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A SURVEY OF ELECTROCHEMICAL METAL WINNING PROCESSES

Contract No. 31-109-38-4212

by

BATTELLE
(COLUMBUS LABORATORIES)

MASTER

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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FINAL REPORT ON

A SURVEY OF ELECTROCHEMICAL METAL WINNING PROCESSES

PREPARED FOR

OFFICE FOR ELECTROCHEMICAL
PROJECT MANAGEMENT
ARGONNE NATIONAL LABORATORY
UNDER CONTRACT NO. 31-109-38-4212

BY

950 0081

BATTELLE
COLUMBUS LABORATORIES
COLUMBUS, OHIO 43201

MARCH 1979

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ABSTRACT

The subject program was undertaken to find electrometallurgical technology that could be developed into energy saving commercial metal winning processes. Metals whose current production processes consume significant energy (excepting copper and aluminum) are magnesium, zinc, lead, chromium, manganese, sodium, and titanium. The technology of these metals, with the exception of titanium, was reviewed.

Growth of titanium demand has been too small to justify the installation of an electrolyte process that has been developed. This fact and the uncertainty of estimates of future demand dissuaded us from reviewing titanium technology.

Opportunities for developing energy saving processes were found for magnesium, zinc, lead, and sodium. Costs for R and D and demonstration plants have been estimated. It appeared that electrolytic methods for chromium and manganese cannot compete energywise or economically with the pyrometallurgical methods of producing the ferroalloys, which are satisfactory for most uses of chromium and manganese.

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

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SUMMARY AND CONCLUSIONS

The metals studied in this survey were magnesium, zinc, lead, chromium, manganese, sodium and titanium. Present processes for producing these metals consume approximately 90 percent of all energy for non-ferrous metals if copper and aluminum are excluded. Iron was excluded from the study also, since there is no history of electrolytic methods being tried for large tonnage production and it was considered unlikely that electrolytic methods can be developed to be competitive with present pyrometallurgical methods. Possible electrolytic methods of making titanium were not investigated in detail because a major producer indicated that there was no saving in energy over present methods and because only minor growth in production and consumption is anticipated in the next twenty years. The near term projected consumption of sodium is a decreasing one due to phase out of tetraethyl lead production. However, present consumption is still about six times that of titanium. It is a versatile chemical and metallurgical reducing agent that could find expanded use if produced more cheaply and with less energy, and development of improved methods of production has not been emphasized in the non-ferrous metallurgical industry where it is regarded more as a chemical than a metal.

New electrolytic methods or modifications of presently used electrolytic methods appear to have the potential of substantially reducing energy for production as compared to that for present processes for magnesium, zinc, lead and sodium. Energy uses for electrolytic chromium and manganese are much higher than for producing the same metal as a ferroalloy by pyrometallurgical methods. The ferro-alloys are suitable for all but minor applications. Therefore, there is little incentive to develop and improve electrolytic methods for chromium and manganese.

Table 1 shows current production volumes and projected production volumes for year 2,000 for the metals studied. Using these figures and the energy use estimated for current processes by Battelle in a study for U.S. Bureau of Mines(1), the energy savings for several processes suggested for further development are shown in Table 2.

TABLE S1. CURRENT AND FORECAST DOMESTIC PRODUCTION VOLUMES

Metal	Production Volumes Current M ton/yr (S ton/yr)	Production Volumes Year 2,000 M ton/yr (S ton/yr)
Magnesium	114,300 (126,000)	357,000 (394,000)
Zinc	394,000 (434,000)	853,000 (940,000) (1)
Lead	549,000 (605,000)	889,000 (980,000) (2)
Chromium (including that in ferrochrome)	246,000 (272,000)	340,000 (375,000)
Manganese (including that in ferromanganese)	382,000 (422,000)	1,500,000 (1,600,000)
Sodium	142,000 (157,000)	145,000 (160,000)
Titanium	14,700 (16,200)	29,000 (32,000)

(1) Assumes 42% (same as present) of predicted consumption of 2.23 million S tons will be domestically produced.

(2) Assumes 41% (same as present) of predicted consumption of 2.4 million short tons will be domestically produced.

TABLE S2. ENERGY SAVINGS FOR PROCESSES REQUIRING FURTHER DEVELOPMENT

		Annual Energy Savings			
		1977		Year 2,000	
Metal	Process	kwh	Kcal (Btu)	kwh	Kcal (Btu)
Magnesium	Refractory Improvements	2 to 4 x 10^{8}	[.5 to 1] x 10^{12} ([2 to 4] x 10^{12})	6 to 12 x 10^{8}	[2 to 3] x 10^{12} ([6 to 13] x 10^{12})
	Hydrodynamic Studies	6 x 10^{8}	1.5 x 10^{12} (6 x 10^{12})	2 x 10^{9}	5 x 10^{12} (21 x 10^{12})
Zinc	Aqueous Chloride Electrolysis	9.8 x 10^{8}*	3.3 x 10^{12} (13. x 10^{12})	2.1 x 10^{9}*	7.1 x 10^{12} (28 x 10^{12})
	Caustic leach and electrolysis	6.1 x 10^{8}	2.1 x 10^{12} (8.2 x 10^{12})	1.3 x 10^{9}	4.5 x 10^{12} (18 x 10^{12})
Lead	Anodic Sulfide Dissolution	-4.5 x 10^{8}	4.6 x 10^{11} (1.8 x 10^{12})	-7.3 x 10^{8}	6.7 x 10^{11} (2.7 x 10^{12})
	Fused Salt Electrolysis of Sulfide	-4.7 x 10^{8}	7.6 x 10^{11} (3.0 x 10^{12})	-7.5 x 10^{8}	1.1 x 10^{12} (4.4 x 10^{12})
Sodium	Lead Cathode and Evaporation	7.0 x 10^{8}	1.8 x 10^{12} (7.2 x 10^{12})	7.0 x 10^{8}	1.8 x 10^{12} (7.2 x 10^{12})

Kwh are for electrolysis.

*Assume 1480 kwh/M ton (1350 kwh/S ton) for zinc and same for chlorine.

The estimated energy savings for improvements in magnesium processes are probably the least accurate, since they depend on projection of as yet undetermined laboratory results to field practice. Energy savings for the caustic zinc process are probably the best estimates since they are based to a considerable extent on pilot plant results and established laboratory results. The projected energy saving for year 2,000 is 4.5 x 10^{12} Kcal (18 x 10^{12} Btu). The caustic zinc process is regarded as the most promising of those considered for further development.

In general, economics, raw materials, and environmental considerations for the new processes are expected to be similar to those for present processes with the exception of lead. Present pyrometallurgical processes for lead may be unacceptable because of air pollution or the expense of avoiding this pollution. Thus, the development of new processes may be mandated regardless of energy savings. The lead processes recommended for development programs are for processes that are alternatives to the fused chloride process now being developed by USBM.

Further development of any of the identified processes should first involve a more detailed analysis of energy savings and economics than was possible in this overall survey.

The section on Suggested Research and Development Programs, page 231, may be considered an adjunct to this summary, as it provides estimates of costs for the various programs proposed and is the culmination of the review effort discussed in other sections of the report.

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(1) "Energy Use Patterns in Metallurgical and Non-Metallic Mineral Processing", Battelle's Columbus Laboratories for U.S. Dept. of Commerce, Phases 4, 5, 6, 7, NTIS PB-245759, PB-246357, PB-261150, PB-2161151. Referred throughout this report as USBM Report.

FINAL REPORT

on

A SURVEY OF ELECTROCHEMICAL (METAL WINNING) PROCESSES

to

ARGONNE NATIONAL LABORATORY

from

BATTELLE
Columbus Laboratories

March 9, 1979

INTRODUCTION

Electrochemical methods have a long history in the winning and refining of metals, and were actually used in the first preparation of some of them, e.g., sodium. Electrochemical methods continue to be used for winning or refining several metals and in some cases have largely supplanted pyrometallurgical processes for new plant construction, e.g., zinc. Processes have been developed in spite of the inherent inefficiency in converting the energy in fossil fuel to electrical energy, which attests to the advantage of the electrochemical methods from the point of view of economics, technical suitability, and environmental considerations.

This project considers the possibilities of saving energy using electrochemical processes for the refining of non-ferrous metals, excluding copper and aluminum. The objective of the project is to find areas of technology that show promise of accomplishing this end after further development.

The method of seeking out such areas for production consists of (1) determining which metals require the most energy, (2) reviewing published information, or technology, including energy use, (3) consulting with the metals producing industries, (4) systematizing the overall technology involved in the metals production, (5) and choosing research and development programs on the basis of energy saved and also technical feasibility, availability of raw materials, economics, including development costs, and environmental impact.

An excellent basis for the subject project was obtained from a prior project sponsored by the USBM (see Summary and Conclusions) at Battelle's Columbus Laboratories (BCL). The effort involved estimating the energy requirements of currently used production processes for commercially important metals and minerals.

UNITS AND CONVERSION FACTORS

The primary units used throughout the report are metric, with English units often given in parenthesis. Weights are expressed as:

Moles	
Kilograms	kg
Pounds	lb
Metric tons	M ton
Short tons	S ton

Energy is expressed as:

Kilowatt hours	kwh
Kilocalories	Kcal
British thermal units	Btu

Data in much of the literature reviewed was in British units, and in the metric system on a molar basis. Most of the calculations were made using Btu or kwh and S tons. The <u>USBM Energy Report</u> uses Btu rather than Kcal. Because of the extensive amount of data given and the complications in exhibiting this in metric units, only the English units are presented.

Following the convention in <u>USBM Energy Report</u> the energy used for producing electric power is assumed to be 2645 Kcal/kwh (10,500 Btu/kwh). This corresponds to an efficiency of 32 percent for the power plant.

For operations involving electrolysis the loss in conversion from A.C. to D.C. plus the loss in voltage between rectifiers and the cell was assumed to be 10 percent.

SELECTION OF METALS REQUIRING SIGNIFICANT ENERGY

Research and development should be directed to those processes for metals where significant amounts of energy can be saved. This is only possible with those metals now requiring a significant amount of energy, which is a product of energy required per ton and the tonnage produced. The energies required to produce a ton of metal were estimated in the project at Battelle for USBM (see Summary and Recommendations). Estimates of domestic annual production volumes have also been published in the USBM Minerals Yearbook. However, production volume estimates are not released for all metals. Consumption and import values are available in some cases where production values are not provided. Consumption includes imports and recycling, but can help to establish the order of magnitude of what a production volume may be. There are little or no data for several metals, but their production volumes and uses are considered to be minor.

For the purpose of making a rough estimate of the comparative energy use for producing the metals to be considered, available information on current production and consumption has been summarized in Table 1.

Blast furnace iron completely dominates the energy use, due to its huge production volume. However, iron was not considered in this study, since it was considered highly unlikely that an electrochemical process could compete with established large-scale pyrometallurgy processes economically or energy-wise. There is no history of electrochemical processes having been tried except for small volume products such as high purity iron powder. Conceivably, direct processes utilizing hydrogen for ore reduction could be developed, utilizing hydrogen produced electrochemically rather than that from petroleum. However, such a process is tied into low-cost and low-energy hydrogen. Methods to produce such hydrogen are receiving worldwide attention and support in other programs.

Only metals with significant domestic production were considered. Some well known metals as nickel and tin have important domestic uses but are largely imported. The USBM is studying methods of producing nickel from domestic ores. Conceivably, a sufficiently low-cost and low-energy process could stimulate domestic production but it is doubtful that domestic production will become significant in this century.

To obtain a rough estimate of the total energy use for producing the metals in Table 1 (excepting iron), the annual energy use values marked with (*) were added. The total is 4.42 x 10^{13} Kcal/yr (1.77 x 10^{14} Btu/yr). The metals can then be rank-ordered according to energy consumption:

Magnesium	33%
Ferromanganese	15%
Zinc	14%
Lead	9%
Ferrochromium	9%
Sodium	7%
Titanium	4%
Other	9%.

Estimates of growth rates in production and consumption of these metals have been made in the following sections. Development of less energy intensive production methods for the remaining metals, currently accounting for 9 percent of the energy use, is not expected to affect the total energy use appreciably. Even a 100 percent increase in volume in the next twenty years for any of these metals would have little impact on energy use.

Sodium and titanium together use approximately 13 percent of the energy. Consumption (and production) of these metals is not expected to increase substantially by the year 2,000 (see following sections). After considerable activity in the 1950's an electrolytic method was developed to produce titanium from the tetrachloride but it is not being used. Titanium Corporation of America (phone conversation) suggests that the process could find use if more capacity is needed but that energy requirements are no less than for current production processes involving reduction with sodium on magnesium. In view of the moderate outlook for growth of the titanium industry a review of current and past technology to find opportunities for reducing energy below that for current practice was not undertaken.

TABLE 1. ENERGY USE FOR METAL WINNING (CURRENT PROCESSES)

Metal	Annual Volume M tons/yr (S tons/yr)	Volume Type (1)	Year of Estimate	Energy Kcal/M ton (Btu/S ton)	Annual Energy Use	
					Kcal (Btu)	Percent of Total
Barium	0.00×10^{0} (0.00×10^{0})	- -	1977	-	-	-
Beryllium	4.54×10^{1} (5.00×10^{1})	C	1977	1.43×10^{9} (5.15×10^{9})	6.50×10^{10} (2.58×10^{11})*	.14
Cadmium	2.72×10^{3} (3.00×10^{3})	P	1977	4.61×10^{7} (1.66×10^{8})	1.26×10^{11} (4.98×10^{11})*	.28
Calcium	2.27×10^{2} (2.50×10^{2})	I	1977	-	-	-
Chromium	2.72×10^{3} (3.00×10^{3})	P	1977	-	-	-
Ferrochromium(3)	2.24×10^{5} (2.47×10^{5})(4)	P	1977	1.70×10^{7} (6.13×10^{7})	3.81×10^{12} (1.51×10^{13})*	8.52
	3.81×10^{5} (4.20×10^{5})	C	1977	1.70×10^{7} (6.13×10^{7})	6.48×10^{12} (2.57×10^{13})	- -
Cobalt	0.00 (0.00)	P	1977	3.45×10^{7} (1.24×10^{8})	-	-
	8.03×10^{3} (8.85×10^{3})	I	1977	3.45×10^{7} (1.24×10^{8})	2.77×10^{11} (1.10×10^{12})	- -

TABLE 1. (Continued)

					Annual Energy Use	
Metal	Annual Volume M tons/yr (S tons/yr)	Volume Type (1)	Year of Estimate	Energy Kcal/M ton (Btu/S ton)	Kcal (Btu)	Percent of Total
Columbium	6.80×10^{1} (7.50×10^{1})	P	1977	-	-	-
Ferrocolumbium(3)	1.81×10^{3} (2.00×10^{3})	I	1977	5.25×10^{7} (1.89×10^{8})	9.53×10^{10} (3.78×10^{11})	-
	7.44×10^{2} (8.20×10^{2})	P	1975	5.25×10^{7} (1.89×10^{8})	3.91×10^{10} (1.55×10^{11})*	0.087
	2.86×10^{3} (3.15×10^{3})	C	1977	5.25×10^{7} (1.89×10^{8})	1.50×10^{11} (5.95×10^{11})	
Gold	2.59×10^{1} (2.85×10^{1}) (2)	P	1977	2.21×10^{10} (7.96×10^{10})	5.72×10^{11} (2.27×10^{12})*	1.28
Iron	7.50×10^{7} (8.27×10^{7})	P	1977	6.42×10^{6} (2.31×10^{7}) (10)	4.81×10^{14} (1.91×10^{15})	-
Lead	6.35×10^{5} (7.00×10^{5})	P	1977	6.11×10^{6} (2.20×10^{7})	3.88×10^{12} (1.54×10^{13})*	8.69
Lithium	-	-	-	-		
Magnesium	1.50×10^{5} (1.65×10^{5})	P	1977	9.95×10^{7} (3.58×10^{8})	1.49×10^{13} (5.91×10^{13})*	33.35

TABLE 1. (Continued)

Metal	Annual Volume M tons/yr (S tons/yr)	Volume Type (1)	Year of Estimate	Energy Kcal/M ton (Btu/S ton)	Annual Energy Use	
					Kcal (Btu)	Percent of Total
Manganese	2.27×10^4 (2.50×10^4)	P	1977	-	-	-
Ferromanganese (3)	4.67×10^5 (5.15×10^5)	P	1977	1.46×10^7 (5.24×10^7)	6.80×10^{12} (2.70×10^{13})*	15.23
	7.89×10^5 (8.70×10^5)	C	1977	1.46×10^7 (5.24×10^7)	1.15×10^{12} (4.56×10^{13})	-
Mercury	1.11×10^3 (1.22×10^3)	P	1977	1.09×10^8 (3.94×10^8)	1.21×10^{11} (4.81×10^{11})*	.27
Molybdenum	2.27×10^3 (2.50×10^3)	P	1977	-	-	-
Nickel	2.34×10^4 (2.58×10^4)	P	1977	4.00×10^7 (1.44×10^8)	9.38×10^{11} (3.72×10^{12})*	2.09
Platinum	5.17×10^1 (5.70×10^1) (5)	C	1977	-	-	-
Potassium	-	-	-	-	-	-
Rare Earths	-	-	-	-	-	-
Selenium	2.52×10^2 (2.78×10^2)	P	1977	8.25×10^7 (2.97×10^8)	2.08×10^{10} (8.26×10^{10})*	.046

TABLE 1. (Continued)

Metal	Annual Volume M tons/yr (S tons/yr)	Volume Type (1)	Year of Estimate	Energy Kcal/M ton (Btu/S ton)	Annual Energy Use	
					Kcal (Btu)	Percent of Total
Silver	1.37×10^{3} (1.51×10^{3})	P	-	3.42×10^{8} (1.23×10^{9})	4.69×10^{11} (1.86×10^{12})*	1.05
Sodium	1.31×10^{5} (1.44×10^{5})	P	1975	2.56×10^{7} (9.20×10^{7})	3.32×10^{12} (1.32×10^{13})*	7.45
Strontium	-	-	-	-	-	-
Tantalum	3.83×10^{2} (4.22×10^{2})	P	1975	6.92×10^{7} (2.49×10^{8})	2.65×10^{10} (1.05×10^{11})*	.059
Tellurium	5.94×10^{1} (6.55×10^{1})	P	1975	2.31×10^{7} (8.32×10^{7})	1.37×10^{9} (5.45×10^{9})*	.003
Tin	5.44×10^{3} (6.00×10^{3})	P	1977	7.08×10^{7} (2.55×10^{8}) (8)	3.36×10^{11}* (1.53×10^{12})	.86
	5.62×10^{4} (6.20×10^{4})	C	1977	7.09×10^{7} (2.55×10^{8})	3.98×10^{12} (1.58×10^{13})	
Titanium	1.46×10^{4} (1.62×10^{4})	C	1977	[1.18×10^{8} (4.23×10^{8}) (6) 1.03×10^{8} (3.70×10^{8}) (7)]	1.61×10^{12} (6.42×10^{12})* (12)	3.62
Tungsten	2.72×10^{3} (3.00×10^{3})	P		9.61×10^{7} (3.46×10^{8})	2.62×10^{11} (1.04×10^{12})*	.59
Vanadium	-	-	-	-	-	

TABLE 1. (Continued)

Metal	Annual Volume M tons/yr (S tons/yr)	Volume Type (1)	Year of Estimate	Energy Kcal/M ton (Btu/S ton)	Annual Energy Use Kcal (Btu)	Annual Energy Use Percent of Total
Ferrovanadium(3)	5.53×10^2 (6.10×10^2) (9)	C	1977	1.36×10^8 (4.91×10^8)	7.56×10^{10} (3.00×10^{11}) *	.17
Zinc	3.81×10^5 (4.20×10^5)	P	1977	1.67×10^7 (6.02×10^7) (11)	6.38×10^{12} (2.53×10^{13}) *	14.28
Zirconium	2.04×10^3 (2.25×10^3)	C	1977	4.14×10^8 (1.49×10^9)	8.44×10^{11} (3.35×10^{12}) *	1.89

(1) P - Production; C - Consumption; I - Imported.
(2) 1,000,000 troy oz/yr.
(3) Cr-60%; Cb-65%; Mn-75%; V-75%.
(4) Calculated from reported volume of contained Cr assuming 65%.
(5) 2,000,000 troy oz/yr.
(6) Reduction with Mg.
(7) Reduction with Na.
(8) Reduction of Bolivian ore.
(9) Calculated from reported volume of contained V assuming 75%.
(10) Blast furnace iron.
(11) Electrowinning method.
(12) Average of energy requirements per ton for Mg and Na reduction.

M Ton - Metric Ton.
S Ton - Short Ton.

*Figures added to determine total energy for production and percentages for each metal.

Unlike titanium, which is used mainly as a structural material, sodium finds use mainly as a chemical reagent. At its present relative price these applications are limited, particularly with the demise of tetramethyl and tetraethyl lead. However, with both a decrease in energy requirements and relative cost, use of sodium as a diverse reducing reagent could expand. If lower energy production is achieved it will also be decreased for sodium-reduced titanium.

The technology of sodium production has received relatively little attention since the advent of the Downs fused chloride process. With other modern developments that have taken place, i.e., materials of construction, a reexamination of the chemistry and technology of sodium production should provide some possible method of reducing energy. For the reasons discussed sodium was chosen for further analysis.

USES, PROCESS MATERIALS, AND FUTURE VOLUME OF METALS USING MOST ENERGY

Introduction

The following sections discuss current and projected uses, raw materials, consumption, and production for magnesium, zinc, lead, chromium and ferrochrome, manganese and ferromanganese, sodium, and titanium. Table 2 shows production for 1977 and that projected for year 2,000. Sources and rational for these estimates are discussed for each metal.

Magnesium

Magnesium enjoys a technological position unique among the metals in common use today. Magnesium is best known for its light weight and high strength-to-weight ratio. However, it has a number of other important characteristics that lead to a wider range of applications. It is an indispensable alloying ingredient or innoculant for a number of other metals. It is the reductant used in the production of such metals as titanium, zirconium, uranium, beryllium and hafnium. It is used for its electrochemical

TABLE 2. CURRENT AND FORECAST DOMESTIC PRODUCTION VOLUMES

	Production Volumes	
Metal	Current M ton/yr (S ton/yr)	Year 2,000 M ton/yr (S ton/yr)
Magnesium	114,300 (126,000)	357,000 (394,000)
Zinc	394,000 (434,000)	853,000 (940,000) (1)
Lead	549,000 (605,000)	889,000 (980,000) (2)
Chromium (including that in ferrochrome)	246,000 (272,000)	340,000 (375,000)
Manganese (including that in ferromanganese)	382,000 (422,000)	1,500,000 (1,600,000)
Sodium	142,000 (157,000)	145,000 (160,000)
Titanium	14,700 (16,200)	29,000 (32,000)

(1) Assumes 42% (same as present) of predicted consumption of 2.23 million S tons will be domestically produced.

(2) Assumes 41% (same as present) of predicted consumption of 2.4 million short tons will be domestically produced.

properties as a sacrificial anode to protect steel structures and equipment from corrosion and as a power-source anode in various types of batteries. It is used for its chemical properties as an intermediate reactant in a number of chemical production processes. Finally, it is the lightest structural metal of proven and demonstrated usefulness in military and consumer applications where weight saving is an important consideration.

Raw Materials

Magnesium is the eighth most abundant element in the earth's crust and the third most abundant metal used in structural applications. Magnesium-bearing raw materials exist abundantly in various forms in all parts of the world(2). The principal raw materials are magnesite ($MgCO_3$), dolomite ($MgCO_3 \cdot CaCO_3$), brucite ($Mg(OH)_2$), olivine ($(Mg,Fe)_2SiO_4$), brines, evaporites*, and seawater. Of these, the ones used predominantly today for the production of magnesium metal are dolomite, brines, and seawater.

Deposits of high-purity dolomite occur throughout the world. The extent of these deposits is considered to be vast. Brines constitute another important raw material for magnesium production. Underground brines are found in many parts of the world, and are frequently associated with oil wells. In addition to underground brines, there are surface brines, the two best known and easily identifiable being the Dead Sea in Israel and the Great Salt Lake in the USA. It has been estimated that the magnesium chloride ($MgCl_2$) content of the Great Salt Lake amounts to 544 million M tons (600 million S tons). Evaporite deposits also exist throughout the world and constitute another very large source of magnesium.

Enormous as all these resources are for magnesium, they are dwarfed by the amount of magnesium in seawater. In Table 3, a partial list of the elements dissolved in seawater is given(3). Magnesium with 12 billion pounds per cubic mile of seawater (1.30×10^9 kg/(km)^3 is the third most abundant solute element in seawater. With an estimated 320 million cubic miles (1333 cubic Kilometers) of seawater in the world, it can be safely stated that there is an essentially inexhaustable reserve supply of raw materials for magnesium.

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*Underground salt deposits that have resulted from natural drying of inland areas.

TABLE 3. PARTIAL SOLUTE COMPOSITION OF SEAWATER(3)

Element	Amount		
	PPM	Pounds/1000 Gallons (approximate)	Pounds/cubic mile (approximate)
Chlorine	18,980	162.0	180,000,000,000
Sodium	10,561	90.0	100,000,000,000
Magnesium	1,272	10.9	12,000,000,000
Sulfur	884	7.6	8,300,000,000
Calcium	400	3.4	3,800,000,000
Potassium	380	3.25	3,600,000,000
Bromine	65	0.56	610,000,000
Carbon	28	0.24	260,000,000
Strontium	13	0.11	120,000,000
Boron	4.6	0.039	43,000,000
Silicon	4	0.034	38,000,000
Fluorine	1.4	0.012	13,000,000

Production and Consumption

The various applications cited earlier and the demand they have created for magnesium have contributed to a well sustained growth in consumption as depicted by the data for the period 1967 to 1977 in Table 4. Actually, during the last 15 years the average compounded growth in consumption has amounted to 6 percent per year. In 1977, total consumption in the United States amounted to 103,420 M ton (114,000 S tons) distributed in the following manner among the principal uses: 54 percent in aluminum alloys, 10 percent in ferrous applications, 8 percent for sacrificial anodes, 9 percent as a chemical reagent, 5 percent as metal reductant and 14 percent in structural applications. Structural applications include aircraft castings, die casting for chain saws, luggage, automotive and other appliances, photo engraving sheet, extrusions for luggage frames and materials handling carts, and miscellaneous other uses.

Table 4 also includes data for production, exports, and imports of magnesium during the 10 year period of 1967-1977. For several years consumption and exports exceeded total production. The short fall was made up by releases from the U.S. government strategic stockpile. This source is now exhausted. The sharp decline in both production and consumption between 1974 and 1975 was due in part to the marked increase in price that occurred at that time. But it is now believed that the major reason for this decrease was the large volume purchases made by users in 1974 in anticipation of a shortage that never materialized. Both production and consumption volume are now again on the increase.

The three principal processes by which primary magnesium can be produced are: (1) fused-salt electrolysis of $MgCl_2$; (2) silicothermic reduction of calcined dolomite (dolime-CaO.MgO); and (3) carbothermic reduction of MgO.

Today magnesium is produced in the USA in four plants having the capacities shown in Table 5. American Magnesium Company and NL Industries use the I.G. Farbenindustrie electrolytic process and The Dow Chemical Company uses its own electrolytic process. The Alcoa Northwest Alloys plant represents the first use of a silicothermic process in the USA for close

TABLE 4. PRODUCTION, CONSUMPTION, EXPORTS AND IMPORTS OF MAGNESIUM METAL FOR THE USA, 1967-1977

	Metric Tons (Short tons)			
Year	Production	Consumption	Exports	Imports
1967	88,038	82,394	11,950	
	(97,406)	(90,825)	(13,173)	
1968	89,244	78,405	17,651	
	(98,375)	(86,427)	(19,457)	
1969	90,615	86,302	24,831	
	(99,887)	(95,132)	(27,372)	
1970	101,611	84,817	32,415	1,304
	(112,007)	(93,495)	(35,732)	(1,438)
1971	112,024	83,611	22,017	1,269
	(123,485)	(92,166)	(24,270)	(1,399)
1972	109,608	94,066	15,841	1,291
	(120,823)	(103,691)	(17,462)	(1,424)
1973	111,067	105,028	35,870	915
	(122,431)	(115,774)	(39,541)	(1,009)
1974	122,469	117,977	41,363	848
	(135,000)	(130,048)	(45,595)	(935)
1975	109,043	85,426	29,134	5,369
	(120,200)	(94,167)	(32,115)	(5,919)
1976	108,831	94,758	12,136	10,441
	(119,966)	(104,453)	(13,378)	(11,510)
1977	114,317	103,419	27,021	11,067
	(126,014)	(114,000)	(29,786)	(12,200)

TABLE 5. PRIMARY MAGNESIUM METAL CAPACITY IN THE UNITED STATES, 1977 and 1981

	Capacity, Metric Tons			
Company	Actual 1977	Projected 1981	Process	Plant Location
Northwest Alloys, Inc. (Alcoa Subsidiary)	22,000	36,000	Magnetherm	Addy, Washington
American Magnesium Company	4,500	4,500	I.G./Electrolytic	Snyder, Texas
NL Industries, Inc.	22,500	22,500	I.G./Electrolytic	Rowley, Utah
The Dow Chemical Company	109,000	109,000	Dow/Electrolytic	Freeport, Texas
TOTAL	158,000	170,000		

to 10 years. This plant was brought on stream in 1977. The Alcoa plant is the only current producer that has projected an increase in capacity by 1981. Today, about 86 percent of primary magnesium capacity in the USA is electrolytic and 14 percent is silicothermic (Magnetherm). The carbothermic process is not used any place in the world today. Although it is basically a thermal reduction process, more than 50 percent of the total energy consumed in the present carbothermic process is electrical. The critical step in this process is the quenching of the Mg vapor emerging from the reactor. This quench must be extremely rapid in order to prevent the reversion of Mg to MgO by reaction with the CO gas produced in the reduction step. Battelle submitted to DOE several years ago a preproposal outlining an advanced concept for achieving a rapid quench and at the same time lowering the total energy required in the process by about 30 percent. Action on this preproposal is awaiting completion of the current DOE project being conducted by MIT on "An Assessment of the Magnesium Primary Production Technology".

Future Consumption

Many factors will affect the future growth of magnesium metal consumption. In several applications, particularly in the non-structural area, there is no substitute for magnesium and its consumption will follow at least the growth pattern of the industries represented by those applications. Use in aluminum alloys, nodularization of iron, and thermal reduction of other metals are examples of such uses. In other areas, however, such as desulfurization of iron and steel and in structural applications, competitive forces are the dominant factor. Magnesium competes with calcium carbide, calcium silicide, lime and rare earths in desulfurization of iron and steel and with aluminum and zinc alloys in structural applications. Industry sources from a careful analysis of all the markets into which magnesium goes are expecting consumption to increase to 145,000 M tons (160,000 S tons) in 1981 and to 186,000 M tons (205,000 S tons) in 1985. Predictions beyond this point are based on extrapolation. The average consumption of magnesium during the last 11 years was 93,000 M tons (102,000 S tons). If the consumption growth rate continues at 6 percent per year, then the consumption in the year 2000 should reach a level of 354,000 M tons (390,000 S tons). The Bureau of Mines(1) has forecasted for the year 2,000 a range of 218,000 to 490,000 M tons (240,000 to 540,000 S tons) and a probable level of 357,000 M tons (394,000 S tons). The latter figure is in complete agreement with the consumption for that year extrapolated from the established annual growth rate.

Attainment of the higher level of the range will require a significant expansion in the use of magnesium for structural applications particularly in automobiles, appliances, hand tools, and other consumer and industrial components. The advantages of magnesium in such applications are well documented and its serviceability has been well demonstrated. The need for weight saving on automobiles is becoming more acute, thus increasing the incentive to use magnesium. One automobile manufacturer has forecasted an usage of 10 to 20 pounds of magnesium alloys per vehicle if the ratio of the price of magnesium to that of aluminum decreases from its present level of 1.9 to about a level of 1.5. This alone represents a consumption of 45 to 90 million kg (100 to 200 million pounds) of magnesium. With the potential of lower cost magnesium through energy-saving production processes and the almost assured further increase in the price of aluminum, the potential of achieving a more favorable price ratio between magnesium and aluminum is very real. Thus, it is not at all unrealistic to predict an almost explosive increase in the demand for magnesium after 1990.

For purposes of estimating energy use, etc., in the report the 1977 production of 114,317 M tons (126,014 S tons) of magnesium metal will be assumed. For the year 2,000 production will be assumed to be the same as the projected consumption of 357,000 M tons (394,000 S tons).

Zinc

Zinc is a versatile metal that has been in use for over 2000 years. Zinc stands third in world wide consumption of nonferrous metals, being surpassed only by aluminum and copper. The United States is a major consumer of zinc, using about 20 percent of the total world supply annually. However, the United States is not a large producer of zinc metal.

Production and Consumption

Zinc metal enters the manufacturing field in four major areas--galvanizing, brass and bronze products, castings, and rolled zinc. Significant quantities of zinc are also consumed as pigments or other chemicals. The U.S. Bureau of Mines(4) estimates that, in 1977, construction materials accounted for 40 percent of consumption; transportation, 27 percent; electrical equipment, 12 percent; machinery and chemicals, 11 percent; and other, 10 percent. Of the zinc metal and concentrates consumed directly, galvanizing accounted for 35 percent of the total; zinc-base alloy, 33 percent; brass and bronze, 14 percent; zinc oxide, 12 percent; and other, 6 percent.

Table 6 presents the production, consumption, and imports of slab zinc for the years 1967-1977. Production was around the 900,000 M tons (1 million S tons) level until 1970 when it started to decline. In 1977 production was less than half that of 1967. There are several reasons for the decline in zinc production. The grade of ore tends to be lower in the United States than zinc ores in the rest of the world. Plants have been closed because they were obsolete and it was not practical to retrofit the plants with environmental controls in order to meet government regulations. Some plants were unable to obtain sufficiently high grade concentrates to compete economically with others who had concentrates.

Four electrolytic zinc plants were operating at the end of 1977. There are in Sauget (East St. Louis) Illinois; Corpus Christi, Texas; Kellogg, Idaho; and Bartlesville, Oklahoma. Two smelting plants, one at Palmerton, Pennsylvania, and one at Monaca, Pennsylvania, were also operating. Total zinc producing capacity was 600,000 M tons (661,000 S tons) annually. A new electrolytic plant at Clarksville, Tennessee, capacity 82,000 M tons (90,000 S tons) per year, is scheduled to open late in 1978 or early in 1979. Environmental concerns may be an obstacle to further expansion of zinc producing facilities. Electrolytic production will minimize some of the problems, but new processes may be needed to reduce the generation of sulfur dioxide.

Consumption of slab zinc has fluctuated around the 900,000 M tons (1 million S tons) level for the past 11 years. The extreme high level in 1973 was due to an increased demand because of the high level of the economy exemplified by the record setting production in the steel and auto industries.

Increased imports of slab zinc have filled the void between decreasing metal production and the level of zinc consumption. This situation probably will continue for some time into the future.

TABLE 6. PRODUCTION, CONSUMPTION, AND IMPORTS OF ZINC METAL IN THE UNITED STATES, 1967-1977

Year	Thousand Metric Tons (short tons)		
	Production	Consumption	Imports
1967	851 (939)	1,122 (1,237)	201 (222)
1968	926 (1,021)	1,210 (1,334)	278 (307)
1969	944 (1,041)	1,241 (1,368)	298 (329)
1970	796 (878)	1,076 (1,187)	244 (270)
1971	694 (766)	1,137 (1,254)	290 (320)
1972	574 (633)	1,286 (1,418)	474 (523)
1973	528 (583	1,364 (1,504)	537 (592)
1974	503 (555)	1,168 (1,288)	489 (540)
1975	397 (438)	839 (925)	344 (380)
1976	452 (499)	1,028 (1,134)	647 (714)
1977[(a)]	394 (434)	944 (1,041)	522 (576)

(a) Estimated

Source: Metal Statistics, 1978.

Future Consumption

According to the U.S. Bureau of Mines(4), primary zinc metal demand is expected to increase at an annual rate of 2.6 percent through 1985. Based on the 1977 consumption of 0.94 million M tons (1.04 million S tons), consumption in 1985 would be 1.2 million M tons (1.3 million S tons). The average yearly consumption of zinc for the 11 years shown in Table 6 was 1.13 million M tons (1.25 million S tons). At an annual growth rate of 2.6 percent, consumption in 1985 would be 1.39 million M tons (1.53 million S tons). There are a number of factors that must be taken into account when forecasting zinc consumption to 1985 and 2,000. The tonnage of zinc diecastings used by the automotive industry has been declining in recent years. This decline has resulted from increased use of aluminum and plastics by the industry in an effort to reduce vehicle weight in order to achieve greater fuel economy. Other coatings or materials such as plastics and electroplated cadmium, as well as special steels can replace zinc in certain areas for corrosion protection. Aluminum can be used in place of brass. Presently there is considerable attention being given to substituting magnesium for zinc diecastings. This situation may be partially changed through greater use of galvanized steel in major markets such as construction and automobiles and trucks.

If the 1977 zinc consumption of 0.94 million M tons (1.04 million S tons) is used as a base and it is assumed that the annual growth rate will be 2.6 percent, consumption in the year 2,000 would be 1.72 million M tons (1.9 million S tons). Based on the average annual consumption of 1.13 million M tons (1.25 million S tons), consumption of slab zinc would be 2.02 million M tons (2.23 million S tons) in the year 2,000.

The Bureau of Mines(1) has also forecasted total U.S. demand for zinc to be between 1.95 and 4.14 million M tons (2.15 and 4.56 million S tons) in the year 2,000, with a probable demand of 2.9 million M tons (3.2 million S tons). This forecast includes 2.49 million M tons (2.75 million S tons) in metallic form and 0.41 million M tons (0.45 million S tons) in nonmetallic form. It is believed that the metallic form also includes zinc recovered from scrap.

The Battelle estimate of 2.02 million M tons (2.23 million S tons) for slab zinc consumption in the year 2,000 may be conservative. However, it is difficult to envision a zinc demand larger than 2.49 million M tons (2.75 million S tons) in the year 2,000 unless there is a considerable upward trend in several zinc markets.

Reserves and Resources

World zinc resources are estimated at about 1.8 billion M tons (2 billion S tons) on a metal content basis(4). Most of these resources are found in conventional-type deposits of stratabound carbonate formations and in massive sulfide ore bodies.

World reserves are estimated at 159 million M tons (175 million S tons), while United States reserves are estimated at 27 million M tons (30 million S tons). Annual domestic mine production of zinc during the past 5 years has been slightly below 450,000 M tons (500,000 S tons) of contained metal, indicating that domestic reserves should be sufficient for several decades. Large reserves exist in Canada, Peru, Other Market Economy Countries, and in the Central Economy Countries.

The United States imports ores, concentrates, and slab zinc. For the past several years Canada has supplied over half of the zinc ores and concentrates to the United States; Mexico, 15 percent; Honduras, 10 percent; and other, 18 percent. Zinc metal imports have come from Canada, 51 percent; Australia, 6 percent; Belgium-Luxembourg, 6 percent; Japan, 5 percent; and other, 32 percent. Slab zinc imports in recent years have been larger than domestic production of slab zinc. In total, zinc imports are providing more than half of our primary consumption.

Dependence on imports to satisfy domestic consumption of any material can be dangerous. Such supplies could be cut off by transportation difficulties, political action by the exporting nations, strikes, or other actions that shut down production facilities. The price of the material may be arbitrarily raised by the exporters so that importers are forced to raise domestic prices with subsequent impact on the U.S. economy.

The principal suppliers of imported zinc to the U.S. - Canada, Honduras, Australia, and Japan--are considered friendly nations. There is little reason to anticipate that these supplies could be cut off for any reason other than a natural calamity.

Lead

Lead is considered to be a useful and probably an essential metal in many applications. It is one of the 4 major nonferrous metals along with aluminum, copper and zinc.

The major uses of lead are in storage batteries for automobiles and other battery-powered vehicles, as an antiknock additive in gasoline, and in cable for the electrical industry. The U.S. Bureau of Mines(1) estimated that, in 1977, batteries accounted for 52 percent of lead consumption; gasoline additives, 19 percent; electrical, 9 percent; ammunition, 6 percent; paints, 7 percent; construction, 2 percent; and other, 5 percent. Although some of the traditional markets for lead, such as gasoline additives and paints, have been declining due to environmental restrictions, there has been growth in the use of lead-acid batteries. This trend is expected to continue and should reach about 540,000 M tons (600,000 S tons) in year 2,000.

Production and Consumption

The annual production, consumption, and imports of lead metal are shown in Table 7. Production of primary lead increased from 345,000 M tons (380,000 S tons) in 1967 to a peak of 624,000 M tons (688,000 S tons) in 1973 and was only 550,000 M tons (605,000 S tons) in 1977. Primary lead production has averaged 43.2 percent of consumption for the past 11 years shown here, secondary recovery has provided about 43.5 percent of lead consumption. The remainder has been supplied by imports. The recovery of lead from secondary sources increased almost every year as shown in the table, and is an important part of the overall lead supply. Lead has excellent corrosion resistance so many lead products remain virtually unchanged during their useful life and are relatively easy to recycle. For example, it is estimated that about 60 percent of the lead in storage batteries is recycled after they are scrapped.

TABLE 7. PRODUCTION, CONSUMPTION, AND IMPORTS OF LEAD METAL IN THE UNITED STATES, 1967-1977

	Thousand Metric Tons (short tons)			
	Production			
Year	Primary	Secondary	Consumption	Imports
1967	344 (380)	502 (554)	1,144 (1,261)	330 (364)
1968	423 (467)	500 (551)	1,205 (1,329)	306 (338)
1969	579 (639)	548 (604)	1,260 (1,389)	252 (278)
1970	615 (678)	541 (597)	1,234 (1,361)	227 (251)
1971	604 (666)	541 (597)	1,298 (1,431)	180 (199)
1972	624 (688)	560 (617)	1,347 (1,485)	177 (196)
1973	624 (688)	593 (654)	1,397 (1,541)	161 (178)
1974	528 (683)	634 (699)	1,450 (1,599)	108 (120)
1975	578 (638)	531 (585)	1,176 (1,297)	96 (106)
1976	597 (659)	565 (623)	1,351 (1,490)	132 (146)
1977 (a)	549 (605)	664 (732)	1,351 (1,490)	236 (261)

(a) Estimated.

Source: Metal Statistics, 1978

Five lead refineries located in Missouri, Idaho, Nebraska, Montana and Texas account for all the production of refined primary lead. There are secondary lead smelters in most areas of the country. The important ones are in the New York, Philadelphia, Baltimore, Cleveland, Chicago, Baton Rouge, Dallas, Los Angeles, and San Francisco areas. The estimated annual refining capacity for primary lead is 725,000 M tons (800,000 S tons).

New plants may be built in the future to satisfy any growth in demand that may develop. However, there are environmental problems in both the mining and refining of lead materials. These are primarily air pollution, waste disposal, and land utilization. Meeting standards of local, state and Federal governments will require substantial capital investments and added operating cost.

Consumption of lead has gradually increased over the 11-year span shown in Table 5. The two peak years were 1973 and 1974 when the U.S. economy was strong.

Imports of primary lead declined from 1967 to 1975 and rose somewhat in 1976 and 1977. One reason for the increased imports in 1977 might be the increase in primary lead prices during the year. The producer price in January was 26 cents per pound, rose to 31 cents by the end of February, and to 32 cents by the end of October. Generally, foreign lead price was 2 to 3 cents per pound lower than that for domestic lead.

Future Consumption

The annual growth rate of lead metal consumption for the past 11 years has been about 1.5 percent, a very modest growth rate. The demand for lead in some markets is expected to grow slowly and to decrease in others. For example, the demand for lead in storage batteries should show a better than average growth due to increased vehicle production. This growth could be offset to some degree by a decrease in lead consumed in gasoline additives. Present governmental regulations require the amount of lead used in gasoline to drop from 1.7 grams per gallon in 1976 to 0.5 gram per gallon by 1980. Although it appears that gasoline consumption will continue to rise, the net effect will be a decrease in the use of lead in gasoline.

The demand for lead has also declined in building construction and electrical cable covering due to substitution of plastics for lead. Soldered food and beverage cans and other containers are being displaced to some extent by steel cans made by different processes and by aluminum cans.

The U.S. Bureau of Mines(4) estimates that the demand for lead should increase at an annual rate of 1.8 percent through 1985. Based on the 1977 lead consumption of 1.4 million M tons (1.5 million S tons), consumption in 1985 would be 1.5 million M tons (1.7 million S tons). The average annual lead consumption for the past 11 years was 1.30 million M tons (1.43 million S tons).

Taking the 1977 lead consumption of 1.4 million M tons (1.5 million S tons) as a base and assuming the annual growth will be 1.8 percent, consumption in 2,000 would be 2.1 million M tons (2.3 million S tons). Based on the 11 years average annual lead consumption of 1.30 million M tons (1.43 million S tons), consumption would be 1.96 million M tons (2.16 million S tons).

The U.S. Bureau of Mines(1) has projected total lead demand to be between 1.61 million M tons (1.78 million S tons) and 3.19 million M tons (3.52 million S tons) in the year 2,000, with a probable demand of 2.20 million M tons (2.43 million S tons). Battelle's best estimate of lead demand in year 2,000 is 2.1 to 2.2 million M tons (2.3 to 2.5 million S tons) based on an annual growth rate of 1.8 percent. Future production should continue to supply about 43 percent of consumption or 889,000 M tons (980,000 S tons).

Reserves and Resources

Total world reserves of lead are estimated at 123 million M tons (136 million S tons). U.S. reserves are estimated to be 25.8 million M tons (28.4 million S tons), while mine production in recent years has been about 540,000 M tons (600,000 S tons) annually. Therefore, at present rates of mine production, U.S. reserves should be adequate for several decades.

United States imports of lead-bearing ores, concentrates and bullion in recent years have varied from 100,000 M tons (110,000 S tons) of contained lead in 1973, to 56,000 M tons (62,000 S tons) in 1977. The major sources of imported ore and matte are Canada, Honduras, Australia, Peru, and West Germany. Imports of lead metal in 1977 were 17.5 percent of total lead consumption.

Because the major suppliers of imported lead are considered to be friendly nations, there is no apparent reason to believe that these shipments would be cut off arbitrarily.

Chromium

Chromium is a widely used and essential material. The industrial uses are primarily in metallurgical, chemical and refractory applications. Its attributes in alloy steels, cast irons, and nonferrous alloys are to enhance properties such as hardenability, creep and impact strengths, as well as resistance to corrosion, oxidation, and wear. Ferrochromium alloys and chromium metal are the prime additives for making alloys. However, ferrochrome alloys are adequate and often technically advantageous for 97 percent of the chromium consumed. Pure chromium is required only for a few specialty applications. Chromite, the major ore containing chromium, is a constituent of refractories widely used in iron and steel processing, nonferrous alloy refining, glassmaking, and cement processing. Sodium dichromate, a basic chromium chemical, is made by leaching chromite with caustic. Chromium chemicals are consumed in the manufacture of pigments, plating compounds, leather tanning and catalysts.

There are materials that can substitute for chromium in many applications, but from a performance and cost standpoint they are not completely satisfactory. Chromium continues to be essential for several high temperature and corrosion resistant alloys, i.e., stainless steels, chromium-cobalt alloys.

Production and Consumption

In 1977, the metallurgical industry consumed 61 percent of chromium used, the refractory industry, 19 percent, and the chemical industry, 20 percent. This report is only concerned with metallurgical applications of chromium in the form of ferrochromium or the pure metal.

Table 8 shows the production, consumption, and imports of chromium, ferroalloys, and chromium metal. The average chromium content of ferrochromium alloys produced was 61 percent, 1967-1977; for alloys consumed it was 61.2 percent. Over the 11 years period chrome content dropped from about 63 percent to about 59 percent for both produced and consumed alloys primarily due to changes in grades being used by steel producers. The average chromium content of imported ferrochromium was 64 percent, 1967-1977, dropping from about 67 percent to 60 percent in recent years.

The relative amounts of the various alloys has also changed in recent years as shown in Table 9. In both production and consumption there is a trend to the lower cost high-carbon ferrochrome and away from low-carbon ferrochrome. This trend is primarily due to the increasing use of the Argon-oxygen-decarburization (AOD) refining of steel. Because these materials are dependent on the metals industry, production, and more particularly consumption, varies with the metals industry performance. During the past 11 years domestic production of ferrochromium and metal has decreased substantially. This is partially due to increased production costs because of pollution controls that make domestic ferrochromium less competitive with imported material. Imported ferrochromium has therefore been able to penetrate the U.S. market to a considerable degree.

In 1976, thirteen plants operated by 8 companies were producing ferrochromium and/or chromium metal. These plants are located in Kentucky, New York, South Carolina, Tennessee, Iowa, West Virginia, Ohio, Mississippi, and New Jersey.

Consumption of ferrochromium and chromium metal fluctuates as does overall metals production, especially that of the iron and steel industry. The peak years for consumption were 1973 and 1974 when over 450,000 M tons (500,000 S tons) were consumed. There was a sharp decline in 1975, and an upswing in 1976-77. In the past 2 years, imports have been approximately equal to 50 percent of total demands.

The ferroalloy industry has always been highly competitive. The upsurge in imported ferrochromium and metal has provided a ceiling on domestic ferrochromium prices, resulting in low profit margins for domestic producers. At least 2 domestic producers also have plants in foreign countries and are a major source of imports into the U.S.

TABLE 8. PRODUCTION, CONSUMPTION, AND IMPORTS OF CHROMIUM FERROALLOYS AND CHROMIUM METAL IN THE UNITED STATES, 1967-1977, TONS*

Year	Metric Tons (short tons)		
	Production	Consumption	Imports
1967	386,309 (425,833)	333,543 (367,669)	52,146 (57,482)
1968	334,444 (368,662)	329,660 (363,389)	54,264 (59,816)
1969	393,239 (433,472)	351,248 (387,185)	55,925 (61,647)
1970	356,251 (392,700)	311,055 (342,880)	37,471 (41,305)
1971	320,781 (353,601)	292,727 (322,677)	77,280 (85,187)
1972	317,840 (350,359)	354,493 (390,762)	131,416 (144,862)
1973	378,971 (417,745)	464,683 (512,226)	145,804 (160,722)
1974	387,758 (427,431)	530,951 (585,274)	148,354 (163,533)
1975	225,519 (248,593)	295,542 (325,780)	290,696 (320,438)
1976	242,336 (267,130)	377,931 (416,598)	220,079 (242,596)
1977	247,354 (272,662)	392,732 (432,913)	203,283 (224,082)

Source: U.S. Bureau of Mines Minerals Yearbooks and Mineral Industry Surveys, 1977.

* Figures include the iron content.

TABLE 9. RELATIVE DOMESTIC PRODUCTION AND CONSUMPTION OF CHROMIUM ALLOYS

Alloy	Percent of Total*			
	1974		1977	
	Production	Consumption	Production	Consumption
Low Carbon Ferrochrome	33	31	20	14
High Carbon Ferrochrome	32	49	50	72
Ferrochrome Silicon	25	17	25	11
Other**	10	3	10	3

* Percents refer to contained chromium.

** Includes pure chromium.

Future Consumption

The U.S. Bureau of Mines(4) forecasts that the demand for primary chromium will increase at an annual growth rate of 3.4 percent through 1985, for a total of 640,000 M tons (700,000 S tons) of contained chromium. This forecast includes the chromium consumed by the refractory and chemical industries as well as that by the metals industry. Based on the 1977 consumption of ferrochromium and chromium metal, demand in 1985 for these materials would be 513,183 M tons (565,687 S tons) of contained chromium. The average annual consumption of ferrochromium and chromium metal for the past 11 years was 366,778 M tons (404,304 S tons) of contained chromium.

The most probable demand for primary chromium in the year 2,000 will be 1.0 million M tons (1.1 million S tons) of contained chromium according to the U.S. Bureau of Mines(2). This represents an annual growth rate of 2.6 percent. Assuming the 1977 consumption as the basis, the demand for ferrochromium and chromium metal would be 708,724 M tons (781,235 S tons) of contained chromium in the year 2,000. Calculated on the 11 year annual consumption, demand in year 2,000 would be 661,888 M tons (729,607 S tons) of contained chromium.

Battelle's best estimate of the demand for ferrochromium and chromium metal in year 2,000 is 680,000 M tons (750,000 S tons) of which approximately 50 percent will be supplied by imports, or 340,000 M tons (375,000 S tons). Production will be about 340,000 M tons (375,000 S tons). These figures are gross weight.

Reserves and Resources

The United States has no economically recoverable reserves of chromite. There are deposits of submarginal resources estimated to contain 1.6 million M tons (1.8 million S tons) of chromium in 20.4 million M tons (22.5 million S tons) of material averaging 8 percent of chromium oxide. Commercial chromite typically runs from 22 to 38 percent chromium content.

Total world chromite reserves are estimated at 2.5 billion M tons (2.7 billion S tons). About 1.8 billion M tons (2 billion S tons) of these reserves are in the Republic of South Africa and 0.5 billion M tons (0.6 billion S tons) in Southern Rhodesia. Turkey and the U.S.S.R. have rather large reserves. The leading exporters of chromite to the United States are Republic of South Africa, Turkey, the U.S.S.R. and the Philippines. The United Nations embargo on Rhodesian chromite has resulted in the United States purchasing less from this source.

Total world resources of chromite are estimated at over 18 billion tons, sufficient to meet demands for several hundred years.

Because the Republic of South Africa and Southern Rhodesia control the vast majority of chromite reserves, any internal problems in these countries or transportation difficulties could quickly reduce the amount of chromite available for world trade. Other suppliers would be willing to make up any deficiencies, but most certainly at much higher prices. It has been evident since the Rhodesian embargo came into being that the United States could be placed in a precarious situation for obtaining chromite in future years because of internal political problems in African nations. This deminishes the impetus to develop less energy intensive processes.

Manganese

The major use of manganese is for the production of iron and steel. This demand far exceeds all other uses of manganese. Manganese acts as a desulfurizer, deoxidizer, and conditioner of steels. It also imparts strength, toughness, hardness and hardenability to iron and steel.

Managanese is used chiefly in the form of ferromanganese, or silicomanganese by the steel industry. Some electrolytic manganese metal is also used, and small quantities of manganese ore are added to steelmaking furnaces.

Manganese is also used as an alloying agent in some nonferrous metals such as aluminum, copper, and magnesium. The additions are usually made in the form of electrolytic manganese or as a master alloy. Manganese dioxide is a component of dry-cell batteries, and manganese chemicals are used in small quantities for various purposes.

There are no economically workable manganese ore deposits (35 percent or more manganese) in the United States. Consequently, we are entirely dependent on imports of ore to satisfy our needs.

Production and Consumption

The steel industry uses large quantities of high-carbon ferromanganese, which can be made either in blast furnaces or in electric furnaces. Medium-carbon ferromanganese, low-carbon ferromanganese, and special grades of ferromanganese are made in electric furnaces. Silicomanganese, or high-silicon ferromanganese is made in electric furnaces.

Two steel companies have made blast furnace ferromanganese off and on for many years. Five companies with plants in Ohio, Kentucky, Tennessee, Oregon, and West Virginia produce ferromanganese in electric furnaces. Electrolytic manganese metal is produced by three companies at plants in Ohio, Mississippi and Tennessee.

Table 10 presents the production, consumption, and imports of ferromanganese and manganese metal for the past decade. The manganese content of the ferromanganese and metal produced in the U.S., 1967-1975, averaged 78.3 percent. Figures for 1976 and 1977 are not yet available. The manganese content of imports averaged 77.7 percent manganese, 1967-1977. In both cases there is very little variation from year to year. Production in the United States gradually declined over the period shown until production in 1977 was only 57 percent of what it had been in 1967. One reason for this is environmental considerations which require large capital expenditures for pollution control measures. Faced with this, several older and obsolete plants have been closed. Another factor is the doubling in tonnage of imports over the past 11 years.

Consumption of ferromanganese is tied directly to the production of raw steel. Because the steel industry has had its ups and downs, manganese demand follows the same curve. About 13 pounds of manganese is consumed in making one ton of raw steel year after year. The average annual consumption of ferromanganese and manganese metal was 892,424 M tons (983,730 S tons) during the period 1967-1977.

TABLE 10. PRODUCTION, CONSUMPTION AND IMPORTS OF FERROMANGANESE AND METAL IN THE UNITED STATES 1967-1977*

Year	Metric Tons (short tons) Production	Consumption	Imports
1967	853,594 (940,927)	890,973 (982,130)	196,205 (216,279)
1968	798,288 (879,962)	922,206 (1,016,559)	184,350 (203,212)
1969	772,938 (852,019)	971,632 (1,071,042)	279,314 (307,891)
1970	757,919 (835,463)	907,739 (1,000,611)	263,941 (290,946)
1971	689,366 (759,896)	815,569 (899,011)	220,244 (242,778)
1972	726,403 (800,723)	878,125 (967,968)	316,189 (348,539)
1973	619,675 (683,075)	1,012,964 (1,116,602)	354,338 (390,591)
1974	493,835 (544,361)	1,011,869 (1,115,395)	382,126 (421,222)
1975	522,365 (575,809	799,707 (881,527)	360,344 (397,212)
1976	445,388 (490,957)	810,714 (893,660)	485,099 (534,731)
1977	488,869 (538,886)	795,163 (876,518)	484,659 (534,246)

Source: U.S. Bureau of Mines Minerals Yearbooks and Mineral Industry Surveys, 1977.

* Figures include the iron content.

Imports of manganese ferroalloys and metal have doubled over the past decade. Two major factors are evident in this situation. The ever increasing costs of pollution control measures have increased production costs and forced closing of some facilities. The second factor relates to ownership of foreign manganese producing facilities. Several U.S. corporations, consumers of manganese ores, have become part owners of mining companies in order to assure themselves a source of supply. Ferroalloy producers have bought into or built ferromanganese facilities in foreign countries. Presumably this allows them to produce alloys more cheaply and enable imports of foreign material to be priced competitively with domestic production. The domestic ferroalloy industry has been in the doldrums for several years.

Future Consumption

Because manganese consumption is basically tied to the steel industry, its future will be governed by the growth of steel production. In turn, steel production will depend on the health of the economy and the tonnage of imported steel brought into the United States.

The U.S. Bureau of Mines(4) estimates that manganese demand will increase at an annual rate of 1.6 percent through 1985. Based on the consumption of 795,164 M tons (876,518 S tons) of ferromanganese in 1977, demand for these alloys would be 903,830 M tons (995,200 S tons) in 1985. Using the average of 892,424 M tons (983,730 S tons) for the past 11 years, demand in 1985 would be 1,013,259 M tons (1,116,927 S tons), about equal to consumption in 1973.

The Bureau of Mines(1) has also forecasted total demand for contained manganese to be between 1.78 and 2.45 million M tons (1.92 and 2.7 million S tons) of contained manganese in the year 2,000. The probable demand is 1.93 million M tons (2.13 million S tons). Assuming a 1.6 percent annual growth from 1977 to 2,000, demand for ferromanganese would be 1.14 million M tons (1.26 million S tons) of contained manganese in the year 2,000. Using the average of 892,424 M tons (983,730 S tons) for the last 11 years, demand in 2,000 would be 1.29 million M tons (1.42 million S tons). The Bureau of Mines figures include all forms of manganese, not just ferromanganese.

Battelle's best estimate of ferromanganese and metal consumption in year 2,000 is the range of 1.35 to 1.63 million M tons (1.5 to 1.8 million S tons) of contained manganese. It is expected that imports will continue to provide at least 50 percent of the demand. Future growth will depend entirely on increased raw steel production.

For energy calculations the 1977 domestic production of contained manganese will be assumed to be 383,000 M tons (422,000 S tons) or 78.3 percent of ferromanganese production. For year 2,000, 1.5 million M tons (1.6 million S tons) will be assumed.

Reserves and Resources

There are no domestic reserves of manganese ore containing 35 percent or more manganese. Attempts have been made to beneficiate low-grade ores found in Arizona, Colorado, and Maine. These have been unsuccessful for technical and economic reasons. Total world reserves of manganese are estimated at 6 billion tons. Major deposits are in Australia, Brazil, Gabon, India, and the Republic of South Africa. The Central Economy Countries also have large reserves of manganese ore.

Total resources of manganese ore are high. One such source is the extensive deposits of manganese nodules on the deep ocean floors. These deposits have been and are being investigated by both U.S. and foreign companies. Although there are technical and legal problems as well as economic concerns associated with mining these nodules, it is conceivable that such mining may be practiced by year 2,000.

The major sources of manganese ore imports by the U.S. during the past several years have been Brazil, 37 percent; Gabon, 31 percent; Australia, 14 percent; Republic of South Africa, 10 percent; and other, 8 percent.

Ferromanganese imports have originated in France, 35 percent; Republic of South Africa, 32 percent; Japan, 14 percent; other, 19 percent. It is aniticipated that these countries will continue to be major exporters of ferromanganese to the United States.

Essentially, complete dependence on foreign sources for raw materials is not a comfortable situation. Presently, the countries exporting manganese ores and ferromanganese to the United States are friendly. However, due to political problems in Africa, it is conceivable that these sources could be cut off. The long shipping distance from Australia and potential interruption in shipping could deter shipments from there. There is less reason to develop lower energy processes for these raw materials than if there were no threat to their availability.

Sodium

Sodium is a soft, malleable, silvery metal made by the electrolysis of sodium chloride in a fused salt bath. Fresh sodium reacts rapidly with moisture, so it must be stored in dry atmospheres.

Production and Consumption

Sodium metal has been used by a number of industries. A major use in the past was the manufacture of sodium cyanide for use in electroplating and in organic reactions. Sodium is consumed in the synthesis of certain dyes, in perfumes, in making tetraethyl lead for gasoline antiknock additives, and in sodium vapor lamps.

Metallic sodium is made by E.I. duPont de Nemours and Company at Niagara Falls, N. Y. and Memphis, Tennessee, by Ethyl Corporation at Baton Rouge, Louisiana and Houston, Texas and by Reactive Metals Company at Ashtabula, Ohio. Production capacity is estimated to be 189,000 tons per year.

The production of metallic sodium is shown in Table 11. Annual production has ranged from a low of 130,000 M tons (144,000 S tons) in 1976 to a high of 160,000 M tons (177,000 S tons) in 1973 during the past 11 years. Average consumption over this period was 145,600 M tons (160,500 S tons) yearly.

Consumption and stocks of sodium metal are not reported by the U.S. Bureau of Mines, nor are such figures available from other standard sources. However, because of the nature of metallic sodium, it is reasonable to assume that most producers and users of sodium do not accumulate large stocks of the metal. Therefore, it is believed that consumption equates to production under normal conditions.

TABLE 11. PRODUCTION OF METALLIC SODIUM IN THE UNITED STATES, 1967-1977

Year	Production Metric Tons	 Short tons
1967	149,527	164,528
1968	141,875	156,391
1969	149,399	164,685
1970	155,356	171,251
1971	138,867	153,075
1972	145,606	160,504
1973	160,483	176,903
1974	157,100	173,174
1975	130,624	143,989
1976	130,634	144,000
1977	142,428	157,000
Avg.	145,603	160,500

Source: U.S. Bureau of Mines Mineral Yearbooks and Mineral Industry Surveys, 1977.

It is estimated that the consumption of metallic sodium in 1974 was about 80 percent in gasoline additives, 7 percent for the reduction of metals, and 13 percent for sodium peroxide manufacture and other miscellaneous uses.

Future Consumption

Consumption of metallic sodium has fluctuated within a rather narrow range for the past decade. A few of the major markets have declined, while new or expanding uses have increased their demand. The largest market for sodium metal, gasoline additives, has shown a decline from the 1972 level. This is the result of regulations by the Environmental Protection Agency limiting the amount of lead in gasoline additives. A lead-sodium alloy, 10 percent by weight of sodium, is used in the manufacture of tetraethyl lead and tetramethyl lead. However, the EPA regulations will reduce the amount of lead in gasoline from 1.7 grams per gallon in 1976 to 0.5 grams per gallon by 1980. Therefore, as the amount of lead in gasoline declines so will the demand for sodium metal decline severely.

The markets for sodium other than in the manufacture of gasoline additives are small and it is difficult to envision their growing fast enough to offset the drop in sodium demand for gasoline additives. This means that new markets must be found during the next several years if sodium production and consumption are to remain at the 145,000 M tons (160,000 S tons) per year level.

Battelle estimates that consumption of metallic sodium will decline over the next few years and should not exceed 145,000 M tons (160,000 S tons) by 2,000. However, if relative cost decreases it could find increased use as a chemical and metallurgical reducing agent.

Reserves and Resources

The reserves and resources of salt in the United States and the rest of the world are virtually unlimited. Domestic reserves consist of huge bedded deposits in northern, southwestern, and central western states.

Large numbers of salt domes are found along the Gulf Coast. Salt lakes and solar evaporated sea salt facilities are found in many areas in the West Coast states.

Vast supplies of salt exist underground as rock salt or as brine in nearly every country of the world. In addition, the oceans are an inexhaustible source of salt. Worldwide salt resources are adequate to meet any foreseeable demands.

The United States normally imports less than 10 percent of its salt consumption and therefore has little reliance on imports.

Titanium Metal

Titanium Metal is produced by the reduction of titanium tetrachloride with either magnesium or sodium under an argon blanket. The titanium tetrachloride is made by chlorinating rutile concentrates (about 95 percent titanium dioxide) in the presence of carbon.

Titanium Metals Corporation of American (TMCA) has developed an electrolytic process for production of sponge titanium that reduces the tetrachloride in a fused salt bath. This material is purer and available in only small quantities.

Production and Consumption

Titanium metal sponge is produced in three plants located in Ohio, Oregon, and Nevada. Titanium ingot is made by the three sponge makers and five other firms. Titanium mill products are produced by 21 companies, of which 14 are located in the east-central region of the country and the others on the west coast.

Because there are only three titanium sponge producers, data for production are not published. Production capacity is estimated at 22,000,000 kg (48,000,000 pounds) per year or 22,000 M tons (24,000 S tons).

Table 12 presents titanium metal data for sponge consumption and imports, scrap metal consumption, ingot production and consumption, and mill product shipments. Imported sponge metal usually is about 25-35 percent of

TABLE 12. TITANIUM METAL DATA, 1967-1977

	Metric Tons (short tons)										
	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977
Sponge Metal											
Imports for Consumption	6,480 (7,144)	3,123 (3,443)	5,211 (5,745)	5,380 (5,931)	2,541 (2,802)	3,454 (3,808)	4,691 (5,172)	6,307 (6,953)	3,801 (4,190)	1,612 (1,778)	2,165 (2,387)
Industry Stocks	2,630) (2,900)	2,358 (2,600)	1,731 (1,909)	2,282 (2,516)	2,471 (2,724)	1,647 (1,816)	1,760 (1,941)	3,467 (3,822)	5,142 (5,669)	3,281 (3,617)	3,216 (3,546)
Government Stocks (DPA Inventory)	18,788 (20,711)	18,788 (20,711)	18,492 (20,385)	18,138 (19,994)	18,138 (19,994)	18,138 (19,994)	29,498 (32,517) (3)	28,217 (31,104)	28,750 (31,692)	29,328 (32,329)	29,328 (32,329)
Consumption	18,199 (20,062)	12,915 (14,237)	18,256 (20,124)	14,890 (16,414)	11,017 (12,145)	11,945 (13,068)	18,300 (20,173)	24,399 (26,896)	15,990 (17,626)	12,079 (13,315)	14,729 (16,236)
Scrap Metal Consumption	5,281 (5,822)	4,264 (4,701)	6,863 (7,566)	6,569 (7,242)	5,578 (6,149)	7,077 (7,802)	9,106 (10,038)	9,615 (10,599)	7,544 (8,316)	8,356 *9,211)	9,878 (10,889)
Ingot(1)											
Production	23,550 (25,950)	17,448 (19,234)	25,845 (28,490)	22,072 (24,331)	16,680 (18,387)	18,385 (20,267)	26,246 (28,932)	32,778 (36,132)	23,187 (25,560)	19,607 (21,614)	23,860 (26,302)
Consumption	23,029 (25,336)	16,622 (18,323)	24,568 (27,082)	21,488 (23,687)	15,474 (17,058)	17,689 (19,499)	23,050 (25,409)	28,633 (31,563)	22,213 (24,486)	19,054 (21,004)	22,898 (25,241)
Net Shipments of Mill Products(2)	12,368 (13,634)	10,795 (11,900)	14,460 (15,940)	13,136 (14,480)	10,197 (11,241)	11,455 (12,627)	13,181 (14,530)	15,824 (17,443)	14,177 (15,628)	13,152 (14,498)	14,030 (15,466)

(1) Includes alloy constituents.

(2) Bureau of the Census, Current Industrial Reports Series BDCF-263.

(3) Total inventory.

Source: U.S. Bureau of Mines Yearbooks and Mineral Industry Surveys.

sponge consumption. The suppliers are Japan, U.S.S.R., and The United Kingdom. Titanium scrap has become an important part of the total titanium metal supply in the United States, with increasing amounts recycled nearly every year.

The consumption of titanium mill products has varied over the past decade from a low of 10,197 M tons (11,241 S tons) in 1971 to a high of 15,824 M tons (17,443 S tons) in 1974. For many years about 90 percent of titanium mill products was consumed by the aircraft industry with the remainder going to other industries. This has changed in the last few years. For example in 1974, about 87 percent of the titanium metal was used in jet engines, airframes, and space and missile applications. The remainder was used in the chemical processing industry and in marine and ordnance applications. In 1977, about 60 percent of the titanium metal was used in jet engines, airframes, and space and missile applications. The remainder was used in the chemical processing industry, power generation, in marine and ordnance applications, and in steel and other alloys.

Future Consumption

Forecasting the future consumption of titanium metal has limited usefulness because of the uncertainties involved. No doubt, airframes, jet engines, and space and missile applications will continue to use over 50 percent of the titanium metal to the year 2,000. How fast industrial applications will grow is unclear at this time because titanium has to prove its worth in these applications due to its somewhat higher cost when compared to other materials such as high nickel steels and superalloys. Presently it appears that supersonic aircraft will not be in production for at least 10 years. Commercial airplane production will probably expand somewhat, depending on the general economies of the United States and many of the Free World Nations. Military aircraft purchases are controlled by the Department of Defense and will vary from year to year with no discernible trend.

Assuming a modest three percent per year growth for titanium sponge consumption, based on the 1977 consumption of 14,700 M tons (16,200 S tons), consumption of titanium ingots would be about 29,000 M tons (32,000 S tons) in the year 2,000. Production in the year 2,000 will be assumed to be the same as consumption.

Reserves and Resources

Rutile concentrates containing about 95 percent of titanium dioxide are the source of titanium metal. There is only one producer of rutile in the United States. Consequently, we depend almost entirely on imported rutile to satisfy our demands. In 1977, 89 percent of the rutile consumed was used in the manufacture of titanium dioxide pigments, about eight percent in miscellaneous applications which include metal and glass fibers, and three percent in welding rod coatings. Ilmenite concentrates containing about 50 percent titanium dioxide are not suitable as a source of titanium tetrachloride because of their low grade.

The United States has limited rutile deposits but large deposits of ilmenite. The large resources of rutile are in Australia, Brazil, and India. Our principal import sources are Australia, Japan and India.

Attempts have been made to upgrade ilmenite to "synthetic rutile". This can be done by lowering the iron oxide content by chemical or by physical concentration. Reasonably acceptable material has been produced, however titanium metal producers have been reluctant to use it because it may not be as good technically and economically as natural rutile in their chlorinators.

Continued reliance on imported rutile could be detrimental if such suppliers were cut off, or if prices become too high. Therefore, continued development of processes to upgrade ilmenite to a satisfactory material that can be readily chlorinated is needed.

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(3) Sverdrup, H. V., Johnson, W. M., Fleming, R. H., "The Oceans", Prentice Hall, New York (1942) p. 176.

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TECHNOLOGY OF MAGNESIUM

Introduction

The principal processes by which primary magnesium can be produced are: (1) fused-salt electrolysis of $MgCl_2$; (2) silicothermic reduction of calcined dolomite (dolime-$CaO.MgO$); and (3) carbothermic reduction of MgO. There are two distinct electrolytic processes in use: (1) the Dow seawater process(A1,A2,A3) using partially dehydrated cell feed, $MgCl_2.1.5H_2O$; and (2) the process developed in Germany by I.G. Farbenindustrie(A4,A5,A6) which requires perfectly anhydrous $MgCl_2$ as cell feed. The silicothermic process using ferrosilicon as the reductant, was developed in Canada as a commercially viable process by L. M. Pidgeon(A7,A8,A9). It was a batch process using a relatively small externally-heated reactor; two different versions of it are now in use. The Magnetherm process developed in France(A10) uses a fluid-slag continuous reactor with a batch-type magnesium condenser. The Amati process, used at Bolzano, Italy, has not been described in the literature but is known to be a batch process using an internally-heated reactor much larger than the Pidgeon reactor. The carbothermic process was developed in Austria by Hansgirg. A detailed analysis of operating variables and costs was made by the U.S. Bureau of Mines(A11). All three processes were used in the USA and various other countries to meet the inordinately large demand for magnesium during World War II. Following the war the demand dropped precipitously and competitive forces competely eliminated the use of thermal reduction processes in the USA for many years.

The Dow Seawater/Electrolytic Process

The Dow Chemical Company operates in Texas the largest primary magnesium producing facility existing in the entire world. The particular site was selected for a number of reasons: (1) availability of a long-term supply of low-cost natural gas for power generation; (2) availability of a large supply of oyster shells as a source of CaO for precipitating $Mg(OH)_2$ from seawater; (3) coastal geography that permitted disposal of spent seawater economically without diluting the intake supply; and (4) availability of large supplies of other needed process materials.

A schematic flow diagram of the Dow seawater/electrolytic process is shown in Figure A1. This is taken from USBM Report(B18) and contains the energy use for each operation. The energy will be discussed later in the report. The plant was originally designed to operate on calcined oyster shells from Galveston Bay as the precipitant for $Mg(OH)_2$ and for many years it operated alternately on oyster shells or caustic soda depending on the chlorine/caustic soda balance in the rest of the Dow Texas plant and in the national economy. However, today restrictions for ecological reasons have been imposed on the harvesting of oyster shells from Galveston Bay and their use has been abandoned in preference for dolime (calcined dolomite).

Currently the principal raw materials for this process are seawater, dolomite, salt, and fuels. Seawater is delivered to the plant by 268,000 liter (71,000 gal)/min pumps through suitable screens to remove fish and debris along an earthen flume that runs the width of the plant. Crushed dolomite is calcined at 1000-1100° C in 2.9 meter (9.5 ft) diameter, 80.8 meter (265 ft) long horizontal rotary kilns. The white-hot dolime is converted to milk of dolime in a rotary slaker and mixed under vigorous agitation with seawater in a concrete flocculator. The degree of agitation and control of pH are critical factors in this operation in order to produce an easily filterable $Mg(OH)_2$ product and to prevent the co-precipitation of $B(OH)_3$ which would be carried through to the electrolytic cell and drastically reduce its operating efficiency.

The limed seawater then goes to 152 meter (500 ft)-diameter Dorr settling tanks from which a 20 percent $Mg(OH)_2$ slurry is harvested and the spend seawater overflows into peripheral launders for subsequent waste disposal. The magnesium hydroxide slurry is filtered, diluted to 50 percent slurry and neutralized with HCl to produce a 35 percent solution of $MgCl_2$. This is then concentrated to 50 percent by evaporation, spray dried at 171° C (340° F) and finally dried in air on shelf driers from which it emerges at 449° C (840° F) as a free-flowing granular solid. It has the approximate composition $MgCl_2.1.5H_2O$ and goes directly to the electrolytic cells.

The Dow Cell is a large steel pot about 1.5 meters (5 ft) wide 1.8 meters (6 ft) deep and 4.0 meters (13 ft) long, externally-fired in a refractory-lined setting. Twenty-two graphite anodes 20 cm (8 inches) in

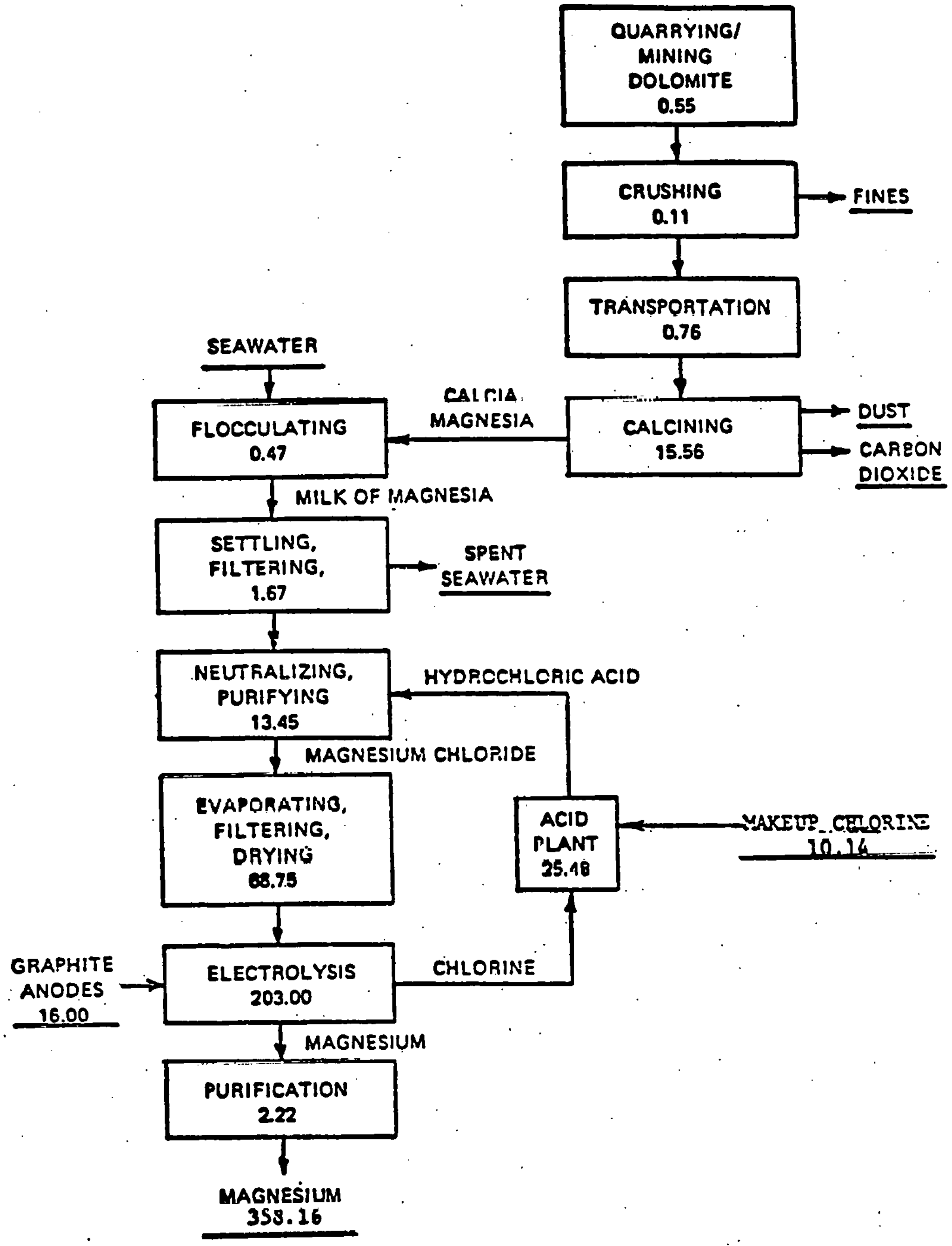

FIGURE A1. PROCESS AND ENERGY FLOWSHEET FOR THE DOW SEAWATER/ELECTROLYTIC PRODUCTION PROCESS (Units are 10^6 Btu/S ton Mg) diameter by 2.7 meters (9 ft) long are suspended through an arched refractory cover in each cell. The steel pot and the steel baffles around each anode act as the cathode. The granular cell feed is introduced into the top of the cell continuously except during metal removal. The fused-salt electrolyte consists of approximately 20 percent $MgCl_2$, 20 percent $CaCl_2$, and 60 percent NaCl and is operated at a temperature between 700° C (1290° F) and 720°C (1330° F) maintained by controlled external gas-firing. Twenty-seven cells are housed in one building and identical buildings are arranged in groups of four each. Thus, a pot line consists of 108 cells of which normally 100 operate in series at any one time. The pot line is serviced by an approximately 100,000 ampere DC circuit with a potential of about 6.3 volts per cell. Cathode current efficiency is about 75 to 80 percent and the DC power requirement is about 18.5 kwh/kg (8.4 kwh per pound) of magnesium produced. During operation molten magnesium is liberated at the cathode, and chlorine gas at the anode. The magnesium rises to the surface of the electrolyte and is directed by inverted troughs to a storage well in front of the cell from which it is pumped into collecting crucibles several times each day, and cast into 9 kg (20 lb) ingots or 18 kg (40 lb) pigs. In addition to chlorine, the effluent gases also contain HCl and water vapor. They are all recycled through the HCl acid plant where an additional 0.5 kg of chlorine per kilogram of Mg produced is added to yield the needed HCl to carry on the process. Chlorine is produced from salt in the Dow diaphragm cells. Thus, the Dow process is a consumer of chlorine. The water in the cell feed causes the corrosion of the graphite anode which may be of the order of 100 kg/M ton (200 lb/S ton) Mg. Total energy consumed and estimated production costs are discussed in a later section.

Anhydrous $MgCl_2$ Electrolytic Process

With the exception of The Dow Chemical Company all other electrolytic magnesium producers use the I.G. Farben process or some modification of it. Modifications of both the feed preparation and the cell are in use. The process was developed in Germany during the twenties and plants using it operated in Bitterfeld (in the Eastern Zone) throughout World War II, at the end of which all magnesium production ceased in that country. It is believed that most of the Bitterfeld plant was relocated in Russia. The critical step in this process is the dehydration of $MgCl_2.6H_2O$. It is relatively easy to proceed to the dihydrate but beyond that special precautions must be taken to prevent the formation of MgO and $MgOCl_2$. I.G. Farben obviated these problems by devloping in the mid-twenties a process for direct chlorination of MgO. The flow diagram for this process is shown in Figure 2. The process needs as its principal raw material a caustic-calcined form of magnesium oxide. In the original process, as developed in Germany, this was obtained by calcining magnesite ($MgCO_3$) at an appropriate temperature to produce the reactive form of MgO. Today, as the process is used by Norsk Hydro, $Mg(OH)_2$ is precipitated from seawater with dolime in the same manner as described for the Dow Texas plant. The $Mg(OH)_2$ is calcined to MgO, mixed with powdered coal and binders, and briquetted. Chlorination is carried out in vertical shaft furnaces electrically heated with the temperature at about 1100-1200° C (2010-2190° F). The resulting anhydrous magnesium chloride is tapped from the bottom of the furnace at about 800-850° C (1470-1560° F) and delivered directly to the electrolytic cells. As shown in the flow diagram, chlorine gas from the magnesium cells is recirculated in the plant to produce $MgCl_2$ but additional chlorine is needed to the extent of 0.5 kg per kilogram of magnesium produced. Thus, this process is also a chlorine consumer.

In the USA, both NL Industries on the Great Salt Lake in Utah and American Magnesium Company in Snyder, Texas, are using the anhydrous magnesium chloride process, but with the difference that the starting material is already a magnesium chloride brine (bittern). In the case of NL Industries their raw material source is the Great Salt Lake where natural evaporation has already increased the $MgCl_2$ concentration to about 7 percent in contrast to seawater where it is 0.5 percent. American Magnesium uses an underground brine running between 2.5 and 5.0 percent $MgCl_2$. The flow diagram for producing magnesium from bitterns prepared by Stein(A12), shown in Figure A3, presents a little more detail than that given for the NL Industries plant by Bauer(A13). The bitterns are concentrated by solar evaporation in large hold ponds almost to saturation (30-36 percent $MgCl_2$). The concentrated brine is reacted with

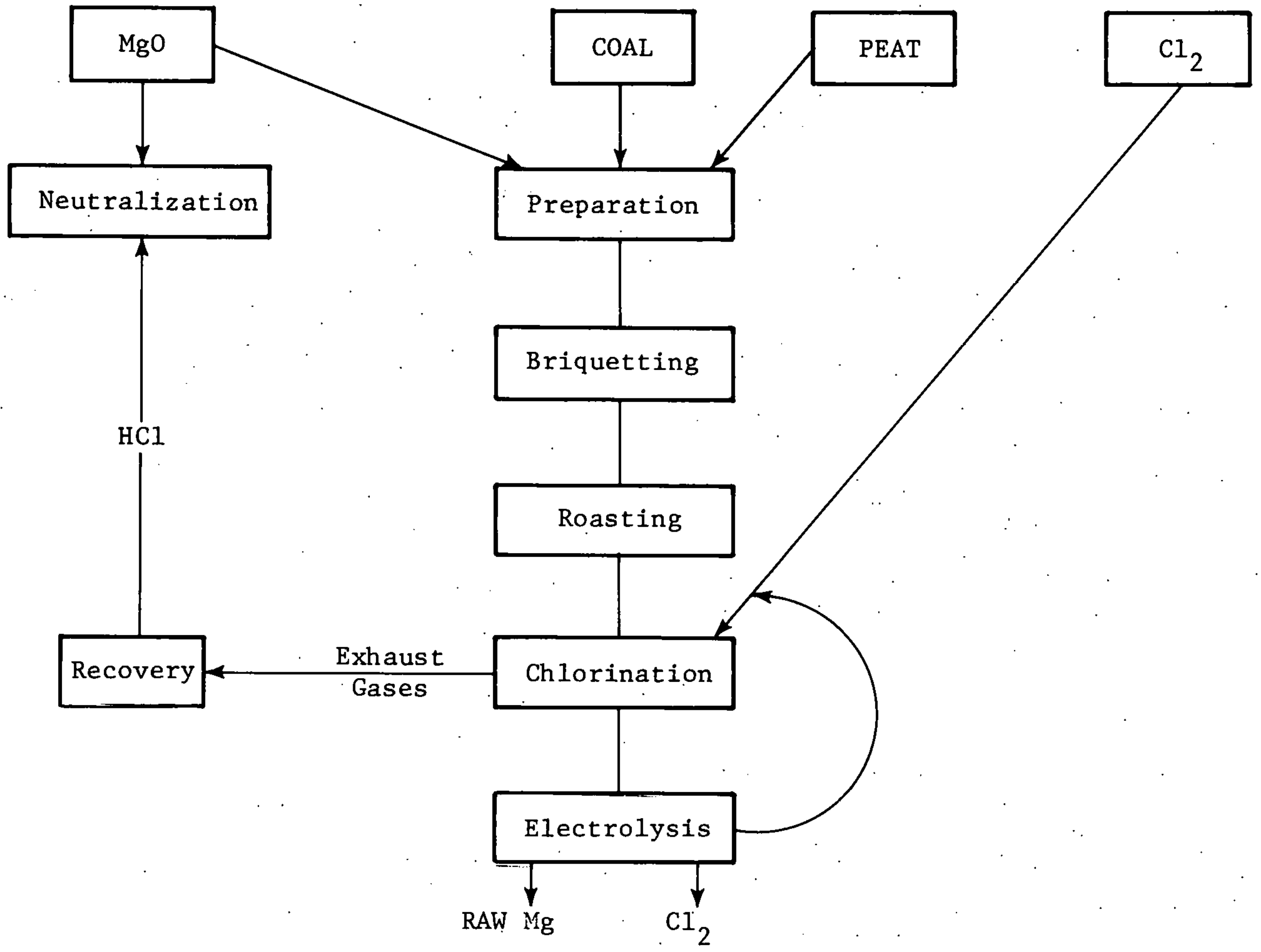

FIGURE 2. I. G. FARBEN ANHYDROUS $MgCl_2$ ELECTROLYTIC MAGNESIUM FLOW DIAGRAM

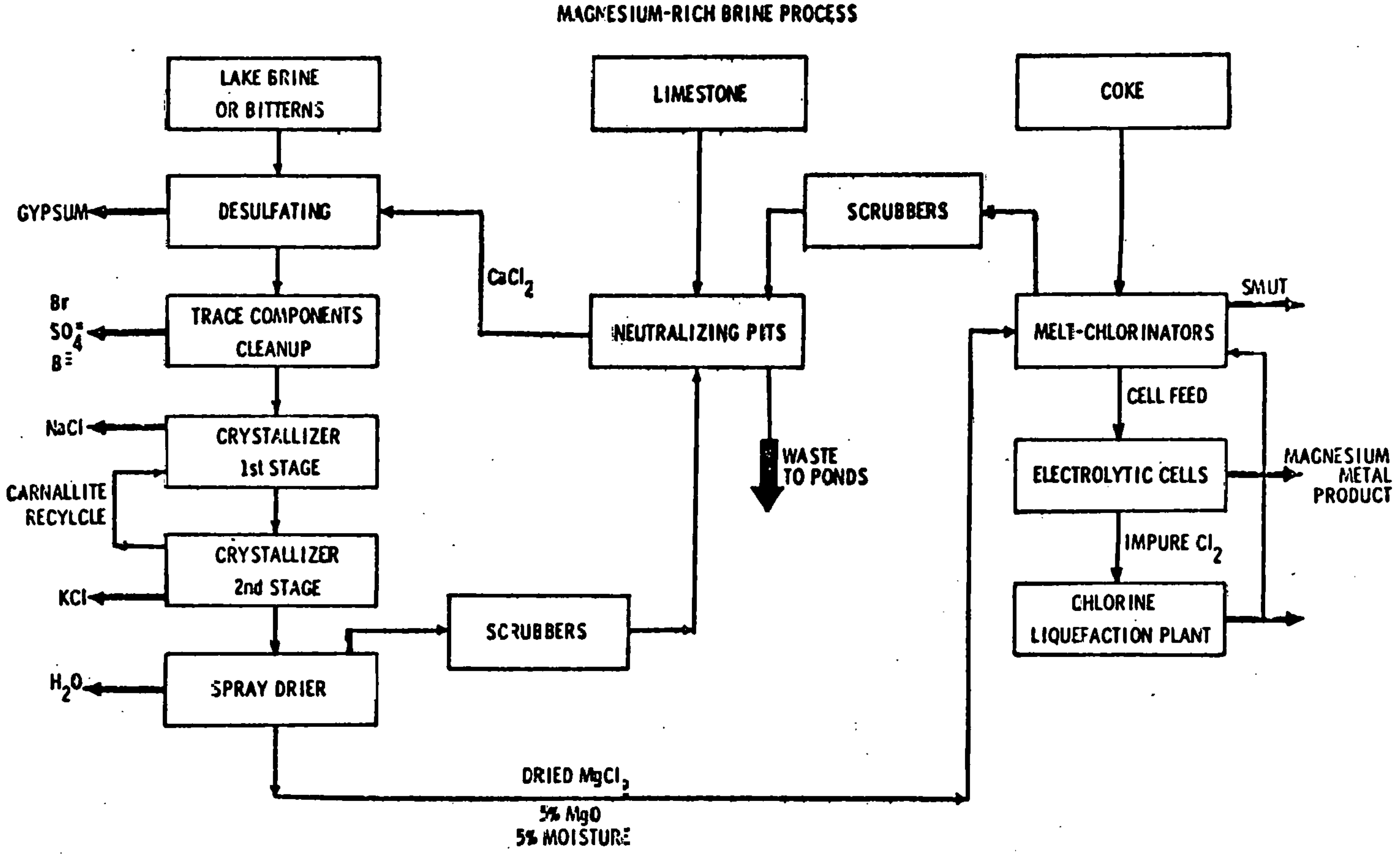

FIGURE A3. FLOW DIAGRAM FOR MAGNESIUM-RICH BRINE ELECTROLYTIC PROCESS

$CaCl_2$ to remove sulfate ion, and then in a series of ion-exchange reactors the small amounts of bromine and boron and the last traces of sulfate ion are removed. The latter step is optional and its use depends on the extent to which these impurities are present and what other means are later provided to counteract their deleterious effects. The diagram presented by Bauer does not provide this step. In a two stage crystallizer, the KCl and NaCl values are recovered separately, and the mother liquor from the second stage is fully saturated $MgCl_2$ solution (36 percent). This is heated to about 93° C (200° F) and conveyed into large vertical shaft spray driers from which the product is $MgCl_2$ containing about 5 percent H_2O, 5 percent MgO, and about 5 percent KCl + NaCl. This product is fused in the melt-chlorinator where it is reacted with chlorine in the presence of carbon to completely remove the H_2O and MgO. The fused, fully anhydrous $MgCl_2$ containing about 5 percent KCl + NaCl goes directly to the electrolytic cells. The off gases from the spray drier and the melt-chlorinator contain HCl gas and are used to react with limestone to produce the $CaCl_2$ needed earlier in the process.

Norsk Hydro has also announced(A14) a bitterns process with some modification from that described above. Their raw material is bitterns imported from Germany and is a by-product of the potash industry. The bitterns are concentrated and de-sulfated as described above. Bromine is removed by passing chlorine through the $MgCl_2$ saturated solution, and boron is removed by an undisclosed process. The saturated $MgCl_2$ solution is converted to solid $MgCl_2$ by spray drying as described above. In the final step, however, the residual moisture is removed by drying in an HCl gas atmosphere at an undisclosed temperature. The effluent HCl gas containing moisture is dried and recirculated.

The I.G. Farben electrolytic cell used with anhydrous $MgCl_2$ differs from the Dow cell in that it has been much smaller, it is refractory-lined and it has no provision for external heating. A schematic drawing of this cell is shown in Figure 4. The original I.G. Farben cell had three carbon anodes and three pairs of steel cathodes as shown in the sketch. To increase production capacity the size was later increased to four carbon anodes; this is the size of the cells currently in use by Norsk Hydro operating at 62,000 amps. Today, cells in Russia (and it is believed the NL Industries cells)

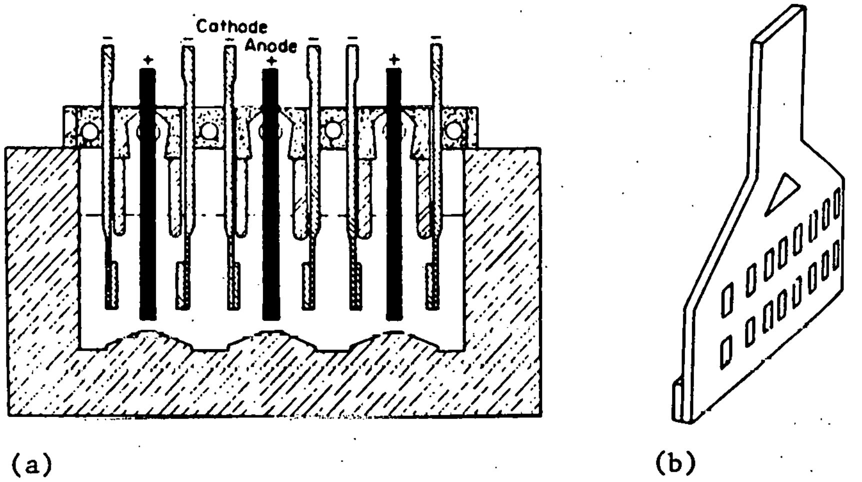

FIGURE A4. THE I.G. FARBEN ELECTROLYTIC CELL

(a) Arrangement of Anodes

(b) Steel Cathode

have 5 anodes and operate at 100,000 amps. A very important feature of this cell design is the refractory semi-wall extending from the roof of the cell to a short distance below the surface of the electrolyte and separating the space above the electrolyte into an anode chamber (box) and a cathode chamber. Materials of construction, design, and life of this semi-wall are critical factors in the operating costs of this cell. Operating conditions are critically adjusted so that the chlorine released at the carbon anode collects in the anode box and the magnesium metal collects in the cathode chamber from where it is directed to a collection trough in front of the cell for periodic removal by pumping or suction. The composition of the electrolyte in this cell is 12 percent $MgCl_2$, 35 percent $CaCl_2$, 28 percent NaCl, and 25 percent KCl. Hoy-Petersen(A15) emphasizes the importance of purity of the anhydrous $MgCl_2$ cell feed and that impurities should not exceed the following amounts: 0.2 percent C, 0.001 percent B, 0.1 percent H_2O, 0.05 percent SO_3, 0.04 percent Fe, 0.005 percent Ti and 0.1 percent $MnCl_2$. The cell is usually operated at about 750° C (1380° F) and in the present large cells current efficiency approaches 90 percent and energy consumption has been reduced to about 15 kwh/kg (7.0 kwh per lb) of magnesium. The freedom from water of the feed also contributes to a low anode consumption, about 0.02 kg per kg of magnesium and to the liberation of chlorine free from the HCl and water vapor.

An important economic advantage of the bitterns anhydrous $MgCl_2$ electrolytic process is the production of by-product chlorine for sale. Theoretically, 2.9 kg of chlorine are produced with every kilogram of magnesium. Bauer(A16) states that at the NL Industries plant the available chlorine for sale is 1.78 kg per kg of magnesium because of the internal consumption of chlorine in the melt-chlorinator. However, Hoy-Petersen(A14) expects that internal usage will be minimal and as much as 2.7 kg of chlorine will be available either for direct sale or for production of chlorinated hydrocarbons in other adjoining Norsk Hydro plants. The complex being planned at Mongstad, Norway, will use the chlorine to produce polyvinyl-chloride.

Silicothermic Magnesium Process

Current electrolytic processes require a magnesium chloride feed. With the Dow seawater process this requires conversion to chloride of all MgO precipitated out. Even where a chloride salt is the raw material, e.g., bitterns, conversion to feed is more than a matter of simple evaporation. Processes that can use magnesium oxide as a feed material avoid the complexities of preparing chloride feed materials and simplify the process in this regard. They also make possible the direct use of calcined dolomite (dolime). The silicothermic process and the magnetherm modification of this process uses magnesium oxide feed, but also requires ferrosilicon that must be separately manufactured.

The silicothermic process as developed by Pidgeon and first commercialized in Canada uses dolomite and ferrosilicon as its primary raw materials. It can be considered that ferrosilicon really is the source of energy needed to reduce magnesium oxide according to the equation:

$$2MgO + (Fe)_xSi \rightarrow 2Mg\uparrow + xFe + SiO_2 \quad .$$

The flow diagram for this process is shown in Figure A5. Dolomite is calcined in a horizontal rotary kiln to produce dolime at 1300-1400° C (2370 to 2550° F) to a dead-burned condition. The dolime is ground, mixed with pulverized ferrosilicon (Fe-Si, 80-85%) and briquetted.

The success of the Pidgeon process depends very much on the design of the retort in which the reaction takes place. Typically the retort has 25 cm (10 inches) internal diameter, 3.8 cm (1.5 inch) wall thickness, and 25 cm (10 feet) of length and is made of either 35Ni-15Cr or 28Ni-12Cr stainless steel. The retorts are set in furnaces with about 50 cm (2 feet) of length extending outside the furnace which forms the cold zone or condenser where the magnesium is collected. A steel liner is placed at the cold end for easy removal of the muff. Dolime/ferrosilicon briquettes are charged, and while they are being heated, vacuum is drawn on the retort reducing the pressure to about 0.1-0.2 mm. The reaction usually takes place at 1150-1175° C (2100-2150° F) and the cycle time is about 9 hours. Each batch produces 20 to 25 kg (44 to 55 lb) of magnesium, which upon removal is remelted and

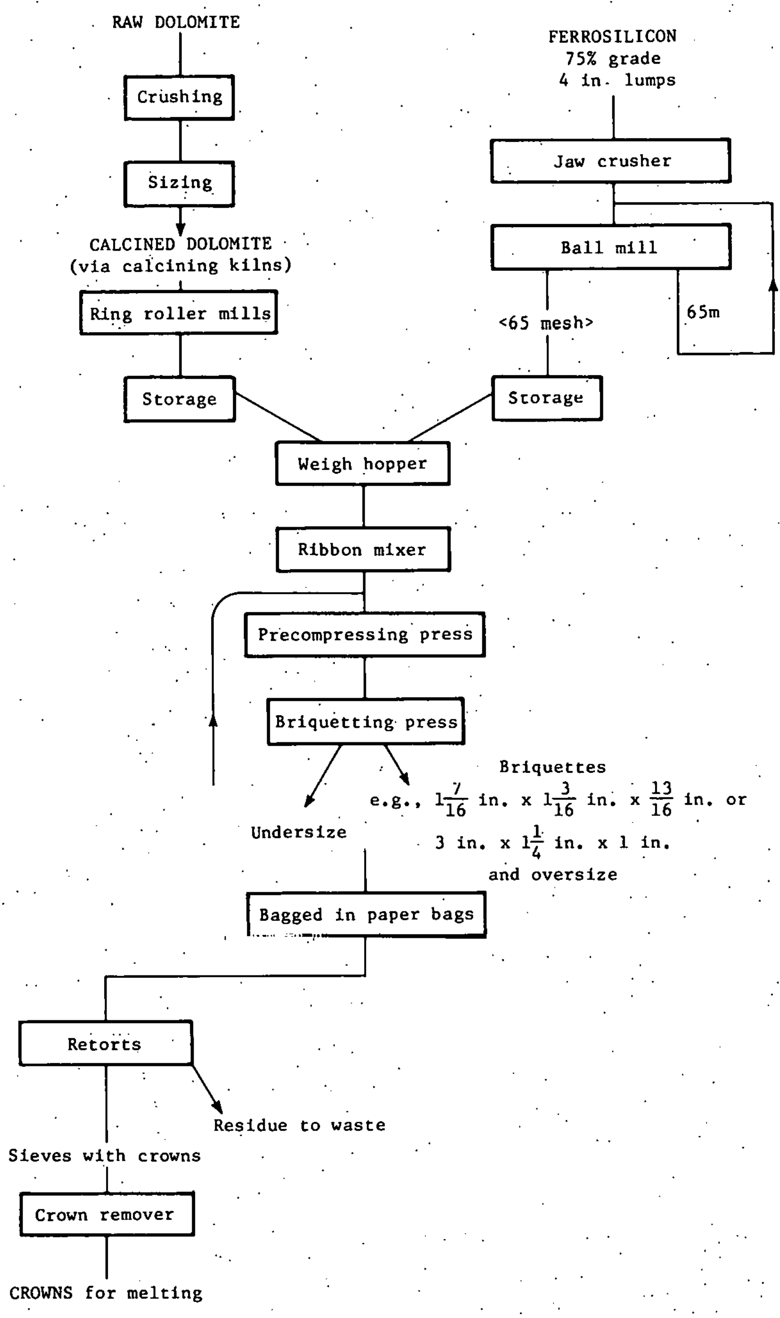

FIGURE A5. PIDGEON SILICOTHERMIC MAGNESIUM PROCESS FLOW DIAGRAM cast into pigs. Silicon efficiency has been reported as averaging about 65 percent. The iron does not enter into the reaction. The SiO_2 formed in the reaction combines with the CaO in dolime to form Ca_2SiO_4. Product purity is equal to or better than the electrolytic grade. The process is described in detail based on the operation of the wartime government plants in Reference A16.

The Magnetherm Process

The magnetherm process is an adaptation of the silicothermic process to provide a reactor that operates semi-continuously(A10). The essential features are shown by the flow diagram in Figure A6 and the sketch of the reaction furnace in Figure A7. As in the Pidgeon process, dolomite and ferrosilicon are the principal raw materials. In addition an 85 percent grade of alumina is added to reduce the melting point of the CaO/SiO_2 (Ca_2SiO_4) slag resulting from the reaction from about 2130° C to 1500° C (3860 to 2730° F) and thus provide a liquid slag in which the reaction is carried out. About 15 percent alumina in the slag is needed to achieve this. Dolomite is calcined at 1300-1400° C (2370 to 2550° F) in horizontal rotary kilns and transferred hot to a storage bin from which it flows directly into the furnace at a temperature no less than 600° C (1100° F). Two other bins directly above the furnace contain the alumina and pulverized ferrosilicon. The original reactors built and operated by Pechiney-Ugine-Kuhlmann in Marignac, France (Figure A7) were 25 cm (10 feet) in diameter and 24.7 cm (9-3/4 feet) high. The reactors are built in three basic sections: (1) the arched roof; (2) the reactor itself; and (3) the condenser. The reactor and the roof may either be flanged together or preferrably welded. The roof is lined with a high-temperature cement and further insulation. The choice of a lining for the reactor proved to be a difficult problem because of the high temperature involved and the reactivity of the slag. Tightly fitted carbon blocks were finally selected and have been giving excellent performance. A somewhat more porous carbon block forms the bottom of the reaction chamber. The furnace lining acts as one electrode and the other electrode is a water-cooled copper tube with a graphite tip coming in through the roof and submerged in the slag.

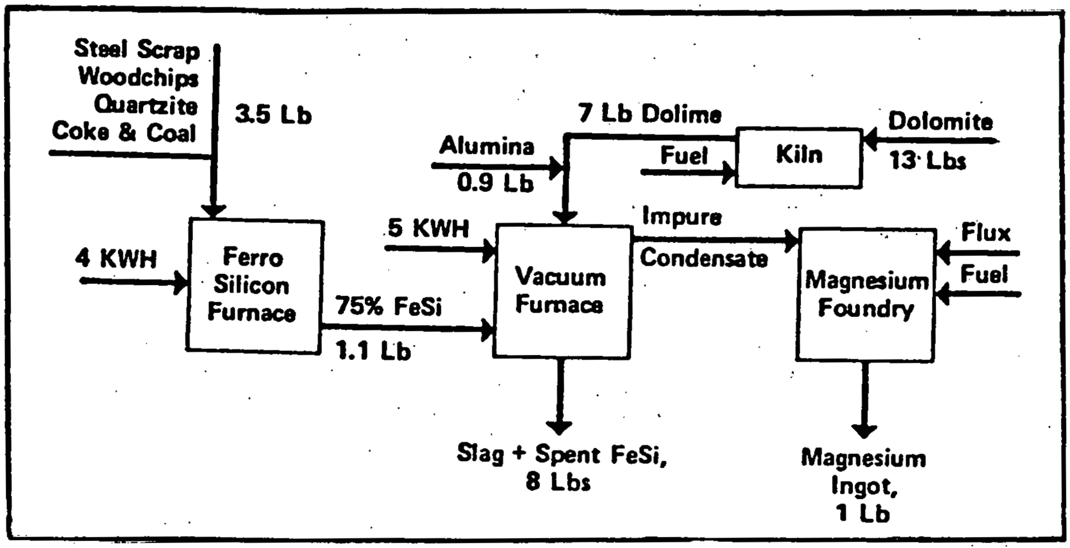

FIGURE A6. MAGNETHERM SILICOTHERMIC MAGNESIUM PROCESS FLOW DIAGRAM

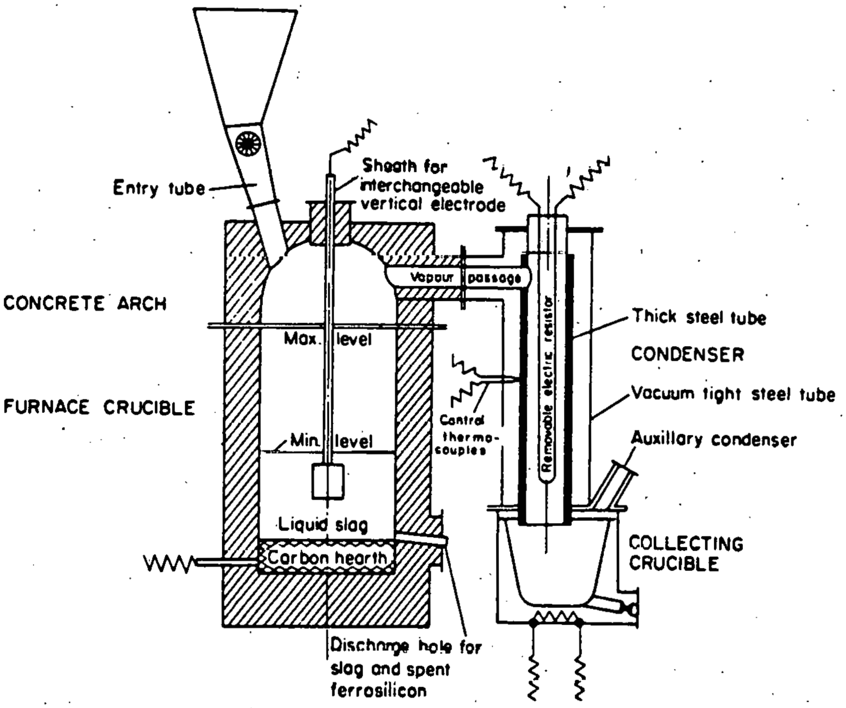

FIGURE A7. MAGNETHERM REACTOR FOR REDUCING DOLIME WITH FERROSILICON USING A LIQUID SLAG

The furnace is heated by electrical resistance with the current introduced through the carbon hearth passing through the molten slag to the electrode submerged in the slag from the roof. The condenser is operated at a temperature of 650 to 700° C (1200 to 1290° F) so that the magnesium vapors issuing from the exhaust passage in the roof are condensed as a liquid and collect in the crucible attached at the bottom. The metal collected in the crucible is maintained at a temperature just below the melting point in order to conserve its sensible heat but still minimize evaporation. The entire system including the raw material bins is run under a vacuum of 25 mm Hg but is capable of being tested down to 5 mm Hg.

A run starts with the surface of the molten slag at the minimum level shown in the sketch in Figure A7. The ferrosilicon is introduced in a continuous stream whereas the dolime and bauxite are added intermittently. Variations of this have been reported and other schemes of adding the reactants are possible. The temperature of the slag and thus the temperature at which the reaction takes place is maintained at 815 C (1500° F). The alumina content of the slag is critical and is controlled by careful adjustment of the rate of introduction. About 1.05 kg of ferrosilicon are used for each kilogram of magnesium produced. When the slag reaches the maximum level, the run is stopped, and the furnace brought to atmospheric pressure, and the slag tapped. The slag and residual ferrosilicon, which is also molten at this temperature, differ sufficiently in density so that they may be separated by decantation, as shown. The residual ferrosilicon is recirculated after grinding. The crucible of condensed magnesium is disconnected from the furnace, removed to the cast-house, the metal refined, and cast into pigs. It is reported that energy required for the reaction is about 10.4 kwh/kg (4.7 kwh/lb) of magnesium produced in addition to the energy represented by the ferrosilicon. The size furnace described here is capable of producing about 910 M tons (1,000 S tons) annually. Furnaces now installed in France produce about 1496 M tons (1,650 S tons) and the furnaces installed in the new Alcoa plant in the USA have an annual capacity of about 2450 M tons (2700 S tons). An important advantage of the Magnetherm process over the Pidgeon process is the semi-continuous operation and the much larger batch sizes which reduce labor cost and improve productivity. A long-term operation of the new

Alcoa plant is needed to demonstrate more reliably the competitive position of this process compared to electrolytic processes. It is, however, more suited for installations of capacity less than 27,200 annual M tons (30,000 annual S tons).

Energy Consumed in Magnesium Production

The standard free energy of formation of MgO is -136.17 kcal/mole (20.1 x 10^6 Btu/S ton Mg) corresponding to 2.95 volts. Standard enthalpy of formation is -143.84 kcal/mole (21.3 x 10^6 Btu/S ton Mg). Thus, the reduction of MgO carried out at the theoretical potential is endothermic and 7.67 kcal/mole of thermal energy must be supplied to maintain a constant temperature.

The standard free energy of formation of $MgCl_2$ is -143.77 kcal/mole or 5.92 x 10^6 Kcal/M ton (21.3 x 10^6 Btu/S ton) Mg corresponding to 3.12 volt. If power conversion losses are 10 percent and fossil energy for electrical production is 2646 Kcal (10,500 Btu)/kwh, the minimum electrical power for reduction at 100 percent current efficiency is 7639 kwh/M ton (6930 kwh/S ton) Mg or 20.21 x 10^6 Kcal/M ton (72.76 x 10^6 Btu/S ton) Mg.

The commercial production of primary magnesium by current technology is an energy-intensive operation. Magnesium plants built in the past were usually located in geographic areas where large amounts of fuel (natural gas, oil, hydropower) were available at the lowest possible cost. There was little concern about the actual amount of total energy consumed in the process. In fact, not until the last few years has there even been a published detailed analysis of the energy consumption in the process. An early attempt in this direction was made by Bravard, Flora and Portal(A17) at the Oak Ridge National Laboratory under the sponsorship of the National Science Foundation. Their study was limited and did not include several factors contributing to the total energy consumed. The results are summarized in the following tabulation.

Energy Consumed to Produce Magnesium by the Seawater/Electrolytic Process According to ORNL(A17)

	10^6 Kcal per M ton (10^6 Btu per S ton) of magnesium metal							
	Thermal		Electrical		Total		kwh/M ton Mg (kwh/S ton Mg) Electrical	
Seawater Treatment	3.78	(13.60)	1.23	(4.42)	5.01	(18.02)	464	(421)
Evaporation	42.66	(153.58)			42.66	(153.58)		
Electrolysis			42.68	(153.64)	42.68	(153.64)	16125	(14,630)
Acid Recovery	3.97	(14.28)			3.97	(14.28)		
TOTAL	50.41	(181.46)	43.91	(158.06)	94.32	(339.52)	16590	(15,050)

A more detailed analysis of the energy consumed in the Dow seawater/electrolytic process has been caried out in 1974/1975 for the Bureau of Mines by Battelle's Columbus Laboratories(A18, A19) as part of a broad study on "Energy Use Patterns in Metallurgical and Nonmetallic Mineral Processing", which covered 83 metals and other important nonmetallic materials. The results of this analysis are shown in Table A1 and on the energy flowsheet in Figure A1, where the energy associated with each major step in the process is clearly identified. It will be noted that the analysis includes not only the obvious consumption of natural gas, electricity, oil, fuel, etc., - but also the energy equivalents of explosives, consumable electrodes, make-up chlorine, etc. Standard factors were used for converting all materials and energy quantities consumed into Btu per short ton of magnesium produced and the 2646 (10,500) factor for converting kwh of electrical energy to Kcal's (Btu's) of fossil fuel equivalent. The energy consumed from this analysis is summarized in the following tabulation.

TABLE A1. ENERGY TO PRODUCE MAGNESIUM BY THE DOW SEAWATER/ELECTROLYTIC PROCESS

	Unit	Units Per Net Ton of Magnesium Metal	10^6 Btu Per Unit	10^6 Btu Per Net Ton of Magnesium Metal *
Quarrying dolomite(1)				
Diesel fuel oil	gal	1.78	0.139	0.25
Other fuels	Btu	—	—	0.13(2)
Electrical energy	kwh	3.48	0.0105	0.04
Explosives	lb	4.34	0.03	0.13
			Subtotal	0.55
Crushing				
Electrical energy	kwh	10.40	0.0105	0.11
Transportation				
Rail (estimated 150 miles)	net ton-mile	1,140.0	0.00067	0.76
Calcining				
Electrical energy	kwh	73.8	0.0105	0.77
Natural gas	ft^3	14,790.0	0.001	14.79
			Subtotal	15.56
Flocculating				
Electrical energy	kwh	44.4	0.0105	0.47
Settling and filtering				
Electrical energy	kwh	158.6	0.0105	1.67
Neutralizing and purifying				
Electrical energy	kwh	121.0	0.0105	1.27
Natural gas	ft^3	12,180.0	0.001	12.18
			Subtotal	13.45
Evaporating, filtering, and drying				
Electrical energy	kwh	171.0	0.0105	1.79
Natural gas	ft^3	66,960.0	0.001	66.96
			Subtotal	68.75
Electrolysis				
Electrical energy	kwh	17,109.0	0.0105	179.64
Natural gas	ft^3	23,360.0	0.001	23.36
Graphite anodes	net ton	0.1	160.0	16.00
				219.00

*Short tons

TABLE A1. (Concluded)

	Unit	Units Per Net Ton of Magnesium Metal	10^6 Btu Per Unit	10^6 Btu Per Net Ton of Magnesium Metal
Acid plant				
Electrical energy	kwh	1,334.0	0.0105	14.01
Natural gas	ft^3	11,470.0	0.001	11.47
Makeup chlorine	net ton	0.49	20.7	10.14
			Subtotal	35.62
Magnesium purification				
Electrical energy	kwh	51.3	0.0105	0.54
Natural gas	ft^3	1,680.0	0.001	1.68
			Subtotal	2.22
Total				358.16

Energy Consumed to Produce Magnesium by
the Seawater/Electrolytic Process According
to Bureau of Mines - Battelle Study

	10^6 Kcal per M ton (10^6 Btu per S ton) of magnesium metal						kwh/M ton Mg (kwh/S ton Mg) Electrical	
	Thermal		Electrical		Total			
Preparation of dolime	4.43	(15.93)	0.29	(1.05)	4.67	(16.81)	110	(100)
Preparation of $MgCl_2$ cell feed	21.98	(79.14)	1.44	(5.20)	23.42	(84.34)	546	(495)
Electrolysis and Metal Refining	6.96	(25.04)	54.50	(196.18)	61.45	(221.22)	20594	(18,683)
Acid Regeneration	3.19	(11.47)	6.71	(24.15)	9.90	(35.62)	2535	(2300)
TOTAL	36.56	(131.58)	62.94	(226.58)	99.44	(358.16)	23787	(21,580)

Although the difference in total energy shown by the two analyses is small, there is a wide disparity in the distribution of energy among the major steps in the process. The Dow Chemical Company has indicated that the Oak Ridge figure is closer to their experience.

In 1974, The Dow Chemical Company had under way a major effort to reduce the energy consumed in producing magnesium(A20). A recent news release(A21) has confirmed the success of this program. Changes have been made in the design of the cell covers, in the method of manufacturing cell feed, in the acid recovery process, and in the use of graphite anodes having lower electrical resistance. The total effect of these improvements has been to lower energy consumption by about 15 to 20 percent to a level of 78 x 10^6 Kcal/M ton (280 x 10^6 Btu/S ton) of magnesium in contrast to the 94.2 - 99.5 x 10^6 Kcal/M ton (339-358 x 10^6 Btu/S ton) shown in the previous analyses. It is stated that by no later than 1985 further improvments will lower the energy consumption for producing magnesium to about 66.67 x 10^6 Kcal/M ton (240 x 10^6 Btu/S ton).

Information on the energy consumption in the bitterns/electrolytic process as reported by Bauer(A13) is presented in Table A2 and summarized in the following tabulation.

Energy Consumed to Produce Magnesium
by the Bitterns/Electrolytic Process at
NL Industries Plant

	10^6 Kcal per M ton (10^6 Btu per S ton) of Magnesium metal							
	Thermal		Electrical		Total		kwh/M ton Mg (kwh/S ton Mg) Electrical	
Preparation of $MgCl_2$ cell feed	24.24	(87.24)	6.81	(24.53)	31.05	(111.77)	2575	(2336)
Electrolysis and Metal Refining	1.06	(3.82)	44.01	(158.42)	45.07	(162.24)	16630	(15087)
Miscellaneous	-5.26	(-18.92)	13.10	(47.16)	7.85	(28.24)	4950	(4491)
SUBTOTAL	20.04	(72.14)	63.92	(230.11)	83.97	(302.25)	24157	(21915)
By-Product Chlorine Credit (1.78 M tons)					10.24	(36.85)		
NET TOTAL					73.73	(265.40)		

Energy consumption and graphite anode consumption are significantly lower in the I.G. Farben cell than in the present Dow cell. But another important factor is the credit resulting from the available by-product chlorine. According to Bauer, the NL Industries will produce 1.78 M tons of chlorine per M ton of magnesium. This compares rather unfavorably with the theoretical amount of 2.9 M tons per M ton of magnesium. The credit of 5.26 x 10^6 Kcal/M ton (18.92 x 10^6 Btu/S ton) of thermal energy taken in the energy calculation is not explained by Bauer.

The energy consumed to produce magnesium by the Magnetherm silicothermic process has been analyzed by Lugagne(A22) and is presented in Table A3. Over 40 percent of the energy consumed is represented by the

TABLE A2. ENERGY TO PRODUCE PRIMARY MAGNESIUM BY THE BITTERNS/ELECTROLYTIC PROCESS(A13)
(NL Industries, Inc.)

	10^6 Kcal/M Ton of Magnesium (10^6 Btu/S Ton of Magnesium)		
	Thermal Energy	Electrical Energy	Total Energy
Solar Evaporation	.53 (1.90)		.53 (1.90)
Brine Evaporation	12.58 (45.30)	0.05 (0.18)	12.63 (45.48)
Evaporation to 29% $MgC\ell_2$	11.12 (40.04)	0.05 (0.18)	11.17 (40.22)
Melt-Chlorination	-	6.71 (24.17)	6.71 (24.17)
Electrolysis	.20 (.72)	43.78 (157.61)	43.98 (158.33)
Graphite Electrodes	.01 (.03)	.19 (.69)	.20 (.72)
Alloying and Casting	.85 (3.07)	.03 (.12)	.89 (3.19)
Motors, Compressors, and Others	-5.26 (-18.92)	13.10 (47.16)	7.85 (28.24)
	20.04 (72.14)	63.92 (230.11)	83.97 (302.23)
Credit for By Product Chlorine 1.78 lb Cl_2/lb Mg x 20.7 x 10^6(a)			10.24 (36.85)
NET TOTAL			73.73 (265.40)

(a) Total energy to produce 1 net ton of liquified chlorine from Reference A18.

TABLE A3. ENERGY TO PRODUCE PRIMARY MAGNESIUM BY THE MAGNETHERM SILICOTHERMIC PROCESS(A22)

	Kwh per Metric Ton (Short Ton)	10^6 BTU per M Ton (S ton)
(a) <u>Ferrosilicon (75 Percent)</u>		
Quartzite: Quarrying and crushing	70 (64)	0.06 (0.22)
Transportation	57 (52)	0.05 (0.18)
Coke Breeze	4,478 (4,062)	3.85 (13.86)
Coal	3,311 (3,003)	2.85 (10.25)
Iron ore pellets	181 (169)	.16 (.56)
Soderberg paste	977 (886)	.84 (3.02)
Transportation	45 (41)	.04 (0.14)
Electrical energy (including ancillary)	26,881 (24,386)	23.12 (83.23)

ferrosilicon used in the process. A considerable amount of additional electrical energy is needed in the reduction step. The process derives a benefit from the by-product slag produced that is sold to the cement industry.

Although the Pidgeon ferrosilicon process represents a very small percentage of the total world production of magnesium, for completeness an analysis of the energy consumed in this process is included in Table A4. The Battelle study is based on information found in the Bureau of Mines report(A19) for the war time plants which did not necessarily operate at the best attainable efficiencies. This shows up as the wide disparity in the energy required to produce ferrosilicon and in the energy used in the retorting operation. Also, if the overall metal yield in these plants was lower than plants operating today, this would also increase the energy consumed per unit weight of final product. In any event, the Magnetherm process has a distinct advantage over the Pidgeon process.

Energy uses for the processes discussed are compared in Table A5. Annual energy values were calculated for each process assuming it alone was used for total annual metal production.

The high energy use for the Dow process is due to the additive effects of (1) need for external heating of the cells (2) high energy use in dehydrating $MgCl_2.6H_2O$ (3) a deficit rather than a credit for chlorine and (4) high consumption of graphite. Dow developed this process and uses it exclusively due to the traditional cheap energy on the Gulf Coast. However, the availability of cheap energy may be at an end or will end shortly. It is probably not feasible to reduce the energy of this process markedly. However, this does not exclude the use of seawater as a source of magnesium in other processes. Chlorine produced by the cell can be used in organic chlorination reactions and the HCl byproduct of chlorination used to neutralize the precipitated MgO (see previous discussion on Norsk Hydro). The total and electrical energy use are similar for the anhydrous and magnetherm processes. The choice of one or the other of these systems in the future will depend in part on which can be developed to require the lesser energy. The energy for the Pidgeon process is high probably because it suffers from the lack of size of the Magnetherm process. A retort produced 22.7 kg (50 lb)

TABLE A4. ENERGY TO PRODUCE PRIMARY MAGNESIUM BY THE PIDGEON SILICOTHERMIC PROCESS

	10^6 Kcal/M Ton Mg Metal (10^6 Btu/S Ton Mg Metal) Thermal	 Electrical	 Total
(a) From Private Communication			
Ferrosilicon Production (1.13 tons)	9.43 (33.93)	27.00 (97.16)	36.42 (131.09)
Dolomitic Lime Production	5.82 (20.96)	8.51 (30.65)	14.34 (51.61)
Briquetting Retorting, & Melting	20.64 (74.31)	-	20.64 (74.31)
TOTAL	35.89 (129.20)	35.51 (127.81)	71.49 (257.01)
(b) From Bureau of Mines-Battelle Study(19,21,22)			
Ferrosilicon Production			47.93 (172.53)
Dolomitic Lime Production			13.59 (48.91)
Briquetting, Retorting, & Melting			32.51 (117.04)
TOTAL			94.03 (338.48)

TABLE A5. COMPARISON OF ENERGY REQUIREMENTS FOR MAGNESIUM PRODUCTION PROCESSES

			Annual Energy Use***			
	Energy/Ton Metal		Yr 1977*		Yr 2000**	
Process	kwh/M ton (kwh/S ton)	10^6 Kcal/M ton (10^6 Btu/S ton)	10^9 kwh	10^{12} Kcal (10^{12} Btu)	10^9 kwh	10^{12} Kcal 10^{12} Btu
Dow Electrolytic (USBM)	23,787 (21,580)	99.50 (358.16)	2.71	11.3 (45.1)	8.50	35.5 (141)
Dow Electrolytic (ORNL)	16,589 (15,050)	94.32 (339.52)	1.89	10.3 (42.3)	5.92	33.5 (133)
Bitterns/Anhydrous Feed Electrolytic	24,157 (21,915)	73.73 (265.40)	2.76	8.4 (33.4)	8.63	26.4 (105)
Magnetherm Silicothermic	20,977 (19,030)	65.85 (237.04)	2.39	7.5 (29.9)	7.50	23.5 (93.3)
Pidgeon Ferrosilicon	-- --	94.03 (338.48)	--	10.7 (42.6)		33.5 (133)

* Assumes production of 114,300 M tons (126,000 S tons).

** Assume production of 357,000 M tons (394,000 S tons).

*** Assumes total annual production by each process.

in an 8-hour run. An obvious way to decrease the energy consumed in the bitterns process is to increase the yield of by-product chlorine. If the chlorine yield in Table A2 is increased to the level of 2.7 kg/kg Mg as anticipated by Norsk Hydro(A17), the total energy consumption would be lowered to 68.3 x 10^6 Kcal/M ton (246 x 10^6 Btu/S ton) of magnesium. Further reduction can be effected by process improvements in the evaporation step and in the electrolysis. Norsk Hydro has stated that they expect to achieve a level of energy consumption in their new process of 61-67 x 10^6 Kcal/M ton (220-240 x 10^6 Btu/S ton).

The Dow Chemical Company also has been reported to have under development a bitterns/electrolytic process which is predicted to lower total energy consumption to 38.9 x 10^6 Kcal/M ton (140 x 10^6 Btu/S ton) of magnesium(A23). The nature of the process has not been made known other than that the maximum amount of by-product chlorine will be available for sale or use in other Dow manufacturing processes. However, it can be safely assumed that at least two major technological improvements must be involved: (1) a new and highly efficient method for producing cell feed; and (2) a completely new electrolytic cell with significantly lower resistance and energy requirements. It is known from the patent literature(A26,A27) that Dow many years ago developed a bipolar cell for electrolysis of magnesium chloride. Among the many advantages of this cell the following were cited: (1) reduction of operating cell voltage (5.0 versus 6.3 volts); (2) reduction of energy consumption from 18.5 to 13.2 kwh/kg (8.4 to 6.0 kwh per pound) of magnesium; and (3) reduction of graphite anode consumption to a very low level. Although it has not been divulged by Dow, there is a very high probability that this cell or a modern and improved version of it is being used in this advanced production process. The laboratory and mini-plant work on this process can be expected in the latter half of the 1980 decade. For still further reductions in energy consumption, and much further down the road, Dow (personal communication) is working on an undisclosed process for producing magnesium that could lower the energy consumption to the level of 25 x 10^6 Kcal/M ton (92 x 10^6 Btu/S ton). However, until the basis for such an estimate is made known, it will be difficult to assess whether such a low energy process can be achieved.

The figure of 38.9 x 10^6 Kcal/M ton (140 x 10^6 Btu/S ton) Mg is drastically lower than for any of the processes discussed and some estimates are useful in determining whether it is in fact possible. A five-volt cell, as described above, operating at 90 percent current efficiency, with 10 percent power conversion loss will require 13,602 kwh/M ton (12,340 kwh/S ton) Mg or 36.1 x 10^6 Kcal/M ton (130 x 10^6 Btu/S ton) Mg at the power plant. Five volts is still substantially above the theoretical potential of 3.1 volt, leaving room for further improvements. In Table A2 preparation of an anhydrous feed requires 31.05 x 10^6 Kcal/M ton (111.77 x 10^6 Btu/S ton) Mg. However, this might be reduced by dehydration in an HCl atmosphere (Norsk Hydro) to 28 x 10^6 Kcal/M ton (100 x 10^6 Btu/S ton) Mg. If 2.9 kg chlorine can be credited/kg Mg the total credit is 16.7 x 10^6 Kcal/M ton (60 x 10^6 Btu/S ton Mg). Thus, the total energy consumption can be estimated as:

$$(130 + 100 - 60) \times 10^6 \text{ Btu/S ton Mg} = (170 \times 10^6 \text{ Btu/S ton Mg})$$
$$47.2 \times 10^6 \text{ Kcal/M ton Mg} \quad .$$

A lower overall energy use than this would require further reduction in energy for feed preparation and/or electrolysis.

Lugagne(A25) has presented concrete plans on how his company is going about reducing energy consumption in the Magnetherm Process. During the next four years they expect to reduce the consumption of all materials by no less than 10 percent and to increase the yield of magnesium by reducing losses in the condensation stage and in the melting and refining. Beyond that and over the next 10-12 years they plan to introduce more energy-efficient ferrosilicon production furnaces, to improve the dolomite and bauxite calcination stage, and to build larger and more efficient reduction furnaces. The total effect of all these improvements is shown by the comparative figures in Table A6. There is no question that the Magnetherm Process does hold promise and that the major improvements anticipated by Dow in the bitterns process will need to be made to compete with it in energy consumption.

In summary, it can be stated that the producers of primary magnesium are aggressively seeking improvements in the processes for producing primary magnesium. A major portion of available research funds are committed

TABLE A6. ENERGY CONSUMPTION TODAY AND IN 1990 IN THE MAGNETHERM SILICOTHERMIC PROCESS(A25)

	10^6 Kcal/M Ton of Magnesium (10^6 Btu/S ton) of Magnesium	
	Today	1990
Ferrosilicon	32.51 (117.04)	24.39 (87.78)
Dolomite, Bauxite, etc.	0.58 (2.08)	0.52 (1.86)
Calcination of Dolomite and Bauxite	11.48 (41.33)	8.00 (28.80)
Electrical Energy in Reduction	31.23 (112.42)	25.80 (92.88)
Melting and Refining	2.21 (7.97)	2.21 (7.97)
Subtotal	78.02 (280.84)	60.92 (219.29)
Credit (Slag and Residual FeSi)	12.17 (43.80)	10.95 (39.40)
Net Total	65.85 (237.04)	49.97 (179.89)

to lowering the total energy required to produce magnesium. However, the impetus for development has been and will be economic. Energy plays a more dominant role in development now than previously because of its increasing cost.

Comparison of Electrolytic Production of Magnesium with Production of Aluminum

Magnesium and aluminum are both active metals produced in quantity by electrolysis. The predominant method for aluminum production is the Hall-Herault process using a fluoride electrolyte and a cell feed of purified aluminum oxide. However, Alcoa has undertaken a considerable development of a method using a chloride bath and an anhydrous aluminum chloride feed. Lewis has reviewed energy use for both technologies(A28). Strelets(A29) has provided an exhaustive review of magnesium technology. Table A7 is a compilation of information from these two sources allowing direct comparison of parameters and results. Information on magnesium is not necessarily consistent with previous information given. The 5.5 volts for the magnesium cell seems low for present commercial cells; 6.3 volts has been used previously as more realistically reflecting actual operating cells. The theoretical cell voltage previously reported was 3.16 volt, based on free energy of formation at 25° C for undiluted $MgCl_2$. Strelets claims to have measured 2.735 volts indicating that there may be further room for improvement before a theoretical value is reached.

Cell amperes and current efficiencies are similar for aluminum and magnesium. The major reason for differences in the cell voltage of the Hall-Herault and magnesium process is the higher (1.0 volt or more) decomposition voltage for the magnesium cell. The lower voltage for the Alcoa process would most likely be due to a lower decomposition voltage and lower IR drop through the electrolyte due to the closer electrode spacing possible. The Alcoa aluminum process and the anhydrous magnesium process both use insoluble graphite anodes, allowing some precision in electrode spacing as compared to the Hall-Herault process or the Dow magnesium process. However, the Alcoa process allows closer electrode spacing than the anhydrous magnesium

TABLE A7. COMPARISON OF ELECTROLYSIS PARAMETERS AND RESULTS FOR ALUMINUM AND MAGNESIUM ELECTROLYSIS CELLS

	Process		
	Hall Herault	Alcoa Chloride	Anhydrous Magnesium
Size, kiloamperes	150	150	100
Current Efficiency	88	86	86
Voltage Drop in Cell			
Anode Bus-Electrolyte	0.7		1.08
Cathode Bus-Electrolyte	0.45		0.43
Through Electrolyte	1.27		1.3
Rev. Potential & Polarization	1.8		2.75
Total	4.22	3.1	5.55
Anode Current Density (amp/cm^2)	0.8 to 1.0	0.8 to 2.3	0.5 to 0.6
Temperature, °C	970	700	700
Electrode Spacing, cm	4.5 to 5.1	1.27 to 1.9	5
Theoretical Voltage	1.1		2.75
Theoretical Energy Use, kwh/kg	6,547		12,108
Actual Energy Use, kwh/kg	28,542	21,454	28,414
Energy Efficiency, percent	22		43

process, probably because of the easier separation of aluminum and chlorine (gas up, metal down) than the magnesium process (gas and metal up). It seems possible, then, that closer spacing could be achieved in the magnesium cell by use of the lighter-than-metal electrolyte. This possibility is further considered under Opportunities for Development. Taking the calculated energy efficiencies at face value is misleading, since a higher reversible potential gives a higher energy efficiency even if other voltage losses are equivalent. The Hall-Herault cell operates at 3.1 volts over the theoretical voltage and the magnesium cell 2.8 volts over theoretical. Therefore the two cells are similar in practical efficiency with a good possibility that the voltage of the magnesium cell can be reduced by at least one volt. With such a reduction its practical efficiency would probably correspond to that of the Alcoa chloride process for aluminum.

Opportunities for Development in Magnesium Production Processes

Two areas of the electrolytic process are important to the efficient and economical operation of these cells. One involves critical materials of construction and the second the cell design to encourage separation of cell products to prevent their recombination.

Materials of Construction

The Dow process was established on the Gulf Coast when energy and raw materials in the area were economic, even though its energy use is substantially higher than that of the other commercial processes. Some engineering improvements are being made as previously described to reduce energy. However, the presence of water in the feed, causing graphite corrosion and need for an adjustable anode, need for externally heating the cell, etc., make substantial energy reduction difficult. Assuming that the Dow process will become obsolete due to its high energy requirements, the anhydrous cell (Figure 4) will be the norm for present designs. This cell is constructed of ceramic materials except for the steel cathode and a container surrounding the outside ceramic walls. The short-lived component in the system is the ceramic separator (called a semi-wall) between anode and cathode. This wears away, becoming thinner and shorter. As this happens the chlorine and molten magnesium which rise to the top of the cell are less efficiently separated, recombination occurs, and current efficiency decreases. Then the cell must be shut down and rebuilt, even though most of the cell components, i.e., cathodes, anodes, walls, roof, may last for a considerably longer period. The rapid deterioration of the semi-wall appears to be associated with the fact that it is subject to a potential gradient due to the voltage drop between anode and cathode, since the same ceramic used elsewhere in the cell is not affected. Of course, the movement of the electrolyte due to the gas lift effect around the semi-wall could also be a contributing factor. If it is assumed that current efficiency is improved by 10 percent through better semi-wall materials (in addition to the economic savings of fewer production interruptions for rebuilding) the annual (1977) energy savings should be:

$$(158.33 \times 10^{6})(.10)(126{,}000) = (2.00 \times 10^{12} \text{ Btu/yr})$$
$$0.50 \times 10^{12} \text{ Kcal/yr} \quad .$$

The Dow patents for a bipolar cell also show ceramic components for the cell which, by the nature of the design , may be subject to deterioration in the vicinity of the junction of the electrodes and ceramic. If the bipolar cell makes possible a reduction of cell potential from 6.3 to 5.0 volts, the 1977 energy saving is:

$$(6.3-5.0)(1999)(10{,}500)(126{,}000)/.9 = (3.8 \times 10^{12} \text{ Btu/yr})$$
$$.96 \times 10^{12} \text{ Kcal/yr}$$

or in year 2,000

$$3.0 \times 10^{12} \text{ Kcal/yr } (11.88 \times 10^{12} \text{ Btu/yr}) \quad .$$

Cell Design

Traditional electrolytic cells have been designed using electrolytes heavier than the molten magnesium. Thus, both chlorine and magnesium rise concurrently to the top of the cell. In addition, the Dow cell consumes graphite at a sufficient rate to require adjustment or feeding of the electrode into the cell. This requirement has made it difficult or impossible to collect chlorine and perhaps contributed also to lowering cell efficiency through recombination of chlorine and magnesium in the electrolyte. The anhydrous cell does not have the graphite feeding problem so chlorine is more easily collected. Current efficiency at the outset can be of the order of 90 percent but decreases as the semi-wall deteriorates.

There is a tradeoff between current efficiency and cell potential. As the cathode-anode spacing is decreased to minimize the voltage, the chlorine and magnesium rising in the cell are brought closer together and recombination is increased, lowering current efficiency. Thus, ignoring semi-wall deterioration for the moment, there is an optimum electrode spacing. Halliday and McIntosh(A28) have been able to demonstrate that the hydrodynamics of the electrolyte and thickness of the gas layer in a 2000-ampere pilot magnesium cell could be simulated by flowing nitrogen through a porous electrode in an aqueous modelling system. While their fused salt cell used an LiCl-KCl electrolyte that is lighter than magnesium, the cell and aqueous system should be applicable with some modification to studying heavier electrolytes as well. Optimizing current efficiency with a possible decrease in cell voltage could add up to an effect equivalent to improvement of 10 percent in current efficiency. For the predicted production volume in the year 2,000 this energy saving would amount to 1.4×10^{12} Kcal (5.6×10^{12} Btu).

It(A26) has been shown that clean steel is preferentially wet by magnesium rather than fused salt. This leads to the concept of a porous cathode through which the magnesium formed on the surface permeates and is collected on the back side. Such a system will allow minimal electrode spacing and could lead to cell potentials as low as 4.0 volts, a 4 volt cell would represent an energy saving in 1977 of:

$$(6.3-4.0)(1999)(10{,}500)(126{,}000)/.9 = (6.8 \times 10^{12} \text{ Btu/yr})$$

$$1.7 \times 10^{12} \text{ Kcal/yr}$$

In year 2,000 energy saving will be:

$$5.3 \times 10^{12} \text{ Kcal/yr}(21.2 \times 10^{12} \text{ Btu/yr}) \quad .$$

Halliday and McIntosh chose to use a low density electrolyte to simplify separation of chlorine and magnesium, since the latter dropped to the bottom of the cell. Electrodes were slightly sloped to enhance the separation as demonstrated in the simulating aqueous system and the fused salt cell. Current efficiencies of over 90 percent were obtained at current densities of 1.5 amp/cm^2 (1400 amp/ft^2), some three times the operating level of the conventional cells. Even at this current density cell potentials of the order of only 5 volts were obtained. Thus, use of these light electrolytes offers a way of improving cell efficiency with energy savings similar to those cited for a 4 volt cell. Use of light electrolytes, based on a composition containing lithium chloride, has been patented by Dow(A27). However, there appears to be no major effort devoted to use of a lighter-than-magnesium electrolyte at the present time. Aluminum cells operate with lighter-than-metal electrolyte which is an advantage over conventional magnesium cells.

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TECHNOLOGY OF ZINC

Introduction

Among nonferrous metals zinc is a relatively important consumer of energy. In the United States the primary zinc industry consumes nearly 25.2×10^{12} Kcal (100×10^{12} Btu) yearly, or an average of 18.1×10^6 Kcal/M ton (65×10^6 Btu/S ton). Of this, about 3.9×10^6 Kcal/M ton (14×10^6 Btu/S ton) is used in mining and concentrating the ore(B1).

The advantages of electrometallurgical processing of zinc concentrates have been well recognized. In fact, since construction of the first commercial plant for sulfate leaching and electrorecovery in 1916 at Great Falls, Montana, there has been steady growth in use of this method. Now all new plants or plans for new zinc plants in the United States are electrolytic. All, so far, are based on leaching roasted concentrates with spent electrolyte containing sulfuric acid, purification of the neutralized solution, and aqueous electrolysis with regeneration of the acid leachant. Only two pyrometallurgical zinc plants are presently operating in the United States. One uses an electrothermic process, the other uses vertical retorts. Energy exclusive of mining and concentrating used in electrothermic reduction of concentrates to metal has been calculated to be 16.7×10^6 Kcal/M ton (60×10^6 Btu/S ton), compared to 12.8×10^6 Kcal/M ton (46×10^6 Btu/S ton) for the average electrolytic plant(B1).

Since the industry is already strongly involved in hydrometallurgical treatment with electrolytic recovery of zinc, there are only two areas in which possible savings in energy by this means can be developed, (1) a different and better procedure for leaching and electrolysis, and (2) by improvements in the various steps presently used for sulfate leaching-purification-electrolysis. Although purification of zinc by electrolytic refining has been done in the past, the metal presently produced is of high purity and there is no need for further refinment on a large scale. In fact, the reverse is true since for galvanizing the high purity electrolytic zinc is purposely debased with cadmium, lead and/or other metals by alloying to produce a galvanizing grade similar to Prime Western zinc.

Recovery Methods for Zinc

Process Steps and Energy Use of Present Electrolytic Sulfate Method

Figure B1 is a flow sheet with estimated energy requirements for the various steps of the electrolytic process now in use worldwide(B1). Table B1 gives more detailed energy data. The ore is mined, crushed, and beneficiated by flotation methods to give a zinc blend concentrate containing from 60 to 70 percent zinc. The benefication plant is usually located near the mine but subsequent treatment is generally remote, necessitating transport of the concentrate. The concentrate is generally wet to minimize dusting, and requires drying prior to roasting. Roasting converts the sulfide to zinc oxide and sulfur dioxide and renders the concentrate soluble in spent acid sulfate electrolyte. Traditional roasting in hearths with a stream of air requires a net input of fuel. Leaching is done with spent electrolyte containing about 150 to 200 g/l of sulfuric acid and 50 g/l of residual zinc sulfate. Leaching consumes essentially all the acid through zinc oxide neutralization and provides a solution containing about 160 to 180 g/l of zinc. The solution is treated to remove impurities such as cadmium, cobalt, nickel, lead, arsenic, etc. Heat and zinc dust are required and the process is complex. However, the total energy use is relatively small.

Electrolysis takes place in tanks with vertical electrodes consisting of aluminum cathodes and silver-lead anodes in a monopolar circuit. These are positioned as closely as possible to each other (shorts during deposition must be avoided) and their weight supported on bus bars. The electrical contacts have traditionally been made to the electrodes by virtue of their weight on the bus. Modern electrodes have dimensions of the order of one m^2 (3' x 3'). Current densities for electrowinning range from 430 to 807 amp/m^2 (40 to 75 amp/ft^2) at 3 to 4 volts and electrolysis is continued for 24 to 48 hours. Cathodes are removed for stripping. In a modern installation up to half of the cathodes in a tank are removed together and stripped with an automatic machine. The stripped zinc is melted and cast.

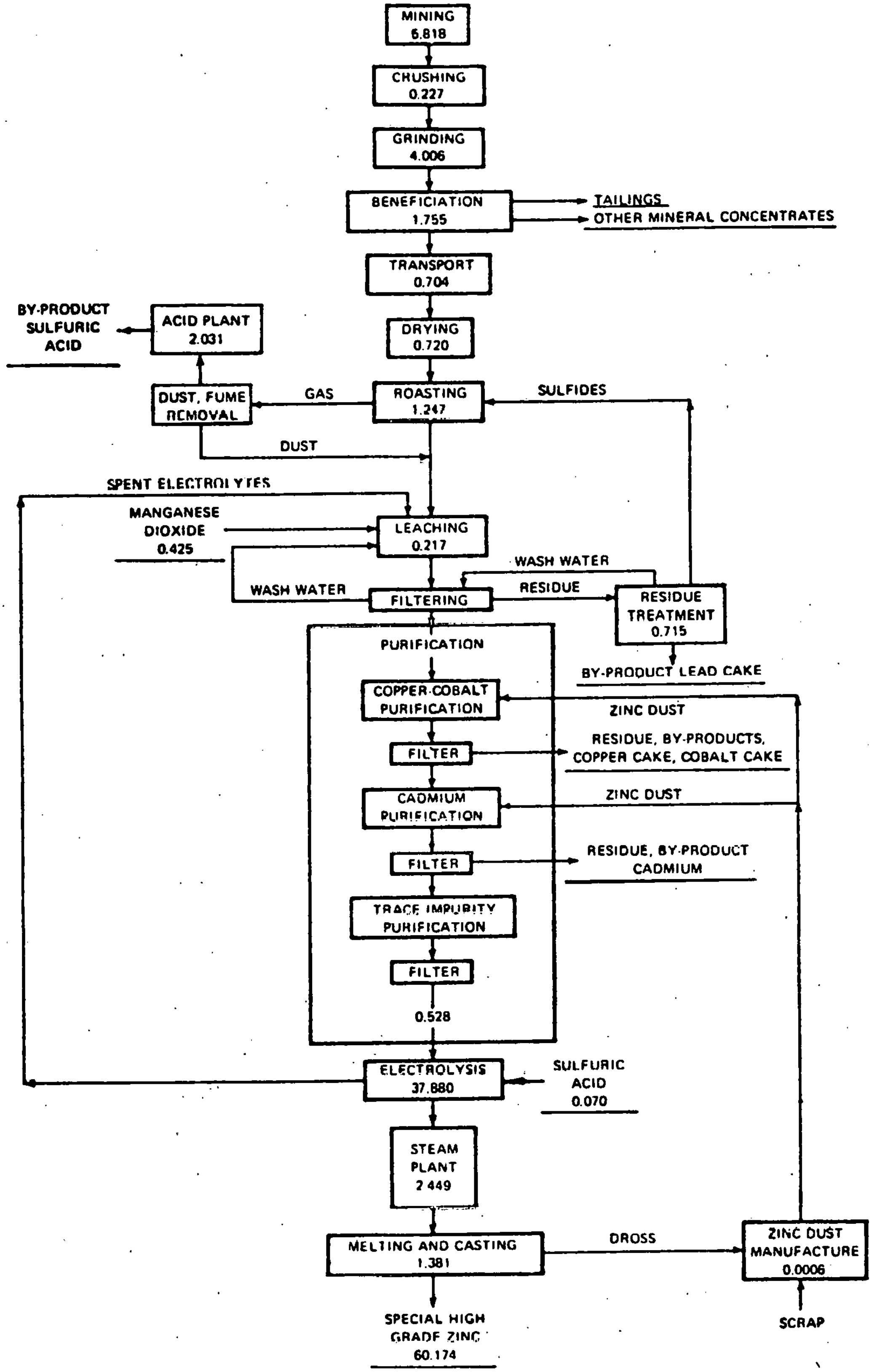

FIGURE B-1. PRODUCTION OF ZINC BY THE ELECTROLYTIC PROCESS

(Figures are Btu/10^6/S Ton of Metal)

TABLE B-1. PRODUCTION OF ZINC BY THE ELECTROLYTIC PROCESS

	Unit	Units per Net Ton* of Zinc	10^6 Btu per Unit	10^6 Btu per Net Ton of Zinc
Mining				
Steel	lb	18.84	0.0175	0.330
Explosives	lb	16.87	0.030	0.506
Electrical energy	kwh	369.3	0.0105	3.878
Diesel fuel oil	gal	7.4	0.139	1.029
Gasoline	gal	0.60	0.125	0.075
			Subtotal	5.818
Crushing				
Electrical energy	kwh	21.6	0.0105	0.227
Grinding and classifying				
Electrical energy	kwh	329.0	0.0105	3.455
Steel	lb	31.5	0.0175	0.551
			Subtotal	4.006
Beneficiation				
Conditioning and flotation	kwh	120.0	0.0105	1.26
Thickening and filtering	kwh	15.7	0.0105	0.165
Organic reagents	lb	2.89	0.020	0.058
Inorganic reagents	lb	42.9	0.005	0.215
Other electrical energy	kwh	5.4	0.0105	0.057
			Subtotal	1.755
Rail Transportation	net ton-mile	1,050.0	0.00067	0.704
Drying concentrates				
Natural gas	ft^3	720.0	0.001	0.720
Roasting				
Electrical energy	kwh	18.9	0.0105	0.198
Natural gas	ft^3	1,049.0	0.001	1.049
			Subtotal	1.247

*Net ton = S ton.

TABLE B-1. (Continued)

	Unit	Units per Net Ton of Zinc	10^6 Btu per Unit	10^6 Btu per Net Ton of Zinc
Sulfuric acid production				
Electrical energy	kwh	247.9	0.0105	2.603
Propane	gal	8.14	0.095	0.773
Credit for sulfuric acid	tons	1.62	0.83	-1.345
			Subtotal	2.031
Leaching				
Electrical energy	kwh	20.6	0.0105	0.217
Manganese dioxide (MnO_2)	lb	85.0	0.005	0.425
			Subtotal	0.642
Residue treatment				
Electrical energy	kwh	10.9	0.0105	0.114
Natural gas for drying	ft^3	601.0	0.001	0.601
			Subtotal	0.715
Solution purification				
Electrical energy	kwh	50.3	0.0105	0.528
Electrolysis				
Sulfuric acid	net ton	0.084	0.83	0.070
Electrical energy	kwh	3,600.0	0.0105	37.800
Inorganic reagents	lb	16.0	0.005	0.080
			Subtotal	37.950
Melting and casting				
Natural gas	ft^3	331.0	0.001	0.331
Electrical energy	kwh	100.0	0.0105	1.050
			Subtotal	1.381
Zinc dust manufacture				
Electrical energy	kwh	0.064	0.0105	0.0006
Natural gas (steam plant)	ft^3	2,449.0	0.001	2.449
Total				60.174

A kwh is assumed equivalent to 10,500 Btu at the power plant.

Certain steps being incorporated into some modern processes, such as treatment of residue for iron removal are not incorporated into Figure B1. These processes and the energy involved will be discussed in subsequent sections.

Electrolysis uses 63 percent of the total energy requirement. The 10.53 x 10^6 Kcal/M ton (37.88 x 10^6 Btu/S ton) Zn corresponds to 3969 kwh/M ton (3600 kwh/S ton) Zn. Other much smaller energy requirements are grinding, 6 percent; roasting, 2 percent; and steam, 4 percent. Thus, savings in energy should be sought by reducing electrolysis power requirements or simplifying the flow sheet to eliminate a substantial number of steps, each of which uses a small increment of the total energy. Zinc plants now planned or under construction, and a few built in recent years, employ a fluidised bed roaster with a heat recovery system that provides essentially all of the process heat requirements of the plant. Thus, as a first approximation the production of 0.62 x 10^6 Kcal (2.449 x 10^6 Btu) from the steam plant in Figure B1 can be eliminated to give a total of 16.03 x 10^6 Kcal/M ton (57.69 Btu/S ton) of zinc. The steam plant must be provided, however, to take over when the roaster is not operating.

Theoretical energies can be approximated from changes in free energy and enthalpy, using standard states but taking account of temperature in some cases.

The overall reaction is:

$$\mathrm{ZnS(s) + O_2(g) \rightarrow Zn\ (s) + SO_2(g)}: 25°\ \mathrm{C}$$

$$\Delta F = -27.48 \text{ Kcal/g mole Zn} = (-1.52 \times 10^6 \text{ Btu/S ton Zn}),$$
$$-.42 \times 10^6 \text{ Kcal/M ton Zn}$$

$$\Delta H = -25.64 \text{ Kcal/g mole Zn} = (-1.42 \times 10^6 \text{ Btu/S ton Zn}),$$
$$-.39 \times 10^6 \text{ Kcal/M ton Zn} \quad .$$

For the electrolysis:

$$\mathrm{ZnSO_4(a{=}1) + H_2O\ (l) \rightarrow Zn(s) + \tfrac{1}{2}\, O_2(g) + H_2SO_4(a{=}1)}: 25°\ \mathrm{C}$$
$$E° = -2.12 \text{ volts}$$

$\Delta F° = 97.77$ Kcal/mole, 1575 kwh/S ton Zn or (5.42×10^6 Btu/S ton Zn), 1.51×10^6 Kcal/M ton Zn ,

$\Delta H° = 110.6$ Kcal/mole Zn or (6.13×10^6 Btu/S ton Zn), 1.70×10^6 Kcal/M ton Zn .

The overall theoretical energy requirement for oxidation of ZnS to zinc and SO_2 is negative. The actual reactions in electrolysis are slightly endothermic. The heat from overvoltages and IR drop in the electrolyte provide more than the heat required to maintain temperature, and the cells must lose heat energy.

Variations and Innovations in Zinc Sulfate Processes

Roasting. As pointed out by Siddle in an excellent review on energy conservation in electrolytic zinc production, heat recovery from roasting is a particularily good area for heat conservation(B2). Some 2.78×10^6 Kcal/M ton (10×10^6 Btu/S ton) of slab zinc is presumably available as evolved heat, assuming 100 percent recovery and using a dry roaster. By using a dry feed fluid-bed roaster 0.46×10^6 Kcal/M ton (1.67×10^6 Btu/S ton Zn) of energy can be saved and converted to evolved heat that would otherwise be used to dry the concentrate. Use of roaster heat depends upon a plant's need for steam generation, steam turbine operations, or even sale outside. Woods(B3) states that 1.1 kg of 40 atm steam can be produced from a kg of concentrate. Thus, steam produced from a concentrate with 50 percent zinc will be 2020 kg/M ton (4040 lb/S ton) Zn. An 100 percent efficient turbine with a 65° C exit temperature would require about 5.4 kg (12 lb) steam/kwh or 18 kg (40 lb)/kwh at 30 percent efficiency. Thus, about 110 kwh/M ton (100 kwh/S ton Zn) can be obtained from the roasting heat. A 90,700 M ton/yr (100,00 S/yr) zinc plant would produce less than 270 M ton/day (300 S ton/day) corresponding to:

$$\frac{(300)(100)}{24} = 1250 \text{ kw} \quad .$$

Thus, the energy available is far too small to set up a separate electrical generating facility, which would also subtract from the process heat otherwise available.

To check the value reported for heat available from roasting the enthalpy of the reaction at 25° C:

$$ZnS + \frac{3}{2} O_2 \rightarrow ZnO + SO_2 : 25° C$$

is -109.0 Kcal/g mole or -6.04 x 10^6 Btu/S ton (1.67 x 10^6 Kcal/M ton) Zn. This is lower than Siddle's value, which however, takes into account metal losses such as those in the leach residue. The residue zinc evolves heat during roasting but does not end up in the slab. Considering average heat capacities and a temperature of 1000° C the enthalpy value is only changed to -109.8 Kcal/g mole of zinc. For purposes of estimation we will use 1.4 Kcal/M ton (5 x 10^6 Btu/S ton) to allow for gas, pumps, handling, etc.

Special Treatment of Ores and Residues

The amount of zinc left in the residue varies rather widely with differences in concentrates treated, and the system of leaching and residue treatment given in different plants. A few years ago, an American electrolytic zinc plant reported 20 percent zinc in the residue, which corresponds to a loss of 8.6 percent of the zinc in the original calcine(B4). At the Risdon electrolytic plant in Tasmania, stockpiled residue contained 22.8 percent zinc; current residue in 1970 contained 22.6 percent zinc. As a generalization the loss of zinc in residue from leaching calcines in 1970 was 7 to 13 percent.

To recover most of the zinc from the normally insoluble zinc ferrite in the residue, the Jarosite process has been developed in Tasmania, Norway, and Spain(B5). By this process, the residue is treated with hot strong sulfuric acid to dissolve the zinc ferrite that is insoluble in spent electrolyte from the cell, and the solution, after removal of insolubles, is partly neutralized and treated with ammonia or a sodium or potassium base to precipitate iron as a complex basic iron sulfate or Jarosite compound.

This gives an iron precipitate that may contain only about 0.5 percent zinc. Thus, at the Risdon plant, from results when operating a pilot plant to treat residue using the Jarosite process, zinc losses in leaching were expected to be reduced from 9.5 percent to about 1 percent.

From recent plant experience at Risdon, Australia the energy required to recover zinc in solution from residue by Jarosite treatment is calculated to be 10.98 x 10^6 Kcal/M ton (39.5 x 10^6 Btu/S ton) as shown in Table B2. Since the solution treated by the Jarosite process must be purified and electrolysed, and the electrowon zinc melted and cast the total energy expenditure for the zinc recovered by Jarosite treatment amounts to 22 x 10^6 Kcal/M ton Zn (79.3 x 10^6 Btu/S ton Zn). This energy requirement is higher than the 16.7 x 10^6 Kcal/M ton Zn (60.2 x 10^6 Btu/S ton Zn) for producing zinc from ore. Thus, disregarding conservation and costs of residue disposal, treatment of residues is not a way to save energy. As noted in Table B2, however, if steam is being wasted, its use for residue treatment could result in a net energy savings per ton of zinc.

A process with similar objectives developed by Vieille Montagne (VM) in France is the Goethite process. This involves a hot acid leach, ferric iron reduction at 90 C, preneutralization, and reoxidation at 90 to 95°C for 5 to 7 hours, with iron removed as a goethite precipitate(B7,B8). As with the Jarosite process, the iron precipitate is readily filterable and zinc loss is low. The economics of the two processes are said to be similar, there is need for sulfuric acid and ammonium or sodium salts for jarosite treatment, and an abundance of steam for solution heating is needed for the goethite procedure. A variation of the VM procedure has been developed by the Electrolytic Zinc Company in Australia whereby the ferric iron is precipitated directly without prior reduction and reoxidation. It is applicable to chloride as well as sulfate solutions. In Japan, the Dowa Mining Company with cooperation of Sheritt Gordon has developed the Hematite Process. Zinc residue from normal leaching is treated with spent electrolyte, makeup sulfuric acid, and sulfur dioxide in a low-pressure autoclave. Excess SO_2 is stripped, copper precipitated with hydrogen sulfide and solution neutralized with limestone. Oxygen is used to precipitate iron as ferric oxide in three stages at 200°C and 21 kg/cm^2 (300 psia) pressure for three hours.

TABLE B2. ENERGY USED IN JAROSITE TREATMENT OF ELECTROLYTIC ZINC PLANT RESIDUE, RISDON*

	Unit	Units per S Ton of Zn Recovered	10^6 Btu per Unit	10^6 Btu per S Ton of Zn Recovered
Steam(1)	S ton	11.09	2.358	26.15
Power(2)	Kwh	457.43	0.0105	4.80
Ammonia	S ton	0.1276	38.64	4.93
Sulfuric Acid	S ton	4.121	0.83	3.42
Flocculent	lb	5.32	0.02	0.11
Compressed Air	M Cu. ft.	17.92	0.005	0.09
Total				39.50

* Communication of September 1, 1978 from Electrolytic Zinc Co. of Australia, Ltd. Laboratories data treating residue from which 15.2 percent zinc is extracted.

(1) Calculated as having to be generated; actually at Risdon waste steam is used which would be credited to another division of the plant.

(2) Power is calculated as generated from steam at a factor of 32.5 percent; with electricity from hydropower the energy consumed in power generation would be less than half that given.

More steam is used in the Geothite procedure than for Jarosite treatment since higher temperatures are needed. Heating requirements for the Hematite process would be expected to be even greater. Thus, the three iron removal processes discussed conserve material at the cost of greater energy use.

Meisal(B8) has reviewed these processes and also described pre-leaching (before roasting) of dolomitic concentrates with dilute sulfuric acid to remove magnesium as is done at Bunker Hill and by Amax. This makes an extra operation but is needed when treating some concentrates. Likewise, in treating oxidized zinc ores which plague the normal leaching plant with soluble silica, success in recovering over 90 percent of the zinc has been secured in an Australian pilot plant operation by completing the neutralization step with limestone to precipitate silica in a filterable form(B9). A novel procedure for separating zinc from soluble silica and other materials was investigated on a laboratory scale(B10). After leaching normally with spent electrolyte, the zinc was salted out as $ZnSO_4 \cdot 7H_2O$ by addition of methanol, ethanol or acetone. After separation, the zinc sulfate crystals were dissolved, purified, and electrolyzed; the organic solvents were recovered for reuse by distillation (It would seem that alkaline leaching would be a more promising method for oxidized and basic zinc ores).

Solvent extraction has been suggested for removing iron from zinc sulfate solutions(B11). By using the zinc salt of the organic "versatic" acid, ferric iron can be removed with a very low zinc loss, i.e., 0.1 percent, which van der Zeeuw compared to up to 3 percent loss in the Jarosite process. Some iron is purposely left for precipitation to carry down arsenic, antimony, and germanium. Iron is stripped with HCl, or more slowly with sulfuric acid, and versatic acid can be regenerated. Since energy involved is essentially that for mixing and pumping solutions, it should compare with that for leaching, except that residence time should be less. Thus, the 0.17×10^6 Kcal/M ton Zn (0.6×10^6 Btu/S ton Zn) given for leaching should be an upper energy limit for solvent extraction.

An old established method for treating low-grade oxidized zinc ores and electrolytic zinc plant leach residue is to add a reducing agent and volatilize the zinc and cadmium in a Waelz kiln. By an improved process, the fumed zinc, lead, and cadmium dust is again run through a rotary kiln with a chloridizing agent to give a zinc calcine and lead-cadmium fume(B12). Recently, a Zileret process has been mentioned by which an iron precipitate is pelletized and heated with a reductant to drive off zinc, lead, cadmium, and indium. The resultant sponge iron containing some copper and silver can then be used effectively for cementation of copper(B13). Thus, an almost complete recovery of useful metals can be made, but not without a considerable expenditure of energy.

Energy use for several of the processes discussed have not been estimated, but qualitatively they are believed to be relatively low. Assume that no energy is required for residue treatment and that 10 percent of the zinc in the original concentrate is recovered from the residue. The zinc from the residue must still go through purification, electrolysis, melting, and casting, requiring 45 x 10^6 Btu/ton Zn. Average energy consumption for the plant is then:

$$(.90)(60.12 \times 10^6) + (.10)(45 \times 10^6) = 58.6 \times 10^6 \text{ Btu/ton Zn} \quad ,$$

or

$$16.3 \times 10^6 \text{ Kcal/M ton Zn} \quad .$$

The energy reduction compared to not treating residue is 2.5 percent. This can be significant to an operating plant if tied in with cost savings, but is not an area in which to undertake a broad-based R and D program aimed at energy savings. However, maximum recovery of zinc from the concentrate provides a saving in natural resources.

<u>Leaching</u>. In normal leaching operations measures have been suggested by Siddle(B2) to produce some energy savings by conserving heat. Thus, he mentions delivering hot calcine directly to the leaching tanks to conserve its sensible heat, if additional heat is needed at this point; covering thickeners; using hot wash water; and blowing filters with

steam where excess steam is available. Drying leach residue, where it is required, takes heat, as about 330 kg/M ton (660 lb/S ton) of water from wet residue must be evaporated. However, the enthalpy change is only of the order of 0.3 x 10^6 Kcal/M ton (1 x 10^6 Btu/S ton). Here use of a double pass dryer is recommended because of its efficiency of about 70 percent compared to 50 percent for a single pass dryer. Overall in normal leaching, energy savings in the leaching department depend too much on individual plant conditions for generalizations except for conclusions reached on treatment of residue to recover more zinc.

Purification. The purification step is a minor user of energy and the potential for research to reduce energy here consequently is small. Where the solution must be heated for purification some energy saving may be effected by choosing a system that requires a lower temperature. For example, by using b-naphthol and sodium nitrite, cobalt and much of the nickel can be removed at around 70°C, whereas with arsenic as an activator with zinc dust a temperature of over 90°C is used. Any new system that gives effective purification without the need for heating the solution would reduce the energy need and certainly would be welcome if it did not carry compensating disadvantages. Thus, a reduction in temperature from 90° to 70°C would result in a reduction in energy 0.14 x 10^6 Kcal/M ton Zn (0.5 x 10^6 Btu/S ton Zn).

Electrolysis. By far, the greatest consumption of energy in an electrolytic zinc plant is in the tank house or electrolysis section. This accounts for about 63 percent of the total or 10.5 x 10^6 Kcal/M ton (38 x 10^6 Btu/S ton). This is 3990 kwh/M ton (3620 kwh/S ton). Obviously, electrolysis would seem to be the place for any major reduction in energy, and much attention has been directed to the problem over the past 60 years. Theoretically, at 100 percent current efficiency, deposition of zinc requires 809 kah/M ton (734 kah/S ton). The standard oxidation potential of zinc in acid solution is -0.76 V and of water to oxygen 1.23 V. Thus, the standard reversible cell potential is 1.99 volts. Theoretical power consumption is consequently 1630 kwh/M ton Zn (1479 kwh/S ton Zn) or 4.3 x 10^6 Kcal/M ton Zn (15.5 x 10^6 Btu/S ton Zn). The theoretical cell voltage for decomposition of zinc chloride is higher (2.12 volts) but the lower overvoltage for chlorine discharge than for oxygen discharge still makes chloride electrolysis potentially attractive.

While the theoretical power consumption does not take account of the actual activity of the zinc in the electrolyte, neglecting this should introduce a relatively small error. Practical energy use is thus more than twice theoretical. Significant losses are due to the IR drop through the electrolyte and overvoltages, particularily at the anode. Bratt(B14) has given a detailed account of the voltage components in a zinc electrowinning cell and his figures are reproduced in Table B3. Assumptions are:

(1) Cells are midway in anode cleaning and zinc deposition cycles

(2) The mean current density is 526 amp/m^2 (50 amp/ft^2)

(3) Temperature is 35° C.

The total cell voltage of 3.5 corresponds to a power consumption of 3079 kwh/M ton Zn (2790 kwh/S ton Zn) or 8.14×10^6 Kcal/M ton Zn (29.3×10^6 Btu/S ton Zn). The loss in converting A.C. to D.C. power is estimated to be 5 percent. An additional loss of 5 percent is assumed to bring power from the rectifiers to the cells. Thus, with the additional 10 percent power requirement, the total consumption is 3418 kwh/M ton Zn (3100 kwh/S ton Zn) or 8.9×10^6 Kcal/M ton Zn (32×10^6 Btu/S ton Zn). These figures compare approximately to those reported by USBM(B1) of 3969 kwh/M ton Zn (3600 kwh/S ton Zn) or 10.53×10^6 Kcal/M ton Zn (37.9×10^6 Btu/S ton Zn).

Anodes. The overpotential at the cathode is relatively small (0.06 volt). However, the anode overvoltage is significant (0.84 volt, 740 kwh/M ton Zn*, 1.96×10^6 Kcal/M ton Zn) as is the IR drop through the solution (0.54 volt, 475 kwh/M ton Zn*, 1.26×10^6 Kcal/M ton Zn). Reduction of the anode overvoltage is thus an obvious problem for R and D, but should be approached with some reservation. Oxygen overvoltage is a problem common to several electrochemical systems such as fuel cells, hydrogen-oxygen production

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*Assume 93 percent current efficiency.

TABLE B3. VOLTAGE COMPONENTS OF OPERATING ZINC ELECTROLYSIS CELL

Component	Basis	Major Causes of Variation	Lead Anodes		Silver-Lead Anodes	
			mV	% total	mV	% total
Cathode						
Reversible potential	(1)	Activity values	- 819	23.1	- 819	24.0
Activation overpotential	(2)	Current density	- 62	1.7	- 62	1.8
Concentration overpotential	(3)	Current density	nil	nil	nil	nil
Effect of potassium anitmonial tartrate	(4)	Conductivity	+ 55	1.5	+ 55	1.6
Effect of glue	(4)	Conductivity	- 40	1.1	- 40	1.2
Effect of 2-naphthol	(4)	Conductivity	- 16	4.5	- 16	4.7
Total cathode potential			- 882	24.9	- 882	25.8
Anode						
Reversible potential	(8)	?	+1217	34.3	+1217	35.7
Oxygen overpotential	(7)	Current density	+ 840	23.7	+ 840	24.6
Concentration overpotential	(5)	Current density	nil	nil	nil	nil
Scale effect	(4)	Time, Scale Thickness	+ 150	4.2	+ 150	4.4
Effect of cobalt	(4)	Conductivity	- 120	3.4	- 10	0.3
Effect of manganese	(4)	Conductivity	- 40	1.1	- 190	5.5
Effect of glue	(4)	Conductivity	+ 20	0.6	+ 10	0.3
Effect of $SrCO_3$	(4)	Conductivity	nil	nil	+ 35	1.0
Alloy effects	(4)	--	nil	nil	+ 120	3.5
Total anode potential			+2067	58.3	+1932	56.7
Conductivity Effects						
Cathode sheet p.d.	(6)	Conductivity	nil	nil	nil	nil
Anode sheet p.d.	(6)	Conductivity	nil	nil	nil	nil
Cathode deposit p.d.	(6)	Conductivity	nil	nil	nil	nil
Solution p.d.	(4)	Concs. Zn, Mg Mn, H_2SO_4	540	15.2	540	15.8
Gas bubbles	(7)	Temp., agitation	54	1.5	54	1.6
Total conductivity effect			594	16.8	495	17.4
Total calculated cell voltage			3.543	100	3.408	100
Average measured plant voltage (without contact or busbar loss)	(4)		3.539		3.483	

(1) Thermodynamics.

(2) Percherskaya and Stender, 1960.

(3) Kortum and Bockris, 1951.

(4) EZ

(5) Kivalo and Vuorio, 1961.

(6) Various conductivity data.

(7) MacMullin, 1963.

(8) Indirectly from cell potential and reversible cathode values.

(From: The Aus. I.M.M. Conference, Tasmania, May, 1977).

See original article for references.

cells, and electrowinning in aqueous solutions. It has consequently received considerable attention from a fundamental and practical standpoint. Support is definitely needed but on a very broad basis rather than a specific practical level. Ettel(B15) includes curves showing that the Dimensionally Stable Anode (DSA) can achieve a saving of 0.4 volts (351 kwh/M ton Zn or .93 x 10^6 Kcal/M ton Zn). However, at a power cost of $.01/kwh he concludes that the power savings do not pay for the cost of leasing. While the DSA has been well proved in chloride solutions its durability is reported to be much less with oxygen evolution. Improved durability would not only have consequences for zinc electrowinning but other applications such as copper electrowinning and water electrolysis.

Anodes can be depolarized with reducing agents, the most readily available one being SO_2 from the roasting operation. The standard electrode potential for oxidation of SO_2 in acid solution is:

$$H_2SO_3 + H_2O \rightarrow SO_4^{=} + 4H^+ + 2\bar{e}: 25° C$$
$$E = + 0.172 \quad .$$

The theoretical cell potential for this reaction combined with zinc deposition is 0.172 + 0.76 = 0.93 volt compared to 1.99 volts for zinc deposition combined with oxygen evolution.

The anodic oxidation of SO_2 in strong sulfuric acid solution is highly irreversible(B55). However, using a catalysed porous carbon electrode an overvoltage of about 0.5 volt has been obtained at 50 ma/cm^2 (46 amp/ft^2). Then the anode potential with SO_2 oxidation is + 0.67 volt compared to the value of 1.23 + 0.8 = 2.1 volts for oxygen evolution. The energy saving for electrolysis with SO_2 is therefore (1.4)(743) = (1040 kwh/S ton Zn) 1146 kwh/M ton or 3.04 x 10^6 Kcal/M ton Zn (10.9 x 10^6 Btu/S ton Zn). The overall cell reaction is:

$$ZnSO_4 + SO_2 + 2H_2O \rightarrow Zn^0 + 2H_2SO_4 \quad .$$

Thus, twice the acid is produced as by anodic oxygen formation and half of this must be removed. In order to maintain a constant sulfuric acid concentration in the bath only half of the zinc sulfate in the neutral cell feed can be converted to zinc. The other half is included in the spent electrolyte, which must be concentrated to commercial acid with crystallization of the zinc sulfate. An ICI patent described in reference (B17) involves concentration of spent electrolyte to 70 percent sulfuric acid and precipitation of essentially all remaining zinc sulfate. Thus the energy for the present method of (1) converting SO_2 from roasting directly to sulfuric acid and electrolysing in a conventional oxygen producing cell should be compared to (2) using SO_2 as a depolarizer and concentrating spent electrolyte by evaporation to produce commercial acid.

The overall reaction is the manufacture of one mole of excess acid for each mole of zinc deposited. Energy for evaporating 17 percent sulfuric acid (190 g/1) to 70 percent acid was estimated from the difference of heat of formation of sulfuric acid at these two concentrations and heat of vaporization at an average vaporization temperature. From data in Table B4 the enthalpy change of the liquid being concentrated is:

$$\Delta H = 6.577 \text{ Kcal/mole } H_2SO_4 \quad .$$

If water is boiled off from 103 to 165° C an average heat of evaporation of 530 cal/g H_2O or 9.54 Kcal/mole H_2O will be assumed. There are 24.89 moles of water vaporized per mole of H_2SO_4 or per mole of zinc deposited with energy use of:

$$(24.89)(9.54) = 237.5 \text{ kcal/mole Zn}$$

$$237.5 + 6.6 = 244.1 \text{ kcal/mole Zn}$$

$$\frac{(244.1)(453)(2000)}{(65.37)(.25)} = (13.5 \times 10^6 \text{ Btu/S ton Zn})$$

$$3.75 \times 10^6 \text{ Kcal/M ton Zn} \quad .$$

This is a rough calculation ignoring energy for heating the liquid and the heat of solution of the zinc sulfate. It nevertheless indicates that the energy saved by using sulfur dioxide as a depolarizer is required for evaporating water. However, this energy use can be approximately halved by use of a double or triple effect evaporator to 1.9×10^6 Kcal/M ton (6.8×10^6 Btu/S ton Zn). One way of reducing

TABLE B4. DATA FOR CALCULATING ENERGY FOR SULFURIC ACID CONCENTRATIONS

Acid Conc, Percent	ΔH_f of H_2SO_4, kcal/mole	B.P., °C	ΔH of vap, Cal/g of H_2O	Moles H_2O per Mole H_2SO_4
18	-211.7	103	576	26.56
70	-205.1	165	682	1.67

the amount of evaporation required would be through use of a cell membrane allowing the anolyte to reach a higher acid concentration, i.e., 34 percent. The trade off here is more difficult to estimate but should be of the same magnitude or greater than with the depolarized cell without a membrane.

The lower anode voltage achievable with a depolarizer allows use of materials other than lead for anodes without encountering deterioration. Various porous electrodes suitable for gas depolarizers have been developed in fuel cell technology. Porous carbonaceous materials should be durable. Cost will depend upon the nature and amount of catalyst required.

Methanol(B16) has been suggested as a depolarizer. Its synthesis from oil is counterproductive to the goals of the project. Methanol or ethanol from natural resources may be justified if it can be proven that energy requirements for their production are not greater than the savings possible through depolarization. However, the disagreement on energy requirements among several who have studied the synthesis problems in detail(B17) suggest that making a separate estimate for the report will not be useful at the present time.

Electrolyte Conductivity. IR drop through the electrolyte can be reduced by increasing its specific conductivity and decreasing the electrode spacing and current density. The concentration of sulfuric acid, a good ionic conductor, in the electrolyte is already high (150 to 175 g/l) so it is doubtful whether substantial improvement can be made through concentration and component changes. Increasing temperature will increase conductivity substantially, but current efficiency drops substantially above 40° C with the present electrolyte unless current density is increased (which itself increases voltage) or the already highly purified solution is made even purer. The current efficiency decrease is due to the increased corrosion of the deposited zinc through local cell action ($Zn + 2H^+ \rightarrow Zn^{++} + H_2$). Decreasing the interelectrode spacing will reduce IR drop but requires that electrodes be very flat and carefully aligned and deposits be smoother and more uniform and probably stripped at an earlier stage than now practiced. Spacing is probably a matter for in-plant improvments in design, operation, etc., and could make possible a maximum saving of 0.2 volt in cell potential

(176 kwh/M ton Zn, .47 x 10^6 Kcal/M ton Zn, 1.68 x 10^6 Btu/ton Zn) if the distance between starting sheets and anodes was reduced by 1.3 cm (0.5 inch).

AC to DC Power Conversion. Modern systems for power conversion consist of step-down transformers and silicon rectifiers. When used to supply DC power at 300 volts or more the conversion efficiency is 95 percent or higher. The theoretical improvement possible for the zinc electrowinning step is thus 3600 x .05 = (180 kwh/S ton of Zn) 198 kwh/M ton Zn or (1.94 x 10^6 Btu/S ton Zn) 0.54 x 10^6 Kcal/M ton Zn. Improving power is a goal for several electrochemical industries, i.e., for copper electrorefining, aluminum and chlorine-caustic production. Annual domestic production of electricity is 2.186 x 10^{12} kwh.* Assuming that 6 percent of the total domestic electrical power is low voltage DC for electrochemical operations, a one percent improvement in conversion efficiency will save:

$$(2.186 \times 10^{12})(.06)(.01) = 1.31 \times 10^{9} \text{ kwh/yr}$$

or

$$0.35 \times 10^{13} \text{ Kcal/yr } (1.38 \times 10^{13} \text{ Btu/yr}) \quad .$$

Reversing Current. Variations in the current flow (pulse, interrupted, asymmetrical, and reverse) have been researched in electroplating and may find application in the electrolytic recovery of zinc. From development work in Bulgaria using a reverse current (changing polarity) with increased current density some rather interesting results were secured that indicate the potential for energy savings$^{(B18)}$. In a small experimental installation in an industrial plant, using reverse current decreased the electrical energy requirement from one to two percent compared to use of a constant current. Productivity was increased substantially because of a denser cathodic deposit and higher current density which permitted a heavier deposit. The possibility of energy conservation by current reversal is due to smoother deposits which may allow closer spacing of electrodes to reduce voltage.

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*Annual Electric Output, November 1, 1977 to November 1, 1978 from Electric Output (EEI) 46 (43) November 1, 1978.

Alternatively the same benefit may be possible with conventional spacing by making possible thicker deposits.

Cathodes. The use of mercury cathodes will be discussed with chloride leaching(B19,B20). There are some interesting possibilities in using mercury cathodes with zinc, such as continuous removal of deposit and metal separations from impure solutions, but two separate electrolysis operations are generally required which increases technical complexity and cost without specific indications of energy savings.

Cathodes of larger dimensions than 1.0 m^2 (9 ft^2) are being used in some new installations which, with increased circulation, give greater capacity. Also, means for automatic stripping are available and being used to an increasing extent(B21). Such changes do not affect the energy consumed appreciably; in fact, automatic stripping requires some mechanical or electrical energy in place of manpower, but reduces cost.

In the last few years experimental work has been done using fluidized bed cathodes. This involves an upward flow of electrolyte causing lifting of small metallic particles which grow with deposition. A diaphragm is used, as well as a current feeder electrode to contact the moving particles. The advantage, of course, is in obtaining continuous operation by removing the cathode particles as they get beyond a certain size and in introducing new seed particles, rather than stripping cathode sheets. Current efficiency suffers, although up to 88 percent has been obtained in some tests(B22). Energy required in one set of experiments using an inclined cell with high current density was 6.8 kwh per Kg of zinc produced or 18.1×10^6 Kcal/M ton (65×10^6 Btu/S ton). This is much greater than present commercial practice. Possibilities of decreasing the voltage below 6 and increasing the current density exist, but at present are not sufficiently encouraging to consider this a really promising method of obtaining any energy savings.

Circulation and Cooling. Various means have been devised to get adequate circulation in the electrolytic zinc cell by forced solution flow and positioning of electrodes. Sparging or the use of compressed air below the electrodes to sweep the electrode surfaces with bubbles has received renewed attention recently. Sparging tests over a two week period in a

South African electrolytic zinc plant indicate no particular improvement in current efficiency, but more compact, smoother deposits are obtainable and less lead has been found in the deposit$^{(B23)}$.

Cell voltage is limited very little by mass-transfer effects at the current densities used, but rather by IR drop and oxygen overvoltage. However, the nature of the deposit can be affected by mass-transfer. At the mass transfer limiting current density powdery deposits are produced$^{(B24)}$. Compact deposits are obtained in the range of 25 to 50 percent of the limiting current density$^{(B28)}$. Thus, if the current density has been increased until some roughness occurs, increasing the agitation and mass transfer can provide more compact deposits, as evidenced in the South African experiments. Smooth compact deposits may allow closer spacing of the electrodes, leading to a reduced voltage and possibly even better mass transfer through increased electrolyte velocity in the narrower space. Assuming an electrolyte conductivity of 0.3 $\text{ohm}^{-1}\ \text{cm}^{-1}$ the voltage at 50 amp/ft^2 through one-inch of electrolyte is 0.45 volt. The energy use is 395 kwh/M ton Zn (359 kwh/S ton Zn) or 1.05×10^6 Kcal/M ton Zn (3.77×10^6 Btu/ton Zn). Thus 5 to 10 percent of the electrolysis power can be saved by decreasing interelectrode distance 1.3 cm (0.5 inch) or more.

Because of the heat generated in electrolysis some cooling normally is required to keep the electrolyte below 40° C. Cooling coils or reduced pressure evaporation have been, and are still, generally used. As pointed out by Siddell (Reference B2), cooling coils require little energy input, but have been largely replaced by evaporation because of the large amount of cool water required, disposal problems for the warm water, and coil cleaning problems. In turn, atmospheric cooling towers, developed in Japanese and European plants, are being installed in two American electrolytic zinc plants, and seem to be the preferred method for the future. The towers apparently are more efficient in energy utilization than the presently used reduced pressure evaporation systems, but in any event consume comparatively little power.

<ins>Reagents</ins>. Various additives are made to the electrolyte during zinc electrodeposition to control cathode growth, prevent deposition of or

adverse effects of impurities, and reduce acid misting. Typically, animal glue or gum arabic or sodium silicate are used as general additives and beta naphthol, strontium carbonate and cresylic acid for more specific effects. The additives can allow closer electrode spacing and reduce IR drop by promoting smoother deposits. However, considering the number of additives that have been studied the probability of finding something that will significantly change energy use seems remote.

Melting and Casting

This operation consumes about 0.39×10^6 Kcal/M ton (1.4×10^6 Btu/S ton) of zinc, (some estimates are as much as 0.51×10^6 Kcal/M ton). Although electric induction furnaces are increasingly favored for melting cathodes, calculations of energy used compared to fuel fired furnaces often are misleading. Thus, at the Porto Marghera electrolytic zinc plant a thermal efficiency of 60 percent is claimed for their induction furnace and only 30 percent for a reverberatory melting furnace using natural gas. This has led to the assumption that changing to electric melting conserves energy. However, since electric energy comes from gas, oil, or coal after sustaining an energy loss of around two thirds in conversion, the actual basic energy consumed is more for the electric induction furnace. The actual comparison on utilization of fuel energy would be 30 percent for the gas fired and 20 percent for the electric furnace. A still greater value favoring the fuel fired furnace might be attained if any of its waste heat could be utilized.

Heat conservation in melting and casting can be obtained by avoiding remelting of the zinc. Thus, alloying or casting into final products can be done with energy efficiency by transferring molten metal to adjacent furnaces as holding vessels rather than casting slabs and later remelting. However, the increase in enthalpy in heating zinc from 25° C to 500° C (M.P. 149° C) is only $.07 \times 10^6$ Kcal/M ton (26×10^6 Btu/S ton). Even a relatively inefficient heating process is not a large energy consumer.

Chloride Leaching and Aqueous Electrolysis

Electrolytic zinc was first produced on an industrial scale by electrolysis of a chloride solution(B26,B27,B28). Known as the Hoepfner process, a small demonstration plant operated in 1892-1895 in Furfurt, Germany, and two other plants using the process were built and operated in Germany. Another, designed by Hoepfner operated in Norwich, England, from 1897 to 1924. The original German plant used a low grade zinc sulfide which was given a salt roast, leached with hot water, the solution purified and electrolyzed in diaphragm cells to give zinc metal and wet chlorine for making bleaching powder. At the English plant ore was given an oxidizing roast and leached with calcium chloride and carbon dioxide. It produced zinc of 99.96 percent purity.

Information by Ralston(B27) from this period shows an energy consumption of 2730 kwh/M ton (2476 kwh/S ton) Zn or 7.22×10^6 Kcal/M ton (26×10^6 Btu/S ton) Zn for the electrolysis itself. However, this was obtained at a relatively low current density, i.e., 161 amp/m^2 (15 amp/ft^2) compared to 538 amp/m^2 (50 amp/ft^2) in a modern zinc plant. The standard oxidation potential for chloride ion to elemental chlorine is 1.35 volts. Combined with -.76 volt for zinc oxidation gives a potential of 2.11 volts for decomposition of aqueous zinc chloride in the standard state at 25° C. This is a higher voltage than the theoretical voltage of 1.99 volts for electrolysis of zinc sulfate solution. Theoretical energy consumption for the zinc chloride solution is 1859 kwh/M ton (1686 kwh/S ton) Zn at 93 percent current efficiency or 4.92 Kcal/M ton (17.7×10^6 Btu/S ton) Zn. Values for the sulfate discussed previously are 1630 kwh/M ton (1479 kwh/S ton) Zn or 4.31×10^6 Kcal/M ton (15.5×10^6 Btu/S ton) Zn.

In spite of the higher theoretical energy, the practical energy requirement for chloride electrolysis probably is lower than for sulfate. The anodic evolution of chlorine is possible at a lower overvoltage, i.e., 0.2 volts with modern platinized titanium anodes as compared to 0.8 volt for oxygen evolution on lead anodes. Therefore, the practical voltage for a chloride cell should be 0.5 volt lower than for a sulfate cell considering the $\sim$0.1 volt difference in reversible potential. The 0.5 volt corresponds to an energy saving of 441 kwh/M ton (400 kwh/S ton) Zn or 1.17×10^6 Kcal/M ton (4.20×10^6 Btu/S ton) Zn. Nikiforov and Stender(B29,B30) have discussed a more modern technology for electrowinning zinc from aqueous chloride solution. Although data are not derived from operating plants, which are nonexistent, a good case can be made for lower energy consumption with chloride electrolysis. The applicable conditions and results are as follows:

Electrolyte:	- Zinc	48 to 80 g/l
	- HCl	30 g/l (ave)
Current Density		500 amp/m^2 (47 amp/ft^2)
Temperature		35°C
Deposition Time		24 hr max
Cell Voltage		3.0 to 3.1 volts
Current Efficiency		>90 percent
Power Consumption		2800 kwh/M ton Zn.

The power consumption probably refers to metric tons, since a calculation for 3.1 volts and 93 percent current efficiency gives 2473 kwh/S ton Zn. Increasing this 10 percent for line and conversion losses gives 2998 kwh/M ton (2720 kwh/S ton) Zn or 7.95×10^6 Kcal/M ton (28.6×10^6 Btu/S ton) Zn. These values compare to 3417 kwh/M ton (3100 kwh/S ton) Zn or 8.89×10^6 Kcal/M ton (32×10^6 Btu/S ton) Zn for the sulfate electrolysis with lead anodes.

Chloride Leaching with Electrolysis of the Molten Salt

Background.(B27,B28) E. A. Ashcroft in England developed a procedure for roasting zinc sulfide ore, leaching with ferric chloride and electrolyzing the solution to regenerate ferric chloride and deposit zinc. This was tested unsuccessfully in Australia in 1896, after which the Swinburn-Ashcroft process was developed as an improvement. By this process, which exemplified work of a number of investigators of that time, zinc sulfide ore was chlorinated dry at a temperature high enough to distill off the sulfur, and the metal chlorides were separated by a rather complex series of metal displacement treatments. After dissolving the remaining chlorides and further purification, the final solution was evaporated to fused zinc chloride for electrolysis to produce zinc and chlorine for reuse. In variations of this method, chlorination under pressure was used, and in a later version the ore was suspended in fused zinc chloride for chlorination. This early electrolysis of fused zinc chloride was used for a time at Broken Hill, Australia, and, later, modifications were tested elsewhere. Troubles, particularly in cell design and formation of basic salts when evaporating the zinc chloride solution, prevented sustained commercial use.

A pilot plant was built in 1924-1925 in Denver to produce zinc chloride by the Malm Process. In this procedure, dry chlorination of zinc sulfide was carried out at a temperature below that necessary to volatilize the sulfur. (Later investigations show need for a temperature over 600°C to chlorinate zinc sulfide effectively(B31)). The chlorinated product was leached out with water, purified, and evaporated to a saleable zinc chloride. In other semi-commercial plants, the fused chloride was electrolyzed to give metal and chlorine for reuse. Test plants were built earlier in Montana, Colorado, Idaho, and Niagara Falls. Mechanical problems and financing difficulties caused eventual abandonment of each of these projects over the years.

Ralston concluded from his work in 1918 on a full-sized cell in Niagara Falls that fused chloride electrolysis had advantages. It avoided use of diaphragms, occupied little space, and simplified the recovery of zinc. The high voltage needed with the cell at that time, 4.5 to 6.0 volts, used too much power compared with aqueous electrolysis. Interestingly, the cost of the Malm operation in 1918, if all costs were charged against zinc in treating complex ores, was calculated to be only 2 cents per pound of zinc metal(B28).

Recent Work. In recent years, attention has been given again to the chloride system of leaching and electrolytic recovery from a fused salt bath. An advantage to chloride leaching, of course, is elimination of the roasting step with its concern over sulfur dioxide disposal and air pollution. An obvious advantage in fused salt electrolysis is withdrawal of molten metal from the cell which eliminates the labor and energy consumed in stripping and melting cathodes when handling zinc from aqueous acid electrodeposition.

Although a number of interesting procedures have been reported in the technical literature, particularly those developed in Europe and

Australia(B32), progress in production and electrolysis of fused zinc chloride is perhaps best exemplified by recent investigations of the US Bureau of Mines(B33-B35). As discussed previously, various methods of obtaining purified zinc chloride have been investigated over the years without general acceptance of any one procedure. To avoid the rather high temperature needed for dry chlorination, a wet chlorination can be used at a much lower temperature. However, the wet method is less selective in attacking the metal values present. The Bureau of Mines investigators have shown that by adding oxygen under pressure, after chlorinating the concentrates, iron is made insoluble as ferric oxide and can be separated with the lead and insoluble residue. Their preferred method at present, then, is to leach zinc or zinc-lead concentrates at 100°C and 50 psi pressure with chlorine, followed by oxygen, remove the elemental sulfur, lead sulfate and iron oxide in the residue by filtration, purify the solutions with zinc dust, evaporate the solution to a molten salt, and electrolyze to produce zinc and recycle chlorine. Although by no means free from possible difficulties in operation, the chlorine-oxygen leaching procedure does give an excellent extraction of zinc and seems to have a reasonable potential for treating complex sulfide concentrates(B36-B39). The theoretical potential for decomposition of pure molten zinc chloride at 450° C is 1.629 volts(B41). This voltage corresponds to 1334 kwh/M ton (1210 kwh/S ton) Zn or 3.53×10^6 Kcal/M ton (12.7×10^6 Btu/S ton) Zn. The activity of $ZnCl_2$ is somewhat reduced in the salt mixture which will raise the theoretical energy values.

Fused salt cells typically rely on the current to internally heat the cell to compensate for enthalpy changes and heat losses. Unlike operations near room temperature, the surroundings do not supply heat. External heat can be provided in some cases, but the materials available for cell construction often cannot withstand the temperatures or provide adequate thermal conductivity. Thus, the theoretical energy requirement should include heat for a positive enthalpy change and fusion of the feed material. The entropy change, $T\Delta S$ for $ZnCl_2(s) \rightarrow Zn(s) + Cl_2(g)$: 25° C is -11.1 Kcal/mole. Energy to fuse ZnCl feed is estimated to be 15 Kcal/mole (ignores heat of solution in fused salt bath). Therefore, there is a total requirement of 26 Kcal/mole Zn equivalent to $26 \times 1.162 \times 10^{-3} = 0.030$ kwh/mole or 458 kwh/M ton (416 kwh/S ton) Zn for internal heating. This value added to the

1334 kwh/M ton (1210 kwh/S ton) Zn for the reversible potential gives a total of 1797 kwh/M ton (1630 kwh/S ton) Zn or 4.72 x 10^6 Kcal/M ton (17 x 10^6 Btu/ton) Zn at the power plant. This energy for fusion and maintaining temperature is about the same as the energy needed in the aqueous sulfate process.

The USBM at Reno operated a pilot cell intermittently at 6.5 volts and 14,500 amp/m^2 (1347 amp/ft^2) and obtained zinc at a current efficiency of 95 percent(B39). Power consumption was estimated to be 5.7 kwh/kg (2.6 kwh/lb) which is 5733 kwh/M ton (5200 kwh/S ton) Zn or 15.17 x 10^6 Kcal/M ton (54.6 x 10^6 Btu/S ton) Zn. This energy consumption is higher than for aqueous electrolysis, but there is a good opportunity for improvement by continuous operation.

Fray(B40) reported an energy consumption of 2.84 kwh/kg (1.29 kwh/lb), 2840 kwh/M ton (2576 kwh/S ton) or 7.50 x 10^6 Kcal/M ton (27 x 10^6 Btu/S ton)Zn) for small scale electrolysis at a current density of 0.77 amp/cm^2 (715 amp/ft^2) and an electrode spacing of 2.0 cm (0.8 inch). Energy losses are due to IR drop in the electrolyte (polarization is negligable) and recombination of zinc and chlorine. Perforated and porous electrodes were effective in reducing recombination. The energy consumption reported by Fray is much lower than reported by USBM and essentially that for aqueous electrolysis. Therefore, fused salt electrolysis appears to offer possibilities for producing zinc at high current density with moderate energy consumption.

Total Energy Requirements for Chloride Processes

Prior discussion has concentrated on the energy use in aqueous and fused salt electrolysis of zinc chloride. However, use of chloride electrolysis affects other steps in the process and the energy involved in these steps. Therefore various options will be examined and total process energy requirements estimated.

Roasting and Leaching. A scheme suggested by Nikiforov and Stender involves roasting the ore to make SO_2 and sulfuric acid. Hydrochloric acid is considered a raw material for leaching and chlorine a product available for other uses, if it does not have to be converted back to acid for leaching. Thus, the chlorine cycle is not a closed one, and this may be an advantage if the processing location is such that it can be tied in with other processes, i.e., chlorination of ethylene to make vinyl chloride and hydrochloric acid. In a remote location the by-product sulfuric acid from roasting may be used to make HCl from salt, and the product chlorine liquified and shipped as a marketable product. However, chlorine may be used for leaching also, to give elemental sulfur and zinc chloride. The USBM process using chlorine plus oxygen provides a zinc chloride solution (estimated 25% $ZnCl_2$). Dry chlorination has also been investigated from time to time(B31).

Ferric chloride leaching without roasting is one option to chlorine leaching(B27), but involves renewing the product ferrous chloride by electrolysis. Also, the electrolytic cell must be designed and operated in a manner that prevents reduction of the ferric chloride at the cathode. Chlorine, of course, is not produced.

Table B5 considers four processes from the standpoint of total energy:

(I) Roasting, HCl leaching, aqueous electrolysis
(II) Chlorine-Oxygen leaching, aqueous electrolysis
(III) Ferric chloride leaching, aqueous electrolysis
(IV) Chlorine-oxygen leaching, fused salt electrolysis.

The energy available from the roasting reaction was previously estimated to be 1.4×10^6 Kcal/M ton (5×10^6 Btu/S ton) Zn. The credit more than cancels out the steam plant whose output is not needed. Electrolysis energy for ferric chloride leaching was calculated from the difference in the reversible oxidation potential +0.77 volts v.s. the potential for chloride oxidation of 1.36 volts. Overvoltages are relatively low for both reactions so ferrous chloride as a depolarizer should reduce cell potential by 0.6 volt, 528 kwh/M ton (479 kwh/S ton) Zn at 93 percent current efficiency or (5.03×10^6 Btu/S ton Zn). The Btu were subtracted from that for chloride electrolysis and rounded off to 6.7×10^6 Kcal/M ton (24×10^6 Btu/ton) Zn.

In the fused salt process, evaporation is required to make the anhydrous cell feed. Scheiner et.al.(B37) report that a pulp density of

TABLE B5. ENERGY USE OF CHLORIDE ZINC PROCESSES

	Process Kcal x 10^6/M ton Zn (Btu x 10^6/S ton Zn)			
	I	II	III	IV
Preparation of Concentrate	4.22(15.2)	4.22(15.2)	4.22(15.2)	4.22(15.2)
Roasting	-1.40(-5.00)	0.0	0.0	0.0
Leaching	2.5(9.0)	0.17(0.6)	0.17(0.6)	0.17(0.6)
Evaporation	--	--	--	(6.7)
Purification and Residue Treatment	0.33(1.2)	0.33(1.2)	0.33)1.2)	0.33(1.2)
Electrolysis	7.95(28.6)	7.95(28.6)	6.67(24)	7.50(27)
Steam Plant	0.69(2.5)	0.69(2.5)	0.69(2.5)	0.69(2.5)
Melting and Casting	0.39(1.4)	0.39(1.4)	0.39(1.4)	0.14(-0.5)
Credits				
Chlorine	-6.25(-22.5)	0.0	0.0	0.0
Total	8.3(30)	14(50)	13(45)	15(53)

I = Roasting, HCl Leaching, Aqueous Electrolysis.
II = Chlorine-Oxygen Leaching, Aqueous Electrolysis.
III = Ferric Chloride Leaching, Aqueous Electrolysis.
IV = Chlorine-Oxygen Leaching, Fused Salt Electrolysis.

50 percent with a concentrate containing 50 percent zinc is used in leaching. Assuming total zinc recovery, 25 g of zinc would be dissolved in 50 g of solution. Allowing an equal weight of water for washing, etc., a ≈25 percent zinc chloride solution would result. Heat of solution for this concentration is less than +15.7 Kcal/mole. There are 10.7 moles of water evaporated per mole $ZnCl_2$. Energy for evaporation is calculated to be 1.9×10^6 Kcal/M ton (6.7×10^6 Btu/S ton) Zn.

The hydrochloric acid for Process I is produced from the roast sulfuric acid. In the process the reactants are heated to 800° C. The enthalpy for the reaction:

$$H_2SO_4(70\%) + NaCl \rightarrow 2HCl(g) + Na_2SO_4 + 2.33\ H_2O$$

is 26.55 Kcal/mole H_2SO_4 at 25° C. Heating the products to 800° C adds 65.13 Kcal/mole for a total of 91.69 Kcal/mole. Heat recovery from such a system would appear difficult. Assuming a 60 percent efficient use of fuel the energy requirement will be 2.36×10^6 Kcal/M ton (8.5×10^6 Btu/S ton) Zn.

Transportation, could be a factor in energy use. If possible, the same transportation vessels may be used for hydrochloric acid into and the chlorine out of the plant. The credit for chlorine, of course, is an overwhelming factor in the low net energy for Process I. A 90,700 M ton/yr (100,000 S ton/yr) zinc plant should produce about 97,000 M ton/yr (107,000 S ton/yr) of chlorine. A plant of this size is average for zinc but is on the small side for chlorine.

The process assumes that either raw chlorine from the cells can be piped to an adjacent chemical plant for use or that a complete liquefaction and tank facility is constructed at the zinc plant.

Other Modifications to Chloride Methods

Electrolytic zinc was made from an aqueous chloride electrolyte in Germany in 1938-1944 using mercury cathodes(B19). The plant was not continued after the war. Zinc-containing amalgam from primary cells was pumped to a second sulfate circuit where the amalgam became the anode. Zinc of high purity was deposited and the procedure was considered to be technically successful. Use of mercury aided in simplifying the purification problem and in zinc removal from the chloride cell, and the whole operation was considered to be an improvement over the Hoepfner cell.

Some experimental work with mercury cathodes has been reported in South Africa, and the concept continues to be of interest in this country(B20). Although there are definite advantages to using a chloride system, and power savings may be attained in using mercury cathodes (probably even with a second refining step), from an environmental standpoint use of mercury may meet strong objections.

Depositing a metal to form an amalgam and decomposing the amalgam anodically to deposit the pure metal has been proposed for many systems and commercially developed for some, i.e., Castner rocking chlorine-caustic cell. The mercury functions as a separation membrane. However, designs have generally been abandoned due to complexity, high labor, difficulty in containing mercury, and so on. With two electrolysis steps there are IR drops through two electrolytes, and polarization at 4 electrode-solution interfaces. There are special circumstances where the two-cell mercury system may work, see Sodium, but development of a suitable semi-permeable membrane would seem to be a more promising direction to go if the goal is to separate chloride and sulfate electrolytes.

Recent work by the U.S. Bureau of Mines on producing zinc chloride in solution from zinc sulfide concentrates may apply to electrolytic recovery, either by an aqueous chloride cell or, after evaporation, by a fused chloride cell. Among many procedures- chlorination, ferric chloride leaching, salt roasting, roasting and chloride leaching, etc. - one of particular interest electrometallurgically has been that of electrolytic oxidation(B36). Using a flow-through diaphragm cell, complex lead-zinc sulfide concentrates in a brine slurry were passed through the anode compartment where hydrochloric and hypochlorous acids formed by electrolysis converted zinc sulfide to zinc chloride and released elemental sulfur. At the cathode sodium hydroxide was formed. Metal extractions of 92 to 100 percent were attained in experimental work. However, under optimum experimental conditions energy consumption on zinc concentrates was 1.4 to 2.3 kwh/kg (3 to 5 kwh/lb). Using 1.42 kwh/kg (3.13 kwh/lb) (enclosed cell) this amounts to over 20×10^6 Kcal/M ton (70×10^6 Btu/S ton) of metal extracted or an excessive power consumption for dissolving the zinc.

Although it may be possible to combine dissolution and electrowinning in one cell to lower the energy use, the total energy requirement still appears to be higher than that for conventional processing.

We conclude that with improved methods available for getting purified zinc chloride from zinc concentrates, and possibilities for improved cell design and operation, the aqueous chloride electrolysis method still merits attention as a possiblity for energy reduction in producing primary zinc. It would appear that its lack of development in the last 25 years has been due to the success of the sulfate process and a lack of materials to handle chlorine. Also, there perhaps has been a reluctance to design and construct a system involving elemental chlorine. Where a zinc plant can conveniently be located near a chlorine consumer that can return byproduct HCl for leaching there should be a real incentive to develop chloride processes. Generally, these circumstances have not existed or been brought about.

Alkaline Leaching and Electrolysis

Investigations to leach zinc ores with alkalis go back to about 1897, but these were laboratory studies. In more recent years, there has been interest in alkaline leaching for zinc sources other than the normal sulfide zinc concentrates. Thus, the Bureau of Mines has looked into the caustic leaching of oxidized zinc ores that could not be concentrated readily and were too low grade to be shipped or caused trouble in acid leaching(B40). A procedure was worked out to leach, purify, and electrolytically recover the zinc as a flake product with caustic soda recycled. Some 85 percent of the metal was recovered from a 21 percent zinc ore with a cell power consumption of 0.68 kwh/kg (1.5 kwh/lb) of zinc or 8.75 x 10^6 Kcal/M ton (31.5 x 10^6 Btu/S ton). Traditionally the deposition of dendrites rather than compact deposits has been considered a disadvantage from the standpoint of handling and obtaining a pure product. However, the advent of "fluidizing" engineering has made it apparent that handling a slurry has production advantages as long as product quality is retained.

Similarly, the Tennessee Corporation has found an alkaline leach to be effective for a high iron concentrate containing 42 percent zinc after giving it a two-stage roast to remove sulfur and, in the second reducing stage, to break up ferrites and render lead and copper less soluble(B41). In a first-stage leaching step at 77°C, some 85-90 percent of the soluble zinc was removed, and by releaching the residue with still hotter strong caustic solution, an overall recovery of 93-97 percent of the zinc in the concentrate was attained. After purification by air oxidation to remove manganese and most of the iron, and by zinc dust to remove copper, lead, cadmium, and residual iron, the solution was electrolyzed. A current efficiency of 93-94 percent was obtained at a current density of 1720 amp/m^2 (160 amp/ft^2) in pilot plant operation. Nickel anodes and magnesium cathodes were used, spaced 2.5 to 5 cm (1 to 2 inches) apart. The dendritic zinc deposit was non-adherent and could be readily collected and removed as a slurry from the cell base. After washing and drying, the zinc sponge could be either pulverized to an unusually reactive powder or melted and cast into slabs meeting high-grade zinc standards.

More recently, Amax has operated an 1360 kg/day (3000 lb/day) pilot plant to recover zinc from a similar type high-iron sulfide concentrate*. They also have found it advantageous to follow the desulfurizing-oxidizing roast with a brief-reducing roast at a lower temperature. The second roast raises recovery from 84 percent to 93 percent. After a simple strong (400 g/l) caustic leach at 90-100°C, the residue is removed, the solution aerated, filtered, purified with zinc dust, and electrolyzed at 1080 amp/m^2 (100 amp/ft^2) with a current efficiency of 95 percent. Power required for electrolysis is estimated conservatively at 3.5 volt, 3300 kwh/M ton (3000 kwh/S ton) Zn or zinc or 8.75 x 10^6 Kcal/M ton (31.5 x 10^6 Btu/S ton), although in some runs a power requirement as low as 3.0 volts, 2866 kwh/M ton (2600 kwh/S ton) Zn has been obtained. The crystalline zinc deposit is collected in hopper-bottomed cells, removed mechanically, and can be sold as such, pulverized to a powder, or briquetted, melted, and cast. Such a system can be readily mechanized. Cells can be covered to prevent irritating caustic spray, and manpower requirements should be low.

Considering the high current density used, which is twice that for the usual sulfate electrolysis, the energy for electrolysis is remarkably low. The use of a higher current density here is a good example of the tendency in electrolysis processes to increase current density when gains

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*Sept., 1978 Communication from Amax Base Metals Research and Development, Inc.

have been made in power consumption. This both balances the power cost with capital and other operating costs to achieve maximum economy.

A 400 g/l (10 molar) caustic solution is used as electrolyte. Standard electrode potentials in basic solution are:

$$Zn + 4OH^- \rightarrow ZnO_2^{=} + 2H_2 + 2e^- \quad E° = -1.215\text{: } 25° \text{ C}$$

$$4OH^- \rightarrow 2O_2 + 2H_2O + 4e^- \quad E° = +0.401\text{: } 25° \text{ C} \quad .$$

The reversible potential is 1.62 volt corresponding to 1326 kwH/M ton (1203 kwh/S ton) Zn or 3.51×10^6 Kcal/M ton (12.63×10^6 Btu/S ton) Zn of electrical plant power at 100 percent current efficiency. The potential is 0.3 volt lower than for sulfate electrolysis (1.99 volt). Nickel is used as an anode in caustic electrolysis and oxygen overvoltage is lower than on lead in acid solution. Nickel anodes find considerable use in potassium hydroxide solution for water electrolysis, and the problem of anodic overvoltage is now under vigorous attack(B42). Use of porous sintered substrates combined with coating with catalysts by such techniques as plasma jet spraying have resulted in anodes that operate at current densities up to 1.0 amp/cm^2 (930 amp/ft^2) with overvoltages of only 0.2 to 0.3 volt.

Thus, it should be realistic to estimate the following voltage components for a caustic zinc electrowinning cell, assuming a current density of 50 amp/ft^2 (0.05 amp/cm^2), and a cell temperature of 60°C for which the conductivity of the electrolyte should be about 0.5 mho(B43):

Cathode	-1.4 v.s. NHE
Electrolyte	0.5
Anode	+0.6 v.s. NHE
Total Cell	2.5 volts.

The interelectrode spacing is assumed to be about 5 cm (two inches). With 93 percent current efficiency and 10 percent power loss between the power into the plant and the cells, the above voltage corresponds to 2425 kwh/M ton (2200 kwh/S ton) Zn or 6.39×10^6 Kcal/M ton (23×10^6 Btu/S ton) Zn. We believe that this is a conservative estimate that could be lowered by reducing interelectrode spacing, etc. Conversely, a similar power consumption could be obtained at a higher current density.

A process flow sheet is shown in Figure B2. Table B6 is an estimate of energy requirements for the various process steps.

Demostrated advantages of alkaline leaching appear to be:

(1) Excellent recovery of zinc from most oxidized ores and from high iron concentrates. Normal roasted zinc sulfide concentrates should be handled at least equally well.

(2) An energy saving in electrolysis of around 30 percent 3.06×10^6 Kcal/M ton (11×10^6 Btu/S ton) over sulfate electrolysis is indicated, with opportunities to increase this margin substantially.

(3) With a non-adherent deposit, or at least one that can be readily removed by occasionally vibrating the cathodes, the cell can be covered to eliminate misting and recover oxygen, if desired.

(4) Permanent electrodes of magnesium and nickel or nickel-coated steel can be spaced close together and tight connections made to busbars to reduce voltage losses. Anodes do not need to be removed and cleaned as with sulfate electrolysis.

(5) With no need to strip cathodes, the tank house can be automated and a substantial saving made in manpower costs.

(6) There appears to be no need for additives to the electrolyte as in sulfate electrolysis, and the system seems to be much less sensitive to adverse effects of various impurities. The comment has been made that deposition of zinc from alkaline electrolytes has the advantage of requiring less purification(B44).

(7) Inexpensive materials of construction can be used. Corrosion is a lesser problem than with an acid electrolyte.

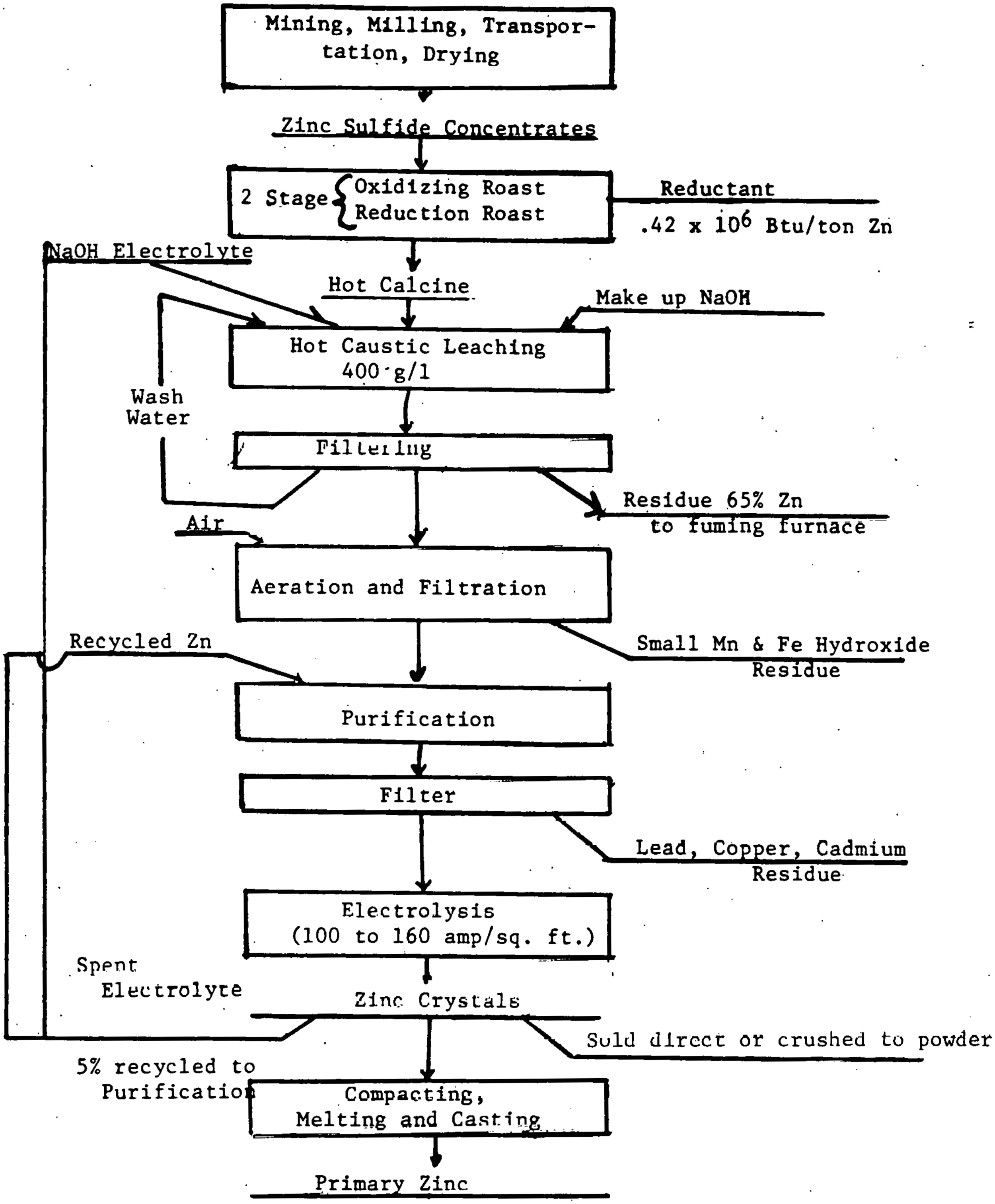

FIGURE B2. ALKALINE ELECTROLYSIS FLOW SHEET

TABLE B6. ENERGY FOR CAUSTIC ZINC PROCESS

Unit Operation	(Kcal/M ton Zn) x 10^6	(Btu/S ton Zn) x 10^6
Preparation of Concentrate	4.22	15.2
Oxidizing Roast	-1.39	-5.0
Reducing Roast	(.28)	(1.0)
Leaching	(.56)	(2.0)
Filtering, Purification	.14	.5
Electrolysis	6.4	23
Steam Plant	.69	2.5
Crystal Collection	(.14)	(0.5)
Compacting, Melting	.39	1.4
Totals	11.4	41

Values in parenthesis are very rough estimates. Heat from first roast is adequate for the reducing roast and only a small amount of carbon is added. Leaching is hot, (100° C) requiring heating of solution.

Disadvantages appear to be:

(1) The second stage or reducing roast constitutes an extra operation over normal sulfate practice. However, this is a simple operation at a temperature of about 750° C, compared to 900° C for the oxidizing stage, and can fully utilize the heat in the hot calcine. The energy supplied by the coal reductant is estimated to be 0.12×10^6 Kcal/M ton ($0.42 \times 10^{+6}$ Btu/S ton) of zinc recovered from a 60 percent zinc calcine. The reducing roast eliminates the need for a Jarosite or Goethite treatment of residue, as in sulfate leaching to get a high overall zinc recovery.

(2) A small amount of caustic soda is needed as make up for losses whereas in sulfate leaching, enough zinc sulfate can be formed in roasting to compensate for losses. By conservation of wash water, this loss of alkali is expected to be very little, but sustained operation is needed to determine how little. Caustic exposed to air will carbonate but this has so far been a minor problem.

(3) The crystalline zinc deposit may need compaction before melting if it is not sold as a powder. This has been demonstrated to be a simple operation and the handling of cathode zinc from the alkaline cells is not expected to use appreciably more energy than the removal, washing, melting, and casting of cathode zinc from sulfate cells.

(4) As a new method, alkaline leaching does not have the background of experience and engineering developments of the sulfate process which make effective operation of a new plant more assured. However, there are potential opportunities for savings in cost, energy, and conservation with such a new process.

Considering both advantages and disadvantages, it would appear that alkaline leaching has an excellent chance to give a substantial saving in energy, as well as using less manpower and being more adaptable to automation the sulfate leaching.

The fact that a dendritic deposit can be considered a large scale primary metallurgical product rather than a specialty item should open up a whole new area for saving energy, labor, and costs. Semi-permanent installation of electrodes is possible, meaning precisely machined sheets can be accurately positioned to give a minimum spacing. A 5 cm (two-inch) spacing has been used, while 2.5 cm (one-inch) should be sufficient.

The deposit can be loosened by frequent vibration, hydraulics, etc., before bridging is likely to occur. The enhanced surface of the deposit and its growth toward the anode will also keep cell voltage at a minimum.

The dendrites from the cells can be pumped around as a slurry, filtered, etc., and handled in a manner more akin to a chemical plant. The concept may have application to metals other than zinc, e.g., copper, lead.

Other Possible Process Innovations for Zinc Recovery

Along with suggested improvements in the various steps of conventional sulfate electrolytic zinc plant operations, there have been a number of radically different approaches to getting the zinc into solution. Much of the impetus to these efforts has been environmental to eliminate the roasting operation, as well as financial, to get a higher overall zinc recovery. In general, the many procedures suggested for leaching to avoid roasting do not result in any saving of energy; rather the energy released in roasting is an asset for generating process steam.

Leaching Innovations

Anodic Oxidation. The Bureau of Mines flow-through diaphragm cell for electrolytic oxidation of lead-zinc concentrates in a chloride system has been discussed under aqueous chloride electrolysis(B44). Similarly, work has been done elsewhere, particularly in Japan and Germany, on anodic dissolution of zinc sulfide in an acid sulfate media. One general procedure, which has been encouraged by the successful Inco development of electrolyzing cast nickel sulfide anodes, has been to electrolyze pressed anodes of zinc sulfide concentrates containing graphite for conductivity(B45).

This is similar to development work in Australia on pressed galena anodes as discussed in the section "Lead". So far, there has been insufficient success experimentally with solid zinc sulfide anodes to warrant any attempt at commercialization. This is largely because of a buildup of elemental sulfur on the anode which prevents adequate mass transfer. Also, the anodes have been fragile and have had a rather high electrical resistance.

Experimental work has been done on using a slurry or suspension of zinc sulfide, as in the Bureau of Mines work with a chloride electrolyte. Early work with a dilute sulfuric acid electrolyte was handicapped by production of considerable hydrogen sulfide. However, by adding sufficient graphite powder or certain other oxidizable reactants to raise the oxidation potential above the level at which hydrogen sulfide was generated, this action was suppressed. Under optimum conditions, 95 percent zinc dissolution was achieved and sulfide was converted almost completely to elemental sulfur(B46). By purification of the zinc sulfate solution, it could be made suitable for electrodeposition to cathode zinc. The operations have not been integrated into one process, and because of the power requirements, as well as complications in operation of a two-step electrolysis, any saving in energy over conventional treatment is doubtful.

Copper Sulfate. Experimental work has been done on leaching zinc-sulfide concentrates directly with copper sulfate solution under pressure at about 220°C(B47). A zinc sulfate solution is formed by the exchange reaction which, after removal of the resultant copper sulfide precipitate and gangue can be purified and electrolyzed. The copper sulfate solution is regenerated by a second pressure leach with spent electrolyte under oxidizing conditions, thereby releasing elemental sulfur. In modifications of this suggested process, to avoid production of excessive amounts of sulfuric acid during cuprous sulfide precipitation, the first pressure leach is done with air or oxygen. This process, like so many others, offers a novel, technically feasible, procedure, but with insufficient economic incentives to replace a more conservative method. Because of the elevated temperature and pressure among other requirements, energy savings over the present roasting-leaching are unlikely. As with other sulfur producing processes the energy from roasting to SO_2, 1.39×10^6 Kcal/M ton or (5×10^6 Btu/S ton Zn) is not obtained.

Ammonia. As a corollary to commercially successful ammonia leaching of copper sulfide concentrates, the Anaconda Company has done experimental work on ammonia leaching of lead-zinc concentrates(B48). The emphasis seems to have been on lead recovery, but flow sheets involve zinc. A slurry of sulfide concentrates is leached by strong agitation with ammonium sulfate and free ammonia, plus oxygen, under slight pressure (under 2.1 kg/cm^2 or 30 psig). The zinc ammonium sulfate solution is filtered off, the ammonia driven off by heating, and the zinc sulfate solution purified and electrolyzed in a conventional cell. There is insufficient information available to calculate energy requirements, particularly from complex ores. Here again power from roasting is not obtained.

Acetic Acid. The use of acetic acid has been suggested as a solvent for zinc in treating oxidized zinc ores. In experimental work, Escadera has found that up to 88 percent of the zinc in a 19 percent oxidized ore from Brazil could be solubilized with remarkably low impurity concentration in the solution(B49). After adding sulfuric acid to the solution (spent electrolyte) acetic acid could be distilled for recirculation, and the resultant zinc sulfate solution could be purified and electrolyzed conventionally. This procedure may be useful for some special situations, but because of acetic acid losses and energy needed for distillation, the total energy required should at least equal that for conventional treatment.

Sulfurous Acid. A sulfite system for leaching complex zinc ores has been described briefly as giving high rates of extraction and is not bothered by halogens in the leachant(B50). After leaching, the zinc is solvent extracted, stripped with sulfuric electrolyte, purified, and electrolyzed conventionally. Too little information is available to estimate energy requirements. However, the system may be integrated into an electrolysis where sulfurous acid depolarizes the anode.

Other. The high pressure sulfuric acid leaching of various metal sulfides, with air or oxygen, over the past 20 years has included attention to zinc although emphasis has been on other metals(B51). From this early work by Professor Forward and Sherritt Gordon, a number of flow sheets involving zinc have been suggested. Since high pressure leaching at elevated temperature is inherently energy intensive compared to conventional roasting-leaching, this area of development will not be discussed in detail. It is of greater interest from an environmental standpoint to avoid roasting and to recover elemental sulfur.

Likewise, solvent extraction has been directed more toward other metals, but a few commercial applications have developed and there are possibilities for it to become a useful step in zinc electrometallurgy(B52). For instance, the Metstep plant in South African (not now in operation) used solvent extraction to remove zinc from a chloride leaching solution, then stripped with sulfuric acid to produce zinc sulfate solution for sulfate electrolysis. If chloride contamination of the sulfate solution can be avoided, this suggests using the more powerful chloride leaching systems for extraction and using present equipment for conventional sulfate electrolysis.

Among many examples of how solvent extraction may be used to effect separation of zinc from other metals, the separation from copper in sulfate solutions can be important. Zinc and copper commonly occur together. The involved electrolysis of a mixed copper-zinc sulfate solution, or the need for an excessive amount of zinc dust for copper removal by displacement, can be avoided by solvent extraction of the zinc or the copper. This makes possible separate electrolysis systems after stripping the organic phase with sulfuric acid electrolyte. A variation on separate extraction of copper and zinc is to exchange one for the other. Use of copper di (2-ethylhexyl) phosphate as the organic extractant to effect a copper-zinc exchange has been patented(B53).

In the San Telmo process of treating pyrite containing copper and zinc sulfides, as 2.8 percent Cu, 3.8 percent Zn and 39 percent Fe, leaching is done with ferric sulfate to release elemental sulfur. Copper is removed by solvent extraction, iron precipitated by the Jarosite procedure, and the zinc concentrated by solvent extraction before electrolysis(B54).

In summary, solvent extraction can be a useful tool in separating zinc in solution from other materials, particularly in treating complex concentrates, but its effect on energy consumption depends on a comparison of specific flow diagrams. However, as stated previously, the energy is probably less than for a typical leaching system, i.e., 0.17×10^6 Kcal/M ton (0.6×10^6 Btu/S ton).

Conclusions

Table B7 compares the estimated and projected energy required for recovering zinc by various processes that have been discussed. The rough estimates require a more careful evaluation before actually undertaking further experimental or pilot plant programs. This should be a first task of such programs. Energy is reported (1) as the Kcal/M ton (Btu/S ton) including fuel for generating electrolysis power (2646 Kcal/kwh or 10,500 Btu/kwh); (2) the kwh for electrolysis assuming a 10 percent loss in electric power for conversion and conduction to cells and (3) annual Kcal or Btu required if the method were used for all domestic production in 1977 and 2,000. We conclude:

(1) The lowest energy used is obtained by cogeneration of marketable chlorine in the electrowinning cell. The energy is lowered mainly because total energy can be allocated to two products rather than one.

(2) Energy may be reduced to 14 x 10^6 Kcal/M ton (50 x 10^6 Btu/S ton) Zn by (a) use of DSA anodes in conventional sulfate electrolysis, and (b) chloride electrolysis using chlorine leaching and (c) fused salt electrolysis. Ferric chloride leaching will reduce energy to 12.5 x 10^6 Kcal/M ton Zn providing a current efficiency of over 90 percent can be obtained.

(3) Caustic leaching and electrolysis can achieve an overall energy use of 12.5 x 10^6 Kcal/M ton (45 x 10^6 Btu/S ton) Zn even at the relatively high current density of 1080 amp/m^2 (100 amp/ft^2). The method has the potential of reducing energy use to 11 x 10^6 Kcal/M ton (40 x 10^6 Btu/S ton) Zn or less.

TABLE B7. ENERGY SAVINGS FOR ZINC WINNING METHODS

Process	Electrical$^{(2)}$ Energy kwh/M ton (kwh/S ton)	Total Energy/ton, 10^6 Kcal/M Ton (10^6 Btu/S ton)	Year 1977		Year 2000	
			10^9 kwh	10^{12} Kcal (10^{12} Btu)	10^9 kwh	10^{12} Kcal (10^{12} Btu)
Average sulfate process (contemporary)	3790 (3600)	16.7 (60)	0.0	0.0	0.0	0.0
Optimum sulfate process	3417 (3100)	15.3 (55)	0.22	0.55 (2.17)	0.47	1.18 (4.70)
With DSA Anodes	3090 (2800)	14.5 (52)	0.35	0.88 (3.47)	0.75	1.89 (7.52)
With SO_2 Depolarizer	2860 (2600)	15.5 (55)	0.43	0.48 (1.74)	0.94	1.04 (3.76)
Aqueous Chloride Process						
Roasting, Chlorine Production	2980 (2700)	8.3(1) (30)	0.39	3.28 (13.0)	0.85	7.10 (28.2)
Chlorine-Oxygen Leaching	2980 (2700)	13.9 (50)	0.39	1.09 (4.34)	0.85	2.36 (9.40)
Ferric Chloride Leaching	2540 (2300)	12.5 (45)	0.56	1.64 (6.51)	1.22	3.55 (14.1)
Fused Chloride Process	2870 (2600)	14.7 (53)	.43	.76 (3.03)	.94	(1.65) (6.58)

TABLE B7. ENERGY SAVINGS FOR ZINC WINNING METHODS (continued)

Process	Electrical(2) Energy kwh/M ton (kwh/S ton)	Total Energy/ton, 10^6 Kcal/M ton (10^6 Btu/S ton)	Year 1977		Year 2000	
			10^9kwh	10^{17} Kcal (10^{12} Btu)	10^9kwh	10^{12} Kcal (10^{17} Btu)
Caustic Process						
1076 amp/m^2(100 amp/ft^2)	2870 (2600)	12.5 (45)	.43	1.64 (6.51)	.94	3.55 (14.1)
538 amp/m^2 (50 amp/ft^2)	2430 (2200)	11.4 (41)	.61	2.07 (8.24)	1.31	4.50 (17.8)

1) Assumes cogeneration of chlorine

2) Electrical energy for electrolysis

3) Assumes 394,000 M ton (434,000 S ton)/yr. or 42% of consumption

4) Assumes 853,000 M ton (940,000 S ton)/yr or 42% of predicted consumption.

(4) Using the roasting SO_2 off-gas to depolarize the anode in the sulfate process can reduce the energy requirement to 15.5×10^6 Kcal/M ton (56×10^6 Btu/S ton) Zn or less. Use of the method will require catalysed porous anodes, and an efficient evaporation and crystallization system for treating cell effluent.

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TECHNOLOGY OF LEAD

Introduction

Lead is comparatively easy to concentrate and smelt by conventional pyrometallurgical techniques. Such techniques are now the only ones for domestic production. Lead occurs predominantly as a sulfide, often with copper and zinc. A relatively pure lead concentrate can often be obtained by physical methods. However, concentrates of lead with other metals, i.e., lead-zinc, can be readily processed as well. The energy required for the usual sinter-blast furnace process is estimated to be about 7.5×10^6 Kcal/M ton (27×10^6 Btu/S ton) of refined lead. Energy use is divided into (USBM Report):

Mining and concentrating	34%
Smelting and drossing	48%
Refining	18%.

This comparison of energy requirements may have to be revised in the future to take account of new pyrometallurgical processes utilizing less energy$^{(C3)}$.

Such processes are concerned with "converting lead sulfide to lead metal and sulfur dioxide much in the manner that copper ores are treated. For the reaction:

$$PbS + O_2 \rightarrow Pb + SO_2$$

the standard enthalpy change is -48.1 Kcal/mole Pb or 0.23×10^6 Kcal/M ton Pb. It is possible that the 48 percent or 3.6×10^6 Kcal/M ton (13×10^6 Btu/S ton) Pb of the total current energy requirement for blast furnace lead could be lowered by at least one-half so that the total energy requirement would be 5.7×10^6 Kcal/M ton (20.5×10^6 Btu/S ton) Pb.

A detailed flow sheet for the conventional process is shown in Figure C1 and data are summarized in Table C1. Proposed air pollution standards, if adapted, could impose severe restraints and/or costs on pyrometallurgical methods in order to meet the standards.

TABLE C1. PRODUCTION OF REFINED LEAD

	Unit	Units Per Net Ton of Lead	10^6 Btu Per Unit	10^6 Btu Per S ton of Lead
Mining				
Electrical energy	kwh	274.7	0.0105	2.88
Explosives	lb	12.55	0.030	0.38
Diesel fuel oil	gal	5.51	0.139	0.77
Gasoline	gal	0.44	0.125	0.06
Steel	lb	13.98	0.0175	0.24
			Subtotal	4.33
Crushing				
Electrical energy	kwh	28.6	0.0105	0.30
Grinding and classification				
Electrical energry	kwh	244.5	0.0105	2.57
Steel	lb	23.44	0.0175	0.41
			Subtotal	2.98
Beneficiation				
Conditioning, flotation and pumping	kwh	89.3	0.0105	0.94
Thickening and filtering	kwh	11.7	0.0105	0.12
Organic reagents	lb	1.46	0.020	0.03
Inorganic reagents	lb	9.29	0.005	0.05
Other electrical energy	kwh	4.0	0.0105	0.04
			Subtotal	1.18
Transportation of concentrates (300 miles rail)	net ton-mile	507.0	0.00067	0.34
Charge preparation				
Electrical	kwh	5.00	0.0105	0.05
Natural gas	ft^3	160.0	0.001	0.16
Limestone	net ton	0.12	0.24	0.03

TABLE C1. (Continued)

	Units	Units Per Net Ton of Lead	10^6 Btu Per Unit	10^6 Btu Per S ton of Lead
Charge Preparation (Cont'd)				
Iron ore	net ton	0.07	0.715	0.05
Sand (silica)	net ton	0.09	0.10	0.01
Sand transportation	net ton-	9.0	0.00067	0.01
			Subtotal	0.31
Sintering				
Electrical energy	kwh	44.8	0.0105	0.47
Natural gas	ft^3	454.05	0.001	0.45
Coke breeze	net ton	0.019	21.0	0.40
Breeze transportation (500 miles by rail)	net ton-mile	9.5	0.00067	0.01
			Subtotal	1.33
Blast furnace				
Electrical energy	kwh	42.5	0.0105	0.45
Natural gas	ft^3	220.0	0.001	0.22
Coke	net ton	0.23	31.5	7.25
Coke transportation (500 miles by rail)	net ton-mile	115.0	0.00067	0.08
			Subtotal	8.00
Drossing				
Electrical energy	kwh	2.30	0.0105	0.02
Natural gas	ft^3	520.0	0.001	0.52
Sulfur	net ton	0.002	5.8	0.01
Sulfur transportation (500 miles by rail)	net ton-mile	1.0	0.00067	0.00
			Subtotal	0.55

TABLE C1. (Continued)

	Unit	Units Per Net Ton of Lead	10^6 Btu Per Unit	10^6 Btu Per S Ton of Lead
Dross reverberatory furnace				
Electrical energy	kwh	2.0	0.0105	0.02
Natural gas	ft^3	782.58	0.001	0.78
Coke Breeze	net ton	0.006	21.0	0.13
Breeze transportation (500 miles by rail)	net ton-mile	3.0	0.00067	0.00
Soda ash	net ton	0.010	18.3	0.18
Soda ash transportation (300 miles by rail)	net ton-mile	3.0	0.00067	0.00
			Subtotal	1.11
Mobile equipment fuel				
Diesel fuel	gal	0.40	0.139	0.06
Sulfuric acid plant				
Electrical energy	kwh	40.5	0.0105	0.43
Natural gas	ft^3	600.0	0.001	0.60
Sulfuric acid product	net ton	0.73	0.83	-0.61
			Subtotal	0.42
Dust collection system				
Electrical energy	kwh	63.69	0.0105	0.67
Sampling				
Electrical energy	kwh	1.44	0.0105	0.02
Natural gas	ft^3	86.61	0.001	0.09
			Subtotal	0.11
Refining				
Softening				
Electrical energy	kwh	2.6	0.0105	0.03
Natural gas	ft^3	754.0	0.001	0.75
			Subtotal	0.78

TABLE C1. (Continued)

	Unit	Units Per Net Ton of Lead	10^6 Btu Per Unit	10^6 Btu Per S ton of Lead
Desilverizing kettles				
Electrical energy	kwh	14.0	0.0105	0.15
Natural gas	ft^3	610.0	0.001	0.61
Zinc spelter	net ton	0.0056	65.0	0.36
Zinc transportation (300 miles by rail)	net ton-mile	1.68	0.00067	0.00
			Subtotal	1.12
Howard presses				
Electrical	kwh	1.0	0.0105	0.01
Retorting				
Natural gas	ft^3	20.0	0.001	0.02
Vaccum dezincing				
Electrical energy	kwh	6.0	0.0105	0.06
Natural gas	ft^3	270.0	0.001	0.27
			Subtotal	0.033
Debismuthizing				
Electrical energy	kwh	14.0	0.0105	0.15
Natural gas	ft^3	1,300.0	0.001	1.30
Calcium	net ton	0.00066	243.6	0.16
Calcium transportation (1,000 miles by truck)	net ton-mile	0.66	0.0024	0.00
Magnesium	net ton	0.00173	350.0	0.61
Magnesium transportation (500 miles by rail)	net ton-mile	0.87	0.00067	0.00
			Subtotal	2.22
Refining and casting				
Electrical energy	kwh	3.0	0.0105	0.03
Natural gas	ft^3	220.0	0.001	0.22

TABLE C1. (Concluded)

	Unit	Units Per Net ton or Lead	10^6 Btu Per Unit	10^6 Btu Per S ton of Lead
Refining and casting (Cont'd)				
Caustic soda (solid NaOH)	net ton	0.001	47.7	0.05
Soda transportation (300 miles by rail)	net ton-mile	0.3	0.00067	0.00
Niter ($NaNO_3$)	net ton	0.00025	42.25	0.01
Niter transportation (300 miles by rail)	mile	0.08	0.00067	0.00
			Subtotal	0.31
General plant (heat, lights, etc.)				
Electrical energy	kwh	14.05	0.0105	0.15
Natural gas	ft^3	150.0	0.001	0.15
			Subtotal	0.30
TOTAL				26.78

Net ton = S ton.

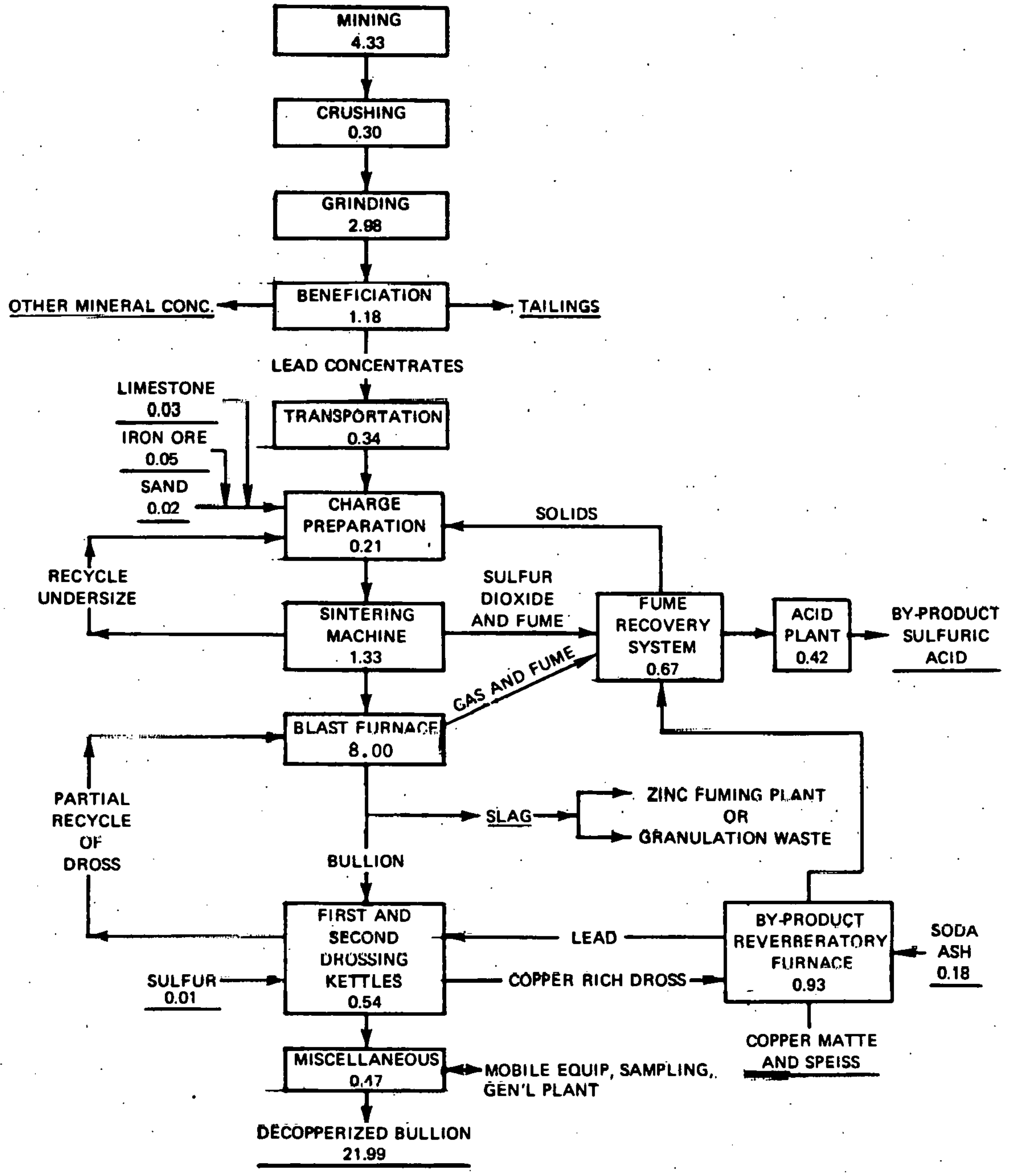

FIGURE C1. PRODUCTION OF REFINED LEAD
(Units in 10^6 Btu/S ton lead)

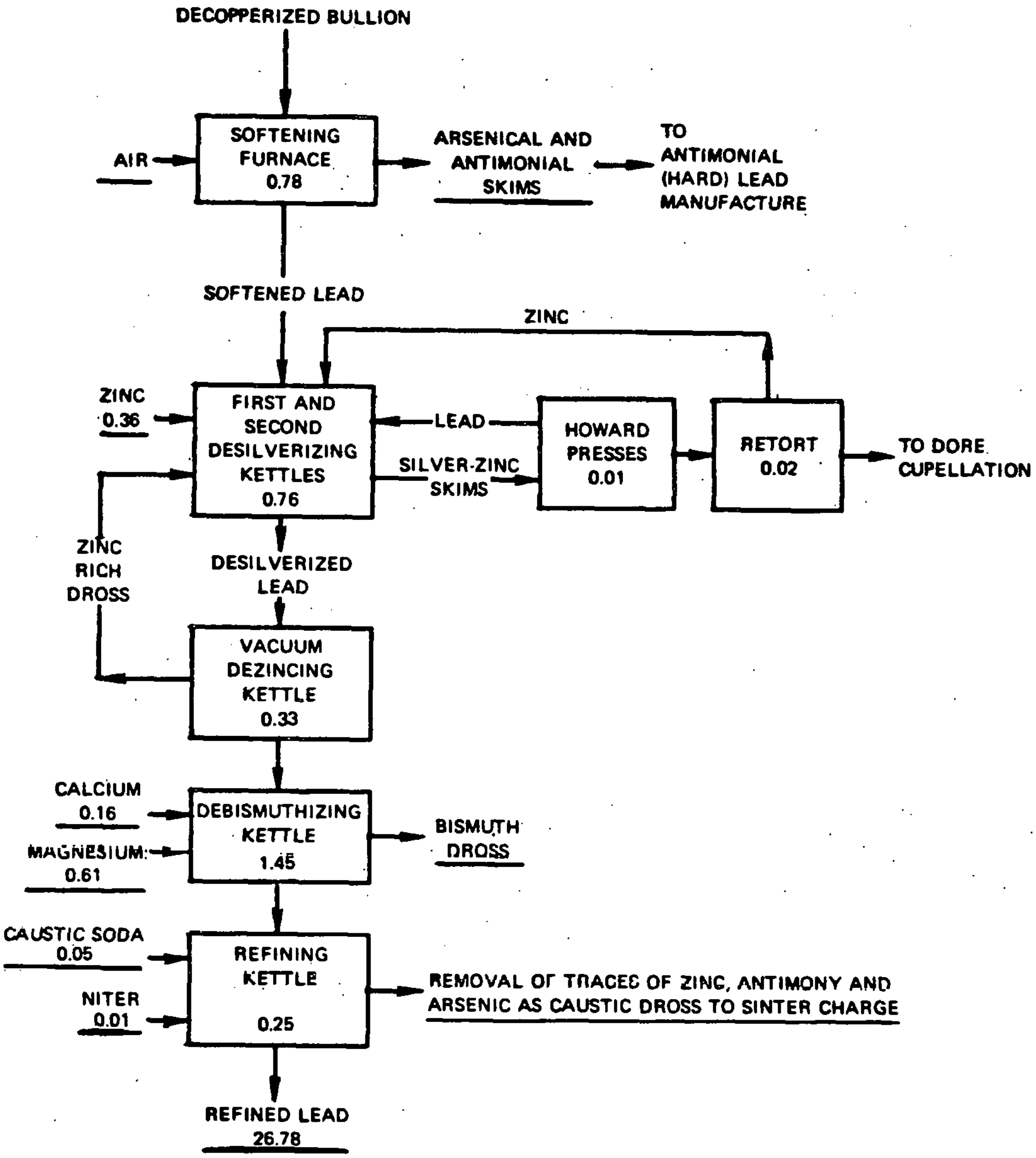

FIGURE C1. PRODUCTION OF REFINED LEAD (Concluded)

Some producers have claimed that technology is not available to restrict emissions to the proposed standard. Additional energy (not estimated) will be needed to power the pollution-control devices. The cost of the control equipment is estimated to be about 20 percent of the total plant cost (see section on Suggested Further Analysis and/or Development of Processes and Appendix). Such restrictions will favor electrometallurgical methods for lead production which are less likely to cause air pollution.

In the following sections the various electrochemical methods for electrowinning and electrorefining that have been proposed or used are reviewed, including historical and more recent descriptions.

Electrometallurgical Processes Based on Chloride Ions

Early Developments

Although hydrometallurgical processes for recovery of lead have not received anywhere near the attention of those for copper, zinc, aluminum, magnesium and may other metals, some processes have been investigated and a few even commercialized to some extent. A few plants outside of the USA refine lead electrolytically. Without going far back in history, mention should be made of early activity in hydrometallurgical treatment of lead ores, particularly in the 1918-1925 period. This is well summarized, with references by Riddell and by Croasdale in Liddell's Handbook(C2).

Most of the work at that time was on acid brine leaching, usually preceded by a chloridizing roast, and the lead was recovered by electrolysis or by cementation on iron. There was sufficient success in this field that hydrometallurgical treatment was competitive with concentration and lead blast furnace smelting. In fact, five commercial brine leaching plants were built in this country and one each in Canada, Australia and England. With improved flotation to treat complex ores and for various reasons (corrosion problems, improvements in smelting, cost of reagents, operating difficulties, etc.) none of these plants operated for more than a few years. In one plant (Kellogg, Idaho) galena concentrates were given a sulfate roast, then leached with hot brine containing chlorine. The lead chloride in solution was electrolyzed in diaphragm cells with insoluble anodes and rotating cathodes.

The spongy lead deposit was melted into bullion containing gold and silver, and chlorine was recycled in the form of bleaching powder. In another process lead chloride was crystallized from a hot brine solution, and the crystals fused and electrolyzed for recovery of molten lead and chlorine. When the older work was reviewed it was evident that modern developments are essentially the same as the older methods with engineering improvements. Attention is directed to these developments(C2,C21) rather than to details of the earlier chlorination, brine leaching, and electrolysis procedures.

Modern Development of Chloride Leaching-Electrolysis Methods.

In the last few years considerable attention has been given by the U.S. Bureau of Mines to hydrometallurgical treatment of lead concentrates. This work is emphasized because it is recent, has been built on past experience and literature reviews, and a reasonable amount of reliable data is available for making comparisons with other methods of lead processing. Also, energy consumption has been measured, although the emphasis of the work was not necessarily on energy reduction. Two lines of attack have been followed in leaching, (a) ferric chloride-brine leaching, and (b) the use of chlorine-oxygen mixtures as an effective leachant. Also, two methods of electrolytic recovery has been investigated, (a) electrolysis of fused lead chloride crystals, and (b) aqueous electrolysis of lead chloride. These are outlined in Figure C2.

Ferric chloride has been shown to be a good leachant for lead sulfide concentrates because of its rapid attack. Thus, at about 100° C over 99 percent of the galena is converted to lead chloride and elemental sulfur in less than 15 minutes. After separation of the sulfur and gangue, the hot lead chloride solution can be cooled to deposit crystals of the chloride which can be separated and lead recovered by electrolysis from a molten salt electrolyte. Chlorine is recovered to regenerate the leachant. Alternately, with simpler equipment, the undissolved lead chloride crystals can be electrolyzed in contact with a horizontal cathode on the bottom of a cell using an aqueous electrolyte. Ferrous chloride is oxidized to ferric chloride anodically or indirectly by chlorine generated in the cell. This latter approach is possibly preferable for small scale operations where capital cost can be minimized. Complex concentrates can be leached

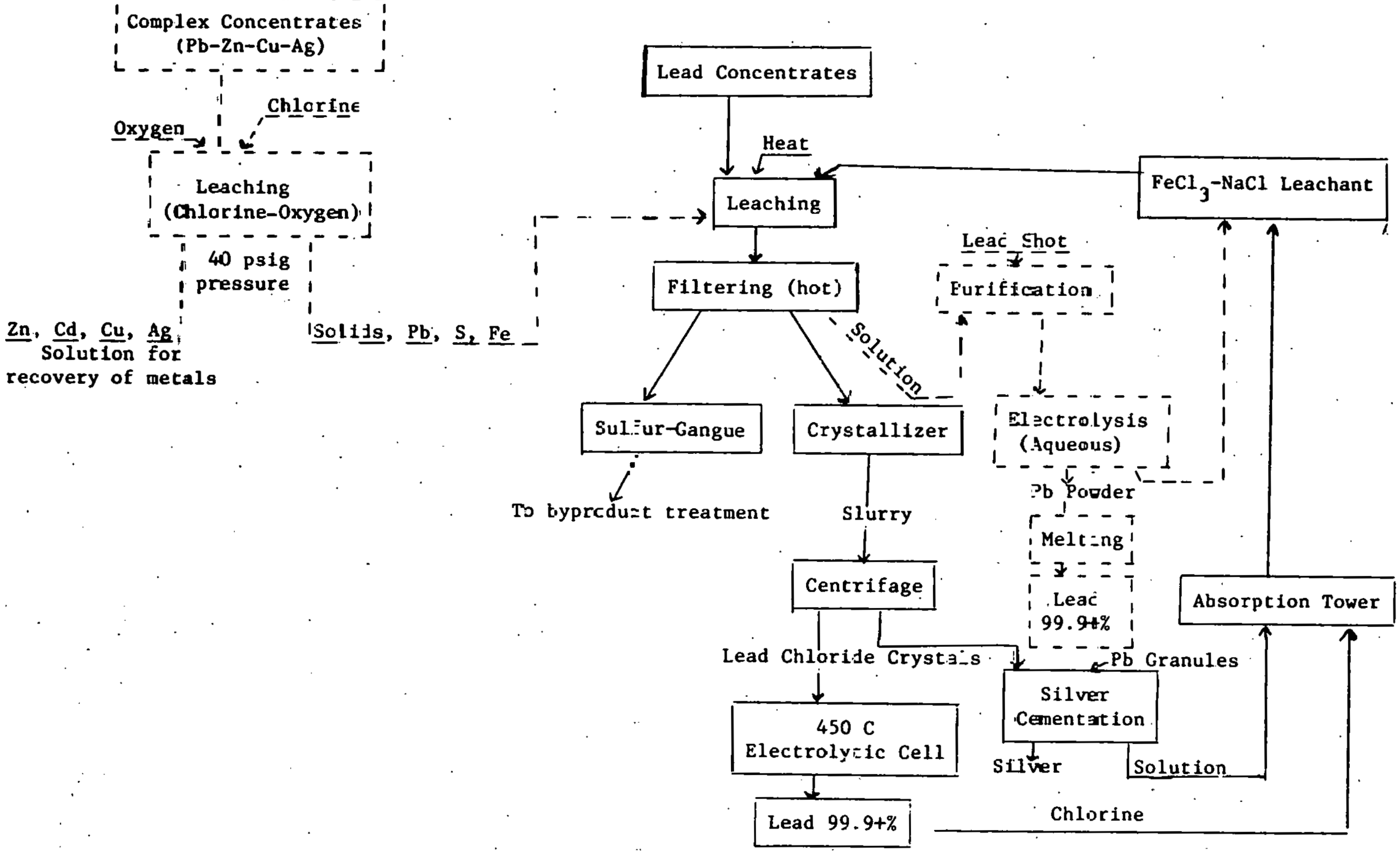

FIGURE C2. BUREAU OF MINES ELECTROHYDROMETALLURGICAL PROCESS FOR RECOVERING LEAD FROM CONCENTRATES with chlorine-oxygen to dissolve zinc, copper, cadmium and silver, and the solid residue containing lead is then leached by the ferric chloride method. These alternate methods are shown by dotted lines in Figure C2.

From an energy consumption standpoint none of these procedures shows a promising reduction over the present conventional method of carbon reduction in a blast furnace. This is particularly true if improved methods of pyrolytic reduction are used to utilize the fuel value in the sulfur in place of using so much coke. It is suggested that direct smelting could reduce the energy to one-half of the sinter-blast furnace procedure(C3). Kahn(C4) has discussed the electrowinning of lead from lead chloride dissolved in $NaCl-CaCl_2$ electrolytes, which differs from the USBM method where the lead chloride is crystallized out.

Theoretical Energy Requirements for Lead Chloride Processes.

In the leaching reactions discussed the reaction products are sulfur and lead complexed with excess chloride ions. If the latter is assumed to be present to the saturation limit its activity is that of solid lead chloride. Thus, the two reactions in the reduction of galena utilizing chloride metallurgy and electrolysis may be considered to be:

$$PbS + 2Cl^- \rightarrow PbCl_2 + S^0 + 2e \qquad (1)$$

$$PbCl_2 \rightarrow Pb^0 + 2Cl^- - 2e \qquad (2)$$

$$PbS \rightarrow Pb^0 + S^0 \qquad (3)$$

Reactions (1) and (2) are general in the sense that a variety of oxidizing agents may react in equation (1) and be regenerated in reaction (2). These agents include chlorine and ferric iron.

Standard state thermodynamic values, including potentials, for several reactions pertinent to the chloride electrometallurgy of lead are shown in Table C2.

Leaching of lead sulfide is carried out in hot (90° C) sodium chloride solution in which the solubility of lead chloride is approximately 75 g/1. Dissolution with chlorine gives off heat ($\Delta H = -63.49$ Kcal/mole Pb).

TABLE C2. REACTIONS IN THE CHLORIDE ELECTROMETALLURGY OF LEAD

Reaction	Temperature °C	E* Volts	ΔF kcal/mole	ΔH kcal/mole	ΔH 10^6Btu/S ton Pb
(1) $PbS+2Cl^- \rightarrow PbCl_2+S^\circ+2e$	25	+0.208	9.59	16.55	0.29
(2) $Pb^\circ+2Cl^- \rightarrow PbCl_2+2e$	25	-0.268	-12.36	- 5.82	-0.10
(3) $Pb^\circ + S^\circ \rightarrow PbS$	25	+0.476	-21.98	-22.38	-0.39
(4) $Pb^\circ + Cl_2 \rightarrow PbCl_2$	25	+1.627	-75.04	-85.68	-1.49
(5) $2Cl^- \rightarrow Cl_2+2e$	25	+1.35	62.72	80.04	--
(6) $Fe^{++} \rightarrow Fe^{+++}+e$	25	+0.771	17.78	9.61	--
(7) $Pb^\circ+Fe^{+++}+2Cl^- \rightarrow PbCl_2+Fe^{+++}+2e$	25	+1.039	-47.98	-24.60	-0.43
(8) $Pb^\circ+Cl_2 \rightarrow PbCl_2$	90	1.62	-74.8	-85.6	--
(9) $Pb^\circ+Cl_2 \rightarrow PbCl_2$	500	1.36	-62.9	-78.9	--
(10) $PbS+FeCl_3 \rightarrow PbCl_2+S^\circ+FeCl_2$	25	--	--	- 2.67	--
(11) $Pb+SO_2 \rightarrow PbS-O_2$	25	--	49.7	48.1	--

*Vs Normal Hydrogen Electrode.

Since 3.86 liters dissolve one mole of lead chloride the enthalpy change is adequate to raise the temperature of the solution only 16° C (assume Cp = 1 Kcal/liter). Thus, auxiliary heat must be supplied for most processes. Leaching with ferric chloride produces negligible heat energy ($\Delta H = -2.67$ Kcal/mole Pb).

Recent work in Australia on leaching zinc-lead sulfide concentrates involved aqueous chloride solutions from which it was assumed lead could be recovered electrolytically from the molten chloride as in the Bureau of Mines procedure(C6). This adds nothing new but confirms present thinking that this is a preferred method of attack.

Comprehensive pilot plant experimentation has been done recently by the Hazen Laboratories along a line of attack similar to that followed by the Bureau of Mines(C7-C8). However, in place of a ferric chloride leach the Hazen approach has been to chlorinate the lead concentrates dry and leach the solid metal chlorides in hot brine. Lead chloride is then crystallized from the solution on cooling and electrolyzed as the molten salt, as in the Bureau of Mines procedure. The chlorine from the electrolysis is then used to chlorinate more concentrate. This procedure is considered to be competitive with conventional pyrometallurgical treatment. Assuming 10 percent of the power required at the cell is needed for auxiliary electrical energy, the total required has been calculated to be 1.2 Kcal/kg (0.55 kwh/lb) of lead or 3.21×10^6 Kcal/M ton (11.55×10^6 Btu/S ton) of lead. Thus, the energy used is about the same as that used in the Bureau of Mines procedure. Theoretical voltages are shown for three cells in Table C3.

The potential with the ferrous ion present provides the lowest cell voltage because of the low potential for ferrous iron oxidation. Oxidation of chloride ion requires more energy. The free energy of formation of lead chloride is lower for the fused salt ($\Delta F = -62.9$ Kcal/mole) than in aqueous solution ($\Delta F = -74.8$ Kcal/mole); hence, the aqueous solution potential is higher.

Practical Energy Requirements for Lead Chloride Processes.

Total energy requirements for the following will be compared:

I Current blast furnace process

TABLE C3. THEORETICAL VOLTAGES AND POWER REQUIREMENTS FOR LEAD ELECTROWINNING

Medium	Anode Oxidation	Potential Volts	Kwh/ M ton (S ton) Pb	Kcal x 10^6/M ton* (Btu 10^6/S ton Pb) at Power Plant
Aqueous	Chloride ion	1.627	466(423)	1.24(4.45)
Aqueous	Ferrous ion	1.04	298(271)	.79(2.84)
Fused salt	Chloride ion	1.36	390(354)	1.03(3.73)

* Includes 10 percent power for electrical conversion and distribution.

II Aqueous leaching; aqueous electrolysis
III Aqueous leaching; aqueous electrolysis of solid lead chloride
IV Aqueous leaching; fused salt electrolysis.

Estimates for energy requirements for the various processes are given in Table C4. The breakdown for the blast furnace was discussed in the introduction and included a value for mining and concentrating which is common to all processes.

Leaching. Haver and Wong(C11) report that heating requirements for ferric chloride leaching, associated with crystallization of lead chloride by cooling, are 1011 Kcal/kg (1825 Btu/lb) Pb (1.01×10^6 Kcal/M ton or 3.65×10^6 Btu/S ton Pb). Independent calculation confirms this heat requirement. Solubilities of lead as chloride in pregnant and stripped solution are reported to be 72 g/l and 18 g/l, respectively. Thus:

$$\frac{207}{(72-18)} = 3.83 \text{ liters/mole Pb crystallized} \quad .$$

Heating from 20° C to 90° C, assuming a specific heat of 1.0 for the solution requires:

$$(3.83)(70) = 268 \text{ Kcal/mole Pb} \quad .$$

Chlorine from electrolysis is used to reoxidize ferrous chloride to ferric chloride which in turn oxidizes the concentrate. The heat of reaction available is the same as direct oxidation of the concentrate by chlorine (63 Kcal/mole Pb). Therefore, the net heat requirement is:

$$268-68 = 205 \text{ Kcal/mole Pb } (995 \text{ Kcal/kg, } 1795 \text{ Btu/lb Pb, } .99 \times 10^6 \text{ Kcal/M ton Pb, } 3.58 \times 10^6 \text{ Btu/S ton Pb}) \quad .$$

These calculations do not allow for extraneous heat loss, which we will assume is 40 percent, and will increase the practical heating

TABLE C4. ESTIMATED TOTAL ENERGY REQUIREMENTS FOR LEAD WINNING PROCESSES

Unit Operations	10^6 Kcal/M ton Pb (10^6 Btu/S ton Pb)			
	I	II	III	IV
Mining, concentrating	2.5(9)	2.5(9)	2.5(9)	2.5(9)
Leaching	--	1.1(4)	1.9(7)	1.9(7)
Purification	--	--	--	--
Reduction	3.6(13)	2.8(10)	1.7(6)	3.1(11)
Refining	1.4(5)	--	--	--
Melting, casting	--	--	--	--
Total	7.5(27)	6.5(23)	6.0(22)	7.5(27)

I = Conventional smelting.

II = Ferric chloride leaching, aqueous electrolysis.

III = Ferric chloride leaching, aqueous electrolysis of crystallized $PbCl_2$.

IV = Fused salt electrolysis.

requirement to 1.7 x 10^6 Kcal/M ton (6 x 10^6 Btu/S ton) Pb. For pumping, filtering, etc., 0.3 x 10^6 Kcal/M ton (1 x 10^6 Btu/S ton) Pb will be added. The total energy consumption is then 2 x 10^6 Kcal/M ton (7 x 10^6 Btu/S ton) Pb. This is the energy associated with obtaining solid lead chloride for use as a feed to a fused salt cell.

Leaching lead concentrate to produce a feed for aqueous chloride electrolysis can involve less energy. Kahn(C4) reports using a temperature of 50° C for aqueous electrolysis. Assuming heat can be conserved following leaching, a hot feed can be used for electrolysis, and that solution is stripped to 18 g/l of lead, the theoretical heat requirement can be reduced to:

$$(3.83)(90-50) -63 = 90 \text{ Kcal/mole Pb}$$

which is equivalent to:

$$0.44 \times 10^6 \text{ Kcal/M ton } (1.57 \times 10^6 \text{ Btu/S ton) Pb} \quad .$$

This is less than half the energy required for the crystallization process and a total energy requirement will be estimated as:

$$(1.57 \times 10^6)/.60 + 1.0 \cong 4 \times 10^6 \text{ Btu/S ton Pb}$$

or

$$1.1 \times 10^6 \text{ Kcal/M ton Pb} \quad .$$

<u>Purification</u>. Purification in the electrowinning processes is not necessary for Processes III and IV where lead chloride is crystallized out with a high purity. The electrowon lead obtained from this feed salt has a purity of 99.99 percent.

The ferric chloride leaches out at least 50 percent of the silver in the concentrate and smaller amounts of copper. Other impurities such as zinc are more electro-negative. The undesirable impurities can be removed by cementation onto lead shot. Thus, deposition of relatively pure lead from aqueous solution should be possible. It is assumed that the energy requirement for cementation is negligible.

Electrolysis. Kahn(C4) electrolyzed a chloride solution starting with 40 g/l of Pb and stripping to 2 to 3 g/l. At 1000 amp/m^2 (92 amp/ft^2) current efficiency was 85 percent and cell potential 3.0 to 3.5 volt. Using the lower voltage the power consumption is:

$$(234.43)(3.0)/.85 = 827 \text{ kwh/S ton Pb or } 912 \text{ kwh/M ton Pb}$$
$$(8.7 \times 10^6 \text{ Btu/S ton Pb or } 2.42 \times 10^6 \text{ Kcal/M ton Pb}) \quad .$$

If there is 10 percent loss in power conversion and bus bars the power consumption is 2.7×10^6 Kcal/M ton (9.7×10^6 Btu/S ton) Pb. In a continuous operation we have assumed deposition from a solution containing 18 g/l of Pb (stripped solution).

The theoretical potential for lead deposition and chlorine evolution from standard states in aqueous solution is:

$$1.36 -(-.13) = \cong 1.5 \text{ volt} \quad .$$

Overpotentials for both reactions probably total no more than 0.5 volt. Specific conductivity of an acid chloride solution is of the order of a few $ohm^{-1}cm^{-1}$. Thus, IR drop need be only 0.2 to 0.3 volt. Therefore, it is possible that cell potential at 1000 amp/m^2 could be reduced to 2.3 volts and energy use to:

$$694 \text{ kwh/M ton (630 kwh/S ton)}$$

or

$$1.86 \times 10^6 \text{ Kcal/M ton } (6.7 \times 10^6 \text{ Btu/S ton) Pb} \quad .$$

Haver, Bixby, and Wong(C21) report cell potentials of the order of 2.0 volts and current efficiencies of 95 percent for cathodic reduction of solid lead chloride at 161 amp/m^2 (15 amp/ft^2) using aqueous sodium chloride (or HCl) electrolyte.

The use of a spent leach solution containing ferrous chloride to depolarize the anode did not reduce voltage as would be predicted theoretically. Results correspond to an energy consumption of 543 kwh/M ton (493 kwh/S ton) Pb or 1.44×10^6 Kcal/M ton (5.2×10^6 Btu/S ton). Allowing 10 percent for conversion and line losses the power consumption is 1.51×10^6 Kcal/M ton (5.8×10^6 Btu/S ton) Pb. This figure is low compared to that for electrolysis with lead in solution and reflects the very low current density used. The restriction on current density seems necessary for solid-state reduction. Even then complete reduction of the crystals is not obtained and the chloride and metal must be separated by fusion. A practical system for continuous electrolysis has not been developed.

Wong and Haver(C19) report results for fused salt deposition. In laboratory cells operated at 7750 amp/m^2 (720 amp/ft^2) potentials of 2.0 volts were obtained with current efficiencies of over 90 percent. External heating was required. An energy consumption, exclusive of external heat, of 0.55 kwh/kg Pb (0.25 kwh/lb Pb) or 551 kwh/M ton or 1.46×10^6 Kcal/M ton (500 kwh/S ton Pb or 5.25×10^6 Btu/S ton Pb) was obtained. In a pilot plant cell operated at a current density of 16,420 amp/m^2 (1526 amp/ft^2) and 5.7 volts no external heat was required and energy consumption was 1.5 kwh/kg Pb (0.68 kwh/lb Pb) or 1499 kwh/M ton Pb or 3.97×10^6 Kcal/M ton Pb (1360 kwh/S ton Pb or 14.3×10^6 Btu/S ton Pb). The higher voltage reflects the higher current density as compared to that in the laboratory cell of 7750 amp/m^2 (720 amp/ft^2). The theoretical heat requirement for the endothermic deposition reaction is 16 Kcal/mole Pb. Heating and fusion of solid $PbCl_2$ cell feed to 500° C requires 15.2 Kcal/mole. The total theoretical heat requirement is 31.2 Kcal/mole Pb. For a two electron reduction the heat produced by overvoltage is:

$$(2)(23.060) = 46 \text{ Kcal/mole/volt} \quad .$$

Therefore, an overvoltage of 0.7 volt is adequate to provide the theoretical heat requirement. Higher voltages are to compensate for heat losses from the cell. The heat losses in the larger cell must be considerable, although perhaps difficult to avoid. For purposes of comparison an optimistic value for electrolysis, including power to maintain cell temperature is 1100 kwh/M ton (1000 kwh/S ton) Pb 3.1 x 10^6 Kcal/M ton (11 x 10^6 Btu/S ton) Pb including conversion and line loss.

Refining. Refining is believed necessary only for the pyrometallurgical process.

Melting, Casting. Theoretical energy to heat solid lead to its melting point (327° C) and melt it is 3.24 Kcal/mole or 16,000 Kcal/M ton (57,000 Btu/S ton). This is a negligible amount of energy compared to that for electrolysis.

The total energy requirement for the blast furnace process is based upon actual production experience while the estimated energies for the electrowinning processes are based upon projections of experimental data. These estimates are probably too low and as much as 1.5 x 10^6 Kcal/M ton (5 x 10^6 Btu/S ton) Pb may have to be added to allow for power for running equipment, steam, etc., needed in a complex plant. Process II requirements might be further reduced by electrolysis at the leach temperature (90° C). In such a case the heat from leaching and electrolysis could be adequate to maintain temperature and the 1.1 x 10^6 Kcal/M ton (4 x 10^6 Btu/S ton) for heating leach solution eliminated. This arrangement would require some careful engineering to integrate leaching, filtration, purification, and electrolysis into a continuous closed cycle. However, deposition of lead as removeable dendrites as with the alkaline zinc process to avoid pulling cathodes, would aid in achieving this goal.

Direct Electrolysis of Lead Sulfide Concentrates

The free energy of formation of lead sulfide (PbS) is only -21.98 Kcal/mole equivalent to +0.476 volts (Reaction 3, Table C1). Therefore, if PbS can be directly electrolyzed to lead and sulfur the energy requirement may be low. Electrolysis has been attempted both by using galena in a compact as an anode or by adding it to a fused salt that will dissolve it.

Use of Lead Sulfide Concentrate in a Soluble Anode.

The most recent effort to use soluble anodes was that by CSIRO in Australia(C22-C26). Galena (lead sulfide) concentrates were pressed with 5.5 percent graphite (for conductivity) into anodes that were electrolyzed at 60° C in perchlorate or fluosilicate electrolyte. Over 90 percent of the lead could be dissolved in this manner. Power for electrolysis (at the cell) was 530 kwh/M ton (480 kwh/S ton) Pb in an initial study and reduced to 395 kwh/M ton (360 kwh/ton) Pb in further work. With conversion losses this would amount to 440 kwh/M ton (400 kwh/S ton) Pb or 1.2×10^6 Kcal/M ton (4.2×10^6 Btu/S ton) Pb at the power plant. This value is low when compared to the minimum of 3.6×10^6 Kcal/ton (13×10^6 Btu/S ton) Pb for leaching plus reduction in chloride processes (Table C4). However, there are formidable problems yet to be overcome with this method.

(1) The maximum current density that was possible is only 160 amp/m^2 (15 amp/ft^2).

(2) The current efficiency of lead dissolution is about 85 percent (the other 15 percent dissolves impurities) thus, lead carbonate, etc., would need to be prepared and added to maintain a constant concentration of electrolyte lead.

(3) Impurities must be removed from a strongly acid electrolyte. Methods remain to be developed.

(4) Preparation of the anodes requires pressing at 0.7 M tons/cm^2 (2 S tons/in^2) and heating to 450° C.

(5) Spent anodes require reprocessing, consisting of leaching to remove lead sulfate and flotation to recover sulfur, graphite, PbS and ZnS.

(6) Refining may be necessary if purification procedures are inadequate.

(7) Estimates of capital and operating costs are high. An estimate for 180,000 M ton (200,000 S ton)/yr plant was $127 million (U.S., 1978). This reflects the present low current density restriction. Process cost was estimated to be $230 (U.S., 1978) per S ton Pb.

Cathro and Sieman(C25) have estimated power requirements along with costs and labor from their conceptual plant design. Power requirements are shown in Table C5. Total energy needs are thus of the order of 4.2×10^6 Kcal/M ton (15×10^6 Btu/S ton) Pb starting with the concentrate. Adding 2.5×10^6 Kcal/M ton (9×10^6 Btu/S ton) Pb for mining and concentrating brings the total to 6.7×10^6 Kcal/M ton (24×10^6 Btu/S ton) Pb compared to 7.5×10^6 Kcal/M ton (27×10^6 Btu/ton) Pb for the sinter-blast furnace process.

The energy calculations were made with little information, leading to a large uncertainty. The energies for forming the anodes and for electrolysis are modest and graphite is recovered by flotation for reuse. The process needs some good technical input on how to increase current density, e.g., increased surface area, and purification techniques and experimental verification to make it practical. Even though estimated energy use is not appreciably less than for conventional processing it should contribute less pollution.

Electrolysis of Lead Sulfide Concentrates Dissolved in a Molten Electrolyte.

Various molten salt electrolytes have been investigated(C27-C34) in an effort to find a practical, workable combination. In early work, as described above, lead sulfide was dissolved in molten lead chloride. A low-melting potassium-sodium chloride mixture has been used as well as lithium chloride-potassium chloride, for example. In the 1930s, a small experimental 272 M ton/yr (300 S ton/yr) plant was operated for several years in Halkyn, Wales, until the war stopped operations. Later, a small pilot plant operated briefly in Canada and another of 1630 M tons/yr (1,800 S ton/yr) capacity was operated in Port Pirie, Australia. The general method has been called the Halkyn process because of the Welsh operation.

TABLE C5. POWER REQUIREMENTS FOR LEAD SULFIDE ANODE PROCESS

Unit Operation	Electric Power		Fuel		Steam		Total
	Kwh/M ton (Kwh/S ton)	Kcal x 10^6/M ton Btu x 10^6/S ton)	GJ/S ton	Kcal x 10^6/M ton (Btu x 10^6/S ton)	M ton S ton	Kcal x 10^6/M ton (Btu x 10^6/S ton)	Kcal x 10^6/M ton (Btu x 10^6/S ton)
Anode Preparation	85(78)	0.23(0.82)	0.34	0.09(0.32)	--	--	0.32(1.14)
Electrowinning	573(520)	1.52(5.46)	1.20	0.31(1.13)	--	--	1.83(6.59)
Electrolyte	64(58)	0.17(0.60)	0.02	0.01(0.02)	1.23(1.36)	3.46(3.81)	1.23(4.43)
$PbSO_4$ leaching	71(64)	0.19(0.67)	0.04	0.01(0.04)	0.54(0.59)	1.50(1.65)	0.66(2.36)
Spent Anode Process	20(18)	0.05(0.19)	0.05	0.01(0.05)	--	--	0.07(0.24)
Lead Concentrate Preparation	4(3)	0.01(0.03)	0.15	0.04(0.14)	--	--	0.05(0.17)
	817(741)	2.16(7.77)	1.80	0.47(1.70)	1.77(1.95)	4.95(5.46)	4.15(14.93)

320 Days/yr for 200,000 tpy plant or 625 tpd

1400 Btu/lb steam or 2.8 x 10^6 Btu/ton steam

1 GJ ≡ 9.48 x 10^5 Btu.

Metal of 99.94 percent purity was produced. Also, work has been done on introducing lead into the bath as lead sulfate in place of the sulfide. Under some conditions cathode efficiencies of 90 to 96 percent were obtained using diaphragm cells.

No definite reason is apparent from the literature as to why the lead sulfide molten chloride process was discontinued. A scum containing impurities such as zinc chloride formed on the surface and required removal. Lead chloride was lost in the operation. We would venture the opinion that the process lost out economically to pyrometallurgical techniques.

Winterhager and Kammel(C33) have provided the most detailed information on the electrochemistry of winning lead from lead sulfide in lead chloride. Theoretical potentials in the range of 0.4 to 0.5 volt for an electrolyte of PbS in $PbCl_2$ at temperatures over 500° C were confirmed by actual EMF measurements and polarographic curves extrapolated to zero current. Use of sodium chloride in the bath lowered the melting point to a minimum of 409° C.

A potential of 0.45 volts corresponds to an energy consumption of 128 kwh/M ton (117 kwh/S ton) Pb or 0.34 x 10^6 Kcal/M ton (1.23 x 10^6 Btu/S ton) Pb, assuming 100 percent current efficiency and 10 percent power conversion loss.

Small-scale electrolysis (100 amperes) was undertaken at an anode current density of 2 amp/cm^2 (1860 amp/ft^2) and cathode current density of 0.9 amp/cm^2 (836 amp/ft^2) with a 3.6 cm (1.4 in) electrode spacing. The cell potential was 3.9 volts and outside heating was required to maintain the 480° C temperature. Lead current efficiency was 97.5 percent. These results correspond to 1148 kwh/M ton (1042 kwh/S ton) Pb with 10 percent conversion loss or 3.04 x 10^6 Kcal/M ton (10.94 x 10^6 Btu/S ton Pb). However, from independent measurements of polarization potentials and electrolyte conductivity, it was estimated that with an average current density of 0.8 amp/cm^2 (5.16 amp/in^2) and an electrode spacing of 2.5 cm, (1.0 in) a cell potential of 2.0 volts could be attained corresponding to 588 kwh/M ton Pb or 1.56 x 10^6 Kcal/M ton Pb (534 kwh/S ton Pb or 5.6 x 10^6 Btu/S ton Pb). Even at this potential, over 75 percent of the energy input merely compensates for heat loss.

TABLE C6. TOTAL ENERGY REQUIREMENT FOR DIRECT ELECTROWINNING OF LEAD SULFIDE CONCENTRATE

Operation	Energy, kwh/M ton (kwh/S ton) Pb	Kcal x 10^6/M ton Pb (Btu x 10^6/S ton Pb)
Mining and Concentrating	--	2.5(9)
Electrowinning	628(570)	1.7(6)
Electrorefining	220(200)	0.6(2)
Auxiliary	--	1.4(5)
Total	850(770)	6.1(22)

An estimate of total energy for lead production has been made in Table C6 assuming a 2.0 volt electrowinning cell. The product from this cell will almost certainly require refining and the energy for the Betts electrolyte process (subsequently discussed) has been included in the total. An additional 1.4 x 10^6 Kcal/M ton (5 x 10^6 Btu/S ton) Pb have been added for miscellaneous operations. The result, 6.1 x 10^6 Kcal/M ton (22 x 10^6 Btu/S ton) Pb is lower than that of the present pyrometallurgical method, 7.5 x 10^6 Kcal/M ton (27 x 10^6 Btu/S ton) Pb. However, the electrolysis method would avoid air pollution or the need for involved means for preventing it. Winterhager and Kammel mention the problem of impurities in the concentrate, which remains to be solved. Insoluble materials are presumably readily removed mechanically. Noble impurities, i.e., copper and silver would be codeposited and concentrated during refining. Soluble, less noble impurities such as zinc would require special procedures for removal as they built up in the bath. King and Welch(C27) have shown that lead and sulfur can dissolve in and recombine in the electrolyte, particularly as the temperature is increased. Also, sulfur-containing coatings can form on the graphite anodes, which could give rise to higher cell voltages. Thus the direct electrolysis of lead sulfide concentrate in fused salts shows promise from an energy standpoint, but significant research and development are still required to make this a practical contemporary process.

Judging from Russian and German experience, as well as the pilot plant work in Wales, Canada, and Australia, the electrolysis of lead sulfide in a molten salt bath has not proceeded to a practical operation(C34-C37). Rather, the Russian investigations have indicated early interest in the Halkyn process, then more attention to using lead chloride electrolysis for refining lead. In the USSR as elsewhere, chief attention recently has been given to improving pyrolytic lead smelting by oxygen flash and other means of by-passing the sintering step and reducing the need for coke(C38).

Other Electrometallurgical Processes for Lead

An interesting laboratory scale study has been made in Australia on oxidizing lead sulfide and dissolving the oxides in ammoniacal ammonium sulfate solution at normal temperature and pressure(C39). The roasting requires that means be used to control pollution. Lead was recovered by electrolysis (or preciptation by steam distillation to remove ammonia). This procedure avoided some of the troubles in brine or amine leaching, but had different troubles of its own. For example, much of the lead produced was in the form of lead peroxide at the anode. Power, required for electrolysis was 0.26 kwh/kg (0.116 kwh/lb) Pb or less than 26 kwh or 0.69 x 10^6 Kcal/M ton (237 kwh or 2.5 x 10^6 Btu/S ton) including anodic lead peroxide Power for electrolysis is one-half or less than for processes previously discussed. It is doubtful that there is a ready market for the lead dioxide, and the removal from the anode could be an expensive operation.

Pressure leaching of galena concentrates has received attention but not to the extent of offering serious competition to conventional lead processing(C40-C42). More work has been done on treating complex or zinc-lead concentrates. Thus, rather extensive work has been done by Sherritt Gordon in Canada, and others elsewhere, on converting lead sulfide to the sulfate by pressure oxidation, removing soluble compounds, and recovering lead from the residue by smelting or by leaching with an organic amine (as ethylenediamine) solution. Lead is removed from the solution by electrolysis using a cell with semi-permeable membranes. So far the smelting routine has been preferred. A variation in treatment after pressure leaching has been to leach with ammoniacal ammonium sulfate solution, followed by electrolysis, but difficulties in getting a high grade product led to conventional smelting of the lead. Pressure leaching-electrolysis appears to be applicable practically only to separation of lead from co-constituents of the ore under unusual circumstances, and not as a primary means of metallic lead recovery.

Electrorefining of Lead

The present conventional method of refining lead pyrometallurgically is effective and uses only a moderate amount of power, estimated to be from 1.33 x 10^6 Kcal/M ton (4.8 x 10^6 Btu/S ton) to as high as 1.9 x 10^6 Kcal/M ton (7 x 10^6 Btu/S ton) of lead for direct operations(C1,C43).

Some energy savings presumably could be made by using the well-established Betts method of electrorefining from a fluosilicate electrolyte. In early work in operating a commercial electrolytic lead refinery, the average energy required was 1 kwh to deposit 8.2 kg (18.1 lbs) of lead or 121.8 kwh/M ton (110.5 kwh/S ton) or 0.32 x 10^6 Kcal/M ton (1.15 x 10^6 Btu/S ton) of refined lead(C2). In more recent electrolytic lead refinery operations in Peru the energy consumed by electrolysis amounted to 189 kwh/M ton (172 kwhr/S ton) or 0.50 x 10^6 Kcal/M ton (1.8 x 10^6 Btu/S ton) of lead(C44). This is somewhat more than required at the Trail, British Columbia, Canada plant where an average voltage of 0.5 V is attained compared with 0.6 V at the Peruvian refinery(C45). A recent paper on energy requirements for electrorefining lead gives 194 kwh or 0.40 x 10^6 Kcal/M ton (136 kwhr or 1.43 x 10^6 Btu/S ton) of lead(C46). However, even using the higher energy figure of Peruvian operation, only 0.50 x 10^6 Kcal/M ton (1.8 x 10^6 Btu/S ton) of lead is needed for electrolysis by the Betts process. This does not include treatment of anode slimes for silver recovery, or melting and casting, but it is obviously much less than pyrolytic treatment where .40 x 10^6 Kcal/M ton (1.45 x 10^6 Btu/S ton) is needed for debismuthizing alone. Figure C3 shows the steps in the pyrolytic and electrorefining process.

Electrorefining gives a high purity product from very impure lead, and is still used commercially in some plants outside of the United States. Although the potential saving in energy is appreciable, its use in the future, as at present, is more dependent on economic considerations and the need for better environmental control*. Where lead contains few impurities, as that from the general Missouri district, the simple pyrometallurgical refining presently used appears to be justifiable, except possibly under the most demanding environmental restrictions. With more complex Rocky Mountain ores the economic advantage of pyrolytic treatment would be somewhat less.

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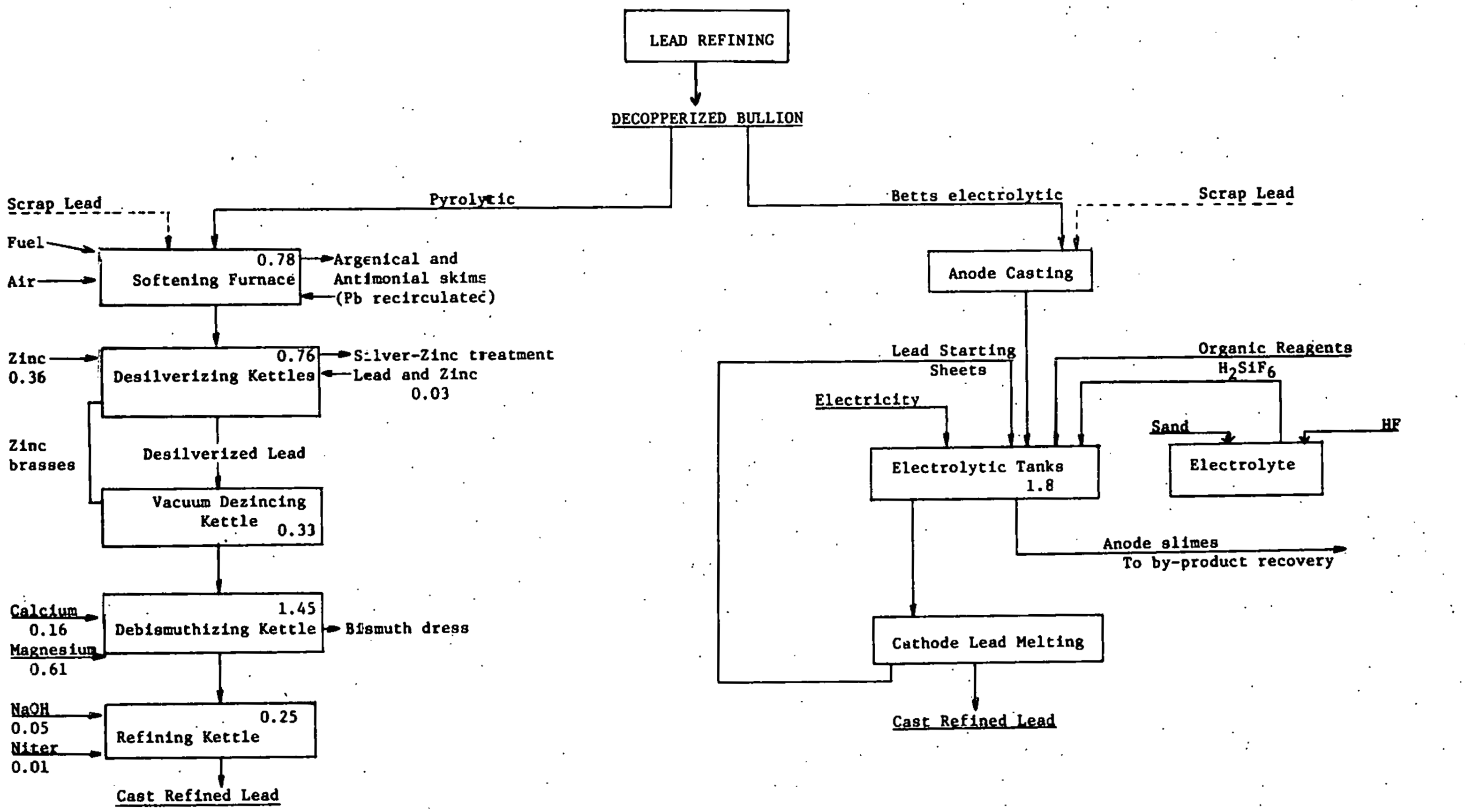
*In phone conversation with Cominco Ltd., it was stated that the Betts process was only justified if appreciable bismuth impurity was present. Otherwise it was not economic. About 25 percent of a zinc plant capital cost is the tankhouse (Communication with Allen Jephson, Consultant to Zinc Industry). Since lead is a heavier metal a smaller tankhouse is required so an estimate would be 12 percent or $12,000,000 assuming $105,000,000 for a 120,000 S ton/yr plant (See Appendix A).



Energy Used: 4.8 X 10^6 Btu/ton of Lead
(Some estimates up to 7.0 X 10^6 Btu/ton)

Energy Used: 1.8 X 10^6 Btu/ton of Lead for electrolysis only.
Estimated 2.8 X 10^6 Btu/ton total

FIGURE C3. COMPARISON OF PYROMETALLURGICAL AND ELECTROHYDROMETALLURGICAL METHODS FOR LEAD REFINING
(Units in 10^6 Btu/S ton)

In an effort to find a better electrolyte for refining lead, development work has been done and a commercial plant operated for four years in Italy, using a sulfamate electrolyte(C47-C49). However, this plant abandoned the sulfamate process for a conventional Betts fluosilicate electrolyte. This resulted in lower costs, less labor and twice the production per cell(C50). There are possibilities for automation in the electrorefining of lead which would reduce labor and costs but would add slightly to overall plant energy needs(C51).

A pilot plant development in Australia for refining lead by fractional crystallization with reflux in place of either pyrolytic or electrolytic means has attracted attention recently(C52). Although energy consumption has been stated as 26 kwh/M ton (24 kwh/S ton) or only $.07 \times 10^6$ Kcal/M ton (0.24×10^6 Btu/ton) this method results in only partial refining, and some additional energy is needed to complete purification--either by electrolytic or pyrolytic methods(C50). It conceivably could diminish the volume of lead to be handled electrolytically and give an overall saving in energy. Too little is known of the practicality of this procedure or its effectiveness in removing all impurities to give an estimate of potential energy saving or economic benefits. The low energy needs reported, and the fact that this method is being seriously regarded by one of the world's largest lead smelter-refineries, indicates that it is a development well worth watching closely.

Considerable attention has been given also to refining lead by fused salt electrolysis, particularly in the USSR(C54-C56). There are many publications by Delimarskii and others on various molten electrolytes and conditions. There are advantages in having a more compact refinery and avoiding the handling of hydrofluoric and hydrofluosilicic acids. However, since the Betts process requires such a low energy it is doubtful that there would be any advantage in going to molten salt electrolysis. Fused salt electrolysis can be used best, presumably, in connection with recovery of lead from ores and concentrates rather than for refining alone.

The Betts process is highly developed and requires minimal energy. There would appear to be little reason to develop it further. It is not used domestically since its use with the sinter blast furnace technique requires capital investment in a separate tankhouse, which is more expensive than installation of pyro-refining equipment integrated with the blast furnace. Electrolyte refining would also increase handling and associated costs. However, increasing energy costs, or need to treat high bismuth concentrates, for which electrolytic refining is most effective, could bring about its domestic use in the future.

Conclusions

The estimated electrical and total energy requirements of the blast furnace process and the various electrolyte processed discussed are compared in Table C7. Within the accuracy of the estimates, i.e., 25 percent, a clear cut energy advantage from any process cannot be assumed. However, it appears that there are several options for which electro-reduction can directly compete in energy use with present pyrometallurgy, such as the fused chloride electrolysis, still being pursued by the USBM. Because of its prior history of development, and possibility for further improvement through simplification of the process and equipment, the direct electrolysis of lead concentrate is a fused bath would appear to warrant further development effort.

Any options will need to compete with improved pyrometallurgical methods where more of the energy in the sulfur of the concentrate is used to reduce (or eliminate) present consumption of coke. This is being done, as in the QSL and Kipcet processes, under conditions leading to commercial utilization in the near future(C57).

We would venture to say that electrolytic methods will require substantially higher energy and will be more expensive to operate than these low energy pyrometallurgical processes under development. However, if conventional control equipment, e.g., scrubbers, do not provide sufficient pollution control, and raise total energy above that for electrolytic methods, electrowinning could assume considerable importance.

TABLE C7. COMPARISON OF ENERGY SAVINGS FOR VARIOUS LEAD WINNING PROCESSES

			Annual Energy Savings	
			Yr 1977**	Yr 2000***
Process	kwh/M ton* (kwh/S ton)	10^6 Kcal/M ton (10^6 Btu/S ton)	10^{12} Kcal 10^{12} Btu	10^{12} Kcal 10^{12} Btu
Current sinter-blast furnace	--	7.5(27)	--	--
Aqueous chloride electrolyte	992(900)	6.4(23)	0.61(2.4)	0.89(3.6)
Aqueous electrolytic reduction of $PbCl_2$ crystals	606(550)	6.1(22)	0.76(3.0)	1.1 (4.4)
Fused chloride electrolysis	1100(1000)	7.5(27)	--	--
Dissolution of pressed anodes	815(740)	6.7(24)	0.46(1.8)	0.67(2.7)
Lead sulfide in fused chloride	850(770)	6.1(22)	0.76(3.0)	1.1 (4.4)

* Electrolysis energy

** Assumes 1977 production of 549,000 M tons (605,000 S tons)

*** Assumes 2000 production of 889,000 M ton (980,000 S tons).

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TECHNOLOGY OF CHROMIUM

Metallic chromium is produced primarily in four forms. Three of these forms are as the ferroalloys: high-carbon ferrochromium, low-carbon ferrochromium and ferrochromium silicon. The fourth form is chromium metal which is produced either by electrolysis or by the aluminothermic process. The relative production and consumption of these forms of chromium were summarized in Table 8 of the section on production and consumption. The ferrochrome alloys are adequate for most applications and often advantageous as compared to pure chromium. The latter is required in only a few specialty alloys, e.g., cobalt-chromium.

Uses of Chromium and its Alloys

Chromium is an essential element in modern industry because of its use in the production of special irons and steels and in nonferrous alloying applications. It is used in stainless, tool, and alloy steels, heat- and corrosion-resistant materials, alloy cast irons, and superalloys. Nonmetallic chromium is used in pigments, metal plating, leather tanning chemicals and refractories for metallurgical furnaces.

Chromium metal (electrolytic and aluminothermic) is used primarily (about 70 percent of total consumption) in superalloys. Other uses are in electrical resistance alloys, aluminum alloys, chromizing and other minor applications.

The use of chromium in metallurgical applications is to promote hardenability, tensile and yield strength, impact strength, resistance to corrosion and/or high temperature oxidation, and wear resistance. The major metallurgical use for chromium is in the production of a variety of stainless steels.

Ferroalloys

The major production of chromium is in the ferroalloy form. All of the ferroalloys are produced in electric furnaces by reduction of chromium ore with carbon.

High-Carbon Ferrochromium. High-carbon ferrochromium is the largest-tonnage chromium ferroalloy. Chromium content ranges from about 65 to 68 percent, carbon content from about 5 to 7 percent, silicon content from 1 to 3 percent, and the balance is essentially iron.

High-carbon ferrochromium is produced directly in a three-phase submerged-arc electric furnace. The furnace is operated continuously with tapping of the ferroalloy at intervals of about 2 hours. The charge to the furnace consists primarily of chrome ore, coke, wood chips, and selected fluxing agents.

Low-Carbon Ferrochromium. The composition of low-carbon ferrochromium is about 67 to 72 percent chromium, 0.03 to 0.10 percent carbon, 0.30 to 1.0 percent silicon and balance iron.

The method for production of low-carbon ferrochromium is somewhat complex. A ferrochromium-silicon alloy (low in carbon content) is produced in a submerged-arc electric furnace, while in another open-arc electric furnace chrome ore fines and lime are melted. Then, in a series of ladle reactions and repourings of mixtures of chrome silicide and ore-lime melt, a low-carbon ferrochromium and a waste slag are produced. The net metallurgical reactions of the series of reladlings is to reduce the Cr_2O_3 and FeO in the chrome ore with the silicon contained in the chrome silicide and to end up with a waste slag low in Cr_2O_3. A low-carbon ferrochromium product results.

Ferrochromium Silicon. The composition of ferrochromium-silicon, or chrome silicide, is about 38 to 41 percent chromium, silicon 38 to 42 percent, carbon at 0.05 percent maximum, and balance iron.

Ferrochromium-silicon is produced directly in a three-phase submerged-arc electric furnace. The charge to the furnace consists of chrome ore, quartzite and/or silica pebble, coke and wood chips. The furnace is tapped about every two hours. The primary use for ferrochromium-silicon is in the production of stainless steels for reducing the oxidized metals in the slag back into the metal.

Chromium Metal

The domestic chromium metal industry presently consists of two producers. They are Union Carbide Corporation, long a dominant factor in the business and a producer of electrolytic chromium, and Shieldalloy Corporation which is a manufacturer of aluminothermic chromium.

A substantial portion of this country's consumption of chromium metal is supplied by imports. These imports are primarily from Japan as electrolytic chromium, and some aluminothermic chromium is imported from the United Kingdom.

The electrolytic process involves the slow deposition of thick, brittle, chromium by the electrolysis of various aqueous solutions of chromium chemicals. After a plating thickness of about 1/8 inch is obtained on a metal cathode, the brittle chromium product is broken free, and deposition on the cathode is continued.

The aluminothermic process involves the self-propagation reduction of high-purity chromium oxide (Cr_2O_3) by finely divided aluminum metal.

Electrolytic Processes. Chromium metal has been produced commercially by two electrolytic processes. One method is the electrolysis of chromic-acid solutions and the other is electrolysis of chromium-alum solutions. Today practically all electrolytic chromium is produced from a solution of the trivalent chromium-alum. This process has definite advantages over plating from the hexavalent chromic acid bath in that at 100 percent current efficiency, theoretically 1545 amp-hr/kg (701 amp-hr/lb) are required to deposit chromium from a trivalent solution, while double that amount is needed for deposition from the hexavalent solution. In actuality, five times as much metal per kilowatt hour of energy is deposited from a trivalent bath, due chiefly to higher current efficiency and lower voltage, as well as the lower valence. Other advantages are lower cost of chromium in the form of chrome alum and fewer toxicity problems. The disadvantages of the chromium-alum process are the requirement of a diaphragm cell and close control of electrolysis conditions.

Chromic Acid Process. The chromic acid electrolyte used for the electrodeposition of chromium metal is essentially the same as that used in chromium plating for decorative work, corrosion resistance, and wear resistance. The limits within which heavy deposits can be produced for use as commercial chromium metal are, however, somewhat narrower than for chromium plating.

The electrolyte is made up of chromic acid with a small amount of sulfuric acid. There is a narrow range in composition of the electrolyte and operating conditions in which current efficiency is a maximum of the order of 15 percent.

Electrolytic chromium produced from the chromic acid electrolyte may contain from 0.01 up to 1 percent of oxygen and considerable hydrogen. The hydrogen is readily eliminated by annealing, but the oxygen is quite difficult to remove.

The cost of producing electrolytic chromium from a chromic acid electrolyte is primarily dependent upon the cost of chromium in chromic acid and the high energy cost resulting from low current efficiencies.

Chromium-Alum Process. The process for electrowinning of chromium from a chromium-alum electrolyte is the result of several years of research by the U.S. Bureau of Mines during the 1940's.

The chrome-alum process is applicable to both low-grade and high-grade ores or concentrates. Chromium ammonium alum for cell feed can be produced directly from chrome ore or concentrates by an acid leach process or from high-carbon ferrochromium. Although chromium-alum can be prepared from leached ore, the large number of steps necessary to produce a sufficiently pure electrolyte renders this process so costly from both operating and construction considerations that it is not used commercially. Instead, the simpler method of acid dissolution of high-carbon ferrochrome is used.

The electrolyte consists of a solution of chromic sulfate, chromous sulfate, and ammonium sulfate. The cell feed is chromium ammonium alum dissolved in water, and is added to the catholyte compartment of a two-compartment cell. The flowsheet for the chromium-alum process using high-carbon ferrochromium at the Marietta plant of Union Carbide is shown in Figure D1.

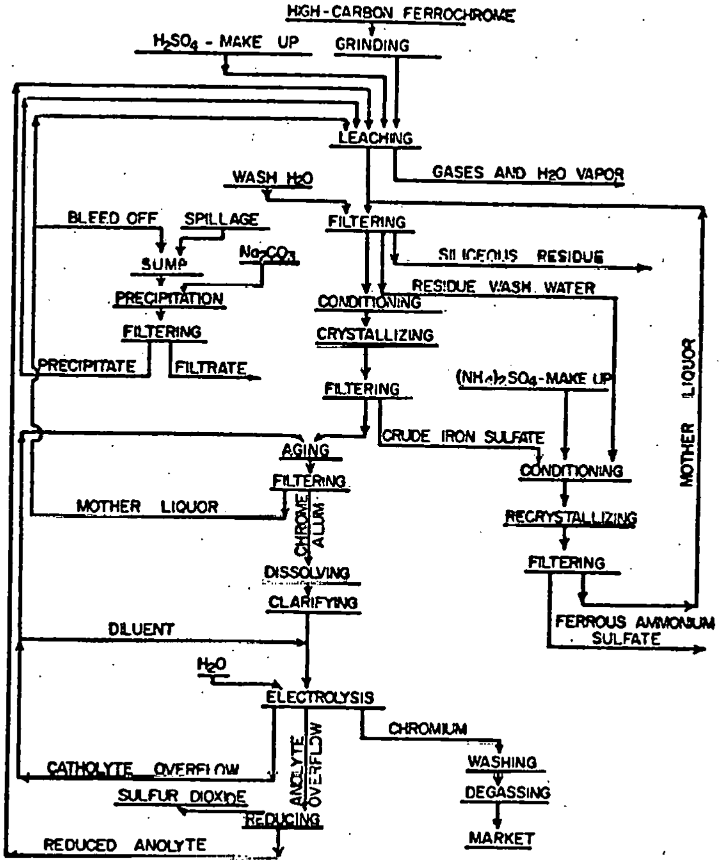

FIGURE D1. FLOWSHEET OF CHROME-ALUM PROCESS AT MARIETTA PLANT FOR ELECTROLYTIC CHROMIUM

Aluminothermic Reduction. The aluminothermic process for the production of chromium metal (and other metals and alloys) is an old European procedure dating back to a period after World War I. The theoretical chemical reaction in the case of chromium metal is:

$$Cr_2O_3 + 2Al = 2Cr + Al_2O_3$$

$$1.46\ \text{kg} + 0.52\ \text{kg} = 1.0\ \text{kg} + 0.98\ \text{kg} + \text{Heat} \quad .$$

The commercialization of this aluminothermic reaction to produce various metals came after the establishment of the Hall process for the production of low-cost aluminum.

The process is carried out as batch operations in simple, refractory-lined vessels. Enough heat must be generated by the exothermic formation of Al_2O_3 to melt the metal product and also to melt the byproduct Al_2O_3. The formation of the fluid slag and metal results in a separation of the slag and metal.

Aluminothermic reduction plants are low capital-cost operations with relatively high material costs. The cost of the chromium oxide (Cr_2O_3) is critical to the production cost of the product. Also, the aluminum is an energy intensive raw material.

Product quality depends mainly on the purity of the oxide and the aluminum powder, and partly on the control of the reduction. Aluminothermic chromium can be produced to a quality either equivalent to or better thaneelectrolytic chromium.

Energy Considerations

The total energy requirements to produce the three principal types of ferrochromium alloys has been determined in a study by Battelle for the U.S. Bureau of Mines[*]. Table D1 gives the details of energy consumption

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[*] "Energy Use Patterns in Metallurgical and Nonmetallic Mineral Processing" (Phase 5 -- Energy Data and Flowsheets, Intermediate-Priority Commodities) September 16, 1975. Prepared by USBM by Battelle Columbus Laboratories NTIS PB-246-357.

TABLE D1. TOTAL ENERGY CONSUMPTION TO PRODUCE HIGH-CARBON FERROCHROMIUM

	Unit	Units Per Net Ton of HC Fe-Cr	10^6 Btu Per Unit	10^6 Btu Per Net Ton* of HC Fe-Cr
Chrome ore				
Mining	net ton	2.50	0.25	0.625
Explosives	lb	1.75	0.030	0.053
Crushing	kwh	10	0.0105	0.105
Concentration	kwh	2.325	0.0105	0.023
Water transportation (7,500 miles)	net ton-mile	17,450	0.00025	4.363
Rail transportation (500 miles)	net ton-mile	1,160	0.00067	0.777
			Subtotal	5.946
Silica pebble				
Mining and screening	net ton	0.213	0.10	0.021
Rail transportation (300 miles)	net ton-mile	64	0.00067	0.043
			Subtotal	0.064
Coke				
Cokemaking	net ton	0.375	31.50	11.813
Rail transportation (300 miles)	net ton-mile	113	0.00067	0.076
			Subtotal	11.889
Wood chips				
Sawing and chipping	kwh	0.5	0.0105	0.01
Heating value of wood	net ton	0.0975	7.28	0.71
Truck transportation (50 miles)	net ton-mile	4.9	0.0024	0.01
			Subtotal	0.73

*Short ton.

TABLE D1. (Concluded)

	Unit	Units Per Net Ton of HC Fe-Cr	10^6 Btu Per Unit	10^6 Btu Per Net Ton of HC Fe-Cr
Refractories	lb	45.0	0.0125	0.563
Carbon electrode manufacture	net ton	0.022	82.00	1.804
Electrode rail transportation (500 miles)	net ton-mile	11.0	0.00067	0.007
			Subtotal	1.811
Alumina scrap rail transportation (200 miles)	net ton-mile	35.8	0.00067	0.02
Electrical energy (smelting)	kwh	3,575.0	0.0105	37.54
Electrical energy (pollution control)	kwh	75.0	0.0105	0.788
General plant energy	kwh	180.0	0.0105	1.89
Crushing and sizing	kwh	1.0	0.0105	0.01
TOTAL				61.25*

*Total energy for the alloy averaging approximately 60 percent chromium.

and Figure D2 is the flowsheet for high-carbon ferrochromium as determined in this study. Similar data for ferrochromium-silicon are shown in Table D2 and Figure D3. Fow low-carbon ferrochromium the data are shown in Table D3 and Figure D4. As can be noted, the energy analyses includes energy for mining ore, transportation, raw materials, reagents, fuels, electricity, pollution control, and miscellaneous items. No similar energy analysis is available for chromium metal.

Table D4 summarizes the available energy data for the production of metallurgical chromium products. The last column gives the electrical energy consumption, and it can be seen that the electrical energy consumed by both electrolytic processes far exceeds the total energy used in the electric-arc furnace ferroalloy processes. The chromium-alum process to produce electrolytic chromium has been in use for over 20 years during which time process conditions have been optimized. However, it should be possible to decrease anode potential and thus lower cell voltage and power requirements. The silver-lead insoluble anodes now used are capable of oxidizing chromic ions to dichromate (standard potential is +1.33 volts v.s. NHE) and probably operate at around +2.0 volts v.s. NHE. This voltage is the standard potential of +1.2 volts for oxygen plus 0.8 volts overvoltage (see section on zinc electrowinning).

A possible improvement is to anodically rather than chemically dissolve the ferrochrome. Standard potentials for iron and chromium are:

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{++} + 2e \qquad -.4402 \text{ volt}$$

$$\mathrm{Cr} \rightarrow \mathrm{Cr}^{+++} + 3e \qquad -.744 \text{ volt} \quad .$$

Assuming that a ferrochromium anode polarizes sufficiently to avoid local cell action (dissolution with hydrogen evolution) we will assume that the anode potential is zero. The saving in energy as compared to use of insoluble anodes is then 2.0 volts. The current efficiency for chromium deposition is about 45 percent. The energy saving with the assumed voltage reduction allowing 10 percent power for AC to DC conversion and line loss is 7550 kwh/M ton (6850 kwh/S ton) Cr or 19.9 x 10^6 Kcal/M ton (71.9 x 10^6 Btu/S ton) Cr. This saving corresponds to a 40 percent decrease in the energy quoted in Table D4.

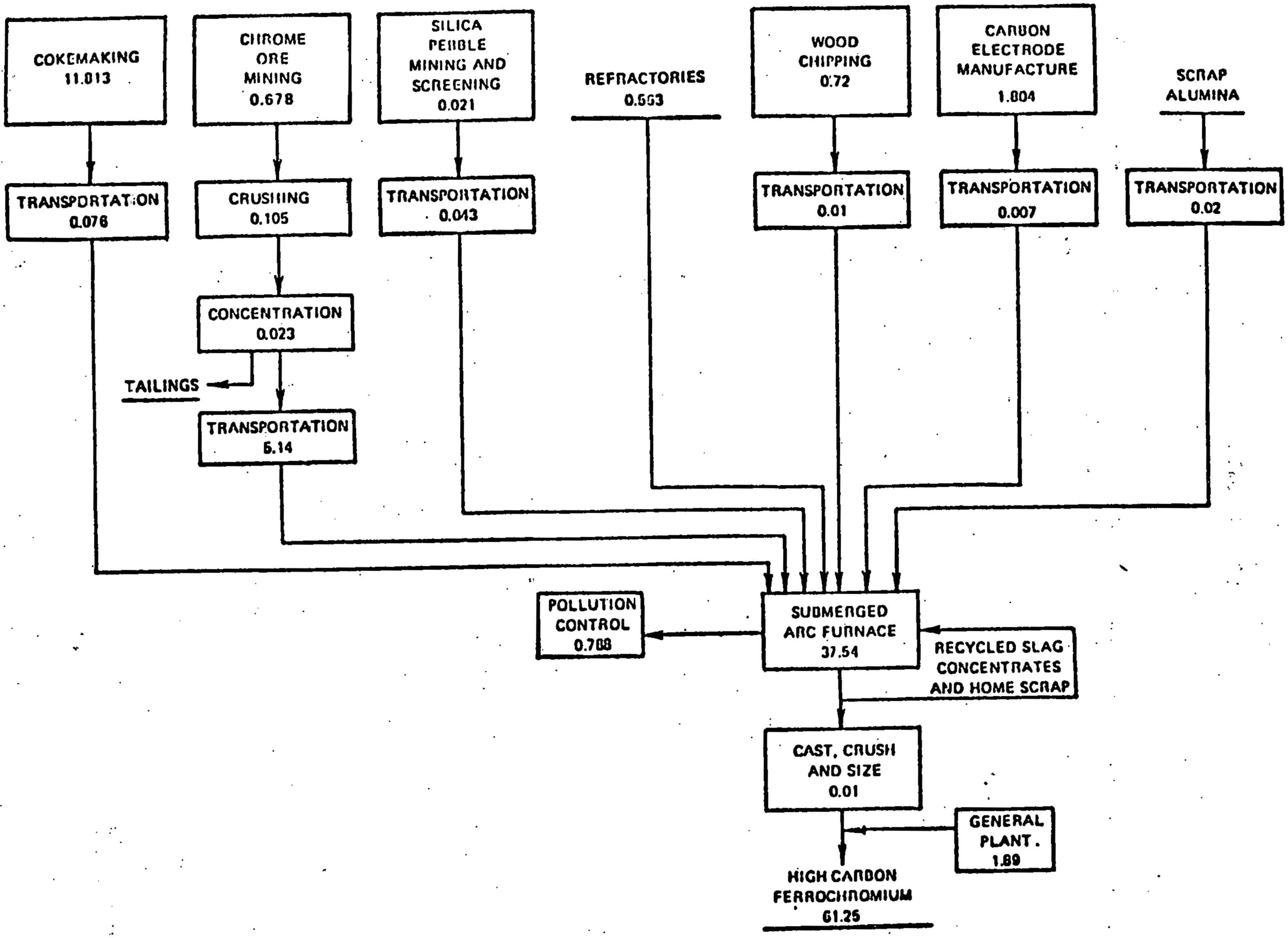

FIGURE D2. UNIT OPERATION AND ENERGY FLOWSHEET FOR THE PRODUCTION OF HIGH-CARBON FERROCHROMIUM (Units are 10^6 Btu/S ton ferrochromium)

TABLE D2. TOTAL ENERGY CONSUMPTION TO PRODUCE FERROCHROMIUM SILICON

	Unit	Units Per Net Ton of Cr-Si	10^6 Btu Per Unit	10^6 Btu Per Net Ton of Cr-Si
Chrome ore				
Mining	net ton	1.25	0.25	0.313
Explosives	lb	0.9	0.030	0.027
Crushing	kwh	5	0.0105	0.053
Concentration	kwh	1.15	0.0105	0.012
Water transportation (7,500 miles)	net ton-mile	8,625	0.00025	2.156
Rail transportation (500 miles)	net ton-mile	575	0.00067	0.385
			Subtotal	2.946
Silica pebble				
Mining and screening	net ton	1.7	0.10	0.17
Rail transportation (300 miles)	net ton-mile	510	0.00067	0.342
			Subtotal	0.512
Coke				
Cokemaking	net ton	0.95	31.50	29.925
Rail transportation (300 miles)	net ton-mile	285	0.00067	0.191
			Subtotal	30.116
Wood chips				
Sawing and chipping	kwh	0.85	0.0105	0.009
Heating value of wood	net ton	0.17	7.28	1.238
Truck transportation (50 miles)	net ton-mile	8.5	0.0024	0.02
			Subtotal	1.267

TABLE D2. (Concluded)

	Unit	Units Per Net Ton of Cr-Si	10^6 Btu Per Unit	10^6 Btu Per Net Ton of Cr-Si
Soderberg paste manufacture	net ton	0.0675	37.92	2.56
Paste rail transportation (500 miles)	net ton-mile	33.75	0.00067	0.023
Refractories	lb	45.0	0.0125	0.563
Electrical energy (smelting)	kwh	7,200	0.0105	75.60
Electrical energy (pollution control)	kwh	800	0.0105	8.40
General plant energy	kwh	360	0.0105	3.78
Refractories	lb	45	0.0125	0.563
TOTAL				125.767*

*Total energy for the alloy averaging approximately 60 percent chromium.

Net ton = S ton.

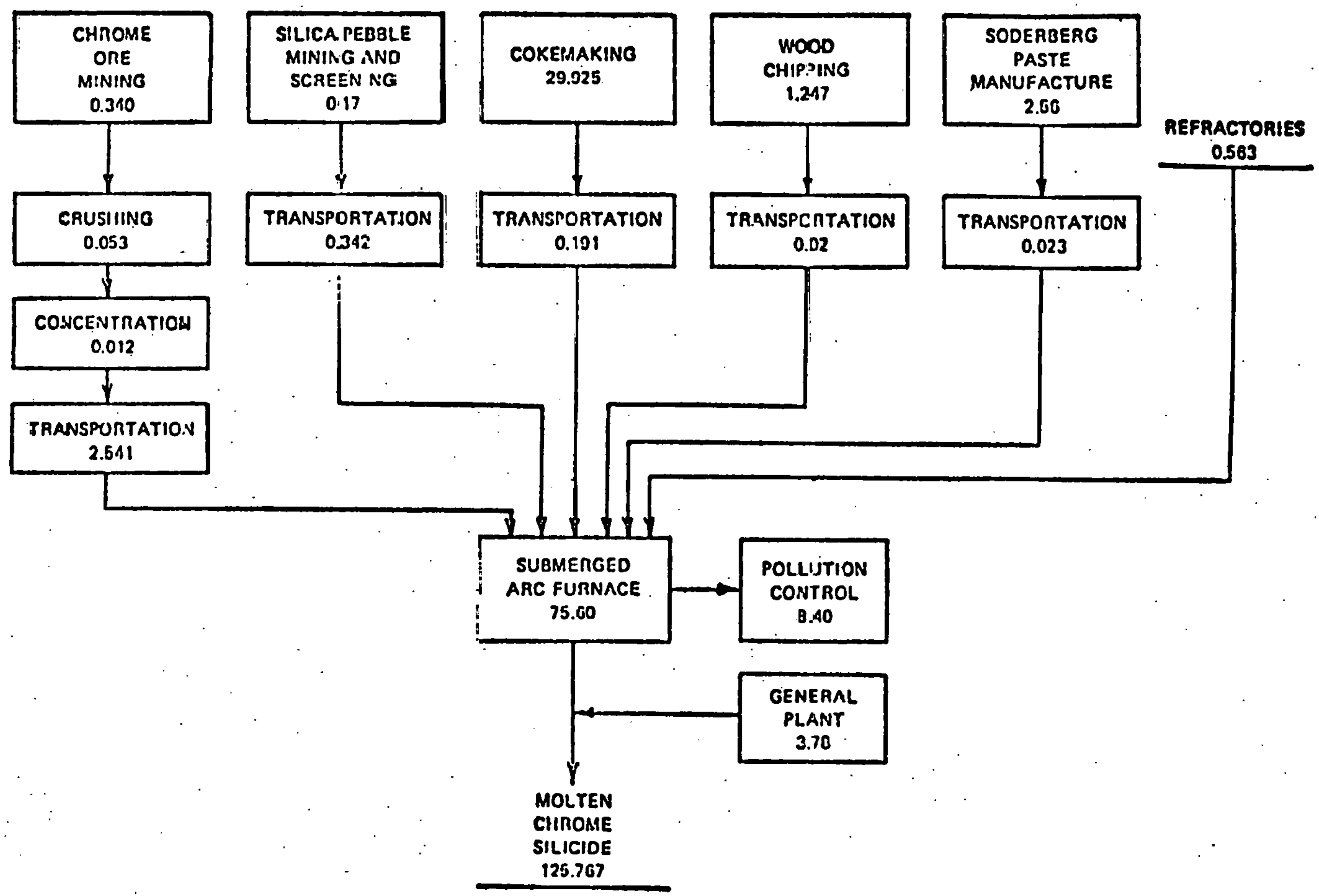

FIGURE D3. UNIT OPERATION AND ENERGY FLOWSHEET FOR THE PRODUCTION OF FERROCHROMIUM-SILICON (Units are 10^6 Btu/S ton chrome silicide)

TABLE D3. TOTAL ENERGY CONSUMPTION TO PRODUCE LOW-CARBON FERROCHROMIUM

	Unit	Units Per Net Ton of LC Fe-Cr	10^6 Btu Per Unit	10^6 Btu Per Net Ton of LC Fe-Cr
Chrome ore				
Mining	net ton	1.70	0.25	0.425
Explosives	lb	1.2	0.030	0.036
Crushing	kwh	6.8	0.0105	0.071
Concentration	kwh	1.55	0.0105	0.016
Water transportation (7,500 miles)	net ton-mile	11,625	0.00025	2.906
Rail transportation (500 miles)	net ton-mile	775	0.00067	0.519
			Subtotal	3.973
Molten chrome silicide	net ton	0.625	125.767	78.604
Lime				
Production	net ton	1.45	8.487	12.306
Transportation	net ton-mile	101.5	0.00067	0.068
			Subtotal	12.374
Carbon electrode manufacture	net ton	0.02	82.00	1.64
Electrode rail transportation (500 miles)	net ton-mile	10	0.00067	0.007
Electrical energy (ore-lime melting)	kwh	2,750	0.0105	28.875
Electrical energy (pollution control)	kwh	150	0.0105	1.575
General plant energy	kwh	140	0.0105	1.47
Cast, crush and size	kwh	5	0.0105	0.053
TOTAL				128.571*

*Total energy for the alloy containing approximately 60 percent chromium.

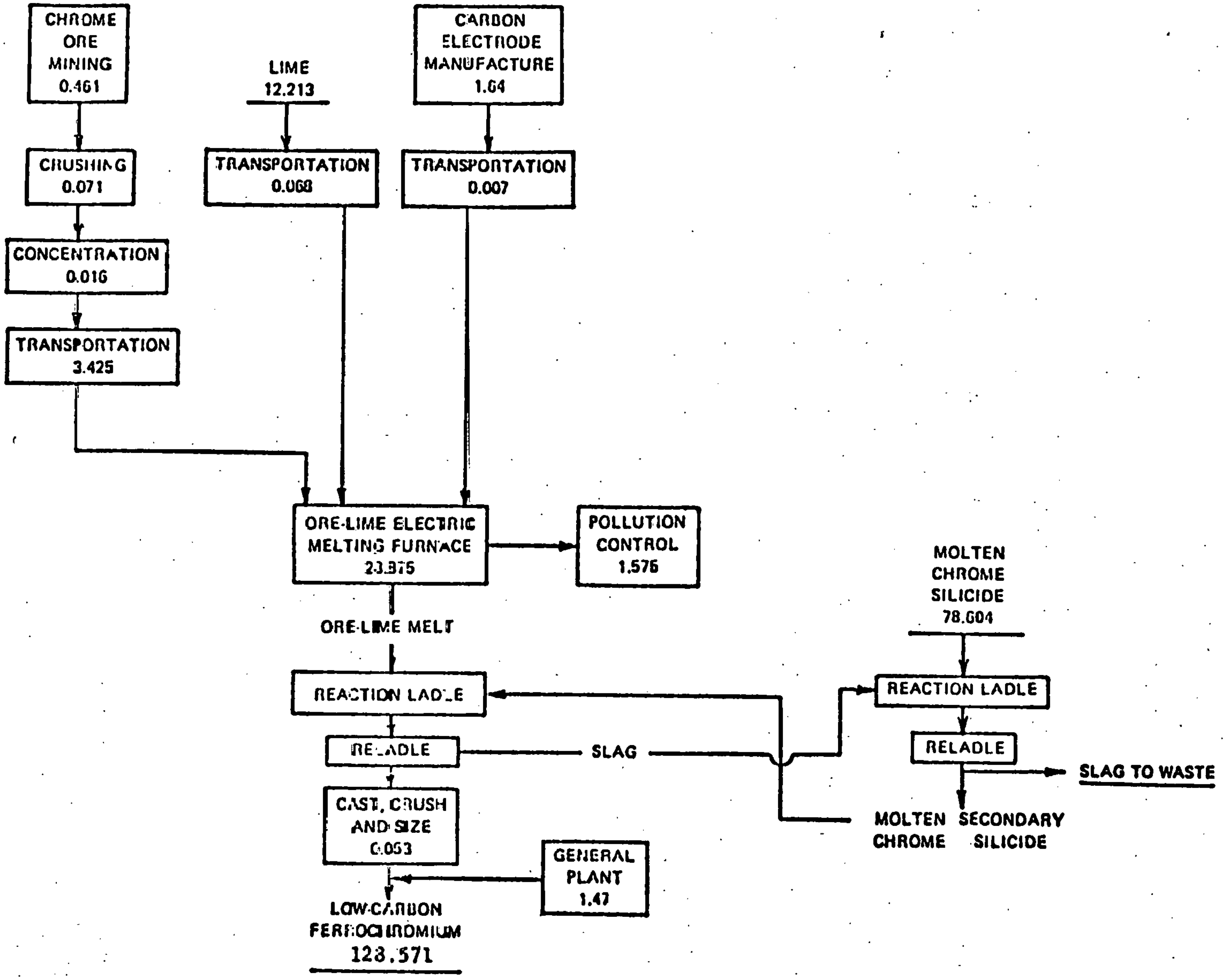

FIGURE D4. UNIT OPERATION AND ENERGY FLOWSHEET FOR THE PRODUCTION OF LOW-CARBON FERROCHROMIUM (Units are 10^6 Btu/S ton chrome silicide)

TABLE D4. ENERGY CONSUMPTION IN PRODUCTION OF METALLURGICAL CHROMIUM PRODUCTS

Chromium Product	Total Energy Consumed (1) Alloy Product 10^6 Kcal/M ton (10^6 Btu/S ton)	Total Energy Consumed (1) Contained Chromium(6) 10^6 Kcal/M ton (10^6 Btu/S ton)	Electrical Energy Consumed (2) Alloy Product 10^6 Kcal/M ton (10^6 Btu/S ton)	Electrical Energy Consumed (2) Contained Chromium(6) 10^6 Kcal/M ton (10^6 Btu/S ton)
High-Carbon Ferrochromium	17.02 (61.25)	28.42 102.3	10.65 (38.33)	17.8 (64)
Low-Carbon Ferrochromium	35.72 (128.57)	59.7 214.	23.05 (82.96)	38.5 (138.5)
Ferrochromium Silicon	34.94 (125.77)	58.3 210.	23.34 (84.0)	39.0 (140)
Electrolytic Chromium Metal				
Chromic Acid Process	-	NA(3)	-	175 (4) (630)
Chrome Alum Process	-	NA(3)	-	49 (5) (176)

(1) Includes energy for mining ore, transportation, raw materials, reagents, fuels, electricity, pollution control and miscellaneous items.

(2) Electrical energy converted at 10,500 Btu per kilowatt-hour.

(3) Not available.

(4) Metallurgy of Chromium and Its Alloys, M. C. Udy, Reinhold Publishing Corporation, New York, 1956, Volume 2, p 45.

(5) Rare Metals Handbook, C. A. Hampel, Reinhold Publishing Corporation, New York, Second Edition, 1961, p 98.

(6) Assumes a 60 percent chromium content.

Sulfur dioxide may be a suitable anode depolarizer with a porous anode. The standard electrode potential for SO_2 oxidation is +.172 volts v.s. NHE. Assume an overvoltage of 0.5 volts (see section on zinc electrowinning) or an anode potential of +0.7 volt. Then the reduction from use of the lead anode is 1.3 volt. Energy saving for this case is 4900 kwh/M ton (4450 kwh/S ton) Cr corresponding to 13.0×10^6 Kcal/M ton (46.8×10^6 Btu/S ton) Cr. The reduction over the present energy requirements would be 27 percent. The volume of pure chromium used is minor compared to the volume of ferrochromium. Thus, what is really sought is an electrolysis method for producing ferrochromium with less energy. In view of the high energy values for the electrolytic processes it appears very unlikely that electrolytic methods can compete with current methods of producing ferrochromium either economically or energy wise.

The price differential, Table D5, reflects the high energy use and more complex processes for producing chromium metal compared to ferrochromes.

Summary

Because of the more-or-less stable market for chromium metal there is little impetus to try and develop new or modified electrolytic processes. Due to energy and price constraints, there is also little likelihood that chromium metal units will be able to capture any of the applications in which ferroalloy chromium units are now being used. Therefore, there is little potential practical motivation to develop a new electrowinning process for ferrochrome or chromium.

TABLE D5. PRICES FOR METALLURGICAL CHROMIUM PRODUCTS IN THE UNITED STATES

Chromium Product	Price of Contained Chromium Dollars/kg (Dollars/lb)
High-carbon ferrochromium	0.82(0.37)
Low-carbon ferrochromium	1.65(0.75)
Ferrochromium-silicon	1.65(0.75)
Electrolytic chromium	6.59(2.99)

Source: Metals Week

TECHNOLOGY OF MANGANESE

Metallic manganese is produced either as a ferroalloy or as electrolytic manganese metal. The primary manganese ferroalloy is high-carbon ferromanganese which can be produced either in a blast furnace or in a submerged-arc electric furnace. Other manganese ferroalloys which are produced and consumed in substantial amounts are medium- and low-carbon ferromanganese and silicomanganese. Relatively low amounts of spiegeleisen (contains 15 to 30 percent manganese, 5 to 7 percent carbon, balance iron) are produced and consumed in the United States. Electrolytic manganese is supplied by domestic producers and foreign sources.

Ferroalloys

Standard high-carbon ferromanganese is produced by two different processes. One method uses a blast furnace with coke as the reductant. Generally, manganese blast furnaces are located within an operating steel plant and the product is used directly in the steel production.

The second process is the usual ferroalloy method which uses submerged-arc electric furnaces. In this process there are two generally accepted practices to produce high-carbon ferromanganese. In one, known as the "high-manganese slag practice", the degree of manganese reduction to metal is limited and a slag is produced which usually contains more than 25 percent manganese. This slag is then used to produce silicomanganese in a separate operation. The silicomanganese can be used to produce low-carbon ferromanganese. The second alternative, known as the "low-manganese slag practice", produces a by-product slag containing only 8 to 12 percent manganese which is discarded. The choice of practice depends upon several factors, including the relative costs of manganese ore and electrical energy and the ability to use a high-manganese slag.

Standard ferromanganese usually contains about 78 percent manganese, 7 percent carbon, 1 percent silicon, and the balance iron.

Electrolytic Manganese

At present the domestic electrolytic manganese metal industry consists of three producers as follows:

Foote Mineral Company, New Johnsonville, Tennessee
Kerr-McGee Chemical Corporation, Hamilton, Mississippi
Union Carbide Corporation, Marietta, Ohio.

Total U.S. capacity is estimated to be about 27,200 M ton (30,000 S tons) per year. Some of the domestic consumption is satisfied by imports. At 5 kwh/lb the electrical energy consumption is 3.0×10^8 kwh (7.9×10^{12} Kcal or 3.15×10^{12} Btu).

Electrolytic Process. The original development of the process for the production of manganese metal by the electrolysis of manganese sulfate solutions was the result of extensive laboratory and pilot plant investigations by the United States Bureau of Mines. The process was brought to the level of commercial production by the Electro Manganese Corporation at Knoxville, Tennessee, in 1939.

In the development of the process it was found that there are several factors pertinent to success*. These factors are summarized as follows:

- Before the manganese in most ores becomes acid soluble it must be converted into the divalent form. This requires a reducing roast.

- Manganese has a high negative value in the electromotive series (-1.18 volt vs. NHE) and nearly all metals plate out of aqueous solution before it. For this reason impurities likely to be deposited must be kept down to a very low level if a high-purity product is to be obtained.

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* Manganese, A. H. Sully, Academic Press Inc., New York, NY, 1955, p 67.

- It is necessary to use a diaphragm cell for the deposition.
- The temperature of the solution must be closely controlled.
- Energy requirements are substantially higher than in the electrowinning of such other metals as copper, nickel and zinc.
- The electrolytes are very corrosive.
- When the current to the cell is stopped the manganese immediately starts to redissolve in the electrolyte.

Sulfur dioxide is added to the anolyte to depolarize the anode, which prevents oxidation of manganous ion to manganese dioxide. The cell voltage based on standard potentials of -1.18 volts for Mn/Mn^{++} and +.17 volts for $H_2SO_3/SO_4^{=}$ is 1.35 volt. This voltage corresponds to a theoretical energy consumption of 1192 kwh/M ton (1172 kwh/S ton) Mn or 3.4×10^6 Kcal/M ton (12.3×10^6 Btu/S ton) Mn for a 32 percent efficient power plant.

Without going into details, the electrolytic process can be considered to consist of four basic steps as follows:

(1) The roasting of the ore
(2) The leaching of the roasted ore
(3) Purification of the leach liquor
(4) Electrodeposition of the metal in a diaphragm cell.

The process flowsheet for electrolytic manganese metal is shown in Figure E1.

Energy Considerations

The total energy requirements to produce high-carbon ferromanganese in the blast furnace and by the submerged-arc electric furnace

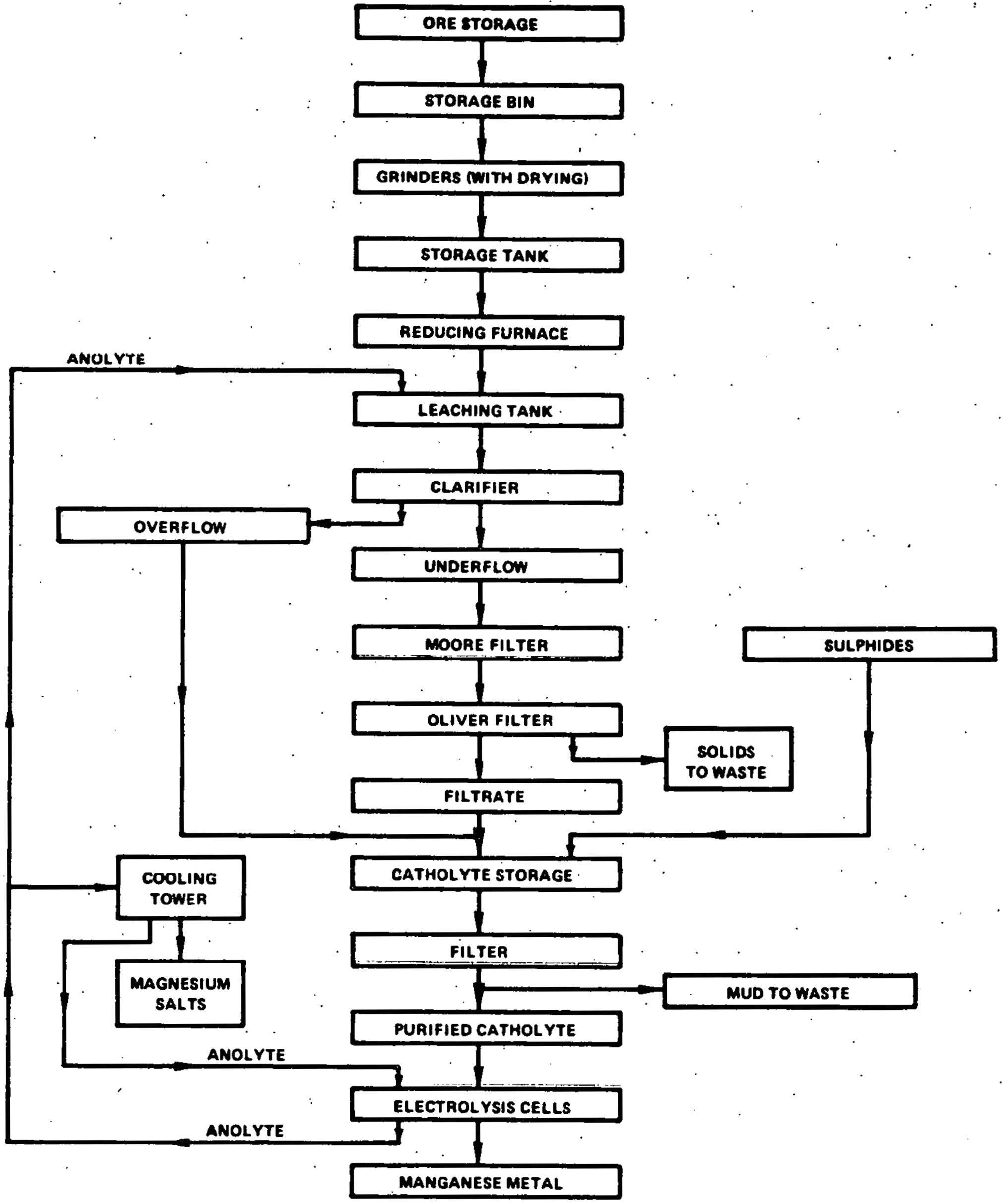

FIGURE E1. PROCESS FLOWSHEET FOR ELECTROLYTIC MANGANESE METAL.

process have been determined in a study by Battelle for the U.S. Bureau of Mines*. Table E1 gives the details of energy consumption and Figure E2 is the flowsheet for the production of electric-furnace high-carbon ferromanganese as determined in the Bureau of Mines study. Similar data for the production of high-carbon ferromanganese by the blast-furnace process are shown in Table E2 and Figure E3. As can be noted, the energy analyses includes energy for mining ore, transportation, raw materials, reagents, fuels, electricity, pollution control, and miscellaneous items. No such detailed energy analysis is available for electrolytic manganese metal.

Table E3 summarizes the available energy data for the production of high-carbon ferromanganese and electrolytic manganese. The very low electrical energy consumption for producing blast-furnace ferromanganese can be attributed to the fact that coke is used to supply the necessary heat and to serve as the reductant. As can be noted, the electrical energy requirement alone for electrolytic manganese is substantially higher than the <u>total</u> energy required for ferromanganese by each of the two processes. The electrowinning cell operates at only about 45 percent current efficiency and at 5 volts. With ferromanganese at 78 percent contained manganese, the energy required for electrolytic manganese is still considerably higher per unit of manganese than for the ferromanganese processes. The energy consumption for electrolytic manganese would have to be reduced to about 6600 kwh/M ton (6,000 kwh/S ton) Mn to be equivalent to that for the total energy required for either of the two ferroalloy processes.

The present electrolytic process for manganese metal is one that has been refined over a period of more than 30 years and has been optimized to a degree. Substantial reduction in energy requirements will require a higher current efficiency along with a reduced cell voltage. Aqueous solution will probably need replacement by fused salts in order to accomplish this along with lower IR drop through the electrolyte. The large items in submerged arc ferromanganese production are the arc furnace and coke making, which account for 11 x 10^6 Kcal/M ton (40.0 x 10^6 Btu/S ton) Mn or about 80 percent of the energy required.

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*"Energy Use Patterns in Metallurgical and Nonmetallic Mineral Processing", (Phase 6-Energy Data and Flowsheets, Intermeditate-Priority Commodities) September 16, 1975. For USBM by Battelle Columbus Laboratories, NTIS PS-246-357.

TABLE E1. TOTAL ENERGY CONSUMPTION TO PRODUCE ELECTRIC-FURNACE HIGH-CARBON FERROMANGANESE

	Unit	Units Per Net Ton of FeMn	10^6 Btu Per Unit	10^6 Btu Per Net Ton of FeMn
Manganese ore				
Mining	net ton	2.2	0.25	0.55
Explosives	lb	1.5	0.030	0.045
Crushing and concentration	kwh	12.0	0.0105	0.126
Water transportation (5,600 miles)	net ton-mile	12,300	0.00025	3.075
Rail transportation (700 miles)	"	1,540	0.00067	1.032
			Subtotal	4.828
Limestone				
Mining and crushing	net ton	0.3	0.104	0.031
Rail transportation (200 miles)	net ton-mile	60	0.00067	0.040
			Subtotal	0.071
Coke				
Cokemaking	net ton	0.50	31.50	15.75
Rail transportation (300 miles)	net ton-mile	150.0	0.00067	0.10
				15.85
Refractories	lb	45.0	0.0125	0.563
Soderberg paste				
Manufacture	net ton	0.02	37.92	0.758
Rail transportation (500 miles)	net ton-mile	10	0.00067	0.007
			Subtotal	0.765
Wood chips				
Sawing and chipping	kwh	0.875	0.0105	0.009
Heating value of wood	net ton	0.175	7.28	1.274
Truck transportation (50 miles)	net ton-mile	8.75	0.0024	0.021
			Subtotal	1.304
Steel scrap	net ton	0.15	0.0	0.0
Scrap transportation (200 miles)	net ton-mile	30	0.00067	0.020
Electrical energy (smelting)	kwh	2,300	0.0105	24.15
Electrical energy (pollution control)	kwh	350	0.0105	3.675
General plant electrical energy	kwh	115	0.0105	1.208
Crushing and sizing	kwh	1.0	0.0105	0.011
Total				52.445

Tons are short tons

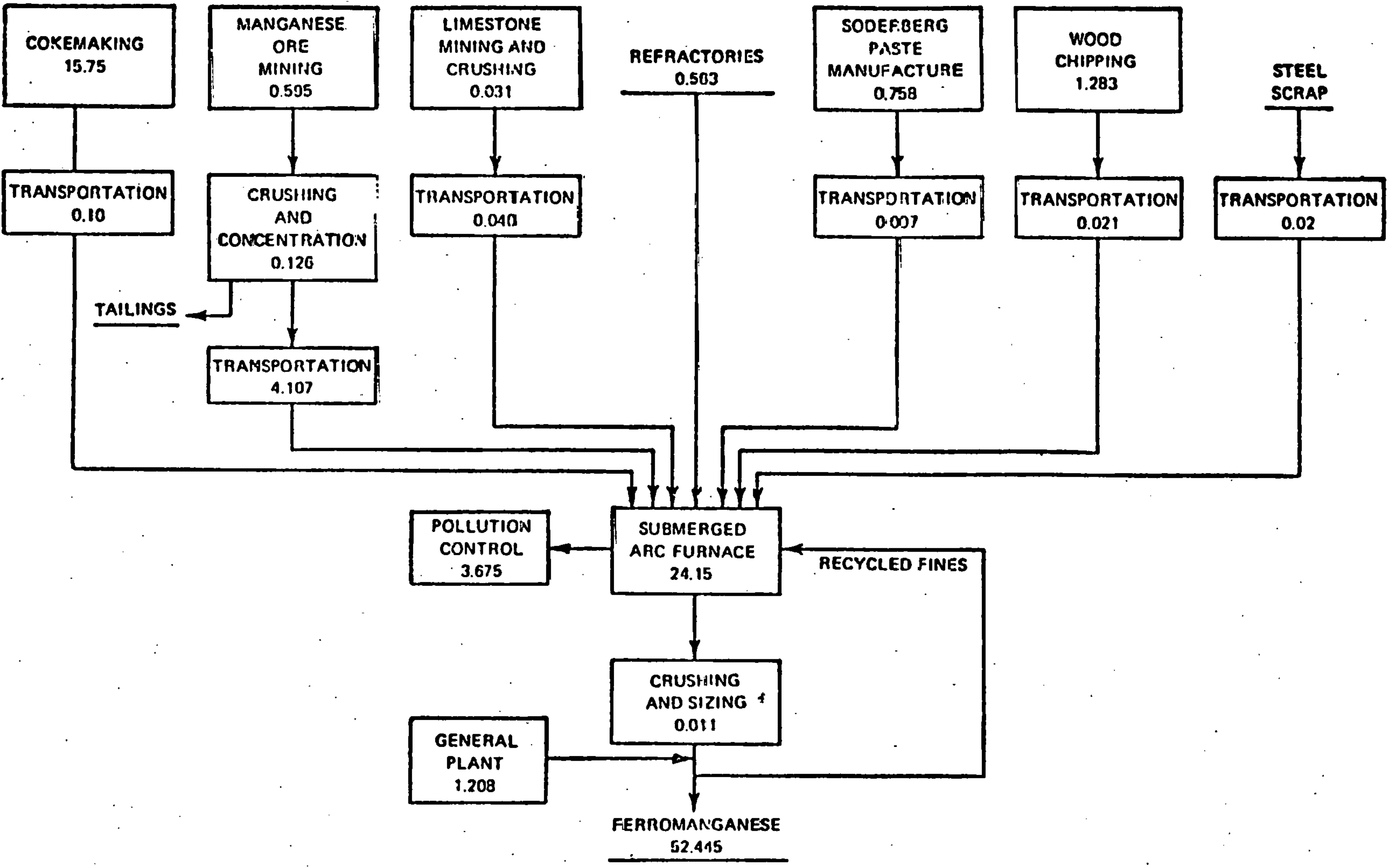

FIGURE E2. UNIT OPERATION AND ENERGY FLOWSHEET TO PRODUCE ELECTRIC-FURNACE HIGH-CARBON FERROMANGANESE

(Units are 10^6 Btu/S ton Ferromanganese)

TABLE E2. TOTAL ENERGY CONSUMPTION TO PRODUCE BLAST-FURNACE HIGH-CARBON FERROMANGANESE

	Unit	Units Per Net Ton of FeMn	10^6 Btu Per Unit	10^6 Btu Per Net Ton of FeMn
Manganese ore				
Mining	net ton	1.93	0.25	0.483
Explosives	lb	1.35	0.030	0.041
Crushing and concentration	kwh	11.0	0.0105	0.116
Water transportation (5,600 miles)	net ton-mile	10,800	0.00025	2.700
Rail transportation (700 miles)	"	1,350	0.00067	0.905
			Subtotal	4.245
Limestone				
Mining and crushing	net ton	0.5	0.104	0.052
Rail transportation (200 miles)	net ton-mile	100	0.00067	0.067
			Subtotal	0.119
Coke				
Cokemaking	net ton	1.423	31.50	44.825
Rail transportation (300 miles)	net ton-mile	430.0	0.00067	0.288
			Subtotal	45.113
Refractories	lb	5.0	0.0125	0.063
Coke oven gas	ft^3	121.0	0.0005	0.061
Blast furnace gas	"	68,000.0	0.00012	8.160
Natural gas	"	325.0	0.001	0.325
Oxygen	"	7,450.0	0.000183	1.363
Steam	lb	1,200.0	0.001	1.200
Electrical energy	kwh	25.0	0.0105	0.263
Crushing and sizing	kwh	1.0	0.0105	0.011
Total consumption				60.923
By-product production				
Blast furnace gas	ft^3	114,000	0.00012	-13.68
Net energy consumption				47.243

Net tons are short tons.

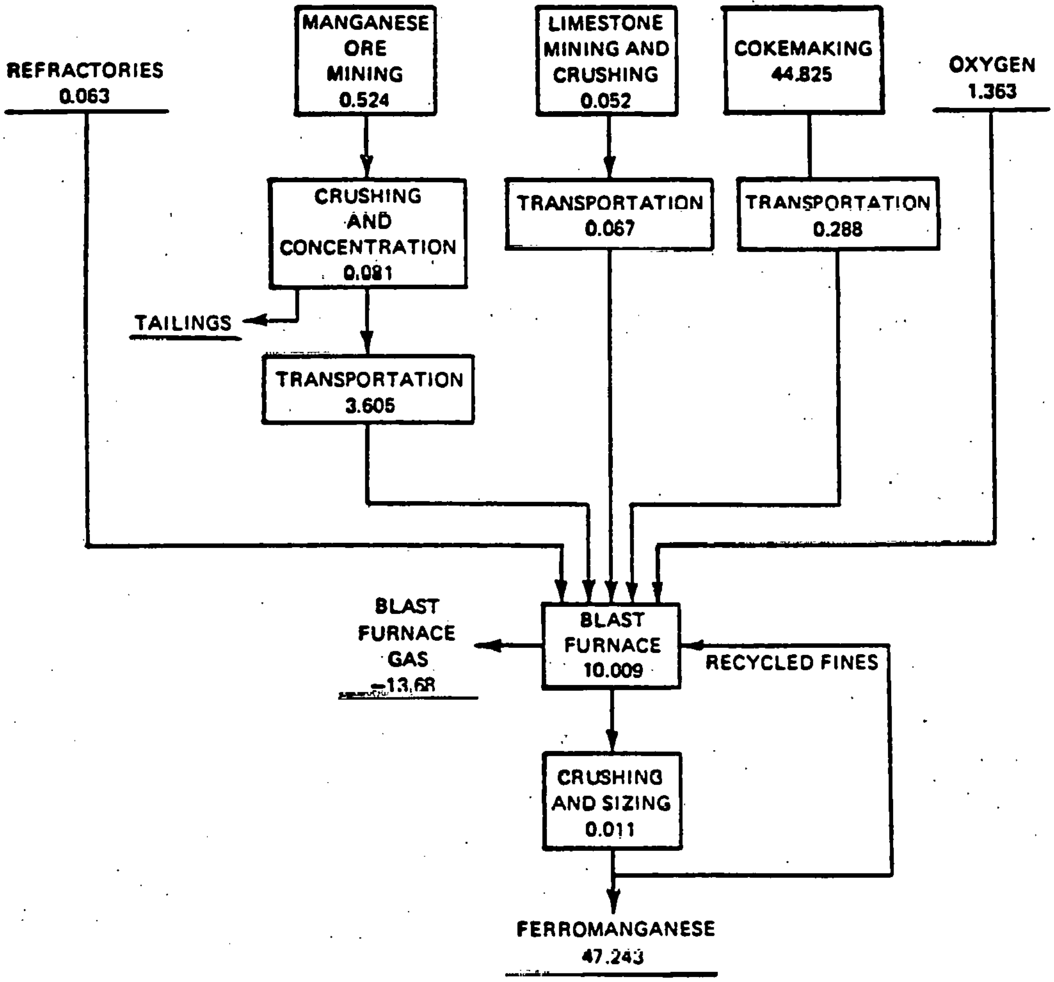

FIGURE E3. UNIT OPERATION AND ENERGY FLOWSHEET TO PRODUCE BLAST-FURNACE HIGH-CARBON FERROMANGANESE

(Units are 10^6 Btu/S ton ferromanganese)

TABLE E3. ENERGY CONSUMPTION IN THE PRODUCTION OF HIGH-CARBON FERROMANGANESE AND ELECTROLYTIC MANGANESE

Manganese Product	Total Energy Consumed 10^6 Kcal/M ton (10^6 Btu/S ton) (1)		Electrical Energy Consumed 10^6 Kcal/M ton (10^6 Btu/S ton) (1)	
	Alloy	Contained Mn	Alloy	Contained Mn
Electric-Furnace High-Carbon Ferromanganese (4)	14.57 (52.45)	19.4 (69.8)	7.73 (27.83)	10.28 (37.9)
Blast-Furnace High-Carbon Ferromanganese (4)	13.12 (47.24)	17.5 (62.8)	0.07 (0.26)	0.09 (0.35)
Electrolytic Manganese Metal	-	-	29.17 (105.0) (3)	

(1) Includes energy for mining ore, transportation, raw materials, reagents, fuels, electricity, pollution control, and miscellaneous items.

(2) Electrical energy converted at 10,500 Btu per kilowatt-hour.

(3) At 5 kilowatt-hours per pound. See: Rare Metals Handbook, C. A. Hampel, Reinhold Publishing Corporation, New York, Second Edition, 1961, p. 275.

(4) Total energy for the alloy containing approximately 75 percent manganese. In a contained manganese base, these figures should be higher by a factor of 1.33.

In the blast furnace process essentially this same total energy is consumed for coke making. Increasing current efficiency to near 100 percent and decreasing cell voltage to 3 volts, (which is still well above theoretical can reduce electrical energy requirements to about 8 x 10^6 Kcal/M ton (30 x 10^6 Btu/S ton) including conversion and line losses of 10 percent. Since other energy elements of manganese alloy production seem relatively small it may be possible to develop an electrolytic method of manganese or manganese alloy production with energy use equivalent to that of present pyrometallurgical processes. However, from the standpoint of this survey it would be difficult to show a possible substantial energy saving.

However, from the standpoint of economics electrolytic manganese could play a larger role by supplanting the equally costly low carbon ferromanganese. The domestic production of ferromanganese alloys in 1977 was distributed as follows:

High carbon ferromanganese	248,987 M tons	(268,950 S tons)
Medium and low carbon ferromanganese	75,840 M tons	(83,600 S tons)
Manganese metal	22,123 M tons	(24,387 S tons).

Although specific figures are not available, the medium carbon ferromanganese production is probably larger than that of low carbon ferromanganese. Assuming equal production of these two products the maximum production for low carbon ferromanganese would have been $\approx$38,000 M tons (42,000 S tons). Therefore, there is the potential for the production of electrolytic manganese to increase to 60,000 M tons (66,000 S tons)/yr.

Prices

The present prices for four types of metallurgical manganese products are shown in Table E4. As can be seen, electrolytic manganese is priced competitively with low-carbon ferromanganese. It is used in preference to the low-carbon grade where it is necessary to have low iron and other impurity levels. Because of the substantial price differential it is not likely that any electrolytic manganese will be used to replace manganese

TABLE E4. PRICES FOR METALLURGICAL MANGANESE PRODUCTS IN THE UNITED STATES

Manganese Product	Price Per Pound of Contained Manganese, dollars
High-carbon ferromanganese	0.24
Medium-carbon ferromanganese	0.38
Low-carbon ferromanganese	0.58
Silicomanganese	0.31
Electrolytic manganese	0.58

SOURCE: Metals Week

units from high- and medium-carbon ferromanganese or silicomanganese. Of course a lower cost electrolytic process could change this balance.

Summary

The markets for manganese metal are expected to grow at a relatively modest rate and present consumption is only about 2.7 percent of total manganese consumption in metallurgical applications. It does not appear that there is any incentive for the development of a completely new electrolytic process because of the lower energy established processes for ferromanganese and the limited potential for increased consumption of pure manganese.

TECHNOLOGY OF SODIUM

Current Methods of Production

The conventional method for production of sodium is by electrolysis of fused sodium chloride (Downs Process). The energy used for the process, estimated in the USBM study, is 25.57 x 10^6 Kcal/M ton (92.041 x 10^6 Btu/S ton)(F1). The breakdown of energy used by process steps is shown in Figure F1 and Table F1. The volatility of sodium has made possible the development of direct reduction processes from sodium salts with carbon, iron carbide(F2), etc., but such processes are not in current use. Most of the processes described operate over 1,000° C which creates materials problems. Rapid chilling is needed to obtain a good yield.

Electrolysis of Sodium Hydroxide

The first electrolytic process used extensively for sodium production utilized fused sodium hydroxide electrolyte, and the best known method was the Castner process(F1). The electrolyte was later displaced by sodium chloride. Nevertheless, the energy requirements of the processes using the two electrolytes should be compared.

The caustic electrolyte must first be manufactured by causticizing sodium sulfate solution or by electrolysis of sodium chloride. The latter is the predominent process. The energy for producing a 50 percent caustic solution (the most common article of commerce) has been estimated to be 9.31 x 10^6 Kcal/M ton (33.5 x 10^6 Btu/S ton) of contained caustic(F3). The allocation of electric power for caustic in chlorine-caustic electrolysis is 1763 kwh/M ton (1600 kwh/S ton). The thermal equivalent of this is 4.67 x 10^6 Kcal/M ton (16.80 x 10^6 Btu/S ton) caustic. The additional energy for dehydration is 14.61 x 10^6 Kcal/M ton (52.6 x 10^6 Btu/S ton) so that total energy for production is of the order of 24 x 10^6 Kcal/M ton (86 x 10^6 Btu/S ton). Details on the estimate for energy to produce anhydrous caustic are in Table F2. The overall reaction of the Castner process is:

$$2NaOH \rightarrow 2Na + H_2 + O_2$$

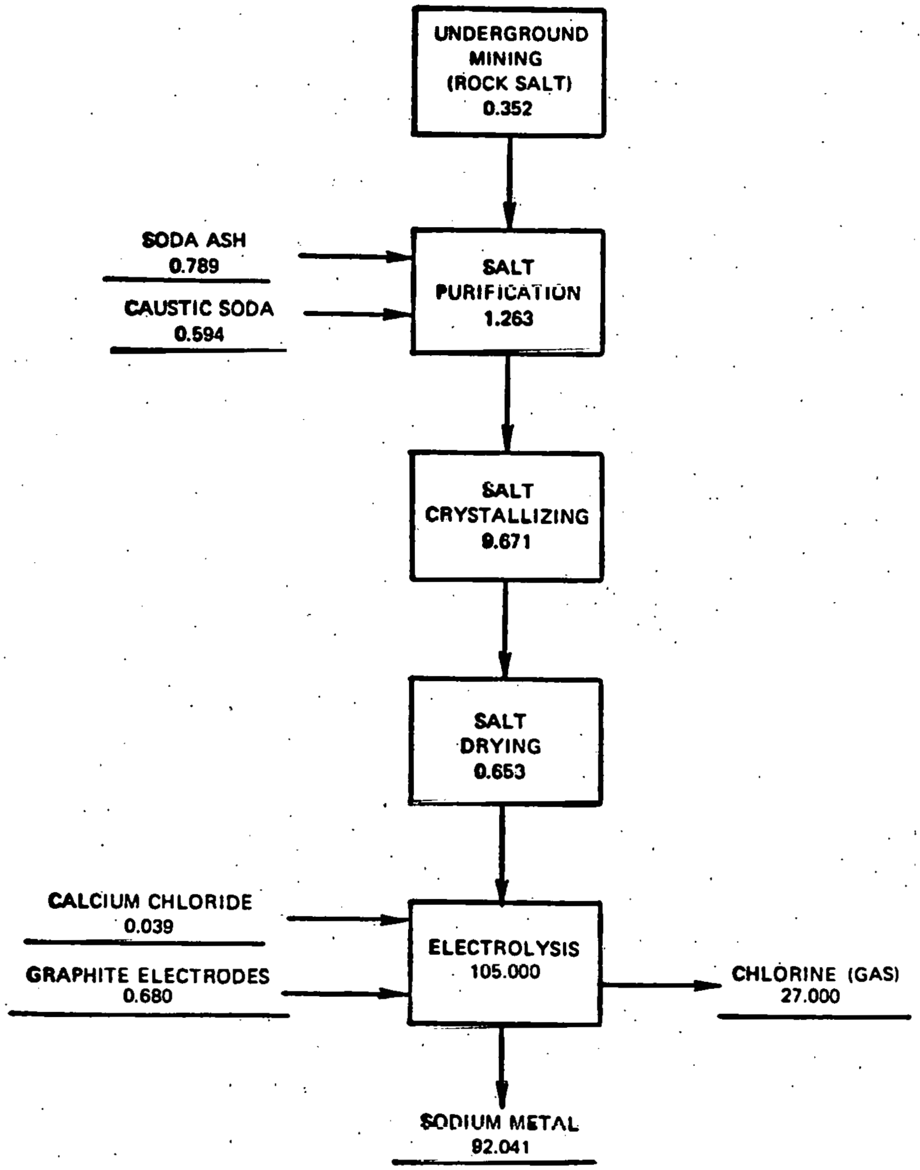

FIGURE F1. PRODUCTION OF SODIUM METAL BY THE DOWNS PROCESS (Units in 10^6 Btu/S Ton).

TABLE F1. PRODUCTION OF SODIUM METAL

	Unit	Units Per Net Ton of Sodium Metal	10^6 Btu Per Unit	10^6 Btu Per Net Ton of Sodium Metal
Mining				
Distillate fuel oil	gal	0.333	0.139	0.046
Electrical energy	kwh	24.20	0.0105	0.254
Explosives	lb	1.72	0.030	0.052
			Subtotal	0.352
Salt purification				
Soda ash	lb	87.7	0.009	0.789
Caustic soda	lb	39.6	0.015	0.594
Steam	lb	849.0	0.0014	1.189
Electrical energy	kwh	7.08	0.0105	0.074
			Subtotal	2.646
Salt crystallizing				
Steam	lb	6,894.0	0.0014	9.652
Electrical energy	kwh	1.78	0.0105	0.019
			Subtotal	9.671
Salt drying				
Electrical energy	kwh	13.10	0.0105	0.138
Steam	lb	368.0	0.0014	0.515
			Subtotal	0.653
Electrolysis				
Calcium chloride	lb	30.0	0.0013	0.039
Graphite electrodes	lb	8.5	0.080	0.680
Electrical energy	kwh	10,000.0	0.0105	105.000
			Subtotal	105.719
Total for co-products				119.041
Total energy input for co-products allocated as follows:(8)				
Sodium metal (1.0 net ton)				92.041
Chlorine (gaseous, 1.5 net tons) *				27.000
Total				119.041

*The chlorine credit in USBM Report was calculated from an estimate of energy for chlorine-caustic production with an electrolytic diaphragm cell. The energy up to the point the two products were simultaneously discharged from the cell was distributed on a weight basis. Energy need to further process the two streams was then assigned to the stream involved. That energy for gaseous chlorine was 18 x 10^6 Btu/S ton Cl_2.

TABLE F2. ENERGY FOR PREPARING ANHYDROUS SODIUM HYDROXIDE

For evaporating the dilute caustic produced in making one pound of Cl_2 the energy is:

To 50% caustic	(6,000 Btu)
To 70% caustic	(6,000 + 12,000) Btu
To anhydrous caustic	(6,000 + 12,000 + 18,000) Btu

The caustic produced with one pound of chlorine is:

$$\frac{40}{35} = 1.14 \text{ lb} \quad .$$

Energy required per pound of contained caustic is:

To 50% caustic	6,000/1.14 = 5263 Btu/lb caustic
To 70% caustic	5263 + 10,526 = 15,789/lb caustic
To anhydrous caustic	15,789 + 15,789 = 31,578/lb caustic

The net energy to prepare anhydrous caustic from 50% caustic is:

$$31{,}579 - 5263 = 26316 \text{ Btu/lb caustic}$$

or

$$(26316)(2000) = 52.63 \times 10^6 \text{ Btu/S ton or}$$

$$14.62 \times 10^6 \text{ Kcal/M ton} \quad .$$

so that, theoretically, twice the coulombs are required as for equivalent production with fused sodium chloride. The electrode potential corresponding to the standard free energy of formation is 3.98 volts, corresponding to a theoretical power requirement of 9268 kwh/M ton (8408 kwh/S ton) Na or 24.5 x 10^6 Kcal/M ton (88 x 10^6 Btu/S ton) Na at the power plant.

The commercial Castner process operates at 5.0 volts and a current efficiency of 36 percent. Assuming a 10 percent loss for AC to DC power, conversion and line loss the power required for electrolysis is:

$$\frac{(96{,}500)(453)(2{,}000)(5.0)}{(3{,}600)(23)(1{,}000)(.36)(.90)} = 16{,}290 \text{ kwh/S ton}$$

or 17,956 Kwh/M ton

This is equivalent to 16,290 x .0105 x 10^6 = 171 x 10^6 Btu/S ton or 47.5 x 10^6 Kcal/M ton. Table F3 is a summary of the energy requirements. In the electrolysis of sodium chloride, a part of the electrolysis energy can be allocated to the chlorine, which is collected and sold (see Table F1 footnote). However, with electrolysis of fused caustic, the sodium metal is the only product of value and all of the energy for the processing steps must be assigned to it. The volumes of hydrogen and oxygen are too small to justify recovery. Of the total requirement of 86.4 x 10^6 Kcal/M ton (311 x 10^6 Btu/S ton), 53 x 10^6 Kcal/M ton (191 x 10^6 Btu/S ton) are required for the <u>two electrolysis steps</u> to produce NaOH first and then Na. The energy requirements are too high to give it further consideration.

Production of Sodium by Electrolysis With Alloying Cathodes

Sodium may be deposited into a mercury cathode from aqueous solution (e.g., NaCl) and into lead from a fused salt electrolyte. The sodium may then be recovered in principle by vaporization or reverse electrolysis.

TABLE F3. PRODUCTION OF SODIUM METAL FROM FUSED CAUSTIC ELECTROLYTE

	kwh/M ton Na (kwh/S ton Na)	Total Kcal x 10^6/M ton Na (Btu x 10^6/S ton Na)
Production of 50 percent Caustic Soda	1,764(1,600)	16.20(58.3)
Evaporation to Solid Caustic	--	14.61(52.6)
Heating to 400 C	--	0.25(0.9)
Electrolysis	17,956(16,290)	47.5(171)
TOTAL		78.3(282)

NaOH property data: Cp, Assume 10 cal/mole; heat of fusion, 2000 cal/mole; MP, 322 C.

Mercury Cathode.

A modern process has been developed by Tekkosha in Japan(F4,F5) utilizing a mercury cathode for electrolysis of brine to form the amalgam. The sodium is recovered from the amalgam in a second cell using a fused mixture of NaOH-NaI-NaCN at a temperature of only 220 to 240°C. Sodium is deposited on a horizontal perforated iron cathode through which it floats to the surface. The bath is saturated with hydrogen to repress the reaction:

$$Na + NaOH \rightarrow Na_2O + H_2 \quad .$$

The small amount of mercury in the sodium (0.1 to 0.5 percent) is removed by subsequent treatment with calcium chloride.

The Tekkosha process is a modern version of old technology that never really reached a practical stage for a sustained length of time(F1,F6). Table F4 is from the Tekkosha reference (F2) and compares sodium production processes.

The listed electrical requirements considerably exceed those calculated from cell voltage and current efficiency. However, assuming that all calculations have the same basis the Tekkosha process offers an energy saving of the order of 2756 kwh/M ton (2500 kwh/S ton) Na (7.22×10^6 Kcal/M ton or 26×10^6 Btu/S ton Na).

The energy of the Tekkosha process can also be estimated independently from information on mercury cathode chlorine cells, and the voltage and current in Table F4 for the second electrolysis step. The data on chlorine and caustic production from USBM(F1) may be utilized. Results are shown in Table F5. Electrolysis in a mercury cathode cell will be assumed to require 3300 kwh/M ton (3000 kwh/S ton) Cl_2, which will include 0.56 M tons (0.62 S tons) Na as amalgam. Allocation of energy to the two products is arbitrary and will be assumed equal. Mining and brine preparation require 156×10^6 Kcal/M ton (2×10^6 Btu/S ton) Cl_2. Therefore, half of this value and half the power will be allocated to 0.56 M tons (0.62 S tons) of sodium. Values under auxiliary energy are very rough estimates, considering that nothing in the other items allows for amalgam pumping and transfer, processing of the product sodium, etc. The total can

TABLE F4. TEKKOSHA'S COMPARISON OF SODIUM PRODUCTION METHODS

	Comparison of Metallic Sodium Processes		
	Castner process	Downs process	Tekkosha process
Bath temperature (°C)	320 330	570 600	220 240
Electrolysis voltage (volt)	4.5 5.0	5.7 6.0	2.5 3.0
Current efficiency (%)	37 40	75 85	96 98
Electricity requirement kwh/S ton of Na (kwh/M ton Na)	29,800* (27,000)	14,300 15,400 (13,000 14,000)	12,100* (11,000)
Salt requirement (ton/ton of Na)	3.0	3.1	2.7
Consumption of electrode	small	very large	negligible
Corrosion of cell	small	large	negligible
Operation environment	mild	no good	good

*Total requirement for 1st cell and 2nd cell.

TABLE F5. ENERGY REQUIREMENTS OF THE TEKKOSHA PROCESS

Operation	kwh/M ton Na (kwh/S ton Na)	Total Kcal x 10^6/M ton Na (Btu x 10^6/S ton Na)
Salt mining and brine preparation	--	0.44(1.6)
Electrolysis I	2645(2400)	6.95(25)
Electrolysis II	3360(3050)	8.89(32)
Auxiliary	550(500)	2.78(10)
TOTALS	6560(5950)	19.2(69)

be compared with 25.5 x 10^6 Kcal/M ton (92 x 10^6 Btu/S ton) Na for the Downs process and represents an energy saving of 20 to 25 percent.

Tobias and Jorne have suggested an alternative to the second electrolysis step of the amalgam in fused salt(F6,F7). This involves the use of propylene carbonate as an aprotic solvent, which is a liquid at room temperature. An advantage of the lower temperature (i.e., 65° C) electrolysis with this solvent is the absence of mercury in the product.

In an example where potassium rather than sodium is formed, a current density of 538 amp/m^2 (50 amp/ft^2) gave a cell potential of 5.0 volts. If sodium were produced under these conditions the energy use is 6472 kwh/M ton (5872 kwh/S ton) Na; (17.14 x 10^6 Kcal/M ton or 61.7 x 10^6 Btu/S ton Na) assuming 10 percent conversion loss.

If these energy values are used for the second electrolysis in Table F5, the total energy requirement is 27.2 x 10^6 Kcal/M ton (98 x 10^6 Btu/S ton) Na, which is slightly more than the requirement for the Downs process. However, further development might lower the energy requirements for non-aqueous electrolysis, and use of such electrolytes should be considered as an alternative to fused salts for the amalgam process.

The conductivity of non-aqueous electrolytes is generally lower than that of aqueous solutions, e.g., 0.01 to 0.001 ohm^{-1} cm^{-1}, so that close electrode spacing and small dimensional tolerances are required. It is necessary to treat the crude propylene carbonate by distillation, adsorption, etc., to remove traces of moisture, and to protect the electrolyte from air to prevent moisture pickup. Also, moisture entrainment by the mercury from the aqueous cell must be avoided. Therefore, careful engineering design will be required for a satisfactory cell using propylene carbonate electrolyte.

An alternative method of recovering sodium from amalgam is to distill off the mercury. A process was patented by Moulton and is discussed by MacMullin(F8). Moulton proposed that the mercury be used in a General-Electric type mercury-steam binary unit. The mercury vapor would enter turbines at 621° C (1150 F) and be rejected at 226° C (438 F). The rejected mercury would be used to produce steam at 211° C (411 F). Fuel consumption for the entire process, including the electrolysis to produce amalgam was estimated to be 5.6 tons of coal/ton of sodium metal. This would correspond to approximately 5.6 x 31.5 x 10^6 = 176.40 x 10^6 Btu/S ton or 49.0 x 10^6 Kcal/M ton Na. This value is much higher than for the Downs process. The productivity of the mercury-steam plant was estimated to be 8800 kwh/M ton (8000 kwh/S ton) of sodium. Of this approximately 4500 kwh are required to make one S ton of sodium as amalgam plus 1.5 S tons of chlorine for which a credit of 27 x 10^6 Btu/S ton can be assumed. Therefore, credit for excess power generation and the chlorine are:

$$\begin{array}{rcl} 3500 \times .0105 \times 10^6 & = & 36.45 \times 10^6 \text{ Btu/S ton or } 10.13 \times 10^6 \text{ Kcal/M ton} \\ 1.5 \times 27 \times 10^6 & = & \underline{40.50 \times 10^6 \text{ Btu/S ton}} \text{ or } \underline{11.25 \times 10^6 \text{ Kal/M ton}} \\ \text{TOTAL} & & 76.95 \times 10^6 \text{ Btu/S ton or } 21.3 \times 10^6 \text{ Kal/M ton} \end{array}$$

The net energy for sodium production would then be reduced to 27.5 x 10^6 Kcal/M ton (99 x 10^6 Btu/S ton) which is still higher than for the Downs process and depends upon the tenuous assumption of using mercury as the fluid in a thermal power system.

Molten Lead Cathode.

Sodium may be deposited and alloyed with a molten lead cathode, but a fused salt electrolyte such as a molten chloride mixture is required. The sodium may then be recovered by a second electrolysis or possibly by distillation. Early cells such as that of Acker and Ashcroft(F2) required about the same power input as the Downs cell. However, an improved 24,000 ampere cell was developed in Germany during WWII, for which current efficiencies of 80 percent and cell potentials as low as 3.5 volts were claimed(F9). A 10 weight percent sodium in lead alloy was produced corresponding to a 50 atomic percent alloy. Under our usual assumption of 10 percent power loss to the cell, the electrolysis power is then 5655 kwh/M ton (5130 kwh/S ton) Na. Of this total, 2480 (2250)* kwh are allocated to the 1.36 M tons (1.5 S tons) of chlorine also formed leaving a net of 3174 kwh/M ton (2880 kwh/S ton) Na or 8.39 x 10^6 Kcal/M ton (30.2 x 10^6 Btu/S ton) Na. Reverse electrolysis to recover sodium metal even with a potential as low as three volts would add at least an additional

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*3000 kwh was assumed for producing 1.0 S ton of chlorine plus 1.0 S ton of caustic and allocated 1500 kwh to each product.

3675 kwh/M ton (3334 kwh/S ton) or give a total of 6500 kwh/M ton (5895 kwh/S ton) or 17.2 x 10^6 Kcal/M ton (61.9 x 10^6 Btu/S ton) Na. The power requirement is less than that of the Downs process.

Distillation of sodium from the lead alloy is possible. Vapor from an alloy containing more than 0.3 atom fraction sodium contains less than 0.004 atom fraction lead at 853°C$^{(F10)}$. Sodium vapor pressure at this temperature is 16.4 Torr. The enthalpy of this vaporization can be estimated, and it is not critically dependent on temperature. Data for 427°C are available$^{(F11)}$.

$$\text{Na}_1\text{(0.3 Mole fraction in Pb) Na}_{(\ell)} \qquad \Delta H = 8{,}200\text{g cal/mole}$$

$$\text{Na}_{(1)} \rightarrow \text{Na}_{(g)} \qquad \underline{\Delta H = 24{,}073\text{g cal/mole}}$$

$$\text{Total} \qquad \Delta H = 32{,}273\text{g cal/mole}$$

$$\frac{453}{23}\ \frac{2{,}000}{252}\ 32{,}273) = 5.04 \times 10^6 \text{ Btu/S ton or } 1.40 \times 10^6 \text{ Kcal/M ton}$$

$$\frac{5.04}{10{,}105} = 480 \text{ kwh/S ton or } 530 \text{ kwh/M ton}$$

In theory, there is a small increment of energy to be added to the 3174 kwh/M ton (2880 kwh/S ton) for forming the sodium lead alloy. Even if the practical requirement for evaporation were 1100 kwh/M ton (1000 kwh/S ton), the total would be 4300 kwh/M ton (3880 kwh/S ton) Na or 11.3 x 10^6 Kcal/M ton (40.7 x 10^6 Btu/S ton) Na. Even with additional energy for auxiliary processing the total energy could be one-half that of the 25 x 10^6 Kcal/M ton (92 x 10^6 Btu/S ton) Na for the Downs Process. The total energy for electrolysis with a lead cathode and vaporization of sodium is estimated in Table F6.

Conclusions

The total energy use and savings, assuming each process is used for the total annual production of 145,000 M tons (160,000 S tons) is shown in Table F7.

TABLE F6. ENERGY REQUIREMENTS FOR THE SODIUM-LEAD ALLOY CATHODE METHOD WITH EVAPORATION

Operation	kwh/M ton Na (kwh/S ton Na)	Total Kcal x 10^6/M ton Na (Btu x 10^6/S ton Na)
Salt Mining and Brine Preparation	--	0.44(1.6)
Electrolysis	3174(2880)	8.4(30.2)
Evaporation	--	2.9(10.5)
Auxiliary	500(500)	1.4(5.0)
TOTALS	3725(3380)	13.1(47.0)

TABLE F7. PROJECTED ENERGY SAVINGS FOR ALTERNATIVE PROCESSES FOR SODIUM METAL PRODUCTION

	Electrical Energy kwh/M ton (kwh/S ton)	Total Energy 10^6 Kcal/M ton (10^6 Btu/S ton)	Energy Savings in Year Shown			
			1977		2000	
			10^9 kwh	10^{12} Kcal (10^{12} Btu)	10^9 kwh	10^{12} Kcal (10^{12} Btu)
Downs-fused NaCl (current)(15)	8542* (7750)	25.5 (92)	0.00	0.00	0.00	0.00
Castner-fused NaOH	17970 (16300)	78.3 (282)	-1.36	-7.66 (-30.4)	-1.36	-7.66 (-30.4)
Tekkosha-two electrolysis(16)	6610 (6000)	19.2 (69)	0.28	0.93 (3.68)	0.28	0.93 (3.68)
Sodium lead-with evaporation	3725 (3380)	13.1 (47)	0.70	1.81 (7.20)	0.70	1.81 (7.20)

*Allows credit of 248 kwh/M ton (2250 kwh/S ton) for chlorine production

**Assumes production of 145,000 M tons (160,000 S tons) in both 1977 and 2000.

The amalgam process proved out in 1972 offers distinct energy savings. The process itself appears suitable for demonstration with critical attention given to containment of the mercury in the system. This appears to have been accomplished in modern chlorine-caustic plants using mercury cathode cells.

The lowest estimated energy is for electrolysis of fused chloride with a lead cathode followed by evaporation of the sodium from the lead. Vaporization of the sodium from lead at 600° C is a part of a process patented by Dow(F12) for producing sodium by carbon reduction of sodium carbonate. Lead contamination of the product is a potential problem. Costs and other factors in the R and D and scale-up of the lead cathode process are further discussed in the later section on Suggested Further Analysis and/or Development of Processes.

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ELECTROCHEMISTRY AND HYDROMETALLURGY

Introduction

The principles of electrochemistry and electrochemical engineering have been applied in an empirical way in hydrometallurgy. Electrowinning and electrorefining in aqueous solutions have usually involved flat-plate anodes and cathodes hung on bus-bars and producing an electrical contact by their own weight. Spacing is as close as practicable considering dimensional tolerances and the uniformity of deposition. Natural convection is common and forced agitation is sometimes used to promote mass transfer. In electrowinning the gas evolved at the anode is a source of forced agitation. In fused salt cells the current often takes on the additional function of maintaining the cell temperature through energy losses resulting from the IR drop through the electrolyte. This is a factor influencing the higher power and current density often used in fused salt cells. Geometries of electrodes in such cells may be parallel, vertical (anhydrous magnesium cell); annular, cylindrical (sodium and Dow magnesium cells) and parallel, horizontal (aluminum reduction cells).

Many fundamental advances in electrochemistry and electrochemical engineering have been made subsequent to the establishment of the electrochemical systems used in even modern metals production plants. Applying some of these advances to practical systems should reduce energy consumption. The general extent of such a reduction is difficult to estimate. However, application of basic engineering principles, where better developed, such as in the petroleum industry, has led to marked process improvements and should do likewise for the electrochemical industry.

In this section, refining or winning cells will be briefly described in electrochemical and hydrodynamic terms, and some actual or possible improvements to metal production systems discussed.

Cell Dynamics

An excellent, brief summary of electrochemical cell theory is given by Newman (1) in his book Electrochemical Systems[G1].

An electrochemical cell can be considered in its simplest arrangement as consisting of an uniformly conducting electrolyte between two electrodes, each with an equipotential surface. The LaPlace equation can then be solved to derive a primary current distribution Kaspar[G2] made such calculations for specific geometries. However, in practice the electrodes do not constitute equipotential surfaces due to the resistances of the electrodes themselves[G3,G4], and the current density dependent polarization near the electrode surface due to non-uniform concentration, and activation energies related to the electron transfer and crystallization in metal deposition. Using these current-dependent boundary conditions, secondary current distribution (closer to the actual distribution for many cases then the primary current distribution) can be calculated. Calculation of primary and secondary current distribution in such systems can be referred to as potential-theory problems.

Currents in an electrowinning or electrorefining cell should not exceed the rate at which metal ions are transported to the cathode or away from a soluble anode. Assuming that this is adequately provided by diffusion as the result of a concentration or potential gradient in a static fluid generally does not explain the current densities that can be attained. In a practical cell the fluid moves either as the result of natural convection or by forced convection from stirring, pumping, or gas evolved at an electrode. Natural convection arises due to a decrease in density as metal ion concentration in the fluid layer adjacent to the cathode is reduced by the deposition process. Conversely, the density is increased adjacent to a soluble anode. Convection enhances the ion transport process as the relatively slower diffusion process is now required only in a thin stagnant layer adjacent to the electrodes.

The fluid motion is described by the Navier-Stokes relation and solution of the hydrodynamics problems in electrochemical cells has followed progress made in other heat and mass-transfer systems. Determination of current density distribution where currents are limited by transport only, can obviously ignore electrolyte conductivity. These constitute convective-transport problems.

In actual electrorefining and electrowinning systems both potential theory and convective transport are involved. Compact deposits are produced at roughly one-third of the transport-limited current density(G5), and powder-type deposits are typically obtained near the limiting current density(G6).

Possible Specific Application of Electrochemical Engineering Theory to Electrohydrometallurgy

Electrode Geometry and Natural Convection

In lead electrorefining the mass transfer to and from the electrodes is promoted by natural convection. The average limiting current density for such a process is inversely proportional to the 1/4 power of electrode length and the total limiting current to an electrode is proportional to the 3/4 power of the length(G7). Therefore, doubling the length of an electrode does not necessarily double the productivity of a tank.

Measurement of Local Mass Transfer in Metal Deposition

In most metal deposition cells the amount of current that can be maintained by mass transfer varies for different areas of the cathode as a result of natural convection and various types of agitation. If a small concentration of a more noble metal is added to the electrolyte, this metal will be deposited over the electrode at its limiting current density(G8). Current above this limit will be used to deposit the metal being refined. Assuming 100 percent current efficiency for deposition of the two metals, analysis of the total amount of metal deposited in a given area along with the determination of its composition makes possible an estimate of the limiting mass transfer possible for the electrorefined metal. By determining total mass and composition of the deposit on various areas, agitation and flow can be adjusted to provide more uniform mass transfer and reduce electrical power.

Use of Non-Planar Electrodes for Electrowinning from Dilute Solutions

The allowable current density decreases with decreasing metal ion concentration and at some point becomes impracticably low. Porous electrodes provide a high surface area, making possible a higher current and faster metal recovery. Flowing the electrolyte through the porous electrode further increases recovery by enhancing mass transfer. Copper has been recovered with these systems(G9). However, they must compete with cementation and solvent extraction processes.

Preparation of Dendritic or Powder Deposits

Powder is deposited at the current density limited by mass transfer. Deposition of powder offers the possibilities of harvesting metal in a continuous system rather than removing cathodes and stripping, or preparing starting sheets of the desired metal. Too high a surface area is undesirable for a good product. This suggests designing a cell for uniform mass transfer over the cathode area and then adjusting current density to a value close to but not at the limiting value. It should be possible to produce a range of deposits varying from coherent to fine powder. An intermediate product should be harvestable and still be of high quality.

Increase in Mass Transfer by Forced Convection

Forced convection has been studied to increase the mass transfer rate and practical current densities for copper electrorefining and electrowinning(G10). Turbulent conditions can be obtained with properly designed air spargers. Smoother deposits make possible closer electrode spacing to compensate for the greater IR drop with the higher current density, e.g., 84 amp/ft^2.

Very High Mass-Transfer Rates Through Forced Turbulent Flow

Forced convection at a sufficient velocity, i.e., 2 m/sec for common aqueous electrolytes, will cause turbulence and a very thin diffusion layer adjacent to an electrode. By this means the limiting and practical current densities can be considerably increased. To minimize the potential drop through an electrolyte at elevated current densities the interelectrode distance must be small.

The development of electrochemical machining utilized these principles since a high current density, i.e., 10 to 100 amp/cm^2 was necessary for practical removal rates, and a close spacing was needed to maintain dimensional tolerance.

The same principles have been applied to electroplating(G11) and more recently proposed for electrowinning zinc(G12).

Preliminary calculations, based upon direct experience with electrochemical machining and electroplating indicate that rotating-drum or continuous-belt cathodes can be plated and stripped in a continuous manner.

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COMPILATION AND ORGANIZATION OF PROCESSES

Electrolysis is only one of many steps in the primary winning of metals. It also may be one of the easier steps for which to determine energy consumption from such well-known parameters as voltage, current, and current efficiency. The diversity of all steps in processing, including the electrolysis, makes it difficult to organize processes into a simple outline. Every ore body is different and in developing a suitable method of metals recovery, all types of physical and chemical treatments are considered to arrive at the best process, starting with the methods of mining the ore and finishing with suitable means of melting and casting the metal into bars, billets, or wire. However, Table H1 is an outline showing some of the variations in the processes that have been examined. A brief description of the major steps follows.

Concentration and Phase Separation

The typical zinc and lead sulfide ores are concentrated by flotation. For magnesium and sodium, precipitation or crystallization (evaporation of water) can be involved although solid feed materials may also be mined directly. Manganese and chromium ores are less subject to physical benefication and involve direct roasting/leaching or pyrometallurgical treatment for hydrometallurgical methods of electrowinning. Where electrorefining rather than electrowinning is involved concentration can be achieved through pyrometallurgical processes to form a sulfide matte or crude metal. These can then be used as soluble anodes for electrolytic cells. Zinc and lead are candidates for the sulfide matte process and crude ferrochrome and ferromanganese for upgrading by electrorefining where the dissolved iron is removed or at least reduced in concentration.

TABLE H1. ORGANIZATION OF PROCESSES IN ELECTROMETALLURGY

Concentration and/or Separation

- Physical Beneficiation
- Precipitation or Crystallization
- Pyrolytic Formation of Separate Matte or Crude Metal Phase

Roasting

- Reducing
- Sulfating
- Chloridizing
- Oxide (dead roast)
- Dehydration

Leaching

- Non-oxidizing - Acidic, Neutral, Basic
- Oxidizing - Oxygen, Chlorine, Ferric Chloride, Anodic

Separation Systems

- Solvent Extraction
- Cell Separators
- Precipitation

Electrochemical

- Electrodeposition
- Anodic Dissolution
- Displacement

Roasting and Leaching

Roasting and leaching are means of concentrating metal values, but are so important to electrometallurgical processes that they are considered under separate sub-headings. The roasting and leaching processes for sulfide ores have been intensively investigated. Copper ores have received most of the attention, but the concepts and results have been applied to zinc and lead.

Roasting. Roasting may be in a reducing atmosphere to segregate metal particles which are then active to leaching as compared to the more refractory ore. Roasting can convert the sulfide to a soluble sulfate or an oxide (dead roast). An advantage of the latter is that the oxide will neutralize the acid produced at an insoluble anode in a sulfate electrowinning process (i.e., zinc). While roasting can be avoided if an oxidizing leach is used, oxidizing roasting provides SO_2 for acid manufacture where acid is marketable, and also is an exothermic reaction that can provide process heat. Chloridizing roasts for sulfide ores have been developed for a long time but depend upon subsequent chloride metallurgy, which has not been promoted for winning metals from sulfides. Dry chlorination of sulfide ores has recently received attention(B31). The fused salt electrolysis of lead and zinc chlorides, which has recently been investigated by USBM, could revive interest in chloridizing roasting.

Leaching. Non-oxidizing leaching solutions, either acid or alkaline, are commonly used on roasted sulfide ores. With unroasted ores, oxidation leaching of the sulfide to a soluble metal ion and a sulfur compound, i.e., elemental sulfur, can be accomplished by chemical agents such as oxygen, chlorine, ferric chloride, and so on. These agents may be generated anodically. Conversely, the leaching may be combined with the electrowinning by use of a cast matte anode or contact of the sulfide pulp with an insoluble anode. It is often difficult to distinguish between direct anodic oxidation of the pulp and indirect oxidation by some redox system, i.e., Fe(II)/Fe(III), present in the electrolyte.

Separation of Solution Components

Following leaching, various methods, including electrochemical ones, are used for separating (and concentrating) components. These methods may remove impurities or recover the desired metal.

Solvent Extraction

Solvent extraction is a useful technique for separating components that may be either the desired metal values or impurities. A metal ion can have a different partition coefficient in one solvent/solution combination than in another. Therefore, the solvent can act as an intermediate to concentrate the metal ion. The poor diffusion rate of a component in a dilute solution to the surface of an extractive solvent is compensated for by the large surface area and short diffusion path when the extractive solvent is intimately dispersed in the dilute solution. The extraction and stripping of solvent to form a more concentrated solution are not energy intensive processes and are frequently preferred to direct electrolysis of dilute solutions utilizing forced flow, porous or fludized bed electrodes, etc., to improve the electrolysis efficiency and minimize power requirements.

Cell Separators

Separators in an electrolytic cell such as semipermeable membranes or porous diaphragms (with or without flow through) constitute a separation technique before rather than after the fact. They either do not allow mixing of soluble anodic and cathodic products, or passage only of selected components.

Thus, in electrorefining, the impure solution from anodic dissolutions can be purified before being sent to the catholyte circuit. This technique is practiced in electrolysis of nickel matte anodes and similar techniques could be used for dissolution of zinc and lead matte anodes, or leaching of the sulfide pulp by anodically generated oxidizers such as chlorine or ferric chloride. There is a voltage drop across membranes due both to their inherent resistance to ion transport and concentration polarization effects at the two surfaces. If the same separation can be accomplished by solvent extraction, energy requirements will generally be less. Energy for solvent extraction was previously estimated to be no more than that for leaching zinc calcine, which is .17 x 10^6 Kcal/M ton (.6 x 10^6 Btu/S ton) Zn. If zinc were deposited in a membrane cell, a 0.3 volt drop across a membrane would require a power consumption of:

$$\frac{(371.942)\ (2000)\ (.3)}{1000} = 233 \text{ kwh/S ton } (256 \text{ kwh/M ton})$$

or

$$(0.0105)\ (223) = 2.34 \times 10^6 \text{ Btu/S ton } (6.5 \times 10^6 \text{ Kcal/M ton})$$

This is not a severe energy penalty and if advantages outweigh cost, increase in cell complexity, etc., membranes may find increased practical use.

Precipitation

The most common use of precipitation in treating leach solutions for the metals under consideration is the removal of iron from zinc sulfate solutions following an oxidation to the ferric state. Sulfide precipitation has been included in some proposed flow sheets. Cobalt precipitation with nitroso-beta-naphthol is a common procedure although the reagent is considered expensive.

Electrochemical Methods of Separation

The most common electrochemical methods of separation utilized in electrometallurgy are (1) electrodepsotion, (2) anodic dissolution or chemicals generation, and (3) displacement (cementation). Since the electron transfer in a complete cell involves both oxidation and reduction, the two can often be used together to advantage. When only reduction or oxidation is used beneficially, there is always an opportunity to find a more effective use for the other. In the technology reviewed there appear to be several opportunities to deposit metal and generate by-product chlorine for sale.

In zinc electrowinning by the sulfate process, cathodic deposition of metal and anodic production of leaching acid are both useful. However, it can be argued that the oxygen produced is wasted and that acid production is unnecessary if a sulfate roast rather than a dead roast is used. Cementation, as used in zinc electrowinning, is an obvious choice for purification because zinc is such an active metal. Thus, the zinc itself can be used to displace the more noble metals and is not a solution contaminant.

Electrorefining provides three opportunities for separation; (1) selective anodic dissolution, (2) electrolyte treatment, and (3) selective deposition. Electrorefining of lead (and copper) is a good example.

Lead dissolves in the fluosilicic acid electrolyte and leaves a mud containing bismuth, antimony, and copper. However, further separation in the electrolyte and at the cathode are hardly required due to the good impurity separation achieved at the anode. Nickel electrorefining involves selective anodic dissolution but also electrolyte treatment. The catholyte is a relatively pure nickel sulfate solution and selective deposition is not a factor in purification. However, some processes involving electrolyte containing both copper and nickel depend upon selective deposition of the copper for separation.

SUGGESTED FURTHER ANALYSES AND/OR DEVELOPMENT OF PROCESSES

Introduction

A number of the processes discussed in the reviews of the technology of individual metals have estimated energy requirements that make them potentially attractive for commercialization. While the technology must be developed in most cases to reach the demonstration or production stage, processes will not be developed unless they are also economically attractive and have an acceptable environmental impact. Also the materials for the process must be available on a long-term basis--at least as available as the source of the metal.

Cost estimates for the undeveloped processes can only be very approximate in most cases. Table II at the end of this section summarizes the estimates of energy savings as compared to current practice for the processes discussed.

Zinc

Present Processes

New construction has been largely for electrolytic zinc plants. Capital costs for two plants built in 1974 averaged approximately $600/M ton yr ($540/S ton yr), Zinc Section, Reference B8). The CE plant cost index* has changed from 165 to 223 since that quotation so that current cost would be $810/M ton yr ($735/S ton yr). Assuming at least this escalation in the future (11 percent/yr) the cost in year 2000 will be $4900/M ton yr ($45000/S ton yr). Contemporary price (December 15, 1978) of zinc is $0.77/kg ($0.35/lb).

No unusual materials are used in conventional zinc electrolysis that would be extremely difficult to obtain or for which substitutes are not available.

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*Chemical Engineering, McGraw Hill.

A modern plant should not cause any serious or unusual environmental problems. The gases generated in fluidized roasting of the ore are collected and converted to acid. Conceivably some metal-containing sludges can arise through neutralization or electrolyte purged from the cell. Also, leach residues (after removal of lead and silver) and iron sulfate residues may constitute a disposal problem. Cadmium and lead are removed prior to electrolysis and therefore these elements should not be present in this sludge.

Alkaline Leaching and Electrolysis

Comparison with Present Process. The alkaline leaching and electrolysis system that has been described is recommended for further study and development because of its estimated modest electrolysis energy requirement of 2425 kwh/M ton (2200 kwh/S ton) Zn and total energy requirement of 5×10^6 Kcal/M ton (18×10^6 Btu/S ton) Zn or lower. The low electrolysis energy reflects the low anode over-voltage and close electrode spacing possible with use of a caustic electrolysis and a system not requiring cathode removal.

Most unit operations in this process are analagous to those in the sulfate method. An additional low energy roasting operation is useful to break down zinc ferrite, but cathode stripping is avoided. A filter and compacting device is used instead. Mild steel to contain caustic will generally be lower in cost than materials for acid sulfate containment. If the desirability of using a higher current density can be demonstrated the amount of material for cell building will be smaller for alkaline than acid systems. We estimate that capital costs for the alkaline process will be as much as 10 to 20 percent less than for the acid process. Operating cost could be substantially less, e.g., 30 percent, through elimination of stripping, and automation of metal dendrite removal, filtering, washing, compacting, melting and casting. Also, lower energy costs are predicted as previously described. Presumably, leach residues will be suitable for further processing for metal values. An electrolyte purge because of carbonate buildup (which has not been a serious problem so far) should require only neutralization for discharge. Thus, no serious environmental problems are foreseen. Raw materials are essentially a small amount of coke or coal and chloride-free caustic, which are readily available raw materials.

R and D Needs. Further study is needed on this process to define the following:

(1) A more accurate estimation of energy use and cost.

(2) Optimum conditions of electrolysis so that good quality dendrites are obtained that are nevertheless removeable. Also, conditions that optimize productivity and energy use.

(3) Optimum conditions for removing, filtering, compacting, and melting dendrites.

Item (1) would involve a more detailed conceptual design using knowledge from prior pilot operations. Item (2) requires a laboratory program followed by a scale-up. Item (3) would involve mainly pilot plant experiments. The costs for these programs are estimated to be:

Conceptual Studies and Small Scale Experimental Work	$ 300,000
Small-Scale Pilot Plant	1,000,000
Large-Scale Pilot Plant	5,000,000
Full Scale Demonstration Plant (90,000 M ton/yr or 100,000 S ton/yr)	$30,000,000.

The amount for the full-scale unit is in addition to the nominal $65,000,000 for formal design and construction and can be considered the amount for shakedown of the plant to solve unanticipated operating problems associated with a new process.

Electrowinning from Aqueous Chloride Solution with By-Product Chlorine

Comparison with Present Processes. By cogenerating zinc metal and chlorine the energy allocated to the zinc can be greatly reduced. The allocation is somewhat arbitrary but a good estimate is 8.3 x 10^6 Kcal/M ton (30 x 10^6 Btu/S ton) Zn which is one-half the energy estimate for the zinc sulfate electrowinning process. The success of a cogeneration process is dependent upon several factors including (1) the basic technology, (2) a convenient market for the chlorine, (3) availability ot hydrochloric acid or a process for making acid.

The capital and operating costs of plants winning zinc and producing chlorine will depend upon the above factors. Capital will change significantly if chlorine liquification and acid production are required as compared to piping chlorine to an adjacent plant that can return acid. Taking as a baseline a capital cost of $100,000,000 for a 90,000 M ton/yr (100,000 S ton/yr) zinc plant we would anticipate that a plant based on chloride would cost at least $125,000,000 without liquification and acid production facilities. This figure amounts to doubling the tankhouse cost.

R & D Needs.

Further study is needed on this process to achieve the following:

(1) A closer analysis of projected energy savings, including a laboratory program to define the best system, e.g., is a diaphragm necessary?

(2) A careful examination of the logistics, economics, and siting of a plant to produce zinc, sulfuric acid, and chlorine.

(3) The scale up of a system from laboratory data and engineering and production data now.

Costs for these programs followed by further scale-up are estimated to be:

Conceptual Studies and Small Scale Experimental Work	$ 500,000
Small Pilot Plant	2,000,000
Large Pilot Plant	10,000,000
Estimated Additional Costs for Full-Scale Demonstration Plant Including Shakedown	75,000,000

Lead

Present Processes

The current sinter-blast furnace process for lead requires 7.5 x 10^6 Kcal/M ton (27 x 10^6 Btu/S ton) with the possibility that this requirement can be reduced by using more of the energy available from the oxidation of sulfide to metal and sulfur dioxide. The capital cost of the lead plants has been estimated to be $105 million for a 109,000 M ton/yr (120,000 S ton/yr) plant (Appendix A). Lead market price (December 10, 1978) was $0.84/kg ($0.38/1b).

The environmental impact of pyrometallurgical lead plants is a matter of considerable discussion at present. The limit of 50 $\mu g/m^3$ of lead for an 8-hour average proposed by OSHA and the quarterly average of 1.5 $\mu g/m^2$ by EPA are considered impractical by most producers, and too lenient by some environmentalists. If technology is not available or if the cost is too great to meet regulations that are imposed, there will be further incentive to develop electrolytic methods.

Raw materials for the lead blast furnace are coke and slag forming constituents, such as limestone, silica sand, iron ore, and rerun slag. These are commonly available materials, and critical shortages are not foreseen.

Direct Electrolysis of Lead Sulfide Concentrates

Comparison with Present Processes. Lead sulfide can be directly electrolyzed either as a pressed anode or dissolved in a molten electrolyte.

Prior work with pressed galena anodes has involved an aqueous chloride electrolyte. However, a fused electrolyte is also possible and could allow an increase in the limiting current density obtained in the aqueous solution (100 amp/m^2 or 15 amp/ft^2).

The capital cost of an electrolytic lead plant is difficult to estimate since there is no precedent in modern times. Cathro and Siemon (Lead Section, Reference A25) made an estimate of $127 million (1978 U.S. dollars) for capital cost of an 180,000 M ton/yr (200,000 S ton/yr) plant. This compares to 105 million for a sinter blast furnace system of 109,000 M ton (120,000 S ton)/yr capacity. The elimination of the sintering in the electrolytic process is compensated for by the probable need for electrolyte preparation and electrorefining of the lead. The capital cost of the latter is probably half of that for a zinc tank house for a 90,000 M ton/yr (100,000 S ton/yr) zinc plant, or $12 million. This added to the prior estimate of $127 million gives a total of about $140,000 for the lead electrolytic plant. This estimate could be subject to large error in view of the uncertainty as to what operations would be required for a fully developed process. However, a linear extrapolation for a sinter-blast furnace plant to 180,000 M ton/yr gives a cost of $175 million. Thus the capital cost for the electrolytic plant appears attractive.

The environmental impact of the electrowinning method for lead should be less than for the sinter-blast furnace process. Air-pollution is not a significant problem with any of the operations, and solutions to be discharged can probably be readily treated to remove contaminants. Disposal of purification sludges is a problem common to many industries at present until suitable landfill sites are made available. Disposition of such sludges will be governed by regulations to be promulgated under the Resource Conservation Recovery Act (RCRA) of 1976. Disposal could be a costly hauling problem if the electrowinning operation is remote from such a site or if offsite disposal is needed.

Raw materials are chlorides, etc., which are readily available. Fluosilicic acid is used for electrorefining and is a readily available byproduct of the phosphate industry. Only makeup quantities are required.

R and D Needs. Considerable technology must be developed to utilize the direct electrolysis process. Experimental work to date has been restricted to laboratory experiments. Further studies are needed to achieve the following:

(1) Define electrolysis conditions and an electrolyte that will allow current densities of the order of 540 amp/m^2 (50 amp/ft^2).

(2) Define a purificiation technique for use on the electrolyte; alternatively, an electrorefining step would be required.

(3) A better estimate of cost and energy for the process based upon results of (1) and (2).

(4) Scale-up of the process if preliminary work appears promising.

Costs for these programs, including scale-up are estimated to be:

Conceptual Studies and Small Scale Experimental Work	\$ 500,000
Small-Scale Pilot Plant	2,000,000
Large-Scale Pilot Plant	10,000,000
Excess Costs for Full-Scale Demonstration	\$75,000,000.

The last item includes the anticipated cost associated with shakedown.

Magnesium

R and D needs for magnesium production concern improvements to the current electrolytic process. These improvements do not change the environmental impact on raw materials used. However, cost and energy consumption may be decreased.

The current capital cost of a magnesium plant is about $3300/annual M ton ($3000/annual S ton). Current price is (December 15, 1978) $2.25/kg ($1.01/lb).

Development of Refractory Materials Resistant to Degradation in the Electrolysis Zone

The problem of degradation of the semiwall in the anhydrous cell and possible problems in the electrolysis zone in other cell designs was discussed in the Magnesium section.

The problem is a difficult one and will require extensive investigation on a laboratory scale before trials in commercial cells. However, the commercial trials themselves should be straightforward and not involve high expenditures or inordinate time to prove out materials. Trials with new designs, of course will be more expensive and lengthy, although with a promising material much of the cell development may be undertaken by producers. Estimates of costs are as follows:

Laboratory development and testing	$2,000,000
Scale-up of processing to produce material of adequate size	2,000,000
Testing in present cells	1,000,000
Preparation of materials for and testing in new cell configurations	$5,000,000.

Improvements in Cell Design

Optimization of cell designs using hydrodynamic modelling with inert gas and aqueous solution and confirmation in a small pilot magnesium cell has been discussed. A decrease in power consumption of 5100 kwh/M ton (4600 kwh/S ton) is believed possible through increased current efficiency from 80 to 90 percent combined with decreased voltage from 6.3 to 5.0 volts or less. A porous, wetted cathode could be a part of this design and eliminate the semiwall in the present anhydrous cell and its attendant corrosion problem. Estimated costs for a design program are:

Small scale hydrodynamic modelling and fused salt electrolysis	$1,000,000
Development of pilot cell	5,000,000
Demonstration cell	$5,000,000.

Sodium

Molten Lead Cathode

Comparison with Conventional Process. The construction and operation of sodium cells are similar in many respects to the magnesium cells. However, the equivalent weight of sodium is approximately twice that of magnesium so the same ampere-hours used in a sodium cell will produce twice the metal that a magnesium cell will. Considering this and the much simpler feed preparation for a sodium cell we will assume that a sodium plant costs only 50 percent as much as a magnesium plant on a same weight basis.

The current capital cost of a magnesium plant is estimated to be $3300/annual M ton ($3000/annual S ton). Cost of a sodium plant is therefore estimated to be $1700/annual M ton ($1500/annual S ton).

The current (December 15, 1978) price of sodium metal is $0.57/kg ($0.26/lb).

A process using a molten lead cathode to form a sodium alloy will have the approximate complexity of construction of a Downs cell with a similar cost. In addition, an evaporative system and condenser will be required. We estimate that the capital cost for equipment will be 20 percent higher than that for the plant using a Downs cell or $2,000/annual M ton ($1850/annual S ton). However, the lower electric energy requirement of 2.47×10^{6} Kcal/M ton (8.9×10^{6} Btu/S ton) should keep operating costs equivalent.

Use of a molten lead cathode and the evaporation of sodium in a separate operation will involve transfer of molten lead between the electrolysis and evaporation operations. In view of stringent requirements expected to be promulgated by EPA for lead emissions, means will need to be provided to keep lead pollution below limits.

Only common chemicals, e.g., salt are required as raw materials.

R and D Needs. The critical need is to determine the efficiency of sodium removal from lead by evaporation. This should be done first on a laboratory scale. Costs for this and subsequent scale-up are estimated as follows:

Laboratory Investigation	$ 100,000
Small-Scale Pilot Plant	1,000,000
Full-Scale Prototype (Single Cell and Evaporation)	$5,000,000.

TABLE 11. ENERGY SAVINGS FOR PROCESSES REQUIRING FURTHER DEVELOPMENT

		Annual Energy Savings			
		1977		Year 2,000	
Metal	Process	kwh	Kcal (Btu)	kwh	Kcal (Btu)
Magnesium	Refractory Improvements	2 to 4 x 10^{8}	[.5 to 1] x 10^{12} ([2 to 4] x 10^{12})	6 to 12 x 10^{8}	[2 to 3] x 10^{12} ([6 to 13] x 10^{12})
	Hydrodynamic Studies	6 x 10^{8}	1.5 x 10^{12} (6 x 10^{12})	2 x 10^{9}	5 x 10^{12} (21 x 10^{12})
Zinc	Aqueous Chloride Electrolysis	9.3 x 10^{8}*	3.3 x 10^{12} (13. x 10^{12})	2.1 x 10^{9}*	7.1 x 10^{12} (28 x 10^{12})
	Caustic leach and electrolysis	6.1 x 10^{8}	2.1 x 10^{12} (8.2 x 10^{12})	1.3 x 10^{9}	4.5 x 10^{12} (18 x 10^{12})
Lead	Anodic Sulfide Dissolution	-4.5 x 10^{8}	4.6 x 10^{11} (1.8 x 10^{12})	-7.3 x 10^{8}	6.7 x 10^{11} (2.7 x 10^{12})
	Fused Salt Electrolysis of Sulfide	-4.7 x 10^{8}	7.6 x 10^{11} (3.0 x 10^{12})	-7.5 x 10^{8}	1.1 x 10^{12} (4.4 x 10^{12})
Sodium	Lead Cathode and Evaporation	7.0 x 10^{8}	1.8 x 10^{12} (7.2 x 10^{12})	7.0 x 10^{8}	1.8 x 10^{12} (7.2 x 10^{12})

Kwh are for electrolysis.

*Assume 1480 kwh/M ton (1350 kwh/S ton) for zinc and same for chlorine.

APPENDIX A

Capital Cost of a Modern Sinter-Blast Furnace Plant for Lead Production--1978*

Size 109,000 M tons (170,000 S tons)/yr

Basic cost of reproducing a conventional plant	$ 47,160,000
Mobile equipment	930,000
Engineering, supervision, procurement	5,145,000
Subtotal	$ 53,235,000
Update for environmental control	
Acid plant	10,000,000
Electric dross furnace	3,900,000
Environmental water and air control equipment	20,000,000
Maintenance equipment	8,000,000
Subtotal	$ 41,900,000
Other costs	
Land	$ 1,000,000
Engineering fees	2,000,000
License fees	1,400,000
Corporate management	2,000,000
Environmental impact statement	2,000,000
Legal fees	1,000,000
Taxes	400,000
Insurance	200,000
Subtotal	$ 10,000,000
Grand Total	$ 105,135,000

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* Source: L. R. Verney, AMAX Corp.

MEETINGS CORRESPONDENCE AND PHONE CONVERSATIONS

Visits

April 26, 1978
USBM, Washington, D.C.
Dr. Thomas Henrie, Assistant Director
Dr. Ralph Kirby, Director of Metallurgy

June 12, 1978
USBM, Rolla, Missouri
Dr. Morris Fine, Research Director

June 13, 1978
USBM, Albany, Oregon
Dr. Rollien Wells, Director of Research

June 14, 1978
USBM, Reno, Nevada
Dr. Marvin Wong

June 15, 1978
USBM, Boulder City, Colorado
Dwight Sawyer, Research Supervisor

August 21, 1978
AMAX, Inc., Greenwich, Connecticut
L. R. Verney, Consulting Metallurgical Engineer

August 22, 1978
AMAX, Inc., Carteret, New Jersey
Dr. William Opie, Director of Development

August 22, 1978
NL Metals/NL Industries, Inc.
Hightstown, New Jersey
G. S. Foerster, Principal Research Scientist

MEETINGS CORRESPONDENCE AND PHONE CONVERSATIONS
(Continued)

August 23, 1978
Natural Resources Group (NJ Zinc)
Gulf and Western Industries
  B. C. Hafford, V.P., R and D

September 20, 1978
St. Joe Minerals Corp., Monaca, Pennsylvania
  Robert Lund, Direction of Research

AMAX - CORRESPONDENCE

August, September, 1978
Electrolytic Zinc Company of Australasia, Ltd.
Tasmonia, Australia
  Mr. R. D. Barker

PHONE CALLS (Those for data, specific information)

May, 1978
Titanium Metals Corporation
Coreapolis, Pennsylvania
  Mr. Ward Minkler

September 13, 1978
Cominco, Ltd.
Trail, British Columbia
  D. J. DeBiosio, General Administration

September 22, 1978
Cities Service Co., Mineral Planning Group, Tulsa, Oklahoma
  Dr. Jack Hulsebos

September, 1978
Dr. Jacob Jorne
Wayne State University
Detroit, Michigan