinning requires 35 × 10^6 BTU/ton Ni. We are therefore able to derive the quantities of electrolytic energy given in Column 2 of Table 28. These values are considered to have a higher degree of uncertainty than those of the other metals considered and are therefore bracketed. The probable forecast for nickel demand by end use for the year 2000 is given in Table 29.

A flow diagram for nickel scrap is given in Fig. 43. Secondary nickel accounted for about 21 percent of the demand in the year 1975.

Much of the information regarding the secondary nickel industry is proprietary and few statistics are available. A.D. Little estimates that 23,000 tons of old scrap and 34,500 tons of new scrap were available in 1976 (3).

Two melting flowsheets have been developed for processing of nickel alloy scrap (3) and these are shown in Figs. 44 and 45. For want of better information, an average value of 15 × 10^6 BTU/ton of product is used to estimate the energy content of recycled nickel alloy. Again this value is somewhat uncertain.

Rough estimates of the total and electrolytic energy saved by recycling nickel in the years 1985 and 2000 are given in Table 30.

4.5.2 Recycling of Nickel Scrap

Nickel scrap is generated during forming and shaping operations in primary processing plants and in fabricating plants which process stainless steels and superalloys. Some obsolete scrap comes from consumer goods. In-house scrap is high for nickel alloys, with stainless and alloy steel products averaging less than 60 percent yield and high-nickel alloys often as low as 20 percent yield.

Stainless steel and superalloy scrap is invariably recycled to produce these materials, whereas Monel alloy is used to make specialty copper-nickel steels which possess high strength and are corrosion resistant. Much of the recycled nickel scrap is runaround scrap in stainless steel mills.

Table 27

U.S. Nickel Demand Forecast (63)
(Thousands of short tons)

	Probable			Year 2000 Forecast Range		Average Annual Growth Rate
	1975	1985	2000	Low	High	Growth Rate 1975-2000 Percent
Primary	155	265	415	300	450	3.0
Secondary	42	100	165	120	190	3.5

Table 28

Energy Consumption in the Production of Primary Nickel in the Years 1985 and 2000

Year	Primary Production (thousands of short tons)	Total Energy, 10^{12} BTU	Electrolytic Energy 10^{12} BTU
1985	(100)	(14)	(1.8)
2000	(270)	(39)	(5.5)

Table 29

End Use of Nickel in the Year 2000 (63)

End Use	Quantity (Thousands of short tons)
Chemicals	115
Petroleum	71
Fabricated Metal Products	46
Transportation	104
Electrical	105
Household Appliances	23
Machinery	37
Construction	45
Other	34
TOTAL	580

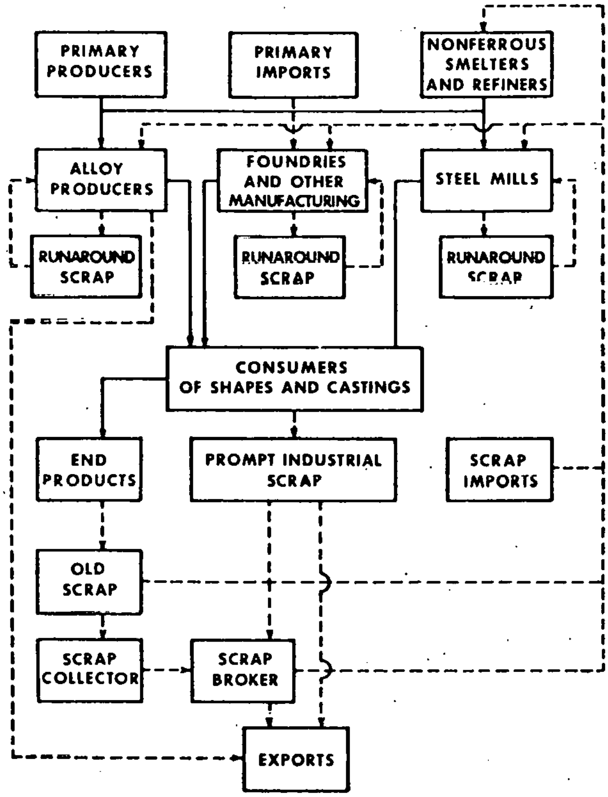
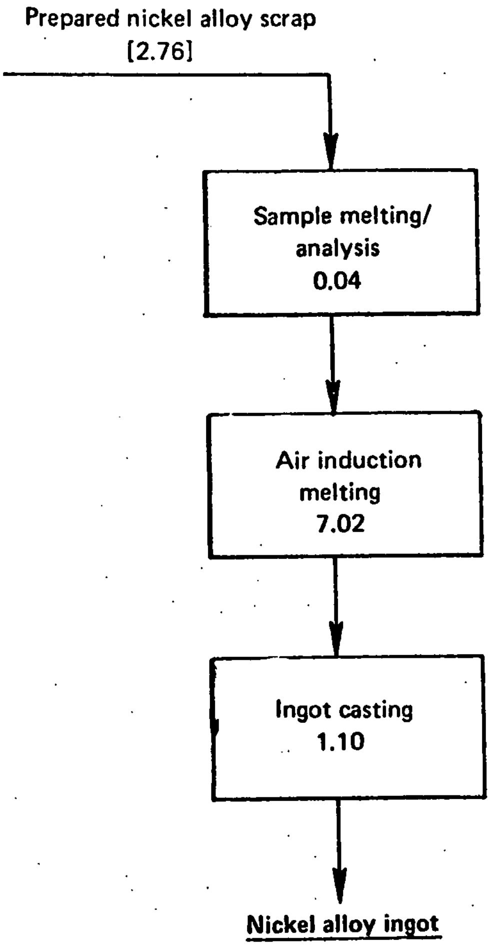


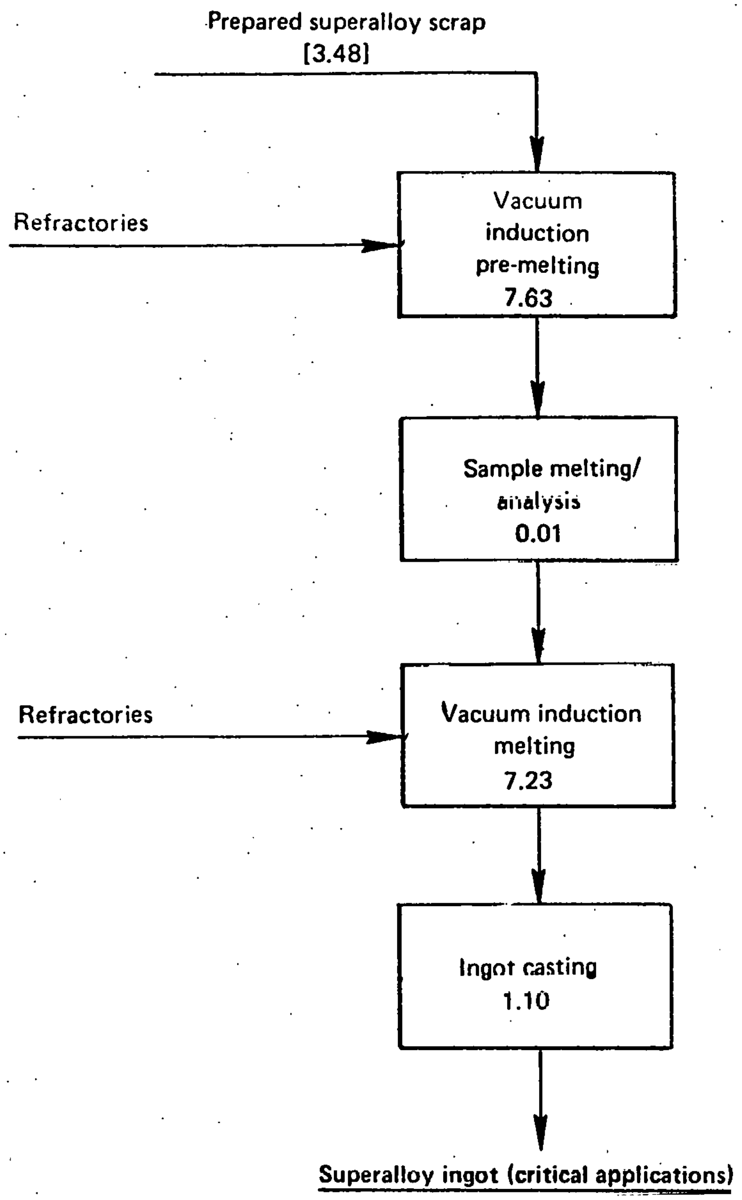
Fig. 43. Nickel scrap flow (63).



SUMMARY

	Million Btu per ton of product
Process energy	10.92
Pollution control energy	0.16
Space heating	0.00
Total energy	11.08

Fig. 44. Nickel alloys: Nickel alloy ingot-making by air induction melting (3).



SUMMARY

	Million Btu per ton of product
Process energy	19.45
Pollution control energy	0.00
Space heating	0.00
Total energy	19.45

Fig. 45. Nickel alloys: Superalloy ingot-making by double vacuum induction melting (3).

Table 30

Energy Saved in Nickel Recycle

Year	Total Energy, 10^{12} BTU	Electrolytic Energy, 10^{12} BTU
1985	(12.9)	(2.1)
2000	(21.3)	(3.3)

Prompt industrial nickel scrap is often sold to steel mills and smelters. Virtually all of nickel scrap from obsolete equipment ends up in steel mills, smelters or foundries.

The refractory nature of the nickel-bearing alloys makes it difficult to separate them into their elements by a hydrometallurgical route, and unless the compositions are known sufficiently well so that it can be remelted, alloy scrap is shipped to Japan or Germany for separation into the elements. Apparently the technology and economics are more favorable in those countries.

The separation of iron, cobalt and nickel from superalloy scrap has been reported by Aue and coworkers (64). Grinding, turnings, solids, etc. are melted together with slag formers to remove non-metals and oil. The metal is then remelted with 3-4% graphite in a high frequency induction furnace. This transforms Mo, W and Cr to carbides. A granulate is fed into titanium baskets and anodically dissolved in a diaphragm cell using a chloride electrolyte. Simultaneous electrodeposition of cobalt or nickel from purified liquor takes place at the cathode. The Mo, W and Cr carbides are treated separately to recover the metals. Solvent extraction, using tertiary alkylamines and selected chloride concentrations, is used to separate iron, cobalt and nickel from the anolyte. The process is not currently practiced commercially.

4.5.3 Conclusions

Improvements in nickel recycling will come about by improved collection and sorting technology. Processes for reclaiming nickel from complex nickel-bearing alloys require further development and may be hydrometallurgical in nature.

4.6 Magnesium

4.6.1 Statistics and Energy Considerations

Magnesium is plentiful in the earth's crust and readily available for commercial production from sea water and brines. The major use is as a nonmetal, primarily for refractories, and only ten percent of total magnesium production is as the metal. More magnesium is used in aluminum alloys than as the unalloyed metal or in magnesium-base alloys. Major uses are aircraft, machinery, consumer products, cathodic protection of iron and steel, and as a reducing agent for the production of titanium, zirconium, hafnium, uranium, and beryllium.

Magnesium is produced in the United States primarily by the Dow electrolytic process. Sea water or brines are mixed with calcined dolomite to precipitate the hydroxide which is then treated with hydrochloric acid to produce a 36% solution of magnesium chloride. The magnesium chloride is further dried to a 75% concentration and fed to electrolytic cells. Chlorine and hydrochloric acid generated at the anode are recycled.

The I.G. Farbenindustrie (IGF) process uses an anhydrous magnesium chloride cell feed to produce primarily chlorine at the anode. Chlorine is sold as a by-product.

Energistics of production by the Dow process are summarized in Fig. 46. One ton of metal produced requires 358×10^6 BTU, of which 203×10^6 BTU is used in electrolysis. Of this latter amount 180×10^6 BTU is electrical energy. Dow Chemical has recently reported (65) that conservation measures have resulted in a 15% reduction of energy requirements for magnesium production.

Forecasts for demand of magnesium as the metal for the years 1985 and 2000 along with data for 1973 are shown in Table 31.

The United States is self-sufficient in magnesium, and its capacity and planned expansions should adequately meet demand through the year 2000.

The total quantity of energy and the electrolytic energy required to supply primary production for the years 1985 and 2000 are given in Table 32.

The probable forecast for magnesium metal by end use for the year 2000 is given in Table 33.

Secondary magnesium originates as magnesium-base alloy sheet, castings, assemblies, etc. After processing, it is generally sold in the form of alloy ingots for use by foundries and pressure die casters, or as cast galvanic anodes for use in cathodic protection of steel pipelines and structures.

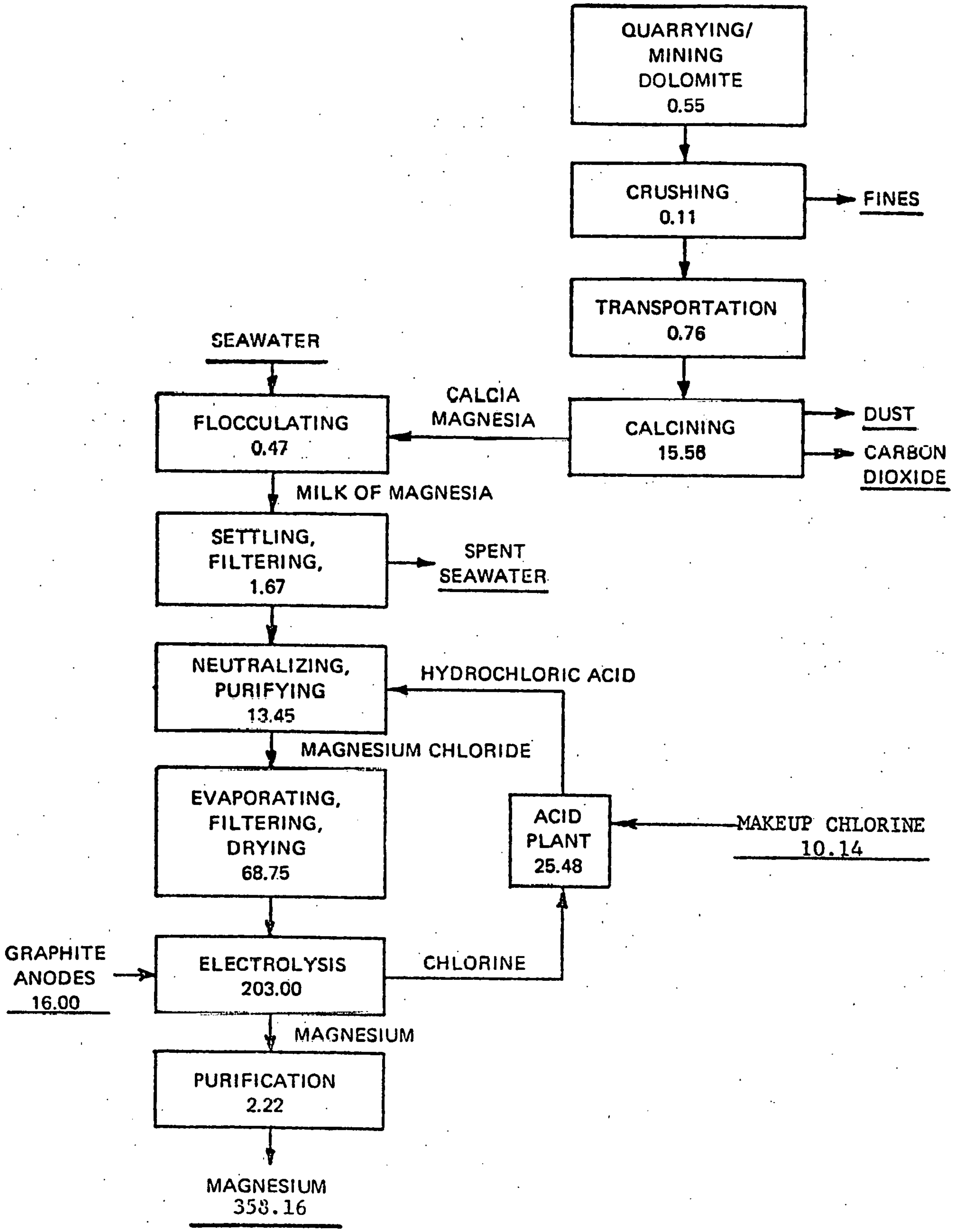


Fig. 46. Production of magnesium metal from seawater (62).

Table 31

U.S. Magnesium Demand Forecast (66)

	Probable			Year 2000 Forecast Range		Average Annual Growth Rate
	1973	1985	2000	Low	High	Growth Rate 1973-2000 (%)
Primary	116	190	365	225	505	4.3
Secondary	4	10	30	15	35	7.8

Table 32

Energy Consumption in the Production of Primary Magnesium in the Years 1985 and 2000

Year	Primary Production (thousands of short tons)	Total Energy, 10^{12} BTU	Electrolytic Energy, 10^{12} BTU
1985	190	68	34
2000	365	130	66

Table 33

End Use of Magnesium Metal in the Year 2000 (66)

End Use	Quantity (thousands of short tons)
Transportation	200
Machinery	100
Chemicals	20
Nonferrous Metals Production	30
Iron and Steel Foundries	20
Other	25
Total	395

During the period 1946 to 1974 magnesium consumption in the United States grew from about 15 thousand tons per year to 145 thousand tons per year. The quantity of recycle magnesium, however, had decreased steadily from about 50% in the late 1940's to only 10% in 1974. Estimates for the year 1975 indicate a doubling of the quantity of magnesium recycle, which is an indication of the success of the aluminum industry campaign to recycle used beverage cans without chlorinating out the magnesium content. Recycle aluminum-base alloys now contribute about 30% of the magnesium used in the aluminum industry.

A flow diagram for magnesium in the U.S. aluminum industry is shown in Fig. 47 for the year 1975.

No energy analysis exists for secondary magnesium recycling, but based on the similarity of properties and procedures we estimate a value of 20×10^6 BTU/ton, which is equivalent to the values used for aluminum. We may now estimate the quantity of energy saved by secondary recycle in the years 1985 and 2000 as well as the electrolytic energy saved in those years and the data are given in Table 34.

4.6.2 Recycling of Magnesium Scrap

Refining of secondary magnesium takes place under the protective action of a flux which usually has a magnesium chloride base and other halide or oxide salts to alter the density and other properties. Three general melting methods have been described: open pot melting where the flux forms a thin fluid film over the surface of the molten metal and may be parted for hand ladling processes; crucible melting in which the flux is skimmed off prior to pouring; and die casting where the flux does not protect the surface but is used to refine the metal. During the die casting process surface protection comes from the use of sulfur dioxide which is maintained in a closed drum over the pot.

Heavy pieces of unalloyed magnesium or standard alloys of known composition are fed directly back to alloying pots and treated in the same manner as virgin ingot. Machine shop scrap and fine clippings and trimmings are melted in the open pot process. Sawings and filings, found in large quantities in foundry operations, are added to a flux heel at a temperature below the melting point of the scrap and the scrap is continuously added with stirring. The mass is then raised above the melting point of the metal and puddling allows the metal to coalesce and the metal may be ladled from the pot. Foundry sprues, heads, gates and risers are cleaned by sand blasting or tumbling and then oven dried before melting. No special refining technique is required. Die casting butts, flashings, drippings, etc. are contaminated with carbonaceous material, and this scrap is puddled in an open pot with flux which acts to coalesce the fine bodies and refine the metal, which may then be transferred to the original casting pot.

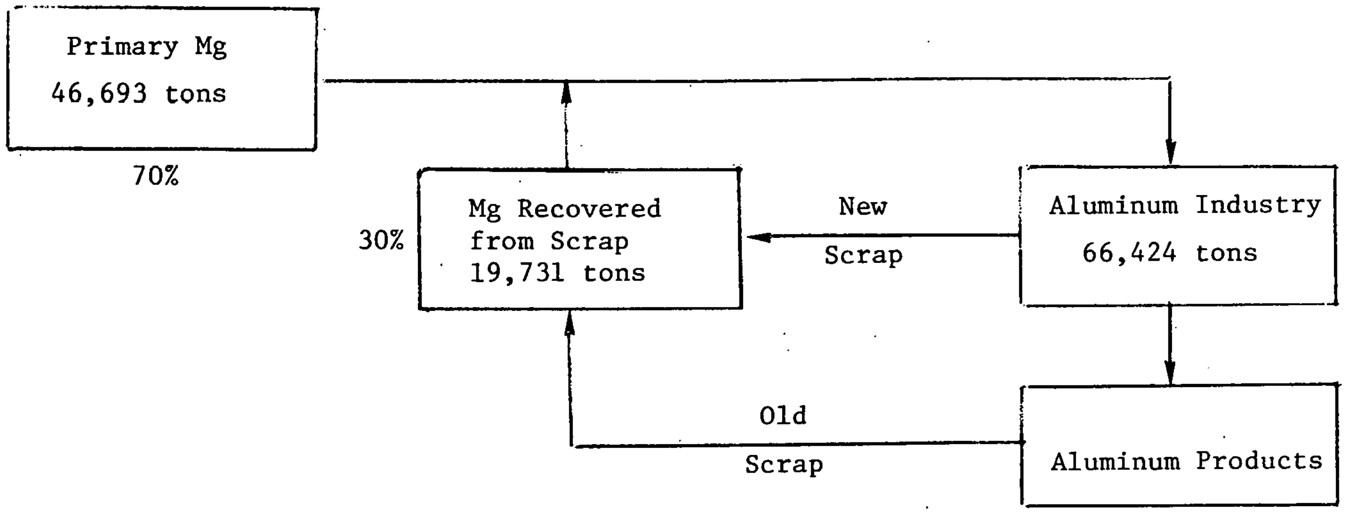


Fig. 47. Magnesium in U.S. aluminum industry in 1975 (67).

Table 34

Energy Saved in Magnesium Metal Recycle

Year	Total Energy, 10^{12} BTU	Electrolytic Energy, 10^{12} BTU
1985	3.4	1.8
2000	10.1	5.4

Fluxes serve the functions of removing certain impurities from the magnesium and protecting the molten metal from contact with the atmosphere. Alkali metals present in magnesium react with magnesium chloride and pass into the flux as chlorides. Magnesium oxide present in the metal also reacts with magnesium chloride, forming the oxychloride which deposits on the bottom of the melt container. Thus the flux refining procedure is capable of removing most of the oxides, nitrides and other non-metallic impurities; however, metallic impurities are not removed by this method. Various metallic additions such as manganese and chromium have beend found to lower the iron content of magnesium. Beryllium and zirconium are also capable of metallic impurity removal. Cobalt halides have been reported to remove silica from magnesium. A number of studies have been published on refining with titanium and titanium compounds in which the titanium is used to remove the non-metallic impurities nitrogen, oxygen and hydrogen from magnesium. It also has been reported that titanium interacts with iron, silicon, manganese, aluminum and zinc in liquid magnesium, decreasing their contents in that sequence.

Sublimation is a powerful technique for purification of magnesium. Here, advantage is taken of the relatively high vapor pressure of magnesium compared with elements which may be present as contaminants. The doubly sublimed material has a very high degree of purity, including purification from alkali and alkaline earth metals. Refining by this method is used only to a limited extent because of high energy and operating costs.

Magnesium may be refined electrolytically in a manner similar to that of the Hoopes cell used in the aluminum refining. In magnesium refining, zinc, lead or copper can be used as the weighting metals. Refining is conducted at about 700°C with anodic current densities of the order of 0.6 to 0.8 amps/cm^2 and cathodic current densities of about 0.6 to 1.0 amps/cm^2 with an interelectrode distance of about 10 cm. The specific energy expenditure during refining is between 9.5 and 10 kWh/kg which is only about 25 to 30% less than that used during electrolytic production of magnesium. The method, therefore, has not been adopted by industry because of high power expenditure and high operating costs.

4.6.3 Conclusions

Increased recycling of magnesium can best be achieved by minimizing demagging operations during the recycle of aluminum scrap. This will require improvements in the recycle technology of wrought aluminum alloys.

4.7 Titanium

4.7.1 Statistics and Energy Considerations

Titanium became important as a metal in the 1950's when the high strength-to-weight ratio of its alloys found use in aerospace applications. Other uses in heat exchangers and condensers depend upon its chemical inertness. The demand for the metallic forms is only about 10% of the total primary demand, 85% going to titanium oxide pigments and 5% to carbides, ceramics and chemicals.

Titanium is produced from the ore rutile which is mined by dredging Australian beach sands. The ore is beneficiated and shipped to the United States for further processing. The concentrate is chlorinated to titanium tetrachloride, which is then purified prior to reduction. Reduction is accomplished with magnesium (Kroll process) or with sodium. Electrolytic reduction of titanium tetrachloride from a molten salt has been under development for a number of years and is reported to have markedly lower energy requirements and simpler pollution controls compared with the Kroll process. The Bureau of Mines projects that by the year 2000 a significant quantity of titanium will be produced in the United States via the electrolytic route (68).

The energistics for production for titanium by the Kroll process and the two-stage sodium reduction process are given in Figs. 48 and 49. No reliable data exist for the energy used in the electrolytic process, but we will assume a requirement of 300×10^6 BTU/ton Ti. It was estimated that in 1975, 65% of the titanium was produced by the Kroll process and 35% by the sodium reduction process. The mix projected for 1985 and 2000 is given in Table 35 together with the weighted average energy content of the metal produced in those years.

The demand for titanium sponge has been highly variable from year to year in the 1970's, ranging from a high of 25 thousand tons in 1973 to a low of 15 thousand tons in 1976. Forecast for U.S. sponge titanium and secondary metal demand for the years 1985 and 2000 are given in Table 36.

Contingencies for the forecast on the high side could result from increased use of titanium in additional structural components of aircraft. The low side could result from the replacement of titanium alloys by fiber reinforced plastic and composite air frames.

The United States has been operating at well below its capacity of about 21 thousand tons per year sponge production. In recent years we have imported about 15 percent of our sponge, mostly from Japan.

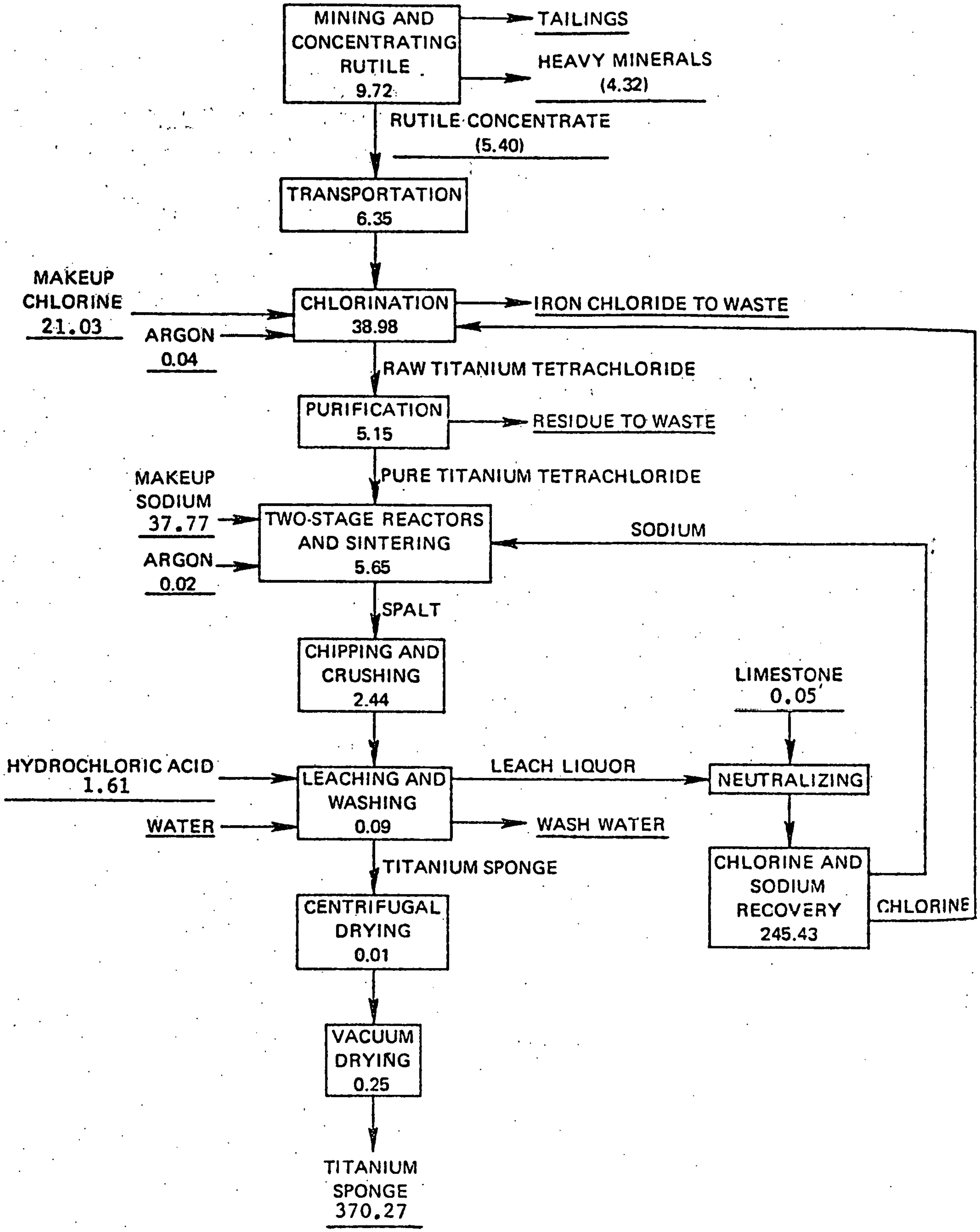


Fig. 48. Production of titanium sponge by the two-stage sodium-reduction process (62).

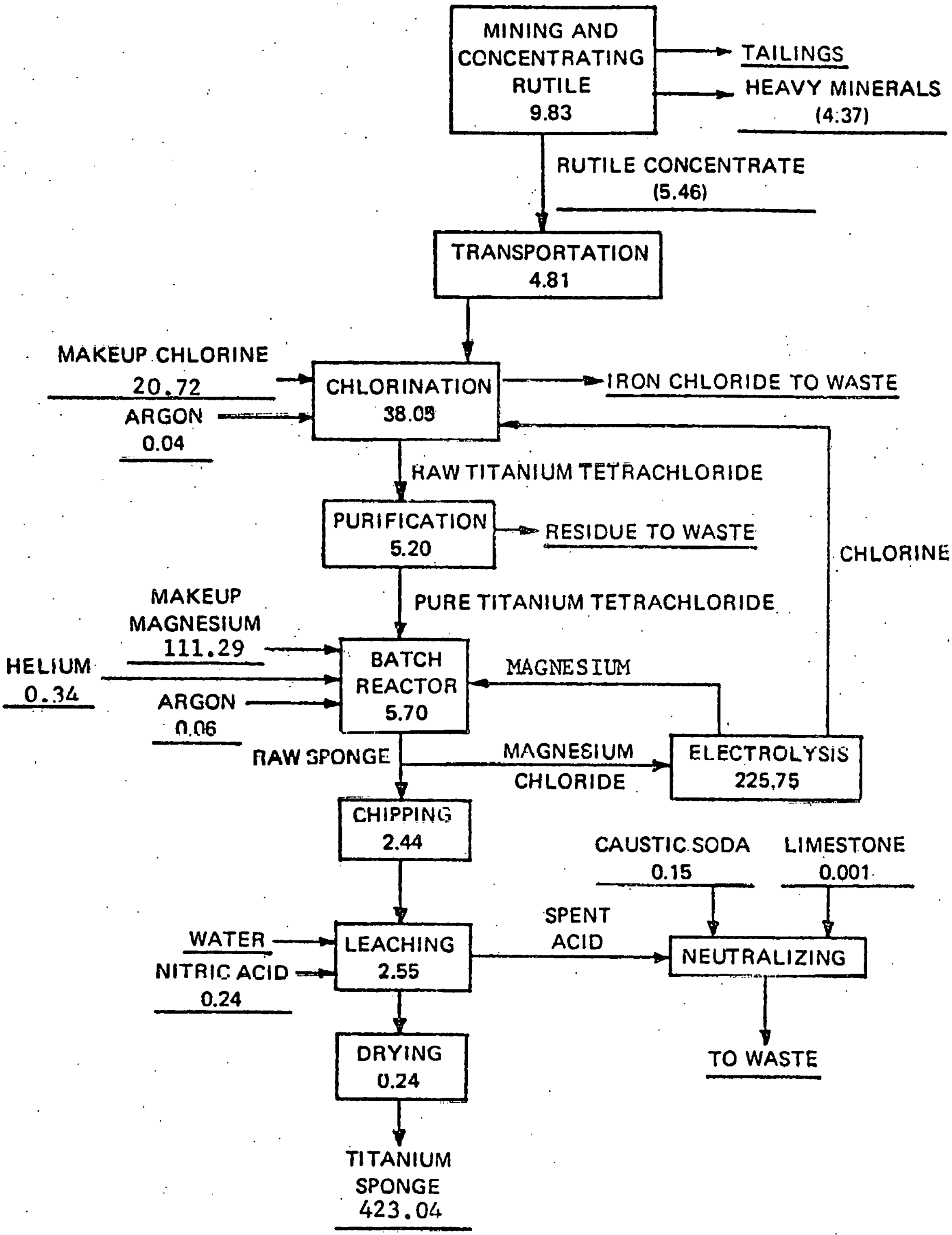


Fig. 49. Production of titanium sponge by the Kroll process (62).

Table 35

Fraction of Titanium Produced by Different Technologies and their Respective Energy Contents

	1975		1985		2000	
	% of Total	10^6 BTU/Ton Energy Contribution	% of Total	Energy Contribution	% of Total	Energy Contribution
Magnesium Reduction	65	275	62	265	40	171
Sodium Reduction	35	130	31	115	31	115
Electrolytic Reduction	-	-	7	21	29	87
Total Energy Content		405		401		373

Table 36

U.S. Titanium Metal Demand Forecast (69)

(thousands of tons)

	Probable		Year 2000 Forecast Range	
	1985	2000	Low	High
Primary	22	40	34	67
Secondary	11	22	15	31

The estimated total energy requirements for primary titanium production for the years 1985 and 2000 are given in Table 37. For the Kroll and sodium reduction processes, the electrolytic component is obtained from the electrolytic energy required to produce the requisite amounts of magnesium and sodium. The electrolytic energy required for electrolytic production of titanium is not reported, but is estimated at approximately 220 × 10^6 BTU/ton Ti.

Titanium scrap is recycled by adding it to a charge of virgin metal and forming a consumable electrode for melting. A flow sheet for this process is depicted in Fig. 50, which indicates the total energy in recycled scrap is about 35 × 10^6 BTU/ton.

The estimated total energy and electrolytic energy saved by recycling titanium scrap in the years 1985 and 2000 are given in Table 38.

Two diagrams depicting the titanium cycle are given in Figs. 51 and 52. For every pound of finished titanium part, 3.8 lbs of scrap are created. Of this, 2.3 lbs represents non-recycled scrap. The recycled titanium scrap represents about 1/3 of the titanium going into ingot production, the other 2/3 coming from primary titanium sponge.

About half of the non-titanium use recycle scrap is lost and the other half goes into steel and aluminum production.

The steel and aluminum industries have kept the price of titanium scrap at a relatively high level. During periods of adequate supply of sponge there is, therefore, no significant incentive for aerospace and superalloy manufacturers to utilize scrap to a higher degree. Furthermore, there is currently no good economical way to separate mixed alloy titanium scrap coming from fabricators and machine shops. It is also difficult to find an economically feasible system to detect inclusions which might be contained in titanium scrap and preclude its remelt use for aerospace applications.

4.7.2 Sources of Scrap

The major sources of titanium scrap are:

- Conversion of sponge to ingot
- Conversion of ingot to mill products
- Manufacture of end products from mill products
- Old scrap from obsolete end items

Table 37

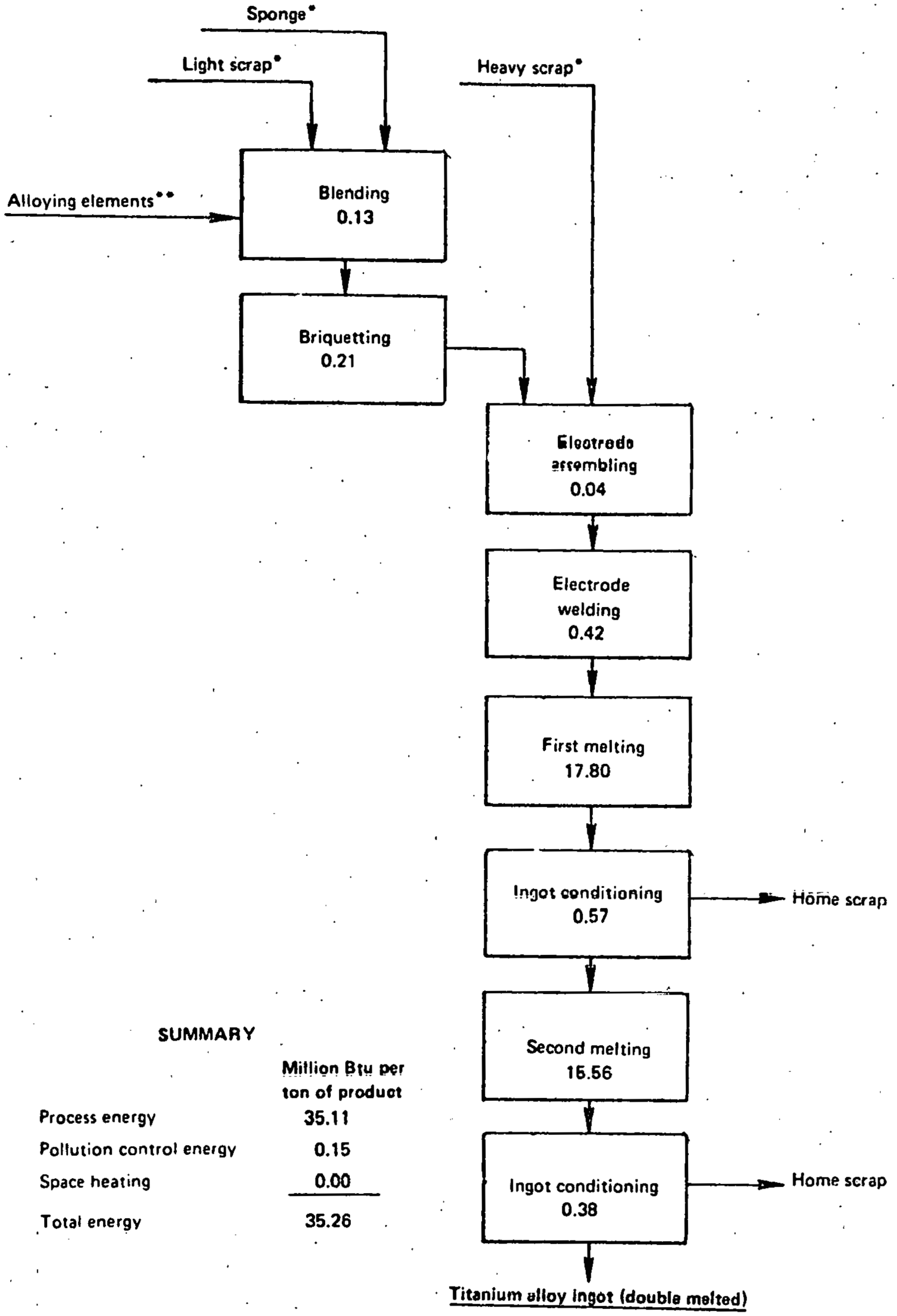
Energy Consumption in the Production of Primary Titanium in the Years 1985 and 2000

Year	Primary Production (thousands of short tons)	Total Energy, 10^{12} BTU	Electrolytic Energy, 10^{12} BTU
1985	22	8.8	6.9
2000	40	14.9	11.5

Table 38

Energy Saved by Titanium Recycle

Year	Total Energy, 10^{12} BTU	Electrolytic Energy, 10^{12} BTU
1985	4.0	3.4
2000	7.4	6.3



SUMMARY

	Million Btu per ton of product
Process energy	35.11
Pollution control energy	0.15
Space heating	0.00
Total energy	35.26

Fig. 50. Titanium: Ingot making by double melting in vacuum arc furnace (3).

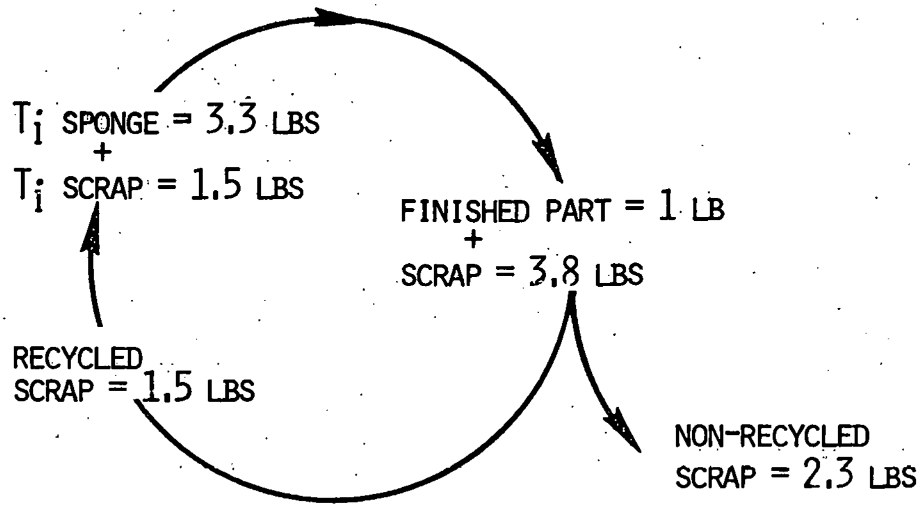
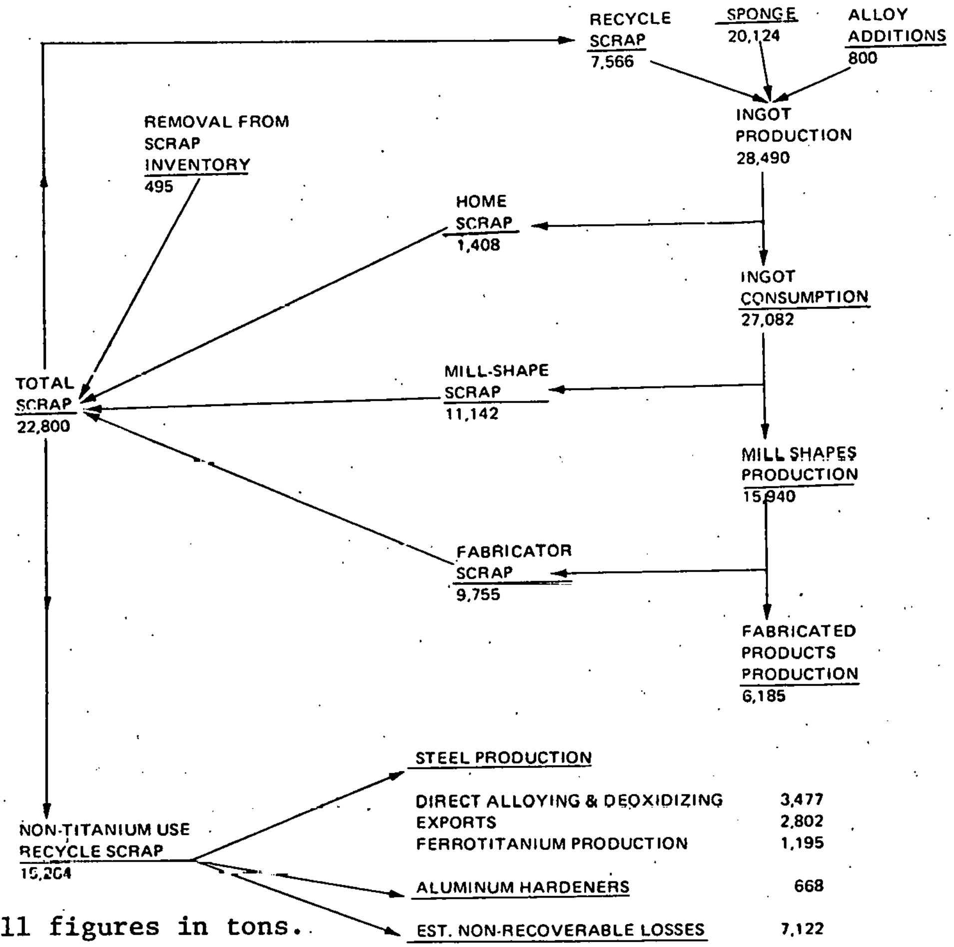


Figure 51. Typical Titanium Cycle



Note: All figures in tons.

Fig. 52. Titanium manufacturing and use cycle for 1969 (70).

A significant amount of scrap is generated by producers of ingot and mill products in the form of ingot ends and collars and as trimmings from bar, plate and sheet. The yield of billet from ingot is usually about 90-95% but under adverse circumstances can be as low as 80%. Product yields from billet average about 65%, but complex products such as tubing may give yields as low as 50%. Large amounts of scrap are generated in converting mill products to finished parts. As an example, for the F-15 aircraft the delivered forging for the fuselage bulkhead weighs about 1300 lbs. and is milled to a final weight of 145 lbs. As an average, the total scrap generated from mill products is about 75%. Of this about 85% is recoverable.

4.7.3 Current Practice in Recycling

Titanium scrap is utilized in three basic ways: (1) recycled to new ingot or castings, (2) recycled to production of steel or aluminum, and (3) converted into noncritical titanium items. Factors affecting the end use include scrap pedigree, cleanliness, form, quantity and end use demand.

There are at least thirty different titanium alloy grades in use,and grade identification is essential to maintain high scrap value. While titanium producers maintain special care in identifying in-house scrap, some fabricators consider the bother uneconomical,and the general scrap may be upgraded by dealers who are knowledgeable in identification procedures.

Producers are reluctant to accept scrap of uncertain pedigree since the quality of their alloys is critical in many uses. However, when scrap prices and qualities are suitable, some outside scrap is utilized. Scrap recycle to titanium ingot is accomplished by cleaning the chips, turnings and small pieces and blending them with sponge to be fed directly into the titanium smelting furnaces. Massive scrap may be consolidated by welding into consumable electrodes. Some massive scrap is converted, by hydriding and crushing, to smaller material prior to consolidation for melting.

Titanium melting is accomplished by the consumable arc process where an arc is struck between a preformed electrode and a molten pool in a copper-cooled mold. A large quantity of the melt is exposed to a vacuum environment and an ingot with little segregation results. The amount of scrap in the charge is limited by the necessity of producing a solid electrode of some integrity, and typically about 25% scrap may be accomodated.

4.7.4 Alternate Processes for Scrap Recycle

Doyle and Love (71) studied physical methods of separating titanium from aerospace scrap. Two density separation processes, the AVCO Ferrofluid and the Frenkel Company fuidized bed, were investigated. Both processes were equally effective in removing most contaminants from alloy scrap, but neither process could remove all contaminants. The minor levels of high density particles in the separated scrap were sufficient to degrade the fatigue life of specimens prepared from it. This is unacceptable for aerospace applications. Alternate melting technologies were recommended as a means of removing the impurity particles.

Direct chlorination of scrap to feed for reduction has been examined as a recycle route but does not appear economically attractive because of the low cost of the natural raw material. Energistically, this route would have little to offer.

The ability of titanium to form subhalides is the basis of a two-stage molten salt process (72) wherein scrap is treated with titanium tetrachloride to form the lower chlorides, $TiCl_2$, and $TiCl_3$, dissolved in a molten salt. The subhalides are subsequently reduced to the metal with sodium or magnesium. Alternatively, reduction could be accomplished electrolytically. The process allows versatility in treating a wide variety of titanium scrap. Economically, the reclamation of scrap not suitable for direct remelting appeared favorable, but the author recognized that the financial rewards anticipated were too small to justify an expensive development program without an industry-wide cooperative effort. Some energy savings may be contemplated by this process if it were applied to scrap that would not be otherwise utilized, since the subhalides, $TiCl_2$ and $TiCl_3$, would require less magnesium or sodium as a reductant compared with $TiCl_4$.

4.7.5 Conclusions

No hydrometallurgical or electrochemical routes for titanium recycle appear worth studying. Better scrap management at the user level and improved methods of sorting would aid in improving recycle.

5.0 CONSIDERATION OF NEW ELECTROCHEMICAL PROCESSES FOR SELECTED SCRAP MATERIALS

5.1 General

The information generated in Section 4 has been utilized to assess the possibility of developing new electrochemical recycle technology. Guidelines for such processes include:

- Potential for significant energy saving.
- Availability of scrap material.
- Feasibility of an electrochemical approach.

We have selected three cases for a more detailed examination:

- Impure wrought aluminum alloy scrap.
- Copper contained in low grade scrap.
- Zinc from metallurgical process dusts.

These are discussed in turn below.

5.2 Molten Salt Electrorefining of Wrought Aluminum Alloy Scrap

5.2.1 General

There is a large energy incentive to increase the recycling of scrap aluminum. Improved physical separations such as better sorting at waste dumps and auto scrap plants and improvements in mechanical and eddy current devices are extremely important. Energy savings and improved aluminum yield can also be envisaged at secondary smelters but these factors are outside the scope of this study.

Although it is not currently a major problem, we project the future necessity of recycling wrought alloy scrap back to wrought products as the demand for this material grows relative to the cast product. Although more careful sorting will help achieve this aim, eventually provision should be made for reducing the level of contaminants such as iron, silicon, copper and lead in recycled aluminum. This could be conveniently effected in an electrorefinery. Since aluminum cannot be refined in the aqueous phase we may consider potential improvements in the Hoopes cell, solid phase electrorefining at low temperature in a molten chloride both, or electrorefining using an organic electrolyte.

5.2.2 Perspective on Molten Salt Electrorefining

We believe that $AlCl_3$-based molten salts afford the best opportunity for economic electrorefining of aluminum. Incorporating suitable organic compounds in the bath could combine the best properties of organic electrolytes (100% current efficiency) with those of molten salt electrolytes (conductivity, stability). A suitable electrolyte might then consist of $AlCl_3$ and NaCl at a temperature below 200°C to which low concentrations ($\sim$100 ppm) of leveling agents, e.g., polycyclic aromatic hydrocarbons or ethers have been added. This system would exhibit the following favorable properties:

- Excellent chemical and electrochemical stability yielding a long bath life.
- Conductivities of $10^{\circ}-10^{-1}$ ohm^{-1} cm^{-1} and low ($\leq$ 200°C) operating temperatures ensuring minimal energy input.
- Thermal and chemical compatibility with a variety of proven organic leveling agents.
- Totally anhydrous and aprotic thus affording plating efficiencies of 100%.
- Inability of the melt to solvate Fe^{+2} thus rendering the refined Al iron-free.

Good stability and conductivity are characteristics of inorganic electrolytes. Scale up and the associated process engineering, have been demonstrated by the Alcoa process which electrowins aluminum from a NaCl/ $AlCl_3$ molten salt (4).

Peled and Gileadi (73) have demonstrated that cathode current efficiencies approaching 100% can be achieved from an $AlBr_3/KB_r$/toluene medium. Moreover, they found that small additions of polycyclic aromatic hydrocarbons (anthracene and napthalene) greatly improved the morphology of the aluminum deposit as well as its purity. We expect that higher molecular weight analogues of anthracene would have a similar effect without participating in the electrochemistry.

The nature of an $AlCl_3$-based electrolyte maintains the anhydrous character. Adventitious water is immediately scavenged by the melt. Thus, with no protic impurities and an aprotic organic leveling agent, cathodic current efficiencies are, in principle, allowed to approach 100%.

An additional important feature of the system is that iron will not dissolve from the anode. Were iron subject to anodic dissolution it would reduce on the cathode concurrently with aluminum, contaminating the product. Boxall and co-workers (74) has shown that in a 50:50 mole % $AlCl_3$:NaCl melt $FeCl_2$ was virtually insoluble. Thus, if aluminum dissolution were being driven at overpotentials sufficiently anodic to oxidize iron, the Fe^{+2} formed would remain bound to the cathode as insoluble $FeCl_2$.

5.2.3 Recommendations

Technology should be developed to enable the low-cost recycling of wrought aluminum alloy scrap to wrought products. We believe that this can be best achieved by a low-temperature aluminum chloride-based molten salt electrorefining process. It is difficult at this time to assess the magnitude of energy savings realizable, but it could be considerable.

5.3 Recovery of Copper from Low Grade Scrap with an Electrohydrometallurgical Process

5.3.1 General

The general outlines of the process requirements for an electrohydrometallurgical process for the recovery of copper from low grade scrap have already been presented (see Fig. 16). All essential operations in the general process sequence have been demonstrated in other applications, and the development of technically and economically successful technology in this instance would involve their adaptation for use on low-grade scrap material. The development effort will have to be focused on the "front end" of the process; technology already exists for treating copper-bearing solutions for metal recovery. The greatest uncertainties, both technical and economic, occur in those sections of the process devoted to handling the raw scrap, pretreating it to render it more suitable for leaching, and leaching the treated scrap.

A key requirement of any successful process will be the ability to handle feed stocks with a wide variety of chemical composition and physical properties. It is known that conventional, pyrometallurgical processes can accept scrap from many sources which differ widely in copper, iron and non-metallic contents and in such physical properties as bulk density and particle size distribution. It is likely that somewhat more attention to scrap preparation will be required for a hydrometallurgical process. The process outline we have presented was developed mainly in response to two considerations: first, it will be necessary to pretreat the scrap by size reduction and densification to achieve acceptable metal recoveries in reasonable leaching times, and second, since the scrap will contain significant amounts of iron and other metallics, the lixiviant/oxidant chosen should be highly selective for copper.

5.3.2 Process Description

An electrohydrometallurgical process for recovering copper from low grade scrap is shown schematically in Fig. 53. The process is based on the use of air as an oxidant and ammonium sulfate as a lixiviant, the latter being chosen as the most appropriate system for use where the dissolution of ferrous material must be minimized. As shown, zinc might also be recovered, if economically justified, from scrap containing significant amounts of brass or zinc alloys. The process plant would logically be divided into seven sections: Scrap storage and retrieval, scrap preparation, scrap leaching, pregnant liquor purification, electrowinning, purge stream treatment, and general plant services. The essential features of each section are summarized below.

5.3.2.1 Scrap Storage and Retrieval

Uncovered storage capacity for 60 days consumption of unsorted, untreated scrap would be needed. Provisions would be made to segregate incoming scrap by type (e.g., massive irony, wire and cable, consumer items) and to accommodate prepared scrap it if can be purchased. Unloading facilities would be provided for rail and truck deliveries as appropriate. Movement of material would be by magnetic and clam shell bucket cranes and tired vehicles as required. The same equipment would be used to charge prepared scrap to the leaching section and remove lights and leached scrap from the plant for disposal. Uncovered storage for 30 days lights and leached scrap would be provided, with unsorted scrap unloading facilities also serving to load process residues for disposal as required.

5.3.2.2 Scrap Preparations

It is likely that the unsorted scrap can be retrieved in two major categories; massive, probably irony, scrap and light scrap associated with material such as wire and consumer scrap. The heavy or massive material would be fed to size reduction equipment to render it more suitable for further processing. Both light and heavy scrap would be shredded to reduce its size. This would release covering material and free metallics from non-metallics insofar as possible and also increase the specific surface area, thereby promoting rapid leaching. The shredded scrap would be subject to air classification steps to remove the lights and the lighter metallic scrap would be baled to reduce the solids volume handled in the leach section. The scrap storage and preparation sections would operate one shift per day, five days per week, while all other plant sections would operate continuously.

5.3.2.3 Leaching

Prepared scrap would be charged, batchwise, to a series of leaching tanks with removable heads. Each tank would be provided with

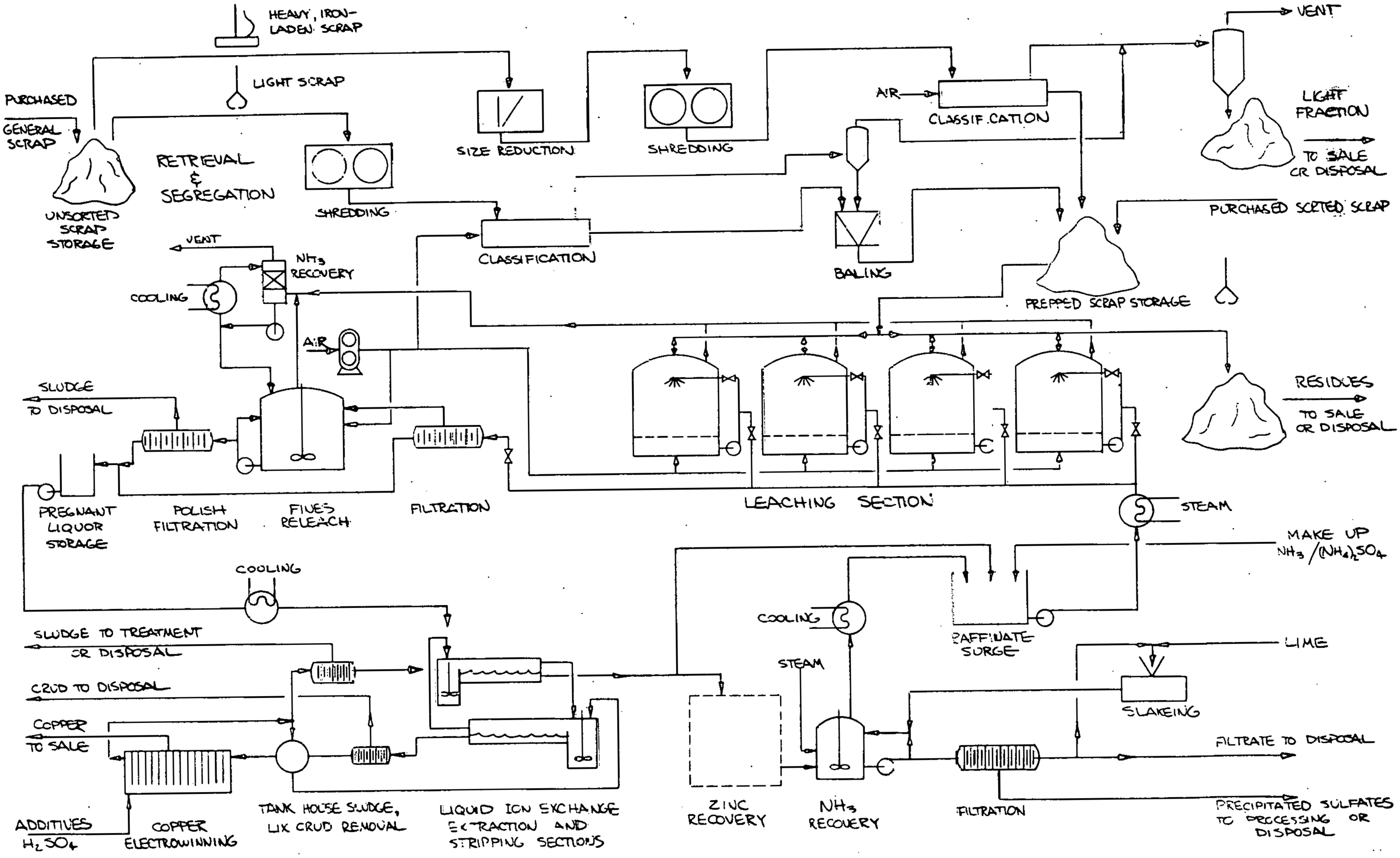


Fig. 53. Electrohydrometallurgical process for the recovery of copper from low-grade scrap.

high volume pumps for circulating leach liquor over the scrap and with sparge nozzles to provide air contact. Vented air would be treated for ammonia recovery. After leaching, the pregnant liquor would be advanced, the scrap allowed to drain, and the bulk of solid residues removed. Some decrepitation of the scrap will inevitably occur, and the fine material will be removed from the liquor and releached to recover additional copper. Residues and sludge will be consolidated for disposal and the pregnant liquor advanced to surge storage to smooth out composition fluctuations.

5.3.2.4 Pregnant Liquor Purification

Copper will be selectively removed from the pregnant liquor by liquid ion exchange using conventional techniques. The required number of extractions and stripping stages will be provided along with equipment for removing organic crud and tankhouse sludge from circulating organic and electrolyte streams.

5.3.2.5 Electrowinning

Copper will be recovered by electrowinning from the liquid ion exchange strip solutions using insoluble lead anodes. The tankhouse will have starter and production sections, but the purge stream will be treated by recycling it to the liquid ion exchange extraction sections.

5.3.2.6 Purge Stream Treatment

Other nonferrous metals, and especially zinc, will be solubilized in the leaching step and must be removed from the circulating leach liquor in a purge stream. If economics are suitable, zinc could be recovered from the purge stream, after pH adjustment, by a liquid ion exchange operation similar to that used to remove copper from the pregnant liquor. The purge stream will contain ammonia and sulfate, however, and the former must be recovered for recycle. This would be accomplished by treating the purge stream with lime to precipitate the sulfates as gypsum and any dissolved heavy metals as hydroxides, and by sparging steam into the mixture to vaporize the ammonia. The latter would be condensed for recycle and the resulting slurry filtered to obtain a sludge suitable for disposal.

5.3.2.7 General Plant Services

General plant services include the provision of utilities - steam, cooling water, and power - and administrative and support services such as laboratory, cafeteria, and administrative areas. These are entirely conventional and appropriate for plants of this type.

5.3.3 Process Material and Energy Balances

The overall process material and energy balances for a plant producing 10,000 tons per year of copper are summarized in Table 39. It must be emphasized that the flow rates for the major inputs and outputs, raw scrap and treated residues, are entirely dependent on the grade and composition of the purchased scrap and the plant capacity. We have somewhat arbitrarily chosen the composition noted, but it is to be expected that in practice, the amount and distribution will be different and highly variable. The copper production rate would be typical of a plant treating scrap from a wide geographic area.

While the equipment for the front end of the process is relatively large, being sized to treat large amounts of low-grade, low-density scrap, the solution handling equipment is relatively small since the pregnant liquor flow rate is only 100 GPM and the purge stream flow would be between 10 and 25 GPM. Thus, process heating and cooling requirements are modest and the requirements for makeup water for process and cooling use and fuel for raising steam are low. The main requirement for power is in electrowinning, although a large connected power is needed for operation of the air classification equipment blower. The process water balance presented here is based on the assumption that the leach residues can be washed free of pregnant liquor, after draining, with a single volume displacement. If washing is more difficult, the extra water would have to be removed with a higher purge stream flow.

The total energy requirement for recovering copper by this process is approximately 60×10^6 BTU/ton, taking a fuel requirement of 10,500 BTU/kWh for power consumed. While this is substantially lower than the energy requirements for primary production ($>100 \times 10^6$ BTU/ton), it is higher than reported for low grade scrap processing by conventional, pyrometallurgical processing ($\sim 40 \times 10^6$ BTU/ton). This is a direct result of the use of an energy intensive electrochemical reduction step in this process. Use of alternative, chemical reduction steps which are currently under development and optimized processing schemes could reduce energy consumption by as much as 25%. If more stringent environmental control requirements impose additional energy costs on conventional processes, an improved hydrometallurgical process sequence would then be competitive from the energy consumption point of view.

5.3.4 Capital and Operating Costs

Capital and operating cost estimates are summarized in Tables 40 and, 41. These costs, derived from factored equipment cost estimates and preliminary material and energy balances, carry an uncertainty of at least 33%.

Table 39

Plant Inputs and Outputs
Recovery of Copper from Low Grade Scrap

Major Inputs	
Low Grade Scrap(1)	45,000 TPY
$(NH_4)_2SO_4$	1,000 TPY
NH_3	50 TPY
H_2SO_4	700 TPY
CaO	1,000 TPY
Liquid Ion Exchange Reagents and Additives	10,000 GPY
Fuel	250×10^9 BTU/yr
Power	35×10^6 kWh
Water	50×10^6 Gal/yr
Major Outputs	
Cathode Copper(1)	10,000 TPY
Separated Light Scrap(1)	∿10,000 TPY
Leached Scrap Residues	∿22,000 TPY
Leached Sludge	∿ 3,000 TPY
Precipitated Sulfate Sludge	2,800 TPY
Tankhouse Sludge and Liquid Ion Exchange Crud	200 TPY
Filtrate and Plant Run Off	20×10^6 Gal/yr
Process Vents(2)	40 MSCPM

---

(1) Scrap assumed to contain 25% copper, recovered at 90% efficiency, and 35% light fraction separated at 66% efficiency.

(2) Cleaned air.

Table 40

Capital Cost Estimate Summary
Copper Recovery from Low Grade Scrap

Plant Section	Physical Plant Costs	
Scrap Storage and Retrieval	$ 500M	
Scrap Preparation	800M	
Leaching	1,600M	
Pregnant Liquor Purification	2,900M	
Electrowinning	6,000M	
Purge Stream Treatment	200M	
Total Physical Plant		$12,000M
Utilities and General Plant Services @ 25% TPPC		3,000M
Direct Plant Cost		15,000M
Engineering, Construction, Fees and Contingency @ 33% DPL		5,000M
Total Fixed Capital		$20,000M
		$ 2,000/Annual Ton

Table 41

Operating Cost Estimate Summary
Copper Recovery from Low Grade Scrap

Materials and Supplies	$ 290M/yr
Utilities and Fuel(1)	1,900
Labor	1,810
Capital Charges(2)	4,000
Total Operating Cost	$8,000M/year
	40¢/lb Cu

---

(1) Fuel @ $2.9/MM BTU, power @ 3.3/kWh.

(2) At 20% TFC

Half of the direct plant costs are associated with the electrowinning section and will be little influenced by changes in plant capacity or the nature of the scrap being processed. Solution handling (liquid ion exchange and purge stream treatment) account for another quarter, so that the "front end" costs, which are most sensitive to scrap type, amount to only 25% of the total. Thus, more complex and expensive scrap preparation and leaching sequences would probably be justified if recoveries could be increased and/or materials handling and disposal problems eased.

Capital charges for maintenance, material and supplies, depreciation, taxes, insurance, etc. are the dominant category of plant operating costs. Therefore a significant process development effort can be justified to decrease the total plant capital costs. In particular, lower cost alternatives to the electrowinning step would be highly desirable.

The total plant labor complement would be approximately 80 personnel, and an average burdened labor rate of $22,000/year has been used. Most of the operating labor is required in the electrowinning plant, and its power consumption amounts to more than 40% of the total utilities costs. Boiler and furnace fuel require another 40%, and the balance is mainly the cost of power consumed in the remainder of the plant. Makeup $(NH_4)_2SO_4$ accounts for one third of the material costs, and would increase directly with the volume of the purge stream to be treated.

The estimated total capital and operating costs of $2000/annual ton and 40¢/lb respectively are both substantially higher than currently borne in the processing of high grade scrap by conventional techniques. In fact, the capital cost is of the same order as would be required for the construction of a new primary smelter and the operating cost is significantly higher than would be required for smelting and refining. The costs of mining and milling would not have to be borne, however. Nevertheless, it appears that it would be necessary to purchase the low grade scrap for a price not exceeding 20¢/lb (delivered) in order to provide a sufficient margin for this type of operation. While this is not out of line with some recently quoted prices, it should be emphasized that these are preliminary estimates and that significant categories of site specific costs have not been considered. These include transportation costs and the net cost of disposal of process wastes. If credits for sale of separated materials do not offset cost of disposal of other wastes, the process economics would be very adversely effected.

5.3.5 Recommendations

No major source of copper scrap has been found which cannot be treated pyrometallurgically followed by electrorefining. Hydrometallurgical processes for copper scrap recovery which utilize electrowinning consume significantly more energy and are more expensive than pyrometallurgical processes. Development of chemical reduction alternatives to the electrowinning of copper are technically feasible and could substantially reduce the energy requirements and cost of the hydrometallurgical alternative.

5.4 Recovery of Zinc from Metallurgical Process Dusts with an Electrohydrometallurgical Process

5.4.1 General

The technology for the recovery of zinc from roasted sulfide ores is well established and can serve as the basis for recovery of zinc from metallurgical process dusts. In both cases, the zinc is present mainly as the oxide, and the technical and economic success depends on obtaining high zinc recoveries while minimizing the dissolution of other dust constituents which would ease problems to zinc electrowinning.

In the case of zinc dusts derived from electric furnace reduction of scrap iron and steel, the key processing problem is to maximize zinc recovery while minimizing iron dissolution. We have developed flow sheets based on the conventional jarosite process for iron removal from roasted zinc sulfide concentrates. In this case, however, the iron removed-to-zinc recovery ratio is quite high because the acid leach step will dissolve a significant amount of iron oxide. It may be possible, however, in some cases to relax the requirement to maximize zinc recovery which would decrease iron removal costs. In these circumstances, the leached residues would be recycled to the electric furnace and the zinc plant would be looked on merely as a zinc removal step in the steel production sequence. In this case, a goethite process would be used for iron removal to reduce the sulfur content of the recycled leach residues.

5.4.2 Process Description

An electrohydrometallurgical process for recovery of zinc from metallurgical process dusts is shown schematically in Fig. 54. The process is based on conventional hydrometallurgical zinc processing technology, and the plant would consist of six sections: dust storage, dust preparation, leaching, solution purification, electrowinning, and general plant services. The features of each section are summarized below.

5.4.2.1 Dust Storage

It is anticipated that the dusts will have been consolidated to increase their density prior to shipment and will be received in drums, by truck, or closed rail cars. Covered, ventilated storage will be provided for 30 days consumption of scrap. Dusts will be removed from containers, if required, and stored in bins for transfer to the dust preparation section by enclosed conveyor.

5.4.2.2 Dust Preparation

The as-received dusts would be wet-milled to break up agglomerates formed to increase shipping density. They would then be washed to remove soluble salts, particularly alkali halides, which would otherwise enter the leaching circuit. The washed, milled dusts would then be fed, at a controlled rate to the leaching section.

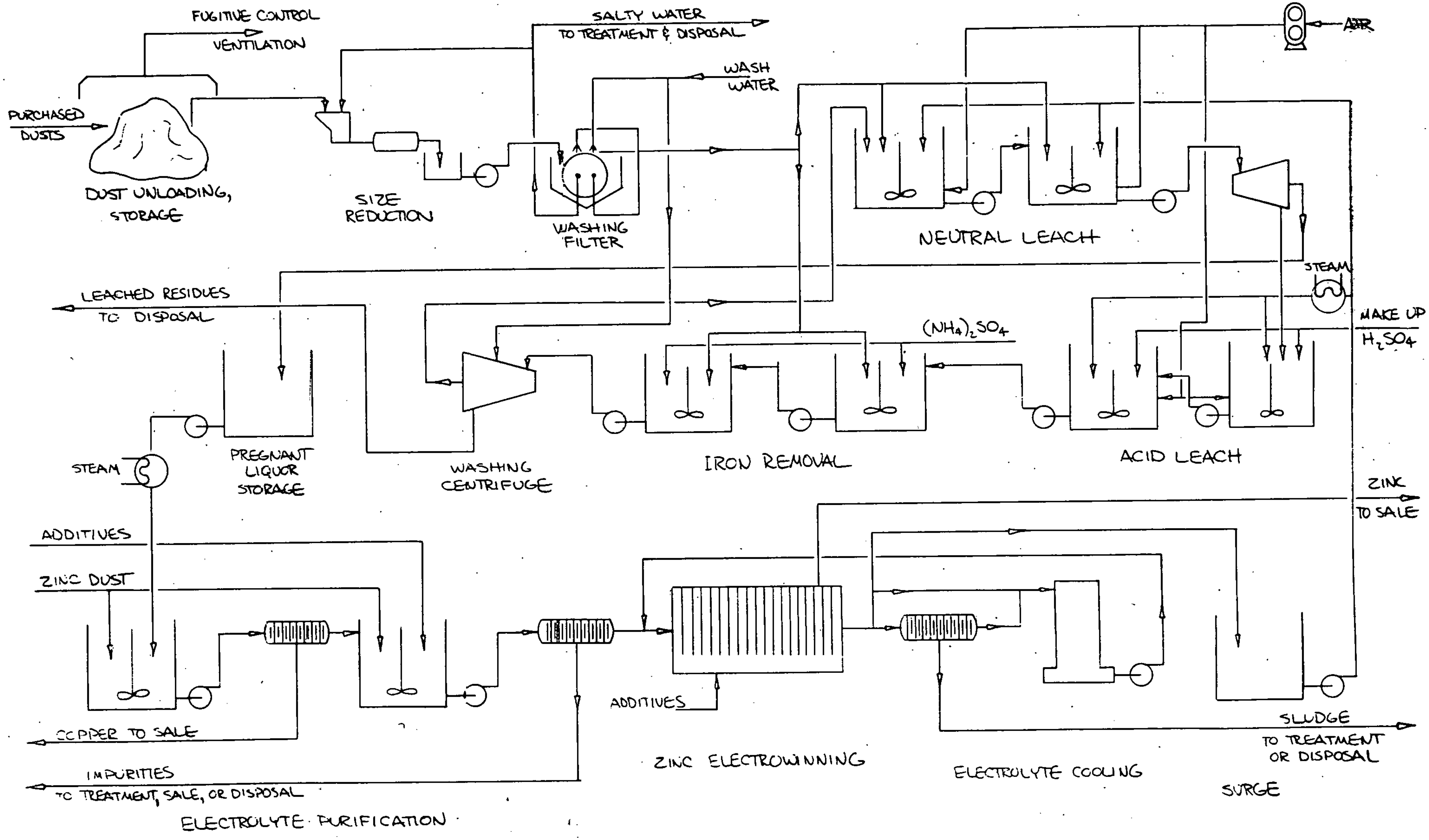


Fig. 54. Electrohydrometallurgical process for the recovery of zinc from metallurgical process dusts.

5.4.2.3 Leaching

The majority of the washed dusts would be fed to a "neutral leach" step in which the relative flow rates of dust and recycled electrolyte are adjusted to maintain the solution pH near neutral. The leaching is carried out in agitated, open top reactors, and the leached slurry is transferred to centrifuges for liquid-solid separation. The separated liquid effluent from neutral leach is sent to surge storage, while the solid residues are releached in hot, acidified electrolyte for additional zinc recovery. The leach effluent from this operation, which will contain significant amounts of dissolved iron, is mixed with unleached dust to raise its pH, and with $(NH_4)_2SO_4$ to precipitate the dissolved iron as ammonium jarosite. The residues from these steps are washed, with the zinc rich filtrate being returned to the neutral leach step.

5.4.2.4 Solution Purification

The solution from the neutral leach step contains copper, nickel and small amounts of other impurities which must be removed almost completely prior to electrowinning. Solution purification is carried out by the stagewise additions of metallic zinc dust and additives to the pregnant liquor. In the first stages, copper displaces metallic zinc and is precipitated from solution. It is then filtered from the reactor effluent while other, more electropositive impurities are removed in the following stages. These impurities, now concentrated, may be sold or treated further if economically justified.

5.4.2.5 Electrowinning

Zinc is recovered directly from the purified pregnant liquor by electrowinning. Standard practice in zinc electrowinning would be followed, and electrolyte cooling would be by direct contact evaporation. The water removal in electrowinning is a major consideration in establishing the process water balance.

5.4.2.6 General Plant Services

General plant services include the provision of utilities and administrative services and, as for the case of copper recovery, are entirely conventional.

5.4.3 Process Material and Energy Balances

The overall process material and energy balances for the recovery of zinc from metallurgical process dusts are summarized in Table 42 . The dust composition selected is typical of electric furnace steelmaking dusts, which is the technology likely to be adopted in regional specialty mills.

Table 42

Plant Inputs and Outputs

Recovery of Zinc from Metallurgical Dusts

Major Inputs	
Zinc Dusts(1)	62,500 TPY
$(NH_4)_2SO_4$	800 TPY
H_2SO_4	1,700 TPY
Metallic Zinc Dust and Additives	200 TPY
Fuel	150×10^9 BTU/hr
Power	38×10^6 kWh/yr
Water	25×10^6 Gal/yr
Major Outputs	
Cathode Zinc(1)	10,000 TPY
Cement Copper	100 TPY
Other Impurities	100 TPY
Leached Residues	52,500 TPY
Tankhouse Sludge	200 TPY
Salt Water and Plant Run Off	20×10^6 GPY
Process Vents	50 MSCFM

---

(1) Dusts assumed to contain 20% Zn, 0.2% Cu recovered at 80% efficiency and 31% Fe of which 10% is dissolved.

The zinc production rate selected would be consistent with the steel mills processing large amounts of galvanized or zinc-rich scrap.

The majority of the solid wastes from the process are leach residues which must be carefully disposed of since they still contain all of the heavy metals present in the raw dusts. If more wash water must be introduced to the leaching circuit than can be disposed of by evaporation in electrowinning, a purge stream treatment step will be required which will increase process complexity and cost. Since the pregnant liquor flow rate is small, about 50 GPM, process heating and cooling requirements are low. The main power demand is for zinc electrowinning, and utilities requirement are lower than for a comparable plant recovering copper.

The total energy required for recovery of electrolytic zinc by this process, taking the fuel equivalent of power at 10,500 BTU/kWh, is approximately 53 × 10^6 BTU/ton. This is slightly lower than the energy requirement for primary production which is about 60 × 10^6 BTU/ton. Current practice in zinc recycling essentially involves distillation of relatively pure, metallic scrap and requires about 25 × 10^6 BTU/ton. There is no figure-of-merit for the recovery of zinc from dusts since this resource is not currently exploited.

5.4.4 Capital and Operating Costs

Capital and operating cost estimates for zinc recovery from metallurgical dusts, summarized in Tables 43 and 44, were derived from factored equipment costs and preliminary material and energy balances and carry a correspondingly high uncertainty.

Even though solution purification techniques must be very carefully worked out, the operations involved can be carried out in relatively simple equipment. The raw dust is not too difficult to handle and is easily leached at moderate process conditions so that the "front end" plant costs are relatively low. Since two thirds of the direct plant costs are associated with zinc electrowinning, significant additional investment in the preparation and leaching sections could be justified if zinc recoveries could be increased from 80 to 90%. This would be true even if somewhat higher amounts of iron were dissolved in the process since the additional capital and operating costs incurred in its removal would be small.

As was the case for copper from low-grade scrap, capital charges dominate the operating costs. Since two thirds of the capital costs are associated with electrowinning, there is little prospect for decreasing operating costs substantially. Half of the materials and supplies costs are associated with zinc dust and additives for solution purification and two thirds of the utility cost is for electrowinning power. The plant labor complement requires about 80 positions, the majority of which are associated

Table 43

Capital Cost Estimate Summary
Zinc Recovery from Metallurgical Dusts

Plant Section	Physical Plant Cost	
Dust Storage	$ 700M	
Dust Preparation	400M	
Leaching	1,700M	
Solution Purification	600M	
Electrowinning	6,600M	
Total Physical Plant		$10,000M
Utilities and General Plant Services @ 25% TPPC		2,500M
Direct Plant Cost		12,500M
Engineering, Construction, Fees and Contingency @ 33% DPC		4,200M
Total Fixed Capital		$16,700
		$ 1,670/Annual Ton

Table 44

Operating Cost Estimate Summary
Zinc Recovery from Metallurgical Dusts

Materials and Supplies	$ 320M/year
Utilities and Fuel(1)	1,700
Labor	1,740
Capital Charges(2)	3,340
Revenues from Copper Sales(3)	(100)
Total Operating Cost	$7,000M/year
	35¢/lb Zn

---

(1) Fuel @ $2.9/MM BTU, power @ 3.3¢/kWh.

(2) At 20% TFC.

(3) At $0.5/lb Cu.

with tankhouse labor. This can be reduced only by utilizing automated material handling equipment, with a corresponding increase in capital related charges.

The total estimated capital and operating costs for recovery of zinc from metallurgical dusts, $1700/annual ton and 35¢/lb, respectively, are far higher than required for the recovery of zinc from metallic scrap by pyrometallurgical techniques. In fact, since electrolytic zinc has recently been selling in the range of 30-35¢/lb, the metallurgical dusts must be made available at no cost for this technology to compete in the primary zinc market. While a steelmaker might set a very low transfer price on the dusts, or make them available for the cost of freight to avoid disposal costs, the costs of disposal of leached residues from the zinc plant would still have to be borne. The projected economics will not leave a sufficient margin to cover any additional costs, let alone an adequate return on investment, unless additional credits can be taken. These might arise from the recycling of leached dusts for iron removal, using a goethite process for iron removed as noted, or from decreased waste disposal costs. In either case, extensive pilot plant work would be required to define the properties of the leach residues.

5.4.5 Recommendations

Zinc-containing metallurgical process dusts are a major untapped resource which is currently an environmental disposal problem. Recycle of electric furnace steelmaking dusts, either as metallic zinc or as zinc oxide, could lead to energy savings of the order of 5 to 10 × 10^{12} BTU/year. A fully integrated hydrometallurgical process for zinc recovery from these dusts is too energy intensive and costly to warrant development. Alternate processes which deserve further consideration are 1) pyrometallurgical processes which combine the dusts with carbon, reduce and vaporize the zinc, and burn the zinc to oxide, and 2) a process which selectively leaches and recovers zinc oxide with concentrated ammonium chloride.

6.0 RECYCLE OF BATTERY COMPONENTS

6.1 Introduction

A major effort is underway in the United States and several countries abroad to develop advanced, high energy secondary battery systems. These batteries would be used in two major applications: electric-powered automobiles and stationary energy storage for load leveling of electric utility power.

For the purpose of this study which is primarily concerned with the recycle of the metals of value, we will consider that each of the proposed secondary batteries will be the battery of choice for both of the contemplated uses. We will thus consider the high volume of metal associated with the large scale recycle of each system.

6.2 Battery Systems Considered

Six systems have been chosen as the most probable to be developed to the point where they are used commercially for the above mentioned missions. The near-term systems which are considered to be available before 1985 include: advanced lead/acid, nickel/zinc, and nickel/iron (75). Future systems, which still have considerable engineering, safety and/or environmental barriers to overcome before they become available in 1990 are: zinc/chlorine, sodium/sulfur, and lithium-aluminum/metal sulfide (75).

Available information on the characteristics of each system, based on the current state of development and projections for the future, has been organized to include:

- Near-term and long-term candidates.
- Physical description of the battery unit for one or both applications.
- Definition of the battery components and the chemical nature of those components in both the charged and discharged state.
- A basis for determining whether a component in a scrapped battery should be recovered or discarded.
- Annual amount of scrap available for near term (1990) and projected (2000) use.
- Definition of the form into which the recovered scrap will have to be converted for reuse.

A summary of all information is given in Table 45. The physical description of each battery system (Columns 2 and 3) is based either on current engineering models or on models proposed by the various facilities involved with developing the systems. The developer is noted in each case. The physical description provides the basis for sizing, handling and processing equipment. Load leveling batteries are much larger and heavier than the corresponding electric vehicle battery.

The major components of each battery system have been itemized to identify those components which must be considered in recycling (Columns 4 and 5). In all systems it has been assumed that the only materials that undergo extensive change are the active materials, usually the electrodes or plates. While the charge and discharge states are described as "same" for many components, it must be acknowledged that there will inevitably be contamination, corrosion or degradation during service. We will assume that in developed systems this occurs only to a minor degree.

In the lead/acid system the active materials are Pb and PbO_2 at the negative and positive electrodes respectively. These interact with the electrolyte, H_2SO_4, and discharge to form $PbSO_4$. Lead-antimony grids are in common use in today's batteries but lead-calcium grids have been featured in the recently developed "maintenance-free" batteries. For this study we will assume that the lead-antimony alloy is retained in batteries for electric vehicle propulsion and load leveling.

In the nickel/zinc system, the active metal electrodes are, in the charged state, NiOOH for the positive electrodes and Zn for the negative electrodes. In the discharged state they are converted to $Ni(OH)_2$ and ZnO. The KOH electrolyte supplies the water for the discharge reaction.

The construction of the nickel/iron battery is similar to that of the nickel/zinc. The nickel positive electrode is identical to the nickel electrode described above. The iron electrode consists of metallic iron in the charged state which is converted to ferrous/ferric hydroxide during two or three discharges. The electrolyte, lithiated KOH, supplies water for the discharge reaction.

The zinc/chlorine system design differs significant from the more conventional designs for the first three systems. The battery section is supported by a sophisticated array of equipment including a gas pump, electrolyte pump, heat exchangers, filters and control valves. The battery section itself is also unique. Both electrodes are graphite substrates that are suspended in an electrolyte consisting of a $ZnCl_2$ solution. The active materials are zinc and chlorine and, in the discharged state, are present in the electrolyte as $ZnCl_2$. In the fully charged state the zinc is plated out onto the negative electrode and the chlorine is absorbed into the porous positive electrode. Chlorine is then stored in a chiller tank as chlorine hydrate.

Table 45

Analysis of Battery Scrap Recovery

Most Probable Battery Systems		Description of Physical Units		Definition and Chemical Nature of Scrap at State of:		Worth Recovery or Discard	U.S. Yearly Amount of Scrap Available (in pounds)		Final Form Required for Reuse
		Electric Vehicle	Load Leveling	Fully Charged	Fully Discharged		Year 1990	Year 2000	
NEAR TERM SYSTEMS	Pb/Acid	12" H 7" W 10" L 65 lbs Typical	~ 49" H ~ 18" W ~ 36" L ~ 2645 lbs (1)	Plates - Pb and PbO_2 Grids - Pb with ~7% Sb Electrolyte - H_2SO_4 Posts } Pb with ~7% Sb Lugs } Cases } Plastic or Separators } Rubber	Pb, PbO_2 and $PbSO_4$ Same Diluted Same Same	Recover Recover Discard Recover Discard	Pb 2.3×10^8 EV*	Pb 2.7×10^9 EV* 7.2×10^9 LL**	Pure Pb and PbO_2 for plates. Pb-Sb @ ~7% for posts & lugs. Pb-Sb @ ~7% for grids.
	Ni/Zn	12" H 7" W 10" L ~62 lbs (2)	No model available at present.	Plates - NiOOH and Zn Electrolyte - KOH Combs, grids } Cu or Ni Connectors } plated Cu Posts - Pb with ~7% Sb Cases } Plastic or Separators } composite	$Ni(OH)_2$ and ZnO Concentrated Same Same Same	Recover Discard Recover Discard Discard	Ni 3.8×10^7 EV Zn 1.7×10^7 EV	Ni 4.5×10^8 EV 1.2×10^9 LL Zn 2.0×10^8 EV 5.2×10^8 LL	Pure Ni or $Ni(OH)_2$ for Ni electrode. Pure Zn or ZnO for Zn electrode.
	Ni/Fe	12" H 7" W 10" L 65 lbs (3)	No model available at present.	Plates - NiOOH and Fe Grids - Steel or Iron Electrolyte - Lithiated KOH Connectors - Steel or Coated Cu Separators - Absorber barrier type Case/Cover - Plastic	$Ni(OH)_2$ and $Fe(OH)_{2\ or\ 3}$ Same Concentrated Same Same Same	Recover Ni Discard† Discard Discard† Discard Discard	Ni 7.1×10^7 EV Fe 3.4×10^7 EV	Ni 8.3×10^8 EV 2.2×10^9 LL Fe 3.9×10^8 EV 1.0×10^9 LL	Pure Ni or $Ni(OH)_2$ for Ni plate.
FUTURE SYSTEMS	Zn/Cl_2 Chlorine hydrate	~ 6" H ~ 8" W ~ 28" L Weight not available. (4)	No model available at present.	Active Materials - Zn and $Cl_2 \cdot < H_2O$ Zn Electrodes Substrate - Graphite Cl Electrode Substrate - Porous Material Electrolyte - $ZnCl_2$ Bus-Bars - Metal Case - Plastic	$ZnCl_2$ in Electrolyte Same Same Concentrated Same Same	Recover Discard† Recover Recover Discard† Discard		Zn 1.7×10^8 EV 4.4×10^8 LL Cl 1.8×10^8 EV 4.8×10^8 LL	Active materials as $ZnCl_2$. *Cl electrode as is, if possible.* Zn electrode - graphite.
	Na/S Ceramic Electrolyte	Cylindrical Cells Grouped in Blocks ~ 17.5" H ~ 13" W ~ 38.5" L Weight not available. (5)	~ 24" H ~ 30" W ~ 60" L Weight not available. (6)	Active Materials - Na and S (liquid) Electrolyte - Beta Alumina Sulfur Media - Porous graphite felt Casing-Steel	Na_2S_x Solid Same Same Same	Recover Discard† Discard Recover		Na 1.6×10^8 EV 4.4×10^8 LL S 2.7×10^8 EV 7.2×10^8 LL	Active materials as pure Na_2S_x. Casing - intact.
	Li-Al/Metal Sulfide	Tubular Housing ~ 8'-10" L ~ 1'-4" dia ~ 660 lbs (7)	~ 80" H ~ 10" W ~ 10" L ~ 970 lbs (8)	Plates - Li-Al Alloy and FeS or FeS_2 Li-Al Grid - SS screen Fe S_x Grid - Fe Electrolyte - LiCl-KCl Molten Eutectic Separators - BN Cloth Casing - Steel	Li_2S and Fe Same Same Same Same Same	Recover Discard† Discard† Recover Recover		Li 4.4×10^8 EV 2.2×10^8 LL Al 1.8×10^9 EV 8.8×10^8 LL FeS_x 2.6×10^9 EV 1.3×10^9 LL	Plates - Li_2S. Bn - as is. Casing - intact.

*EV = Electric Vehicle.
**LL = Load Leveling.
†Discard to further scrap recovery.

(1) CRD Batteries
(2) ERC
(3) Westinghouse
(4) Energy Dev. Assoc.
(5) Ford
(6) General Electric
(7) Eagle-Picher
(8) Argonne

The sodium/sulfur battery is a high temperature system where the active materials, sodium and sulfur/polysulfide, are molten at operating conditions (300-350°C) while the electrolyte is a solid. Current designs involve the use of cylindrical cells with sodium at the center core and a ceramic electrolyte, beta-alumina, separating it from the outer core which contains the sulfur. The sodium reservoir serves as the negative electrode while the sulfur is the positive electrode. Both materials react on discharge to form solutions of general composition Na_2S_x which may be liquid or solid depending on composition.

The lithium-aluminum/metal sulfide battery also operates at elevated temperatures (400-475°C). The candidate metal sulfide for the positive electrode is at present either FeS or FeS_2. The active cathode is a 20 weight percent alloy of lithium in aluminum. The current cell design calls for a central positive electrode, FeS_x, sandwiched between two negative electrode Li-Al plates. Upon discharge, lithium is depleted from the alloy and reacts with the iron sulfide to form Li_2S and Fe. Reactions occur in a molten electrolyte of LiCl-KCl eutectic. Of special concern to this system is the high cost of the plate separators that are capable of functioning in such a hostile environment. Boron nitride is considered to be the most likely candidate at present.

6.3 Rationale for Recycle Methodology

With the component parts and chemical nature of the systems defined above, an evaluation was made as to what would be recovered and what could be discarded during reprocessing (Column 6). A discarded item or material may be considered either to be sold to another scrap operation, or relegated to final disposal depending on economic considerations. The recover-discard rationale was based on three criteria:

- Component cost due either to raw material or fabrication.
- Material availability to meet projected demand (secondary material may have to be recycled).
- Environmental impact of discarding large quantities of toxic materials may not be feasible or disposal costs may be prohibitive.

However, because of the large size, load leveling batteries will permit recycle of more components than their electric vehicle counterparts. Therefore, the information presented in Column 6 pertains more to the electric vehicle batteries. The differences in recoverability will be discussed further in the next section on recovery processes.

To arrive at the amounts of scrap generated in the United States by the battery systems discussed above, several assumptions were made:

- Each battery system is the only system in production.

- Only two sources of battery scrap exist - electric vehicle and peak load leveling applications.

- All vehicular batteries have an average 3-year life and load leveling batteries have an average 10-year life.

Based on the above criteria it is evident that the first scrap will be available from a near term system vehicular battery about 3-years after their 1985 commercial introduction. By 2000 both near term and future systems for both applications will be contributing scrap. On this basis, 1990 and 2000 were chosen as sample years. The magnitude (kWh or (MWh) of the battery demand has been derived from projections made by Argonne National Laboratory (76). From the calculated usage of each battery application it was then possible to estimate the quantity of active material available assuming 100% recovery as scrap (77). These data are given in Columns 7 and 8.

Although the final form in which battery scrap components will be available has not been fully defined, we have carried out a preliminary evaluation of the specifications which might be required for the various recycled components (Column 9). Suggested assembly details for each battery system, as given in the literature, define the chemical and physical form of the raw materials that go into the initial battery construction. With the exception of the lead/acid battery, manufacturing processes utilizing scrapped battery components are not practiced commercially.

Three classes of scrap components must be considered in the recycle process:

- Active material such as electrodes.

- Auxiliary materials such as posts, lugs, grids, etc.

- Materials unique to specific systems.

Active and auxiliary components are common to all systems. Unique components are found in the future systems where, for example, the chlorine electrode in the zinc/chlorine battery is apt to be very expensive and its performance is highly dependent on its physical form. If it is to be reclaimed from a scrapped battery then it must be recovered intact and, preferably, be easily cleaned by simple physical methods. The beta-alumina solid electrolyte of the sodium/sulfur battery would also have to be recovered in its original physical form since the major cost of the component is in its fabrication. Similar arguments hold for the boron nitride cloth from the lithium-aluminum/iron sulfide battery.

The acceptable form of recovered battery scrap is dependent on several factors:

- The ability of the manufacturing process to accept other than the elemental form of the active material, e.g., can the lithium-aluminum alloy be used directly in recycle?
- Whether the battery is produced in the charged or discharged state with active material in the same chemical form as it occurs in the scrap battery.
- Whether the functionality of the recycled material is more influenced by its physical or chemical form.

While each system that has been identified has some or all of these factors already defined, assumptions have been made for all construction details which bear on recovery and reuse. For example, we assume that the zinc/chlorine battery will be constructed with recycle in mind so that recovery of components like the intact chlorine electrode will be possible.

6.4 Conceptual Battery Recycle Processes

Material handling, physical and chemical purification steps for each of the six battery systems studied are presented schematically in Figs. 55 through 66.

For each battery system two recycle processes are presented: one for electric vehicle batteries and a second for the much larger-sized load leveling batteries. Since there are significant design differences for the two applications, the recovery systems are inherently different. The most pronounced differences exist in the "front end" operations of handling and access to the internal components (see Tables 46 and 47).

Since detailed mechanical designs, specifics of construction techniques, raw material purity requirements, and the physical state of the components in the used batteries cannot be fully defined at present, the flowsheets presented are somewhat speculative. We have attempted, however, to identify all of the operations which would be required to separate and purify the various components for recycle. The flowsheets have been based on the assumption that existing technology will be used whenever possible to minimize risk, even at some economic penalty. In addition, physical separation steps are preferred to chemical separations because of the inherently lower capital costs and energy requirements.

The lead/acid flowsheets are shown in Figs. 55 and 56. Sulfuric acid will be recovered for recycle from the load leveling battery only. The acid recycle may turn out to be a maintenance item done periodically

Table 46

Characterization of Electric and Load Leveling Batteries

	Electric Vehicle Batteries	Load Leveling Batteries
Size	Small in size, low in weight and inexpensively constructed.	Large in size, high in weight and constructed with long life cycle in mind.
Environment	Designed to cope with vibrations and abrupt changes in motion.	Designed for stable repetitive service environment.
Temperature	May be subject to conditions above and below normal operating temperature limits.	Will operate under controlled temperature conditions.
Electrolyte	Systems using room temperature electrolytes may have impurities introduced with electrolyte makeup.	Chemistry of makeup electrolyte carefully controlled.

Table 47

Characterization of Recovery Processes for Electric Vehicle and Load Leveling Batteries

	Electric Vehicle Batteries	Load Leveling Batteries
Collection	Gathered from many small sources, each with a different service history.	Components recycled directly at load leveling site insofar as possible.
Dismantling	Separate battery components at a central location from a general mix by a series of mechanical and chemical processes.	Recover major components by mechanical removal from the carefully disassembled batter unit.
Reclaiming	Convert segregated streams of multiple chemical composition to a variety of useful products.	Recover as many components as possible with minimal further processing to reconstruct new battery.

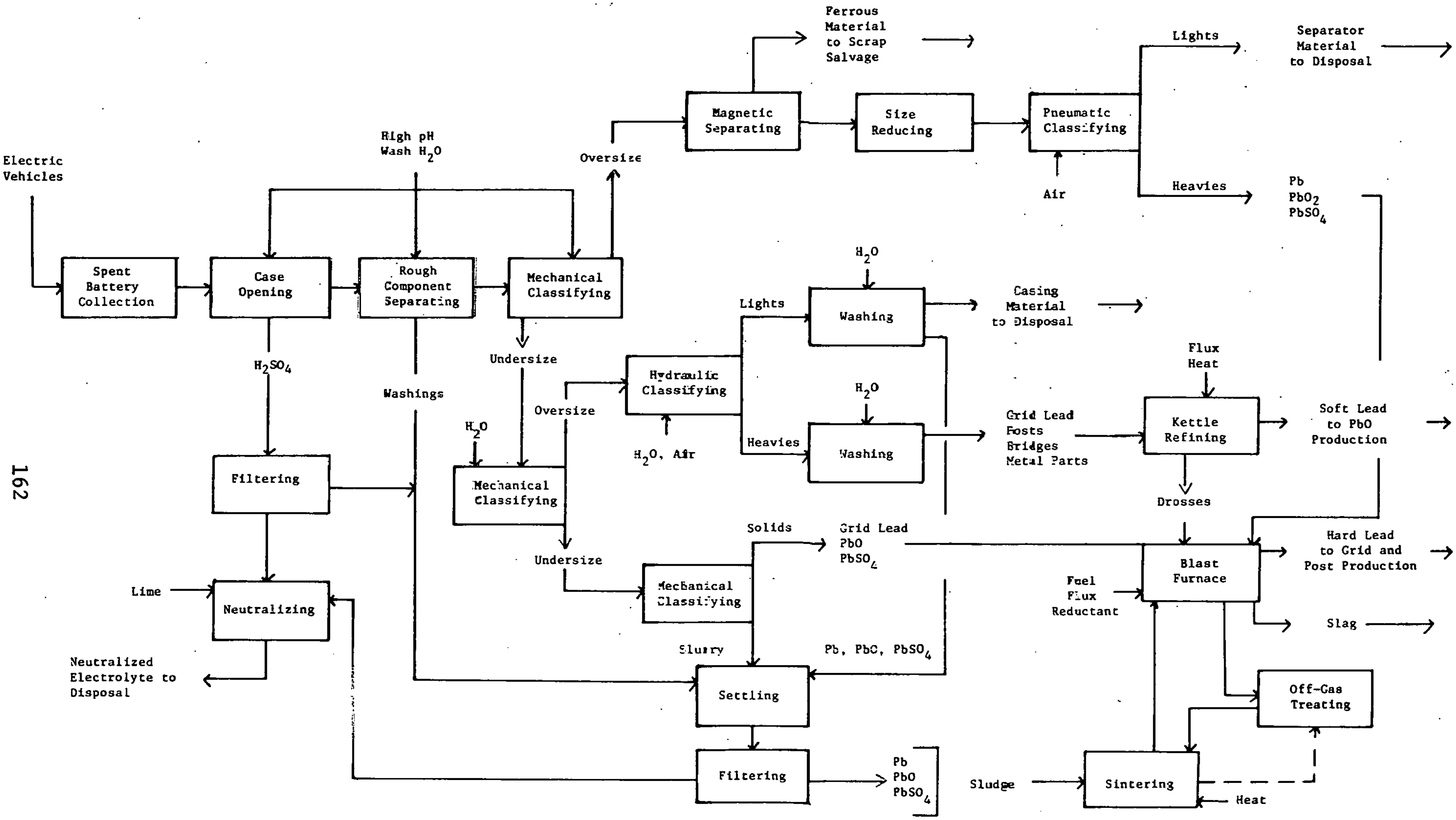


Fig. 55. Electric vehicle - lead-acid battery recovery flowsheet.

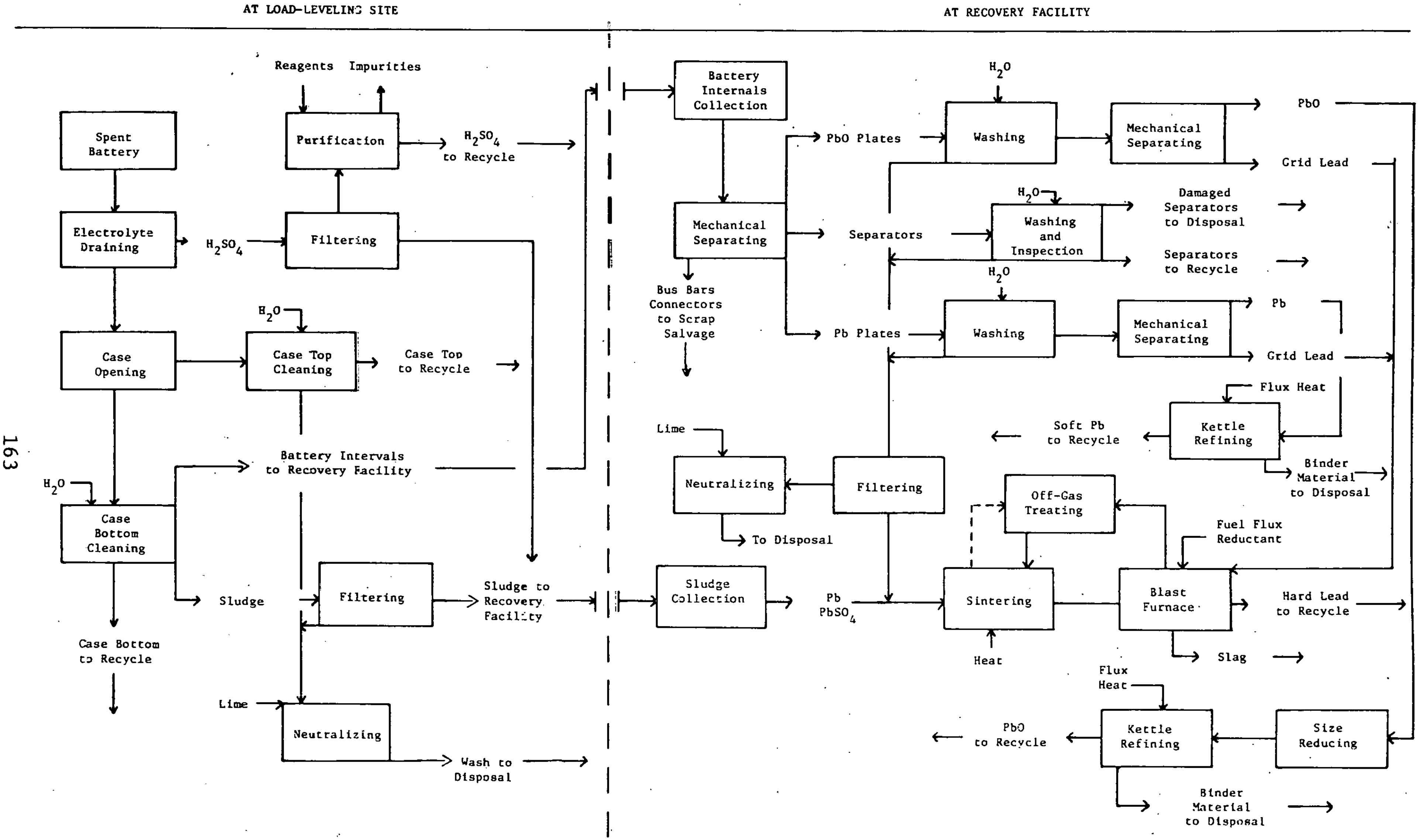


Fig. 56. Load-leveling - lead-acid battery recovery flowsheet.

rather than at battery termination. Both flowsheets are based on recycle processes currently used to recovery SLI batteries and utilize pyrometallurgical processes for the final chemical refining steps.

The nickel/zinc and nickel/iron flowsheets are shown in Figs. 57 through 60, respectively. The recovery processes are very similar, except that the iron plates of the nickel/iron battery are not reprocessed but are sent directly to salvage. The success of these flowsheets depends on the ability to separate the plates as "cleanly" as possible. This factor should be a key design consideration in battery manufacture. Another important design consideration involves the use of cobalt hydroxide, $Co(OH)_2$, in the fabrication of the nickel plates. Under current nickel plate manufacturing technology, the $Co(OH)_2$ is added to improve plate life and integrity. Since the plates are separated and dissolved to recover their nickel content, a nickel-cobalt separation step would have to be added if the cobalt is present. While this can be done using existing technology, the process becomes more complex with the inclusions of the cobalt removal step.

Zinc/chlorine battery recycle flowsheets are depicted in Figs. 61 and 62. As noted previously, a major portion of the recycle operation will consist of the maintenance or overhaul of the auxiliary equipment associated with the battery. The ease and success of recycling the porous chlorine electrode will be very dependent on its design and construction. Based on the literature describing the proposed manufacturing approach, it was decided that the recycled materials be recovered in the form of $ZnCl_2$ solution since the manufacturing facilities will have capacity for $ZnCl_2$ storage as a raw material. It appears that the batteries will be produced in the discharged state and then charged at the production facility. We assume then that the bulk of the raw material demand will be in the form of $ZnCl_2$, which is also easier to store and handle than liquid chlorine.

The sodium/sulfur battery recovery flowsheets are given in Figs. 63 and 64. Here, the solvent N,N-dimethylacetamide (DMAC) is instrumental in the non-destructive separation of the inner and outer cell components and also in dissolving sodium and its sulfides. Because of the reactivity of sodium, much of the recycle operation will have to be conducted in a dry environment, typically at levels below 2% absolute humidity. The recycled final form will be Na_2S_x rather than pure sodium because of the stability and ease of handling of the sulfide.

The last two flowsheets for the lithium-aluminum/iron sulfide battery recovery are shown in Figs. 65 and 66. In this system, ether serves as a selective solvent for removing the KCl component of the electrolyte. This, in turn, facilitates separation of the inner and outer cell components. At later stages in the process, methyl alcohol is used to dissolve lithium and its sulfide. The properties of lithium also require that much of the reprocessing be done in a dry environment.

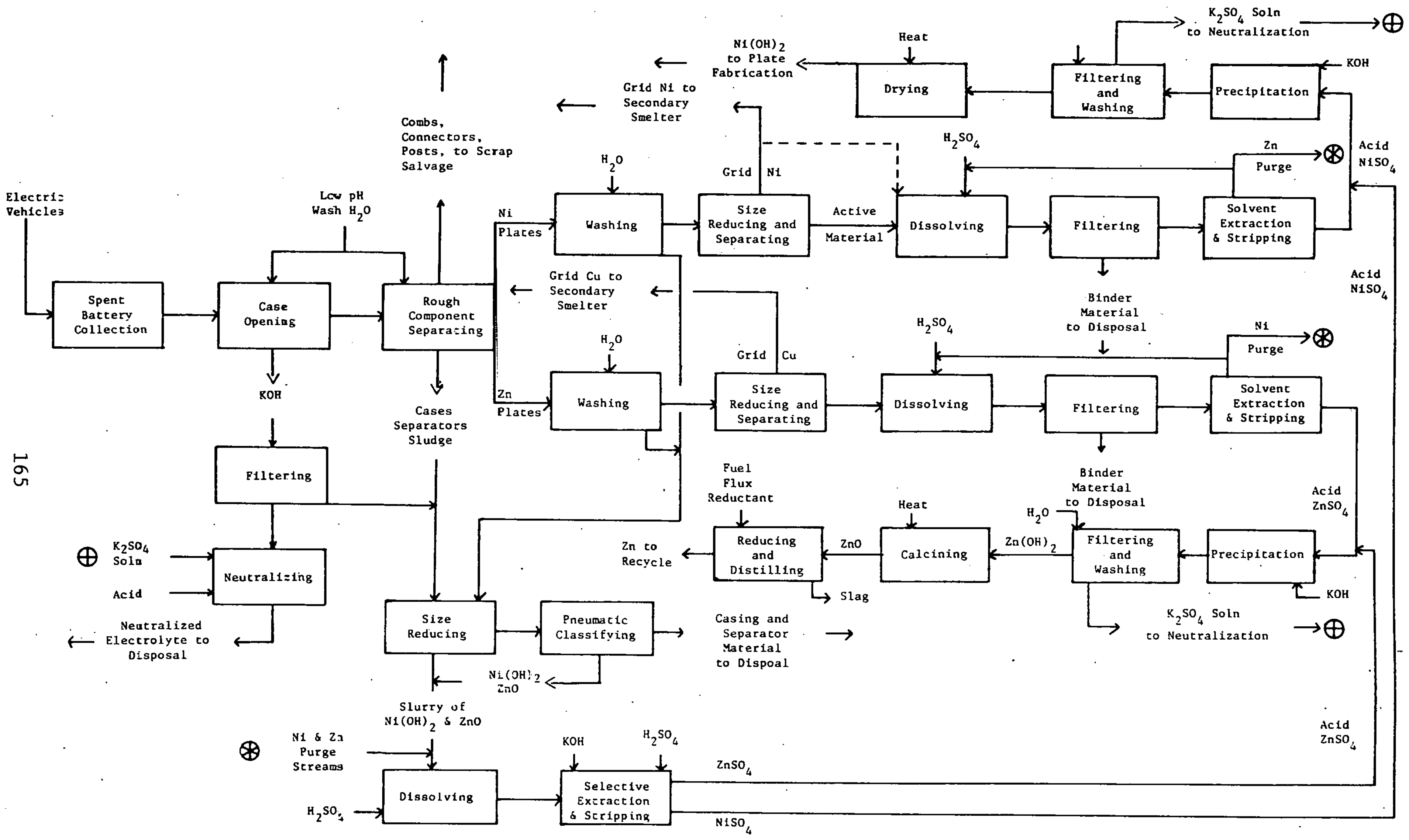


Fig. 57. Electric vehicle - nickel-zinc battery recovery flowsheet.

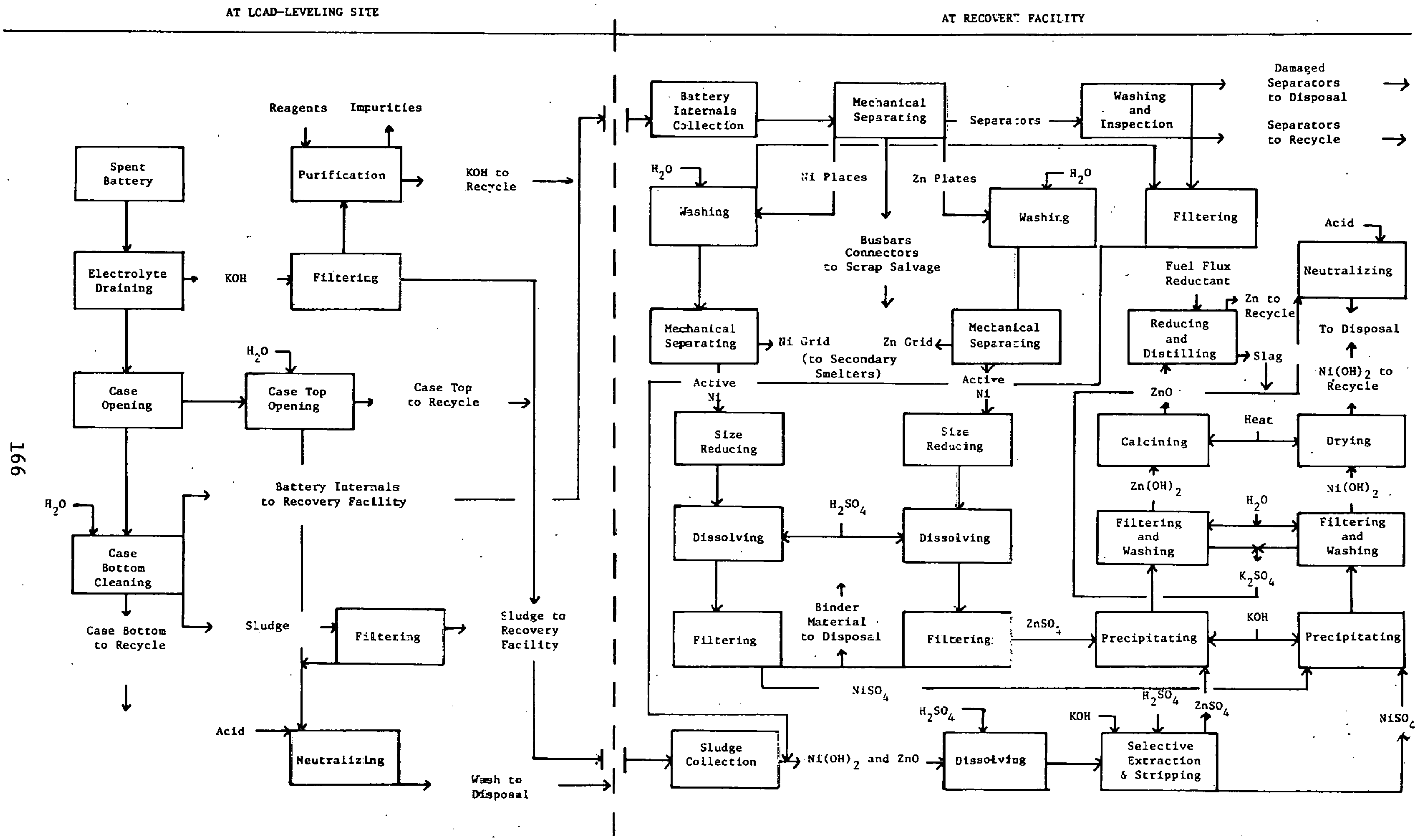


Fig. 58. Load-leveling - nickel-zinc battery recovery flowsheet.

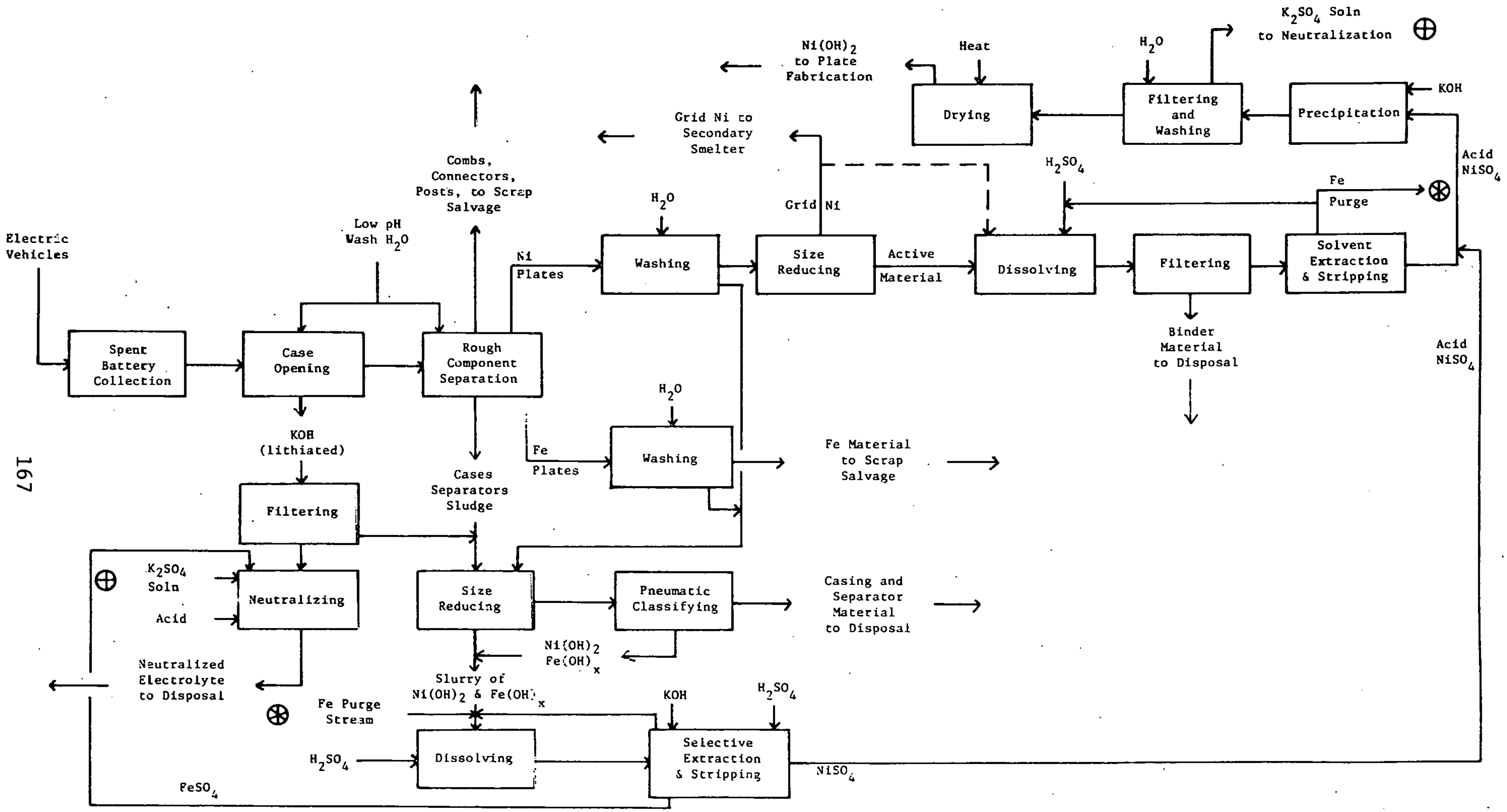


Fig. 59. Electric vehicle - nickel-iron battery recovery flowsheet.

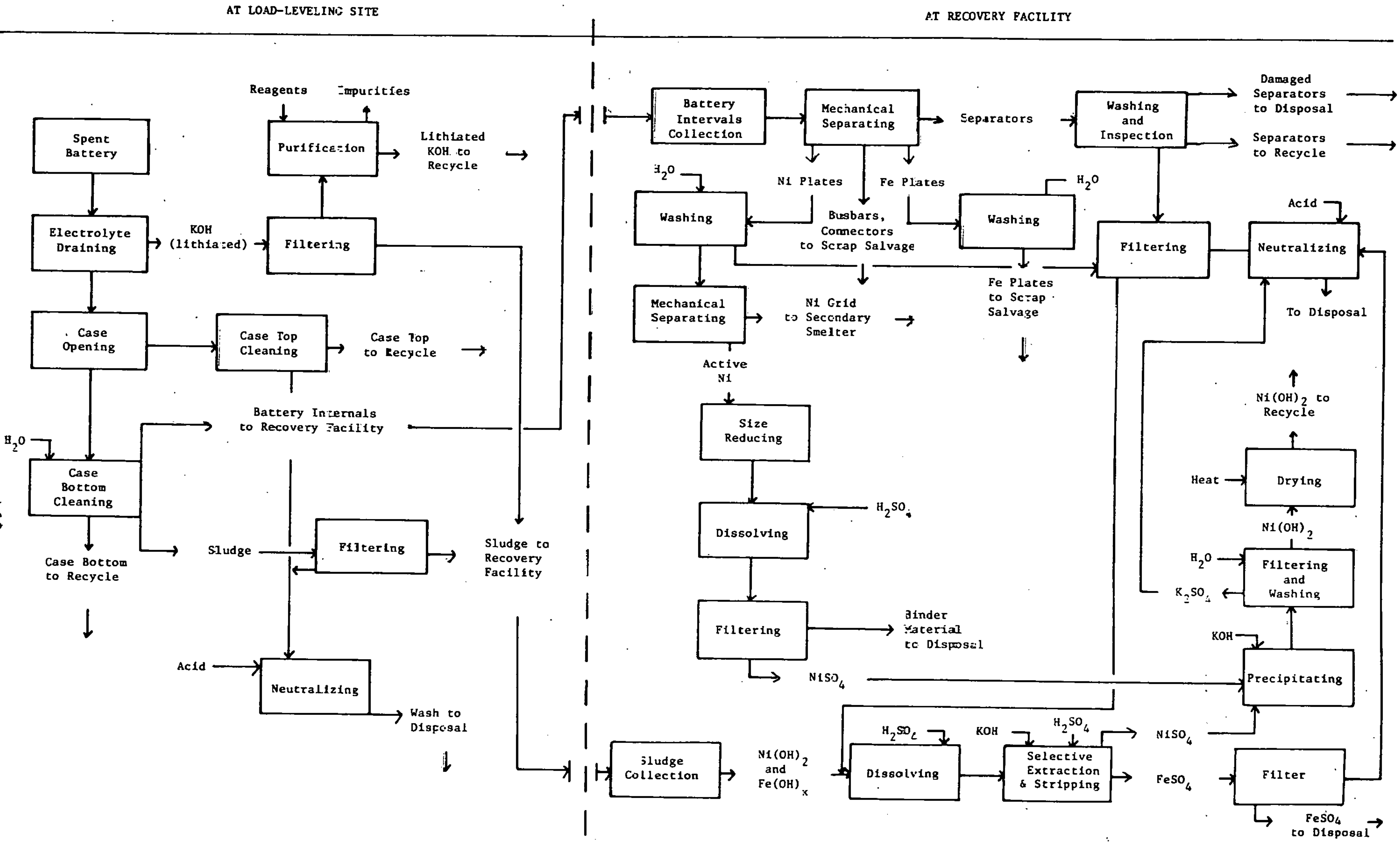


Fig. 60. Load-leveling - nickel-iron battery recovery flowsheet.

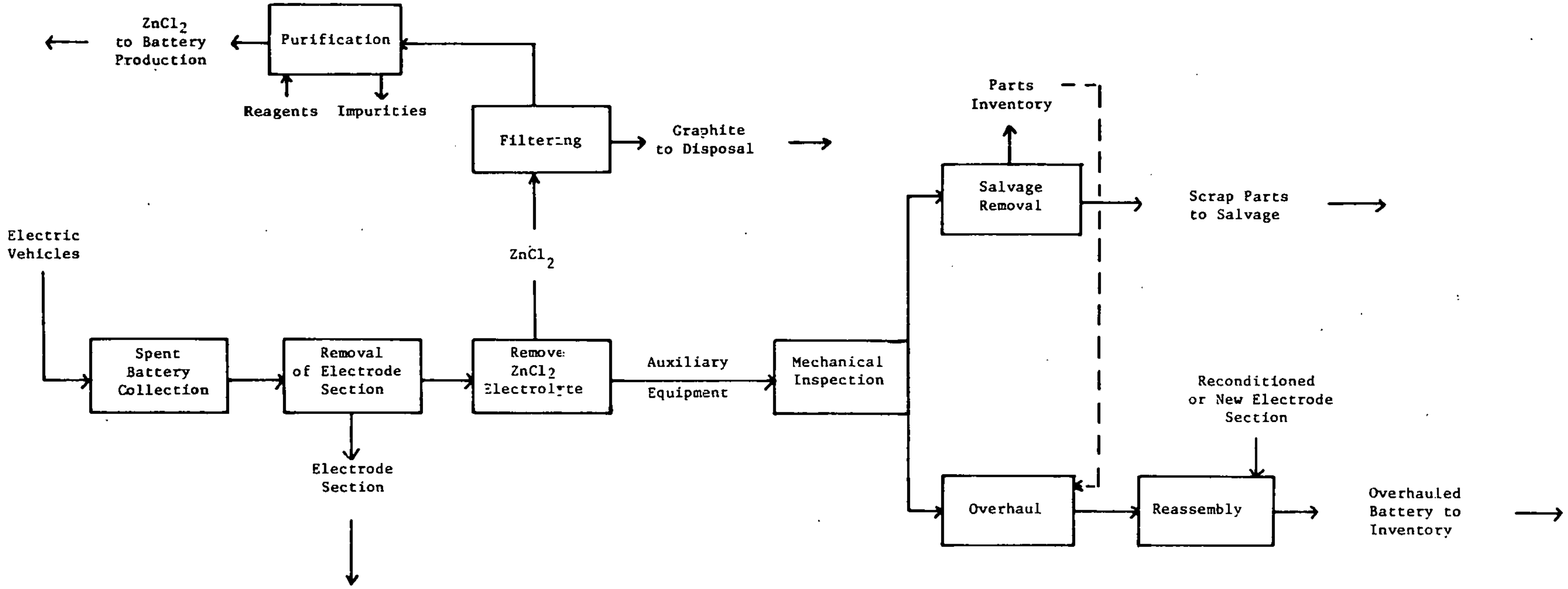


Fig. 61. Electric vehicle - zinc-chlorine battery recovery flowsheet.

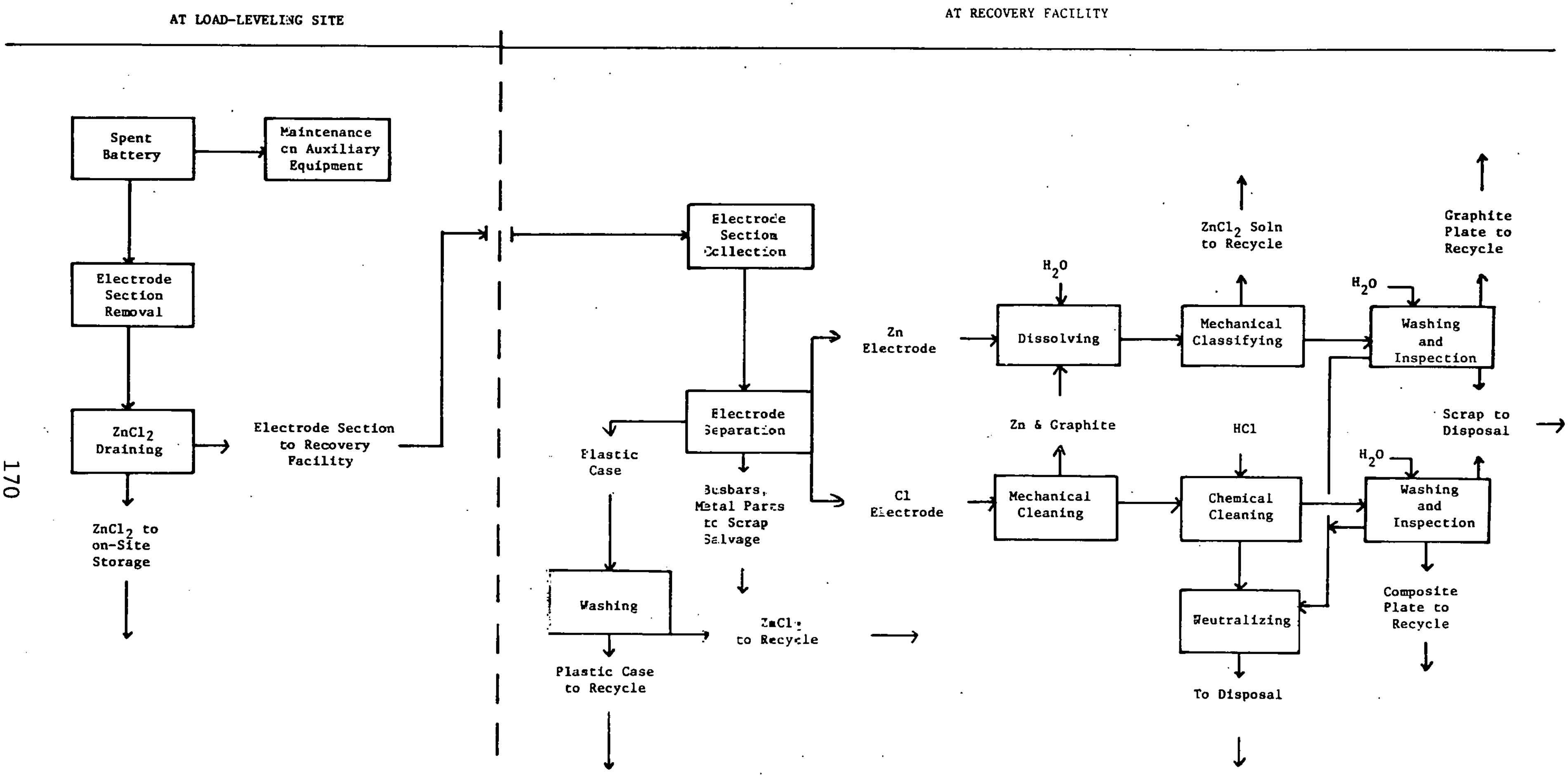


Fig. 62. Load-leveling - zinc-chlorine battery recovery flowsheet.

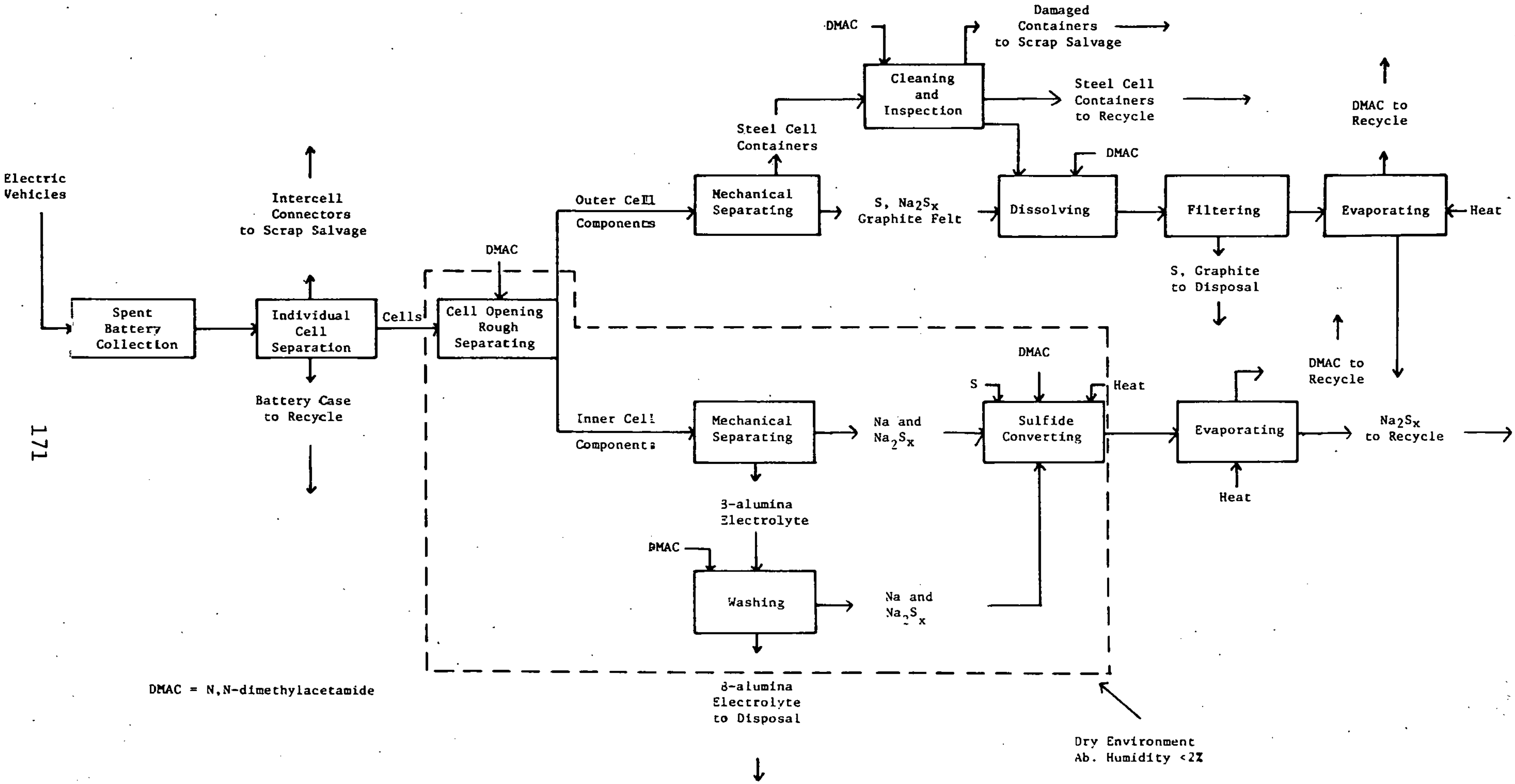


Fig. 63. Electric vehicle - sodium-sulfur battery recovery flowsheet.

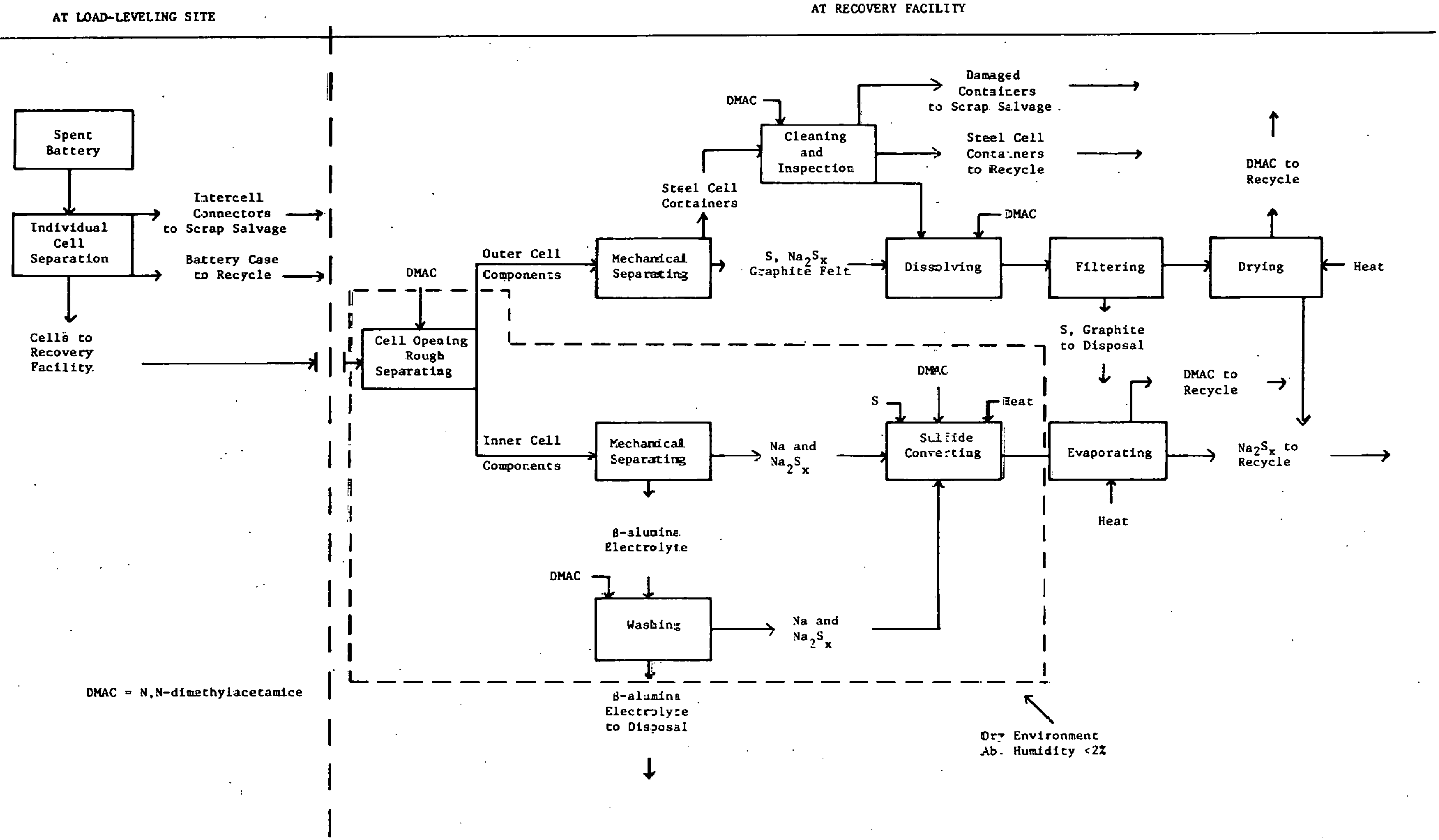


Fig. 64. Load-leveling - sodium-sulfur battery recovery flowsheet

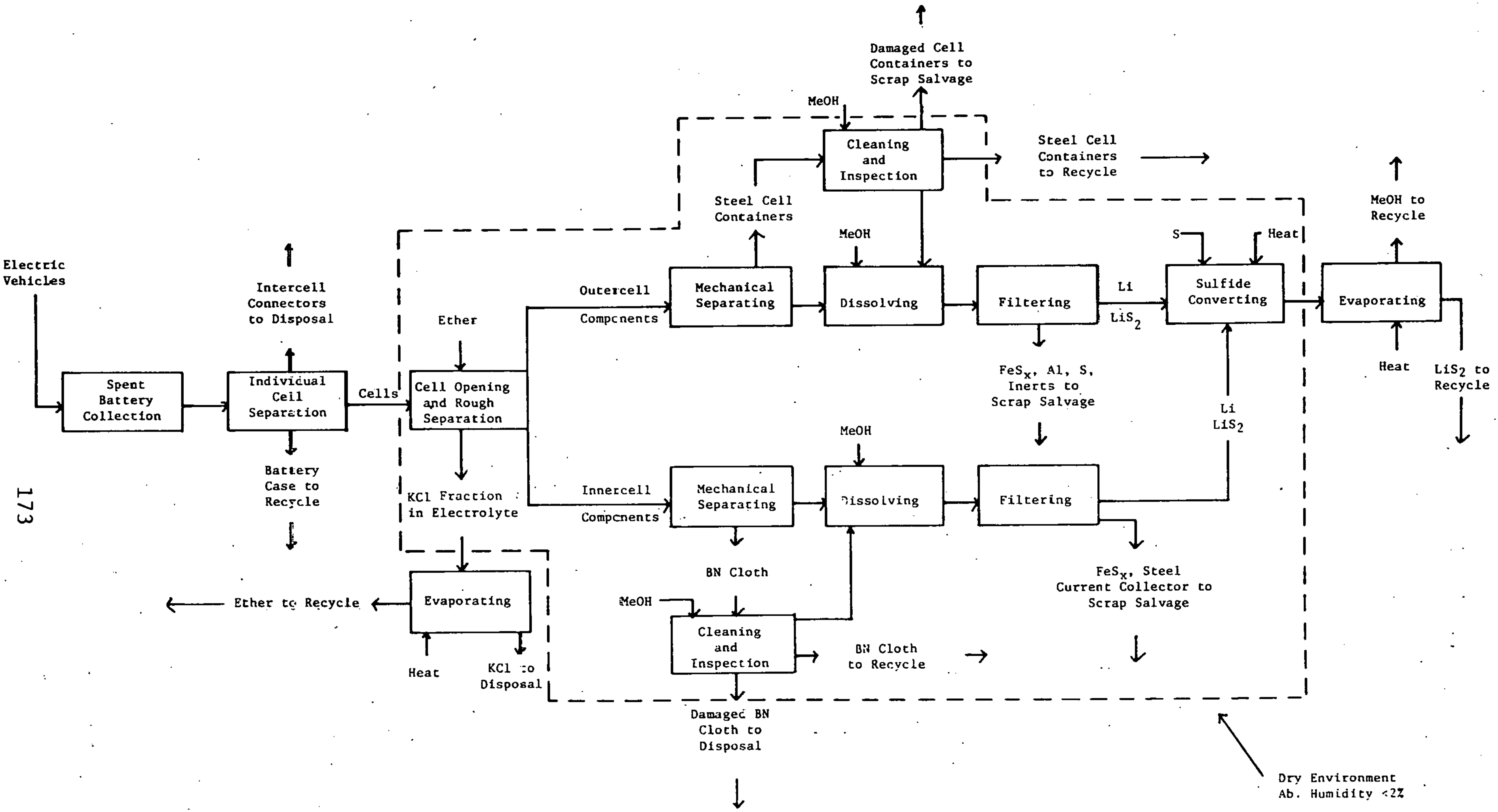


Fig. 65. Electric-vehicle - lithium-aluminum-metal sulfide battery recovery flowsheet.

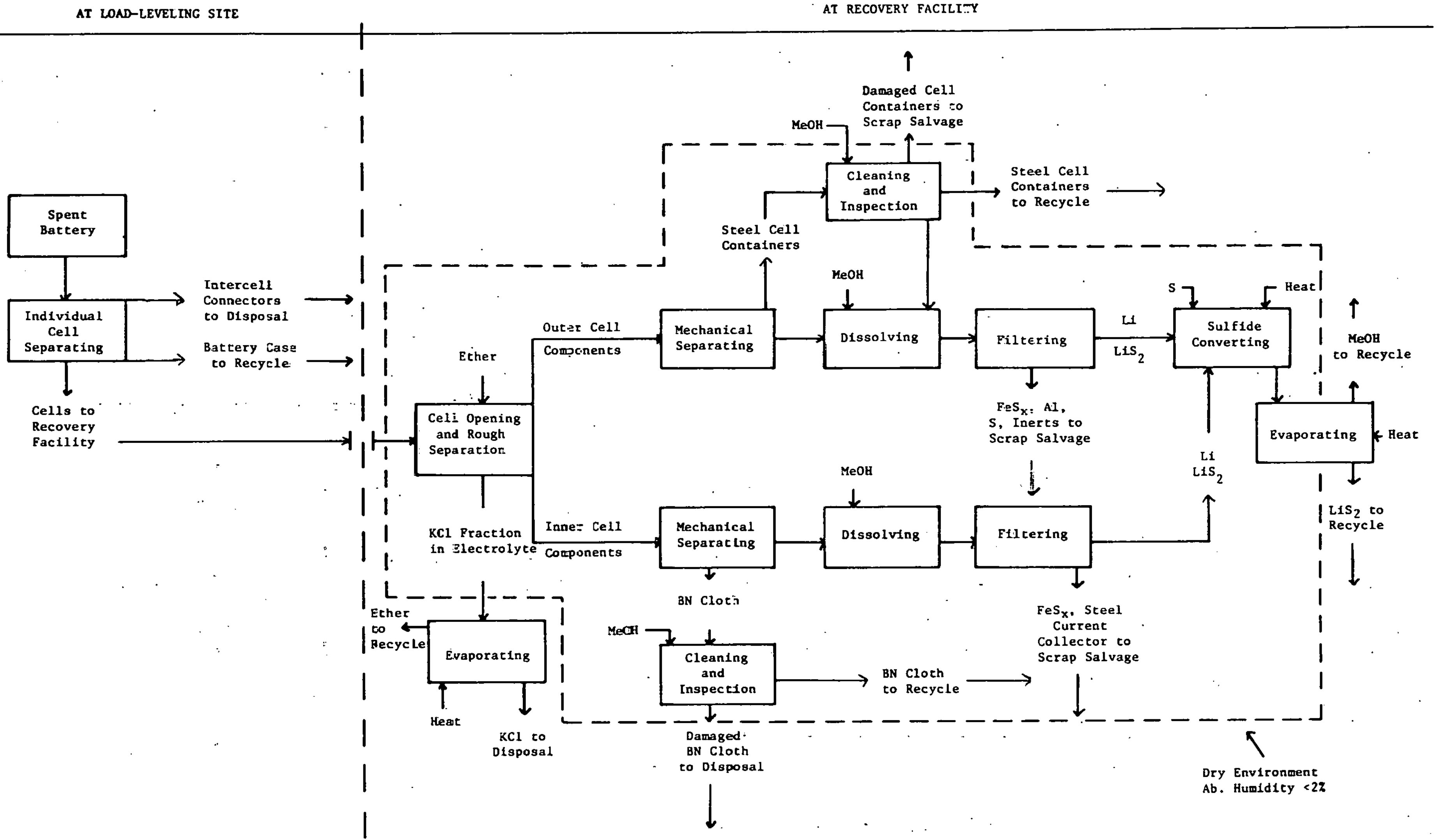


Fig. 66. Load-leveling - lithium-aluminum-metal sulfide battery recovery flowsheet.

The near-term battery systems, lead/acid, nickel/zinc and nickel/iron all lend themselves to a general recovery scheme of:

- Mechanical classification
- Hydrometallurgical separation
- Pyrometallurgical conversion.

Electrohydrometallurgical recovery processes are not justified for reasons that were presented earlier in this report for the specific metals lead, nickel and zinc. The advanced battery systems also involve mechanical classification, but the degree of sophistication required will be greater and will probably involve more intense operator intervention. Aqueous metallurgical processing cannot be utilized with the high temperature systems because of the reactivity of the metals with water. However, the use of selected solvents under carefully controlled conditions is feasible to effect necessary separations.

6.5 Recommendations

The recycle flowsheets presented above must be considered of a preliminary nature. They can, however, be used for rough economic scoping analysis.

Significant uncertainty exists about the final form of the various batteries, especially for the more advanced concepts. It is also not known which of the systems will actually be developed commercially. Further funding for more detailed studies of battery recycle should be provided as additional information is generated and when input is required to establish the economic viability of a particular battery system.

7.0 REFERENCES

1. Energy Use Patterns in Metallurgical and Non-metallic Mineral Processing (Phase 4 - Energy Data and Flowsheet, High Priority Commodities) Battelle Columbus Laboratories, Report PB-245 759, 1975.

2. Aluminum, Mineral Commodity Profiles MCP-14, Bureau of Mines, May 1978.

3. C. L. Kusik and C. B. Kenahan, Energy Use Patterns for Metal Recycling, U.S. Bureau of Mines Report IC 8781, 1978.

4. J. G. Peacey and W. G. Davenport, Journal of Metals, July 1974, pp. 25-28.

5. A. G. Szekely, Met. Trans. B, 7B, 1976, pp. 259-270.

6. A. G. Szekely, An Alternative to Chlorine Fluxing of Aluminum: The SNIF Process, in Proceedings of the Second International Aluminum Extrusion Technology Seminar, November 15-17, 1977, pp. 35-41.

7. J. L. Dewey, U.S. Patent 3,163,895, January 5, 1965.

8. J. D. Edwards, F. C. Frary and Z. Jeffries, The Aluminum Industry, Aluminum and its Production, McGraw-Hill, New York, 1930, pp. 321-327.

9. R. C. Howie and D. W. Macmillan, J. Applied Electrochem. 2, 1972, pp. 217-222.

10. W. G. Davenport and G. A. Capuano, in Physical Chemistry of Process Metallurgy: The Richardson Conference, Institution of Mining and Metallurgy, London, England, 1973, pp. 77-84.

11. Development Sciences, Inc., Sandwich, Mass., 1976.

12. D. A. Schultz, Journal of Metals, January 1978, pp. 14-20.

13. Private communication, Kennecott Copper Corp.

14. Copper - 1977, Mineral Commodity Profiles MCP-13, Bureau of Mines, June 1977.

15. F. P. Haver and M. M. Wong, Recovering Elemental Sulfur from Nonferrous Minerals: Ferric Chloride Leaching of Chalcopyrite Concentrate, U.S. Bureau of Mines RI 7474, 1971.

16. F. P. Haver, R. D. Baker and M. M. Wong, Improvements in Ferric Chloride Leaching of Chalcopyrite Concentrate, U.S. Bureau of Mines RI 8007, 1975.

17. T. A. Phillips, Economic Evaluation of a Process for Ferric Chloride Leaching of Chalcopyrite Concentrate, U.S. Bureau of Mines IC 8699, 1976.

18. D. E. G. Maschmeyer, E. F. Milner and B. M. Parekh, CIM Bulletin, Feb. 1978, pp. 27-35.

19. H. J. Schoreder, Bureau of Mines, private communication, July 1978.

20. V. A. Ettel, CIM Bulletin, July 1977, pp. 179-187.

21. F. V. Carrillo, M. H. Hibpshman and R. D. Rosenkranz, Recovery of Secondary Copper and Zinc in the United States, U.S. Bureau of Mines IC 8622, 1974.

22. S. H. Langer, T. D. Kaun, and M. A. Nametz, Journal of Metals, July 1976.

23. E. D. Smith, U.S. Patent 3,832,162, Aug. 27, 1974.

24. D. Pearson, Reclamation Industries, July 1972, pp. 10-11.

25. T. W. Hummel and P. C. Schroy, U.S. Patent 3,865,580, Feb. 11, 1975.

26. T. K. Savage, H. L. Pinkerton, A. K. Graham, U.S. Patent 3,054,736, Sept. 18, 1962.

27. Efficient Processing of Nonstandard Secondary Copper - Bearing Secondary Material, V. F. Bogdashev, S. S. Naboichenko, I. F. Khudyakov, Tsvetnye Metally, 1975, pp. 40-43.

28. A. J. Parker, Search, 4, 1973, pp. 426-432.

29. E. P. Foster, Air Products and Chemicals Corporation, private communication, 1978.

30. D. M. Muir, A. J. Parker, J. H. Sharp and W. E. Waghorne, Hydrometallurgy, 1, 1975, pp. 61-77.

31. E. Mohri and M. Yamada, Recovery of Metals from the Dusts of Flash Smelting Furnace in World Mining and Metals Technology, Proceedings of a Joint Meeting of MMIJ-AIME, Denver, Colorado, Sept. 1-3, 1976.

32. W. R. N. Snelgrove, A Hydrometallurgical Process for the Recovery of Copper and Zinc from Alloy Scrap, presented at Canadian Institute of Mining and Metallurgy Meeting, Montreal, August 28-31, 1978.

33. W. L. Faith, D. B. Keyes and R. L. Clark, Industrial Chemicals, Third Edition, John Wiley & Sons, New York, 1965.

34. Zinc, Mineral Commodity Profiles MCP-12, U.S. Bureau of Mines, May 1978.

35. P. G. Barnard, A. G. Starliper, W. M. Dressel and M. M. Fine, Recycling of Steelmaking Dusts, U.S. Bureau of Mines TRR52, 1972.

36. C. A. Holley and T. H. Weidner, New Processes for Converting Steelmaking Fumes into Low-Zinc Pellets, Presented at Chicago Regional Technical Meeting, AISI, Chicago, October 14-16, 1969.

37. G. G. W. Thom and A. A. F. Schuldt, Can. Min. and Met. Bull. No. 59, 1966, pp. 1229-1233.

38. L. W. Higley and H. H. Fukubayaski, Method for Recovery of Zinc and Lead from Electric Furnace Steelmaking Dusts, in Proc. 4th Miner. Waste Utilization Symp., Chicago, May 7-8, 1974, pp. 295-302.

39. M. O. Holowaty, A Process for Recycling of Zinc-Bearing Steelmaking Dusts, Presented at AIME Annual Mtg, New York March 2, 1971.

40. J. E. Allen, U.S. Patent 3,850,613, Nov. 26, 1974.

41. American Metal Market, Japanese Perfect Process in Recycling Furnace Dust, March 5, 1971.

42. Journal of Metals, Japan Watching, 26, 1974, p. 52.

43 Can. Min. and Met. Bull. 68, No. 761, 1975, p. 123.

44. H. G. Hudson and R. Brandiff, U.S. Patent 3,905,882, Sept. 1975.

45. E. G. Valdez and K. C. Dean, Experiments in Treating Zinc - Lead Dusts from Iron Foundries, U.S. Bureau of Mines RI 8000, 1975.

46. H. E. Powell, H. Fukubazashi, L. W. Higley and L. L. Smith, Recovery of Zinc, Copper and Lead-Tin Mixtures from Brass Smelter Flue Dusts. U.S. Bureau of Mines RI 7637, 1972.

47. L. W. Higley and M. M. Fine, Electric Furnace Steelmaking Dusts - A Zinc Raw Material, U.S. Bureau of Mines RI 8209, 1977.

48. G. Socolescu and A. Socolescu, Metallurgia 27, 1975, pp. 575-578.

49. H. Reinhardt and H. D. Ottertun, U.S. Patent 3,966,569, June 1976.

50. R. B. Sudderth, J. P. Clitheroe and G. A. Kordosky, The Sulfite System - A New Hydrometallurgical Process for Zinc, presented at AIME Meeting, Denver, Colorado, February 1978.

51. W. H. Burrows, U.S. Patent 3,849,121, Nov. 19, 1974.

52. Lead - 1977, Mineral Commodity Profiles MCP-9, U.S. Bureau of Mines, December 1977.

53. R. C. Anderson, Resource Recovery and Conservation, 2, 1977, pp. 193-209.

54. V. S. Esyutin and D. N. Nurgaliev, Tsv. Metally, 1975, pp. 32-34.

55. F. P. Haver and M. M. Wong, Ferric Chloride-Brine Leaching of Galena Concentrate, U.S. Bureau of Mines Report RI 8105, 1976.

56. F. P. Haver, C. H. Elges, D. L. Bixby and M. M. Wong, Recovery of Lead from Lead Chloride by Fused Salt Electrolysis, U.S. Bureau of Mines Report RI 8166, 1976.

57. F. P. Haver, D. L. Bixby and M. M. Wong, Aqueous Electrolysis of Lead Chloride, U.S. Bureau of Mines Report RI 8276, 1978.

58. G. C. Bratt and R. W. Pickering, Met. Trans. 1, 1979, pp. 2141-2199.

59. Yu. A. Koz'min et al., Tsv. Metally, 11 (9), Sept. 1970, pp. 49-51.

60. D. Marthales, Tages-Anzeiger, August 22, 1978.

61. T. Nikolov and N. Liakov, Neue Hütte, 19, 1974, pp. 591-594.

62. Energy Use Patterns in Metallurgical and Nonmetallic Mineral Processing (Phase 5 - Energy Data and Flowsheets, Intermediate Priority Commodities), Report PB-246 357, 1975.

63. Nickel - 1977, Mineral Commodity Profiles MCP-4, U.S. Bureau of Mines, July 1977.

64. A. Aue, L. Skjntare, G. Bjorling, H. Reinhardt and J. Rydberg, *Proceedings Int. Solvent Extr. Conf. 1971*, *Vol. 1*, pp. 447-450.

65. Dow Saves on Magnesium, Chemical Marketing Reporter, May 22, 1978.

66. Mineral Facts and Problems, U.S. Bureau of Mines Bulletin 667, 1976.

67. J. G. Mezoff, Trends in Recycling of Magnesium in the U.S.A., 1977.

68. L. E. Lynd, U.S. Bureau of Mines, private communication, 1978.

69. Titanium, Mineral Commodity Profiles MCP-18, U.S. Bureau of Mines, August 1978.

70. Summary Report on the Strategic Materials Reclamation Seminar, Report AMFL-TM-LT-75-1, May 1974.

71. J. R. Doyle and K. T. Love, *Light Metals 1976*, *Volume 1*, Met. Soc. of AIME, pp. 571-584.

72. J. Glasser in *Titanium Science and Technology, Proceedings of the Second International Conference*, R. Jaffee, Ed. Plenum, New York, 1973, pp. 285-297.

73. E. Peled and E. Gileadi, J. Electrochem. Soc., *123*, 1976, pp. 15-19.

74. L. G. Boxall, H. L. Jones and R. A. Osteryoung, *Ibid.*, 121, 1974, pp. 212-219.

75. U.S. Dept. of Energy, Environmental Development Plan, Publication No. DOE/EDP-0015, 1978, p. 52.

76. A. A. Chilenskas, G. J. Bernstein and R. O. Ivins, Lithium Requirements for High Energy Lithium-Aluminum/Iron Sulfide Batteries for Load-Leveling and Electric-Vehicle Applications, 1976. A Symposium on U.S. Lithium Resources and Requirements by the Year 2000, Lakewood, Colorado, Table 1, p.6, Table 2, p.9.

77. National Battery Advisory Committee to DOE, Resource and Conservation Subcommittee, Advanced Battery Materials Resource Requirements Survey for Electric Vehicle Application, 1978.