

EPA-600/2-77-023o
February 1977

Environmental Protection Technology Series

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

EPA-600/2-77-023o
February 1977

INDUSTRIAL PROCESS PROFILES
FOR ENVIRONMENTAL USE
CHAPTER 15
BRINE AND EVAPORITE CHEMICALS INDUSTRY

by

P. E. Muehlberg, B. P. Shepherd, J. T. Redding,
and H. C. Behrens
Dow Chemical
Freeport, Texas 77541

Terry Parsons
Radian Corporation
Austin, Texas 78766

Contract No. 68-02-1319

Project Officer
Alfred B. Craig
Metals and Inorganic Chemicals Branch
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

LIBRARY

DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory - Cincinnati, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

TABLE OF CONTENTS

CHAPTER 15

	<u>Page</u>
INDUSTRY DESCRIPTION.....	1
Raw Materials.....	2
Products.....	3
Companies.....	4
Environmental Impact.....	5
Bibliography.....	6
INDUSTRY ANALYSIS.....	7
Brine and Evaporite Chemicals Industry Processes.....	8
Borax and Boric Acid Segment Processes.....	11
Chlorine-Caustic Segment Processes.....	12
Lithium Chemicals Segment Processes.....	13
Magnesium Metal Segment Processes.....	14
Potash Segment Processes.....	15
Sodium Metal Segment Processes.....	16
Process Descriptions	
Process No. 1. Screening/Chlorination.....	39
Process No. 2. Bicarbonate Removal.....	41
Process No. 3. Solution Mining.....	43
Process No. 4. Shaft Mining.....	45
Process No. 5. Open-Pit Mining.....	48
Process No. 6. Coarse Crushing.....	50
Process No. 7. Settling/Filtration.....	52
Process No. 8. Carbonation/Filtration.....	54
Process No. 9. Solidification.....	61
Process No. 10. Evaporation/Solidification.....	66
Process No. 11. Drying.....	92
Process No. 12. Drying/Calcination.....	108
Process No. 13. Solar Evaporation.....	113
Process No. 14. Washing/Draining.....	123
Process No. 15. Froth Flotation.....	125

TABLE OF CONTENTS (Continued)

CHAPTER 15

	<u>Page</u>
Process No. 16. Filtration.....	130
Process No. 17. Liquid-Liquid Extraction.....	135
Process No. 18. Stripping.....	137
Process No. 19. Dissolution (Salt Cavern).....	139
Process No. 20. Crystallization/Filtration.....	140
Process No. 21. Brine Desulfurization.....	143
Process No. 22. Acidification.....	144
Process No. 23. Chlorination/Stripping.....	146
Process No. 24. Gravity Separation.....	149
Process No. 25. Spent Brine Neutralization.....	151
Process No. 26. Distillation.....	154
Process No. 27. Iodine Stripping.....	156
Process No. 28. Iodine Absorption.....	158
Process No. 29. Iodine Reduction.....	160
Process No. 30. Iodine Oxidation.....	162
Process No. 31. Iodine Finishing.....	164
Process No. 32. Digestion.....	166
Process No. 33. Lithium Carbonate Separation.....	168
Process No. 34. Clarifying.....	171
Process No. 35. Dissolution/Clarifying.....	173
Process No. 36. Carbonation.....	178
Process No. 37. Absorption.....	180
Process No. 38. Calcination/Slaking.....	183
Process No. 39. Ammonia Regeneration.....	186
Process No. 40. Dechlorination.....	189
Process No. 41. Mercury Cell Electrolysis.....	191
Process No. 42. Diaphragm Cell Electrolysis.....	193
Process No. 43. Sodium Amalgam Decomposition.....	195
Process No. 44. Cooling/Compression.....	197
Process No. 45. Liquefaction.....	199
Process No. 46. Crushing/Grinding.....	201

TABLE OF CONTENTS (Continued)

CHAPTER 15

	<u>Page</u>
Process No. 47. Leaching/Clarifying.....	205
Process No. 48. Calcination.....	209
Process No. 49. Fusion/Grinding.....	211
Process No. 50. Tabling.....	214
Process No. 51. Wet Grinding.....	216
Process No. 52. Debrining.....	218
Process No. 53. Sulfur Combustion.....	219
Process No. 54. Leaching.....	221
Process No. 55. Hargreaves Process.....	223
Process No. 56. Neutralization.....	225
Process No. 57. Evaporation/Filtration.....	227
Process No. 58. Electrolysis.....	229
Process No. 59. Hydrochloric Acid Formation.....	232
Process No. 60. Fusion.....	233
Process No. 61. Filtration/Crystallization.....	234
Process No. 62. Calcination/Grinding.....	235
Process No. 63. Digestion.....	239
Process No. 64. Leaching/Filtration/Evaporation.....	241
Process No. 65. Dissolution.....	244
Process No. 66. Electrolytic Chlorate Production.....	246
Process No. 67. Sodium Chlorate Drying.....	248
 Appendix A - Raw Material List.....	 251
 Appendix B - Product List.....	 257
 Appendix C - Company/Product List.....	 261

LIST OF FIGURES

CHAPTER 15

<u>Figure</u>		<u>Page</u>
1	Sample Process Description Format.	9
2	Chemical Tree - Brine and Evaporite Chemicals Industry	10
3	Principal Raw Material Sources	17
4	Magnesium Chemicals from Brines.	18
5	Sodium Chloride and Bitterns from Seawater . . .	19
6	Chemicals from Great Salt Lake	20
7	Chemicals from Searles Lake, Upper Level	21
8	Chemicals from Searles Lake, Lower Level	22
9	Chemicals from Bristol Lake, Salduro Marsh and Texas Brines	23
10	Bromine Recovery from Various Brines	24
11	Chemicals from Michigan Brines	25
12	Iodine Recovery from Michigan Brines	26
13	Lithium Carbonate from Two Different Brine Sources.	27
14	Solvay Soda Ash and Sodium Bicarbonate	28

LIST OF FIGURES (Continued)

CHAPTER 15

<u>Figure</u>		<u>Page</u>
15	Chlorine and Caustic Soda Via Electrolysis. . .	29
16	Borax, Boric Acid, and Colemanite from Evaporites.	30
17	Potassium Chloride from Sylvinite	31
18	Potassium Sulfate from Langbeinite and Sylvite.	32
19	Soda Ash from Trona	33
20	Magnesium and Chlorine Via $MgCl_2$ Electrolysis .	34
21	Sodium Metal Via Downs Cell	35
22	Lithium Chloride, Sodium Iodide and Sodium Bromide	36
23	Sodium Chlorate Via Electrolysis.	37
24	Lithium Values from Spodumene	38

LIST OF TABLES

CHAPTER 15

<u>Table</u>		<u>Page</u>
1	Utilities Consumed by Various Applications of Process 9.	64
2	Function of Various Applications of Process 10 .	68
3	Input Materials to Various Applications of Process 10	72
4	Utilities Consumed in Various Applications of Process 10.	79
5	Waste Streams Resulting from Various Applications of Process 10.	83
6	Function and Input Materials for Applications of Process 11.	94
7	Operating Parameters and Utilities for Applications of Process 11	98
C-1	Company/Product List	262

ACKNOWLEDGEMENTS

This catalog entry was prepared for EPA by Dow Chemical U.S.A., Texas Division, under Contract No. 68-02-1329, Task 7. The contributions of P. E. Muehlberg, B. P. Shepherd, J. T. Reding, and H. C. Behrens in preparing this report are gratefully acknowledged.

Helpful review comments from C. Fred Gurnham and Alan D. Randolph were received and incorporated into this chapter.

BRINE AND EVAPORITE CHEMICALS INDUSTRY

INDUSTRY DESCRIPTION

The Brine and Evaporite Chemicals Industry encompasses all first-level inorganic compounds derived from subterranean brines, from existing or historic salt lakes, and from seawater. Additionally, certain second-level inorganic compounds derived from these sources are included in the industry when produced in the same facility as the parent compound.

Within the industry thus defined, six industry segments are recognized. These have been assigned the following titles:

- Borax and Boric Acid
- Chlorine-Caustic
- Lithium Chemicals
- Magnesium Metal
- Potash
- Sodium Metal

A wide diversity of both raw materials and products, in types of operations, and in individual process parameters is characteristic of the industry. This fact and the existence of many recycle streams result in an apparent complexity of flow diagrams. The latter are shown on 22 individual flow-sheets, many of them interrelated through flows of intermediate products.

The 78 identified end products of the industry were produced in a total of 280 separate facilities (1972) from 21 raw materials.

The size of a single facility varies from an estimated half-dozen employees recovering salt or calcium chloride brine at Bristol Lake, California, to between 1,500 and 2,000 employees engaged in processing bedded salt and subterranean brine to chlorine, caustic, bromine, and compounds of magnesium and calcium. In the former example, the equipment involved might be valued at a few hundred thousand dollars, while the total fixed investment in the latter instance might reach one-quarter billion dollars.

Total employment in the industry is estimated here to lie somewhere between 70,000 and 120,000 persons during the present biennium. A more precise estimate is prevented by the undifferentiated employment statistics for single facilities conducting operations in two or more industries.

The combined dry-basis weight of all products leaving the industry during 1972 approximated 55 million metric tons. This amount of net industry product was produced from an estimated 90 million metric tons of mined, dry raw materials (evaporites) plus 300 million cubic meters of seawater, subterranean brines, and salt lake brines.

The industry is distinctly raw material oriented. With few exceptions, production facilities are located close to raw material sources. Exceptions are the facilities for upgrading certain crude intermediate materials into end-products and the cases of prior existence of a center of population near a recent raw materials find.

The average growth rate for the entire industry during the past five years has been about two percent per year. The chlorine-caustic segment individually experienced a growth rate of nearly 10 percent during the same period.

The need for process steam and the energy-intensive character of the chlorine-caustic, magnesium metal, and sodium metal segments account for the relatively high proportion of on-site power generation within the industry. About thirty (estimated here) industry plants generate a major portion of their electrical energy requirements. These plants are usually either multi-product facilities or are located in relatively sparsely populated regions. Searles Lake, and Boron, California, and Green River, Wyoming, are examples of the latter.

Raw Materials

Industry raw materials are typically unmined ores in place, unproduced brines in subterranean reservoirs or in lakes, and seawater. Generally, industry companies control their raw materials, either by fee ownership, lease, or royalty payment. Limestone, sulfuric acid, and sulfur are the only raw materials supplied from sources outside the industry. In most situations, notably in the case of rock salt, a considerable portion of the mined material is sold directly by the producing company for consumption both inside and outside the industry.

A total of 21 distinct industry raw materials are included in the general categories mentioned above. A complete list of these, along with their compositions, is given in Appendix A.

With three exceptions all the raw materials are considered nontoxic. Sulfuric acid is both toxic and corrosive. Kernite and native borax are moderately toxic.

Four general types of adverse environmental impact occur in producing the raw materials:

- Fugitive atmospheric emissions of particulates (dusting) in open-pit mining.
- Creation of tailings piles, mounds of stripped overburden, and "cratered" landscapes in both shaft mining and open-pit mining operations.
- Disposal of spent brines, bitterns, and other waste liquors.
- Inadvertent leaks and spills of liquid raw materials, as in cases of pipeline ruptures.

Products

Approximately 45 percent of the combined gross tonnage of all industry end products is consumed by the industry itself in producing other industry end products. ("The chemical industry feeds on itself.") About the same fraction of the total combined tonnage of end products leaving the industry is consumed by other chemical industries. The most notable specific example of this situation is the 24 million metric tons of salt (NaCl) used by the industry for producing chlorine, caustic soda, and soda ash, out of the total gross salt production (1972) of 40 million metric tons.

Annual net production varies widely among the 78 industry products. The five products listed below accounted for about 90 percent (estimated) of the combined tonnage of all products leaving the industry during 1972. Tonnages leaving the industry are expressed in (estimated) millions of metric tons per year on a dry-weight basis.

•Salt, all forms	16
•Caustic soda, all forms	10
•Chlorine, gas and liquefied	9
•Soda ash, Solvay and natural	7
•Potash, total weight	4

The combined annual net production of the five products listed below accounted for less than 0.1 percent of the combined tonnage of all products leaving the industry during 1972.

- Lithium nitrate
- Lithium oxide
- Lithium peroxide
- Lithium iodide
- Iodine

Except for potash and some of the individual small-production lithium compounds, all of the industry end products have a

wide spectrum of uses outside the industry. The largest single tonnage use (or use category) outside the industry for ten industry end products is given below. Numbers are estimates in millions of metric tons per year for the period 1972 through 1974.

•Salt	8	Highway use
•Chlorine	6	Chlorinated organics
•Potash chemicals	4	Fertilizers
•Soda ash	3	Glass
•Caustic soda	1	Pulp and paper
•Sodium sulfate	0.8	Kraft paper
•Magnesium hydroxide	0.6	Refractories
•Bromine	0.3	Motor fuel antiknock
•Calcium chloride	0.3	Highway use
•Borax	0.2	Glass and ceramics

The myriad of other uses for industry end products range from medicinals through detergents to cattle feed and vary from a few hundred kilograms to several million metric tons per year.

A complete list of industry end products is shown in Appendix B.

Companies

The industry included a total of 140 companies during 1972. The companies differ widely from aspects of total size, total number of industry products manufactured, degree of participation in nonindustry production, and total tonnage produced. There are also considerable differences in the number of companies producing any one industry product.

Extremes in total size are represented by a company recovering calcium chloride from Bristol Lake in California with an estimated total of a dozen employees to multiindustry, multifacility organizations exemplified by Allied Chemical Corporation or Dow Chemical U.S.A., each with more than twenty thousand employees and each with greater than five thousand persons working inside the industry.

Considerably more than one-half of the industry companies make at least two industry end products. Dow Chemical U.S.A., Foote Mineral Company, and Lithium Corporation of America each produce more than 15 industry end products. Several dozen companies, notably the producers of salt, produce but a single industry product. Several dozen other companies also produce end products belonging to other industries.

Total combined annual net tonnage of industry end products produced by any one company varies from a few hundred

kilograms (estimated) of lithium chemicals produced by a chemical specialty company to greater than seven million metric tons of various end products produced by Dow Chemical U.S.A.

Salt is produced by 53 companies. Elemental iodine is produced by only one.

A complete list of companies competing within the industry is shown in Appendix C.

Environmental Impact

Disposal of spent brines is the chief environment-related problem continually facing the industry. At least two companies were forced to cease their Solvay-type operations producing soda ash during the past three years because an acceptable means of disposal of weak calcium chloride brine was lacking. Generally, reinjection of waste liquors into subterranean strata is the disposal method employed at inland facilities. Waste bitters are usually sluiced into tidewater at seaboard locations with little or no adverse environment effects.

Dusting, tailings piles, and "cratered" landscapes, mentioned above, under "Raw Materials," occur almost entirely in sparsely populated, near-desert locations. Adverse environmental impact is therefore minimal.

Elimination of atmospheric emissions of "sniff" chlorine from chlorine-caustic facilities has been almost entirely implemented throughout the industry, usually through use of caustic exhaust scrubbers.

Several cases of liquid chlorine release from railroad cars or barges, resulting from collisions or derailments, are reported each year.

U. S. Borax and Chemical Corporation successfully concluded a three-year, ten-million-dollar dust abatement program in 1972 at Boron, California.

Little mention is made, in this chapter, of indirect wastes, as from leaks, spills and clean up operations. It is not the intent, in this study, to overlook such wastes. They are less significant here than in most other industries, but they are real, nonetheless, and should be considered in any comprehensive study of wastes from individual processes.

Bibliography

- (1) Chlorine Institute Pamphlet 10: North American Chlor-Alkali Industry Plants and Production Data Book, New York, Chlorine Institute, Inc., January 1975.
- (2) Eilertson, D. E. Potash, In: Minerals Yearbook, 1972, Schreck, A. E. (ed.), Washington, U. S. Department of the Interior, 1974, I:1055-1967.
- (3) Keyes, W. F., Potash in 1974, In: Mineral Industry Surveys, Washington, U. S. Dept. of the Interior, March 1974, 9 p.
- (4) Keyes, W. F., personal communication, May 1975.
- (5) Klingman, C. L., personal communication, May 1975.
- (6) MacMillan, R. T., Salt, In: Minerals Yearbook, 1972, Schreck, A. E. (ed.), Washington, U. S. Dept. of the Interior, 1974, I-235-236.
- (7) McCaleb, K. E. (ed.), Chemical Economics Handbook, Menlo Park, Stanford Research Institute.
- (8) Reed, A. H., Calcium and Calcium Compounds, In: Minerals Yearbook, 1972, Schreck, A. E. (ed.), Washington, U. S. Dept. of the Interior, 1974, I:235-236.
- (9) Wang, K. P., Boron, In: Minerals Yearbook, 1972, Schreck, A. E. (ed.), Washington, U. S. Dept. of the Interior, 1974. I:217-221.

INDUSTRY ANALYSIS

Published data pertaining to some of the processes shown here are either mutually conflicting, incomplete, or simply do not exist. This situation is particularly true for information pertaining to emissions. In these cases a general range is given here for the probable types of equipment used and for operating parameters. The nature and quantity of emissions is then inferred from known characteristics of similar equipment operating on closely related materials.

Published technological data for the entire industry are organized for display in a sequence of 22 flowsheets, Figures 3 through 24. The entire sequence diagrammatically describes the operations of the industry as a whole without regard to the existence of industry segments; i.e., no single flow-sheet completely describes any one of the six industry segments.

The interior of each of the rectangular "process blocks" appearing on the flowsheets represents at least one, and usually several, of the sequential, real processes of the prototype operations depicted by the flowsheets. In the ensuing context, the word "process" refers to what occurs inside the process block.

A number has been assigned to each of the process blocks, uniquely identifying the process it represents with an appropriate title and with a process description. Where substantially the same process is used more than once throughout the industry, its process number and title remain unchanged; i.e., more than one process block may bear identical numbers and titles.

Flag symbols at the upper right-hand corner of the process block are used to indicate the nature of the waste streams, if any, discharged from the process--a circle for atmospheric emissions, a triangle for liquid wastes, and a rhombus for solid wastes. The flags do not differentiate between inadvertent (fugitive) and designed wastes.

A verbal process description has been written to characterize each process further, to relate it to other processes, and to quantify its operating parameters. Where the same process finds application in a number of industry operations, the various elements of the process description are divided into sub-elements, each identified with a lower case letter. Each sub-element relates to a specific industry operation. The same letter designation is retained in each element to identify information specific to particular industry operations. In cases where the same process is used in a large number of industry operations, its process description may contain the data in tabular form.

A sample process description format is illustrated on Figure 1, showing the type of information given.

The set of completed process descriptions immediately follows the sequence of flowsheets.

As an overview of the material flow of the entire industry, a chemical tree, Figure 2, has been included under the subject heading immediately following.

Brine and Evaporite Chemicals Industry Processes

Twenty-six industry products are produced outside any recognizable industry segment. Each of these is listed below, along with the figure numbers of the flowsheets which collectively describe all stages of its production. The product is emergent on figures whose numbers are underlined.

Bromine

Figures 3, 7, 10

Calcium chloride, 35% liquor

Figures 3, 9, 11

Calcium chloride, 78% flake

Figures 3, 9, 11

Calcium chloride, anh. flake

Figures 3, 11

Magnesium carbonate trihydrate

Figures 3, 4

Magnesium carbonate, basic

Figures 3, 4

Magnesium chloride, 32% liquor

Figures 3, 4, 9

Magnesium chloride, 46% liquor

Figures 3, 6

Magnesium chloride, 50% flake

Figures 3, 4

Magnesium hydroxide, slurry

Figures 3, 4

Magnesium hydroxide, dried

Figures 3, 4

Magnesium oxide, caustic-calcined

Figures 3, 4

Magnesium oxide, dead-burned

Figures 3, 4

Magnesium sulfate (epsom salt)

Figures 3, 4

Hydrochloric acid (note paragraph following)

Figures 3, 17, 18

STRIPPING

1. Function

A brief description of Process 18, entitled "Stripping", is given here.

2. Input Materials

All materials entering the process are identified here and quantified in metric units per metric ton of the principal end product produced in the operation.

3. Operating Parameters

Listed here is available information on pertinent operating variables and general operating conditions, such as temperature, pressure, flow rates, catalysts, if any, and equipment size.

4. Utilities

Identified and quantified in metric units per metric ton of principal end product.

5. Waste Streams

Liquid wastes, solid wastes, and emissions to the atmosphere are identified here and quantified in metric units per metric ton of principal end product.

6. EPA Source Classification Code

Given here if one exists.

7. References

Information sources are listed here using the format prescribed by the EPA style manual, "Interim Specifications for OR & M Grant, Contract and In-House Reports."

FIGURE 1. SAMPLE PROCESS DESCRIPTION FORMAT

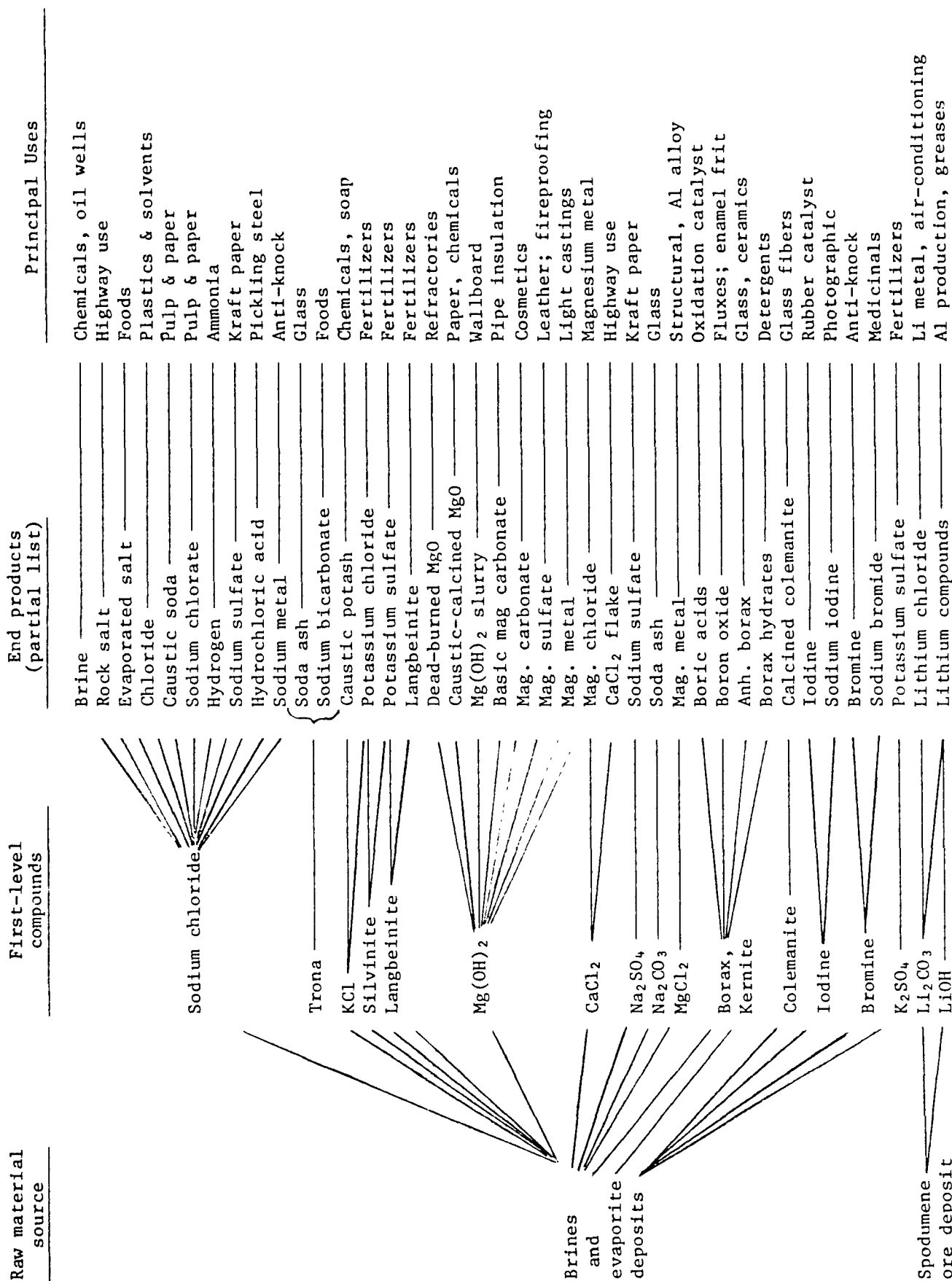


FIGURE 2. CHEMICAL TREE - BRINE AND EVAPORITE CHEMICALS INDUSTRY

Iodine

Figures 3, 12

Sodium bicarbonate

Figures 3, 14

Sodium bromide

Figures 3, 10, 22

Sodium carbonate

Figures 3, 7, 8, 14, 19

Sodium chloride, brine

Figure 3

Sodium chloride, crude, dried

Figures 3, 5

Sodium chloride, crude, washed

Figures 3, 5, 6

Sodium chloride, refined

Figures 3, 5, 11

Sodium chloride, rock salt

Figure 3

Sodium iodide

Figures 3, 12, 22

Sodium sulfate (note paragraph following)

Figures 3, 6, 7, 8, 9, 24

The Hargreaves-type process, shown on Figure 18, specifically for producing hydrochloric acid and potassium sulfate, additionally is intended to be exemplary for the production of hydrochloric acid plus sodium sulfate by the Hargreaves process and by the Mannheim process, using as raw materials, respectively, sodium chloride plus sulfur, and sodium chloride plus sulfuric acid. The latter two processes are not shown on any of the following flowsheets.

Borax and Boric Acid Segment Processes

The products of this segment are defined here as first-level inorganic borates and forms of boric acid. The end products are thus the various hydrates of sodium tetraborate (borax), anhydrous borax, various forms of boric acid, fused boron oxide, and calcium borate. Sodium sulfate is a by-product of the segment.

Facilities of the segment are located entirely in Kern, Inyo, San Bernardino, San Mateo, and Los Angeles counties, California. They account for all the domestic production and the major portion of the world supply of boron products.

Sources of the boron values are mainly near-surface deposits of borax, kernite, and colemanite, and, secondarily, the brine of Searles Lake.

Five companies operate ten facilities inside the segment. One of these, U. S. Borax and Chemical Corporation, has more than 70 percent of the estimated 650 thousand metric tons annual B_2O_3 capacity.

About one-half of the total tonnage of end products is exported. Production of glass (principally fibers), enamel frits, and detergents accounts for an estimated 75 percent of domestic consumption.

Processes of the segment operations are diagrammed on the flowsheets shown on the figures listed below. Flowsheets showing the emergent products are indicated by underlined numbers.

Figures 3, 7, 8, 16.

Chlorine-Caustic Segment Processes

This large-tonnage segment consists of companies electrolyzing mainly sodium chloride brine and, to a much lesser extent, potassium chloride brine to obtain five products. Chlorine, sodium hydroxide (caustic soda), sodium chlorate, and potassium hydroxide are four products of the segment and are also industry end products. The hydrogen, always co-produced with any of the other four, is an industry by-product.

Competing within the segment are 33 producers conducting electrolysis operations in 68 installations. Six of the companies producing chlorine and caustic soda also make caustic potash. Eight recover hydrogen beneficially in a total of 18 facilities. Sodium chlorate is produced by a total of 9 companies, 5 of whom produce chlorine and caustic soda.

Five companies collectively produce about 70 percent of the segment output:

Dow Chemical U.S.A.
PPG Industries, Incorporated
Diamond Shamrock Corporation
Hooker Chemical Corporation
Allied Chemical Corporation

The segment produced approximately 9 million metric tons of chlorine during 1972 and about an equal tonnage of caustic soda. Caustic potash production traditionally equals about 3 percent of that of caustic soda. Sodium chlorate production tonnage is slightly less than that of caustic potash. Co-produced hydrogen is usually flared, but the number of installations beneficially recovering it is increasing.

Most of the chlorine and most of recovered hydrogen are used captively to make other chemicals belonging to other industries. During 1974 more than 65 percent of the chlorine was consumed in the manufacture of plastics monomers, chlorinated solvents, and other organic chemicals. The largest single use for caustic soda occurs in the manufacture of pulp and paper, where between 12 and 15 percent of its total consumption is used. Caustic potash is used mainly in producing soap and in manufacturing other potassium compounds. The chief use for sodium chlorate is in the pulp and paper industry.

Processes conducted by the industry segment are diagrammed on the flowsheets shown on the figures listed below. Figure numbers are underlined for flowsheets showing the emergent products.

Chlorine, caustic soda, and hydrogen: Figs. 3,5,11,15
(Figure 15 is also exemplary for caustic potash.)

Sodium chlorate and hydrogen: Figs. 3,5,11,23

Fifty percent caustic soda, as a by-product of the lithium segment, is also shown on Figure 24.

Lithium Chemicals Segment Processes

The two principal end products of the segment are lithium carbonate and lithium hydroxide. From these two first-level compounds are derived 29 second-level lithium chemicals, also included in the segment. Crude phosphoric acid and 50 percent sodium hydroxide solution are by-products of the segment.

Raw materials are spodumene ore*, mined exclusively in North Carolina, the subterranean brine of Silver Peak, Nevada, and the brine of Searles Lake, California.

Ten companies compete within the segment with operations conducted in a total of 12 facilities. Of these ten companies, three are major tonnage producers, producing either the carbonate or the hydroxide. Foote Mineral Company is believed to be the major producer, with an estimated 40 to 50 percent of the total segment output tonnage. It processes both spodumene ore and brines. The minority large-tonnage producer, Kerr-McGee Chemical Corporation, division of Kerr-McGee Corporation, produces from Searles Lake brine an estimated 15 to 20 percent of the total segment output.

*Because of the increasing importance of their brine source, lithium compounds are included in the Brine and Evaporite Chemicals Industry. Spodumene ore, a nonevaporite, is believed to be the current major source.

Production and capacity information is officially withheld. Total annual segment capacity in 1972, estimated here, was between 10 and 20 thousand metric tons of Li_2O equivalent. Annual production of some of the second-level lithium chemicals is believed to approximate less than several hundred kilograms.

Principal consumption areas for lithium chemicals are aluminum cell bath, ceramics, greases, and large air-conditioning installations.

Processes included in the segment are diagrammed on the flow-sheets shown on the figures listed below. Principal end products are shown emergent on flowsheets indicated by underlined figure numbers.

Lithium carbonate:	Figs. 3, 7, <u>13</u> , <u>24</u>
Lithium chloride:	Figs. 3, 7, <u>13</u> , <u>22</u> , 24
Lithium hydroxide:	Fig. <u>24</u>
Crude phosphoric acid:	Figs. <u>3</u> , 7, <u>13</u>
50% sodium hydroxide:	Fig. <u>24</u>

Figure 22, in addition to showing the production of lithium chloride, is also exemplary for the production of many of the second-level lithium compounds.

Magnesium Metal Segment Processes

In all three operations of this segment, primary magnesium metal is produced as end product by the electrolysis of magnesium chloride. Two of the operations are also net producers of co-generated chlorine, a by-product of the segment. Of the latter two operations, one derives magnesium chloride from the brine of Great Salt Lake; the other, from subterranean brine of western Texas. The third operation, at Freeport, Texas, depends partly on seawater and partly on dolomitic lime for its supply of magnesium ion. It is a net consumer of chlorine.

Three companies currently (1975) compete within the segment. Dow Chemical U.S.A. produced between 85 and 95 percent of the 1974 total domestic production of primary magnesium in its facilities at Freeport, Texas. The other two companies--N L Industries, operating at Rowley, Utah, and American Magnesium Company, at Snyder, Texas--have entered the segment during the past five years. Their facilities, not yet under capacity operation, will collectively represent an estimated 30 to 35 percent of total domestic capacity.

A potential fourth producer, Aluminum Company of America, has a plant under construction at Addy, Washington, to employ an electrothermal process.

Total domestic production of primary magnesium during 1973 is estimated to be 120 thousand metric tons, representing a 4 to 5 percent annual growth rate for the segment during the previous five-year period. An equal or greater growth rate is anticipated for the next five years.

About one-fourth of the domestic production is exported. The principal areas of domestic consumption are in aluminum alloys, structural products, and in organic chemical production.

Operations of the industry are diagrammed on the flowsheets shown on Figures 3, 6, and 20. Metallic magnesium emerges as end product on Figure 20.

Potash Segment Processes

Companies populating the Potash Segment mine bedded potash ores, recover potassium values from salt lakes, and produce large-tonnage quantities of several potassium salts which they market almost entirely to the Phosphate Rock and Basic Fertilizer Materials Industry.

Total production of the segment during 1974 was reported to be 2.36 million metric tons of K_2O equivalent (estimated here to be 4 million metric tons total weight). This total was produced in 12 separate facilities located in New Mexico, Utah, California, and Texas.

Bedded potash ores of the Carlsbad, New Mexico, area account for approximately 70 percent of total raw material supply. The remainder comes from wet-mined ore at Moab, Utah, and from the brines of Searles Lake, California, Great Salt Lake, and Salduro Marsh, Utah.

Specific end products of the segment are potassium chloride, potassium sulfate, and magnesium potassium sulfate (langbeinite). The latter is intended here to include the so-called "manure salts." Potassium hydroxide, an industry end product, is produced in the Chlorine-Caustic Segment.

Ten companies operate in the industry segment. All of these produce other products.

Imports of potash, currently (1975) exceeding domestic production, do not play a role in the industry. Imported potash is either acquired directly by companies outside the industry (usual) or, if received by industry companies, does not undergo further processing prior to resale.

Annual production has remained almost constant over the past seven years, experiencing a slight decline recently. Despite the current increased demand for fertilizers, a zero segment growth is forecast in view of available Canadian imports.

Approximately 55 percent of the total segment capacity resides in the facilities of the four largest producers, named in order of decreasing capacity:

International Minerals & Chemical Corporation
Duval Corporation
Potash Company of America
AMAX Chemical Corporation

Figure numbers of flowsheets collectively describing all stages of production of each of the end products of the segment are listed below. The end product is emergent on figures whose numbers are underlined.

Potassium chloride: Figs. 3, 7, 9, 17
Potassium sulfate: Figs. 3, 6, 7, 8, 18
Magnesium potassium
sulfate: Figs. 3, 18

Sodium Metal Segment Processes

The companies competing within this segment electrolyze molten sodium chloride to produce metallic sodium as end product. The co-produced chlorine is a segment by-product.

Three companies conduct operations in a total of five facilities. Two of the three--E. I. duPont de Nemours and Ethyl Corporation--each operate two facilities, collectively representing about 80 percent of the total domestic capacity.

Between 80 and 90 percent of the total sodium metal consumption is in production of lead alkyls used in motor fuel anti-knock fluids.

Segment operations are shown on Figures 15 and 21, with the metallic sodium emerging as product shown on the latter-named figure.

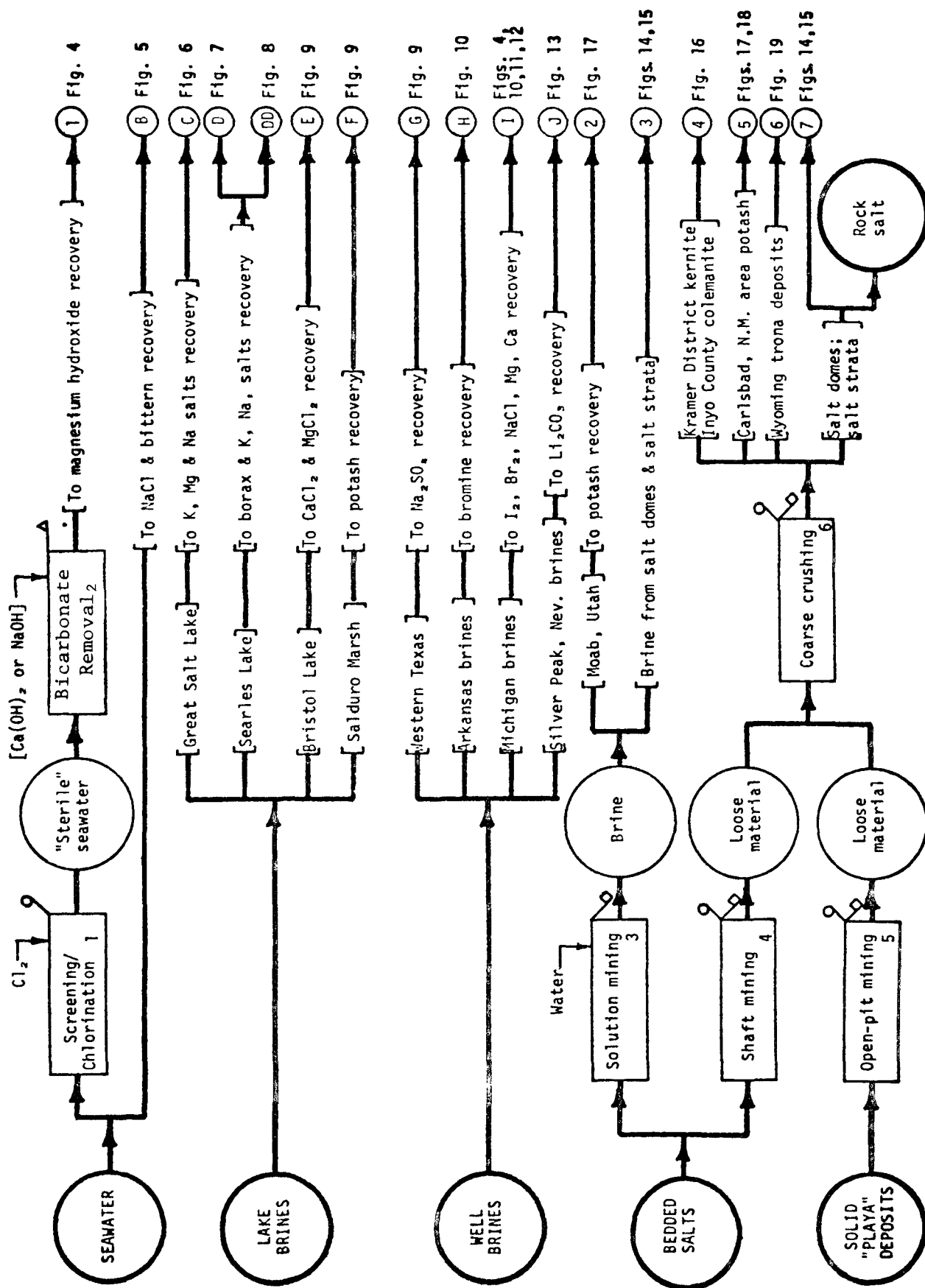


FIGURE 3. PRINCIPAL RAW MATERIAL SOURCES

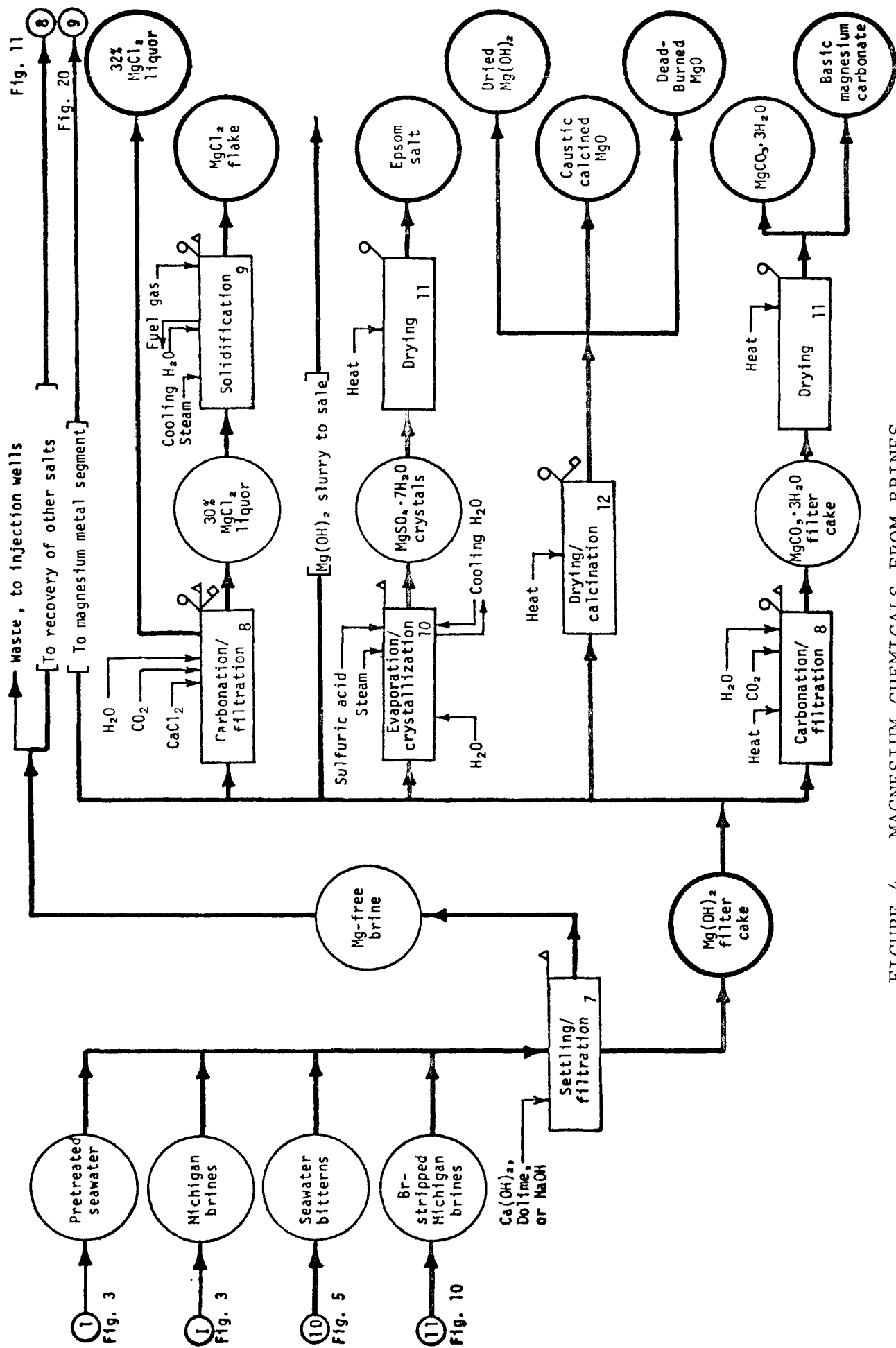


FIGURE 4. MAGNESIUM CHEMICALS FROM BRINES

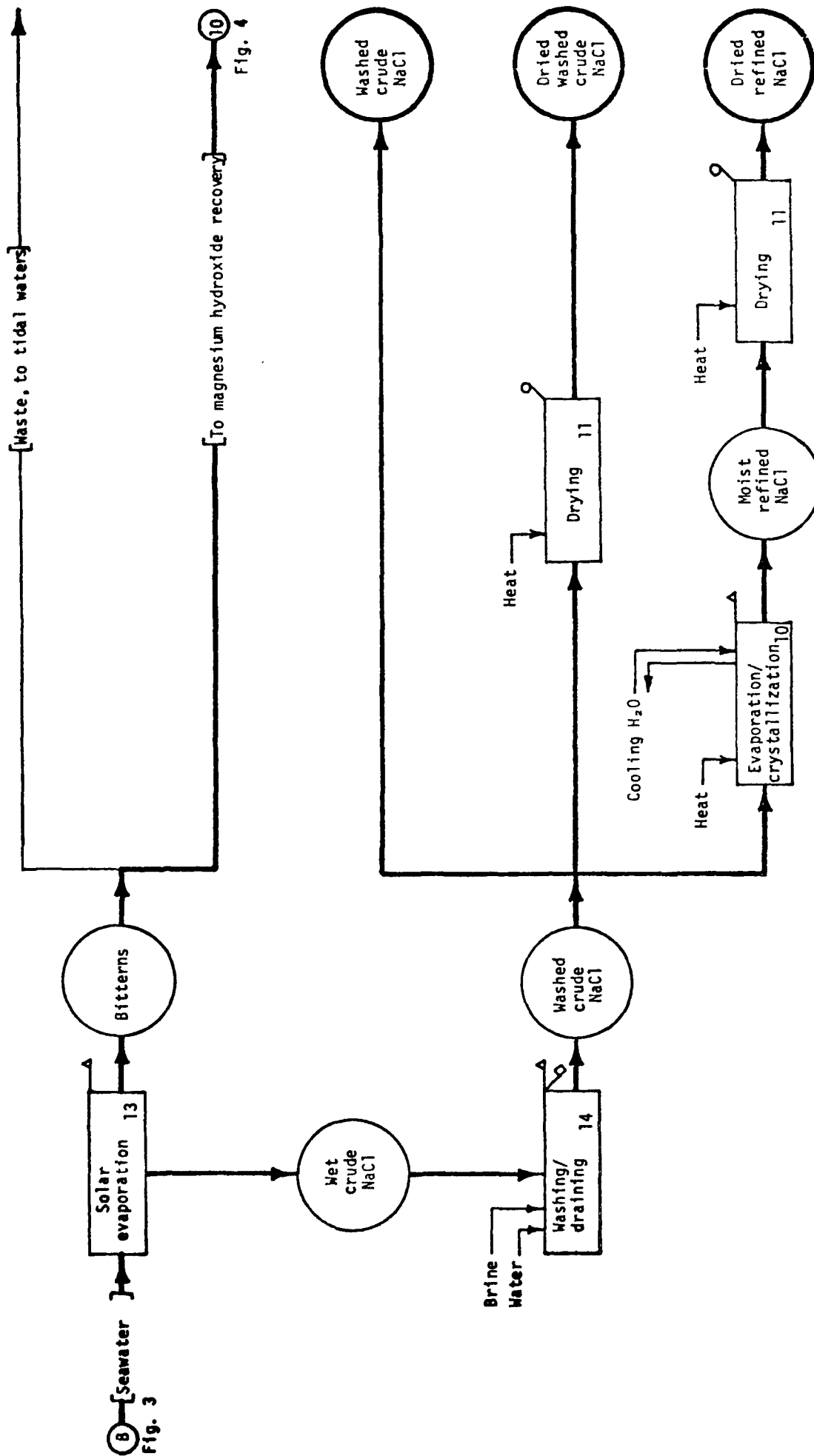


FIGURE 5. SODIUM CHLORIDE AND BITTERNS FROM SEAWATER

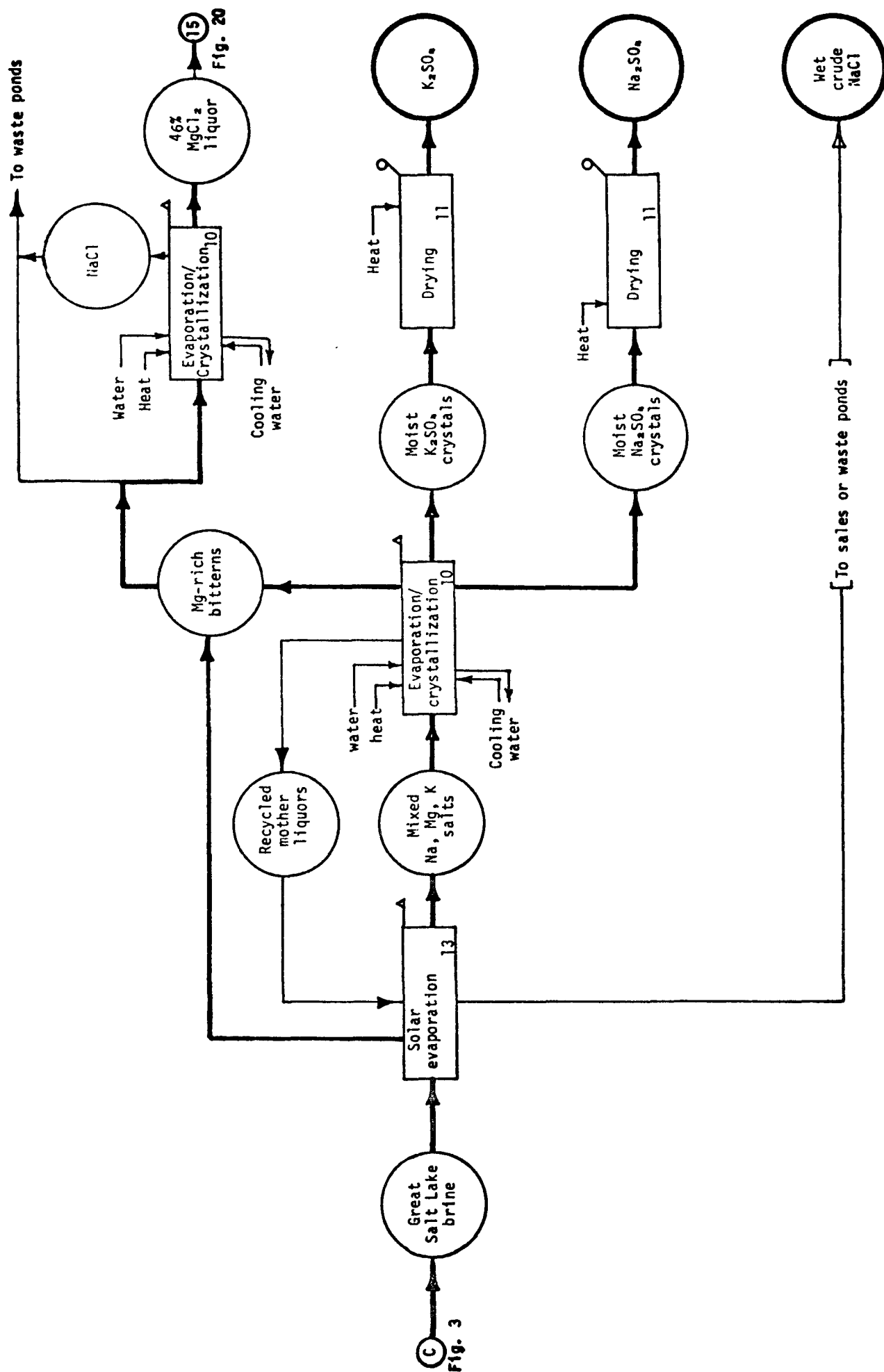


FIGURE 6. CHEMICALS FROM GREAT SALT LAKE

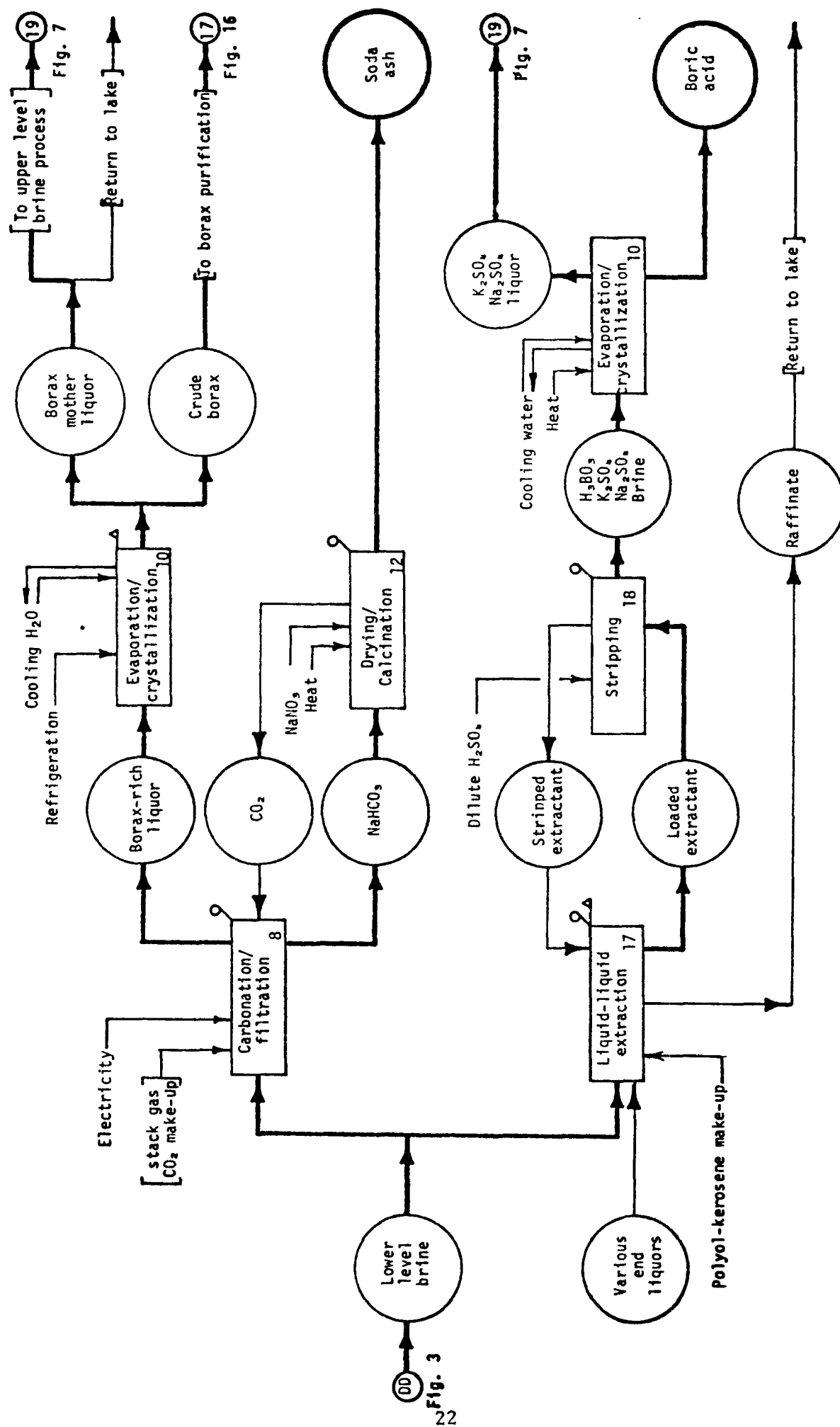


FIGURE 8. CHEMICALS FROM SEARLES LAKE, LOWER LEVEL

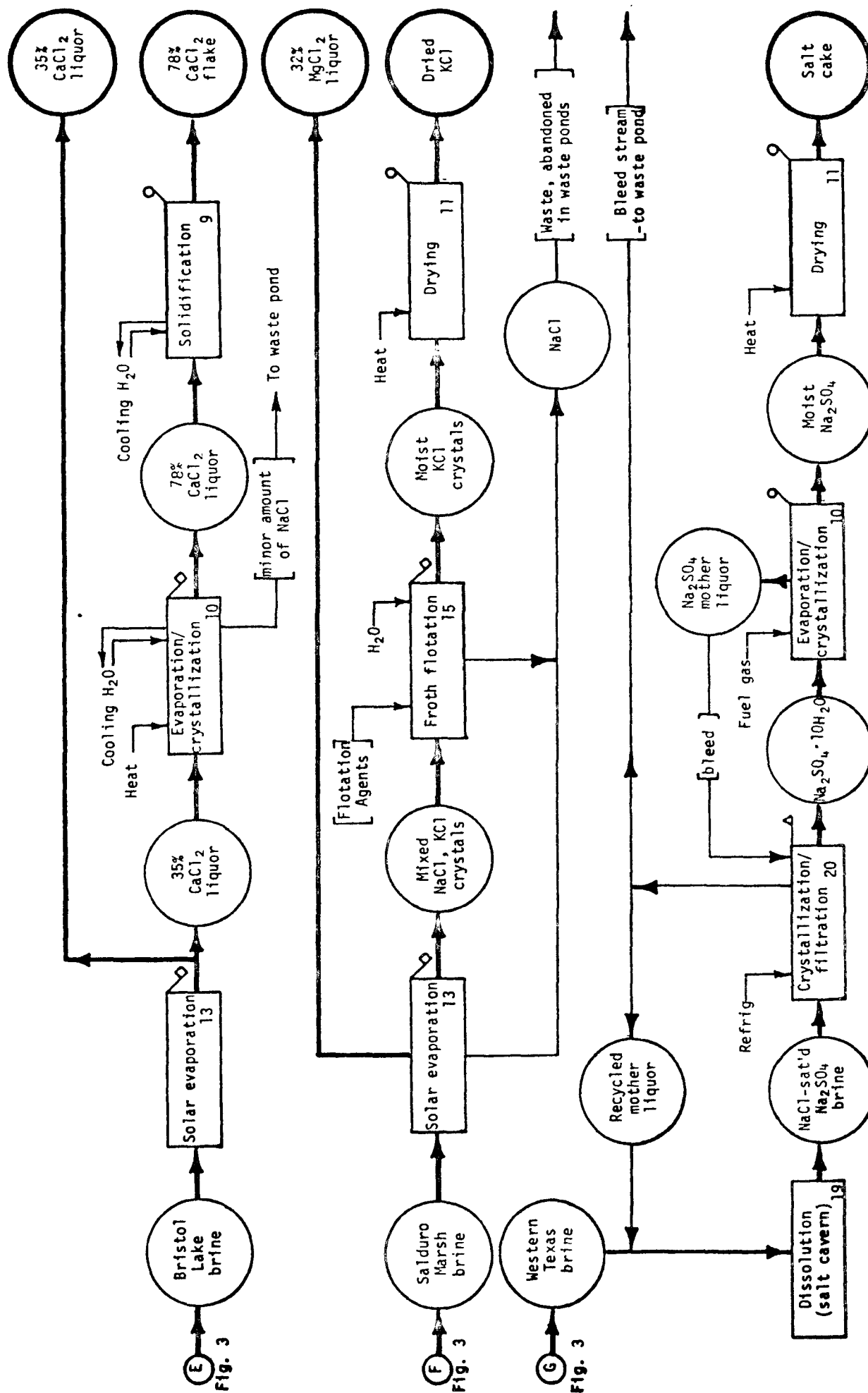


FIGURE 9. CHEMICALS FROM BRISTOL LAKE, SALDURO MARSH AND TEXAS BRINES

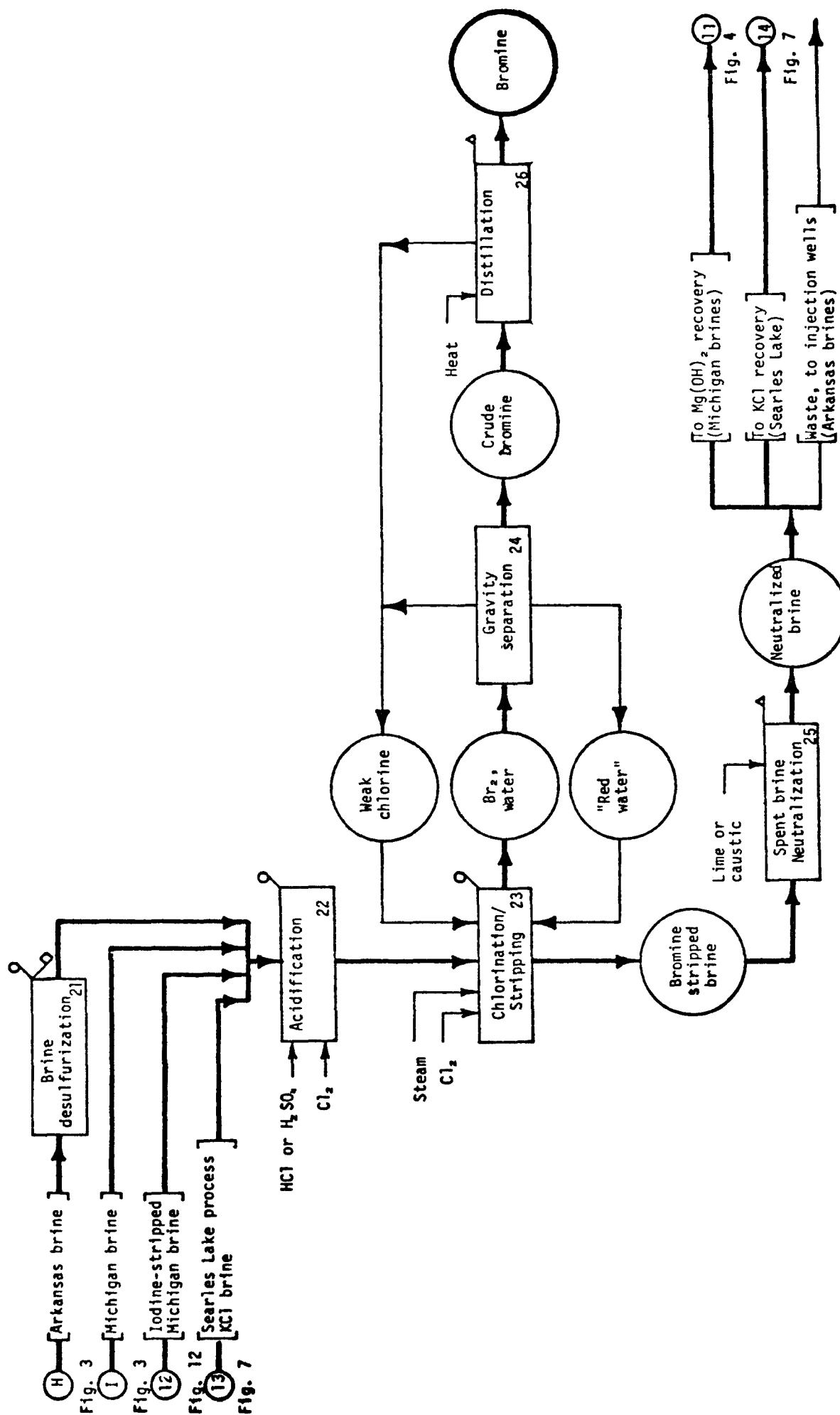


FIGURE 10. BROMINE RECOVERY FROM VARIOUS BRINES

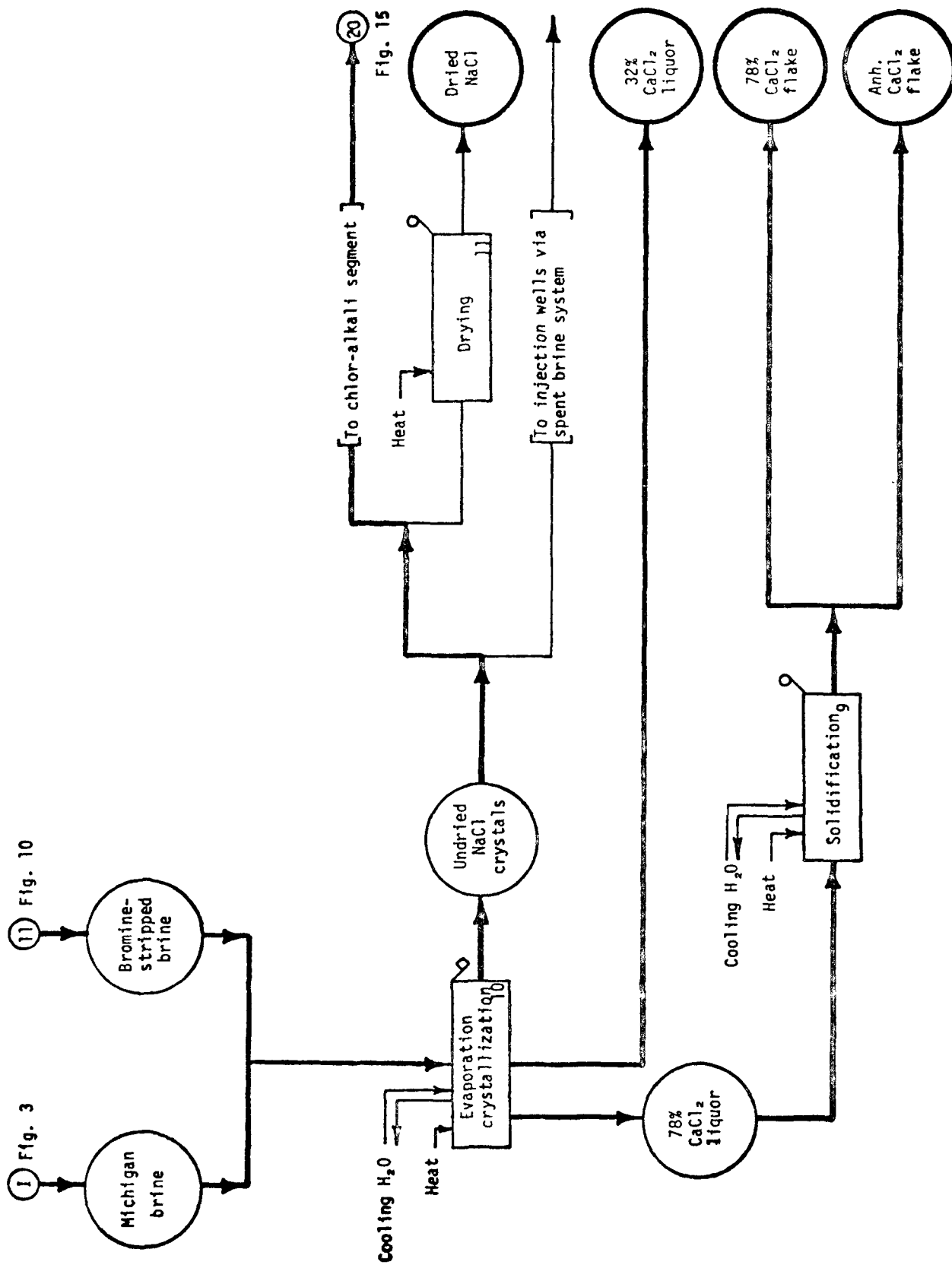


FIGURE 11. CHEMICALS FROM MICHIGAN BRINES

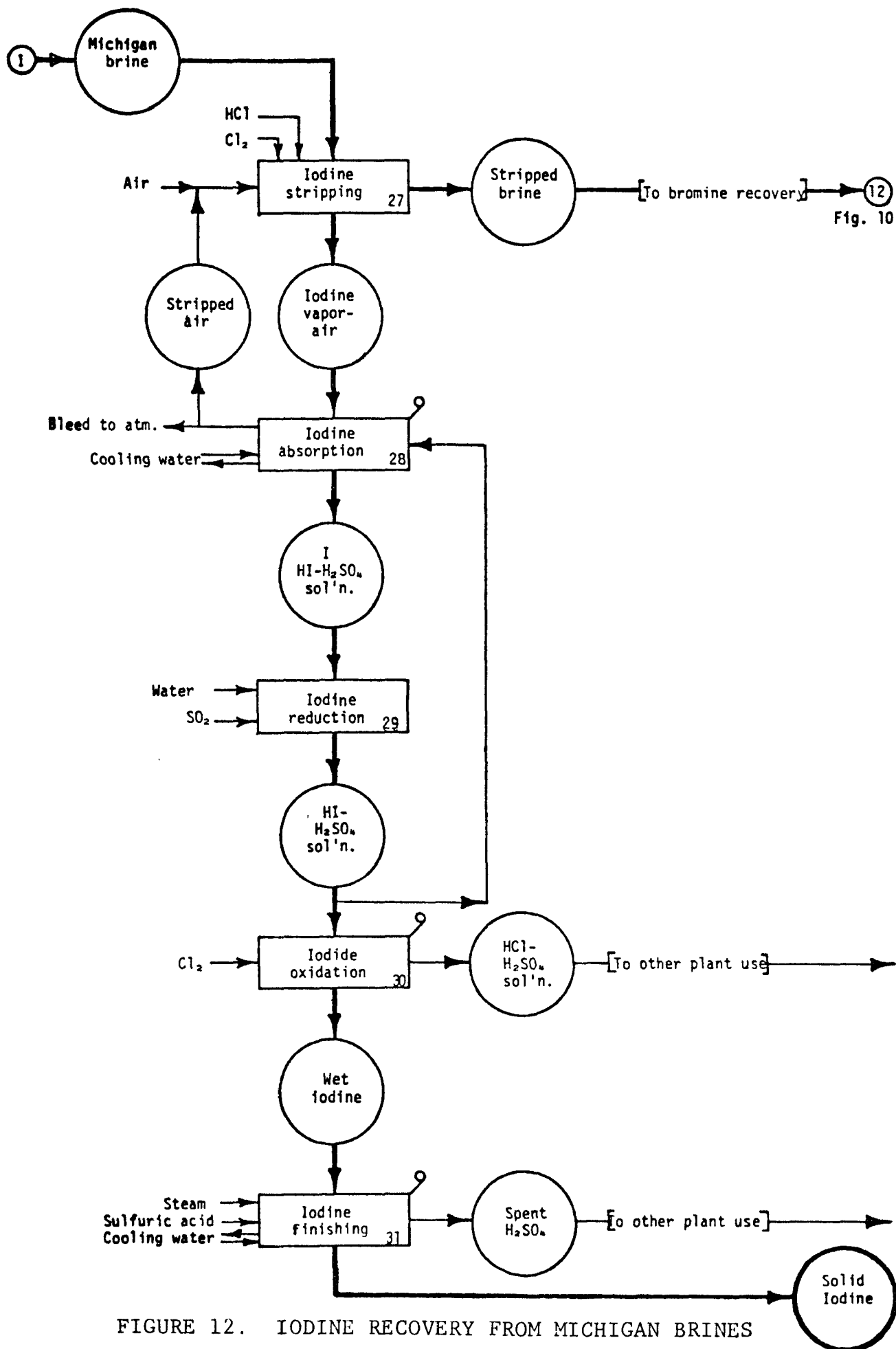


FIGURE 12. IODINE RECOVERY FROM MICHIGAN BRINES

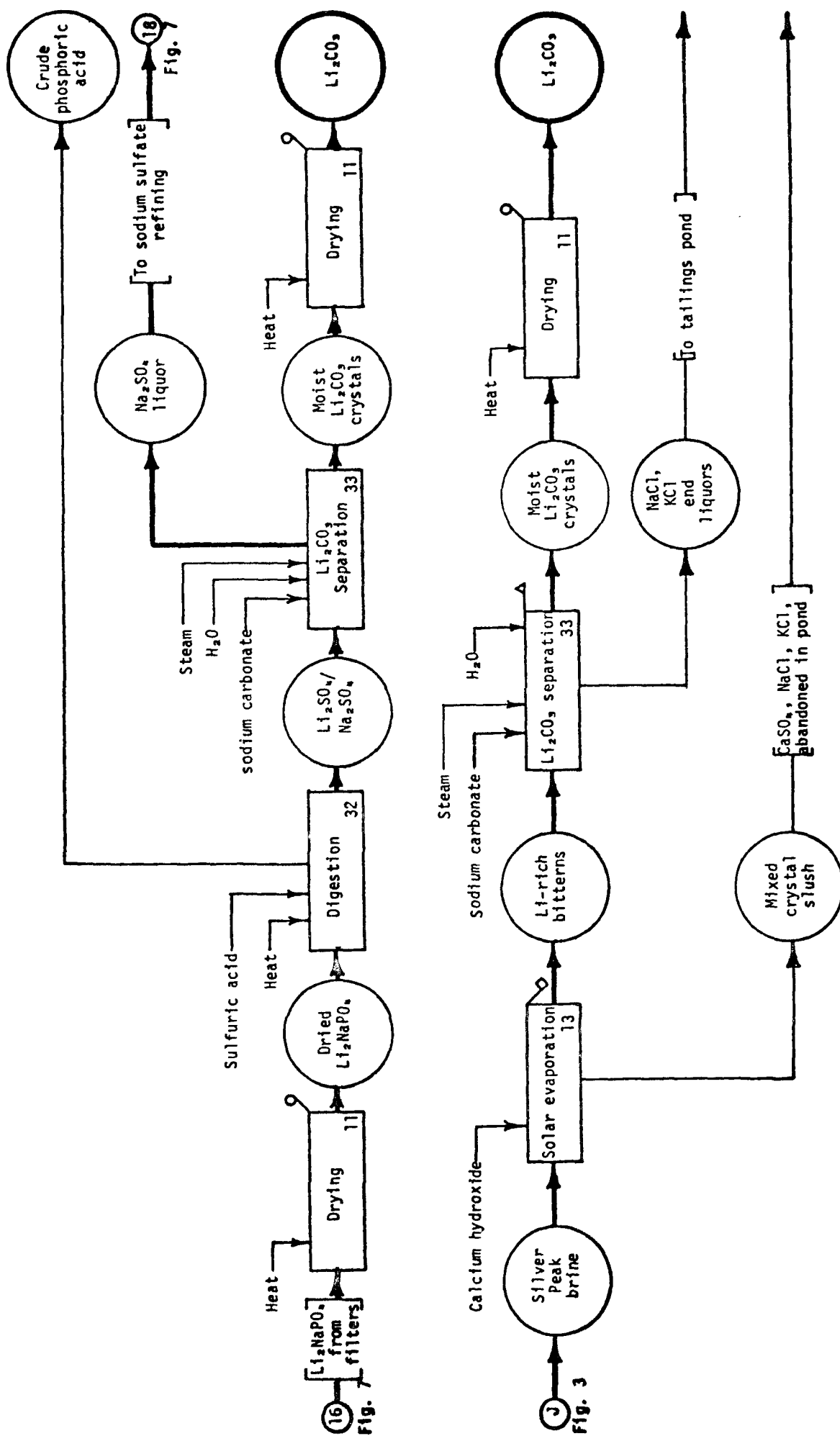


FIGURE 13. LITHIUM CARBONATE FROM TWO DIFFERENT BRINE SOURCES

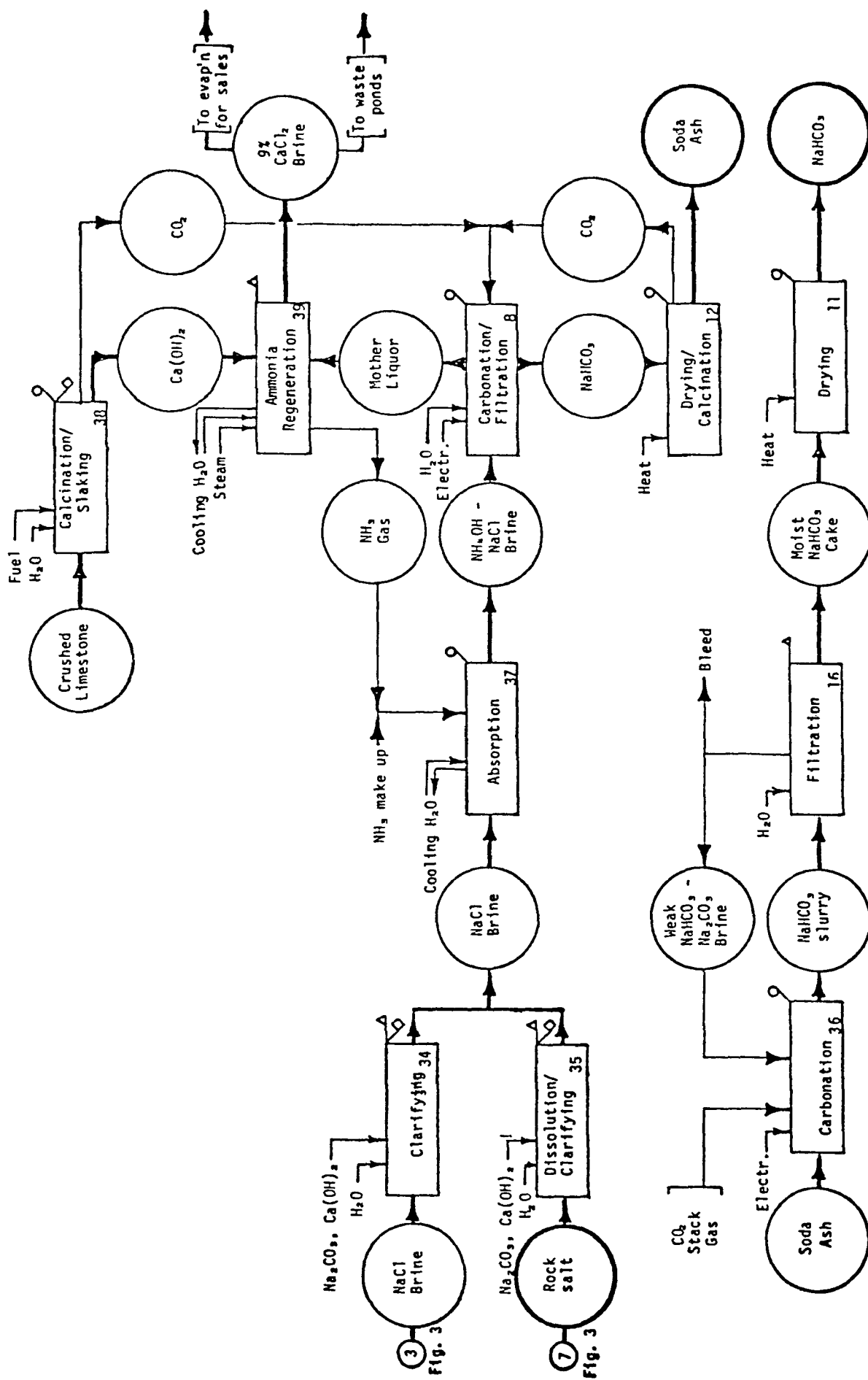


FIGURE 14. SOLVAY SODA ASH AND SODIUM BICARBONATE

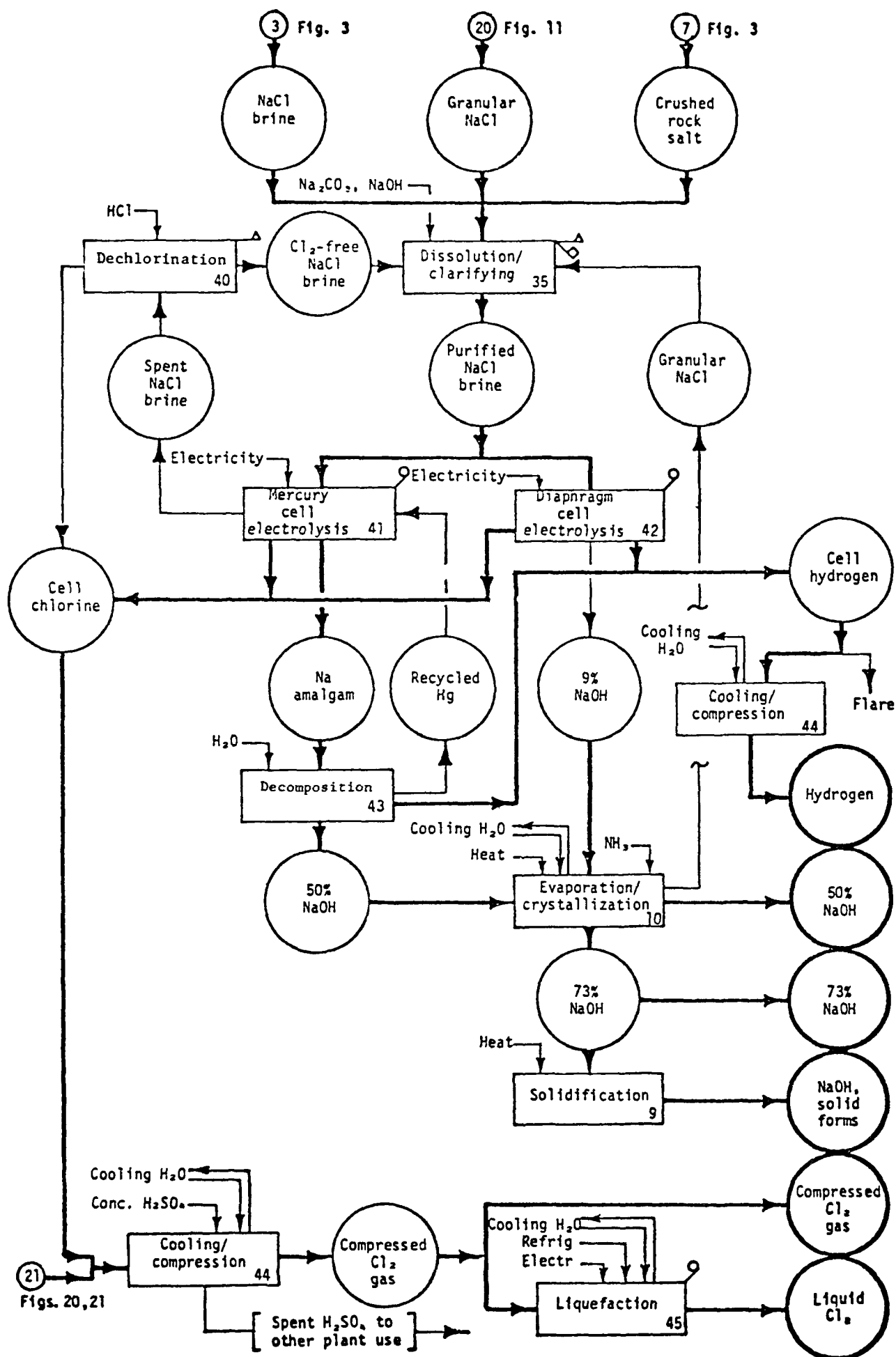


FIGURE 15. CHLORINE AND CAUSTIC SODA VIA ELECTROLYSIS

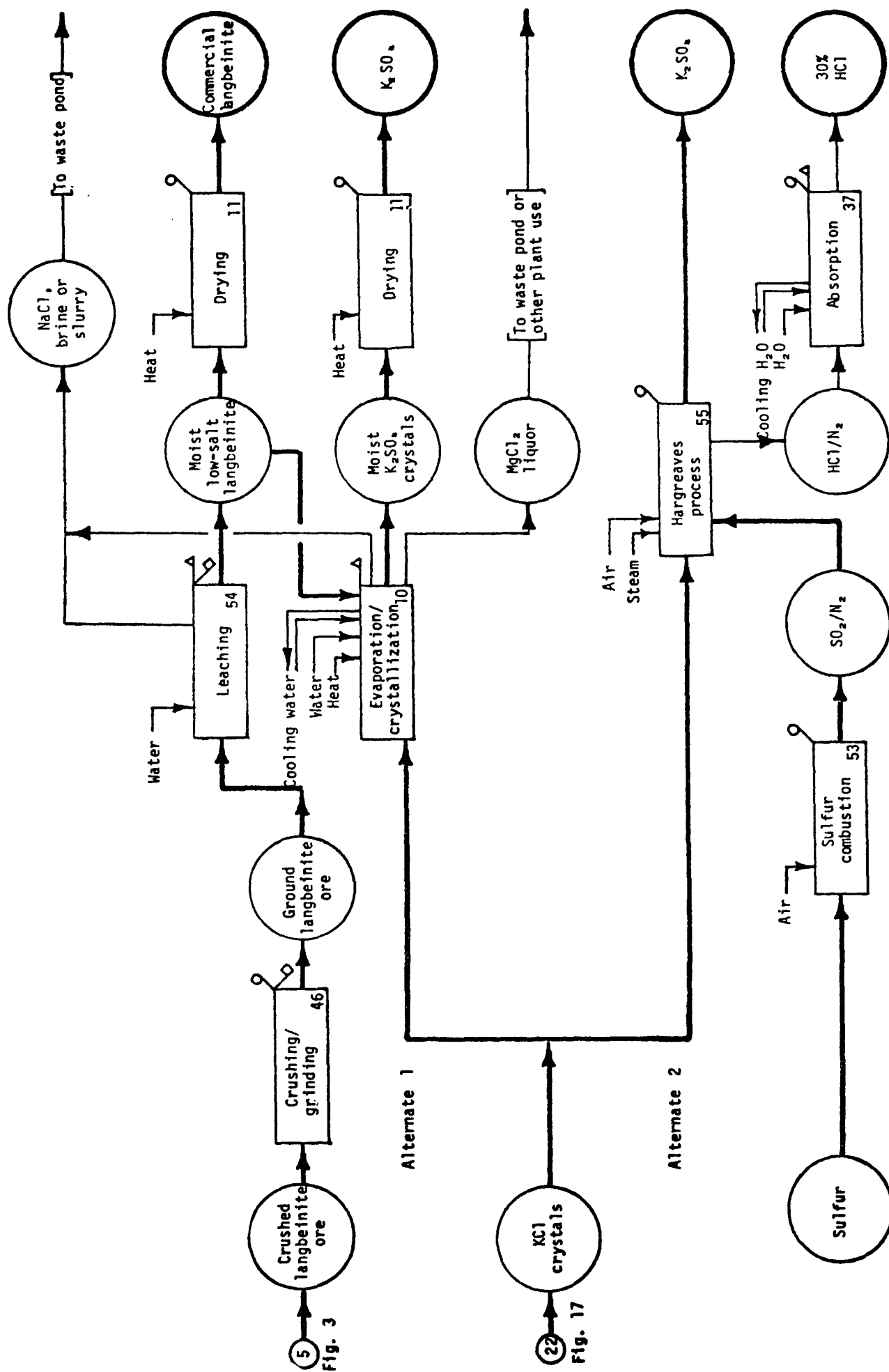


FIGURE 18. POTASSIUM SULFATE FROM LANGBEINITE AND SYLVITE

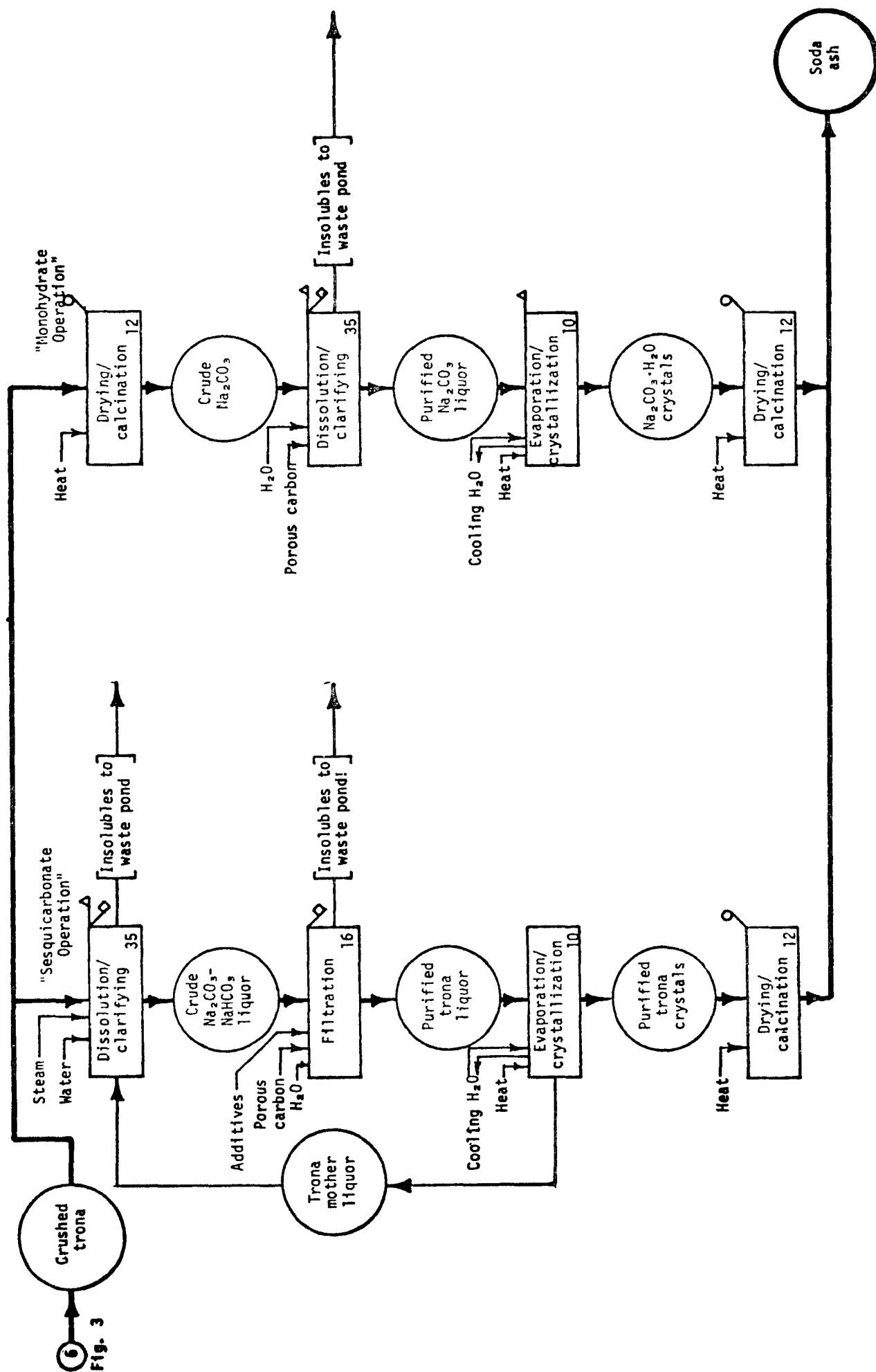


FIGURE 19. SODA ASH FROM TRONA

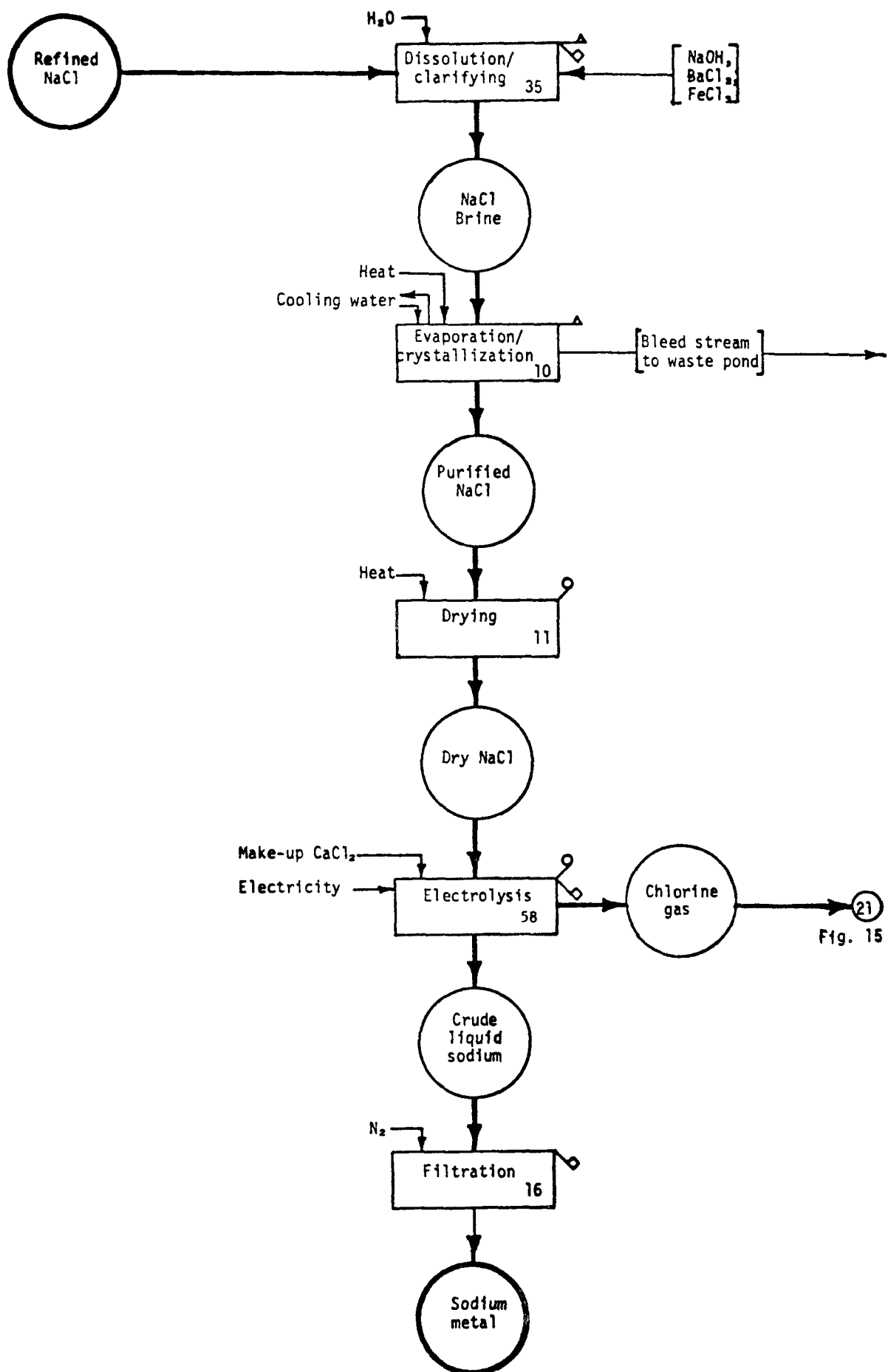


FIGURE 21. SODIUM METAL VIA DOWNS CELL

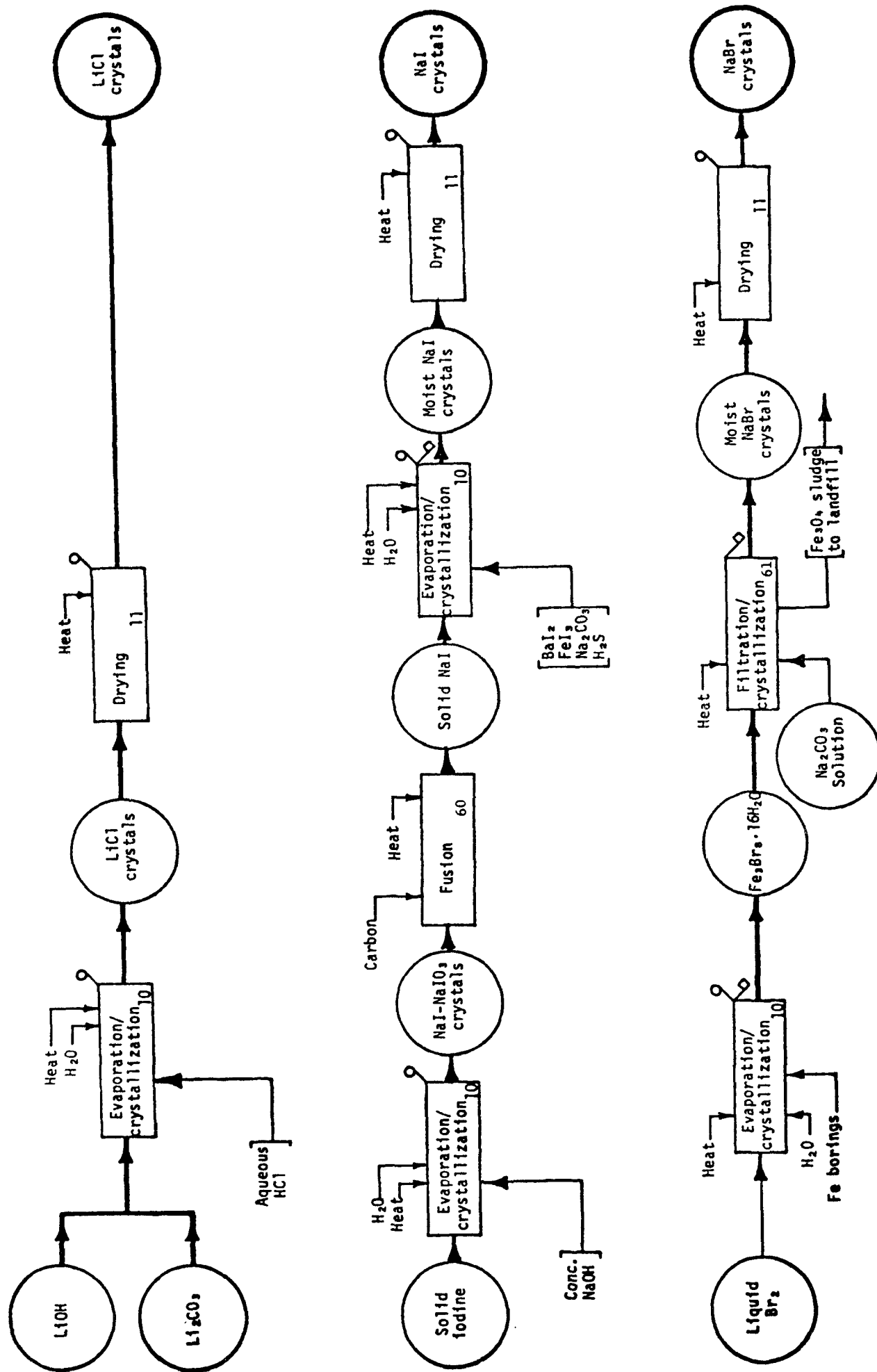


FIGURE 22. LITHIUM CHLORIDE, SODIUM IODIDE AND SODIUM BROMIDE

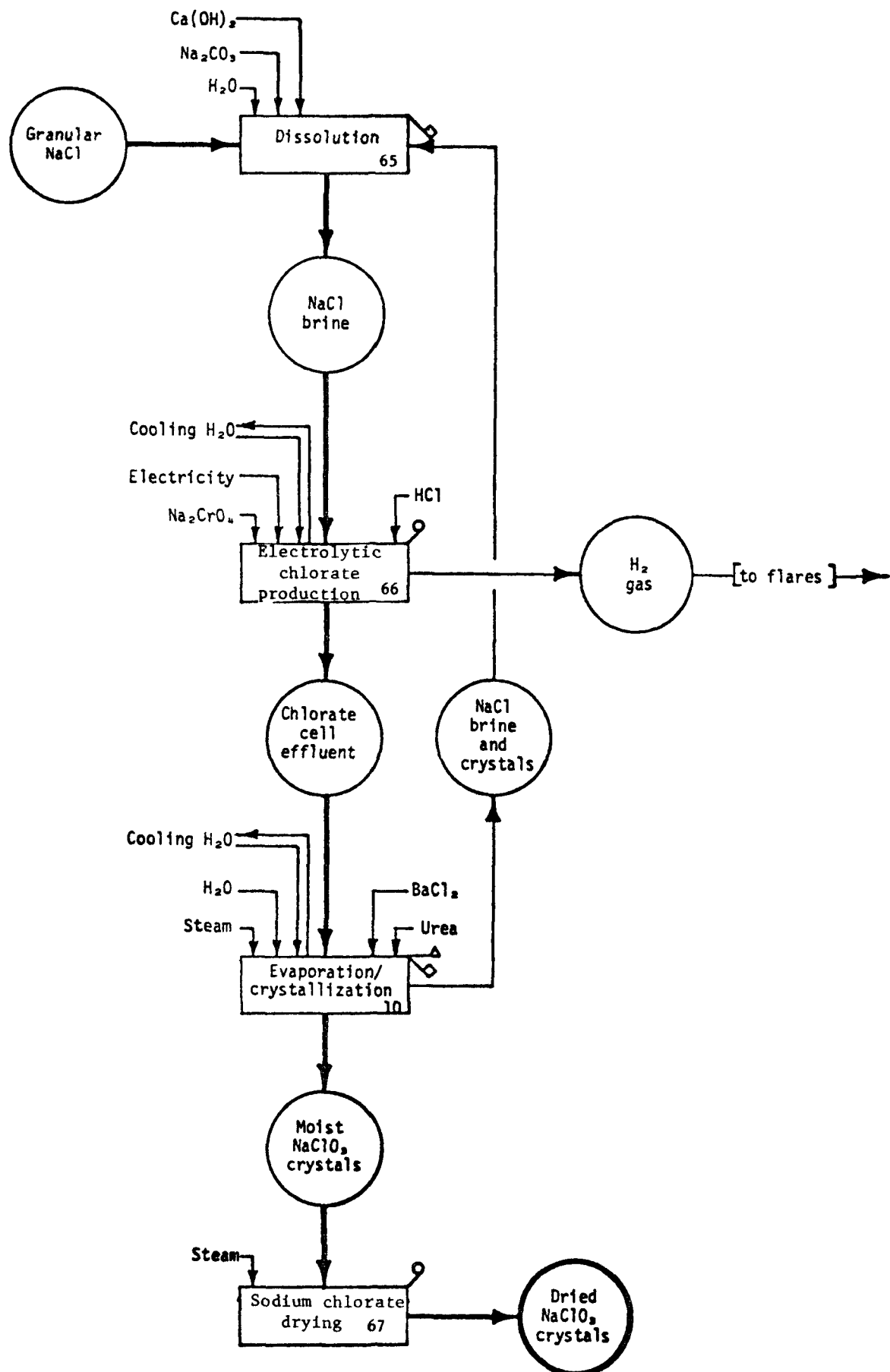


FIGURE 23. SODIUM CHLORATE VIA ELECTROLYSIS

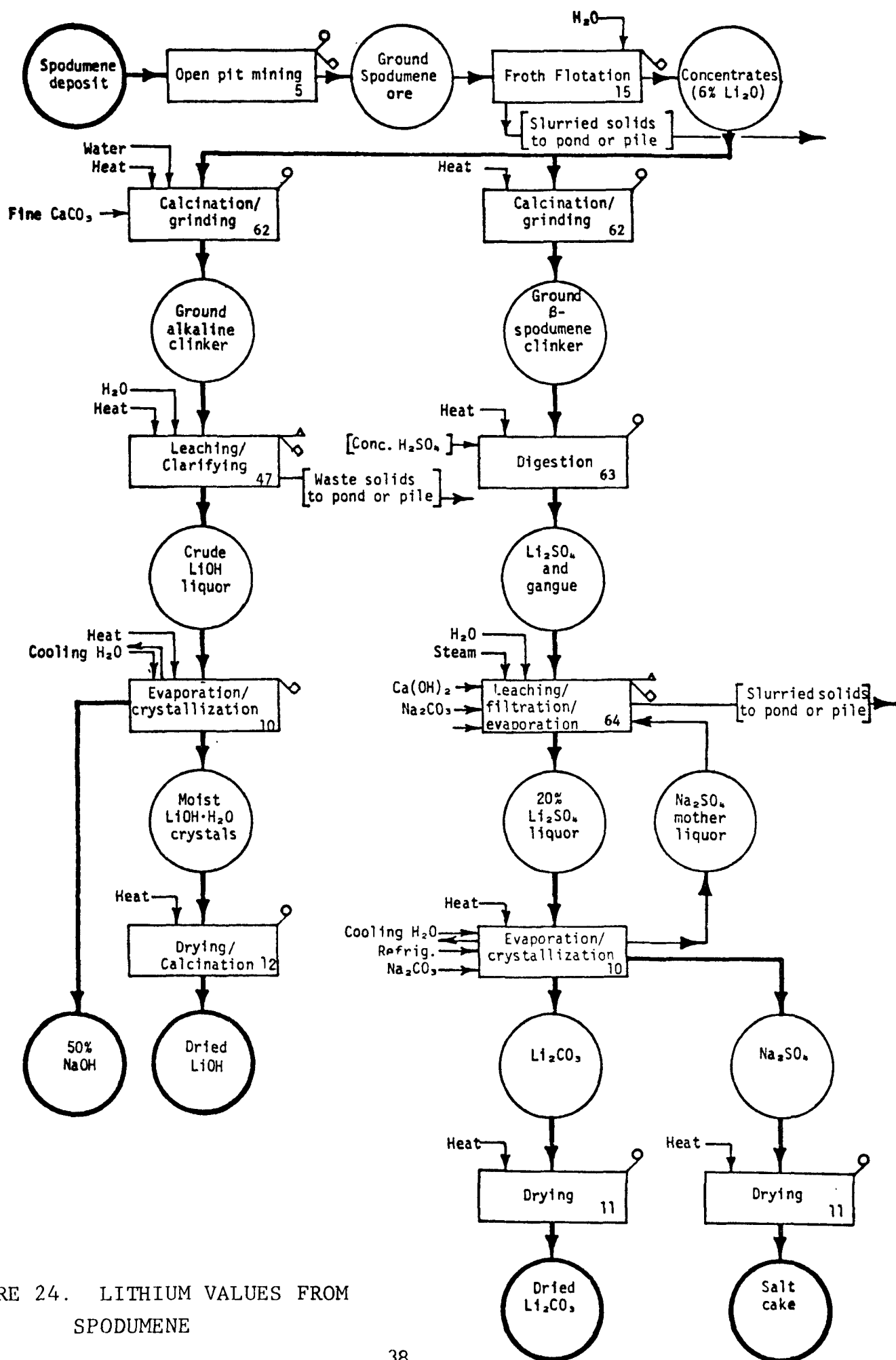


FIGURE 24. LITHIUM VALUES FROM SPODUMENE

SCREENING/CHLORINATION1. Function

This process (see Figure 3) accomplishes two objectives: (1) removes floating debris from seawater prior to the latter's entry into intake pump suctions and seawater pipelines; and (2) kills marine organisms present in raw seawater, thereby preventing fouling of seawater pumps and pipelines.

Trash screens are usually about 3-cm² mesh of corrosion resisting alloy wire. Screens are either removable or of self-cleaning "roller towel" type. Screens are usually protected by a steel-bar grizzly. Chlorinating equipment may be of standardized off-the-shelf design.

This process also includes seawater pumping. The screened/chlorinated seawater is forwarded to Process 2.

2. Input Materials

Raw seawater - Quantities required in cubic meters per metric ton of product assuming 3.3% salinity and 100% extractive efficiencies:

Mg(OH) ₂	340
Mg metal	800

Chlorine - Kilograms of Cl₂ (average) per metric ton of:

Seawater	0.002
Mg(OH) ₂	0.6
Mg metal	1.5

3. Operating Parameters

Prevailing near-shore salinity and temperature - Depends on exact location of intake.

Chlorination - Either by diffuse bubbling of chlorine gas below the surface of seawater in flumes or by injection into pipelines. Chlorination may be either continuous or intermittent at 12-hour intervals and is usually controlled to approximately 1 ppm residual Cl₂.

4. Utilities

Electric energy consumption (for pumping seawater) expressed in kWh per metric ton of product, assuming same seawater conditions named in 2 above, and assuming 10-foot total head and 75% overall efficiency of pump-motor unit:

Mg(OH) ₂	3 to 4
Mg metal	8 to 9

5. Waste Streams

Amount of Cl₂ entering atmosphere is sufficient to detect by smell in immediate vicinity.

Trash recovered from screens is incinerated or buried.

6. EPA Source Classification Code

None established.

7. References

Mangum, D. C., B. P. Shepherd, and W. F. McIlhenny. Methods for Controlling Marine Fouling in Intake Systems. U. S. Department of the Interior, Washington, D. C. Office of Saline Water R & D Progress Report No. 858. (PB 221 909). June 1973. 124 p.

Shepherd, B. P., P. G. LeGros, J. C. Williams, and D. C. Mangum. Intake Systems for Desalting Plants. U. S. Department of the Interior, Washington, D. C. Office of Saline Water R & D Progress Report No. 678. April 1971. 222 p.

White, G. C. Handbook of Chlorination. New York, Van Nostrand Reinhold. 1972. 744 p.

BICARBONATE REMOVAL1. Function

This process (see Figure 3) eliminates or substantially reduces the concentration of bicarbonate ions plus suspended solids contained in seawater from Process 1. It also increases the level of purity of the Mg(OH)_2 precipitated in Process 7, Figure 4.

Major equipment includes agitated flocculator, plus settling ponds or thickening tanks.

This process may be bypassed if the Mg(OH)_2 subsequently produced is used for production of magnesium metal.

2. Input Materials

Quantities of materials per metric ton of product (typical):

	<u>For Mg(OH)_2</u>	<u>For Mg metal</u>
"Sterile" seawater	340 m ³	800 m ³
Ca(OH)_2 , or	90 kg	220 kg
NaOH	97 kg	240 kg

3. Operating Parameters

The process is conducted at ambient temperatures. A clarifying tank is typically about 160 meters (500 feet) in diameter by 4 meters (12 feet) side wall depth for a seawater flow of 80 cubic meters per minute (20,000 gpm).

Additions of Ca(OH)_2 or NaOH are typically controlled to precipitate approximately 5% of the total magnesium content, corresponding to pH values in the neighborhood of 9.5.

4. Utilities

Approximately 5 kW for clarifier tank plus, typically, 50 kW for flocculator tank. Total electric power expressed in kWh per metric ton of product:

Mg(OH)_2	2 to 4
Mg metal	5 to 10

5. Waste Streams

The sole waste stream is a slurry of CaCO_3 and clay particles suspended in seawater, typically carrying 150 grams total suspended solids per liter. The waste stream is innocuous. Depending upon conditions, it may be:

- Diluted with seawater and discharged into the tidal system.
- Neutralized with dilute HCl , the resulting neutral solution then being discharged into tidewater.
- Discharged into diked ponds, where further thickening occurs, qualifying the disposal as landfill operation.

6. EPA Source Classification Code

None established.

7. References

Schambra, W. P. The Dow Magnesium Process at Freeport, Texas. Trans. Am. Inst. Chem. Eng. 41:35-51, January 1945.

SOLUTION MINING1. Function

This process (see Figure 3) obtains the desired mineral in solution form at the surface, by dissolving the underground mineral deposit with injected water. This process applies to the recovery of sodium chloride from salt domes and layered deposits at several locations and to the recovery of sylvinite at Moab, Utah.

Equipment consists essentially of high-pressure pumps and piping. The latter, both for injection water and solution, is typically contained inside casing cemented into both overburden and producing formation. Solution tubing may be concentric with injection water tubing, or be contained in separate well casing.

This process includes storage for both water and solution and equipment for water treating. The NaCl brine is forwarded to Process 34, Figure 14, or Process 35, Figure 15.

2. Input Materials

In the case of solution mining salt domes for NaCl recovery, the total weight of solids dissolved from the deposit is only slightly greater than the weight of NaCl produced.

Approximately 2.5 metric tons of sylvinite ore are dissolved per metric ton of KCl produced.

3. Operating Parameters

Injection water temperatures vary seasonally between 0° and 25°C. Recovered brine temperatures are as high as 35°C.

A typical salt "well" may produce between 250 and 1,000 metric tons per day of NaCl.

In sylvinite mining, between 4 and 12 cubic meters per minute (1,000 to 3,000 gpm) is the typical flow from an extraction well.

4. Utilities

Water requirement in cubic meters per metric ton of product:

NaCl	2.8 to 3.0
KCl	7.0 to 8.0

5. Waste Streams

Fragments of anhydrite, gypsum and sand are carried in the brine from the solution cavity of a salt dome. This is settled out in a pond or tank. Their ultimate disposal is by landfill (abandonment in pond). This waste is estimated at <0.5% by weight of the NaCl in the recovered brine.

Solid wastes of sand and clay particles are believed to result from solution mining potash, but no quantitative information is available.

6. EPA Source Classification Code

None established

7. References

Jackson, D. Solution Mining Pumps New Life into Cane Creek Potash Mine. Eng./Min. J. 174:59-69. July 1973.

SHAFT MINING1. Function

This process (see Figure 3) brings ore to the surface from a relatively deep ore body using dry, mechanical methods and without the necessity of removing the overburden. (Similar to classical concept of coal mining.)

This process usually involves sinking a central shaft. Mining proceeds by "room-and-pillar", or similar methods, employing various devices of attacking the ore in place: drilling and blasting, use of "continuous mining" equipment, etc.

Equipment is identical or similar to that used in underground coal mining: rock drills, undercutters, front-end loaders, roof-bolting equipment, belt conveyors, central elevator, etc.

2. Input Materials

Subsurface ore deposits are the starting materials for this process. The weight of ore removed per metric ton of end product varies widely from mine to mine for any one material. Estimates of this ratio are:

Halite to crushed rock salt:	<1.02:1
Sylvinite to granular KCl:	2.5:1 to 4:1
Langbeinite to K_2SO_4 :	1.1 to 1.5:1
Trona to soda ash:	1.4 to 1.6

3. Operating Parameters

A typical scale of mining operations for a single mine in terms of product output in thousands of metric tons per year capacity:

Crushed rock salt:	800 to 1,500
KCl plus K_2SO_4 :	500 to 1,000
Soda ash:	500 to 1,500

4. Utilities

Electric power is the chief form of energy used in underground mining operations. Requirements are 1 to 20 kWh per metric ton of any of the products mentioned in this process description.

5. Waste Streams

Mining operations are inherently dusty. Dust-laden air in the underground galleries, frequently containing gaseous products of blasting, is carried by the ventilating system and exhausted to the atmosphere in undisclosed quantities and concentrations.

From a practical standpoint, there are no liquid emissions from underground mining operations of evaporites.

Solid wastes associated with shaft mining processes result directly from crushing, screening and sizing processes and in this study are listed in the descriptions of the latter.

6. EPA Source Classification Code

3-05-022-01 Mine-Grind/Dry

7. References

- First Symposium on Salt. Bersticker, A. C. (ed.). Cleveland, Northern Ohio Geological Society, 1963. 661 p.
- Harley, G. T., and G. E. Atwood. Langbeinite--Mining and Processing. Ind. Eng. Chem. 39: 43-47, January 1947.
- Jacobs, J. J. Potassium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, John Wiley and Sons, Inc., 1968. 16: 369-400.
- Kellogg, H. H. Energy Efficiency in the Age of Scarcity. Journal of Metals. 26: 25-29, June 1974.
- Magraw, R. M. New Mexico Sylvinites. Ind. Eng. Chem. 30: 861-871, August 1938.
- Second Symposium on Salt. Raw, J. L. (ed.). Cleveland, Northern Ohio Geological Society, 1966. 443 p.
- Third Symposium on Salt. Raw, J. L. and L. Dellwig (ed.). Cleveland, Northern Ohio Geological Society, 1970. 486 p.
- Turrentine, J. W. Potash in North America. ACS Monograph Series, No. 91. New York, Reinhold, 1943. 186 p.
- von Perbandt, L. K. Salt Mining. In: Sodium Chloride. ACS Monograph Series, No. 145. Kaufmann, D. W. (ed.). New York, Reinhold, 1960. p. 109-126.

White, N. C., and C. A. Arend, Jr. Potash Production at Carlsbad. Chem. Eng. Progr. 46: 523-531, October 1950.

OPEN-PIT MINING

1. Function:

The process (see Figure 3) recovers ore from an orebody, by removing the overburden, either prior to or during the removal of the ore itself. This process is applicable to the mining of kernite and colemanite.

Equipment employed includes power shovels, draglines, front-end loaders, scrapers, bull dozers, dump trucks, conveyor belts, blasting equipment and other excavating and earth-moving machinery.

The process may include the steps of crushing, grinding, and drying. The mined ore is forwarded to Process 6.

2. Input Materials

The unmined ore is the input material. Ratios of weight of ore mined to weight of product recovered are estimated as follows for the products involved in this process:

Kernite to B_2O_3 contained in products: 4 to 5
Colemanite to calcined colemanite: 1.3 to 2.0

3. Operating Parameters

As an indication of the scale of specific open-pit mining processes applied to kernite and colemanite, typical mining capacities of a single operation are given below in thousands of metric tons per year of the stated material. These values have been inferred from published information.

Kernite	1,000
Colemanite	150

4. Utilities

Most equipment is usually powered by self-contained internal combustion prime-movers, consuming gasoline or diesel fuel. Other units use compressed air. In some cases electrical energy is used, supplied either by trolleys or trailing cables. Total energy consumption obviously varies over a wide range, depending on type and depth of overburden and identity of the ore.

Total consumption of energy in all forms is estimated to vary from 2 to 20 kWh per metric ton of end products involved.

It is conjectured that fresh water may be consumed for dust abatement. Quantitative information is unavailable.

5. Waste Stresms

Open pit mining is inherently a dusty process, producing considerable quantities of particulate emissions from the blasting, crushing and loading steps. Inadequate quantitative information is available.

Particle size range of atmospheric emissions in kernite mining is 0.5 to 20 microns. These dusts amount to an estimated 4 to 5 kilograms per metric ton of B_2O_3 contained in the various forms of borate end-products.

6. EPA Source Classification Code

3-05-023-01	Mining/Processing
3-05-040-01	Open Pit-Blasting
3-05-040-02	Open Pit-Drilling
3-05-040-03	Open Pit-Cobbing

7. References

Chem. Wk. 109: 39-40, August 11, 1971.

Kellogg, H. H. Energy Efficiency of the Age of Scarcity. Journal of Metals. 26:25-29 June 1974.

Wang, K. P. Boron. In: Minerals Yearbook, 1971. Schreck, A. E. (ed.). Washington, U. S. Bur. Mines, U. S. Dept. of the Interior, 1973. 1:228.

Woodmansee, W. C. The Mineral Industry of California. In: Minerals Yearbook, 1971. Schreck, A. E. (ed.). Washington, U. S. Bur. Mines, U. S. Dept. of the Interior, 1973. 2:139.

COARSE CRUSHING1. Function

This process (see Figure 3) reduces the maximum size of large lumps of ore to sizes permitting accommodation by subsequent handling equipment such as stockpile conveyors, storage hoppers or railcar and truck loading equipment. This process may be required on only a portion of the ore mined and in some operation is omitted entirely.

Equipment used includes any of several types of primary crushers such as jaw crushers, cone crushers and roll crushers. Screens and other size-separation equipment may be included.

2. Input Materials

Coarser fractions of the mined ore: ~1 metric ton per metric ton of product.

3. Operating Parameters

Capacities of crushing equipment employed vary as much as several hundred metric tons per hour. Crushed material output varies from 5-cm lumps to 4- or 8- mesh. Crushing equipment may be located both inside the mine and at the surface.

4. Utilities

Input electrical energy varies with hardness of ore and size-reduction ratio, between 0.5 and 5 kWh per metric ton crushed product, corresponding to estimated electrical energy inputs per metric ton of finished product as follows:

NaCl (from rock salt)	1 to 2
KCl (from sylvinite)	3 to 6
Calcined colemanite	2 to 3
Borax decahydrate (from kernite)	1 to 2
Soda ash (from trona)	4 to 5

5. Waste Streams

Particulate atmospheric emissions almost invariably accompany crushing and dry screening processes. No

quantitative information is available on the materials considered here.

Solid waste streams consisting of the gangue material may be separated from the ore in amounts estimated between 1% and 10% of the feed weight. The identity of the gangue is listed below for some of the ores under consideration.

<u>Ore</u>	<u>Usual gangue</u>
Rock salt	Anhydrite, sand, gypsum
Sylvinite	Clay, anhydrite, sand
Colemanite	Clay
Trona	Shale

6. EPA Source Classification Code

3-05-040-30 Primary Crusher
3-05-022-01 Mine-Grind/Dry
3-05-040-34 Screening

7. References

Lincoln, T. W., and A. L. Stern. Size Reduction and Size Enlargement. In: Chemical Engineers' Handbook, 4th Edition. Perry, R. H., C. H. Chilton, and S. D. Kirkpatrick (ed.). New York, McGraw-Hill, 1963. p. 8:1-64.

Turrentine, J. W. Potash in North America. ACS Monograph Series No. 91, New York, Reinhold, 1943. 186 p.

White, N. C., and C. A. Arend, Jr. Potash Production at Carlsbad. Chem. Eng. Progr. 46:523-531, October 1950.

SETTLING/FILTRATION1. Function

This process (See Figure 4) obtains magnesium hydroxide in the form of washed filter cake from various brines and semi-processed liquors from Processes 1 and 2, Figure 3.

Magnesium hydroxide is precipitated from the brine in an agitated flocculator tank by the addition of lime, dolime or caustic soda and then allowed to settle out and thicken in settling tanks. The thickened sludge is filtered and water-washed to yield a filter cake containing approximately 35 weight percent magnesium hydroxide. The filter cake is forwarded to Process 56, Figure 20, or Processes 8, 10, or 12, Figure 4.

2. Input Materials

These may be seawater or any other surface brine, bitterns resulting from the solar evaporation of seawater, or natural underground brines (notably well brines from various formations underlying the state of Michigan). The magnesium content of these materials varies from approximately 0.12% Mg in the case of seawater, through 0.8% Mg in some Michigan brines, to as high as 7% in the case of seawater bitterns.

Typical quantities of input materials per metric ton of magnesium hydroxide recovered:

Seawater	300 to 350 cubic meters
Seawater bitterns	5 to 7 cubic meters
*Ca(OH) ₂ or	1.3 metric tons
*NaOH	1.4 metric tons

*An excess of approximately 20% is required if the Mg(OH)₂ is used to produce magnesium metal.

3. Operating Parameters

In the case of seawater, sizes of settling or thickening tanks are typically 50 to 80 meters in diameter by 3 meters side wall depth, or may be square ponds approximately 150 meters on edge, equipped with several raker

arms. One 60-meter diameter settling tank is required to produce approximately 35 metric tons per day of magnesium hydroxide.

4. Utilities

The major consumer of electrical energy in this process is the agitator (circulating pump) in the flocculator tank. This uses about 80% of the 13 kWh total per metric ton of magnesium hydroxide in the case of seawater.

5. Waste Streams

The supernatant spent brine from the settling tanks and the filtrate (identical in composition to the former) are the two waste streams. Together, they amount to between 300 to 350 cubic meters per metric ton of magnesium hydroxide. These streams are usually neutralized with waste HCl prior to discharge. In the case of seawater, the waste stream is discharged into tide water. In the case of Michigan brines, the stream of spent brine is used to beneficially recover sodium and calcium chlorides or may be sent to injection wells.

6. EPA Source Classification Code

None established

7. References

Schambra, W. P. The Dow Magnesium Process at Freeport, Texas. Trans. Am. Inst. Chem. Eng. 41:35-51, January 1945.

CARBONATION/FILTRATION1. Function

- *a. For magnesium chloride production (Figure 4) - To form magnesium chloride solution from magnesium hydroxide, calcium chloride and carbon dioxide. The process includes the sequential steps of carbonation, thickening, filtration, displacement washing, and evaporation. Equipment consists essentially of a carbonation tank, thickeners, and filters (which may be of either the continuous rotary or the Moore type), and evaporators. The latter may be either steam-tube or vertical falling-film evaporators.
- b. For magnesium carbonate production (Figure 4) - To form either magnesium carbonate crystals [$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$] or basic magnesium carbonate [$5\text{MgO} \cdot 4\text{CO}_2 \cdot 6\text{H}_2\text{O}$] from a magnesium hydroxide slurry and carbon dioxide. Essential equipment includes a carbonating tank, and thickening and filtration equipment. The latter may be either Moore filters or continuous rotary vacuum filters.
- c. For Searles Lake brine (lower level) (Figure 8) - To form and to recover sodium bicarbonate from lower level brine of Searles Lake. Addition of carbon dioxide converts the sodium carbonate in solution to sodium bicarbonate. The sodium bicarbonate precipitates from solution and is removed by filtration.

The mechanism of carbonation (acidification in general) shifts the borax equilibrium from the soluble metaborate form to the crystallizable tetraborate form, resulting in an increased yield of borax. Sodium bicarbonate can be separated from the borax due to the metastability of borax at the lower supersaturations occurring in carbonation towers.

The process consists of sequential steps of carbonation, settling, filtration, and displacement washing.

Essential equipment consists of a series of carbonating towers, settling tanks, and continuous rotary filters.

- d. For production of soda ash by the Solvay Process (Figure 14) - to form and to remove sodium bicarbonate from a

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

sodium chloride brine saturated with ammonia. Addition of carbon dioxide causes sodium bicarbonate to precipitate from solution, with the formation of ammonium chloride in solution.

The process includes the steps of carbon dioxide compression, carbonation, filtration, and displacement washing.

Major equipment employed consists of:

- Centrifugal compressors for compressing stack gas and recycled carbon dioxide.
- Several carbonating towers in series ("Solvay Towers").
- Coolers for removing heat of reaction released in the carbonating towers. These are either tube-and-shell exchangers, submerged pipe coils, or water-sprayed pipe banks.
- Filtration equipment, either rotary vacuum filters or centrifuges.

2. Input Materials

- a. Washed magnesium hydroxide, calcium chloride solution, and carbon dioxide (flue gas or lime-kiln stack gas) are fed to the process in the quantities listed, as metric tons per metric ton of $MgCl_2$ product, assuming 100% recovery efficiencies:

$Mg(OH)_2$	-----	0.61
$CaCl_2$	-----	1.16
CO_2	-----	0.46

(equivalent to 250 cubic meters of free, 100% CO_2)

- b. Washed magnesium hydroxide and carbon dioxide (flue gas or lime kiln stack gas) are fed to the process in the quantities listed, as metric tons per metric ton of $MgCO_3 \cdot anh.$ product, assuming 100% recovery efficiencies:

$Mg(OH)_2$	-----	0.7
CO_2	-----	0.5

(equivalent to 280 cubic meters of free, 100% CO_2)

- c. Raw brine from the lower structure and carbon dioxide (flue gas, plus recycled calciner gas) are fed to the process in the estimated quantities shown per ton of soda ash produced:

Raw brine-----20 cubic meters
 Make-up CO₂-----0.1 metric ton
 (50 cubic meters of free, 100%
 CO₂)

- d. Ammonia-saturated sodium chloride brine and carbon dioxide (flue gas plus lime kiln stack gas) are fed to the process. The quantities of materials actually consumed in the process (weight entering minus weight leaving) per metric ton of soda ash produced are estimated as follows:

NaCl-----1.1 metric tons
 CO₂-----0.5 metric ton

Total quantities of materials entering the process, in metric tons per metric ton of soda ash produced are estimated as follows :

NaCl-----1.5 metric tons
 NH₃-----0.5 metric ton
 CO₂-----1.2 metric tons

The numbers given above indicate the considerable quantities of materials that are required to be recycled.

3. Operating Parameters

- a. The process is conducted at atmospheric temperatures and pressures. Flue gas is required at a typical gage pressure of about one kg/cm².
- b. Process is conducted at atmospheric temperatures and pressures. Flue gas or lime kiln stack gas is required at gage pressure of about 1 kg/cm².
- c. Process operates at atmospheric temperature and atmospheric pressure, except for the flue gas (12% CO₂) and recycled carbon dioxide from calciners (about 75% CO₂) which is required at approximately 3 kg/cm² gage pressure.

Carbonating towers are approximately 7 meters in diameter x 21 meters high. Six towers are required to produce approximately 180 metric tons per day of soda ash. Three primary towers intake 12% CO₂ and three secondary towers intake 75% CO₂. Towers are operated as fully-flooded bubble towers. Dorr thickening tanks and rotary vacuum drum filters are used.

- d. Maximum temperature of carbonation is controlled to 28°C, and pressures at the top of carbonating towers are slightly greater than atmospheric.

Towers are 28 meters high and are operated as liquid-filled bubble towers, in series-connected pairs. Strong CO₂ (73 to 77%), recycled from calciners, enters the bottom of secondary towers. Lime kiln stack gas (37 to 42% CO₂) enters the middle of the secondary towers and also the base of the primary towers. Nitrogen, containing 3 to 7% CO₂, is collected from the top of both towers and recycled to the ammonia absorption system. Carbon dioxide gas pressures of 3.2 kg/cm² are required.

Conversion of sodium chloride approximates 75% per pass. The presence of about 80% more ammonia than is stoichiometric is required in the feed.

4. Utilities

- a. Total electric power requirement is estimated to be 90 to 100 kWh per metric ton of MgCl₂, most of which is used for carbon dioxide (flue gas) compression.

Fresh water for displacement washing of calcium carbonate filter cake is estimated at 1.1 cubic meter per metric ton of magnesium chloride.

- b. Total electric power requirement is estimated to be 100 to 120 kWh per metric ton of magnesium carbonate, most of which is consumed in flue gas compression.

Fresh water for displacement washing of magnesium carbonate filter cake is estimated at 0.8 cubic meter per metric ton of magnesium carbonate.

A heat source, usually low pressure steam, is needed to heat to boiling the slurry of MgCO₃•3H₂O prior to its filtration in the case of basic magnesium carbonate production. This is estimated to be between 500,000 and 600,000 kcal per metric ton of basic magnesium carbonate.

- c. Total electric power requirement is estimated to be 100 to 120 kWh per metric ton of soda ash produced, most of which is consumed in compression of CO₂-bearing gases.

Fresh water required for displacement washing of bicarbonate filter cake is estimated at 0.1 cubic meter per metric ton of soda ash. Cooling water is required to remove 350,000 to 450,000 kcal per metric ton of soda ash produced.

- d. Total electric energy requirement is estimated to be 150 kWh per metric ton of soda ash, most of which is consumed in compressing CO₂-bearing gases.

Fresh water required for displacement washing of bicarbonate filter cake is inferred from published information to be between 0.05 and 0.15 cubic meter per metric ton of soda ash.

5. Waste Streams

- a. Carbon dioxide is vented to the atmosphere from the carbonating tanks (Figure 4).

An undisclosed fraction of the spent wash water from the filters is wasted to the main spent brine system for eventual injection to the brine source formation. Principal dissolved constituent is magnesium chloride.

Sole solid waste is calcium carbonate filter cake. Depending on economics, this is used to produce lime and carbon dioxide, or is slurried in water and ponded, eventually becoming landfill. This amounts to approximately 0.05 metric tons of solids per metric ton of magnesium chloride.

- b. Carbon dioxide is vented to the atmosphere from the carbonating tanks (Figure 4).

Filtrate from the magnesium carbonate filters is the sole liquid waste stream. This quantity is estimated to be 6 to 10 cubic meters per metric ton of magnesium carbonate.

- c. Carbon dioxide from the top of secondary absorber towers constitutes the sole atmospheric emission (Figure 8).

There are no solid wastes emitted.

There are no liquid waste streams. Clears from thickening tanks and filtrate from bicarbonate filters are forwarded to Process 10 for borax recovery; spent wash water is recycled to carbonating towers.

- d. Approximately 0.05 kg of gaseous ammonia per metric ton of soda ash enters the atmosphere during transfer of sodium bicarbonate filter cake to Process 12 (Figure 14).

There are no liquid or solid waste streams.

6. EPA Source Classification Code

- a. None established
- b. None established
- c. 3-01-021-02 Handling
- d. 3-01-021-02 Handling

7. References

- a. Boeglin, A. F., and T. P. Whaley. Magnesium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. New York, John Wiley & Sons, Inc., 1967. 12:708-736.

- b. Havighorst, C. R., and S. L. Swift. Magnesia Extraction from Seawater. Chem. Eng. New York. 72:84-86, September 2, 1965.

Schambra, W. P. The Dow Magnesium Process at Freeport, Texas. Trans. Amer. Inst. Chem. Eng. 41:35-51, January 1945.

Schreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw Hill, 1967. 183-185.

- c. Bixler, G. H., and D. L. Sawyer. Boron Chemicals from Searles Lake Brines. Ind. Eng. Chem. 49:322-333, March 1965.

Hightower, J. V. New Carbonation Technique - More Natural Soda Ash. Chem. Eng. 58:162-163, May 1951.

Nies, N. P. Boron Compounds (Oxides, Borates). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, John Wiley & Sons, Inc., 1964. 3:608-652.

Plant Expansion at Trona Boosts Soda Ash and Borax Capacity. Chem. Eng. 56:102-103, April 1949.

- d. Deutsch, Z. G., C. C. Brumbaugh, and F. H. Rockwell.
Alkali and Chlorine Industry. In: Kirk-Othmer
Encyclopedia of Chemical Technology, 2nd Edition.
Standen, A. (ed.). New York, John Wiley & Sons, Inc.,
1963. 1:668-758.

Shreve, R. N. Chemical Process Industries, 3rd
Edition. New York, McGraw-Hill, 1967. 227-231.

SOLIDIFICATION

1. Function

The process yields some solid form of the desired material from solution:

- *a. Magnesium chloride in the form of 50% flake and anhydrous powder from nominally 30% magnesium chloride liquor. (See Figure 4).
- b. 78% calcium chloride flake from 78% calcium chloride liquor. (See Figure 9).
- c. Calcium chloride in the forms of 78% flake, 78% pellets and anhydrous flake from Michigan brines (See Figure 11).
- d. Sodium hydroxide in the forms of flake, beads and drummed solid from 73% sodium hydroxide solution. (See Figure 15).
- e. Magnesium chloride in the form of electrolysis cell feed (See Figure 20).

The following sequential steps are included in the process:

- a. Evaporation (30% to 50% $MgCl_2$)
Flaking
Drying (if anhydrous form is desired)
Packaging (in bags)
- b. Flaking
Packaging (in bags)
- c. Flaking
Drying (if anhydrous form is desired)
Packaging (in bags)
- d. Evaporation (to molten 99.5% solid), or
Flaking (to 99% flakes), or
Pelletizing
Packaging (in drums)

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

- e. Flaking
Drying

Major equipment generally consists of the following:

- a,b,c: Steam-heated "boil-down" kettles
- a,b,c,d,e: Water-cooled flaking rolls
- a,c,e: Shelf dryer or fluidized-bed dryer
- d: Flash-type, tube evaporators;
gas-fired furnaces; "shot-towers"
- a,b,c: Standardized drumming equipment for
single-trip drums

2. Input Materials

- a. Concentration of feed liquor may vary between 20% and 30% magnesium chloride. Quantity required, in cubic meters per metric ton of product:

For 50% flake: 2 to 2.5
For anhydrous flake: 4 to 5
- b. Quantity of 78% CaCl_2 feed liquor per metric ton of 78% flake is approximately 0.6 cubic meter.
- c. Quantity of 78% CaCl_2 feed liquor in cubic meters per metric ton of product:

For 78% CaCl_2 flake: approximately 0.6
For anhydrous flake: approximately 0.7
- d. Quantity of 73% sodium hydroxide solution required per metric ton of any one of the three solid forms (drummed solid, flake or beads) is approximately 0.8 cubic meter.
- e. Quantity of 50% magnesium chloride liquor required per metric ton of magnesium metal produced is 6 cubic meters.

3. Operating Parameters

- a. Process operates at atmospheric pressure. Temperature of boiling 50% MgCl_2 liquor in boil-down kettles is in the range of 155°C to 175°C (46% to 50% MgCl_2). A typical size for a flaking roll is 1 meter diameter x 1.25 meters long, water-cooled internally.
- b,c. Process operates at atmospheric pressure. Temperature range of the boiling nominally 78% CaCl_2 liquor in open boil-down kettles is 187°C to 195°C.

- d. Process operates at various temperatures and pressures. Typical are:
- 120°C and slightly greater than atmospheric pressure for 73% NaOH entering gas-fired tube furnaces.
 - 480°C and approximately 370 mm. Hg absolute pressure for NaOH stream inside tube furnaces.
 - 500°C and 150 mm. Hg absolute pressure for molten anhydrous NaOH inside vacuum flash tank.
 - 400°C and atmospheric pressure for molten anhydrous NaOH entering "shot tower", or flowing to flaker roll.
- e. Process operates at atmospheric pressure. Typical temperatures are:
- 155°C to 175°C in boil-down kettles and 175°C for flaking-roll feed.
 - 180°C to 250°C temperature range of air to shelf driers or spray driers.

4. Utilities

Utilities consumed by each of the applications of Process 9 are shown in Table 1.

5. Waste Streams

- a. NaCl crystals precipitated during the concentration step amount to approximately 20 kg NaCl per metric ton of 50% MgCl₂ flake produced. The NaCl crystals are removed in filter presses, slurried in water, and are eventually injected into the producing formation.

If anhydrous MgCl₂ flake is produced, entailing further drying of the 50% flake in an atmosphere of HCl, atmospheric emissions of gaseous HCl usually result. No quantitative information is available.

Detectable quantities of MgCl₂ particles and HCl vapor constitute an atmospheric emission from boil-down kettles and flaking rolls.

- b,c. Atmospheric emissions of HCl vapor are possible at flaking-roll temperature resulting from catalyzed decomposition of CaCl₂. No quantitative information is available.

Table 1. UTILITIES CONSUMED BY VARIOUS APPLICATIONS OF PROCESS 9

Process application	Per metric ton of:	Fuel gas, 10 ³ kcal	28 kg/cm ² steam 10 ³ kcal	Electrical energy kWh	Cooling water cu.m.	Remarks
a.	50% MgCl ₂ flake	None	1000 - 1500	5 - 10	8 - 15	30% MgCl feed, boil-down kettles, flaker
b., c.	78% CaCl ₂ flake	None	<10	5 - 10	10 - 15	Flakers
d.	NaOH flake	800 - 1000	<10	20 - 40	20 - 30	Tube furnace, flash tank, flaker
e.	Mg metal	4000 - 5000	None	70 - 140	80 - 160	Flaker and shelf dryer

- d. No waste streams or emissions
- e. Detectable amounts of undivulged quantities of HCl, MgCl_2 particles and MgO particles are present in the exhaust air stream from MgCl_2 dryers of any type, whether spray dryers, shelf dryers, or fluidized-bed dryers.

Detectable amounts of MgCl_2 particles and HCl vapor constitute an atmospheric emission from boil-down kettles and MgCl_2 flakers.

A bleed stream from the recycled liquor from the scrubber towers of MgCl_2 dryers of any type constitutes a liquid waste. The main flow of scrubber tower effluent is recycled to Process 58, but the bleed-stream is neutralized with NaOH and is either discharged into tidewater, or sent to injection wells. Composition of the bleed-stream is typically 2% HCl and 3% MgCl_2 in aqueous solution. Its quantity is in the range of 10 to 20 liters per metric ton of Mg metal produced.

6. EPA Source Classification Code

a,b,c,d,e: None established

7. References

- a. Boeglin, A. F. and T. P. Whaley. Magnesium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. New York, John Wiley & Sons, Inc., 1967. 12:708-736.
- b,c,d. Deutsch, Z. G., C. C. Brumbaugh, and F. H. Rockwell. Alkali and Chlorine Industry. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, John Wiley & Sons, Inc., 1963. 1:668-758.
- e. Schambra, W. P. The Dow Magnesium Process at Freeport, Texas. Trans. Am. Inst. Ch. Eng. 41:35-51, January 1945.

EVAPORATION/CRYSTALLIZATION1. Function

Essentially, the process creates at least two physically separable phases from a single input material, for example, the formation of sodium chloride crystals plus mother liquor from sodium chloride brine. The separation and recovery of the phases may occur in another process, or be effected in subsequent steps of this process. If separation is accomplished in this process, then any or all of the following steps may be included:

- Evaporation
- Crystallization
- Dissolution
- Filtration
- Centrifuging
- Displacement washing
- Decantation washing
- Thickening
- Exchange cooling and heating
- Evaporative cooling
- Drying (of filter cakes on filter drum)
- Chemical reaction

The process steps named may be arranged in any sequence and may occur several times. Many internal recycle flows may be required.

Generally the fundamental process steps are evaporation and crystallization, occurring almost always in the order named.

In the present context, the process may involve many separate flows of both input materials and intermediate products. Also, two of the input materials may chemically react; for example, magnesium hydroxide with sulfuric acid in the production of Epsom salt.

The process may include any of the following equipment:

- Horizontal steam-tube evaporators
- Vertical-tube evaporators
- Falling-film evaporators
- Boil-down kettles
- Direct-fired evaporators

Submerged combustion evaporators
Vacuum crystallizers
Crystallizing pans
Moore filters
Vacuum drum filters
Belt filters
Pressure filters
Centrifuges
Thickener tanks
Dissolving tanks
Vacuum coolers
Heat exchangers

Table 2 lists the specific functions of the various applications of Process 10.

2. Input Materials

Table 3 lists the compositions of the input materials, and the quantity of each consumed per metric ton of principal end-product, for each of the applications of Process 10.

3. Operating Parameters

- *a. •Neutralization of $\text{Mg}(\text{OH})_2$ conducted at atmospheric temperature and pressure.
•Evaporation of MgSO_4 liquor commences at 105°C in multi-effect evaporators and crystallization of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ at $50^\circ\text{--}60^\circ\text{C}$ (estimated) in vacuum crystallizers.
•Equipment sized for 100-200 metric tons per day.
- b. •Evaporation of NaCl brine in multi-effect basket-type evaporators commences at about $110^\circ\text{--}120^\circ\text{C}$ and crystallization is at 600 to 700 mm. Hg vacuum.
•Equipment sized for about 200-250 metric tons NaCl per day; evaporators are about 3 to 4 meters diameter by about 12 to 13 meters high.
- c. •Process generally conducted at atmospheric pressure.
•Low temperature (estimated 10°C) required if process involves separation of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals.
•Actual crystallization paths employed are not disclosed.
- d. •Open boil-down kettles operate at atmospheric pressure and inside a temperature range of 155°C to 175°C for 46 to 50% MgCl_2 liquor.

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

Table 2. FUNCTION OF VARIOUS APPLICATIONS OF PROCESS 10

Process application	Process shown on fig:	Produces:	From:	Equipment used; remarks
*a.	4	Epsom salt crystals ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$)	$\text{Mg}(\text{OH})_2$ filter cake & H_2SO_4	Lined, agitated tanks; vert- tube evaporators; vacuum X-tallizers; vacuum rotary filters
b.	5	Refined salt crystals (NaCl)	Crude "solar" salt	Multi-effect, vert.-tube evaps. w/salt chest. vacuum filter-dryer
c.	6	1) K_2SO_4 crystals, 2) Na_2SO_4 crystals, and 3) MgCl_2 -rich mother- liquor	Several complex salts of Na, K, Mg, SO_2 , Cl	Probably vacuum X-tallizers; no factual information
d.	6	1) 46% MgCl_2 liquor, and 2) Waste NaCl crystals	30% MgCl_2 bittern	Probably open boil-down kettles; operation may now be inoperative
e.	7	1) Br-rich KCl brine, 2) Li-rich burkeite liquor 3) KCl crystals, 4) Crude borax, 5) Na_2SO_4 crystals, and 6) $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ crystals	Upper-level Searles Lake brine; various mother liquors	Multiple-effect evaporators, vacuum crystallizers, rotary vacuum filters, centrifuges, pachuca tanks, thickening tanks

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

Table 2 (Continued). FUNCTION OF VARIOUS APPLICATIONS OF PROCESS 10

Process application	Process shown on fig:	Produces:	From	Equipment used; remarks
f.	8	1) Crude borax, and 2) Borax mother-liquor	Borax-rich liquor	Refrig. X-tallizer; Dorr thickeners; Oliver filters
g.	8	1) Crude boric acid, and 2) $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$ liquor	Aqueous strip-liquor from Process 18	2-effect evap.-X-tallizers; carbon adsorption column; heat exchangers
h.	9	1) 78% CaCl_2 liquor 2) NaCl crystals (wasted)	35% CaCl_2 bittern from Salduro Marsh brine	Either boil-down kettles or vert.-tube evap.; minor amount NaCl ppts.
i.	9	1) Moist Na_2SO_4 crystals, and 2) Recycled mother-liquor	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals	Submerged-combustion evap.; minor amount recycled
j.	11	1) Undried NaCl crystals, 2) 32% CaCl_2 liquor, and 3) 78% CaCl_2 liquor	Mg-free $\text{CaCl}_2\text{-NaCl}$ brine	Vert.-tube evaporators
k.	15	1) 50% NaOH, 2) 73% NaOH, and 3) NaCl crystals	9% NaOH cell effluent; 50% NaOH from Hg-cells (for 73% NaOH only)	Vert.-tube steam evaps.; gas-fired falling-film
l	16	1) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, undried, or 2) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$, undried	Crude $\text{Na}_2\text{B}_4\text{O}_7$ liquor, or crude borax crystals	Vert.-tube evaps., vacuum crystallizers, centrifuges; pressure-filters; settling tanks; hydroclones

Table 2 (Continued). FUNCTION OF VARIOUS APPLICATIONS OF PROCESS 10

Process application	Process shown on fig:	Produces:	From:	Equipment used; remarks
m.	16	1) Undried H_3BO_3 , and 2) Na_2SO_4 liquor	$Na_2B_4O_7 \cdot 10H_2O$ crystals (or liquor); H_2SO_4	Rubber-lined, agitated tanks, vacuum crystallizers, centrifuges.
n.	18	1) Moist K_2SO_4 crystals, 2) $MgCl_2$ liquor, and 3) $NaCl$ (waste)	KCl (crystals or brine), and leached, low-salt langbeinite	Agitated dissolving tanks, thickening tanks, Oliver filters, Bird continuous centrifuges, vert.-tube evaps., vacuum crystallizers
o.	19	1) Purif. trona crystals ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$)	Purif. trona liquor	Struthers-Wells evap.-crystallizers, hydroclones, cont. centrifuges
p.	19	$Na_2CO_3 \cdot H_2O$ crystals	Purif. Na_2CO_3 liquor	Evaporator-crystallizers thickening tanks, cont. centrifuges, carbon-packed adsorption column
q.	21	Doubly-refined $NaCl$ brine	Purif. $NaCl$ brine	Vac. crystallizing evaps.; vacuum filters
r.	22	$LiCl$ crystals	Either: Li_2CO_3 , or $LiOH$, and aqueous HCl	Batch equipment: probably open boil-down kettles with steam coils; vac. evaporators may be used; heated crystallizing pans

Table 2 (Concluded). FUNCTION OF VARIOUS APPLICATIONS OF PROCESS 10

Process application	Process shown on fig:	Produces:	From:	Equipment used; remarks
s.	22	NaI-NaIO ₃ crystal mixture	Iodine crystals, and 50% NaOH	Batch equipment: porcelain bathtubs with steam coils; vac. filter; manual transfer
t.	22	Purified moist NaI crystals	Fused, crude, NaI (lumps)	Batch equipment, identical to "s", above
u.	22	Fe ₃ Br ₈ ·16H ₂ O crystals	Liquid Br ₂ , iron borings & turnings, water	Batch equipment: porcelain bathtubs with steam coils; vacuum filters; manual transfer
v.	23	1) Moist NaClO ₃ crystals 2) NaCl crystals 3) Mother liquor	Electrolysis cell effluent cont'g 200-600 g/l NaClO ₃	Sand filter for removing graphite; double-effect evap.; crystallizer-tanks; belt filter for NaCl; centrifuge for NaClO ₃
w.	24	1) Undried LiOH·H ₂ O crystals, and 2) 50% NaOH solution	Crude LiOH liquor	Probably vert.-tube evaps. and vac. crystallizers
x.	24	Undried Li ₂ CO ₃ crystals, Na ₂ SO ₄ (salt cake), and mother liquor (recycled)	20% Li ₂ SO ₄ liquor	Agitated reaction tanks, batch centrifuges; refrigerated crystallizers; probably submerged comb. evaps. for Na ₂ SO ₄

Table 3. INPUT MATERIALS TO VARIOUS APPLICATIONS OF PROCESS 10

Process application	Major input materials		Remarks
	Material and approximate composition	Quantity consumed per m. ton of (product)	
* a.	1) $\text{Mg}(\text{OH})_2$ filter cake: 50% $\text{Mg}(\text{OH})_2$ 2) 77% H_2SO_4 3) H_2O	1) 0.5 m. ton; ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) 2) 0.3 cu.m. ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) 3) 1 cu. m. ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$)	Estimated
b.	Crude "solar" salt: 99% NaCl	1.02 m. ton; (refined NaCl)	Estimated
c.	Total solids input: astrakanite leonite kainite carnallite	4.8 m. ton; (K_2SO_4)	Estimated. 3-5 cu.m. process water req'd.
d.	MgCl_2 bittern: 30% MgCl_2 0.5% NaCl	5 cu.m.; (46% MgCl_2 liquor)	Estimated. 1 m. ton process water req'd.
e.	Searles Lake brine (upper level), ppm: Na - 111,000 K - 26,000 Li - 80 Cl - 121,000 SO_4 - 45,000 CO_3 - 27,000 Br - 850 B_4O_7 - 12,200	900 cu.m. (Br_2) 1,900 cu.m. (Li_2CO_3) 35 cu.m. ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$) 17 cu.m. (KCl) 12 cu.m. (Na_2SO_4) 16 cu.m. (Na_2CO_3)	Approximate stoichiometric requirements. Process water is required for many re-crystallizations in this process. Quantitative information is unavailable.

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

Table 3 (Continued). INPUT MATERIALS TO VARIOUS APPLICATIONS OF PROCESS 10

Process application	Major input materials		Remarks
	Material and approximate composition	Quantity consumed per m. ton of (product)	
f.	NaHCO ₃ mother liquor: 2.1% Na ₂ B ₄ O ₇ 3.2% KCl 7% Na ₂ SO ₄ 17% NaCl	25 cu.m.; (Na ₂ B ₄ O ₇ ·5H ₂ O)	Value inferred
g.	Strip liquor: 9% H ₃ BO ₃ 7% K ₂ SO ₄ 24% Na ₂ SO ₄	8.5 cu.m.; (H ₃ BO ₃)	Gross estimate; handbook values; inferred conditions
h.	35% CaCl ₂ liquor: approximately 1.5% NaCl	1.6 cu.m.; (78% CaCl ₂ flake)	Estimated
i.	Na ₂ SO ₄ ·10H ₂ O crystals	2.3 m. tons; (Na ₂ SO ₄)	Approximate stoichiometric amount
j.	CaCl ₂ solution (35%-40%) approximately 1.5% NaCl	1.6 cu.m.; (78% CaCl ₂ flake)	This process may also occur prior to Mg(OH) ₂ recovery
k.	Cl ₂ -cell effluent (diaphragm cells only), approx.: NaOH - 9% NaCl - 15%	9 cu.m.; (NaOH flake)	
	Decomposer effluent (Hg-cells only): NaOH - approx. 50%	1.3 cu.m.; (NaOH flake)	Process applies to Hg-cell operation only if 73% NaOH is produced.

Table 3 (Continued). INPUT MATERIALS TO VARIOUS APPLICATIONS OF PROCESS 10

Process application	Major input materials		Remarks
	Material and approximate composition	Quantity consumed per m. ton of (product)	
l.	1) Crude $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ crystals, or	1) 1.30 m. tons; ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$)	1) Theoretical basis
	2) Crude $\text{Na}_2\text{B}_4\text{O}_7$ liquor: approx. 30% $\text{Na}_2\text{B}_4\text{O}_7$	2) 1.9 cu.m.; ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$)	2) Gross estimate
m.	1) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (fines), and	1) 1.56 m. tons; (H_3BO_3)	1) Theoretical basis
	2) H_2SO_4	2) 2.4 m. tons; (H_3BO_3) (100% basis)	2) Theoretical basis
n.	1) KCl crystals: nominally 98% KCl, and	1) 0.6 m. tons; (K_2SO_4)	Process water required in unknown amounts.
	2) Low-salt langbeinite: (est'd 90% $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$)	2) 0.9 m. tons; (K_2SO_4)	
o.	Purif. trona liquor: $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ - 30% (estimated)	4.5 cu.m.; (Na_2CO_3)	Estimated for temperature of 100°C
p.	Purif. Na_2CO_3 liquor: approx. 32% Na_2CO_3	2.7 cu.m.; (Na_2CO_3)	Gross estimate
q.	Purif. NaCl brine	8.3 cu.m.; (Na metal)	Handbook value
r.	1) Li_2CO_3 crystals, or	1) 0.87 m. ton; (LiCl)	Stoichiometric amounts
	2) $\text{LiOH} \cdot \text{H}_2\text{O}$ crystals, and	2) 0.6 m. ton; (LiCl)	
	3) 30% HCl	3) 0.8 m. ton (anh. basis) (LiCl)	
	4) Water	4) 1-5 cu.m.; (LiCl)	
			4) Gross estimate.

Table 3 (Concluded). INPUT MATERIALS TO VARIOUS APPLICATIONS OF PROCESS 10

Process application	Major input materials		Remarks
	Material and approximate composition	Quantity consumed per metric ton of (product)	
s.	1) Iodine crystals, 2) 50% NaOH, and 3) Water	1) 0.9 m. ton; (NaI) 2) 0.5 m. ton; (NaI) 3) 1-5 cu.m.; (NaI)	Estimated 3) Gross estimate
t.	1) Fused NaI lumps 2) Water	1) 1.05 m. tons; (NaI) 2) 1-5 cu.m.; (NaI)	Estimated 2) Gross estimate
u.	1) Liquid Br ₂ , 2) Iron turnings, and 3) Water	1) 0.65 m. ton; (NaBr) 2) 0.21 m. ton; (NaBr) 3) 3 cu.m.; (NaBr)	Stoichiometric amounts Stoichiometric amounts
v.	1) Cell effluent: 200-600 g/l NaClO ₃ 2) BaCl ₂ for CrO ₄ ⁼ removal 3) Urea for ClO ⁻ removal	1) 2-3 cu.m. (NaClO ₃) 2) 1-2 kg (NaClO ₃) 3) 2-3 kg (NaClO ₃)	1) Depends on cell operation 2) Estimated 3) Estimated
w.	Crude LiOH liquor: 10% LiOH (estimated)	9 cu.m.; (LiOH)	Estimated
x.	1) Li ₂ SO ₄ liquor: 20% Li ₂ SO ₄ , 1% Na ₂ SO ₄ , and 2) Na ₂ CO ₃	1) 15 cu.m.; (Li ₂ CO ₃) 2) 1.45 m.ton; (Li ₂ CO ₃)	Estimated Stoichiometric amount

e. •Pressure - Generally, all process steps are conducted close to atmospheric pressure.

•Temperatures -

- 1) KCl brine, containing KBr, is made by dissolving KCl crystals; it leaves the process at 95° to 105°C (estimated) and is recycled to the process at 105° to 110°C (estimated).
 - 2) Burkeite liquor, containing Li values, is made from burkeite crystals; it exits from and re-cycles to the process within an estimated temperature range of 75° to 90°C.
 - 3) KCl is crystallized from KCl-Na₂B₄O₇ liquor (burkeite mother liquor) at 38°C.
 - 4) Borax pentahydrate is crystallized at 24°C; seeding required.
 - 5) Mixtures of burkeite, Na₂CO₃, NaCl, and NaLi₂PO₄ are crystallized from a mixture of raw brine plus mother liquor within an estimated range of 115° to 125°C. Na₂SO₄•10H₂O crystals are removed at 22°C, mixed with NaCl brine, and recrystallized as Na₂SO₄•anh. at 17°C.
 - 6) Na₂CO₃•10H₂O crystallized at 5°C.
Na₂CO₃•H₂O crystallized at 90° to 95°C (estimated).
- f. Process conducted at atmospheric pressure and at a temperature of 20°C to crystallize and filter off borax decahydrate.
- g. Atmospheric pressure; estimated temperature range is 50° to 60°C.
- h. Atmospheric pressure; estimated temperature is 185°C for 78% CaCl₂.
- i. Atmospheric pressure; estimated temperature of 110°C.
- j. •Process conducted in multiple-effect evaporators and in boil-down kettles.
- Temperature range is 60° to 185°C.

k. •Operating conditions:

For evaporating to 50% NaOH--

60° to 170°C temperature range and pressure range of 660 mm. Hg vacuum to 2 kg/cm² absolute pressure; liquor cooled to 20°C for final NaCl crystallization.

For salt extraction by liquid ammonia--

60°C and 28 kg/cm².

For evaporating to 73% NaOH--

132°C and 700 mm. Hg vacuum.

For producing anhydrous NaOH in tube furnace--

Most severe conditions are 330°C; atmospheric pressure.

•Ammonia makeup required for final NaCl removal by liquid ammonia extraction process is estimated at 2 kg NH₃ per metric ton of 100% NaOH.

- l. Vacuum-cooled; approximately 65°C for crystallizing borax pentahydrate; 35° to 50°C (estimated) for crystallizing borax decahydrate.
- m. Atmospheric pressure; estimated temperature range for crystallizing H₃BO₃ is 25° to 35°C.
- n. Atmospheric pressure; 25°C is optimum temperature for crystallizing K₂SO₄.
- o. •Range of pressures from initially atmospheric down to 700 mm. Hg vacuum; temperatures from 90°C (estimated) initial down to 60°C final.
•Na₂S added for corrosion control. Surfactants used to prevent foaming.
- p. Essentially atmospheric pressure; temperature of evaporation is maintained constant at approximately 100°C.
- q. Usual pressure range from 2 kg/cm² gage down to 680 mm. Hg vacuum, corresponding to temperature range of about 135°C down to 55°C.
- r. •Atmospheric pressure; estimated temperature range of evaporation is 110° to 120°C if boildown kettles are used.
•Crystallization temperature must be maintained above 95°C to prevent formation of LiCl•H₂O crystals.
- s. Atmospheric pressure; estimated evaporating temperature - 110° to 115°C; crystallization probably at room temperature.

- t. Atmospheric pressure; estimated evaporating temperature 110° to 115°C; crystallization probably at room temperature.
- u. Atmospheric pressure; evaporating temperature is probably less than 100°C to prevent decomposition of $\text{Fe}_3\text{Br}_8 \cdot 16\text{H}_2\text{O}$.
- v. •Temperature range in double-effect evaporators is probably 60° to 120°C, corresponding to approximately 0.2 to 1.5 kg/cm² absolute pressure.
•Temperature of NaClO_3 crystallization is estimated at 40° to 60°C.
- w. •Pressure range of triple effect-evaporation probably commences at 1 to 2 kg/cm² gage and finishes at 650 to 700 mm. Hg vacuum, corresponding to estimated boiling temperatures initially near 160°C and finally near 60°C.
•Final temperature of crystallization of $\text{LiOH} \cdot \text{H}_2\text{O}$ is probably in the range of 30° to 40°C.
•Recrystallization of $\text{LiOH} \cdot \text{H}_2\text{O}$ is necessary.
•NaOH mother liquor is recycled within the process for lithium recovery.
- x. •Atmospheric pressure; precipitation, filtration, and washing of Li_2CO_3 is conducted close to 100°C.
•Mother liquor is chilled close to 0°C for separation of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals. Latter are subsequently redissolved for crystallization of Na_2SO_4 in temperature range of 110° to 115°C, probably in submerged combustion evaporators.

4. Utilities

Utilities consumed by various applications of Process 10 are shown in Table 4.

5. Waste Streams

Table 5 lists the identity and estimated quantity of the principal waste streams associated with the various applications of Process 10.

6. EPA Source Classification Code

a. through z: None established

Table 4. UTILITIES CONSUMED IN VARIOUS APPLICATIONS OF PROCESS 10

Process application	Per metric ton of:	Electrical energy kWh	Heat 10^3 kcal (source)	Cooling water cu.m.	Others, or remarks
* a.	MgSO ₄ ·7H ₂ O	20 - 50	250 - 350 (steam)	8 - 25	Estimated values 1 cu.m. process water
b.	Refined NaCl	40 - 80	500 - 800 (steam)	25 - 50	Estimated values
c.	K ₂ SO ₄	50 - 100	200 - 500 (steam)	10 - 25	Gross estimates. Utilities required depend on degree of integration with solar evaporation. 3 to 5 cu.m. process water
d.	46% MgCl ₂ liquor	20 - 40	400 - 600 (steam)	nil.	Estimated values
e.	"Average product" **	30 - 200	300 - 1500 (steam)	20 - 100	Gross estimates
f.	Na ₂ B ₄ O ₇ ·5 H ₂ O	10 - 30	<1 m. ton (steam)	80 - 160	Gross estimates. Steam used for ejectors. 150 kcals removed by NH ₃ refrig. (net of regen. cooling)
g.	H ₃ BO ₃	50 - 150	500 - 1000 (steam)	25 - 75	Gross estimates

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

** Per metric ton of a composite of the individual products in the same proportion as they are represented in the total production of the operation.

Table 4 (Continued). UTILITIES CONSUMED IN VARIOUS APPLICATIONS OF PROCESS 10

Process application	Per metric ton of:	Electrical energy kWh	Heat 10 ³ kcal (source)	Cooling water cu.m.	Others, or remarks
h.	78% CaCl ₂ flake	2 - 5	1000 - 1500 (steam)	10 - 20	Gross estimates
i.	Salt cake (Na ₂ SO ₄)	4 - 6	800 - 1500 (fuel gas)	Minor amounts	Estimated values. Elec. energy chiefly for compressing combust. air
j.	Anh. CaCl ₂ flake	60 - 100	1300 - 2600 (steam)	70 - 140	Estimates assume all CaCl ₂ produced is anh. CaCl ₂ flake
k.	Solid NaOH	100 - 150	2000 - 3000 (steam)	10 - 15	Estimates assume all NaOH produced is anh. solid NaOH
l.	Na ₂ B ₄ O ₇ ·5H ₂ O	10 - 20	400 - 800 (steam)	30 - 60	Gross estimate, assuming all product is Na ₂ B ₄ O ₇ ·5H ₂ O
m.	H ₃ BO ₃	30 - 60	800 - 1600 (steam)	50 - 100	Gross estimate, assuming all product is H ₃ BO ₃ crystals
n.	K ₂ SO ₄	40 - 80	800 - 1600 (steam)	50 - 100	Gross estimates
o.	Soda ash (Na ₂ CO ₃)	15 - 30	20 - 40 (steam)	10 - 20 (additional to regen. cooling)	Gross estimates

Table 4 (Continued). UTILITIES CONSUMED IN VARIOUS APPLICATIONS OF PROCESS 10

Process application	Per metric ton of:	Electrical energy kWh	Heat 10^3 kcal (source)	Cooling water cu.m.	Others, or remarks
p.	Soda ash (Na_2CO_3)	30 - 60	500 - 800 (steam)	25 - 40	Estimated values; water requirement assumes no regen. cooling
q.	Na metal	100 - 200	1200 - 2000 (steam)	60 - 100	Estimated values
r.	LiCl crystals	20 - 40	700 - 1000 (steam)	None	Gross estimates
s.	NaI crystals	0.2 - 2	1000 - 2000 (steam)	None	Gross estimates; electrical energy for portable transfer pumps
t.	NaI crystals	0.2 - 2	1000 - 2000 (steam)	None	Same as for "s", above
u.	NaBr crystals	0.2 - 2	800 - 1600 (steam)	None	Gross estimate. Electr. energy for portable transfer pumps
v.	NaClO	40 - 60	400 - 800 (steam)	30 - 60	Gross estimate
w.	LiOH	80 - 160	2000 - 3000 (steam)	100 - 150	Gross estimate

Table 4 (Concluded). UTILITIES CONSUMED IN VARIOUS APPLICATIONS OF PROCESS 10

Process application	Per metric ton of:	Electrical energy kWh	Heat 10 ³ kcal (source)	Cooling water cu.m.	Others, or remarks
x.	Li ₂ CO ₃	100 - 150	300 - 600 (steam), plus 3000 - 4000 (fuel gas)	20 - 30	Gross estimates. Cooling H ₂ O and most of electrical energy for chilling mother-liquor and compressing combustion air, respectively. 30 x 10 ³ kcal of NH ₃ refrig. required to chill mother liquor to 0°C, assuming 80% regenerative cooling

Table 5. WASTE STREAMS RESULTING FROM VARIOUS APPLICATIONS OF PROCESS 10

Process application	Shown on fig:	Identity of Waste	Quantity of waste	Per m. ton of:	Disposition or remarks
a.	4	Mother liquor, containing NaCl & CaCl ₂	<10 liters	MgSO ₄ ·7H ₂ O	Intermittent bleed stream combined with main plant effluent & reinjected
b.	5	Mother liquor containing MgCl ₂ , CaCl ₂ , etc.	<10 liters	Refined NaCl	Minor bleed stream, discharged into tidewater
c.	6	1) NaCl (slurry or brine) 2) MgCl ₂ bittern	1) 0.5-1.0 m. tons NaCl 2) 0.5-3.0 m. tons MgCl ₂	K ₂ SO ₄	Both streams returned to Great Salt Lake. MgCl ₂ wasted only if none sold.
d.	6	NaCl (slurry)	0.2-0.3 m. tons NaCl	46% MgCl ₂	Returned to Great Salt Lake
e.	7	Slurry of NaCl in	3 - 7 cu. m.	"Average product"*	Gross estimate. Waste stream returned to Searles Lake
f.	8	Borax mother liquor ("spent brine")	15 - 25 cu. m.	Na ₂ B ₄ O ₇ ·5H ₂ O	Gross estimates. Discharged only during periods of low demand for Na ₂ SO ₄ and KCl. Returned to Searles Lake
g.	8		--	--	No waste streams

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

** Per metric ton of a composite of the individual products in the same proportion as they are represented in the total production of the operation.

Table 5 (Continued). WASTE STREAMS RESULTING FROM VARIOUS APPLICATIONS OF PROCESS 10

Process application	Shown on fig:	Identity of waste	Quantity of waste	Per m. ton of:	Disposition or remarks
h.	9	NaCl (crystals or slurry)	<.01 m. tons NaCl	78% CaCl ₂	Discharged to waste pond
i.	9	Atmosphere discharge: Smog of micron-size Na ₂ SO ₄ particles plus condensed water vapor	1000 - 2000 cu.m. smog at discharge point. <1 kg Na ₂ SO ₄ particles (est'd)	Na ₂ SO ₄	Discharge is <u>suspected condition only</u> . Particle size distribution unknown
j.	11	NaCl	1.3 - 1.6 m. tons (max., if no NaCl used beneficially)	Anh. CaCl ₂ flake	Estimate assumes all CaCl ₂ is anh. flake. NaCl is dissolved and sent to injection wells. <u>No discharge may exist if NaCl is sold or used</u>
k.	15	--	--	--	No waste streams
l.	16	--	--	--	No waste streams
m.	16	--	--	--	No waste streams
n.	18	1) NaCl brine 2) MgCl ₂ liquor: 14 - 15% MgCl ₂	<0.1 m. ton NaCl 2 - 3 cu.m.	K ₂ SO ₄ K ₂ SO ₄	Gross estimates
o.	19	--	--	--	No waste streams; Liquor recycled to Process 35.

Table 5 (Continued). WASTE STREAMS RESULTING FROM VARIOUS APPLICATIONS OF PROCESS 10

Process application	Shown on fig:	Identity of waste	Quantity of waste	Per m. ton of:	Disposition or remarks
p.	19	Bleed-stream: 32% Na ₂ CO ₃ solution	<10 liters	Na ₂ CO ₃	Gross estimate. Stream required to purge soluble impurities
q.	21	Bleed-stream: 26% NaCl solution	<10 liters	NaCl	Gross estimate. Stream required to purge soluble impurities
r.	22	Atmospheric emission of aqueous HCl mist	<1 liter liquid as droplets	LiCl	Suspected only, if Li ₂ CO ₃ used. Mist results from CO ₂ foam
s.	22	Iodine vapor	<0.1 kg I ₂	NaI	Small batch process
t.	22	1) Sludge or filter cake, mixture of: BaSO ₄ , Fe(OH) ₃ , Heavy metal sulfides 2) H ₂ S fumes (atmospheric emission)	<5 kg total solids	NaI	Small batch process, disposition unknown, probably buried. Gross estimate
			<0.1 kg H ₂ S	NaI	H ₂ S used to remove sulfides
u.	22	1) Bromine vapor (atmospheric emission) 2) Insol. residue from iron: C plus SiO ₂	<0.5 kg Br ₂ <1 kg	NaBr NaBr	Small batch process Gross estimate

Table 5 (Concluded). WASTE STREAMS RESULTING FROM VARIOUS APPLICATIONS OF PROCESS 10

Process application	Shown on fig:	Identity of waste	Quantity of waste	Per m. ton of:	Disposition or remarks
v.	23	1) BaCrO ₄ 2) Bleed stream	1) ~3 kg 2) ~1 liter	NaClO ₃ NaClO ₃	1) Disposition unknown 2) Surmised only; disposition unknown
w.	24	Suspended material from ore: R ₂ O ₃ , SiO ₂ , etc.	<1 kg	LiOH	Gross estimate. Cake from filter presses
x.	24	--	--	--	No waste streams

7. References

Process
Applic.

- a Boeglin, A. F., and T. P. Whaley. Magnesium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1967. 12:733.
- b VerPlank, W. E., and R. P. Heizer. Salt in California. Calif. Dept. of Nat'l. Res., Div. of Mines, Bulletin 175, San Francisco, 1958. 168 p.
- c Hadzeriga, P. Some Aspects of the Physical Chemistry of Potash Recovery by Solar Evaporation of Brines. Trans. Soc. Min. Eng. 229:169-174, June 1964.
- Potassium Chloride and Potassium Sulfate. Chem. Eng. 57:168-171, January 1950.
- c,d Smith, E. E., and H. J. Andrews, Mining Great Salt Lake A \$75 Billion Reserve of Lithium, Magnesium, Potash, and Sodium Salts. Unpublished paper presented at Meeting of Am. Inst. Min. Eng., Los Angeles, February 21, 1967.
- e Bach, R. D., C. W. Kamienski, and R. B. Elliott. Lithium and Lithium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York Interscience Publishers, 1967. 12:530-546.
- Bixler, G. H., and D. L. Sawyer. Boron Chemicals from Searles Lake Brines. Ind. Eng. Chem. 49:322-333, March 1957.
- Jacobs, J. J. Potassium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1968. 16:371-397.
- Mumford, R. W. Potassium Chloride from the Brine of Searles Lake. Ind. Eng. Chem. 30:872-877, August 1938.
- Hies, N. P. Boron Compounds (Oxides, Borates). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York Interscience Publishers, 1964. 3:621-650.

- e Plant Expansion at Trona Boosts Soda Ash and Borax Capacity. Chem. Eng. 56:102-103, April 1949.
- Robertson, G. R. Expansion of the Trona Enterprise. Ind. Eng. Chem. 34:133-137, February 1942.
- Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1967. 905 p.
- Teeple, J. E. The Industrial Development of Searles Lake Brine. ACS Monograph Series, No. 19, New York, Reinhold, 1929. 182 p.
- Turrentine, J. W. Potash in North America. ACS Monograph Series, No. 91. New York, Reinhold, 1943. 186 p.
- Woodmansee, W. C. The Mineral Industry of California. In: Minerals Yearbook 1971, Schreck, A. E. (ed.). Washington, U. S. Dept. of Interior, Bur. of Mines, 1973. 2:119-168.
- f Bixler, G. H., and D. L. Sawyer. Boron Chemicals from Searles Lake Brines. Ind. Eng. Chem. 49:322-333, March 1957.
- Hightower, J. V. New Carbonation Technique - More Natural Soda Ash. Chem. Eng. 58:162-163, May 1951.
- Mumford, R. W. Potassium Chloride from the Brine of Searles Lake. Ind. Eng. Chem. 30:872-877, August 1938.
- Nies, N. P. Boron Compounds (Oxides, Borates). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1964. 3:621-650.
- Plant Expansion at Trona Boosts Soda Ash and Borax Capacity. Chem. Eng. 56:102-103, April 1949.
- Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1967. 905 p.
- Turrentine, J. W. Potash in North America. ACS Monograph Series, No. 91. New York, Reinhold, 1943. 186 p.
- Woodmansee, W. C. The Mineral Industry of California. In: Minerals Yearbook 1971, Schreck, A. E. (ed.). Washington, U. S. Dept. of Interior, Bur. of Mines, 1973. 2:119-168.

- g Havighorst, C. R. New Process Separates Borates from Ore by Extraction. Chem. Eng. (New York). 70:228-232, November 11, 1963.
- Woodmansee, W. C. The Mineral Industry of California. In: Minerals Yearbook 1971, Schreck, A. E. (ed.). Washington, U. S. Dept. of Interior, Bur. of Mines, 1973. 2:119-168.
- h Hadzeriga, P. Some Aspects of the Physical Chemistry of Potash Recovery by Solar Evaporation of Brines. Trans. Soc. Min. Eng. 229:169-174, June 1964.
- i Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley and Sons, 1965. 852 p.
- j VerPlank, W. E., and R. F. Heizer. Salt in California. Calif. Dept. of Nat'l. Res., Div. of Mines, Bulletin 175, San Francisco, 1958. 168 p.
- k Deutsch, Z. G., C. C. Brumbaugh, and F. H. Rockwell. Alkali and Chlorine Industry. In: Kirk-Othmer Encyclopedia of Chemical Technology, Standen, A. (ed.). New York, Interscience Publishers, 1963. 1:671-702, 740-756.
- l Bixler, G. H., and D. L. Sawyer. Boron Chemicals from Searles Lake Brines. Ind. Eng. Chem. 49:322-333, March 1957.
- Nies, N. P. Boron Compounds (Oxides, Borates). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1964. 3:621-650.
- m Bixler, G. H., and D. L. Sawyer. Boron Chemicals from Searles Lake Brines. Ind. Eng. Chem. 49:322-333, March 1957.
- Nies, N. P. Boron Compounds (Oxides, Borates). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1964. 3:621-650.
- n Harley, G. T., and G. E. Atwood. Langbeinite, Mining and Processing. Ind. Eng. Chem. 39:43-48, January 1947.

- n Jacobs, J. J. Potassium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1968. 16:371-397.
- Potassium Chloride and Potassium Sulfate. Chem. Eng. 57:168-171, January 1950.
- Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1967. 905 p.
- Turrentine, J. W. Potash in North America. ACS Monograph Series, No. 91. New York, Reinhold, 1943. 186 p.
- White, N. C., and C. A. Arend, Jr. Potash Production at Carlsbad. Chem. Eng. Progr. 46:523-530, October 1950.
- o,p Rau, E. Sodium Compounds (Carbonates). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1969. 18:458-468.
- q Lemke, C. H. Sodium. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1969. 18:432-457.
- Sittig, M. Sodium Its Manufacture, Properties, and Uses. ACS Monograph Series, No. 133. New York, Reinhold, 1956. p. 33.
- r Bach, R. D., C. W. Kamieniski, and R. B. Elletstad. Lithium and Lithium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1967. 12:530-546.
- s,t Jacobs, J. J. Potassium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1968. 16:371-397.
- Two Men and a Tub, Chem. Wk. 73:77-83, December 5, 1953.

- u Jacobs, J. J. Potassium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1968. 16:371-397.
- v Clapper, T. W., and W. A. Gale. Chloric Acid and Chlorates. In: Kirk-Othmer Encyclopedia of Chemical Technology, Standen, A. (ed.). New York, Interscience Publishers, 1964. 5:50-59.
- Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1967. 905 p.
- w,x Bach, R. D., C. W. Kamienski, and R. B. Ellestad. Lithium and Lithium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1967. 12:530-546.
- Luckenback, W. F. Lithium (Annual Review, 1967). Eng./Min. J. 168:152, February 1967.

DRYING

1. Function

The process removes, almost always by evaporation, at least a portion of the water contained in the input material, thereby yielding a product of lower total water content. "Drying" generally involves only the removal of "free" water, as opposed to the intended function of "Drying/Calcination" (Process 12), which generally alters the input composition in additional ways, including the removal of combined water.

Input materials may be liquids or solids, but the product is always a solid. The product of the drying process is usually the end product of the operation, but in some cases may be an intermediate product, transferred to a subsequent process.

The process may occasionally include the following additional steps:

- Grinding
- Cooling
- Screening

The specific type of equipment used in drying processes depends both on economics and on the chemical and physical nature of the substances involved. The equipment types in general use in the various applications of Process 11, described below, include:

- Rotary - direct fired
 - externally heated
 - steam-coil heated
 - cocurrent
 - countercurrent
 - double-cone (batch)
- Shelf
- Tray
- Pan
- Tunnel
- Spray
- Fluidized bed
- Belt
- Hot-air drying cycle on continuous filters

Most of the types of dryers mentioned above may be operated in continuous, intermittent-continuous, or batch modes, and are represented in a wide range of production capacities. Double-cone and tray dryers are usually for small outputs and are usually operated batchwise.

The specific function and type of dryer used in each of the applications of Process 11 are listed in Table 6.

Rotary coolers are usually used for cooling the dried product, although water-jacketed trough-and-screw coolers are sometimes employed.

2. Input Materials

The identity and estimated quantity of the respective input materials fed to the various applications of Process 11 are listed in Table 6.

3. Operating Parameters

Operating temperatures are listed in Table 7.

4. Utilities

Quantities of heat and electrical energy consumed are listed in Table 7.

5. Waste Streams

All types of solids-drying equipment, when producing dry bulk solids, invariably release particulate matter to the atmosphere as a fugitive emission. Most frequently, fine particles of the substance being dried are carried suspended in the exhaust air issuing from the dryer. Even when little or no air is used as the direct heating agent, as is the case with a steam-coil dryer or a double-cone dryer, dusts arise in the discharging and the immediately subsequent handling of the dried product.

Generally, direct-fired rotary dryers generate the highest absolute quantity of particulate matter per unit of product. Conversely, indirectly heated dryers, represented by steam-tube or double-cone rotating types, usually produce the smallest amount of dust per unit of product.

Table 6. FUNCTION AND INPUT MATERIALS FOR APPLICATIONS OF PROCESS 11

Process Applic.	Shown on Fig.	Produces	Type of Equipment	Input Material: Amount used in m. tons per m. ton of (product)	Remarks
* a	4	MgSO ₄ •7H ₂ O crystals	Rotary; heated from ext. steam coils, in- ternal lifting vanes	Moist MgSO ₄ •H ₂ O: 1.05 to 1.1 (dry MgSO ₄ •7H ₂ O)	Some drying on filter
b	4	1) MgCO ₃ •3H ₂ O, or 2) 5 MgO•4CO ₂ • 6H ₂ O	Spray dryer, shelf dryer, or tray dryer. (for both products)	MgCO ₃ •3H ₂ O filter cake: 1) 2 to 2.5 (MgCO ₃ •3H ₂ O) 2) 2.7 to 3.0 (5MgO•4CO ₂ •6H ₂ O)	Inferred type; Gross estimate
c	5	Crude NaCl	Rotary; direct-fired	Moist, crude NaCl: 1.04 to 1.06 (dry, refined NaCl)	Estimated
d	5	Refined NaCl	1) Dried on filter; 2) Rotary; direct fired	Moist, refined NaCl: 1.04 to 1.06 (dry, refined NaCl)	Estimated
e	6	K ₂ SO ₄	Rotary, direct-fired	Moist K ₂ SO ₄ : 1.05 to 1.1 (dry K ₂ SO ₄)	Gross estimate
f	6	Na ₂ SO ₄	Rotary, direct-fired	Moist Na ₂ SO ₄ : 1.05 to 1.1 (dry Na ₂ SO ₄)	Gross estimate

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

Table 6 (Continued). FUNCTION AND INPUT MATERIALS FOR APPLICATIONS OF PROCESS 11

Process applic.	Shown on Fig:	Produces	Type of Equipment	Input Material: Amount used in m. tons per m. ton of (product)	Remarks
g	7	1) KCl 2) K ₂ SO ₄ 3) Na ₂ SO ₄	Rotary, direct-fired	Respective moist materials: 1.05 to 1.1 (respective dry products)	Gross estimate
h	9	KCl	Rotary, direct-fired	Moist KCl: 1.05 to 1.1 (dry KCl)	Gross estimate
i	9	Na ₂ SO ₄	Rotary, direct-fired	Moist Na ₂ SO ₄ : 1.05 to 1.1 (dry Na ₂ SO ₄)	Gross estimate
j	11	NaCl	Rotary, or Roto- louver type	Moist NaCl: 1.04 to 1.06 (dry NaCl)	Gross estimate
k	13	Li ₂ NaPO ₄	Type undisclosed probably steam-coil heated rotary	Moist Li ₂ NaPO ₄ : (9 to 18 (Li ₂ CO ₃))	Gross estimate
m	13	Li ₂ CO ₃	Type undisclosed;	Moist Li ₂ CO ₃ : 1.05 to 1.1 (Li ₂ CO ₃)	Gross estimate
n	14	NaHCO ₃	Usually belt dryers	Moist NaHCO ₃ : 1.09 to 1.18 (dry NaHCO ₃)	Published values

Table 6 (Continued). FUNCTION AND INPUT MATERIALS FOR APPLICATIONS OF PROCESS 11

Process applic.	Shown on Fig.	Produces	Type of Equipment	Input Material: Amount used in m. ton per m. ton of product)	Remarks
o	16	1) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	1) Tray; possibly rotary	Respective moist materials: 1.04 to 1.06 (Respective dried products.)	Published values
		2) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$	2) Rotary or tray		
p	16	H_3BO_3	Undisclosed type; probably tray	Moist H_3BO_3 : 1.05 to 1.1 (dry H_3BO_3)	Gross estimate
q	17	KCl	Rotary	Moist KCl: 1.05 (dry KCl)	Inferred moisture content
r	18	Commercial langbeinite ($\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$)	Rotary	Moist langbeinite: 1.05 (dry langbeinite)	Inferred moisture content
s	18	K_2SO_4	Rotary	Moist K_2SO_4 : 1.05 (dry K_2SO_4)	Inferred moisture content
t	21	NaCl	Probably rotary	Moist NaCl: 1.05 (dry NaCl)	Inferred moisture content
u	22	LiCl	Probably tray or double-cone	Moist LiCl: 1.05 to 1.1 (dry LiCl)	
v	22	NaI	Double-cone, or tray; probably vacuum	Moist NaI: 1.05 to 1.1 (dry NaI)	

Table 6 (Concluded). FUNCTION AND INPUT MATERIALS FOR APPLICATIONS OF PROCESS 11

Process applic.	Shown on Fig:	Produces	Type of Equipment	Input Material: Amount used in m. ton per m. ton of (product)	Remarks
w	22	NaBr	Double-cone, or tray; maybe vacuum	Moist NaBr: 1.05 to 1.1 (dry NaBr)	
x	24	Li ₂ CO ₂	Undisclosed type, probably steam-coil rotary	Moist Li ₂ CO ₃ : 1.05 to 1.1 (dry Li ₂ CO ₃)	
y	24	Na ₂ SO ₄	Probably rotary	Moist Na ₂ SO ₄ : 1.05 to 1.1 (dry Na ₂ SO ₄)	

Table 7. OPERATING PARAMETERS AND UTILITIES FOR APPLICATIONS OF PROCESS 11

Process applic.	Shown on Fig:	Operating parameters (atmospheric pressure, unless noted)	Utilities consumed			Remarks
			Heat 10 ³ kcal (form)	Electrical energy kWh	Basis Per m. ton of:	
* a	4	120°C inlet air; 30°C to 40°C max. material temperature	100 - 200 (steam)	10 - 20	Dry MgSO ₄ •7H ₂ O	Gross estimate
b	4	1) <150°C, may be vacuum 2) 80 to 100°C	1) 2,000 - 3,000 (steam) 2) 3,000 - 4,000 (steam)	20 - 30	1) MgCo ₃ •3H ₂ O 2) 5MgO•4CO ₂ • 6H ₂ O	Gross estimate
c	5	180° to 200°C material temperature	100 - 150 (gas)	10 - 20	Dry, crude NaCl	Heat estimated; temperature published
d	5	180° to 200°C material temperature	100 - 150 (gas)	10 - 20	Dry, refined NaCl	Heat estimated; temperature published
e	6	200° to 250°C material temperature	100 - 200 (gas)	10 - 20	Dry K ₂ SO ₄	Gross estimate
f	6	200° to 250°C material temperature	100 - 200	10 - 20	Dry Na ₂ SO ₄	Gross estimate
g	7	1) through 3) 200° to 250°C material temperature	1) through 3) 100 - 200	10 - 20	1) Dry KCl 2) Dry K ₂ SO ₄ 3) Dry Na ₂ SO ₄	Gross estimate
h	9	200 to 250°C material temperature	100 - 200	10 - 20	Dry KCl	Gross estimate

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

Table 7 (Continued). OPERATING PARAMETERS AND UTILITIES FOR APPLICATIONS OF PROCESS 11

Process applic.	Shown on Fig:	Operating parameters (atmospheric pressure, unless noted)	Utilities consumed			Basis Per m. ton of:	Remarks
			Heat 10 ³ kcal (form)	Electrical energy kWh			
i	9	200 to 250°C material temperature	100 - 200	10 - 20	Dry Na ₂ SO ₄	Gross estimate	
j	11	180 to 200°C material temperature	100 - 150	10 - 20	Dry NaCl	Gross estimate	
k	13	150 to 200°C material temperature	100 - 200 (probably steam)	15 - 30	Dry Li ₂ CO ₃	Gross estimate	
l	13	150 to 200°C material temperature	50 - 150 (probably steam)	10 - 20	Dry Li ₂ CO ₃	Gross estimate	
m	13	150 to 200°C material temperature	100 - 200 (probably steam)	10 - 20	Dry Li ₂ CO ₃	Gross estimate	
n	14	80°C air temp.; <50°C material temperature	150 - 300 (steam)	20 - 30	Dry NaHCO ₃	Temperature published, heat estimated	
o	16	1) 50 to 60°C material temp. 2) 50 to 100°C material temp.	100 - 200 100 - 200	10 - 20 10 - 20	1) Dry Na ₂ B ₄ O ₇ •10H ₂ O 2) Dry Na ₂ B ₄ O ₇ •5H ₂ O	Temperature published, heat estimate inferred	
p	16	80 to 100°C material temperature	150 - 300	10 - 15	Dry H ₃ BO ₃	Inferred	
q	17	200 to 250°C material temperature	100 - 200	10 - 20	Dry KCl	Gross estimate	

Table 7 (Concluded). OPERATING PARAMETERS AND UTILITIES FOR APPLICATIONS OF PROCESS 11

Process applic.	Fig:	Operating parameters (atmospheric pressure, unless noted)	Utilities consumed			Basis Per m. ton of:	Remarks
			Heat 10 ³ kcal (form)	Electrical energy kWh			
r	18	200 to 250°C material tempeature	100 - 200	10 - 20	Dry	langbeinite	Gross estimate
s	18	200 to 250°C material temperature	100 - 200	10 - 20	Dry	K ₂ SO ₄	Gross estimate
t	21	180 to 200°C material temperature	100 - 150	10 - 20	Dry	NaCl	Gross estimate
u	22	120 to 150°C material temperature	50 - 100	40 - 60	Dry	LiCl	Gross estimate
v	22	<100°C material temperature	50 - 100	40 - 60	Dry	NaI	Inferred temperature
w	22	<100°C material temperature	50 - 100	40 - 60	Dry	NaBr	Inferred temperature
x	24	200 to 250°C material temperature	80 - 150	10 - 20	Dry	Li ₂ CO ₃	Gross estimate
y	24	200 to 250°C material temperature	400 - 800	15 - 30	Dry	Na ₂ SO ₄	Gross estimate

In light of the above generalization, each of the applications of Process 11 produces atmospheric emissions of fine particles of the respective material being dried. Almost no factual information is available on either the quantity or the distribution of the particulates from any of the specific applications. Published information on the airborne dust from rotary lime kilns is the basis for estimating the range of the amount of particulate emissions from direct-fired rotary dryers:

0.05 to 0.15 metric tons per metric ton of product, when operating without control equipment.

0.0005 to 0.02 metric tons per metric ton of product, when operating with emission control equipment. The latter may include spray chambers, bag-filters, cyclones, and electrostatic precipitators.

Estimated quantity of airborne particulates from spray dryers is in the range given above.

Estimated quantity of airborne particulates from non-air swept dryers is less than 0.005 metric tons per metric ton of product.

6. EPA Source Classification Code

a to e. None established
f. 3-01-036-02 Kilns
g to n. None established
o to q. None established
r. 3-05-040-33 Ore Dryer
s to y. None established

7. References

k,l,x,y.
Bach, R. O., C. W. Kamienski, and R. B. Ellestad.
Lithium and Lithium Compounds. In: Kirk-Othmer
Encyclopedia of Chemical Technology, 2nd Edition,
Standen, A.(ed.). New York, Interscience Publishers,
1967. 12:529-556.

- m. Barrett, W. T., and B. J. O'Neal, Jr. Recovery of Lithium from Saline Brines using Solar Evaporation. In: 3rd Symposium on Salt. Rau, J. L., and L. F. Dellwig (ed.). Cleveland, Northern Ohio Geological Society, 1970. 2:47-50.
- k,o,p. Bixler, G. H., and D. L. Sawyer. Boron Chemicals from Searles Lake Brines. Ind. Eng. Chem. 49:322-334, March 1957.
- a. Boeglin, A. F., and T. P. Whaley. Magnesium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, Interscience Publishers, 1967. 12:708-736.
- w. Clough, R. W. Miscellaneous Heavy Chemicals. In: Reigels Handbook of Industrial Chemistry, 7th Edition. Kent, J. A. (ed.). New York, Reinhold, 1974. p. 137.
- i,y. Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley and Sons, Inc. 1965. 852 p.
- e. Hadzeriga, P. Some Aspects of the Physical Chemistry of Potash Recovery by Solar Evaporation of Brines. Trans. Soc. Min. Eng. 229:169-174, June 1964.
- r,s. Hartley, G. T., and G. E. Atwood. Langbenite--Mining and processing. Ind. Eng. Chem. 39:43-47, January 1947.
- b. Havighorst, C. R. and S. L. Swift. Magnesia Extraction from Seawater. Chem. Eng. (New York). 72:84-86, September 2, 1965.
- c,d. Hester, A. S., and H. W. Diamond. Salt Manufacture. In: Modern Chemical Processes. Murphy, W. J. (ed.). New York, Reinhold, 1956. 4:152-163.
- n. Hou, T. P. Alkali and Chlorine Production. In: Roger's Industrial Chemistry, 6th Edition. Furnas, C. C. (ed.). New York, Van Nostrand, 1942. 1:402-450.
- q. Jackson, D., Jr. Solution Mining Pumps New Life Into Cane Creek Potash Mine. Eng./Min. J. 174:59-69, July 1973.

g,e,q,r,s,v,w.

Jacobs, J. J. Potassium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A.(ed.). New York, Interscience Publishers, 1968. 16:371-397.

t. Lemke, C. H. Sodium. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, Interscience Publishers, 1969. 18:432-457.

General:

Lewis, C. J., and B. B. Crocker. The Lime Industry's Problem of Airborne Dust. J. Air Pollution Contr. Assoc. 19:31-39, January 1969.

q. Magraw, R. M. New Mexico Sylvinit. Ind. Eng. Chem. 30:861-871, August 1938.

General:

McCormick, P. Y., R. L. Lucas, and D. F. Wells. Section 20. In: Chemical Engineer's Handbook, 4th Edition. Perry, R. H. (ed.). St. Louis, McGraw-Hill, 1963. p. 20-1 to 20-96.

g. Mumford, R. W. Potassium Chloride from the Brine of Searles Lake. Ind. Eng. Chem. 30:872-877, August, 1938.

m. Nevada Brine Supports a Big New Lithium Plant. Chem. Eng. (New York). 73:86-88, September 15, 1966.

o,p. Nies, N. P. Boron Compounds (Oxides, Borates). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A.(ed.). New York, Interscience Publishers, 1964. 3:621-650.

e,q,r,s.

Potassium Chloride and Potassium Sulfate. Chem. Eng. (New York). 57:168-171, January 1950.

n,u. Rau, E. Sodium Compounds (Carbonates). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A.(ed.). New York, Interscience Publishers, 1969. 18:458-468.

g. Robertson, G. R. Expansion of the Trona Enterprise. Ind. Eng. Chem. 34:133-137, February 1942.

- b. Schambra, W. P. The Dow Magnesium Process at Freeport, Texas. Trans. Amer. Inst. Chem. Eng. 41:35-51, January 1945.
- b,g,k,l,q,s.
Shreve, R. N. Chemical Process Industries, 3rd Edition, New York, McGraw-Hill, 1967. 905 p.
- t. Sittig, M. Sodium, Its Manufacture, Properties, and Uses. ACS Monograph Series, No. 133. New York, Reinhold, 1956. p. 33.
- f. Smith, E. E., and H. J. Andrews. Mining Great Salt Lake--A \$75 Billion Reserve of Lithium and Sodium Salts. Unpublished paper presented at February 21, 1967 meeting of Am. Inst. Min. Eng., Los Angeles.
- g. Tuple, J. E. The Industrial Development of Searles Lake Brine. ACS Monograph Series, No. 19, New York, Reinhold, 1929. 182 p.
- g,q,r,s.
Turrentine, J. W. Potash in North America. ACS Monograph Series, No. 91. New York, Reinhold, 1943. 186 p.
- v. Two Men and a Tub. Chem. Wk. 73:77-83, December 5, 1953.
- c,h,j.
VerPlank, W. E., and R. F. Heizer. Salt in California. Bulletin 1975, California Dept. of Nat'l. Res. San Francisco. March 1958. 168 p.
- q,r,s.
White, N. C., and C. A. Arend, Jr. Potash Production at Carlsbad. Chem. Eng. Progr. 46:523-531, October 1950.
- g,h. Woodmansee, W. C. The Mineral Industry of California. In: Minerals Yearbook 1971. Schreck, A.E.(ed.). Washington, U. S. Dept. of the Interior, Bur. of Mines, 1973. 2:119-168.

DRYING/CALCINATION1. Function

Generally, the process alters the chemical composition of the input material by heating and simultaneously removes all or most of the "free" water. Most frequently, the chemical changes involved are the removal of combined water and carbon dioxide.

The various applications of the process may include any of the following steps:

- Grinding (of input material or intermediate product)
- Product cooling
- Product briquetting
- CO₂ recovery

Essential equipment may be identical or similar to that used for drying, and is usually represented by one of the following types:

- Rotary
 - Direct-fired
 - Externally heated
 - Steam-coil heated
 - Cocurrent
 - Countercurrent
- Shelf
- Tray
- Pan
- Spray
- Fluidized bed

Any of the types of dryer-calciners mentioned above may be operated in continuous, intermittent-continuous, or batch modes, and are represented in a wide range of production capacities. Rotary dryer-calciners and rotary coolers are the type most frequently encountered in the various applications of Process 12.

Table 8 identifies the specific applications of Process 12 and lists the types of equipment used.

2. Input Materials

The identity and quantity of the input materials corresponding to each of the applications of Process 12 are given in Table 8.

Table 8. APPLICATIONS AND INPUT MATERIALS TO PROCESS 12

Process application	Shown on Fig:	Produces:	Type of Equipment	Input material: Amount used in m. tons per m. ton of (product)	Remarks
*a	4	1) Dried $Mg(OH)_2$, or 2) Caustic-calcined MgO , or 3) Dead-burned MgO	Rotary, direct fired kilns; rotary coolers. Same equipment for all products with product depending on temperature.	$Mg(OH)_2$ filter cake: 1) 50% $Mg(OH)_2$ 2 m. tons; [Dried $Mg(OH)_2$] 2) 50% $Mg(OH)_2$ 3 m. tons; (MgO) 3) 50% $Mg(OH)_2$ 3 m. tons; (MgO)	3) Additives of alumina, silica, CaO , or irox oxides are made to the 50% $Mg(OH)_2$ filter cake to lower the sinter temp. These additives are as high as 0.5 m. ton per m. ton of MgO .
b	7	Soda ash (Na_2CO_3)	Steam heated rotary kilns; rotary coolers.	Moist $Na_2CO_3 \cdot H_2O$: 1.3 m. tons; (Na_2CO_3)	Produces high density ash (1538 kg/m ³).
c	8	Soda ash	Direct fired kilns; rotary coolers.	Moist $NaHCO_3$: 2 m. tons; (Na_2CO_3)	CO_2 recovered & compressed for re-use. Produces low density ash (560 kg/m ³) $NaNO_3$ is added to bleach the product. Often this soda ash is converted to $Na_2CO_3 \cdot H_2O$ and recalculated to get dense ash.

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

Table 8 (Concluded). APPLICATIONS AND INPUT MATERIALS TO PROCESS 12

Process application	Shown on Fig:	Produces:	Type of Equipment	Input material: Amount used in m. tons per m. ton of (product)	Remarks
d	14	Soda ash (Na_2CO_3)	Steam heated rotary kilns; rotary coolers.	Moist NaHCO_3 : 2 m. tons; (Na_2CO_3)	CO_2 recovered & compressed for re-use. Produces low density ash (560 kg/cm^3). Often this soda ash is converted to $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ and recalcined to get dense ash.
e	19	Soda ash	Steam-heated rotary kilns; rotary coolers	Purified trona X-tals: 1.5 m. ton; (Na_2CO_3)	Double calcining sometimes to increase density from 800 kg/m^3 to 960 kg/m^3
f	19	Crude Na_2CO_3	Steam heated rotary kilns; rotary coolers	Crushed trona ore: 1.6 m ton; (Na_2CO_3)	Soda ash contains silicates and soluble organics. This material is forwarded to Process 35.
g	19	Soda ash (Na_2CO_3)	Steam heated rotary kilns; rotary cooler	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ 1.3 m. ton; (Na_2CO_3)	Produces high density ash (960 kg/m^3).
h	24	Dried LiOH	Steam heated rotary dryers.	Moist $\text{LiOH} \cdot \text{H}_2\text{O}$ crystals 1.8 m. ton; (LiOH)	$\text{LiOH} \cdot \text{H}_2\text{O}$ may be the dominant product rather than LiOH .

3. Operating Parameters

- *a. 1) Dried $\text{Mg}(\text{OH})_2$
Kiln temperature is 200° to 250°C . Pressure is atmospheric.
- 2) Caustic-calcined MgO
Kiln temperature is 400° to 600°C . Pressure is atmospheric.
- 3) Dead-burned MgO
Kiln temperature is 1800°C at the sintering section. Residence time in the kiln is 2.5 to 4 hours.
- b. Na_2CO_3 from $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (Searles Lake, upper level)
 - Calcination temperature is 125°C (estimated)
 - Pressure is atmospheric.
- c. Na_2CO_3 from NaHCO_3 (Searles Lake, lower level)
 - The calciner temperature reaches 400°C .
 - Pressure is atmospheric.
- d. Na_2CO_3 from the Solvay Process
 - Final Na_2CO_3 temperature is 175° to 225°C .
 - Pressure is atmospheric.
 - Steam-heated calciners with a capacity of 360 metric tons per day are 2.5 meters in diameter by 30 meters long containing finned tubed.
- e. Na_2CO_3 from $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ (Wyoming)
 - Calcination temperature is 200°C .
 - Temperature for gas-fired calciners is 250°C .
 - Pressure is atmospheric.
- f. Crude Na_2CO_3 from trona ore (Wyoming)
 - Temperature is 150° to 200°C .
 - Pressure is atmospheric.
- g. Na_2CO_3 from $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (Wyoming)
 - Calcination temperature is 125°C (estimated).
 - Pressure is atmospheric.

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

h. Dried LiOH

- Temperature is 200°C
- Pressure is slightly below atmospheric.

4. Utilities

a. 1) Dried $\text{Mg}(\text{OH})_2$ product

- Natural gas
100 cubic meters per metric ton dried $\text{Mg}(\text{OH})_2$
- Electrical energy
10 to 20 kWh per metric ton dried $\text{Mg}(\text{OH})_2$

2) Caustic-calcined MgO

- Natural gas
150 cubic meters per metric ton MgO
- Electrical energy
10 to 20 kWh per metric ton MgO

3) Dead-burned MgO

- Natural gas
200 cubic meters per metric ton MgO
- Electrical energy
10 to 20 kWh per metric ton MgO

b. Na_2CO_3 from $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (Searles Lake)

- Steam
0.5 metric tons per metric ton Na_2CO_3
- Electrical energy
10 to 20 kWh per metric ton Na_2CO_3

c. Na_2CO_3 from NaHCO_3 (Searles Lake)

- Natural gas
120 cubic meters per metric ton Na_2CO_3
- Electrical energy
10 to 20 kWh per metric ton Na_2CO_3

d. Solvay Na_2CO_3 from NaHCO_3

- Steam (30 kg/cm²)
2 metric tons per metric ton Na_2CO_3
- Electrical energy
10 to 20 kWh per metric ton Na_2CO_3

- e. Na_2CO_3 from $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ (Wyoming)
 - Steam
1 metric ton per metric ton Na_2CO_3
 - Electrical energy
10 to 20 kWh per metric ton Na_2CO_3
- f. Crude Na_2CO_3 from trona ore (Wyoming)
 - Steam
1 metric ton per metric ton crude Na_2CO_3
 - Electrical energy
10 to 20 kWh per metric ton Na_2CO_3
- g. Na_2CO_3 from $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (Wyoming)
 - Steam
0.5 metric tons per metric ton Na_2CO_3
 - Electrical energy
10 to 20 kWh per metric ton Na_2CO_3
- h. Dried LiOH
 - Steam (30 kg/cm²)
1 metric ton per metric ton LiOH
 - Electrical energy
10 to 20 kWh per metric ton LiOH

5. Waste Streams

- a. Particulate emissions in the kiln exhaust gases to the atmosphere vary with the recovery equipment used. Good practice should limit emissions to less than 0.001 metric ton per metric ton $\text{Mg}(\text{OH})_2$ or MgO .

Some under-burned and over-burned MgO is collected during start-ups and periods of erratic operation. This material is used as landfill. No quantitative information is available.

- b,c,d, Particulate emissions in the kiln exhaust gases
- e,f,g. to the atmosphere vary with the recovery equipment used. Good practice should limit these emissions to less than 0.001 metric ton per metric ton Na_2CO_3 .
- h. Particulate emissions in the dryer exhaust gases to the atmosphere are estimated to be less than 0.001 metric ton per metric ton of LiOH .

6. EPA Source Classification Code

a through h: None established

7. References

- a. Boeglin, A. F., and T. P. Whaley. Magnesium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, Interscience Publishers, 1967. 12: 724-728.

Havighorst, C. R. Magnesia Extraction from Seawater. Chem. Eng. (New York). 72:84-86, August 2, 1965.

- b. Hightower, J. V. The Trona Process. . . and its Unique Features. Chem. Eng. (New York). 58:104-106, August 1951.

- b,d,g. Deutsch, Z. G., C. C. Brumbaugh, and E. F. Rockwell. Alkali and Chlorine (Sodium Carbonate). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, Interscience Publishers, 1963. 1:712-758.

- b,e,g. Sommers, H. A. Soda Ash from Trona. Chem. Eng. Progr. 56:76-79, February 1960.

- c. Nies, N. P. Boron Compounds (Oxides, Borates). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, Interscience Publishers, 1964. 3:636.

Plant Expansion at Trona Boosts Soda Ash and Borax Capacity. Chem. Eng. (London). 56:102-103, April 1949.

- d. McCormick, P. Y., R. L. Lucas, and D. F. Wells. Section 20. In: Chemical Engineers' Handbook, 4th Edition. Perry, R. H. (ed.). St. Louis, McGraw-Hill, 1963. p. 20-15 to 20-31.

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1967, p. 230.

- e,f,g. Rau, E. Sodium Compounds (Carbonates). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, Interscience Publishers, 1960, 18:461-465.
- h. Bach, R. D., C. W. Kamienski, and R. B. Ellestad. Lithium and Lithium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1967, 12:545.

SOLAR EVAPORATION1. Function

- *a. As applied to "solar salt" production at tidewater locations (Figure 5) - The process evaporates seawater in open, diked ponds, producing moist crystals of crude sodium chloride (NaCl) bulk-loaded in tramcars or dump trucks. The crude salt is forwarded to Process 14, Figure 5. Seawater "bitterns", the mother liquor from the NaCl crystallization, also result as a by-product.

The process includes the sequential steps of:

- Seawater intaking (gravity flow or pumping)
- Transporting partially evaporated seawater ("pickle") through pond system (gravity flow or pumping)
- Discharging bitterns
- Salt (NaCl) harvesting

Ponds may be hundreds of hectares in area, and generally about one meter in depth, with compacted clay floor. Harvesting equipment includes elaborate, specially constructed motorized equipment, front-end loaders, bulldozers, dump trucks, locomotive-drawn tramcars, and belt conveyors.

- b. As applied to processing Great Salt Lake brine (Figure 6) - The process evaporates brine from Great Salt Lake to obtain a moist mass of mixed crystals of sodium chloride (NaCl) and several double salts, including astrakanite ($\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$), leonite ($\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$), kainite ($\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$), and possibly carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$). The NaCl is generally unwanted. A magnesium chloride bittern is also obtained as a potentially marketable by-product. The mixed crystals are forwarded to Process 10, Figure 6.

Sequential process steps and equipment used are almost identical to those in a, above.

-
- * Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

- c. As applied to processing Searles Lake brine (Figure 7) - This process is a recently (1973) commenced alternative to some of the steps of Process 10, Figure 7.

The process crystallizes sodium chloride (NaCl) from Searles Lake brine by solar evaporation. (It is surmised that the brine is pumped from the upper crystal body of the lake.) The process is restricted to amounts such that only NaCl precipitates. The NaCl solids are wasted or periodically harvested by outside contractors as a crude NaCl product. The process is conducted solely as a brine preconcentrator.

The process includes the following sequential steps:

- 1) Brine pumping and gathering
- 2) Solar evaporation
- 3) Crystal harvesting
- 4) Bittern removal for further processing

- d. As applied to processing brine from Bristol Lake, California (Figure 9) - The process evaporates brine pumped from Bristol Lake, obtaining a nominal 35% calcium chloride (CaCl_2) liquor, whose actual CaCl_2 content approaches 40%. Sodium chloride (NaCl) crystallizes from the brine but is abandoned in the solar ponds.

The process includes the sequential steps of pumping brine into the solar ponds and pumping 35% CaCl_2 liquor from the ponds into tank cars, either as a marketable product or for transfer to Process 10, Figure 9.

- e. As applied to processing brine from Salduro Marsh, Bonnevillle, California (Figure 9) - Process obtains crystalline mixtures of sodium chloride (NaCl), potassium chloride (KCl), and double salts of potassium and magnesium, such as kainite ($\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$) and carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), by evaporating brine pumped from Salduro Marsh in solar evaporating ponds. The mixed crystals are forwarded to Process 15, Figure 9. A final bittern containing approximately 32% MgCl_2 is also obtained. This is sometimes sold as a by-product.
- f. As applied to processing brine at Silver Peak, Nevada (Figure 13) - The process removes sodium chloride (NaCl) and potassium chloride (KCl) plus smaller quantities of magnesium hydroxide

[Mg(OH)₂], and calcium sulfate (CaSO₄) from lithium-bearing well brine by solar evaporation. The concentrated brine is forwarded to Process 33, Figure 13 for lithium recovery.

Process includes the following sequential steps:

- Brine production and gathering
- Solar evaporation
- Bittern pumping

- g. As applied to recovery of sylvinite (mixed KCl-NaCl) from brine resulting from solution-mining potash deposits at Moab, Utah (Figure 17) - Process recovers mixed crystals of potassium chloride (KCl)-sodium chloride (NaCl) by evaporating the KCl-NaCl brine forwarded from Process 3, Figure 3. The mixed crystal slush or slurry is pumped to Process 51, Figure 17.

Equipment consists of diked, earthen-bottom, PVC-lined solar evaporating ponds, crystal-harvesting equipment consisting of specialized scraper-loaders, slurry pumps, and pipeline system.

2. Input Materials

- a. Seawater. Depending upon prevailing coastal salinities, between 38 and 45 cubic meters are required per metric ton of crude NaCl produced. Seawater from the "open sea" has the following composition with respect to the major dissolved ions:

<u>Ion</u>	<u>ppm</u>
Chlorine	19,360
Sodium	10,767
Magnesium	1,297
Sulfate	2,652
Calcium	408
Potassium	388
Bromine	66
Bicarbonate	140

The concentration of the ions shown above in coastal waters may vary widely; from 50 to 120% of the concentrations shown is a typical range.

- b. Brine from the northern arm of the Great Salt Lake has the following typical composition (1963-1965), with seasonal variations:

<u>Ion</u>	<u>ppm</u>
Magnesium	12,200
Potassium	7,200
Sulfate	23,800
Chloride	149,200
Sodium	80,000

In practice, the specific brine consumption may differ widely from the values given above, depending on ability to market and upon the specific method of operation.

- c. Brine from the upper crystal body of Searles Lake has the following approximate composition:

<u>Ion</u>	<u>ppm</u>
Sodium	111,400
Potassium	25,700
Lithium	80
Chloride	120,900
Bicarbonate	1,100
Carbonate	26,900
Sulfate	45,600
Tetraborate	12,200

Per metric ton of each of the products of interest currently produced, the quantities of raw brine theoretically required are:

<u>Product</u>	<u>Brine Required (cubic meters)</u>
Na_2SO_4	12.4
Na_2CO_3	16.8
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$	36.2
KCl	17.0

- d. Brine from Bristol Lake typically contains the following quantities of calcium chloride (CaCl_2) and sodium chloride (NaCl):

CaCl_2	14%
NaCl	14%

On a theoretical basis, the quantity of brine required per metric ton of CaCl_2 (100% basis) is 6.3 cubic meters.

- e. Brine collected from Salduro Marsh has the following typical composition:

<u>Dissolved Constituent</u>	<u>Percent</u>
NaCl	18 to 24
KCl	0.8 to 1.2
MgCl ₂	0.9 to 1.2
MgSO ₄	0.2 to 0.3
CaSO ₄	0.3 to 0.4
LiCl	0.03 to 0.04

On a theoretical basis, the brine required per metric ton of each of the desired products, currently produced is:

<u>Product</u>	<u>Brine Required (cubic meters)</u>
KCl	69 to 104
MgCl ₂	69 to 93
(100% basis in 32% solution)	

The actual brine requirement is probably at least 150% of the values listed above.

- f. Well-brines at Silver Peak, Nevada, typically have the following composition:

<u>Ion</u>	<u>Percent</u>
Sodium	6.2
Potassium	0.8
Magnesium	0.04
Lithium	0.04
Calcium	0.05
Sulfate	0.71
Chloride	10.1

On a theoretical basis, 430 cubic meters of brine are required per metric ton of Li₂CO₃ produced.

An undisclosed quantity of calcium hydroxide, estimated to be 0.7 metric tons per metric ton of Li₂CO₃, is added to the brine entering the first pond, to precipitate magnesium as Mg(OH)₂.

- g. The brine fed to the solar ponds is a saturated aqueous solution of KCl and NaCl, containing about

12% KCl and 20% NaCl at 34°C. Theoretically, 7 cubic meters of this brine are required to produce 1 metric ton of KCl product.

Approximately 2.5 metric tons of mixed crystals from the solar ponds are required per ton of KCl produced.

3. Operating Parameters

Items a through g. All solar evaporation processes are necessarily operated at prevailing year-round atmospheric temperatures. Annual net evaporation rate, rainfall pattern, and temperature pattern are critical factors.

- a. The following parameters partially describe the solar evaporation of seawater on the California coast:
 - Annual net evaporation rate is 85 to 110 cm.
 - Water of San Francisco Bay typically contains 26.5 gms. NaCl per liter.
 - Ratio of evaporating pond area to crystallizing pond area is about 15:1.
 - Salt is harvested once per year. Specific production rate is approximately 85 metric tons NaCl per year per hectare of total pond area.
 - Total solar pond area in salt production on the California coast is between 13,000 and 17,000 hectares.
- b. Annual net evaporation rate ranges from 80 to 106 cm. Approximately 5,600 hectares of solar ponds adjoining Great Salt Lake are devoted to K_2SO_4 - Na_2SO_4 recovery.
- c. Only an estimated 20% of the total brine taken from Searles Lake is processed in solar ponds.
- d. Scale of $CaCl_2$ recovery operations at Bristol Lake. is undisclosed.
- e. Production of KCl from Salduro Marsh brine approximates 55,000 metric tons per year (1971).
- f. Annual net evaporation rate averages 145 cm. Total solar pond area is approximately 1,590 hectares and has capacity to produce between 4,500 and 6,000 metric tons per year of Li_2CO_3 .

- g. Temperature of brine from Process 3 is invariant at 34°C, governed by prevailing temperature in mine at approximately 1,000 meters subsurface.

Approximately 180 hectares of pond area are required to sustain an annual production rate of 275,000 metric tons of KCl product.

Crystal slurry harvested from solar ponds and pumped to Process 51 averages 35% solids.

4. Utilities

Electrical energy - Estimates of consumption for driving pumps is shown below. Where applicable, this includes well-pumps.

- a. Between 0.5 and 1.5 kWh per metric ton of NaCl.
- b. Between 0.75 and 1.5 kWh per metric ton of K₂SO₄.
- c. Between 1 and 2 kWh per metric ton of Na₂SO₄.
- d. Between 0.2 and 0.3 kWh per metric ton of CaCl₂ (100% basis).
- e. Between 2 and 3 kWh per metric ton of KCl.
- f. Between 250 and 400 kWh per metric ton of Li₂CO₃.
- g. Estimated electrical energy required to fill solar ponds with brine is 20 kWh per metric ton of KCl produced.

Estimates of fuel required to power crystal-harvesting equipment, where applicable, would be based on data too remote to produce meaningful numbers.

Water - Fresh or brackish water is required to flush or dissolve unwanted NaCl crystals from the solar ponds at Great Salt Lake. The requirement is estimated to be 15 to 30 cubic meters per metric ton of K₂SO₄ produced.

5. Waste Streams

- a. Unless marketed, the final bitterns (mother liquor) from crystallizing ponds constitute a waste stream and are drained into tidewater. The quantity is

approximately 1 cubic meter per metric ton of crude NaCl produced, and the composition at a specific gravity of 30°Be is typically:

NaCl	12.5%
MgCl ₂	8.7
MgSO ₄	6.1
KCl	1.9
MgBr ₂	0.18

- b. Between 6 and 10 metric tons of NaCl per metric ton of K₂SO₄ produced is returned to Great Salt Lake in the form of a solution or slurry of crystals, amounting to 15 to 30 cubic meters per ton of K₂SO₄.

A MgCl₂-rich bittern, sometimes wasted by being returned to Great Salt Lake, is estimated to contain 1 metric ton of MgCl₂ per metric ton of K₂SO₄ produced. Stream size is estimated to be 4 cubic meters per metric ton of K₂SO₄. This stream is sometimes combined with another stream from Figure 4 and the total forwarded to Process 10, Figure 4.

- c. This process is relatively new (1972). No information on waste streams is available.
- d. Approximately one metric ton of NaCl crystals are abandoned in solar ponds per ton of CaCl₂ produced.
- e. NaCl crystals (16 to 20 metric tons per metric ton of KCl) are abandoned in solar ponds. There are no liquid waste streams.
- f. A total of 64 metric tons of solids per metric ton of Li₂CO₃ produced are abandoned in solar ponds.

Composition of solids varies from pond to pond, from impure NaCl to a mixture of NaCl, KCl, and glaserite (3Na₂SO₄•K₂SO₄).

- g. A slurry consisting of solid NaCl crystals plus clay particles in NaCl brine is discharged to tailings ponds. The total amount of solids discharged is estimated at 1.5 to 1.8 metric tons per metric ton of KCl produced.

6. EPA Source Classification Code

a through g: None established

7. References

- a. VerPlank, W. E., and R. F. Heizer. Salt in California. Bulletin 175, San Francisco, California Dept. of Nat'l. Res., March 1958, 168 p.
- b. Glassett, J. M., and B. J. Anderson. The Recovery of Salts from the Waters of Great Salt Lake. Bulletin No. 21, University of Utah, Salt Lake City, May 1964, 80 p.
- Handy, A. H., and D. C. Hahl. Great Salt Lake: Chemistry of the Water. In: Guidebook to the Geology of Utah, No. 20: The Great Salt Lake. Stokes, W. L. (ed.). Salt Lake City, Utah Geology Soc., 1966, p. 135-151.
- Smith, E. E., and H. J. Andrews. Mining Great Salt Lake - A \$75 Billion Reserve of Lithium, Magnesium, Potash and Sodium Salts. Unpublished paper presented at the Meeting of the Amer. Inst. of Mining Eng., Los Angeles, February 21, 1967.
- c. Shreve, R. N. Chemical Process Industries. 3rd Edition. New York, McGraw-Hill, 1967, p. 287.
- c,d. Woodmansee, W. C. The Mineral Industry of California. In: Minerals Yearbook - 1971, Shreck, A. E. (ed.). Washington, U. S. Dept. of the Interior, 1973. 2:119-168.
- d. VerPlank, W. E., and R. F. Heizer. Salt in California. Bulletin 175, San Francisco, California Dept. of Nat'l. Res., March 1958, 168 p.
- e. Hadzeriga, Pablo. Some Aspects of the Physical Chemistry of Potash Recovery by Solar Evaporation of Brines. Trans. Am. Inst. Min. Met. Petr. Eng., Soc. Min. Eng. of AIME. 229:169-174, June 1964.
- Mitko, F. C. The Mineral Industry of Utah. In: Minerals Yearbook - 1971, Shreck, A. E. (ed.). Washington, U. S. Dept. of the Interior, 1973. 2:723-738.
- f. Barrett, W. T., and B. J. O'Neill, Jr. Recovery of Lithium from Saline Brines using Solar Evaporation. In: Third Symposium on Salt. Rau, J. L., and L. F. Dellwig (ed.). Cleveland, Northern Ohio Geological Society, 1970. 2:47-50.

Nevada Brine Supports a Big Lithium Plant. Chem.
Eng. 73:86-88, Aug. 15, 1966.

- g. Jackson, Daniel, Jr. Solution Mining Pumps New
Life into Cane Creek Potash Mine. Eng./Min. J.
174:59-69, July 1973.

WASHING/DRAINING1. Function

This process (See Figure 5) further removes impurities, namely clay and adhering bitterns, from harvested salt.

Harvested salt is discharged from dump cars into a concentrated brine pit. Centrifugal pumps move the slurry to a spiral classifier. There a countercurrent concentrated brine wash separates dirt from the harvested salt. The salt is then screened to remove large clay balls before entering a log washer, where the remaining clay balls are broken up. The salt proceeds to an inclined dewatering drag containing a fresh water rinse that further removes magnesium-containing salts. The salt is then conveyed to storage, Process 10 or Process 11.

2. Input Materials

Harvested salt contains about 97.8% NaCl. Its impurities include clay, gypsum, and adhering bitterns.

3. Operating Parameters

A double 0.6 by 6 meter spiral classifier has a capacity of 136 metric tons of salt per hour. The screens are 2 1/2-cm mesh, followed by double steel 0.6 by 6 meter log washers. The inclined dewatering drag is 3 by 30 meters.

4. Utilities

Fresh water - Rinse for dewatering drag - approximately 0.05 cubic meter per metric ton of NaCl.

5. Waste Streams

All drain streams are pumped to a wash brine circulating pond where dirt and gypsum settle, constituting a land-fill disposal method. The estimated sediments are 0.001 to 0.01 metric ton per metric ton of NaCl.

Fresh brine make-up replaces a small pond bleed-off to prevent accumulation of magnesium salts. This bleed

stream is estimated to be 0.05 cubic meter per metric ton of NaCl. The bleed stream is discharged into tidewater.

6. EPA Source Classification Code

None established.

7. References

VerPlank, W. E., and R. F. Heizer. Salt in California. Bulletin 175, San Francisco, California. Dept. of Nat'l. Res., March 1958. 168 p.

FROTH FLOTATION1. Function

- *a. As applied to the separation of dilithium sodium phosphate from burkeite liquor at Searles Lake, California (Figure 7) - The process recovers a froth of dilithium sodium phosphate (Li_2NaPO_4) crystals from burkeite ($\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$) liquor forwarded from Process 10, (see Figure 5). The Li_2NaPO_4 froth is forwarded to Process 16, Figure 7 and the Li-stripped burkeite liquor is returned to Process 10 for further processing.

Major equipment consists of specialty designed, vertical, cylindrical flotation tanks.

- b. As applied to potassium chloride recovery from mixed crystals of potassium chloride and sodium chloride (Figure 9) - The process separates crystals of potassium chloride (KCl) from a mixture of KCl crystals and sodium chloride (NaCl) crystals received from Process 13. The KCl crystals are forwarded to Process 11, while the NaCl crystals are wasted.

Essential equipment consists of banks of flotation cells of conventional design.

The step of wet-grinding the feed crystals may be included.

- c. As applied to the recovery of KCl from natural sylvinite (mixed KCl-NaCl) in the Moab, Utah and the Carlsbad, N.M. areas (Figure 17) - The process separates KCl crystals from a slurry of mixed KCl-NaCl crystals received from Process 51. The KCl crystals are then forwarded either to Process 11, or to the potassium sulfate (K_2SO_4) operations shown on Figure 18. The NaCl crystals are wasted.

The process application is almost identical to that of b, above, and uses similar equipment.

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

In most cases, KCl crystals are froth-floated away from NaCl crystals, but the reverse situation is also commercial.

- d. As applied to lithium-value recovery from spodumene ores (Figure 24) - The process recovers a lithium-rich concentrate from ground spodumene ore (a lithium silicate, $\text{LiAlSi}_2\text{O}_6$). The ground ore is received from Process 5. The concentrated spodumene from the froth is forwarded to Process 62 of either of two alternative operations for lithium recovery. The gangue material is wasted to a tailings pond or pile.

Major equipment is similar to that of b, above.

The process includes the initial step of slurring the input ore in water.

2. Input Materials

- a. Burkeite liquor, prepared in Process 10 by dissolving burkeite crystals in hot water, is fed to the process. The liquor is actually a slurry of fine Li_2NaPO_4 crystals. An approximation of the feed slurry composition entering the process is:

Na_2SO_4	22%
Na_2CO_3	8%
Li_2NaPO_4 (in suspension)	0.4%
H_2O	69.6%

Approximately 350 cubic meters of this slurry is required per metric ton of Li_2CO_3 produced.

Various flotation agents, usually soaps and kerosene, are added to the entering slurry in amounts believed to be 10 to 20 kilograms per metric ton of Li_2CO_3 .

- b. The principal input stream is a KCl-NaCl crystal slush, received from Process 13, containing about 30% of KCl on a dry basis. The crystals are believed to be slurried in a saturated KCl-NaCl brine from an internal recycle flow, and then wet-ground prior to flotation.

Estimated consumption of the KCl-NaCl mixture is 3 to 4 metric tons per metric ton of KCl produced.

Estimated requirement of make-up water is 1 to 2 cubic meters per metric ton of KCl produced.

Various flotation agents, usually aliphatic amines, are added to the flotation cell feed slurry in amounts estimated between 1 and 5 kilograms per ton of KCl produced.

- c. Principal input stream consists of a pumpable slurry of a mixture of KCl-NaCl crystals in saturated NaCl-KCl brine. Overall slurry compositions vary widely with exact identity of sylvinite ore mined. A typical composition is:

Suspended KCl	6%
Suspended NaCl	12%
Saturated brine	82%

Approximately 15 cubic meters of the slurry are required per metric ton of KCl produced.

Various conditioners, depressants and flotation agents are added to the entering stream in amounts estimated between 1 and 5 kilograms per metric ton of KCl produced.

- d. The principal input stream is finely ground spodumene ore containing 0.5 to 1.0 percent Li. Estimated requirement of the ore is 20 to 40 metric tons per metric ton of Li_2CO_3 produced.

An estimated 80 to 150 cubic meters of water per metric ton of Li_2CO_3 is required to slurry the ore. Most of the water may be recycled.

Various conditioners, depressants and flotation agents are required in amounts estimated between 50 and 100 kilograms per metric ton of Li_2CO_3 produced.

3. Operating Parameters

- a. Process is conducted at 40°C (estimated) and at atmospheric pressure.

Only one operation exists producing Li_2CO_3 via Li_2NaPO_4 . This produces an estimated 2,000 metric tons per year Li_2CO_3 , corresponding to a volume flow entering the process estimated to be 1.5 to 2.0 cubic meters per minute.

- b. The process is conducted at atmospheric pressure and ambient temperature.
- c. Process is conducted at ambient temperatures and at atmospheric pressure.

A typical operation produces approximately 500,000 metric tons per year of KCl corresponding to a flow of slurry entering the process estimated to be 14 to 20 cubic meters per minute.

- d. Process is believed to be conducted at ambient temperature and at atmospheric pressure.

Two companies conduct operations which process spodumene ore. Total annual production of Li_2CO_3 at one of these is estimated to be 5,000 metric tons.

4. Utilities

Consumption of electrical energy is estimated to be:

- a. 50 to 100 kWh per metric ton of Li_2CO_3
- b,c. 60 to 80 kWh per metric ton of KCl
- d. 400 to 800 kWh per metric ton of Li_2CO_3

5. Waste Streams

- a. The process produces no waste streams.
- b,c. Almost all applications of Process 15 to the recovery of KCl from KCl-NaCl mixtures discard the NaCl crystals, pumping them in slurry form to a tailings pond, where they eventually constitute a solid waste pile, or landfill. Clear brine may be recycled to the process.

The quantity of NaCl wasted varies widely with ore quality. Estimates place the quantity between 2 and 3 metric tons per metric ton of KCl produced.

- d. Approximately 10 to 30 metric tons of ore tailings result per metric ton of Li_2CO_3 produced. Tailings are wasted to a tailings pile. At times tailings may be further beneficiated with respect to Al and Si content and supplied to the ceramic industry.

6. EPA Source Classification Code

- a. None established.
- b,c. 3-05-040-32 Ore concentrator
- d. 3-05-040-32 Ore concentrator

7. References

- a,d. Bach, R. O., C. W. Kamienski, and R. B. Ellestad. Lithium and Lithium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, Interscience Publishers, 1967. 12:530-533.
- a. Bixler, G. H., and D. L. Sawyer. Boron and Boron Compounds from Searles Lake Brines. Ind. Eng. Chem. 49:322-334, March 1957.
- b. Hadzeriga, P., Some Aspects of the Physical Chemistry of Potash Recovery by Solar Evaporation of Brines. Trans. Soc. Min. Eng. 229:169-174, June 1964.
- a. Hightower, J. V. The Trona Process---and its Unique Features. Chem. Eng. (New York) 58:104-106, August, 1951.
- c. Magraw, R. M. New Mexico Sylvinite. Ind. Eng. Chem. 30:861-871, August 1938.
- c. Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, Inc., 1967. p. 286-299.
- b,c,d. Taggart, A. F. Flotation. In: Handbook of Mineral Dressing. New York, John Wiley & Sons, Inc., 1945. p. 12-01 to 12-130.
- b,c. Turrentine, J. W. Potash in North America. ACS Monograph Series, No. 91. New York, Reinhold, 1943. p. 105-175.
- c. White, N. C., and C. A. Arend, Jr. Potash Production at Carlsbad. Chem. Eng. Progr. 46:523-531, October 1950.

FILTRATION1. Function

- *a. As applied to the recovery of lithium values from burkeite liquor at Searles Lake, California (Figure 7) - The process recovers a filter cake of dilithium sodium phosphate (Li_2NaPO_4) crystals, washed free of sodium sulfate (Na_2SO_4) and sodium carbonate (Na_2CO_3), from a slurry of Li_2NaPO_4 froth in residual burkeite ($\text{NaCO}_3 \cdot 2\text{Na}_2\text{SO}_4$) brine.

The Li_2NaPO_4 froth forwarded from Process 15, containing considerable quantities of Na_2CO_3 , Na_2SO_4 and water, is filtered. washed free of burkeite brine and transferred to Process 11 (see Figure 13). The filtrate and wash water is recycled to Process 10 for recovery of Na_2CO_3 and Na_2SO_4 .

The specific type of filtration equipment has not been disclosed. Either centrifuges or continuous rotary vacuum filters are practical. If the latter are used, then the process step of partially drying Li_2NaPO_4 cake on the filter may be included.

- b. As applied to production of sodium bicarbonate from soda ash (Figure 14) - The process recovers a moist washed filter cake of fine sodium bicarbonate (NaHCO_3) crystals from a slurry of NaHCO_3 in sodium carbonate (Na_2CO_3) brine received from Process 36. The NaHCO_3 cake is transferred to Process 11, and the filtrate and wash water are recycled to Process 36.

The process step of displacement-washing the NaHCO_3 cake is included

Major equipment consists of continuous vacuum rotary drum filters and batch-type centrifuges.

- c. As applied to soda-ash recovery from mined trona ore (Figure 19) - The process removes a relatively small amount of organics plus any suspended solids from

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

the crude trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) liquor forwarded from Process 35. The clear, purified trona liquor produced is forwarded to Process 10.

The steps of removal of organic materials with porous carbon added to the crude feed liquor and displacement washing the filter cake are included.

Equipment consists of agitated holding tanks (inferred) for carbon addition, and Sweetland® pressure filters.

- d. As applied to metallic calcium removal in sodium metal production (Figure 21) - The process mechanically removes suspended impurities contained in the crude molten sodium metal produced in the electrolytic cell of Process 58. Suspended impurities consist of calcium metal, calcium chloride and sodium oxide. The product of the process is molten sodium metal of approximately 99.95% purity.

The subsequent step of packaging in tank cars and drums is also included in the process. This step is conducted under a padding of gaseous nitrogen.

Equipment consists of a specially designed filtration device using alloy wire mesh filter elements and operating under a padding of nitrogen.

2. Input Materials

- a. Quantitative composition of the Li_2NaPO_4 froth (or slurry) is undisclosed. A gross estimate is:

Li_2NaPO_4 (suspended)	20%
Na_2SO_4 (dissolved)	6%
Na_2CO_3 (dissolved)	18%
Water	56%

Between 7 and 8 cubic meters of slurry are required per metric ton of Li_2CO_3 produced.

- b. Estimated composition of the feed slurry entering the process is:

NaHCO_3 (suspended)	32 to 36%
NaHCO_3 (dissolved)	4 to 5%
Na_2CO_3 (dissolved)	5 to 6%
Water	50 to 60%

Approximately 4 cubic meters of the feed slurry are required per metric ton of sodium bicarbonate produced.

- c. Estimated quantity of the crude trona liquor entering the process is between 4 and 5 cubic meters per metric ton of soda ash produced. It is estimated to contain between 26 and 30 percent trona.
- d. Estimated quantity of crude molten sodium metal entering the process is 1.1 metric tons per metric ton of sodium produced.

The crude molten sodium contains an estimated 3 percent total impurities. About 6 percent of crude sodium entering the process leaves with the sludge removed.

3. Operating Parameters

- a. The process operates at atmospheric pressure and within a temperature range estimated to be 75° to 100°C. Wash-water temperature is believed to be nearly 100°C.
- b. The process operates at atmospheric pressure and at approximately 40°C.
- c. Operating pressure of the Sweetland® pressure filters is pump discharge pressure, probably 5 to 7 kg/cm².

Porous carbon, in undisclosed amounts, is added to the crude Na₂CO₃ liquor to remove organic impurities and to de-colorize the liquor.

Diatomaceous earth is used as a filter-aid. Temperature is estimated to be 90° to 100°C.

- d. The process operates principally at 0.1 to 0.3 kg/cm² below atmospheric pressure, with intermittent surges, to slightly above atmospheric pressure for "back-washing" the filter elements. Normal operating temperature is 100°C. Nitrogen padding is used.

4. Utilities

- a. Electrical energy consumption is estimated to be between 5 and 10 kWh per metric ton of Li₂CO₃ produced.

Wash-water consumption is estimated to be between 0.5 and 1.0 cubic meters per metric ton of Li₂CO₃ produced.

- b. Electrical energy consumption is estimated to be between 15 to 20 kWh per metric ton of NaHCO₃ produced.

Wash-water consumption is estimated to be between 0.5 and 1.0 cubic meters per metric ton of NaHCO_3 produced.

- c. Electrical energy consumption is estimated to be between 2 and 4 kWh per metric ton of Na_2CO_3 produced.

Wash-water required is estimated to be between 0.05 and 0.1 cubic meter per metric ton of Na_2CO_3 produced.

- d. Estimated consumption of electrical energy is between 5 and 10 kWh per metric ton of Na produced.

Estimated consumption of nitrogen for purging and padding is probably close to 1.0 cubic meter (STP) per metric ton of Na produced.

5. Waste Streams

- a. No waste streams are produced. All filtrate and wash-water is reprocessed.
- b. A bleed stream of a solution of about 5 percent NaHCO_3 is discharged if the operation is not integrated with a Solvay operation. The bleed is presumably discharged into natural streams. Its estimated quantity is less than 10 liters per metric ton of NaHCO_3 .
- c. Solid waste, consisting of a mixture of spent carbon, diatomaceous earth and slimes is discharged from the process. It is probably conveyed as a slurry to a tailings pond. Its quantity is estimated at less than 0.05 metric ton per metric ton of Na_2CO_3 produced.
- d. Approximately 0.1 metric ton of sludge results per metric ton of Na produced. Sludge composition approximates:

Na metal	70%
Ca metal, CaCl_2 , NaCl , Na_2O	30%

Sludge disposition is undisclosed.

6. EPA Source Classification Code

a through d: None established

7. References

- a. Bach, R. O., C. W. Kamienski, and R. B. Ellestad. Lithium and Lithium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology. 2nd Edition, Staden, A. (ed.). New York, Interscience Publishers, 1967. 12:529-556.
- Bixler, G. H., and D. L. Sawyer. Boron Chemicals from Searles Lake Brines. Ind. Eng. Chem. 49:322-334, March 1957.
- Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1967. 905 p.
- b. Hou, T. P. Alkali and Chlorine Production. In: Rogers Industrial Chemistry, 6th Edition, Furnas, C. C. (ed.). New York, Van Nostrand, 1942. 1:402-450.
- Rau, E. Sodium Compounds (Carbonates). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1969. 18:458-468.
- c. Rau, E. Sodium Compounds (Carbonates). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1969. 18:458-468.
- d. Gilbert, H. N. Purifying Light Metals. U.S. Patent 1,943,307. Jan. 16, 1934.

LIQUID-LIQUID EXTRACTION1. Function

This process (see Figure 8) recovers sodium and potassium borates from Searles Lake brine (presumably from the lower-level salt body), producing them in solution in an organic extractant. The borates are then stripped from the extractant in Process 18.

Brine and the immiscible extractant are agitated together in a closed contacting tank after which the two liquid phases are allowed to separate by gravity in a separator tank. The two tanks plus the required pumps and agitators comprise the essential equipment.

2. Input Materials

Searles Lake brine (lower-level), containing approximately 4,000 ppm boron in the form of poly- and metaborate ions, 18,000 ppm potassium ion, and much higher concentrations of sodium ion, is required in the ratio of 35 to 40 cubic meters per metric ton of boric acid (H_2BO_3) produced.

Boron, potassium, and sodium values are also extracted from weaker plant brines and end liquors by this process.

The extractant is apparently a kerosene solution of polyols. Make-up quantities of fresh extractant, required to replenish loss from its slight solubility in the spent-brine raffinate, are not divulged. The kerosene make-up alone is estimated at 8 to 10 liters per metric ton of boric acid (H_3BO_3).

3. Operating Parameters

The process is operated at atmospheric temperature and pressure. Total brine flow capacity is estimated between 4 and 12 cubic meters per minute.

4. Utilities

Electric power consumption, principally for agitation and pumping, is estimated between 30 and 80 kWh per metric ton of boric acid (H_3BO_3).

5. Waste Streams

Kerosene vapor is the only atmospheric emission (inferred). Quantitative information is not available.

Spent brine, 35 to 40 cubic meters per metric ton of H_3BO_3 , is the only liquid waste stream. It is returned to Searles Lake. Estimated kerosene content: ~200 ppm.

There are no solid wastes.

6. EPA Source Classification Code

None established

7. References

Havighorst, C. R. AP&CC's New Process Separates Borates from Ore by Extraction. Chem. Eng. 70:228-232, November 11, 1963.

STRIPPING1. Function

The process (see Figure 8) recovers an aqueous solution of boric acid, potassium sulfate, and sodium sulfate from the loaded extractant from Process 17. Also, this process includes the step of adsorption of organic materials on porous carbon.

The loaded extractant is stripped of the recoverable values by washing with sulfuric acid. The solution formed is forwarded to Process 10 for separation of boric acid.

Essential equipment consists of an agitated contactor tank, a separator tank, a carbon-packed adsorption column, all plastic or rubber-lined, and heat exchangers.

2. Input Materials

An undivulged amount of loaded extractant plus 25 percent (estimated) aqueous sulfuric acid is fed to the process. The requirement of the latter is approximately 2.5 metric tons H_2SO_4 (100% basis) per metric ton of boric acid (H_3BO_3).

3. Operating Parameters

The process operates at atmospheric pressure and at a temperature estimated to be 50°C.

4. Utilities

Electric power requirement is estimated to be 20 to 40 kWh per metric ton of boric acid (H_3BO_3).

5. Waste Streams

Kerosene vapors are the only atmospheric emission (inferred). Quantitative information is not available.

6. EPA Source Classification Code

None established

7. References

Havighorst, C. R. AP&CC's New Process Separates Borates from Ore by Extraction. Chem. Eng. 70:228-232, November 11, 1963.

DISSOLUTION (SALT CAVERN)1. Function

The process (see Figure 9) saturates natural sodium sulfate brine with sodium chloride in order to suppress the solubility of sodium sulfate during its separation in Process 20. This process also includes the immediately prior step of brine production. Process 19 is similar to solution mining. The sodium sulfate brine is injected into a cavity in a salt stratum and subsequently is forced to the surface, saturated with NaCl.

2. Input Materials

Natural sodium sulfate wells of Gains County, Texas, contain 7 to 11 percent sodium sulfate (Na_2SO_4) and smaller percentages of sodium chloride and magnesium chloride. Ten to 14 cubic meters of brine are required per metric ton of sodium sulfate (Na_2SO_4) produced.

A gross estimate of the quantity of sodium chloride dissolved from the salt cavern is 1 metric ton per metric ton of sodium sulfate produced.

3. Operating Parameters

Estimated salt cavern temperature is 30° to 35°C

4. Utilities

Estimated power consumption is 50 to 70 kWh per metric ton of sodium sulfate.

5. Waste Streams

There are no waste streams.

6. EPA Source Classification Code

None established

7. References

Faith, L. F., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 2nd Edition. New York, John Wiley & Sons, Inc., 1957. 852 p.

CRYSTALLIZATION/FILTRATION1. Function

- *a. Production of sodium sulfate from Gaines County, Texas brine (Figure 9) - The process crystallizes Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) from the sodium chloride-sodium sulfate brine obtained from Process 19 and then filters the Glauber's salt crystals from the mother liquor. Essential equipment includes a brine chiller, crystallizing tank, and a rotary drum filter or centrifuge.
- b. Production of potassium chloride from Sylvinite (Figure 17) - The process crystallizes potassium chloride (KCl) from a sodium chloride-potassium chloride liquor forwarded from Process 47, then filters the potassium chloride crystals from the mother liquor. The crystals are air-dried on the filter.

The process includes the sequential steps of:

evaporative cooling
crystallization
settling (thickening)
filtration
crushing and screening
packaging (railroad cars)

Essential major equipment consists of evaporative coolers, crystallizer tanks, settling tanks, continuous rotary drum filters with provisions for drying, crushing rolls, and vibrating screens.

2. Input Materials

- a. Sodium sulfate brine, saturated with sodium chloride from Process 19, has the following approximate composition:

Na_2SO_4	7 to 11%
NaCl	23 to 25%
MgCl_2	not divulged

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

The quantity of brine entering Process 20 is estimated to be 13 to 20 cubic meters per metric ton of sodium sulfate produced. This quantity includes recycled mother liquor.

- b. Sodium chloride-potassium chloride leach liquor from Process 47 is estimated to have the following composition:

KCl	22 to 24%
NaCl	14 to 16%

The quantity of liquor entering the process, including recycled KCl, is estimated to be between 7 and 8 cubic meters per metric ton of potassium chloride produced.

3. Operating Parameters

- a. Crystallizers operate at -7° to -9°C , and at atmospheric pressure.

Tube-and-shell exchangers chill incoming brine with cool mother liquor leaving the process. Final brine cooling is by ammonia refrigeration coils.

- b. The temperature of the incoming NaCl-KCl brine from Process 47 is between 105° and 110°C , and is cooled in direct-contact condensers to 25° to 27°C prior to entry into crystallizer-settling tanks. Filtration is conducted at 27°C . Filtration occurs at atmospheric pressure. Cooling occurs at 0.1 kg/cm^2 absolute pressure.

4. Utilities

- a. Estimated electrical energy consumption, including refrigeration requirement, is 60 to 80 kWh per metric ton of sodium sulfate produced.

Cooling water requirement is estimated at 10 to 15 cubic meters (once-through basis) per metric ton of sodium sulfate produced.

- b. Estimated electrical energy consumption is 15 to 20 kWh per metric ton of potassium chloride produced.

Approximately 50 cubic meters of cooling water (once-through basis) are required for barometric condensers.

Steam is consumed by ejectors (estimated less than 0.01 metric tons per metric ton of Na_2SO_4).

5. Waste Streams

- a. There are no atmospheric emissions or solid wastes.

A portion of the mother liquor recycled from Process 20 to Process 19 is bled off to intermediate waste storage ponds and thence to injection wells. The quantity of bleed is estimated to be between 2 and 4 liters per metric ton of sodium sulfate produced.

- b. There are no atmospheric emissions or waste flows.

6. EPA Source Classification Code

- a. None established
b. None established

7. References

- a. Faith, L. F., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 2nd Edition. New York, John Wiley & Sons, Inc., 1957. 852 p.
- b. Jacobs, J. J. Potassium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1966. 16:369-400.
- Magraw, R. M. New Mexico Sylvinite. Ind. Eng. Chem. 30:861-871, Aug. 1938.
- Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1967. 905 p.
- Turrentine, J. W. Potash in North America. New York, Reinhold, 1943. 186 p.
- White, N. C., and Carl A. Arend. Potash Production at Carlsbad. Chem. Eng. Progr. 46:523-530, October 1950.

BRINE DESULFURIZATION

1. Function

This process (See Figure 10) permits the evolution of traces of hydrogen sulfide gas (H_2S) from brine produced from the Smackover formation in Arkansas. The hot brine from wells is held in a surge pond to allow H_2S gas to be evolved and to be oxidized to elemental sulfur in the atmosphere. The elemental sulfur formed floats on the brine as scum.

This process includes the step of brine production from the formation.

2. Input Materials

Arkansas brine, containing between 3,500 and 5,000 ppm bromine, yields 170 to 250 cubic meters per metric ton of bromine.

3. Operating Parameters

Ambient temperature and atmospheric pressure.

4. Utilities

Electrical energy (includes brine production) - 400 to 1,200 kWh per metric ton of bromine.

5. Waste Streams

Gaseous H_2S - Detectable quantities evolved into surrounding atmosphere. No quantitative information is available.

Elemental Sulfur - Collected as elemental sulfur and buried (landfill). No quantitative information is available.

6. EPA Source Classification Code

None Established.

7. References

None. (Information presented above is based on first-hand knowledge.)

ACIDIFICATION1. Function

This process (See Figure 10) lowers the pH of bromide-containing brine by addition of hydrochloric acid (HCl). Enough chlorine (Cl_2) may also be added to the brine at this point to oxidize a portion of the bromide to elemental bromine (Br_2).

The following brines are treated with HCl before entering Process 23:

- a. Process 21 Arkansas (Smackover formation)
- b. Raw Michigan brine (various formations)
- c. Process 27, Figure 12 Iodine-stripped Michigan brine
- d. Process 10, Figure 7 Potassium chloride brine (intermediate product in Searles Lake operations)

Enough HCl (or H_2SO_4) is added to decrease the pH of the brines to approximately 3.5. An undivulged portion of the Cl_2 necessary to oxidize bromide to Br_2 may also be added to the brines.

2. Input Materials

Bromide-containing brines - m^3 per metric ton of Br_2 :

- a. 170 to 250
- b. 600
- c. 350
- d. 200

HCl (on a 100 percent HCl basis) -

- a,c. Sufficient to adjust the pH to 3.5 (quantity used is not divulged)
- b,d. 0.008 to 0.009 metric tons per metric ton of Br_2

Cl_2 -

- a,b,c. A portion of the 0.45 metric tons per metric ton of Br_2 is required to oxidize bromide to bromine. The remainder is added in Process 23.

- d. None. Chlorine is added in Process 23.
3. Operating Parameters
- a,b,c,d.
- Temperature - 70 to 80°C
- Pressure - slightly above atmospheric
- pH of brine - approximately 3.5
4. Utilities
- Electrical energy consumption per metric ton of Br₂:
- a. 10 kWh
b. 30 kWh
c. 20 kWh
d. 10 kWh
5. Waste Streams
- None
6. EPA Source Classification Code
- None established
7. References
- b. Faith, W. L., D. B. Keyes, and R. L. Clark.
Industrial Chemicals, 3rd Edition. New York, John
Wiley & Sons, Inc., 1965. 852 p.
- d. Robertson, G. R. Expansion of the Trona Enterprise.
Industrial and Engineering Chemistry. 34:133-137
February 1942.
- a,b,c,d.
Stenger, V. A. Bromine. In: Kirk-Othmer
Encyclopedia of Chemical Technology, 2nd Edition.
Standen, A. (ed.). New York, John Wiley and Sons,
Inc., 1964. 3:750-766.

CHLORINATION/STRIPPING1. Function

This process (See Figure 10) completes the oxidation by chlorine (Cl_2) of the bromide ion in acidified brine coming from Process 22. It also strips elemental bromine (Br_2) from the brine by the use of a counter-current flow of steam upward through a packed tower.

The major liquid stream, entering the tower near the top is the acidified, and partially chlorinated brine from Process 22. An additional liquid stream, water saturated with Cl_2 and Br_2 , is recycled to the tower from Process 24 and Process 26. Gaseous Cl_2 , injected into the tower at several points, and the low-pressure steam admitted at the bottom are the major gaseous streams. A stream of non-condensable gases from Process 24, containing Cl_2 and Br_2 is fed to the tower near the top.

Br_2 vapor, plus unreacted Cl_2 are carried by the steam from the top of the tower to a condenser. The two condensed liquid phases then flow to Process 24. The stripped brine flows from the tower bottom to Process 25.

2. Input Materials

Acidified brine from Process 22, originating from any one of the respective sources listed below:

- *a. Process 21, Arkansas (Smackover formation) -
170 to 250 cubic meters per metric ton of Br_2 , or
- b. Raw Michigan brine (various formations) -
600 cubic meters per metric ton of Br_2 , or
- c. Process 27, Figure 12, iodine-stripped Michigan brine -
350 cubic meters per metric ton of Br_2 .
- d. Process 10, Figure 7, potassium chloride brine formed in the Searles Lake operations - 200 cubic meters per metric ton of Br_2 .

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

•Cl₂ :

- a,b,c. The remaining portion of the 0.45 metric ton Cl₂ per metric ton of Br₂ that is required to oxidize bromide to Br₂. (Some Cl₂ was added in Process 22).
d. 0.45 metric ton per metric ton of Br₂

•Steam:

- a,b,c,d. 2 to 15 metric tons per metric ton of Br₂

•Non-condensable gases containing Cl₂ and Br₂ from Process 24:

- a,b,c,d. Undivulged quantity.

3. Operating Parameters

- a,b,c,d.
•Temperature is 85 to 95°C
•Pressure is slightly above atmospheric
•The pH of the brine is approximately 3.5
•The oxidation-reduction potential of the brine is 0.88 to 0.97 volts (platinum versus saturated calomel).

4. Utilities

- a,b,c,d.
•Cooling Water
30 to 100 cubic meters per metric ton of Br₂

5. Waste Streams

- a,b,c,d.
•A gas stream containing primarily non-condensable gases is vented to the atmosphere. This stream contains some Cl₂ and Br₂. The Cl₂ plus Br₂ portion of the stream is estimated to be less than 0.001 metric ton per metric ton of Br₂ product.

6. EPA Source Classification Code

None established

7. References

- a,b,c,d.
Stenger, V. A. Bromine. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, John Wiley and Sons, Inc., 1964. 3: 750-766.

Yaron, F. Chapter 1. In: Bromine and Its Compounds. Jolles, Z. E. (ed.). London, Ernest Benn, Limited, 1966. p. 3-42.

- d. Robertson, G. R. Expansion of the Trona Enterprise. Industrial and Engineering Chemistry. 34: 133-137, February 1942.

GRAVITY SEPARATION1. Function

This process (See Figure 10) separates crude liquified bromine (Br_2) from water and noncondensable gases.

The condensed halogen and water-laden vapors from Process 23 flow to a corrosion-resistant gravity separator. The high-density crude bromine exits the bottom through a trap and goes to Process 26. Lower density water saturated with Br_2 and chlorine (Cl_2) is returned to the stripping tower of Process 23. Noncondensable gases containing some Br_2 and Cl_2 are returned to the upper part of the stripping tower of Process 23.

The contexts referred to below are:

- *a. Arkanses brine
- b. Michigan brine
- c. Iodine-stripped Michigan brine
- d. Searles Lake process potassium chloride brine

2. Input Materials

a,b,c,d.

Condensed vapors from Process 23 (primarily Br_2 , Cl_2 , and water) - 2 cubic meters per metric ton of Br_2

3. Operating Parameters

a,b,c,d.

Temperature is approximately 0 to 10°C above ambient, pressure is approximately atmospheric.

4. Utilities

a,b,c,d. None

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

5. Waste Streams

a,b,c,d. None

6. EPA Source Classification Code

None established

7. References

a,b,c,d.

Stenger, V. A. Bromine. In: Kirk-Othmer
Encyclopedia of Chemical Technology, 2nd Edition,
Standen, A. (ed.). New York, John Wiley and Sons,
Inc., 1964. 3750-766.

Yaron, F. Chapter 1. In: Bromine and Its Compounds,
Jolles, Z. E. (ed.). London, Ernest Benn, Ltd., 1966.
p. 3-42.

SPENT BRINE NEUTRALIZATION1. Function

This process (See Figure 10) neutralizes the acidity of the bromine-stripped brine effluent from Process 23 preparatory to disposal of further processing.

Lime (CaO) or caustic soda (NaOH) is added to the bromine-stripped brine leaving Process 23. Usually the neutralized brine is cooled by exchanging heat with brine entering Process 22. The neutralized bromine-stripped brine is then either:

- *a. Arkansas brine - Returned to original source strata.
- b. Michigan brine - Forwarded to Process 7, Figure 4.
- c. Iodine-stripped Michigan brine - Forwarded to Process 7, Figure 4.
- d. Searles Lake process potassium chloride brine - Forwarded to Process 10, Figure 7.

2. Input Materials

Bromine-stripped brines - m³ per metric ton of Br₂:

- a. 170 to 250
- b. 600
- c. 350
- d. 200

Lime (CaO) - metric tons per metric ton Br₂:

- a. 0.007
- b. 0.02
- c. 0.01
- d. 0.008

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

3. Operating Parameters

Temperature -

a,b,c,d.

90°C entering the neutralizer

40 to 90°C after exchanging heat with brine
entering Process 22

Pressure -

a,b,c,d. Near atmospheric

pH -

a,b,c,d. Entering at approximately 3.5. Exiting at
approximately 7.

4. Utilities

Electrical energy -

a. Primarily for pumping bromine-stripped brine into
source strata.

50 kWh per metric ton of Br₂

b,c,d.

Primarily for pumping bromine-stripped brine to the
next process.

Less than 20 kWh per metric ton of Br₂

5. Waste Streams

Bromine-stripped neutralized brine -

a. 170 to 250 cubic meters per metric ton of Br₂
returned to source strata

b,c,d. None

6. EPA Source Classification Code

None established

7. References

a,b,c,d.

Stenger, V. A. Bromine. In: Kirk-Othmer Encyclo-
pedia of Chemical Technology, 2nd Edition, Standen,
A. (ed.). New York, John Wiley and Sons, Inc.,
1964. 3: 750-766.

Yaron, F. Chapter 1. In: Bromine and Its Compounds,
Jolles, Z. E. (ed.). London, Ernest Benn, Ltd.,
1966. p. 3-42.

DISTILLATION1. Function

This process (See Figure 10) separates halogenated hydrocarbons and water saturated with chlorine (Cl_2) from crude bromine (Br_2) coming from Process 24.

Crude Br_2 from Process 24 is fed to a distillation column. Higher-boiling halogenated hydrocarbons are removed from the bottom of the column. Bromine and Cl_2 boil off the top and are cooled in a reflux condenser. Most of the cooled chlorine returns to Process 23, whereas the cooled liquid bromine goes to a final distillation column. Bromine with a purity of 99.8% is the bottom product from the column, while a rich chlorine overhead stream is returned to Process 23.

The contexts referred to below are:

- *a. Arkansas brine
- b. Michigan brine
- c. Iodine-stripped Michigan brine
- d. Searles Lake process potassium chloride brine

2. Input Materials

Crude Br_2 -

a,b,c,d. 1.1 metric ton per metric ton of Br_2 product.

3. Operating Parameters

Temperature -

a,b,c,d. Temperature ranges from ambient to 100°C .

Pressure -

a,b,c,d. Near atmospheric.

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

4. Utilities

- Steam:

a,b,c,d. 0.4 metric ton per metric ton of Br₂

- Cooling water:

a,b,c,d. 10 metric tons per metric ton of Br₂

- Electrical energy:

a,b,c,d. Less than 1 kWh per metric ton of Br₂

5. Waste Streams

- Halogenated hydrocarbons (liquid); burned in sludge-pit:

a,b,c,d.

Undivulged quantities estimated to be less than
0.01 metric ton per metric ton of Br₂.

6. EPA Classification Code

None established

7. References

a,b,c,d.

Stenger, V. A. Bromine. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, John Wiley and Sons, Inc., 1964. 3: 750-766.

IODINE STRIPPING1. Function

This process (see Figure 12) recovers elemental iodine (I_2) as a dilute vapor in air from Michigan brines. Steps involved include acidification, oxidation and air stripping.

A brine stream containing approximately 40 ppm I_2 is sprayed into a steel tower lined with acid-proof brick and packed with ceramic rings. Hydrochloric acid and chlorine are injected into the brine feed line ahead of the tower. A large counter-current flow of air strips the released elemental I_2 from the brine spray and conveys it to Process 28.

2. Input Materials

- Michigan brine, containing approximately 40 ppm iodine -
23,000 cubic meters per metric ton of iodine
- Hydrochloric acid -
0.3 metric ton (100% basis) per metric ton of iodine
- Chlorine -
0.28 to 0.30 metric tons per metric ton of iodine
- Air -
90,000 to 120,000 cubic meters per metric ton of iodine.

3. Operating Parameters

Ambient temperature and atmospheric pressure.

4. Utilities

- Electrical energy -
approximately 4000 kWh per metric ton of iodine

5. Waste Streams

None

6. EPA Source Classification Code

None established

7. References

Sawyer, F. G., M. F. Ohman, and F. E. Lusk. Iodine from Oil Well Brines. Industrial and Engineering Chemistry. 41: 1547-1552, August 1949.

IODINE ABSORPTION

1. Function

This process (see Figure 12) removes iodine (I_2) from the iodine-laden air coming from Process 27 and absorbs it into an acid solution.

Cooled iodine-laden air flows up through an acid-proof packed tower. A counter-flow of HI- H_2SO_4 solution from Process 29 absorbs the iodine vapor from the air. The air is returned to the iodine stripping tower of Process 27.

2. Input Materials

• Iodine-laden air -

90,000 to 120,000 cubic meters per metric ton of iodine

• HI- H_2SO_4 solution -

80 to 100 cubic meters per metric ton of iodine

3. Operating Parameters

Up to 10°C above ambient temperature
Atmospheric pressure

4. Utilities

• Cooling water -

250 cubic meters per metric ton of iodine

5. Waste Streams

• Air-bleed to the atmosphere -

Iodine content is undisclosed but estimated to be very minute. The total bleed is less than 1 percent of the air input into Process 27.

6. EPA Source Classification Code

None established

7. References

Development Document for Proposed Effluent Limitations for the Significant Inorganic Products Segment of the Inorganic Chemicals Manufacturing Point Source Category (Draft). General Technologies Corporation. December 1973.

Sawyer, F. G., M. F. Ohman, and F. E. Lusk. Iodine from Oil Well Brines. Industrial and Engineering Chemistry. 41: 1547-1552. August 1949.

IODINE REDUCTION1. Function

This process (see Figure 12) reduces elemental iodine to iodide. The iodine enters this process from Process 28, where it was absorbed into a HI-H₂SO₄ solution.

Sulfur dioxide is dissolved into the HI-H₂SO₄ solution in an acid-proof vessel to reduce absorbed iodine to hydroiodic acid. A portion of the acid solution is recycled to Process 28 to absorb additional iodine. The remainder of the solution is forwarded to Process 30.

2. Input Materials

- HI-H₂SO₄ solution containing absorbed iodine -
80-100 cubic meters per metric ton of iodine
- Sulfur dioxide -
0.25 metric ton per metric ton of iodine
- Water -
23 cubic meters per metric ton of iodine

3. Operating Parameters

Ambient temperature and atmospheric pressure

4. Utilities

- Electrical energy -
4 to 5 kWh per metric ton of iodine

5. Waste Streams

None

6. EPA Source Classification Code

None established

7. References

Development Document for Proposed Effluent Limitations for the Significant Inorganic Products Segment of the Inorganic Chemicals Manufacturing Point Source Category (Draft). General Technologies Corporation. December 1973.

Sawyer, F. G., M. F. Ohman, and F. E. Lusk. Iodine from Oil Well Brines. Industrial and Engineering Chemistry. 41: 1547-1552. August 1949.

IODIDE OXIDATION1. Function

This process (see Figure 12) oxidizes iodide in the HI-H₂SO₄ solution from Process 29. The resulting iodine precipitates, and is ultimately forwarded to Process 31.

The HI-H₂SO₄ solution from Process 29 is forwarded to a brick-lined conical precipitating tank. Chlorine gas is bubbled into the solution from Pyrex® tubes. The chlorine oxidizes the iodide to iodine. The iodine precipitates and passes through a porcelain valve into a wooden box filter. The wet iodine cake collects on a Saran® filter cloth and then is transferred to Process 31. The HCl-H₂SO₄ filtrate is used elsewhere in the plant.

2. Input Materials

- HI-H₂SO₄ solution -
23 cubic meters per metric ton of iodine
- Chlorine -
0.28 metric ton per metric ton of iodine

3. Operating Parameters

Ambient temperature and atmospheric pressure

4. Utilities

None

5. Waste Streams

Detectable but unquantified amount of chlorine may escape to the atmosphere.

6. EPA Source Classification Code

None established.

7. References

Development Document for Proposed Effluent Limitations for the Significant Inorganic Products Segment of the Inorganic Chemicals Manufacturing Point Source Category (Draft). General Technologies Corporation. December 1973.

Sawyer, F. G., M. F. Ohman, and F. E. Lusk. Iodine from Oil Well Brines. Industrial and Engineering Chemistry. 41: 1547-1552. August 1949.

IODINE FINISHING1. Function

This process (See Figure 12) melts the wet iodine from Process 30, pours the molten iodine into ingots, pulverizes the ingots, and packages the crushed iodine.

Wet iodine from Process 30, along with strong sulfuric acid (over 60%), is heated in a steam-jacketed kettle. The acid chars residual organic impurities and removes water from the iodine. After prolonged heating, the sulfuric acid is poured off the top of the kettle, after which the molten iodine is poured into enamel-lined slop sinks. After cooling, the iodine ingots are crushed and packaged in wooden kegs. The wet sulfuric acid is used elsewhere in the plant.

2. Input Materials• Wet iodine -

1.1 metric ton per metric ton of iodine

• Sulfuric acid (over 60% H_2SO_4) -

0.2 to 0.3 cubic meter of acid solution per metric ton of iodine.

3. Operating Parameters

Temperature is 120° to 160°C.
Pressure is atmospheric.

4. Utilities• Steam -

100,000 to 200,000 kcal per metric ton of iodine.

• Cooling water -

1 to 2 cubic meters per metric ton of iodine.

• Electrical energy -

1 to 2 kWh per metric ton of iodine.

5. Waste Streams

- Water vapor containing a detectible but unquantified amount of iodine escapes to the atmosphere.

6. EPA Source Classification Code

None established

7. References

Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Significant Inorganic Products Segment of the Inorganic Chemicals Manufacturing Point Source Category (Draft). General Technologies Corporation. December 1973.

Sawyer, F. G., M. F. Ohman, and F. E. Lusk. Iodine from Oil Well Brines. Industrial and Engineering Chemistry. 41: 1547-1552. August 1949.

DIGESTION1. Function

The process (see Figure 13) generates mixed crystals of lithium sulfate (Li_2SO_4) and sodium sulfate (Na_2SO_4) from a filter cake of dilithium sodium phosphate (Li_2NaPO_4) by treatment of the latter with sulfuric acid (H_2SO_4). A mother liquor containing a high concentration of phosphoric acid (H_3PO_4) is also produced. The process also includes the subsequent step of centrifuging the mixed sulfates from the phosphoric acid mother liquor and the step of concentrating the mother liquor by evaporation to a marketable, crude phosphoric acid.

The mixed sulfate crystals are forwarded to Process 33.

2. Input Materials

Between 1.8 and 1.9 metric tons of Li_2NaPO_4 from Process 11 are required per metric ton of Li_2CO_3 produced. Approximately two metric tons of concentrated H_2SO_4 are consumed per metric ton of Li_2CO_3 produced.

3. Operating Parameters

The process is conducted at atmospheric pressure at a temperature of 115°C .

It is estimated here that the average production rate of Li_2CO_3 at one of the plants operating on Searles Lake brine is between 5 and 8 metric tons per day. This relatively small rate would indicate either batchwise or intermittent-continuous modes of operation.

4. Utilities

Electric energy consumption is estimated here to be in the range of 15 to 20 kWh per metric ton of Li_2CO_3 produced.

Steam consumption, probably at a gage pressure of 10 kg per cm^2 , is estimated to be between 1 and 2 metric tons per metric ton of Li_2CO_3 produced.

5. Waste Streams

There are no known atmospheric, liquid, or solid wastes.

6. EPA Source Classification Code

None established.

7. References

Bach, R. O., C. W. Kamienski, and R. B. Ellestad.
Lithium and Lithium Compounds. In: Kirk-Othmer
Encyclopedia of Chemical Technology, 2nd Edition,
Standen, A. (ed.). New York, Interscience Publishers,
1966. 12:529-556.

Bixler, G. H., and D. L. Sawyer. Boron Chemicals from
Searles Lake. Ind. Eng. Chem. 49:322-332, March 1957.

Shreve, R. N. Chemical Process Industries, 3rd Edition.
New York, McGraw-Hill, 1967. 905 p.

LITHIUM CARBONATE SEPARATION1. Function

- *a. In lithium carbonate production from Searles Lake brine (see Figure 13) - The process obtains moist lithium carbonate (Li_2CO_3) crystals from a mixed crystal mass of lithium sulfate (Li_2SO_4) and sodium sulfate (Na_2SO_4), obtained as a centrifuge cake from Process 32. The process comprises the sequential steps of dissolution of the mixed sulfate crystals in water, precipitation of Li_2CO_3 by addition of sodium carbonate (Na_2CO_3) solution and centrifuging the resulting slurry to obtain a moist, washed cake of Li_2CO_3 crystals.

Sodium sulfate (Na_2SO_4) liquor is obtained as a by-product and is forwarded to Process 10, Figure 7, for Na_2SO_4 recovery.

- b. In lithium carbonate production from Silver Peak, Nevada brine (see Figure 13) - Moist lithium carbonate (Li_2CO_3) crystals are obtained from the "bitterns" resulting from Process 13. The moist crystals are forwarded to Process 11 for drying.

The process comprises the sequential steps of precipitation of Li_2CO_3 from the bitterns by addition of sodium carbonate (Na_2CO_3) solution and filtration of the resulting slurry on a belt-filter.

2. Input Materials

- a. The mixed Li_2SO_4 - Na_2SO_4 crystals entering the process contain between 7 and 8 percent lithium on a dry weight basis. Between 2.5 and 2.6 metric tons of the crystals are consumed per metric ton of Li_2CO_3 produced.

Between 1.45 and 1.50 metric tons (100% basis) of sodium carbonate (Na_2CO_3) are required per metric ton of Li_2CO_3 produced.

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

- b. The bitterns fed to the process contain between 3 and 6 percent lithium chloride (LiCl), 11 percent potassium chloride (KCl), and approximately 22 percent sodium chloride (NaCl). Between 15 and 30 cubic meters of bitterns are consumed per metric ton of Li_2CO_3 produced.

Between 1.45 and 1.50 metric tons (100% basis) of sodium carbonate are required per metric ton of Li_2CO_3 produced.

3. Operating Parameters

- a,b. The process is conducted at atmospheric pressure. It is conjectured that the precipitation and filtration steps at both the Searles Lake and Silver Peak locations are conducted at temperatures near 100°C .

The relatively small estimated average production rates (between 5 and 8 metric tons per day for the Searles Lake operation and between 15 and 25 metric tons per day for Silver Peak, Nevada) indicate either batchwise or intermittent-continuous modes of operation.

4. Utilities

- a. Total consumption of electrical energy is estimated to be between 15 and 30 kWh per metric ton of Li_2CO_3 produced.

Steam, probably at a gage pressure near 10 kg/cm^2 , is needed to heat process water. Assuming no heat recovery, the steam requirement is estimated to be between 1.5 and 2.0 metric tons per metric ton of Li_2CO_3 .

Total process water requirement, including process steam make-up, is estimated to be between 10 and 12 cubic meters per metric ton of Li_2CO_3 .

- b. Total consumption of electrical energy is estimated to be between 20 and 40 kWh per metric ton of Li_2CO_3 produced.

Steam, probably at a gage pressure near 10 kg/cm^2 , is required to heat the entering bitterns and the wash water. Assuming 75 percent heat recovery, the steam consumption is estimated to be between 1.0 and 3.0 metric tons per metric ton of Li_2CO_3 produced.

Estimated water consumption, including process steam makeup, is between 1.5 and 4.0 cubic meters per metric ton of Li_2CO_3 produced.

5. Waste Streams

- a,b. There are no atmospheric emissions from the process as operated at either Searles Lake or Silver Peak.
- b. At Silver Peak, the process discharges the mother liquor from the Li_2CO_3 precipitation. This is a brine containing about 10 percent KCl and 24 percent NaCl. It is estimated to amount to between 18 and 36 cubic meters per metric ton of Li_2CO_3 produced. It is impounded and allowed to evaporate, leaving behind 6 to 12 metric tons of solids per metric ton of Li_2CO_3 produced.

6. EPA Source Classification Code

None established.

7. References

- a. Bach, R. O., C. W. Kamienski, and R. B. Ellestad. Lithium and Lithium Compounds. Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1967. 12:529-556.

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1967. 905 p.
- b. Barrett, W. T., and B. J. O'Neal, Jr. Recovery of Lithium from Saline Brines using Solar Evaporation. In: Third Symposium on Salt, Rau, J. L., and L. F. Dellwig (ed.). Cleveland, Ohio, Northern Ohio Geological Society, 1970. 2:47-50.

Luckenbach, W. F. Year's End Report on Lithium. Eng./Min. J. 168:152, February 1967.

CLARIFYING1. Function

The process (see Figure 14) removes calcium, magnesium, and heavy metal ions from saturated sodium chloride brine. Controlled additions of soda ash and lime cause the ions to form insoluble compounds which form a mud precipitate. The process occurs in settling tanks. Clarified brine is fed to Process 37.

2. Input Materials

Saturated sodium chloride brine - 5.7 cubic meters per metric ton of soda ash.

Soda ash (Na_2CO_3) - Quantity varies depending primarily on total calcium in brine. In one case, 0.031 metric ton per metric ton of soda ash was used.

Lime (CaO) - Quantity varies depending primarily on total magnesium in brine. In one case, 0.0036 metric ton per metric ton of soda ash was used.

3. Operating Parameters

The process is conducted at atmospheric pressure and ambient temperature.

4. Utilities

Electrical energy is used primarily for pumping. The requirement is less than 10 kWh per metric ton.

5. Waste Streams

The underflow mud from settling tanks which consists primarily of calcium carbonate and magnesium hydroxide is transferred to pondage. Solids become landfill, while water evaporates or flows into natural streams. The size of this stream depends on the quantity of calcium and magnesium in the brine. In one case, this stream was 0.1 cubic meter per metric ton soda ash. It contained 0.06 metric ton solids per metric ton soda ash.

6. EPA Source Classification Code

None established

7. References

Deutsch, Z. G., C. C. Brumbaugh, and F. H. Rockwell.
Alkali and Chlorine Industry. In: Kirk-Othmer Encyclo-
pedia of Chemical Technology, 2nd Edition, Standen,
A. (ed.). New York, John Wiley & Sons, Inc., 1963.
1:668-758.

DISSOLUTION/CLARIFYING1. Function

In general, the process forms a relatively impure solution by dissolving a crude material in water. It then removes dissolved or suspended contaminants from the solution by some combination of the steps of precipitation, settling and filtration. The specific functions of the several applications of the process are listed below.

- *a. As applied to the production of soda ash by the Solvay operation (see Figure 14) - The process dissolves rock salt (NaCl) in water, forming a saturated NaCl brine containing undesired minor concentrations of calcium (Ca) and magnesium (Mg) ions plus suspended insolubles. The Ca and Mg are precipitated by addition of NaOH and Na_2CO_3 , and removed either by settling and filtration or settling alone. The purified brine is forwarded to Process 37.

Essential equipment consists of agitated dissolving tanks, settling tanks, and in some cases, continuous filters.

- b. As applied to the preparation of saturated NaCl brine for the electrolytic production of chlorine and caustic (see Figure 15) - The process application is almost identical to "a", above, except that in most operations the NaCl recovered from the evaporation of caustic (Process 10) is also added to the agitated dissolving tanks. Additionally, alternative NaCl sources may be either granular salt, or solution-mined NaCl brine. In the latter case, the dissolution step is omitted. The clarified brine from this process is forwarded to Process 41 or 42.
- c. As applied to the "Sesquicarbonate" operations for production of natural soda ash (see Figure 1) - The process forms a saturated aqueous solution of trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) by dissolving crushed trona

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

in hot mother liquor recycled from Process 10, and subsequently clarifying the solution by settling out the insoluble gangue material. The clarified trona liquor is forwarded to Process 16 for further purification.

Essential equipment consists of agitated dissolving tanks and Dorr-type settling tanks or clarifiers.

- d. As applied to the "Monohydrate" operation for production of natural soda ash (see Figure 19) -
Crude soda ash received from Process 12 is dissolved in water to form a saturated aqueous sodium carbonate (Na_2CO_3) solution, which is then forwarded to Process 10 for recovery of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ crystals.

Essential equipment consists of agitated dissolving tanks, settling tanks, and continuous filters.

- e. As applied to the preparation of re-purified NaCl for the electrolytic production of sodium metal in the Downs cell (see Figure 21) - The process application is similar to that described in "a" and "b", above except that already-purified NaCl is the raw material, and the degree of purity of the brine produced is higher. The sulfate content of the entering NaCl is removed in the process by precipitation with BaCl_2 . The purified brine is forwarded to Process 10.

2. Input Materials

- a. Quantity consumed per metric ton of Na_2CO_3 produced -

Rock salt	1.5 to 1.6 metric tons
Water	4 to 6 cubic meters
Sodium hydroxide	5 kilograms (estimated)
Sodium carbonate	20 kilograms (estimated)

- b. Quantity consumed per metric ton of Cl_2 produced -

Rock salt, (or granular)	1.8 to 2.0 metric tons
Salt brine, (alternative input)	6 to 7 cubic meters
Water (for dry- salt input)	5 to 6 cubic meters
Sodium hydroxide	5 kilograms (estimated)
Sodium carbonate	20 kilograms (estimated)

c. Quantity consumed per metric ton Na₂CO₃ produced -

Crushed trona	1.4 to 1.5 metric tons
Make-up water	1 to 2 cubic meters (gross est.)
Recycled mother liquor	2 to 3 cubic meters (gross est.)

d. Quantity consumed per metric ton Na₂CO₃ produced -

Crude Na ₂ CO ₃	1.1 to 1.2 metric tons
Water	3.5 to 4 cubic meters
Porous carbon	undisclosed quantity, estimated 20 kilograms

e. Quantity consumed per metric ton Na metal produced -

NaCl	3.5 to 4.0 metric tons
NaOH	2 to 5 kilograms (estimated)
BaCl ₂	0.5 to 1.0 kilogram
FeCl ₃	2 to 3 kilograms
Water	9 to 11 cubic meters

3. Operating Parameters

a,b,e. Atmospheric pressure and temperature slightly above ambient.

c. Atmospheric pressure and near the atmospheric boiling point of saturated trona liquor, estimated to be 95° to 100°C.

d. Atmospheric pressure and temperatures slightly below the atmospheric boiling point, 95° to 100°C.

4. Utilities

a,d. Per metric ton Na₂CO₃ produced -

Electrical energy consumed	10 to 15 kWh (gross est.)
----------------------------	---------------------------

b. Per metric ton Cl₂ produced -

Electrical energy consumed	5 to 15 kWh (gross est.)
----------------------------	--------------------------

c. Per metric ton Na₂CO₃ produced -

Electrical energy consumed	15 to 20 kWh
Low pressure (2 kg/cm ²) steam	0.5 to 1.0 metric ton (gross est.)

e. Per metric ton Na metal produced -

Electrical energy consumed 25 to 40 kWh (gross est.)

5. Waste Streams

- a. Underflow slurry from settling tanks, or slurried filter cake, consisting of $\text{Mg}(\text{OH})_2$, CaCO_3 , and clay particles, is presumed to be wasted to tailings ponds. Solids become landfill; water evaporates, or is sluiced to natural streams. Estimated quantity: 10 to 20 kg total solids, plus 0.1 to 0.3 cubic meters water per metric ton Na_2CO_3 produced.
- b. Slurries similar in composition to those of "a", above are also presumed to be wasted to tailings ponds. Estimated quantity: 10 to 20 kg solids plus 0.1 to 0.2 cubic meters H_2O per metric ton Cl_2 produced.
- c,d. Solids, consisting principally of gangue materials (clay, shale and sand), plus some finely divided CaCO_3 and $\text{Mg}(\text{OH})_2$, is wasted to tailings ponds or piles. It is presumed the solids are conveyed in slurry form. Estimated quantity: 0.09 to 0.12 metric tons solids, plus 0.5 to 0.7 cubic meters water (presumed) per metric ton of Na_2CO_3 produced.
- e. Slurries similar in composition to those of "a", above but containing additionally approximately 1 kg BaSO_4 per metric ton Na metal, are wasted presumably by similar means.

Estimated quantity: 10 to 15 kg solids plus 0.1 to 0.15 cubic meters water per metric ton of Na metal produced.

6. EPA Source Classification Code

a through e: None established

7. References

- a. Deutsch, Z. G., C. C. Brumbaugh, and F. H. Rockwell. Alkali and Chlorine. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1963. 1:668-758.
- Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, Inc., 1965. p. 664-667.
- Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, Inc., 1967. p. 225-230.
- b. Deutsch, Z. G., C. C. Brumbaugh, and F. H. Rockwell. Alkali and Chlorine. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1963. 1:668-758.
- c,d. Rau, E. Sodium Compounds (Carbonates). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1969. 18:461-464.
- e. Lemke, C. H. Sodium. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1969. 18:442-445.
- Sittig, M. Sodium, Its Manufacture, Properties and Uses. New York, Reinhold Publishing Corporation, 1956. 529 p.

CARBONATION1. Function

The process (see Figure 14) converts soda ash (Na_2CO_3) to sodium bicarbonate (NaHCO_3) by carbonation with stack gas.

Soda ash is dissolved in a weak solution of soda ash and sodium bicarbonate recycled from Process 16 and contacted in an absorption tower with a countercurrent flow of CO_2 (stack gas). The most common tower used is the classical Solvay tower, equipped with stacked, single bubble-cap sections positioned above cooling sections. The carbonated slurry is forwarded to Process 16.

2. Input Materials

Soda ash - 0.63 to 0.7 metric ton per metric ton of sodium bicarbonate.

Stack gas containing 16 to 20 percent CO_2 - 800 to 900 cubic meters per metric ton of sodium bicarbonate.

Recycled brine from Process 16 containing some soda ash and sodium bicarbonate - 3 to 5 cubic meters per metric ton of sodium bicarbonate.

3. Operating Parameters

The process is conducted at atmospheric pressure and at a temperature of 40°C .

4. Utilities

Electrical energy - 100 to 200 kWh per metric ton of sodium bicarbonate (gross estimate).

5. Waste Streams

Tail gas from carbonating towers is discharged to the atmosphere. This is mainly nitrogen and carbon dioxide. Estimated quantities are 650 to 750 cubic meters N_2 plus 10 to 50 cubic meters CO_2 per metric ton of NaHCO_3 .

6. EPA Source Classification Code

None established

7. References

Deutsch, Z. G., C. C. Brumbaugh, and F. H. Rockwell. Alkali and Chlorine. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1963. 1:668-758.

Faith, W. L., B. D. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, Inc., 1965. 852 p.

Shreve, R. N. Chemical Process Industries. New York, McGraw-Hill, 1966. 905 p.

ABSORPTION1. Function

- *a. In its application to the Solvay process (See Figure 14) for soda ash, this process produces ammoniated NaCl brine by absorbing NH_3 gas in purified, saturated NaCl brine.

Nearly saturated sodium chloride brine, previously purified, is fed into a cylindrical absorption tower, countercurrent to a gas flow containing a high concentration of ammonia. The ammoniated brine is carbonated during and/or following the absorption process.

- b. In the Hargreaves-type process, this process (See Figure 18) absorbs the HCl gas produced in Process 55 in water to form a 30% hydrochloric acid solution. A mixture of HCl and N_2 gas from a Hargreaves-type process reactor is fed into a vessel countercurrent to a water stream. The absorption of HCl in water is highly exothermic, requiring significant cooling. The corrosiveness of hydrochloric acid necessitates use of Karbate for construction of the heat exchanger and absorption tower. The exit N_2 gas is scrubbed with water or NaOH solution in a packed tower.

2. Input Materials

- a. Sodium chloride brine - 5.7 cubic meters per metric ton of soda ash

Ammonia (makeup only) - 1 kg per metric ton of soda ash

- b. HCl/ N_2 gas mixture - 1230 cubic meters per metric ton of HCl (100% basis)

Water - 2.33 cubic meters per metric ton of HCl (100% basis)

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

3. Operating Parameters

- a. Exit liquid temperature - 25°C
Exit liquid concentration - 83 g. NH₃ per liter of brine
- b. Exit liquid temperature - 25°C
Exit liquid concentration - 30% HCl solution

4. Utilities

- a. Non-contact cooling water - 3 to 3.5 cubic meters per metric ton of soda ash
- b. Non-contact cooling water (once-through basis) - 35 cubic meters per metric ton of HCl (100 basis)

5. Waste Streams

- a. Atmospheric discharge - approximately 0.05 kg NH₃ per metric ton of soda ash produced.
- b. Nitrogen gas is vented to the atmosphere in a stream estimated to be 615 cubic meters per metric ton of HCl (100% basis).

A NaCl - NaOH solution is wasted to ponds from the tail-gas scrubber. This is estimated to contain 5% NaCl and 5% NaOH. Its amount is estimated to be 30 kg of solution per metric ton of HCl (100 % basis) produced.

6. EPA Source Classification Code

- a. None established
- b. None established

7. References

- a. Deutsch, Z. G., C. C. Brumbaugh, and F. H. Rockwell. Alkali and Chlorine. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A.(ed.) New York, Interscience Publishers, 1963. 1:668-758.

Shreve, R. N. Chemical Process Industries, 3rd Edition. pp. 227-229, New York, McGraw-Hill, 1966.

- b. Jacobs, J. J. Potassium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, Interscience Publishers, 1968. 16:369-400.

Kleckner, W. R., and R. C. Sutter. Hydrochloric Acid. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A.(ed.). New York, Interscience Publishers, 1968. 11:307-337.

Shreve, R. N. Chemical Process Industries, 3rd Edition, New York, pp. 343-346, McGraw Hill, 1966.

CALCINING/SLAKING1. Function

The process (see Figure 14) forms calcium hydroxide slurry ($\text{Ca}(\text{OH})_2$), or "milk-of-lime", by calcining limestone (CaCO_3), then slaking the resulting calcium oxide (CaO) in an excess of water. Carbon dioxide (CO_2) gas is also formed in the process, resulting from both the calcination of the limestone, and as a product of combustion of the fuel, usually coke.

The $\text{Ca}(\text{OH})_2$ slurry is transferred to Process 39 for regenerating ammonia. Part of the CO_2 , as stack gas, is compressed and conducted to Process 8 for brine carbonation.

The steps of cooling and cleaning a portion of the CO_2 -containing kiln stack gas is included in the process. Essential equipment consists of vertical "stack" kilns, rotary slakers, and cyclone separators.

2. Input Materials

The process consumes the following typical quantities of input materials per metric ton of soda ash (Na_2CO_3) produced:

Crushed limestone	1.2 metric tons
Fuel (almost always coke)	0.08 to 0.11 metric tons
Slaking water	2 to 2.5 cubic meters

3. Operating Parameters

Pressure - Essentially atmospheric.

Maximum kiln temperature - 1000° to 1300°C

Maximum slaker temperature - approximately 100°C

A typical stack kiln is 20 to 30 meters total height by 3.5 to 6 meters cylinder diameter, and can produce 250 to 400 metric tons CaO per day.

4. Utilities

Heat (supplied by the coke mentioned above) required per metric ton of soda ash produced - 0.7 to 0.8×10^6 kcal.

Electrical energy consumption - Grossly estimated to lie between 10 and 20 kWh per metric ton of soda ash produced.

5. Waste Streams

Uncollected kiln exhaust gases, vented to the atmosphere, are estimated to amount to 1,000 to 1,200 standard cubic meters per metric ton of soda ash produced. The exhaust gases contain about 35 to 40 percent CO₂ (lower if kiln is fueled with natural gas), oxides of sulfur if high-sulfur coal is burned, water vapor, and nitrogen. Particulates are almost always present and consist of fly ash, lime, and limestone dust. A stack kiln, operating without solids-collecting equipment on exhaust, produces exhaust gases containing typically 0.7 to 2.3 grams or particulates per cubic meter. These values correspond to 0.7 to 2.7 kilograms per metric ton of soda ash produced. Operating with glass bag filters on the exhaust stream, the same kiln might produce exhaust gases containing 5 to 10 percent of the values mentioned above.

Chemical composition (by weight percent) of the particulates in the exhaust gases is typically:

CaO	66
CaCO ₃	23
Ca(OH) ₂	6.4
MgO	1.4
CaSO ₄	1.2
Heavy metal oxides	1.0
Acid insolubles	1.0

The size range of the particulates emitted during operation without the use of collection equipment is 30 percent below 5 microns and 10 percent below 2 microns.

Solid wastes (handled as a slurry) discharged from rotary lime slakers consist of Ca(OH)₂ (inadvertent), CaCO₃, CaO (overburned lime), heavy metal oxides, and acid insolubles. Their particle-size distribution is typically 0.07 mm to 2 mm diameter. The quantity varies with the purity of the limestone used. This is typically as high as 20 kg per metric ton of soda ash produced. The ultimate disposal is used as landfill.

6. EPA Source Classification Code

None established

7. References

Deutsch, Z. G., C. C. Brumbaugh, and F. H. Rockwell. Alkali and Chlorine (Sodium Carbonate). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1963. 1:707-740.

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, Inc., 1965. p. 664-667.

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, Inc., 1967. p. 225-230.

AMMONIA REGENERATION1. Function

The process (see Figure 14) recovers both the "free" ammonia and the "fixed" ammonia (NH_4Cl) from the mother liquor received from Process 8. All the recovered ammonia, as NH_3 , together with some recovered CO_2 , is then recycled to Process 37.

Essential equipment consists of two stripping columns and an agitated lime reaction tank. The two columns are sometimes combined, one above the other, each forming a section of a structurally single tower.

2. Input Materials

A typical composition, by weight percent, of the mother liquor received from Process 8 is estimated to be:

NaCl	5.4
NH_4Cl	13.0
"Free" NH_3 (as NH_4OH , carbonates & carbamate)	2.3
Total CO_2 (as carbonate & carbamate)	2.7
Water	76.7

The estimated consumption of mother liquor is between 6 and 7 cubic meters per metric ton of soda ash produced.

Consumption of milk-of-lime, or calcium hydroxide slurry ($\text{Ca}(\text{OH})_2$), is estimated to be between 2.0 and 2.6 cubic meters per metric ton of soda ash produced. This corresponds to 0.8 to 0.85 metric tons of $\text{Ca}(\text{OH})_2$ per metric ton of soda ash produced.

The composition of the milk-of-lime usually varies between 300 and 390 gms $\text{Ca}(\text{OH})_2$ per liter of slurry.

3. Operating Parameters

The process is operated at pressures slightly greater than atmospheric, typically up to 0.5 kg/cm² gage pressure.

Operating temperatures vary inside the stripping columns: approximately 100°C throughout most of the height, and 50° to 60°C at the top of the "free" column.

The two stripping columns (the "free" still, and the "fixed" still) are approximately 35 and 15 meters high, respectively, for a wide range of production capacities. If the two columns are combined, the total height can reach 55 meters.

For daily capacities of about 700 metric tons Na_2CO_3 , column diameters are 3.5 to 4.0 meters.

Still-columns may contain bubble-cap plates, or may be coke-packed.

The lime reaction tank requires violent agitation.

4. Utilities

Consumption of low-pressure steam (1.0 to 1.5 kg/cm² gage), is estimated to be 1 to 2 metric tons per metric ton of soda ash produced.

Cooling water consumption is grossly estimated to be between 10 and 15 cubic meters per metric ton of soda ash produced.

Estimated electrical energy consumption is 5 to 8 kWh per metric ton of soda ash produced.

5. Waste Streams

Between 10 and 11 cubic meters (9 to 10 metric tons) of waste liquid is discharged per metric ton of soda ash produced. The composition of this liquid in weight percent is estimated to be:

CaCl_2	9
NaCl	3 to 4
$\text{Ca}(\text{OH})_2$, suspended	0.5 to 1.0
Water	balance

The stream also contains fractional percentages of R_2O_3 , SiO_2 and CaSO_4 .

The stream may be processed for economic recovery of CaCl_2 , but usually is discharged to natural streams.

Solid waste, chiefly CaSO_4 , is discharged at annual tower cleanout periods. This is estimated to amount to less than 0.1 kg per metric ton of soda ash produced. Probable disposal method is as landfill.

It is suspected that detectable quantities of NH_3 gas are inadvertently discharged to the atmosphere. These are estimated to be less than 0.1 kg NH_3 per metric ton of soda ash produced.

6. EPA Source Classification Code

3-01-021-01 Ammonia Recovery

7. References

Deutsch, Z. G., C. C. Brumbaugh, and F. H. Rockwell. Alkali and Chlorine (Sodium Carbonate). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1963. 1:707-740.

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, Inc., 1965. p. 664-667.

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, Inc., 1967. p. 225-230.

DECHLORINATION1. Function

This process removes dissolved chlorine from the spent sodium chloride brine used in a mercury electrolysis cell for chlorine production (See Figure 15).

The brine stream exiting a mercury electrolysis cell contains dissolved chlorine in the form of hypochlorite. The stream is treated with hydrochloric acid to reduce chlorine solubility. It then is fed to a flash vessel where practically all of the chlorine is evolved along with water vapor. Chlorine and water are separated in another vacuum column. Chlorine is fed to the chlorine product line leaving the electrolysis cell. The water flows out as waste. The dechlorinated brine is recycled to Process 35 for resaturation with salt.

2. Input Materials

Spent Brine Containing Dissolved Cl_2 - approximately 40 cubic meters brine per metric ton of Cl_2 produced.

HCl - 0.03 cubic meters of 32% HCl per metric ton of Cl_2 produced.

3. Operating Parameters

The chlorine collection manifold operates at a slight vacuum. The flash tank pressure is typically 0.28 kg per square centimeter (6" Hg) absolute. The temperature ranges from approximately 80°C (175°F) in the acidification tank to 75°C (165°F) in the flash vessel to 60°C (135°F) in the water-chlorine separation column.

4. Utilities

Electrical energy requirements are less than 5 kWh per metric ton of chlorine.

5. Waste Streams

0.6 cubic meter water per metric ton chlorine produced.

6. EPA Source Classification Code

3-01-008-05 Air-Blow Mercury Cell Brine

7. References

Deutsch, Z. G., C. C. Brumbaugh, and F. H. Rockwell.
Alkali and Chlorine Industry (Chlorine). In: Kirk-
Othmer Encyclopedia of Chemical Technology, 2nd Edition,
Stand n, A. (ed.). New York, Interscience Publishers,
1963. 1:671-702.

Yen, Y. C. Chlorine, Supplement A. Stanford Research
Institute, Menlo Park, California. Process Economics
Program, Report No. 61A. May 1974. 256 p.

MERCURY CELL ELECTROLYSIS1. Function

This process (see Figure 15) separates sodium chloride brine from Process 35 into chlorine gas and a sodium-amalgam in an electrolytic cell that uses mercury as the cathode.

Most cells are constructed with a flat-bottomed steel trough. Mercury flows across the bottom and serves as the cathode. Sodium chloride brine flows between the mercury and coated titanium anodes. The anodes are shaped as flat plates parallel to the mercury surface and are supported from a cell cover. The cell cover material is inert to chlorine gas corrosion. Chlorine gas evolves from the anode and collects beneath the cell cover prior to forwarding to Process 44.

Sodium combines with the mercury to form an amalgam. The sodium-mercury amalgam flows to Process 43. The spent brine, containing some chlorine, goes to Process 40.

2. Input Materials

Brine saturated with dry sodium chloride -
1.7 metric tons of purified NaCl per metric ton of chlorine.

3. Operating Parameters

Volts per cell	4.1-4.5
Current density	
(amps/cm ²) cathode	0.59-1.35
Salt conversion	~15%
Brine flow	~40 cubic meters per metric ton of chlorine
Mercury flow	20-25 cubic meters per metric ton of chlorine
Pressure	approximately atmospheric
Temperature	75-85°C (167-185°F)

4. Utilities

Electrical energy requirements for electrolysis -
3500 kWh per metric ton of chlorine.

5. Waste Streams

Some leakage of chlorine gas around cell-cover seams may occur. The estimated quantity is less than 0.0001 metric ton per metric ton of chlorine.

6. EPA Source Classification Code

3-01-0008-02 Liquefaction/Mercury Cell

7. References

Deutsch, Z. G., C. C. Brumbaugh, and F. H. Rockwell. Alkali and Chlorine Industry (Chlorine). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1963. 1:671-702.

Yen, Y. C. Chlorine, Supplement A. Stanford Research Institute, Menlo Park, California. Process Economics Program, Report No. 61A. May 1974. 256 p.

DIAPHRAGM CELL ELECTROLYSIS1. Function

This process (See Figure 15) separates sodium chloride brine into chlorine and hydrogen gas and sodium hydroxide solution in an electrolytic cell containing a diaphragm to separate the gaseous products.

Brine is fed continuously from Process 35. It flows from the anode compartment through an asbestos diaphragm into the cathode compartment. The brine then leaves the cell. Chlorine gas forms at the graphite anode and is collected in an overhead manifold for transporting to Process 44. Hydrogen gas and sodium ions collect at the iron cathode. The hydrogen is collected in a separate manifold for transporting to another application of Process 44. The sodium hydrolyzes into sodium hydroxide in the brine. The brine is collected for transporting to Process 10.

2. Input Materials

Purified brine saturated with sodium chloride - 1.8 metric tons of sodium chloride per metric ton of chlorine.

3. Operating Parameters

Volts per cell	3.8
Current density	
(amps/cm ²) cathode	0.11
Salt conversion	~50%
Brine flow	
(m. ³ /m. ton of Cl ₂)	~13
Pressure	~ atmospheric
Temperature (°C)	~90

4. Utilities

Electrical power for electrolysis - 3,000 kWh per metric ton of chlorine

5. Waste Streams

Some leakage of chlorine gas around cell-cover seams may occur. It is estimated to be less than 0.0001 metric tons per metric ton of chlorine produced.

6. EPA Source Classification Code

3-01-008-01 Liquefaction-Diaphragm

7. References

Deutsch, Z. G., C. C. Brumbaugh, and F. H. Rockwell. Alkali and Chlorine Industry (Chlorine). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, Interscience Publishers, 1963. 1:671-702.

Yen, Y. C. Chlorine, Supplement A. Stanford Research Institute, Menlo Park, California, Process Economics Program, Report No. 61A. May 1974. 256.

SODIUM AMALGAM DECOMPOSITION1. Function

This process decomposes the sodium amalgam transported from Process 41 by adding purified water to the mercury stream (See Figure 15).

Purified water is fed to the mercury stream, usually countercurrent to the amalgam flow. Through the use of a short-circuited electrode system, the sodium leaves the amalgam and combines with water to form sodium hydroxide in the electrolyte. Hydrogen gas is generated at the iron or graphite cathode. This gas is collected and forwarded to Process 44.

Water is added at a rate to produce a 50% sodium hydroxide solution essentially free of sodium chloride. This solution is forwarded for use as an end product or for further concentration in Process 10. The sodium-stripped mercury is returned to Process 41 for reuse.

2. Input Materials

- Mercury-sodium amalgam -
 ~20 cubic meters per metric ton of chlorine.
- Purified water -
 ~1.6 cubic meters water per metric ton of chlorine.

3. Operating Parameters

Water flow is adjusted to obtain the desired sodium hydroxide concentration (~50%). The operating pressure is approximately atmospheric and the temperature is approximately 80°C (180°F).

4. Utilities

Electrical energy for water and mercury pumps is approximately 15 kWh per metric ton of chlorine.

5. Waste Streams

None.

6. EPA Source Classification Code

None established

7. References

Deutsch, Z. G., C. C. Brumbagh, and F. H. Rockwell.
Alkali and Chlorine Industry (Chlorine). In: Kirk-
Othmer Encyclopedia of Chemical Technology, 2nd Edition,
Standen, A. (ed.). New York, Interscience Publishers,
1963. 1:671-702.

COOLING/COMPRESSION1. Function

This process (See Figure 15) cools and compresses the chlorine and hydrogen gases produced in electrolysis cell processes.

- *a. Chlorine gas from electrolysis cells is collected in manifolds at a slight vacuum, cooled in suitably corrosion resistant heat exchangers and transported through sulfuric acid drying towers. Water is the non-contact cooling medium. The sulfuric acid is recirculated in towers countercurrent to the chlorine flow to remove moisture from the gas. Either rotary or reciprocating compressors with special seals are used to compress the chlorine for ultimate packaging or liquefaction. The sulfuric acid enters the drying towers at a concentration above 90% and leaves at about 60% for other plant use.
- b. Hydrogen gas is cooled by direct contact with cooling water prior to being compressed by conventional types of positive displacement compressors.

2. Input Materials

- a. Chlorine leaving electrolysis cells - 1.2 to 1.5 metric tons of chlorine-laden vapor per metric ton of chlorine product.

Sulfuric acid (>99% purity) - ~0.05 cubic meters per metric ton of chlorine.
- b. Hydrogen leaving electrolysis cells - 0.04 to 0.4 metric tons of hydrogen-laden vapor per metric ton of chlorine produced.

3. Operating Parameters

- a. The temperature of the cooled chlorine is approximately 40°C. The absolute pressure before entering Process 45 is 2 to 3 kg per square centimeter.

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

- b. The temperature of the cooled hydrogen is approximately 30°C. The final pressure is usually 1.2 to 2 kg per square centimeter.

4. Utilities

Electrical energy -

- a. 10 kWh per metric ton of chlorine for chlorine compression.
- b. 2 kWh per metric ton of chlorine for hydrogen compression.

Cooling Water -

- a. 2 to 8 cubic meters per metric ton of chlorine.
- b. Less than 1 cubic meter per metric ton of chlorine.

5. Waste Streams

- a. None
- b. None

6. EPA Source Classification Code

None established

7. References

Deutsch, Z. G., C. C. Brumbaugh, and F. H. Rockwell. Alkali and Chlorine Industry (Chlorine). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, Interscience Publishers, 1963. 1:671-702.

Yen, Y. C. Chlorine, Supplement A. Stanford Research Institute, Menlo Park, California, Process Economics Program, Report No. 61A. May 1974. 256.

LIQUEFACTION1. Function

This process liquefies chlorine gas by successive stages of compression with interstage cooling, plus a final cooling with a refrigerant.

Chlorine gas at absolute pressures from 2 to 3 kilograms per square centimeter is compressed further and then cooled for condensation. Noncondensable diluent gases are vented to a scrubber system to recover their chlorine content. Some plants include a packed tower in which a countercurrent liquid chlorine stream is used to remove low-boiling organics from the chlorine gas.

2. Input Materials

Chlorine gas containing 1 to 10 percent noncondensable diluent gases.

3. Operating Parameters

The final chlorine absolute pressure varies from 5 to 10 kilograms per square centimeter. The final temperature is -10° to 30°C (10° to 72°F).

4. Utilities

Electrical energy requirement is approximately 40 to 80 kWh per metric ton of chlorine. This includes chlorine compression and refrigerant compression requirements. Cooling water requirement for the compressor intercooler is approximately 1 cubic meter per metric ton of chlorine. Refrigeration requirements are approximately 90,000 kcal at -20°C per metric ton of chlorine (30 tons at 0°F per metric ton of chlorine).

5. Waste Streams

Noncondensables amounting to 0.02 metric ton per metric ton of chlorine produced are vented to the atmosphere. This stream has gone through a Cl_2 scrubber and contains less than 0.2 ppm Cl_2 .

6. EPA Source Classification Code

None established

7. References

Deutsch, Z. G., C. C. Brumbaugh, and F. H. Rockwell. Alkali and Chlorine Industry (Chlorine). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1963. 1:671-702.

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals. New York, John Wiley & Sons, Inc., 1950. p. 216-217.

Yen, Y. C. Chlorine. Process Economics Program Report No. 61A. Menlo Park, California, Stanford Research Institute, May 1974. 256 p.

CRUSHING/GRINDING1. Function

In general, the essential function of the process is size reduction of the input material necessitated by a requirement of a subsequent process or process step. The specific functions of the various applications of the process are given below.

- *a. As applied to processing of colemanite ore (see Figure 16) - The process further reduces the size of coarse-crushed colemanite ore from Process 6, Figure 3, to permit handling by conveyors and trucks and to satisfy requirements of calcination equipment of Process 48. Ore beneficiation by screening (surmised) may be a process step.

The operation became operative relatively recently (1971). Information identifying the types of equipment used is unavailable. Jaw crushers, hammermills, or roll-crushers are possibilities.

- b. As applied to the processing of sylvinite (KCl-NaCl) ore (see Figure 17) - The process further reduces the size range of coarse-crushed sylvinite ore, received from Process 6, Figure 3, to the fineness necessary for the "unlocking" of the unit crystals of sylvite (KCl) and halite (NaCl). The ground material is then forwarded to either Process 47, Process 50, or Process 51.

Screening steps (size separation) are usually included.

Essential equipment may be one or several of the following types:

hammermill
raymond pulverizer
cone crusher
vibrating or shaking screens

-
- * Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

- c. As applied to the processing of langbeinite ($K_2SO_4 \cdot 2MgSO_4$) ore (See Figure 18) - The process further reduces the size range of coarse-crushed langbeinite ore, received from Process 6, Figure 3, to the degree of fineness required for the rate-of-solution separation of halite ($NaCl$) from the langbeinite ($K_2SO_4 \cdot 2MgSO_4$) in Process 54.

The process includes the step of screening.

Essential equipment may be identical to that listed in "b", above.

2. Input Materials

- a. Colemanite ore ($Ca_2B_6O_{11} \cdot 5H_2O$ plus clay gangue) - Gross estimate of amount consumed is 1.5 to 2.0 metric tons per metric ton of calcined colemanite produced.
- b. Coarse-crushed sylvinite ore (12 cm maximum lump dimension) - Estimated quantity consumed is 2 to 4 metric tons per metric ton of KCl produced.
- c. Coarse-crushed langbeinite ore - Estimated quantity consumed is 1.1 to 1.5 metric tons per metric ton of K_2SO_4 produced.

3. Operating Parameters

- a. No quantitative information is available. Gross estimate of size required of process output is less than 1-cm size lumps.

Operation is designed to process approximately 130,000 metric tons per year of raw ore.

- b. Sylvinite is ground to the following size ranges:

4-mesh to 14-mesh for input to Process 47
6-mesh to 100-mesh for input to Process 50
20-mesh to 40-mesh (estimated) for input to Process 51

Annual capacities of a single operation are in the range of 300 to 800 thousand metric tons of KCl .

- c. Particle size range of ground langbeinite ore is typically 80 percent between 8-mesh and 80-mesh.

4. Utilities

Estimated electrical energy consumption -

- a. 2 to 5 kWh per metric ton of calcined colemanite.
- b. 4 to 8 kWh per metric ton of KCl.
- c. 3 to 6 kWh per metric ton of K_2SO_4 .

5. Waste Streams

a,b,d. It is surmised that particulate fugitive emissions to the atmosphere result from all three applications of the process. It is inferred that this dusting would be particularly troublesome in crushing colemanite (application a).

No quantitative information is available pertaining to either absolute quantities or particle size distribution.

6. EPA Source Classification Code

a,b,c. None established

7. References

Chem. Wk. 109:39-40, August 11, 1971.

Cramer, T. M. Production of Potassium Chloride in New Mexico. Ind. Eng. Chem. 30:865-867, August 1938.

Harley, G. T., and G. E. Atwood. Langbeinite - Mining and Processing. Ind. Eng. Chem. 39:43-47, January 1947.

Jacobs, J. J. Potassium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1968. 16:371-383.

McGraw, R. M. New Mexico Sylvinite. Ind. Eng. Chem. 30:861-864, August 1938.

Potassium Chloride and Sulfate. Chem. Eng. New York. 57:168-171, January 1950.

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, Inc., 1967. p. 294-298.

Turrentine, J. W. Potash in North America. New York, Reinhold Publishing Corp., 1943. p. 135-171.

White, N. C., and C. A. Arend, Jr. Potash Production at Carlsbad. Chem. Eng. Progr. 46:523-530, October 1950.

Woodmansee, W. C. The Mineral Industry of California. In: Minerals Yearbook 1971, Schreck, A. E. (ed.). Washington, U.S. Dept. Interior, Bur. Mines, 1973. 2:139.

LEACHING/CLARIFYING1. Function

- *a. As applied to processing borax and kernite from the Kramer District at Boron, California (Figure 16) -
The process produces clear borax ($\text{Na}_2\text{B}_4\text{O}_7$) liquor from crushed kernite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$) and borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) ores, forwarded from Process 6, Figure 3. The borax liquor is forwarded to Process 10.

The following sequential process steps are included:

Leaching
Wet screening
Countercurrent thickening and washing

Major equipment consist of steam-heated leach tanks, vibrating screens, and clarifiers (thickening tanks).

- b. As applied to potassium chloride production at Carlsbad, New Mexico (Figure 17) - The process uses a sodium chloride (NaCl)-potassium chloride (KCl) brine, recycled from Process 10, to extract KCl from ground sylvinites (mixed NaCl - KCl crystals), forwarded from Process 46, producing a hot liquor saturated with both KCl and NaCl . The liquor is forwarded to Process 20.

The process includes the sequential steps of:

Leaching, including brine-heating
Countercurrent thickening
Centrifuging and washing

Major equipment consists of agitated leach tanks, thickener-clarifier tanks and continuous centrifuges.

- c. As applied to processing calcined lithium ore (spodumene) concentrates at Kings Mountain, N.C. (Figure 24) - The process extracts lithium hydroxide

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

(LiOH) from the β -spodumene clinker resulting from Process 62, producing an impure LiOH liquor which is subsequently purified in Process 10.

The following sequential steps are included:

Leaching
Thickening and clarifying
Filtration and washing

Major equipment consists of thickening tanks and a continuous drum filter (the latter is inferred).

2. Input Materials

- a. Estimated amount of crushed ore entering the process is about 1.7 metric tons per metric ton of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ produced. (Based on assumed weight ratio of gangue to ore of 1:1 and assumed mole ratio of borax to kernite of 1:1).

- b. The composition of the brine recycled to this process from Process 10 is:

11% KCl
20% NaCl
69% H_2O

Approximately 6 cubic meters of recycled brine are required per metric ton of KCl produced.

The composition of the ground sylvinite entering the process varies with ore quality. A typical composition might be:

30% KCl
70% NaCl

Approximately 3.5 metric tons of ground sylvinite of this composition would be required per metric ton of KCl produced.

- c. Alkaline clinker entering the process contains typically about 1% to 1.3% Li. About 25 to 30 metric tons of ground clinker are required per metric ton of LiOH produced.

Leach water amounts to 10 to 15 metric tons per metric ton of LiOH.

3. Operating Parameters

- a. Leaching is conducted at approximately 100°C, and at atmospheric pressure. Gangue (clay plus rock) in thickener underflow ranges from 2 cm. diameter to 60-mesh. Leach-tanks are 8 cubic meter capacity. Each of four thickener tanks is 70 meters in diameter by 2.5 meters side wall depth.
- b. Process operates at atmospheric pressure and about 150°C. Brine recycled from Process 10, enters this process at 25° to 27°C. Recycled brine flow is typically 2 to 3 cubic meters per minute.
- c. Leaching is conducted at elevated temperatures, probably in excess of 75°C and at atmospheric pressure.

4. Utilities

Estimated requirements are:

	Water, m. ³	Steam, low pressure (m. tons)	Electrical energy (kWh)	Per m. ton of
a.	4.2	2.0	5 to 10	B ₂ O ₃ equiv.
b.	<0.1	0.3 to 0.5*	5 to 10	KCl
c.	10 to 15	1.0 to 1.5	35 to 50	LiOH

* Assuming 75% heat recovery.

5. Waste Streams

- a. Slimes and sand are discharged from thickeners as slurries and larger size material is rejected by shaking screens. Collectively, all wastes evolve into solids wasted to tailings piles, and amount to an estimated 0.7 metric ton per metric ton of Na₂B₄O₇•10H₂O produced.
- b. NaCl, wasted to tailings pond, is estimated at 2.3 metric tons per metric ton KCl produced.

Slimes and insolubles are estimated at 0.2 metric ton per metric ton of KCl and are also discharged to tailings pond.

- c. Total solid wastes are estimated at 25 to 30 metric tons per metric ton LiOH produced. Conjectured method disposal is to transport a slurry of the solids to tailings pond or pile.
- a,b,c. A part of the aqueous portion of the slurries carrying the above solid wastes to pondage might reach natural streams. No quantitative estimate of the liquids is available.
6. EPA Source Classification Code
- a,b,c. None established
7. References
- a. Nies, N. P. Boron Compounds (Oxides, Borates). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A.(ed.). New York, Interscience Publishers, 1964. 3:609-652.
- b. Cramer, T.M. Production of Potassium Chloride in New Mexico. Ind. Eng. Chem., 30:865-867, August 1938.
- Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, Inc., 1967. p. 294-495.
- Turrentine, J. W. Potash in North America. ACS Monograph Series, No. 91. New York, Reinhold Publishing Corp., 1943. p. 135-167.
- White, N. C., and Carl A. Arend, Jr. Potash Production at Carlsbad. Chem. Eng. Progr., 46:523-530, October 1950.
- c. Bach, R. O., C. W. Kamienski, and R. B. Ellestad. Lithium and Lithium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A.(ed.). New York, Interscience Publishers, 1967. 12:530-533.
- Faith, W. L., O. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, Inc., 1965. p. 492-494.

CALCINATION

1. Function

The process (see Figure 16) removes the water of hydration from crushed colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$) ore received from Process 46 prior to rail shipment of the calcined material as end product. The chief objective of water removal is weight reduction. The product weighs 78 percent of the input material per unit of contained boron.

The sole existing operation began in 1971. Little quantitative information is available.

The steps of cooling and product screening are presumably included in the process.

Essential equipment presumably consists of an oil-fired rotary kiln, rotary cooler, and vibrating, or shaking screens.

2. Input Materials

Crushed colemanite ore. Some gangue material (clay) may be present.

Estimated consumption is 1.3 to 1.5 metric tons per metric ton of calcined colemanite.

3. Operating Parameters

Pressure - Atmospheric

Estimated temperature range of calcination - 250° to 350°C

No information is available on size requirement for kiln feed.

4. Utilities

(Per metric ton of calcined colemanite):

Heat, presumably supplied by combustion of fuel oil -
Estimated 0.7×10^6 to 1.0×10^6 kcal.

Electrical energy - Estimated 20 to 30 kWh.

5. Waste Streams

(Per metric ton of calcined colemanite):

If beneficiation of the calcined product is required, a solid waste of gangue material could result. This may amount to as much as 0.1 metric ton.

Atmospheric emissions of fine particulates of calcium borate and gangue are surmized. Inferred from known characteristics of limestone calcination in rotary kilns, the quantity may be in the range of 30 to 90 kilograms.

No factual information is available

6. EPA Source Classification Code

None established

7. References

Chem. Week. 109:39-40, August 11, 1971.

Woodmansee, W. C. The Mineral Industry of California.
In: Minerals Yearbook 1971, Schreck, A. E. (ed.).
Washington, U.S. Dept. of Interior, Bur. of Mines, 1973.
2:139.

FUSION/GRINDING1. Function

- *a. As applied to production of anhydrous borax (Figure 16) - The process converts borax decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) from Process 10 into ground, fused, anhydrous borax ($\text{Na}_2\text{B}_4\text{O}_7$). The following sequential process steps are included:

Calcination
Fusion
Cooling
Crushing and grinding
Size separation
Packaging

Equipment consists of:

Rotary calciner
Specially-designed fusion furnace
Pan coolers or chilling rolls
Roll crushers and rod mill
Shaking screens
Bagging or drumming equipment

- b. As applied to production of anhydrous boric acid (boric oxide) (Figure 16) - The process converts boric acid (H_3BO_3) from Process 10 into ground, fused, anhydrous boric acid or boric oxide (B_2O_3). The process steps and equipment are identical with those described in "a", above.
- c. As applied to production of boron oxide (Figure 16) - The process converts borax pentahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$) from Process 10 and concentrated sulfuric acid (H_2SO_4) into ground, fused, boron oxide (B_2O_3).

The process steps are similar to those of "a", above, except that a product of fused, impure Na_2SO_4 is obtained, which is eventually dissolved and forwarded to Process 10 (see Figure 7).

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

The "anhydrous boric acid" produced in "b" above has a higher purity level than the "boron oxide" produced here. Theoretically, the two substances are chemically identical.

2. Input Materials

- a. Theoretically, 1.9 metric tons of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) are required per metric ton of $\text{Na}_2\text{B}_4\text{O}_7$ produced. Either dry or moist borax may be fed. It is impracticable to use $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ as feed, because of excessive dusting.
- b. Theoretically, 1.9 metric tons of H_3BO_3 are required per metric ton of B_2O_3 produced.
- c. Theoretically, 1.71 metric tons of borax pentahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$) and 0.6 metric ton of concentrated sulfuric acid are required per metric ton of B_2O_3 produced.

3. Operating Parameters

- a. Fusion furnace is of special design, is gas-fired from above, and continuously fed. Molten charge is supported by a bed of solid feed. Rotary calciners are 2.5 meters diameter x 22.5 meters long, are fed concurrent to 760°C gases exhausting from fusion furnace. Maximum temperature of about 980°C . All equipment operates at atmospheric pressure.
- b. Very similar to those of "a", above, except that temperatures are lower. Molten charge temperature is probably about 800°C to 850°C .
- c. Little quantitative information is available. Fusion furnace operates at 800°C to 900°C , yielding a two-phase melt: upper layer of B_2O_3 and lower layer of Na_2SO_4 . Operation is at atmospheric pressure.

4. Utilities

- a,b,c. Estimated total heat input is in neighborhood of 0.5 to 1.5×10^6 kcal per metric ton of product.

5. Waste Streams

- a,b,c. There are no designed waste streams. It is inferred that particulate emissions (dusting) to the atmosphere from calciners, fusion furnace

and crushing equipment is a problem. Fumes of SO_3 are probably emitted by the boron oxide fusion furnace.

6. EPA Source Classification Code

None established

7. References

Bixler, G. H., and D. L. Sawyer. Boron Chemicals from Searles Lake Brines. Ind. Eng. Chem. 49:322-333, March 1957.

Nies, N. P. Boron Compounds (Oxides, Borates). In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A.(ed.). New York, John Wiley, & Sons, Inc., 1966. 3:608-652.

TABLING1. Function

The process (See Figure 17) separates potassium chloride (KCl) crystals and sodium chloride (NaCl) crystals from the crystal mixture (fine sylvinite) forwarded from Process 46. The principal product is actually a slurry of KCl crystals in saturated KCl-NaCl brine, forwarded to Process 52. The NaCl crystals are usually wasted to a tailings pond, although sometimes are dried and sold.

This process does not effect as clean a separation of KCl from NaCl as either the hot-leach method or the froth-flotation method. Consequently, it is being replaced by the latter two processes.

This process also includes the steps of:

- Slurrying of ground sylvinite crystals in makeup water and recycled brine.
- De-sliming the crystal slurry.
- De-brining the NaCl crystal fraction.
- De-brining and recycling a "middlings" crystal fraction.
- Wet screening the "middlings" fraction.

2. Input Materials

Principal entering material is a mixture of fine crystals of KCl and NaCl containing particles of gangue. Its weight composition varies widely with quality of sylvinite ore used, ranging between 25 and 50 weight percent of KCl.

A stream of brine, saturated with KCl and NaCl, enters the process as a recycle flow from Process 52. Its quantity is estimated to be between 5 and 10 cubic meters per metric ton of KCl produced.

Addition of minor amounts of "collecting agents" and oil may be necessary to enhance the difference in crystal densities of KCl and NaCl. Quantitative information is unavailable.

3. Operating Parameters

Process is conducted at atmospheric pressure and normal room temperatures.

A typical operation produces approximately 200,000 metric tons per year of KCl, corresponding to a flow of slurry entering the process of 3 to 6 cubic meters per minute.

4. Utilities

Estimated requirements per metric ton of KCl produced:

Makeup water	0.5 to 1 cubic meter
Electrical energy	5 to 10 kWh

5. Waste Streams

Depending upon the quality of sylvinite ore, between 2 and 3 metric tons of NaCl are wasted to tailings ponds per metric ton of KCl produced. A part of the aqueous portion of this stream may reach natural streams. No quantitative estimate of the liquid waste is available.

6. EPA Source Classification Code

None established

7. References

Jacobs, J. J. Potassium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1966. 16: 376.

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1967. p. 295.

Turrentine, J. N. Potash in North America. ACS Monograph Series, No. 91. New York, Reinhold Publishing Company, 1943. p. 135-167.

WET GRINDING

1. Function

The process (See Figure 17) reduces the particle size of sylvinite crystals forwarded from either Process 13, as conducted at Moab, Utah, or Process 46, as conducted at Carlsbad, New Mexico, in order to "unlock" intermeshed crystals of potassium chloride (KCl) and sodium chloride (NaCl). The product is a slurry of NaCl and KCl crystals of approximately 100-mesh size suspended in saturated KCl-NaCl brine forwarded to Process 15.

The process includes the steps of brine addition and wet size classification.

Rod mills or ball mills are the principal equipment, with wet screens, spiral classifiers, drag classifiers, and hydroclones included as auxiliaries.

2. Input Materials

Approximately 2 to 3 metric tons of coarse-ground sylvinite (NaCl-KCl crystal mixture) enter the process per metric ton of KCl produced. This ratio varies with ore composition.

Between 10 and 15 cubic meters (estimated) of saturated KCl-NaCl brine per ton of KCl produced also enter the process as a recycle flow from Process 15.

3. Operating Parameters

The process is conducted at atmospheric pressure and normal room temperatures.

A typical operation produces approximately 200,000 metric tons per year of KCl. This production rate corresponds to average, continuous-flow rates of approximately one metric ton per minute of entering coarse-ground sylvinite ore and 3 to 5 cubic meters per minute of recycled brine.

4. Utilities

Estimated electrical energy consumption per metric ton of KCl produced is 10 to 20 kWh.

5. Waste Streams

Estimated amount of clay particles discharged to tailings ponds as slimes from hydroclones and thickeners is 0.1 metric ton per metric ton KCl produced. A part of the aqueous portion of this stream may reach natural streams. No quantitative estimate of the liquid waste is available.

6. EPA Source Classification Code

3-05-022-01 Mine-Grind/Dry

7. References

Jacobs, J. J. Potassium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1966. 16:374-376.

Magraw, R. M. New Mexico Sylvinite. Ind. Eng. Chem. 30:861-864, August 1938.

White, N. C., and C. A. Arend, Jr. Potash Production at Carlsbad. Chem. Eng. Progr. 46:523-533, October 1950.

DEBRINING1. Function

The process recovers potassium chloride (KCl) crystals from the slurry of KCl crystals in saturated brine forwarded from Process 50. Principal equipment consists of drag classifiers, but may include centrifuges if the KCl crystals are to be washed (See Figure 17).

2. Input Materials

The estimated composition of the slurry entering the process is:

Suspended KCl	10 to 15%
Saturated brine	85 to 90%

Approximately 10 cubic meters of entering slurry is required per metric ton of KCl produced.

3. Operating Parameters

The process is conducted at atmospheric pressure and normal room temperature.

4. Utilities

Electrical energy consumption is estimated to be less than 3 kWh per ton of KCl produced.

5. Waste Streams

No wastes are generated.

6. EPA Source Classification Code

None established

7. References

White, N. C., and C. A. Arend, Jr. Potash Production at Carlsbad. Chem. Eng. Progr. 46:523-531, October 1950.

SULFUR COMBUSTION1. Function

The process (See Figure 18) converts elemental sulfur, either solid or liquid, into sulfur dioxide (15 to 19% SO_2) by combustion in air. The sulfur dioxide is conducted to Process 55.

Commonly used essential equipment consists of a sulfur melting chamber, a rotating cylindrical sulfur vaporizer, where partial combustion takes place, and a combustion chamber in which the sulfur vapor is completely burned and which also heats the melting chamber. If solid sulfur is used, a feeding device is included, usually a small screw conveyor. If liquid sulfur is fed, the melting chamber is unnecessary.

2. Input Materials

Either solid (lump or powder) or liquid sulfur is fed. The choice is based on economics. In either case approximately 0.2 metric ton of sulfur is consumed in producing 1 metric ton of K_2SO_4 .

3. Operating Parameters

Equipment operates generally at atmospheric pressure. A slight negative gage pressure is maintained inside the vaporizer and combustion chamber to minimize atmospheric emission of sulfur dioxide.

Temperature ranges are between 250° and 350°C in the melting chamber, 500° to 700°C in the vaporizer, and 700° to 850°C in the combustion chamber.

A typical capacity for sulfur-burning equipment is between 10 and 15 metric tons of sulfur per day. Larger units are available.

4. Utilities

Between 1 and 2 kWh of electrical energy are required per metric ton of K_2SO_4 produced.

5. Waste Streams

Minor periodic emissions of sulfur dioxide (SO₂) into the atmosphere are unavoidable during normal operation of the equipment. No quantitative information is available.

6. EPA Source Classification Code

None established

7. References

Jacobs, J. J. Potassium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1968. 16:369-400.

Kleckner, W. R., and R. C. Sutter. Hydrochloric Acid. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1966. 11:310-311.

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1966. p. 343-346.

LEACHING1. Function

The process (See Figure 18) removes sodium chloride (NaCl) from ground langbeinite ($K_2SO_4 \cdot 2MgSO_4$) ore forwarded from Process 46. The removal is accomplished by selectively dissolving the NaCl from the langbeinite.

The process includes the consecutive steps of pulping (slurry formation), wet classification, settling, and centrifuging. Major equipment includes rotary washing tumblers, Dorr classifiers, wet cyclones, and either centrifuges or rotary drum filters.

The wet product is forwarded to Process 11.

2. Input Materials

Between 2.5 and 2.8 metric tons of crushed langbeinite ore from Process 46 are consumed per metric ton of dried langbeinite (98% $K_2SO_4 \cdot 2MgSO_4$) produced. A typical screen analysis of the crushed ore feed is:

<u>Mesh</u>	<u>Cumulative % Retained</u>
4	0
6	2
8	12
10	25
14	40
20	55
28	67
200	97

3. Operating Parameters

The process operates at atmospheric temperature and pressure. Control of washing time (contact time) and ore-water ratio are critical parameters.

Typical equipment sizes for a plant producing 500 metric tons per day of product are:

Dorr classifier (2 in series)	7.7 m dia x 2.5 m deep
Settling cone (1)	5.5 m dia
Byrd solid-bowl centrifuge (1)	1.0 m dia x 1.25 m face

4. Utilities

Total water requirement approximates 6 cubic meters per metric ton of dried langbeinite.

Estimated electrical energy consumption is between 6 and 12 kWh per metric ton of dried langbeinite.

5. Waste Streams

There are no atmospheric emissions.

Total quantity of liquid wastes is approximately 6.5 cubic meters per metric ton of dried langbeinite, comprising a 20 to 22% sodium chloride brine. This is ponded.

Solid wastes consist of a variable quantity of fine mud and slimes suspended in the waste brine, estimated less than 0.3 metric tons per metric ton of dried langbeinite.

6. EPA Source Classification Code

None established

7. References

Hartley, G. T., and G. E. Atwood. Langbeinite - Mining and Processing. Ind. Eng. Chem. 39:43-47, January 1947.

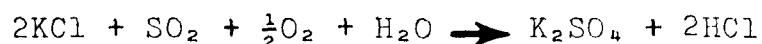
Jacobs, J. J. Potassium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1968. 16:381-384.

Turrentine, J. W. Potash in North America. New York, Reinhold, 1943. p. 181.

White, N. C., and C. A. Arend, Jr. Potash Production at Carlsbad. Chem. Eng. Progr. 46:523-530, October 1950.

HARGREAVES PROCESS1. Function

The process (See Figure 18) forms potassium sulfate (K_2SO_4) and gaseous HCl by reacting potassium chloride (KCl), sulfur dioxide (SO_2), steam, and air:



The sulfur dioxide is forwarded from Process 53, and the potassium chloride from either Process 15 (Figure 17), or Process 20 (Figure 17).

The process is a modification of the classical Hargreaves process for production of salt cake. It includes the steps of briquetting, reaction, cooling, grinding, and packaging (RR cars) of the K_2SO_4 produced.

Major equipment consists of briquetting rolls, reaction furnace (multiple chambers in cyclic countercurrent operation), and a rotary cooler.

2. Input Materials

Approximately 0.38 metric tons of SO_2 (100% basis) are consumed per metric ton of K_2SO_4 produced. This is equivalent to 782 standard cubic meters of 17% SO_2 gas.

Between 0.85 and 0.90 metric ton of potassium chloride is consumed per metric ton of K_2SO_4 produced.

3. Operating Parameters

All steps of the process are conducted at essentially atmospheric pressure. The reaction furnaces are operated under a slightly negative pressure to minimize atmospheric emissions. Temperatures inside the reaction mass are maintained between 400° and 650°C (690°C is the melting point of the KCl- K_2SO_4 eutectic). Temperature is controlled by admission of additional air, since the reaction is exothermic. Heat is added initially only to bring a reaction mass up to temperature.

Reaction chambers are stationary and are manifolded to effect flow of SO_2 countercurrent to the passage of KCl.

Quantities in excess of stoichiometric amounts of both steam and air are used.

4. Utilities

Estimated requirement of low pressure steam is 0.5 metric ton per metric ton of K_2SO_4 produced.

Estimated electrical energy consumption is less than 5 kWh per metric ton of K_2SO_4 produced.

The consumption of fuel gas is negligible, less than 10 cubic meters per metric ton of K_2SO_4 .

5. Waste Streams

Fugitive emissions of gases containing both SO_2 and HCl are conjectured in the vicinity of the reaction furnaces during the periodic operation of the gas flow valving. Specific information is not available.

6. EPA Source Classification Code

None established

7. References

Hartley, G. T., and G. E. Atwood. Langbeinite---Mining and Processing. Ind. Eng. Chem. 39:43-47, January 1947.

Jacobs, J. J. Potassium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1968. 16: 381-397.

Kleckner, W. R., and R. C. Sutter. Hydrochloric Acid. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1966. 11:312.

Turrentine, J. W. Potash in North America. New York, Reinhold, 1943. p. 181.

White, N. C., and C. A. Arend, Jr. Potash Production at Carlsbad. Chem. Eng. Progr. 46:523-530, October 1950.

NEUTRALIZATION1. Function

This process (See Figure 20) neutralizes magnesium hydroxide $[\text{Mg}(\text{OH})_2]$ filter cake received from Process 7, Figure 2, with make-up hydrochloric acid (HCl) and HCl recycled from Process 59 to produce magnesium chloride (MgCl_2) liquor.

Filter cake is introduced into an agitated neutralizer tank, along with a controlled stream of hydrochloric acid. A stream of H_2SO_4 is also introduced in an amount equivalent to soluble calcium present. The resulting, impure MgCl_2 brine or liquor is forwarded to Process 57.

2. Input Materials

Washed, filtered 35% $\text{Mg}(\text{OH})_2$ filter cake -

8 metric tons per metric ton of magnesium metal.

H_2SO_4 -

0.2 metric tons (100% basis) per metric ton of magnesium metal.

HCl -

3.5 metric tons (100% basis) per metric ton of magnesium metal.

3. Operating Parameters

The process is conducted at atmospheric pressure and at temperatures between 40° and 50°C .

4. Utilities

Electrical energy -

10 kWh per metric ton of magnesium metal.

5. Waste Streams

Mists of MgCl_2 are caused by breaking of CO_2 bubbles. The MgCl_2 in these mists is less than 0.001 metric ton per metric ton of magnesium.

6. EPA Source Classification Code

None established

7. References

Comstock, H. B. Magnesium and Magnesium Compounds.
U.S. Government Printing Office, 1973.

McIlhenny, W. F. Dissolved Deposits. Society of Mining
Engineers Handbook, 1973. 2:Article 20.4.1.

Schambra, W. P. The Dow Magnesium Process at Freeport,
Texas. Trans. Amer. Inst. Chem. Eng. 41:35-51,
January 1945.

EVAPORATION/FILTRATION1. Function

This process (See Figure 20) concentrates a 30 to 34% magnesium chloride (MgCl_2) solution to 50 to 55% MgCl_2 and also removes impurities.

Direct-fired or submerged combustion evaporators are used to concentrate the MgCl_2 solution from Process 56. The more concentrated MgCl_2 solution is cooled by vacuum evaporation, sent to settling tanks, and then through filters where calcium sulfate, sodium chloride, and magnesium hydroxide are deposited. The filtered MgCl_2 solution is then further concentrated to 50 to 55% in steam-heated, boil-down kettles. The 50 to 55% MgCl_2 stream then goes to Process 9.

2. Input Materials

MgCl_2 solution (30 to 34% MgCl_2) -

10 cubic meters per metric ton of magnesium metal.

3. Operating Parameters

Temperatures are approximately 115°C (240°F) in the first evaporation step, 40°C (100°F) in the settling step, ambient in the filtration step, and 175°C (345°F) in the final evaporation step.

Pressures are atmospheric for all these steps except for the vacuum evaporation, which is at an absolute pressure of 0.2 kg per square centimeter.

4. Utilities

Electrical energy -

Less than 10 kWh per metric ton of magnesium metal.

Natural gas -

100 to 200 cubic meters per metric ton of magnesium metal.

Steam (28 kg/cm²) -

3 to 5 metric tons per metric ton of magnesium metal.

Quench water -

25 cubic meters per metric ton of magnesium metal.

Filter wash water -

0.5 cubic meters per metric ton of magnesium metal.

5. Waste Streams

Combustion gases from submerged combustion evaporator -

Contain detectable amounts of $MgCl_2$, HCl , and MgO .
Quantitative information is unavailable.

Filter cake slurry (primarily calcium sulfate and sodium chloride) -

0.1 metric ton solid per metric ton of magnesium is
slurried with 0.5 cubic meter water per metric ton
of magnesium. The slurry is discharged to tidewater.

6. EPA Source Classification Code

None established

7. References

Comstock, H. B. Magnesium and Magnesium Compounds.
U.S. Government Printing Office, 1963.

Gross, W. H. Magnesium and Magnesium Alloys. In:
Kirk-Othmer Encyclopedia of Chemical Technology, 2nd
Edition, Standen, A. (ed.). New York, John Wiley and
Sons, Inc., 1967. 12:661-708.

McIlhenny, W. F. Dissolved Deposits. Society of
Mining Engineers Handbook, 1973. 2:Article 20.4.1.

ELECTROLYSIS1. Function

- *a. As applied to the production of magnesium metal (See Figure 20) - The process forms magnesium metal (Mg) and gaseous chlorine (Cl₂) by electrolysis of the solid magnesium chloride (MgCl₂) received from Process 9.

Granular MgCl₂ is added to a bathtub-shaped steel cell containing a bath of fused salts. High-amperage electrical current is passed through the bath to generate molten elemental Mg and Cl₂ gas. The Mg is dipped from the top of the bath and cast into ingots. The Cl₂ is collected and conveyed to Process 59, or alternatively, to Process 44 (See Figure 15).

- b. As applied to the production of sodium metal (See Figure 21) - The process forms sodium metal (Na) and gaseous chlorine (Cl₂) from the sodium chloride (NaCl) received from Process 11.

Dry purified NaCl is fed to the Downs cell. The latter is a closed, refractory-lined steel box with separate anode and cathode compartments. High-amperage electrical current is passed through the bath to generate a molten mixture of Na and calcium (Ca). The molten alloy flows upward into a compartment sealed to protect the Na from oxidation. The molten alloy flows to Process 16, and the gaseous Cl₂ is transferred to Process 44 (See Figure 15).

2. Input Materials

- a. MgCl₂ feed (Solid granules, containing 72 to 78% MgCl₂, 0.5% CaCl₂, 1% NaCl, 1 to 2% MgO, remainder water) -

5 metric tons per metric ton of Mg.

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

Graphite anodes -

0.1 metric ton per metric ton of Mg.

b. NaCl (Dry purified) -

3 metric tons per metric ton of Na.

Graphite anodes-

0.01 to 0.02 metric tons per metric ton of Na.

3. Operating Parameters

a. Mg cell temperature is 700°C.

Cell pressure is approximately atmospheric.

The cell bath contains 20% MgCl₂, 20% CaCl₂, 57% NaCl, 2% KCl, 1% CaF₂.

b. Downs (Na) cell temperature is 580°C.

The cell bath contains 58 to 59% CaCl₂, 41 to 42% NaCl. (There may be some use of NaCl-CaCl₂-BaCl₂ baths).

4. Utilities

Electrical energy -

a. 19,000 kWh per metric ton of Mg.

b. 13,000 kWh per metric ton of Na.

Natural gas -

a. 10 to 100 cubic meters per metric ton of Mg.

5. Waste Streams

a. Chlorine gas collection system leakage - Absolute amount is not divulged. Ventilation systems are designed to maintain less than 1 ppm Cl₂.

Sludge consisting primarily of CaCl₂, MgCl₂, NaCl, and MgO - 0.1 metric ton per metric ton of Mg.

b. Chlorine gas collection system leakage - Absolute amount is not divulged.

Sludge consisting primarily of NaCl and CaCl₂ - 0.002 to 0.005 metric tons per metric ton of Na.

6. EPA Source Classification Code

- a. None established
- b. None established

7. References

- a. Gilroy, D. The Electrowinning of Metals. In: Industrial Electrochemical Processes, Kuhn, A. T. (ed.). New York, Elsevier Publishing Company, 1971. p. 175-217.

Schambra, W. F. The Dow Magnesium Process at Freeport, Texas. Trans. Amer. Inst. Chem. Eng. 41:35-51, January 1945.

- b. Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley and Sons, Inc., 1965. 852 p.

Kuhn, A. T. The Chlor-Alkali Industry. In: Industrial Electrochemical Processes, Kuhn, A. T. (ed.). New York, Reinhold Publishing Corporation, 1956. 529 p.

Sittig, M. Sodium (Its Manufacture, Properties, and Uses). New York, Reinhold Publishing Corporation, 1956. 529 p.

HYDROCHLORIC ACID FORMATION1. Function

This process (See Figure 20) forms hydrochloric acid (HCl) from the chlorine (Cl_2) gas recycled from Process 58 by reacting the latter with steam.

Chlorine gas, formed by electrolysis in Process 58, is collected by suction fans and conveyed to a refractory checker-work, regenerative-type furnace. The Cl_2 is converted to HCl gas, which is absorbed in water to form hydrochloric acid. The latter supplies the major fraction of the HCl consumed in Process 56.

The absorption of HCl gas constitutes a step in the process.

2. Input Materials

Cl_2 - 2 to 2.5 metric tons per metric ton of magnesium (Mg).

3. Operating Parameters

Temperature is 1200°C , and pressure is atmospheric.

4. Utilities

Methane - 300 cubic meters per metric ton of Mg.

Process water for absorption tower - 5 to 7 cubic meters per metric ton of Mg.

Steam - 0.9 to 1 metric ton per metric ton of Mg.

5. Waste Streams

Combustion products leaving the absorption tower - 1200 cubic meters per metric ton of Mg.

6. EPA Source Classification Code

3-01-011-02 Byproduct w/Scrubber

7. References

Schambra, W. P. The Dow Magnesium Process at Freeport, Texas. Trans. Amer. Inst. Chem. Eng. 41:35-51, January 1945.

FUSION1. Function

This process (See Figure 22) reduces the iodates contained in a mixture of sodium iodide and sodium iodate crystals from Process 10 to iodides, by complete fusion in a smelting pot at 600°C. Addition of charcoal assures complete conversion of the iodates. This process is typically an overnight batch operation. The sodium iodide (NaI) is forwarded to Process 10.

2. Input Materials

Sodium iodide - sodium iodate crystal mixture - 1.06 to 1.08 metric tons per metric ton of NaI (estimated).

3. Operating Parameters

Temperature of fusion charge - 600°C.

Pressure - atmospheric.

4. Utilities

Heat (fuel gas or fuel oil) - 500,000 kcal per metric ton of NaI.

5. Waste Streams

None

6. EPA Source Classification Code

None established

7. References

Jacobs, J. L. Potassium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1968. 16:392.

Two Men and a Tub. Chem. Wk. 73:77-83, December 5, 1953.

FILTRATION/CRYSTALLIZATION

1. Function

This process (See Figure 22) forms sodium bromide (NaBr) from ferrosferric bromide hexadecahydrate ($\text{Fe}_3\text{Br}_8 \cdot 16\text{H}_2\text{O}$) crystals from Process 10 by the addition of aqueous sodium carbonate.

2. Input Materials

$\text{Fe}_3\text{Br}_8 \cdot 16\text{H}_2\text{O}$ crystals - 1.33 metric tons per metric ton of NaBr crystals (stoichiometric).

Soda ash (added as 20 to 30% solution) - 0.52 metric tons (100% basis) per metric ton of NaBr crystals (stoichiometric).

3. Operating Parameters

Reaction is conducted at ambient temperatures and atmospheric pressure as a small-scale batch operation.

Crystallization and filtration are both conducted at atmospheric pressure and at temperatures between 55° and 100°C.

4. Utilities

Heat - 2 to 2.5 metric tons of steam per metric ton of NaBr.

5. Waste Streams

Ferric oxide sludge to landfill - 0.28 metric ton per metric ton of NaBr (stoichiometric).

6. EPA Source Classification Code

None established

7. References

Clough, R. W. Miscellaneous Heavy Chemicals. In: Riegel's Handbook of Industrial Chemistry, 7th Edition, Kent, J. A. (ed.). New York, Reinhold Publishing Corporation, 1974. p. 137.

CALCINATION/GRINDING1. Function

This process (See Figure 24) has two applications. The basic function of the process in the two operations is the same, but operating conditions and procedure differ sufficiently to describe the two applications separately.

- *a. In the Foote Mineral Company operation, the process converts spodumene ore concentrates received from Process 15, containing lithium values in chemically unreactive form, to finely ground material, containing soluble lithium hydroxide (LiOH). The ground product is then forwarded to Process 47.

The following sequential steps are included:

- Mixing ground limestone, ore concentrates, and water.
- Calcination of the resulting slurry.
- Cooling
- Grinding

Essential equipment consists of:

- Agitated mixing tanks (surmised)
- Rotary, coal-fired kiln
- Rotary cooler
- Hammermill (surmised grinding equipment type)

- b. In the Lithium Corporation of America operation, the process converts the α -spodumene content of spodumene ore concentrates, received from Process 15, to the more reactive β -spodumene. The calcined concentrates are then ground and forwarded to Process 63.

The following sequential process steps are included:

- Calcination
- Cooling
- Grinding

* Separate industry operations employing the process are identified with a specific lower case letter which is retained as an identifier in each element of this process description.

Major equipment comprises:

- Rotary kiln
- Rotary cooler (surmised type)
- Ball mills

2. Input Materials

a. Per metric ton of LiOH produced:

Spodumene ore concentrates (containing 5 to 6% Li_2O) - 11 to 13 metric tons.

Finely ground limestone - 38 to 45 metric tons.

Water - 50 to 60 cubic meters (gross estimate).

b. Per metric ton of Li_2CO_3 produced:

Spodumene ore concentrates (containing 5 to 6% Li_2O) - 6 to 8 metric tons.

3. Operating Parameters

a. Pressures for all steps of the process - atmospheric.

Kiln discharge temperature - 1030° to 1050°C.

Clinkers discharged by kiln - about 2 to 3 centimeters diameter.

Rotary kiln - 3.1 meters diameter x 105 meters long. (for estimated annual capacity, about 5,000 metric tons LiOH).

Ground product - 50 to 100 mesh (estimated).

b. Pressures for all steps of the process - atmospheric.

Maximum temperature of kiln load - 1075° to 1100°C.

Kiln size - 75 meters long (for estimated annual capacity <5,000 metric tons Li_2CO_3).

Ball-milled product - approximately 100 mesh.

4. Utilities

a. Per metric ton of LiOH produced:

Heat (in form of coal) - 40×10^6 to 80×10^6 kcal (gross estimate).

Electrical energy - 150 to 300 kWh (gross estimate).

- b. Per metric ton of Li_2CO_3 produced:

Heat (in form of fuel gas) - 5×10^6 to 8×10^6 kcal (gross estimate).

Electrical energy - 150 to 300 kWh (gross estimate).

5. Waste Streams

- a. Quantities are per metric ton of LiOH produced:

Surmised fugitive emissions to atmosphere of particulate material (ore and limestone) escaping the kiln-exhaust quencher - Quantitative information on amount and particle-size distribution unavailable. Estimated to be between 0.1 and 1 metric ton, depending on type of dust collectors on kiln exhaust.

Surmised fugitive emissions to atmosphere of particulate material (calcined clinker) from clinker cooler and from grinding equipment - Quantitative information on quantity and particle-size distribution unavailable. Estimated to be between 5 and 50 kilograms, depending on type of dust collection system used.

Kiln discharge into atmosphere - Between 20×10^3 and 35×10^3 standard cubic meters of CO_2 .

- b. Quantities are per metric ton of Li_2CO_3 produced:

Surmised fugitive emission to atmosphere of particulate material (ore dust) escaping the kiln - Quantitative information on amount and particle-size distribution is unavailable. Estimated to be between 10 and 200 kilograms total solids, depending on type of dust collectors used on kiln and grinding equipment.

Surmised fugitive emissions to atmosphere of particulate material (clinker dust) from clinker cooler and grinding equipment - Quantitative information is unavailable. Estimated to be between 0.1 and 1 kilogram, depending on type of dust collection system used.

Kiln discharge into atmosphere - Between 4×10^3 and 7×10^3 standard cubic meters of CO_2 (gross estimate).

6. EPA Source Classification Code

a. None established

b. None established

7. References

Bach, R. O., C. W. Kamienski, and R. B. Ellestad. Lithium and Lithium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1967. 12:530-533.

Ellestad, R. B., and C. W. Kamienski. Lithium. In: Chemical and Process Technology Encyclopedia, Considine, D. M. (ed.). New York, McGraw-Hill, Ind., 1974. p. 700.

DIGESTION1. Function

The process (See Figure 24) converts the lithium (Li) values of calcined spodumene ore received from Process 62, to water-soluble lithium sulfate (Li_2SO_4) by reaction with concentrated sulfuric acid. The digested ore is forwarded to Process 64.

Essential equipment comprises one or more heated reaction chambers. It is surmised that these are operated batch-wise and may be rotating cylinders. The method of heating is unknown but may be by external firing with oil or coal.

2. Input Materials

Per metric ton of Li_2CO_3 produced:

Calcined spodumene ore, containing approximately 5 to 6% Li_2O equivalent - 6 to 8 metric tons.

93% H_2SO_4 (66% Be acid) - 0.8 to 0.85 cubic meter of acid (1.4 to 1.6 metric tons H_2SO_4).

3. Operating Parameters

The process is conducted at atmospheric pressure (surmised) and at temperatures ranging between 200° and 250°C .

Time required for digestion is not published, but is estimated here to be less than one hour.

4. Utilities

Per metric ton of Li_2CO_3 produced:

Heat (supplied by combustion of either coal or fuel oil - 300×10^3 to 600×10^3 kcal (gross estimate).

Electrical energy consumption - 30 to 60 kWh (estimated).

5. Waste Streams

Surmised fugitive emissions of SO_3 mist may occur during charging or discharging periods of digestion vessel, if

operation is batchwise. Factual information is unavailable. Estimated quantity is less than 2 kg SO₂ per metric ton of Li₂CO₃ produced.

6. EPA Source Classification Code

None established

7. References

Bach, R. O., C. W. Kamienski, and R. B. Ellestad. Lithium and Lithium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1967. 12:530-533.

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley and Sons, Inc., 1965. p. 492-494.

LEACHING/FILTRATION/EVAPORATION1. Function

The process recovers the soluble lithium (Li) values from acid-digested spodumene ore received from Process 63, producing impure 20% lithium sulfate (Li_2SO_4) liquor, which is forwarded to Process 10 (See Figure 24).

The following major sequential steps are included:

- Leaching digested ore (gangue plus solubles) with water and with recycled mother liquor.
- Neutralization of the leachate with ground limestone.
- Clarifying (implied) and filtration of the leachate.
- Evaporation of the leachate to a concentration of 20% Li_2SO_4 .
- Clarifying (surmised) and filtration of the impure 20% Li_2SO_4 solution for removal of previously precipitated CaCO_3 and $\text{Mg}(\text{OH})_2$.

Major essential equipment includes:

- Open-top leach tanks (presumed)
- Agitated neutralization tanks
- Settling tanks
- Rotary vacuum filters (presumed type).
- Five-effect vacuum evaporators.

2. Input Materials

Quantities expressed are per metric ton of Li_2CO_3 produced.

Major input is acid-digested spodumene ore (containing 5 to 6% Li_2O) - 6 to 8 metric tons.

Recycled mother liquor from Process 10 containing soluble Li values at estimated concentrations between 0.2 and 0.4% Li - 9 to 12 cubic meters of solution, containing 0.025 to 0.035 metric tons Li.

Total water added - 7 to 8 cubic meters (gross estimate).

Ground limestone - 0.2 to 0.5 metric tons consumed (gross estimate).

Hydrated lime - 0.02 to 0.05 metric tons consumed (gross estimate).

Soda ash, added as 30% solution for Ca removal - 0.5 to 2.0 metric tons Na_2CO_3 .

3. Operating Parameters

Leaching, clarifying, and filtration steps - conducted at atmospheric pressure and in temperature range estimated to be 40° to 70°C.

Range of physical conditions during evaporation, conducted in a five-effect evaporator (gross estimate) - 3 kilograms per square centimeter absolute pressure and 135°C to 630 millimeters Hg vacuum and 50°C.

Second clarifying and filtration - conducted at approximately 50°C and at atmospheric pressure (inferred).

4. Utilities

Quantities expressed are per metric ton of Li_2CO_3 produced.

Steam (presumed at 3.5 kilograms per square centimeter absolute pressure) - 2 to 4 metric tons (estimated).

Cooling water (at least a part of this may be identical with the make-up water mentioned under 2, above) - Up to 50 cubic meters (once-through basis).

Electrical energy - Between 100 and 200 kWh (gross estimate of total amount consumed).

5. Waste Streams

Quantities expressed are per metric ton of Li_2CO_3 produced.

Solid wastes - 5 to 7 metric tons of fine inert gangue, 0.02 to 0.05 metric tons (gross estimate) of $\text{Mg}(\text{OH})_2$, and up to 1.5 metric tons (gross estimate) of finely divided CaCO_3 . All the solids mentioned are discharged from the process as slurries (presumed). It is surmised that the solids are settled out and abandoned in tailings ponds or piles.

Water - At least part used to transport the waste solids to tailings ponds is not recycled. Presumably it evaporates from the tailings ponds or is wasted to natural streams. A gross estimate of the quantity is 3 to 5 cubic meters.

6. EPA Source Classification Code

None established

7. References

Bach, R. D., C. W. Kamienski, and R. B. Ellestad. Lithium and Lithium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1967. 12:530-533.

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley and Sons, Inc., 1965. 852 p.

DISSOLUTION1. Function

The process (See Figure 23) forms saturated sodium chloride (NaCl) brine from:

- Make-up granular NaCl
- NaCl crystals plus mother liquor, both recycled from Process 10.
- Make-up softened water.

The saturated brine thus produced constitutes the feed to the electrolytic cell of Process 66.

Included in the process are the steps of clarifying and filtration of the NaCl brine.

Major equipment consists of agitated dissolving tanks, a retention or settling tank, and filtration equipment, presumed to be a sand filter.

2. Input Materials

Per metric ton of sodium chlorate (NaClO_3) produced:

Make-up NaCl - Between 0.55 and 0.60 metric tons.

Recycled NaCl - Estimated between 0.1 and 0.3 metric tons. The quantity varies with operating conditions of the subsequent electrolysis. Estimated quantity of NaClO_3 in recycled mother liquor is 0.3 metric tons.

Make-up water - Estimated between 1.5 and 1.7 cubic meters.

Sodium carbonate (Na_2CO_3) and $\text{Ca}(\text{OH})_2$ for Mg and Ca removal - Less than 5 kilograms each.

3. Operating Parameters

All equipment is operated at atmospheric pressure. Possible exception is the filtration equipment. Pressure filters, if used, may require pressures up to 3 to 4 kilograms per square centimeter.

Temperatures are estimated in the range of 35° to 40°C.

4. Utilities

Electrical energy consumption is estimated to be between 10 and 20 kWh per metric ton of NaClO₃ produced.

5. Waste Streams

Depending on the amount of impurities present in both the make-up salt and make-up water, up to 20 kilograms of solids per metric ton of NaClO₃ is discharged in the back-washings from the sand filter. The solids are chiefly magnesium hydroxide and calcium carbonate. The filter back-washings are presumably ponded. The settled solids constitute a landfill.

6. EPA Source Classification Code

None established

7. References

Clapper, T. W., and W. A. Gale. Chloric Acid and Chlorates. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1964. 5:50-59.

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1966. p. 255-256.

ELECTROLYTIC CHLORATE PRODUCTION1. Function

Sodium chlorate (NaClO_3) and hydrogen gas (H_2) are produced in a diaphragmless electrolytic cell by the electrolysis of saturated sodium chloride (NaCl) brine received from Process 65 (See Figure 23). The cell effluent is forwarded to Process 10, Figure 23. The hydrogen gas is assumed to be flared.

Essential equipment consists of a series of rectangular steel cells, operated without diaphragms between the cathode and anode surfaces. Graphite anodes are usually employed, spaced close to the steel cathodic surfaces. Cells are estimated to be approximately 0.5 meter by 2.5 meter by 1.2 meter high, and are water-cooled internally by pipe coils.

2. Input Materials

Per metric ton of sodium chlorate (NaClO_3) produced:

Saturated NaCl brine from Process 65 - Estimated 2.3 cubic meters (2.7 metric tons), containing about 0.9 metric tons NaCl and some recycled NaClO_3 .

Sodium chromate (for corrosion protection and hypochlorite suppression) - Estimated 1 to 2 kilogram.

Hydrochloric acid (for pH control) - Estimated 6 to 12 kilogram of HCl .

Graphite consumed by anode degradation - 10 to 20 kilograms.

3. Operating Parameters

Cells operate at atmospheric pressure and inside a temperature range of 40° to 45°C .

Optimum pH of cell brine is 6.8 to 7.0.

Anodic current density is in the range of 1,000 to 1,300 amperes per square meter.

Concentration of NaClO_3 in cell effluent varies within a broad range, depending on exact method of operation, estimated from 200 to 600 grams per liter.

4. Utilities

Per metric ton of sodium chlorate (NaClO_3) produced:

Electrical energy (D.C. current for electrolysis) -
5,000 to 5,200 kWh.

Cooling water - Estimated 150 to 170 cubic meters.

Gaseous nitrogen, bled into the cell to provide a slight positive internal pressure - Estimated 5 to 10 standard cubic meters.

5. Waste Streams

Fugitive emissions of gaseous chlorine from cell and cell-fittings (surmised) - Estimated less than 0.1 ppm Cl_2 in air in the vicinity of the cell.

Emission to the atmosphere of water vapor from the flared hydrogen gas - Estimated approximately 0.5 metric tons of H_2O per metric ton NaClO_3 , representing an estimated 700 standard cubic meters of hydrogen.

6. EPA Source Classification Code

None established

7. References

Clapper, T. W., and W. A. Gale. Chloric Acid and Chlorates. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1964. 5:50-59.

Creighton, H. J., and W. A. Kohler. Principles and Applications of Electrochemistry, 2nd Edition. New York, John Wiley and Sons, Ind., 1944. 2:283-287.

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1966. p. 255-256.

SODIUM CHLORATE DRYING

1. Function

The process (See Figure 23) reduces the water content of the moist sodium chlorate (NaClO_3) crystals received from Process 10, from an estimated 5% to approximately 0.2%. The dried NaClO_3 is the end product of the operations.

Rotary dryers and batch tray dryers are alternatively employed. Both types are steam-coil heated externally.

2. Input Materials

Moist NaClO_3 crystals containing an estimated 5% free moisture - 1.05 metric tons per metric ton of NaClO_3 produced.

3. Operating Parameters

Drying NaClO_3 is a critical and potentially hazardous process. The material must not be subjected to even moderately high temperatures. Information on precise drying temperatures is not available. It is surmised here that air-swept dryers (rotary or tray type) are used, preventing the NaClO_3 from contacting any surface hotter than an estimated 40° to 45°C .

The NaClO_3 must be prevented from contacting any organic materials, or any reducing agent.

Use of cyclone collectors and glass-cloth bag-filters on dryer exhausts is imperative.

Accumulations of NaClO_3 dust from seal leakages must be prevented.

4. Utilities

Per metric ton of dry NaClO_3 produced:

Low-pressure (1 to 2 kilogram per square centimeter) steam - Estimated 0.2 metric tons.

Electrical energy - Estimated 15 to 25 kWh.

5. Waste Streams

Fugitive emissions of NaClO_3 dust particles to the atmosphere are presumed to be of very small magnitude. Information about precise values are unavailable. Estimated amount is less than 0.01 kilogram per metric ton of NaClO_3 produced, assuming control devices are operative.

6. EPA Source Classification Code

None established

7. References

Clapper, T. W., and W. A. Gale. Chloric Acid and Chlorates. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, Interscience Publishers, 1964. 5:50-59.

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1966. p. 255-256.

APPENDIX A
RAW MATERIALS LIST

APPENDIX A

RAW MATERIAL LIST

Composition and Occurrence Information

1. Seawater

- Concentration in ppm of the ten most prevalent dissolved elements in "normal" seawater:

Cl	-	18,360
Na	-	10,768
Mg	-	1,298
S	-	900
Ca	-	408
K	-	388
Br	-	66
C	-	28
Sr	-	14
B	-	5

- Relative proportion of elements listed is invariant.
- Absolute concentrations at shore locations vary typically between 70% and 110% of values listed.

2. Michigan subterranean brines commercially exploited

Typical composition in ppm of brines obtained from three members of the Sylvania formation:

<u>Dissolved Constituent</u>	<u>Marshall</u>	<u>Dundee</u>	<u>Monroe</u>
Na	50,100	55,044	20,444
K	998	nil	8,794
Ca	35,900	32,432	68,468
Mg	8,890	7,650	9,307
Cl	168,212	164,877	188,283
Br	1,500	1,500	2,600
I	nil	nil	38

3. Nevada subterranean brine

- Typical concentration in percent, of dissolved ions in Silver Peak Playa brine, Clayton Valley, Esmeralda County, Nevada.

Na	-	6.2
K	-	0.8
Mg	-	0.04
Li	-	0.04
Ca	-	0.05
SO ₄	-	0.71
Cl	-	10.1

Appendix A (Continued)

- Producing formation lies 100 to 250 m below surface.

4. Arkansas brine

- Typical concentration in percent, of dissolved ions in brine from the Smackover formation near Magnolia, Arkansas:

Na - 6.35
Cl - 9.65
Br - 0.45 to 0.52

- Producing formation lies approximately 1,800 m below surface.

5. Western Texas brines

- Typical composition in percent, of brine from reservoir underlying Howard, Glasscock and Scurry counties:

NaCl - 12.0
MgCl₂ - 11.0
CaCl₂ - 0.78
KCl - 0.23
Br - 0.13

- Typical concentration of Na₂SO₄ in brine from reservoir underlying Ward and Terry counties:

9% - Na₂SO₄

6. Great Salt Lake brine

Typical concentrations in ppm:

	<u>Northern Arm. (G.S.L. Min. & Chem. Corp.)</u>	<u>Southern Arm. (NL industries)</u>
Na	82,800	71,900
Mg	12,420	7,960
K	7,120	4,870
Ca	100	136
Li	60	35
Cl	146,280	132,000
SO ₄	25,200	15,600
HCO ₃	350	397

7. Searles Lake brine

Typical concentrations in ppm:

Appendix A (Continued)

	<u>Upper stratum</u>	<u>Lower stratum</u>
Na	111,400	117,100
K	25,700	18,400
Li	80	40
Cl	120,900	111,600
SO ₄	45,600	40,600
CO ₃	26,900	36,800
HCO ₃	1,100	nil
B ₄ O ₇	12,200	12,000
B ₂ O ₄	nil	4,900
Br	850	710
As	160	160

8. Bristol Lake brine

Typical composition in percent:

CaCl₂ - 14
NaCl - 14

9. Salduro Marsh brine

Average composition in percent:

NaCl - 18 to 24
KCl - 0.8 to 1.2
MgCl₂ - 0.9 to 1.2
MgSO₄ - 0.2 to 0.3
CaSO₄ - 0.3 to 0.4
LiCl - 0.03 to 0.04

10. Sodium chloride

Composition range of bedded deposits and salt domes, in weight percent:

NaCl, deposit average: 80 to 99
NaCl, individual layers: up to 100
Anhydrite, overall: 0 to 2
Br, intracrystalline: 0 to 0.01
Mg, overall: 0 to 0.5

11. Sylvinite

- Composition range of bedded deposits of New Mexico and Utah, weight percent:

KCl - 15 to 40
NaCl - 60 to 85

- Interspersed with clay, sand, and anhydrite.

Appendix A (Continued)

12. Langbeinite ($2 \text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$)

Inferred composition range of bedded deposits of the Carlsbad, New Mexico area:

50 to 90% langbeinite

13. Trona ($\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$)

Reported average composition of bedded trona of the Green River formation in Wyoming:

95 to 96% $\text{NaHCO}_3 \cdot 2\text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$

14. Kernite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$)

- Inferred composition of kernite deposits of Kern County, California:

55% B_2O_3

- Deposit is associated with borax.

15. Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)

- Inferred composition of borax deposits of Kern County, California:

30% B_2O_3

- Deposit is associated with kernite

16. Colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$)

- Major deposit is near Death Valley Junction, Inyo County, California.
- Assay of ore body is not available.

17. Spodumene ($\text{LiAlSi}_2\text{O}_6$)

Typical lithium content of the spodumene ore deposits near Kings Mountain and Bessemer City, North Carolina:

1 to 2% Li_2O

18. Sulfur (S); purchased raw material

Usually contains between 99.5 and 99.95% sulfur.

Appendix A (Concluded)

19. Sulfuric acid (H_2SO_4); purchased raw material

Commercial acid usually contains either 95 to 98% H_2SO_4 or about 80% H_2SO_4 .

20. Lime (CaO or $\text{Ca}(\text{OH})_2$); purchased raw material

Typical composition range:

CaO	95 to 97%
CaCO_3	- 1 to 2%
SiO_2	- 0.5 to 3%
R_2O_3	- 0.5 to 3%

21. Dolime ($\text{CaO} \cdot \text{MgO}$); usually a purchased raw material

Typical composition range:

MgO	- 37 to 41%
CaO	- 55 to 58%
SiO_2	- 0.5 to 3%
R_2O_3	- 0.5 to 3%

22. Limestone (CaCO_3); usually a purchased raw material

Typical composition range:

CaCO_3	- 95 to 99%
SiO_2	- 0.5 to 1.5%
R_2O_3	- 0.5 to 1.5%

APPENDIX B
PRODUCT LIST

APPENDIX B
PRODUCT LIST

Industry by-products are indicated by an *.

Products

Boric acid - H_3BO_3
Boric acid anhydride - B_2O_3
Boron oxide - fused B_2O_3
Bromine, elemental - Br_2
Calcium borate (calcined colemanite) - $2 \text{CaO} \cdot 3\text{B}_2\text{O}_3$
Calcium chloride, 35% liquor - CaCl_2
Calcium chloride, 78% flake - CaCl_2
Calcium chloride, anh. flake - CaCl_2
Chlorine, gas - Cl_2
Chlorine, liquefied - Cl_2
Hydrochloric acid, 30% solution - HCl
*Hydrogen, gas - H_2
Iodine, elemental - I_2
Lithium acetate - $\text{LiC}_2\text{H}_3\text{O}_2$
Lithium aluminate - LiAlO_2
Lithium amide - LiNH_2
Lithium bromate - LiBrO_3
Lithium bromide - LiBr
Lithium carbonate - Li_2CO_3
Lithium chloride - LiCl
Lithium cobaltate - Li_2CoO_2
Lithium fluoride - LiF
Lithium fluoroborate - LiBF_4
Lithium hydride - LiH
Lithium hydroxide - LiOH
Lithium hypochlorite - LiClO
Lithium iodide - LiI
Lithium iodide trihydrate - $\text{LiI} \cdot 3\text{H}_2\text{O}$
Lithium manganite - Li_2MnO_3
Lithium metaborate - LiBO_2
Lithium metaphosphate - LiPO_3
Lithium metasilicate - Li_2SiO_3
Lithium molybdate - Li_2MoO_4
Lithium nitrate - LiNO_3
Lithium nitride - Li_3N
Lithium orthophosphate - Li_3PO_4
Lithium orthosilicate - Li_4SiO_4
Lithium oxide - Li_2O
Lithium peroxide - Li_2O_2
Lithium sulfate - Li_2SO_4
Lithium sulfide - Li_2S
Lithium tetraborate - $\text{Li}_2\text{B}_4\text{O}_7$
Lithium titanate - Li_2TiO_3
Lithium zirconate - Li_2ZrO_3
Magnesium, metal - Mg

Appendix B (Concluded)

Magnesium carbonate trihydrate - $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$
Magnesium carbonate, basic - $5 \text{MgO} \cdot 4\text{CO}_2 \cdot 6\text{H}_2\text{O}$
Magnesium chloride, 32% liquor - MgCl_2
Magnesium chloride, 46% liquor - MgCl_2
Magnesium chloride, 50% flake - MgCl_2
Magnesium hydroxide, slurry - 35-50% $\text{Mg}(\text{OH})_2$
Magnesium hydroxide, dried - $\text{Mg}(\text{OH})_2$
Magnesium oxide, caustic-calcined - MgO
Magnesium oxide, dead-burned - MgO
Magnesium potassium sulfate (commercial langbeinite) - $2\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$
Magnesium sulfate (Epsom Salt) - MgSO_4
*Phosphoric acid, crude, 50% - H_3PO_4
Potassium chloride - KCl
Potassium hydroxide - KOH
Potassium sulfate - K_2SO_4
Sodium, metal - Na
Sodium bicarbonate - NaHCO_3
Sodium bromide - NaBr
Sodium carbonate (soda ash) - Na_2CO_3
Sodium chlorate - NaClO_3
Sodium chloride, dried crude - NaCl
Sodium chloride, dry refined - NaCl
Sodium chloride, rock rock salt - NaCl
Sodium chloride, saturated brine - NaCl
Sodium chloride, washed, crude - NaCl
Sodium hydroxide, 50% liquor - NaOH
Sodium hydroxide, 75% liquor - NaOH
Sodium hydroxide, solid - NaOH
Sodium iodide - NaI
Sodium sulfate, anh. (salt cake) - Na_2SO_4
Sodium tetraborate, anhydrous (anhydrous borax) - $\text{Na}_2\text{B}_4\text{O}_7$
Sodium tetraborate decahydrate (borax) - $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
Sodium tetraborate pentahydrate - $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$

APPENDIX C
COMPANY/PRODUCT LIST

Table C-1. COMPANY/PRODUCT LIST^a

Company name	Location of operation (city and state)
Boric acid:	
Orthoboric acid - H_3BO_3	
Anhydrous boric acid - B_2O_3	
Kerr-McGee Corporation	Trona, California
Kerr-McGee Chemical Corporation, subsid.	
Stauffer Chemical Company	San Francisco, California
Industrial Chemicals Division	
U. S. Borax and Chemical Corporation	Wilmington, California
<u>Boron oxide - B_2O_3</u>	
Eagle-Picher Industries, Inc.	
Electronics Division	Miami, Oklahoma
	Quapaw, Oklahoma
Stauffer Chemical Company	
Industrial Chemicals Division	San Francisco, California

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)	Annual capacity (thousands of metric tons)
<u>Bromine, elemental - Br₂</u>		
Arkansas Chemicals, Inc.	El Dorado, Arkansas	27
Dow Chemical U.S.A.	Ludington, Michigan	7
	Magnolia, Arkansas	16
	Midland, Michigan	48
Ethyl Corporation		
Brine Products Division	Magnolia, Arkansas	59
Great Lakes Chemical Corporation	El Dorado, Arkansas	32
Kerr-McGee Corporation		
Kerr-McGee Chemical Corporation, subsid.	Trona, California	1
Northwest Industries, Inc.		
Michigan Chemical Corporation, subsid.	El Dorado, Arkansas	7
	St. Louis, Michigan	2
<u>Calcium borate (calcined colemanite)</u>		
Tenneco, Inc.		
Tenneco Oil Company, division	Death Valley Junction, California	
U. S. Borax and Chemical Corporation		
U. S. Borax Research Corporation, subsid.	Anaheim, California	

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)	Annual capacity (thousands of metric tons)
Calcium chloride - CaCl_2 : Anhydrous flake 78% flake and pellets 35% liquid		
Allied Chemical Corporation Industrial Chemicals Division	Syracuse, New York	290
Diamond Shamrock Corporation Diamond Shamrock Chemical Company Agricultural Division	Greens Bayou, Texas	
Dow Chemical U.S.A.	Ludington, Michigan) Midland, Michigan)	630
Geothermal Energy & Minerals Corporation	Imperial Valley, California	n.a.
Hill Brothers Chemical Company	Amboy, California	
National Chloride Company of America	Amboy, California	
Northwest Industries, Inc. Michigan Chemical Corporation, subsid.	St. Louis, Michigan	72
Occidental Petroleum Corporation Hooker Chemical Corporation, subsid. Electrochemical & Specialties Divisions	Tacoma, Washington	
Shell Chemical Company Industrial Chemicals Division	Norco, Louisiana	n.a.

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)	Annual capacity (thousands of metric tons)
Chlorine - Cl ₂ : Gas (pipeline delivery) Liquefied		
Allied Chemical Corporation Industrial Chemicals Division	Acme, North Carolina) Baton Rouge, Louisiana) Brunswick, Georgia) Moundsville,) West Virginia) Syracuse, New York)	535
Aluminum Company of America	Point Comfort, Texas	150
American Magnesium Company	Snyder, Texas	23
BASF Wyandotte Corporation Industrial Chemicals Group	Geismar, Louisiana) Port Edwards, Wisconsin) Wyandotte, Michigan)	500
Brunswick Pulp & Paper Company Brunswick Chemical Company, subsid.	Brunswick, Georgia	25
Champion International Corporation Champion Papers Division	Canton, North Carolina Pasadena, Texas	16 13

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)	Annual capacity (thousands of metric tons)
Chlorine (cont'd)		
Diamond Shamrock Corporation		
Diamond Shamrock Chemical Company		
Electro Chemicals Division	Deer Park, Texas) Delaware City, Delaware) Mobile, Alabama) Muscle Shoals, Alabama) Painesville, Ohio)	1,035
Dow Chemical U.S.A.	Freeport, Texas) Midland, Michigan) Oyster Creek, Texas) Pittsburg, California) Plaquemine, Louisiana)	1,850 1,435
E. I. duPont de Nemours & Company, Inc.		
Industrial Chemicals Department	Memphis, Tennessee) Niagara Falls, New York) Corpus Christi, Texas)	305
Organic Chemicals Department		
Freon® Products Division		
Ethyl Corporation	Baton Rouge, Louisiana) Pasadena, Texas)	207
FMC Corporation		
Chemical Group		
Industrial Chemical Division	South Charleston, West Virginia	255

Table C-1 (Continued). COMPANY/PRODUCT LIST

<u>Company name</u>	<u>Location of operation (city and state)</u>	<u>Annual capacity (thousands of metric tons)</u>
<u>Chlorine (cont'd)</u>		
Georgia-Pacific Corporation Chemical Division	Bellingham, Washington Plaquemine, Louisiana	43 260
The B. F. Goodrich Company B. F. Goodrich Chemical Company, division	Calvert City, Kentucky	97
Hercules, Inc. Coatings & Specialty Products Department	Hopewell, Virginia	16
Inland Chemical Corporation	Newark, New Jersey	38
Kaiser Aluminum & Chemical Corporation Kaiser Chemicals Division	Gramercy, Louisiana	173
Linden Chlorine Products, Inc.	Linden, New Jersey	147
Mobay Chemical Corporation Industrial Chemicals Division	Cedar Bayou, Texas	65
Monsanto Company Monsanto Industrial Chemicals Company	Sauget, Illinois	80
N L Industries, Inc. Magnesium Division	Rowley, Utah	140
Northwest Industries, Inc. Velsicol Chemical Corporation, subsid.	Memphis, Tennessee	21

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)	Annual capacity (thousands of metric tons)
<u>Chlorine (cont'd)</u>		
Occidental Petroleum Corporation		
Hooker Chemical Corporation, subisd.		
Hooker Chemicals & Plastics Corp., subisd.		
Electrochemical & Specialty Chems. Div.	Montague, Michigan) Niagara Falls, New York) Tacoma, Washington) Taft, Louisiana)	830
Olin Corporation		
Designed Products Division	Charleston, Tennessee) Augusta, Georgia) McIntoch, Alabama) Niagara Falls, New York)	526
Industrial Products & Services Division		
Pennwalt Corporation		
Chemical Division	Calvert City, Kentucky) Portland, Oregon) Tacoma, Washington) Wyandotte, Michigan)	305
PPG Industries, Inc.		
Chemical Division		
Industrial Chemical Division	Barberton, Ohio) Corpus Christi, Texas) Lake Charles, Louisiana) Natrium, West Virginia) Guayanilla, Puerto Rico)	1,000 165
PPG Industries (Caribe)		
RMI Company	Ashtabula, Ohio	n.a.

Table C-1 (Continued). COMPANY/PRODUCT LIST.

Company name	Location of operation (city and state)	Annual capacity (thousands of metric tons)
<u>Chlorine (cont'd)</u>		
Shell Chemical Company Base Chemicals Division	Deer Park, Texas	122
Sobin Chemicals, Inc.	Ashtabula, Ohio Orrington, Maine	33 67
Stauffer Chemical Company Industrial Chemical Division	Henderson, Nevada) Le Moyne, Alabama) St. Gabriel, Louisiana)	315
Texaco, Inc. Jefferson Chemical Company, Inc., subsid.	Port Neches, Texas	49
Vicksburg Chemical Company	Vicksburg, Mississippi	29
Vulcan Materials Company Chemicals Division	Wichita, Kansas	82
Weyerhaeuser Company	Longview, Washington	86

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
<u>Hydrochloric acid, 30% to 37% HCl^b</u>	
Allied Chemical Corporation Industrial Chemicals Division	Baton Rouge, Louisiana Syracuse, New York
Allied Chemical Corporation Specialty Chemicals Division	Baton Rouge, Louisiana Danville, Illinois Elizabeth, New Jersey Moundsville, West Virginia Syracuse (Solvay), New York
BASF Wyandotte Corporation Industrial Chemicals Group	Wyandotte, Michigan
*Climax Chemical Company	*Monument, New Mexico
Continental Oil Company Conoco Chemicals	Baltimore, Maryland
Detrex Chemical Industry, Inc.	Ashtabula, Ohio
Diamond Shamrock Corporation Diamond Shamrock Chemical Company Agricultural Division Electro Chemicals Division	Greens Bayou, Texas Belle, West Virginia Painesville, Ohio
Dow Chemical U.S.A.	Freeport, Texas

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
<u>Hydrochloric acid (cont'd)</u>	
E. I. duPont de Nemours & Co., Inc. Industrial Chemicals Department	*Cleveland, Ohio East Chicago, Indiana Linden, New Jersey
FMC Corporation Chemical Group Industrial Chemical Division	Baltimore, Maryland Nitro, West Virginia
*Ideal Basic Industries, Inc. Potash Company of America, division	*Dumas, Texas
Inland Chemical Corporation	Newark, New Jersey
Jones-Hamilton Company	Newark, California
Lehigh Valley Chemical Company	Glendon, Pennsylvania
Mobay Chemical Corporation Industrial Chemicals Division	Cedar Bayou, Texas New Martinsville, West Virginia
Monsanto Company Monsanto Industrial Chemicals Company	Everett, Massachusetts Sauget, Illinois
Montrose Chemical Corporation of California	Henderson, Nevada
*Morton International, Inc. Morton Chemical Company, division	*Weeks Island, Louisiana

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
<u>Hydrochloric acid (cont'd)</u>	
Northwest Industries, Inc. Velsicol Chemical Corporation, subsid.	Chatanooga, Tennessee
Occidental Petroleum Corporation Hooker Chemical Corporation, subsid. Hooker Chemicals & Plastics Corporation, subsid. Electrochemical & Specialty Chemicals Division	Montague, Michigan Niagra Falls, New York
Pennwalt Corporation Chemical Division	Calvert City, Kentucky Portland, Oregon Tacoma, Washington Wyandotte, Michigan
PPG Industries, Inc. Chemical Division Industrial Chemical Division	Barberton, Ohio Lake Charles, Louisiana Natrium, West Virginia
Reichhold Chemicals, Inc.	Tacoma, Washington
Rohm and Haas Company	Philadelphia, Pennsylvania
Sobin Chemicals, Inc. Montrose Chemical Division	Newark, New Jersey
Stauffer Chemical Company Agricultural Chemical Division	Cold Creek, Alabama Mt. Pleasant, Tennessee

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
<u>Hydrochloric acid (cont'd)</u>	
Stauffer Chemical Company Industrial Chemical Division	Dominguez, California Fort Worth, Texas Henderson, Nevada Louisville, Kentucky
Specialty Chemical Division Union Carbide Corporation Chemicals and Plastics Division	Gallipolis Ferry, West Virginia Institute, West Virginia South Charleston, West Virginia Texas City, Texas
*Vulcan Materials Company Chemicals Division	*Denver City, Texas Geismar, Louisiana Wichita, Kansas

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)	Daily capacity (1,000 m ³)
<u>Hydrogen - H₂</u>		
(List includes only companies in Brine and Evaporite Chemicals Industry known to beneficially recover hydrogen from electrolysis cells.)		
Allied Chemical Corporation Specialty Chemicals Division	Moundsville, West Virginia	67
Diamond Shamrock Corporation Diamond Shamrock Chemical Company Electro Chemicals Division	Deer Park Texas) Delaware City, Delaware) Mobile, Alabama) Muscle Shoals, Alabama) Painesville, Ohio)	44
Dow Chemical U.S.A.	Midland, Michigan) Freeport, Texas)	233
Pennwalt Corporation. Chemical Division	Portland, Oregon	30
PPG Industries, Inc. Industrial Chemical Division	Barberton, Ohio) Corpus Christi, Texas) Lake Charles, Louisiana) Natrium, West Virginia) Guayanilla, Puerto Rico	n.a. n.a.
PPG Industries (Caribe)		n.a.

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)	Daily capacity (1,000 m ³)
<u>Hydrogen (cont'd)</u>		
Stauffer Chemical Company Industrial Chemical Division	Henderson, Nevada) Le Moyne, Alabama) St. Gabriel, Louisiana)	n.a.
Vulcan Materials Company Chemicals Division	Wichita, Kansas	n.a.
<u>Iodine, elemental - I₂</u>		
Dow Chemical U.S.A.	Midland, Michigan	
<u>Lithium acetate - LiC₂H₃O₂</u>		
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina	
<u>Lithium aluminate - LiAlO₂</u>		
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina	
<u>Lithium amide - LiNH₂</u>		
Foote Mineral Company	Exton, Pennsylvania	

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
<u>Lithium amide (cont'd)</u>	
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
<u>Lithium bromate - LiBrO₃</u>	
City Chemical Corporation	Jersey City, New Jersey
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
<u>Lithium bromide - LiBr</u>	
Foote Mineral Company	Exton, Pennsylvania
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
Mallinckrodt, Inc. Medicinal Division	St. Louis, Missouri
<u>Lithium carbonate - Li₂CO₃</u>	
Foote Mineral Company	Exton, Pennsylvania
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
<u>Lithium carbonate (cont'd)</u>	
Kerr-McGee Corporation	
Kerr-McGee Chemical Corporation, subsid.	Trona, California
<u>Lithium chloride - LiCl</u>	
Foote Mineral Company	Exton, Pennsylvania
Gulf Resources & Chemical Corporation	
Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
Mallinckrodt, Inc.	
Industrial Chemicals Division	St. Louis, Missouri
<u>Lithium cobaltite - Li₂CoO₂</u>	
Gulf Resources & Chemical Corporation	
Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
<u>Lithium fluoride - LiF</u>	
Foote Mineral Company	Exton, Pennsylvania
	Silver Peak, Nevada
General Telephone & Electronics Corporation	
GTE Sylvania, Inc., subsid.	
Chemical & Metallurgical Division	Towanda, Pennsylvania

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
<u>Lithium fluoride (cont'd)</u>	
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
Kawecki Berylco Industries, Inc.	Boyertown, Pennsylvania
Kewanee Oil Company Harshaw Chemical Company, division Crystal & Electronic Products Department	Solon, Ohio
<u>Lithium fluoroborate - LiBF₄</u>	
Foote Mineral Company	Exton, Pennsylvania
Pennwalt Corporation Ozark-Mahoning Company, subsid.	Tulsa, Oklahoma
Ventron Corporation Alfa Products Division	Beverly, Massachusetts
<u>Lithium hydride - LiH</u>	
Foote Mineral Company	Exton, Pennsylvania
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
<u>Lithium hydroxide - LiOH</u>	
Footo Mineral Company	Exton, Pennsylvania
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
<u>Lithium hypochlorite - LiClO</u>	
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
<u>Lithium iodide - LiI</u>	
City Chemical Corporation	Jersey City, New Jersey
Footo Mineral Company	Exton, Pennsylvania
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
Kewanee Oil Company Harshaw Chemical Company, division Crystal & Electronic Products Department	Solon, Ohio
Mallinckrodt, Inc. Industrial Chemicals Division	St. Louis, Missouri

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
<u>Lithium iodide, trihydrate - $\text{LiI} \cdot 3\text{H}_2\text{O}$</u>	
Footo Mineral Company	Exton, Pennsylvania
<u>Lithium manganite - Li_2MnO_3</u>	
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
<u>Lithium metaborate - LiBO_2</u>	
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
G. Frederick Smith Chemical Company	Columbus, Ohio
Ventron Corporation Alfa Products Division	Beverly, Massachusetts
<u>Lithium metaphosphate - LiPO_3</u>	
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
<u>Lithium metasilicate - Li_2SiO_3</u>	
Footo Mineral Company	Exton, Pennsylvania New Johnsonville, Tennessee

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
<u>Lithium metasilicate (cont'd)</u>	
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
<u>Lithium molybdate - Li_2MoO_4</u>	
City Chemical Corporation	Jersey City, New Jersey
Engelhard Minerals & Chemicals Corporation Philipp Brothers Division S. W. Shattuck Chemical Company, Inc., subsid.	Denver, Colorado
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
<u>Lithium nitrate - LiNO_3</u>	
Footo Mineral Company	Exton, Pennsylvania
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
Mallinckrodt, Inc. Industrial Chemicals Division	St. Louis, Missouri

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
<u>Lithium nitride - Li_3N</u>	
Footo Mineral Company	Exton, Pennsylvania
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
<u>Lithium orthophosphate - Li_3PO_4</u>	
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
<u>Lithium orthosilicate - Li_4SiO_4</u>	
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
<u>Lithium oxide (Lithia) - Li_2O</u>	
Footo Mineral Company	Exton, Pennsylvania
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
<u>Lithium perchlorate - LiClO_4</u>	
Footo Mineral Company	Exton, Pennsylvania
G. Frederick Smith Chemical Company	Columbus, Ohio

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
<u>Lithium peroxide - LiO_2</u>	
Barium and Chemicals, Inc.	Steubenville, Ohio
Footo Mineral Company	Exton, Pennsylvania
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
<u>Lithium sulfate - Li_2SO_4</u>	
Footo Mineral Company	Exton, Pennsylvania
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
Mallinckrodt, Inc. Industrial Chemicals Division	St. Louis, Missouri
<u>Lithium sulfide - Li_2S</u>	
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
<u>Lithium tetraborate - $\text{Li}_2\text{B}_4\text{O}_7$</u>	
City Chemical Corporation	Jersey City, New Jersey

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
<u>Lithium tetraborate (cont'd)</u>	
Foote Mineral Company	Exton, Pennsylvania
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
<u>Lithium titanate - Li_2TiO_3</u>	
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
<u>Lithium zirconate - Li_2ZrO_3</u>	
Gulf Resources & Chemical Corporation Lithium Corporation of America, Inc., subsid.	Bessemer City, North Carolina
<u>Magnesium, metal - Mg</u>	Annual Capacity (1,000 m. tons)
American Magnesium Company	Snyder, Texas 30
Dow Chemical U.S.A.	Freeport, Texas 120
NL Industries, Inc. Magnesium Division	Rowley, Utah 45

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
Magnesium carbonate - MgCO_3	
Basic magnesium carbonate - $\text{MgO} \cdot 5\text{CO}_2 \cdot 6\text{H}_2\text{O}$	
Combustion Engineering, Inc. C-E Minerals Division	Camden, New Jersey
Kaiser Aluminum & Chemical Corporation Kaiser Refractories Division	Moss Landing, New Jersey
Mallinckrodt Chemical Works Industrial Chemicals Division	St. Louis, Missouri
Merck & Company, Inc. Merck Chemical Division	South San Francisco, California
Mineral Research & Development Corporation	Concord, North Carolina
Morton International, Inc. Morton Chemical Company, division	Manistee, Michigan
Northwest Industries, Inc. Michigan Chemical Corporation, subsid.	St. Louis, Michigan
Tamms Industries Company Western Division	Bellflower, California

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
Magnesium chloride - $MgCl_2$	
32% liquor	
46% liquor	
50% flake	
73-75% granules	
Dow Chemical U.S.A.	Freeport, Texas Ludington, Michigan
FMC Corporation Chemical Group Industrial Chemical Division	Chula Vista, California
Gulf Resources & Chemical Corporation Great Salt Lake Minerals & Chemicals Corporation, subsid.	Ogden, Utah
Kaiser Aluminum & Chemical Corporation Kaiser Chemicals Division	Wendover, Utah
Mallinckrodt Chemical Works Industrial Chemicals Division	St. Louis, Missouri
Mineral Research & Development Corporation	Concord, North Carolina
N L Industries, Inc. Magnesium Division	Rowley, Utah
Richardson-Merrell, Inc. J. T. Baker Chemical Company, subsid.	Phillipsburg, New Jersey

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
<u>Magnesium chloride (cont'd)</u>	
Titanium Metals Corporation of America TIMET Division	Henderson, Nevada
<u>Magnesium oxide - MgO caustic calcined dead burned</u>	
<u>Magnesium hydroxide - $Mg(OH)_2$ dried hydrate slurry</u>	
Basic Incorporated Basic Chemicals Division	Port St. Joe, Florida
Combustion Engineering, Inc. C-E Minerals Division	Camden, New Jersey Greeneville, Tennessee
Corning Glass Company Corchem Company, subsid.	Pascagoula, Mississippi
Dow Chemical U.S.A.	Freeport, Texas Ludington, Michigan Midland, Michigan
General Electric Company Chemical and Metallurgical Division Plastics Department	Fittsfield, Massachusetts

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
<u>Magnesium oxide and Magnesium hydroxide (cont'd)</u>	
Glasrock Products, Inc. Muscle Shoals Electrochemical Company, div.	Tuscumbia, Alabama
The Greyhound Corporation Armour and Company, subsid. Armour Pharmaceutical Company, subsid. Reheis Chemical Company, division	Berkeley Heights, New Jersey
Kaiser Aluminum & Chemical Corporation Kaiser Refractories Division	Moss Landing, California
Mallinckrodt Chemical Works Industrial Chemicals Division	St. Louis, Missouri
Merck & Company, Inc. Merck Chemical Division	South San Francisco, California
Morton-Norwich Products, Inc. Morton Chemical Company, division	Manistee, Michigan
Northwest Industries, Inc. Michigan Chemical Corporation, subsid.	St. Louis, Michigan
Norton Company	Worcester, Massachusetts
Sterling Drug, Inc. Glenbrook Laboratories Division	Gulfport, Mississippi

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
<u>Magnesium potassium sulfate - $2\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$ (commercial langbeinite)</u>	
International Minerals & Chemical Corporation Agricultural Operations	Carlsbad, New Mexico
Pennzoil Company Duval Corporation, subsid.	Carlsbad, New Mexico
<u>Magnesium sulfate heptahydrate - $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Epsom salts)</u>	
Allied Chemical Corporation Specialty Chemical Division	Marcus Hook, Pennsylvania
Dow Chemical U.S.A.	Midland, Michigan
Giles Chemical Corporation	Waynesville, North Carolina
Mallinckrodt Chemical Works Industrial Chemicals Division	St. Louis, Missouri
Philadelphia Quartz Company	Berkeley, California
<u>Phosphoric acid - H_3PO_4</u>	
Kerr-McGee Corporation Kerr-McGee Chemical Corporation, subsid.	Trona, California

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)	Annual capacity (thousands of metric tons)
Potassium chloride - KCl		
AMAX, Inc. AMAX Chemical Corporation, division	Carlsbad, New Mexico	1,000
Freeport Minerals Company National Potash Company, subsid.	Carlsbad, New Mexico	580
Ideal Basic Industry, Inc. Potash Company of America, division	Carlsbad, New Mexico	1,100
International Minerals & Chemical Corp, Agricultural Operations	Carlsbad, New Mexico	730
Kaiser Aluminum & Chemical Corporation Kaiser Chemicals Division	Wendover, Utah	110
Kerr-McGee Corporation Kerr-McGee Chemical Corporation, subsid.	Hobbs, New Mexico Trona, California	600 450
Mississippi Chemical Corporation Mississippi Potash, Inc., subsid.	Carlsbad, New Mexico	365
Pennzoil Company Duval Corporation, subsid.	Carlsbad, New Mexico	580
Texasgulf, Inc. Agricultural Division	Moab, Utah	545

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)	Annual capacity (thousands of metric tons)
Potassium hydroxide - KOH (caustic potash)		
Allied Chemical Corporation Industrial Chemicals Division Specialty Chemicals Division	Syracuse, New York Marcus Hook, Pennsylvania	32 n.a.
Diamond Shamrock Corporation Diamond Shamrock Chemical Company Electro Chemicals Division	Deer Park, Texas Delaware City, Delaware Muscle Shoals, Alabama	n.a. 24 55
Monsanto Company Monsanto Industrial Chemicals Company	Sauget, Illinois	55
Occidental Petroleum Corporation Hooker Chemical Corporation, subsid. Electrochemical & Specialties Divisions	Niagara Falls, New York	80
Pennwalt Corporation Chemical Division	Calvert City, Kentucky Wyandotte, Michigan	22 n.a.
PPG Industries, Inc. Chemical Division Industrial Chemical Division	Corpus Christi, Texas	9

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)	Annual capacity (thousands of metric tons)
Potassium sulfate - K_2SO_4		
Allied Chemical Corporation Specialty Chemicals Division	Marcus Hook, Pennsylvania	n.a.
Great Western United Corporation Great Western Sugar Company, subsid.	Johnstown, Colorado	11
Gulf Resources & Chemical Corporation Great Salt Lake Minerals & Chemicals Corporation, subsid.	Ogden, Utah	220
Ideal Basic Industries, Inc. Potash Company of America, division	Dumas, Texas	16
International Minerals & Chemical Corp. Agricultural Operations	Carlsbad, New Mexico	455
Kerr-McGee Corporation Kerr-McGee Chemical Corp., subsid.	Trona, California	46
Pennzoil Company Duval Corporation, subsid.	Carlsbad, New Mexico	345
Sodium, metal - Na		
E. I. duPont de Nemours & Company, Inc. Industrial Chemicals Department	Memphis, Tennessee Niagara Falls, New York	32 38

Table C-1 (Continued). COMPANY/PRODUCT LIST

<u>Company name</u>	<u>Location of operation (city and state)</u>	<u>Annual capacity (thousands of metric tons)</u>
<u>Sodium, metal (cont'd)</u>		
Ethyl Corporation	Baton Rouge, Louisiana Pasadena, Texas	41 27
RMI Company	Ashtabula, Ohio	34
<u>Sodium bicarbonate - NaHCO₃</u>		
BASF Wyandotte Corporation Industrial Chemicals Group	Wyandotte, Michigan	38
Church & Dwight Company, Inc. Specialty Chemicals Division	Green River Wyoming Syracuse, New York	90 90
Diamond Shamrock Corporation Diamond Shamrock Chemical Company Soda Products Division	Painesville, Ohio	30
Hummel Chemical Company, Inc.	South Plainfield, N. J.	n.a.
<u>Sodium bromide - NaBr</u>		
J. Q. Dickinson & Company	Malden, West Virginia	
Dow Chemical U.S.A.	Midland, Michigan	

Table C-1 (Continued). COMPANY/PRODUCT LIST

<u>Company name</u>	<u>Location of operation (city and state)</u>	<u>Annual capacity (thousands of metric tons)</u>
<u>Sodium bromide (continued)</u>		
Kewanee Oil Company		
Harshaw Chemical Company, division		
Crystal & Electronic Products Dept.	Solon, Ohio	
Morton International, Inc.		
Morton Chemical Company, division	Manistee, Michigan	
<u>Sodium carbonate - Na₂CO₃ (soda ash)</u>		
Natural soda ash producers:		
Allied Chemical Corporation		
Industrial Chemicals Division	Green River, Wyoming	1,000
FMC Corporation		
Chemical Group		
Industrial Chemical Division	Green River, Wyoming	1,600
Kerr-McGee Corporation		
Kerr-McGee Chemical Corporation, subsid.	Trona, California	145
*Stauffer Chemical Company		
Industrial Chemical Division	West End, California	145
Stauffer Chemical Company of Wyoming	Green River, Wyoming	2,230

* Merged as a division of Kerr-McGee Corporation

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)	Annual capacity (thousands of metric tons)
<u>Sodium carbonate (continued)</u>		
Synthetic (Solvay) soda ash producers:		
Allied Chemical Corporation	Baton Rouge, Louisiana	715
Industrial Chemicals Division	Syracuse, New York	910
Specialty Chemicals Division	Marcus Hook, Pennsylvania	n.a.
BASF Wyandotte Corporation	Wyandotte, Michigan	725
Industrial Chemicals Group		
Diamond Shamrock Corporation		
Diamond Shamrock Chemical Company	Painesville, Ohio	725
Soda Products Division		
Olin Corporation		
Agricultural Chemicals Division	Lake Charles, Louisiana	345
PPG Industries, Inc.		
Chemical Division		
Industrial Chemical Division	Corpus Christi, Texas	245
<u>Sodium chlorate - NaClO₃</u>		
Brunswick Pulp & Paper Company		
Brunswick Chemical Company, subsid.	Brunswick, Georgia	6
Georgia-Pacific Corporation		
Chemical Division	Bellingham, Washington	4

Table C-1 (Continued). COMPANY/PRODUCT LIST

<u>Company name</u>	<u>Location of operation (city and state)</u>	<u>Annual capacity (thousands of metric tons)</u>
<u>Sodium chlorate (cont'd)</u>		
Huron Chemicals of America, Inc.	Naheola, Alabama	4
	Riegelwood, North Carolina	6
Kerr-McGee Corporation		
Kerr-McGee Chemical Corporation, subsid.	Hamilton, Mississippi	30
	Henderson, Nevada	30
Occidental Petroleum Corporation		
Hooker Chemical Corporation, subsid.		
Hooker Chemicals & Plastics Corp., subsid.		
Electrochemical & Specialty Chemicals Division	Columbus, Mississippi	56
	Niagara Falls, New York	14
	Taft, Louisiana	40
Pacific Eng'g & Production Co. of Nevada	Henderson, Nevada	6
Penn-Olin Chemical Company	Calvert City, Kentucky	28
Pennwalt Corporation		
Chemical Division	Portland, Oregon	14
PPG Industries, Inc.		
Chemical Division		
Industrial Chemical Division	Lake Charles, Louisiana	14

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (county and state)	Type of product
Sodium chloride - NaCl		
Dried, crude (solar) salt - 1		
Dry, refined salt - 2		
Rock salt - 3		
Saturated brine - 4		
Washed crude (solar) salt - 1		
Acme Salt Company Box 420 Erick, Oklahoma 73645	Harmon, Oklahoma	2
Akzona, Inc. International Salt Company, division Clarks Summit, Penn. 18411	Iberia, Louisiana Wayne, Michigan Livingston, New York Schuyler, New York Cuyahoga	2,3 3 3 2 2,3
Allied Chemical Corporation Industrial Chemical Division P. O. Box 1219-R Morristown, New Jersey 07960	Iberville, Louisiana Onondaga, New York Marshall, West Virginia	4 2,4 4
American Salt Corporation 3142 Broadway Kansas City, Missouri 64111	Rice, Kansas Tooele Utah	2,3 1,2
BASF Wyandotte Corporation 1609 Biddle Avenue Wyandotte, Michigan 48192	Ascension, Louisiana Wayne, Michigan	4 4

Table C-1 (Continued). COMPANY/PRODUCT LIST

<u>Company name</u>	<u>Location of operation (county and state)</u>	<u>Type of Product</u>
<u>Sodium chloride (cont'd)</u>		
Blackmon Salt Company Route No. 1 Freedom, Oklahoma 73842	Woods, Oklahoma	2, 4
Cargill, Inc. 1620 Northstar Center Minneapolis, Minnesota 55402	Reno Kansas St. Mary, Louisiana Tompkins, New York St. Martin, Louisiana	2 3 3 2
Diamond Crystal Salt Company 916 South Riverside St. Clair, Michigan 48079	Iberia, Louisiana St. Clair, Michigan Summit, Ohio	2, 3 2 2, 4
Diamond Shamrock Corporation 1100 Superior Avenue Cleveland, Ohio 44114	Lake, Ohio Chambers, Texas	4 4
DOMTAR Chemicals, Inc. P. O. Box 8 New Iberia, Louisiana 70560	St. Mary, Louisiana	3
Dow Chemical U.S.A. 2020 Dow Center Midland, Michigan 48640	Iberville, Louisiana Midland, Michigan Brazoria, Texas	4 4 4
Excelsior Salt Works, Inc. P. O. Box 267 Pomeroy, Ohio 45769	Meigs, Ohio	2

Table C-1 (Continued). COMPANY/PRODUCT LIST

<u>Company name</u>	<u>Location of operation (county and state)</u>	<u>Type of Product</u>
<u>Sodium chloride (cont'd)</u>		
FMC Corporation Industrial Chemicals Division Box 8127 South Charleston, West Virginia 25303	Tyler, West Virginia	4
Fallon Development Corporation Huck Salt Company, Subsid. Route 2, Box 33 Fallon, Nevada 89406	Churchill, Nevada	2
Freeport Minerals Company Box 61520 New Orleans, Louisiana	Jefferson, Louisiana Plaquemines, La. (2 facil.) Terrebonne, Louisiana	4 4 4
Gramercy, KACC P. O. Box 337 Gramercy, Louisiana 70052	Ascension, Louisiana	4
Guanica Puerto Rico	Mayaguez District	1
Gulf Resource & Chemicals Corporation Great Salt Lake Minerals & Chemical Corporation, subsid. Box 1190 Ogden, Utah 84402	Weber, Utah	1,2
Hardy Salt Company P. O. Box 449 St. Louis, Missouri 63166	Manistee, Michigan Williams, North Dakota Tooele, Utah	2 2,4 1,2

Table C-1 (Continued). COMPANY/PRODUCT LIST

<u>Company name</u>	<u>Location of operation (county and state)</u>	<u>Type of Product</u>
<u>Sodium chloride (cont'd)</u>		
Ideal Basic Industries, Inc. Potash Company of America, division Box 31 Carlsbad, New Mexico 88220	Eddy, New Mexico	3, 4
Independent Salt Company Box 36 Kanopolis, Kansas 67454	Ellsworth, Kansas	3
Interpace Corporation Carey Salt Company, division 1800 Carey Blvd. Hutchinson, Kansas 67501	Reno, Kansas (2 plants)	2, 3
Kaiser Aluminum & Chemicals Corporation Kaiser Chemicals Division 300 Lakeside Drive Oakland, California 94604	Ascension, Louisiana	4
Lake Crystal Salt Company Box 1149 Ogden, Utah 84402	Box Elder, Utah	1, 2
The Leslie Salt Company P. O. Box 364 Newark, California 94560	Alameda, California Napa, California San Mateo, California San Bernardino, Calif.	2 1, 2 1, 2 2, 3

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (county and state)	Type of Product
<u>Sodium chloride (cont'd)</u>		
Metropolitan Water District of Southern California P. O. Box 54153 Los Angeles, California 90054	San Bernardino, Calif.	1,2
Mississippi Chemical Corporation Mississippi Potash, Inc., subsid. Box 101 Carlsbad, New Mexico 88220	Eddy, New Mexico	2,3,4
Montex Chemical Company 104 East 3rd Monahans, Texas 79756	Ward, Texas	4
Morton International, Inc. Morton Salt Company, division 110 N. Wacker Drive Chicago, Illinois 60606	Reno, Kansas Iberia, Louisiana Manistee, Michigan St. Clair, Michigan Wyoming, New York Yates, New York Lake, Ohio Wayne, Ohio Van Zandt, Texas Salt Lake, Utah	2 2,3 2 2 2 3 3 2 2,3 1,2
National Chloride Company of America Std. Salt & Chemical Company, division Suite 803 - Wilflower Bldg. 615 S. Flower Street Los Angeles, California 90017	San Bernardino, Calif.	1,2

Table C-1 (Continued). COMPANY/PRODUCT LIST

<u>Company name</u>	<u>Location of operation (county and state)</u>	<u>Type of Product</u>
Sodium chloride (cont'd)		
Northwest Industries, Inc. Michigan Chemical Corporation, subsid. 351 E. Ohio Street Chicago, Illinois 60611	Gratiot, Michigan	2
Occidental Petroleum Corporation Hooker Chemical Corporation, subsid. P. O. Box 295 Montague, Michigan 49437	Muskegon, Michigan	4
Olin Corporation 120 Long Ridge Road Stamford, Connecticut 06904	Washington, Alabama Cameron, Louisiana	4 4
Oliver Bros. Salt Company P. O. Box 155 Mt. Eden, California 94557	Alameda, California	1,2
Pacific Salt and Chemical Company 4262 Wilshire Blvd. Los Angeles, California 90021	San Bernardino, Calif.	1,2
Pennwalt Corporation 4655 Biddle Avenue Wyandotte, Michigan 48192	Wayne, Michigan	4
Pennzoil Company Duval Corporation, subsid. Box 511 Carlsbad, New Mexico 88220	Eddy, New Mexico	4

Table C-1 (Continued). COMPANY/PRODUCT LIST

<u>Company name</u>	<u>Location of operation (county and state)</u>	<u>Type of Product</u>
Sodium chloride (cont'd)		
Phillips Petroleum Company Exploration and Production Dept. Bartlesville, Oklahoma 74004	Hutchinson, Texas	4
Pioneer Water Company, Inc. Box 1196 Eunice, New Mexico 88231	Lea, New Mexico	4
Ponce Salt Industries Puerto Rico	Mayaguez District	1
Albert Poulson Salt Company Redmond, Utah 84652	Sanpete, Utah	3
PPG Industries, Inc. Industrial Chemical Division One Gateway Center Pittsburgh, Pennsylvania 15222	Calcasieu, Louisiana Summit, Ohio Duval, Texas Marshall, West Virginia	4 2, 4 4 4
Redmond Clay and Salt Company, Inc. Redmond, Utah 84652		3
Sal de Borinquen Puerto Rico	Mayaguez District	1
Southwest Salt Corporation 714 West Olympic Blvd. Los Angeles, California 90015	San Bernardino, California	1, 2

Table C-1 (Continued). COMPANY/PRODUCT LIST

<u>Company name</u>	<u>Location of operation (county and state)</u>	<u>Type of Product</u>
<u>Sodium chloride (cont'd)</u>		
Tanaka Hawaiian Salt 663 North King Street Honolulu, Hawaii 96817	Honolulu, Hawaii	1,2
Texas Brine Corporation 2000 West Loop South Houston, Texas 77027	Harris, Texas Jefferson, Texas Matagorda, Texas	4 4 4
Union Carbide Corporation Mining and Metals Division 270 Park Avenue New York, New York 10017	Montrose, Colorado	4
United Salt Corporation 2000 West Loop South Houston, Texas 77027	Fort Bend, Texas Harris, Texas	2 3
Utah Salt Company Suite 1P, 2150 South 3rd West Salt Lake City, Utah 84115	Tooele, Utah	1,2
Vulcan Materials Company Chemicals Division P. O. Box 545 Wichita, Kansas 67201	Sedgwick, Kansas Yoakum, Texas	4 4
The Watkins Salt Company, Inc. P. O. Box 150 Watkins Glen, New York 14891	Schuyler, New York	2,4

Table C-1 (Continued). COMPANY/PRODUCT LIST

<u>Company name</u>	<u>Location of operation (county and state)</u>	<u>Type of Product</u>
<u>Sodium chloride (cont'd)</u>		
Western Salt Company P. O. Box 149 San Diego, California 92112 Long Beach Salt Company, division	San Diego, California Kern, California	1,2 1,2
	<u>Location of operation (city and state)</u>	<u>Annual capacity (thousands of metric tons)</u>
Sodium hydroxide - NaOH (caustic soda) 50% liquid 73% liquid flake solid		
(No differentiation is made between product forms produced by any one company.)		
Allied Chemical Corporation Industrial Chemicals Division	Acme, North Carolina) Baton Rouge, Louisiana) Brunswick, Georgia) Moundsville, W. Va.) Syracuse, New York) Marcus Hook, Pa.	578
Specialty Chemicals Division		
Aluminum Company of America	Point Comfort, Texas	170

Table C-1 (Continued). COMPANY/PRODUCT LIST

<u>Company name</u>	<u>Location of operation (city and state)</u>	<u>Annual capacity (thousands of metric tons)</u>
<u>Sodium hydroxide (cont'd)</u>		
Barton Chemical Corporation	Chicago, Illinois	n.a.
BASF Wyandotte Corporation	Geismar, Louisiana)	
Industrial Chemicals Group	Port Edwards, Wisc.)	583
	Wyandotte, Michigan)	
Brunswick Pulp & Paper Company	Brunswick, Georgia	31
Brunswick Chemical Company, subsid.		
Champion International Corporation	Canton, North Carolina	19
Champion Papers Division	Pasadena, Texas	15
Chemtech Industries, Inc.	Solvay, New York	n.a.
Eastern Division		
Diamond Shamrock Corporation	Deer Park, Texas)	
Diamond Shamrock Chemical Company	Delaware City, Delaware)	
Electro Chemicals Division	Mobile, Alabama)	1,113
	Muscle Shoals, Alabama)	
	Painesville, Ohio)	
Dow Chemical U.S.A.	Freeport, Texas)	
	Midland, Michigan)	
	Oyster Creek, Texas)	3,633
	Pittsburg, California)	
	Plaquemine, Louisiana)	

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)	Annual capacity (thousands of metric tons)
<u>Sodium hydroxide (cont'd)</u>		
Ethyl Corporation	Baton Rouge, Louisiana	65
FMC Corporation Chemical Group Industrial Chemical Division	South Charleston, W. Va.	281
Georgia-Pacific Corporation Chemical Division	Bellingham, Washington Plaquemine, Louisiana	48 277
The B. F. Goodrich Company B. F. Goodrich Chemical Company, division	Calvert City, Kentucky	108
Hercules, Inc. Coatings & Specialty Products Department	Hopewell, Virginia	19
Inland Chemical Corporation	Newark, New Jersey	43
Kaiser Aluminum & Chemical Corporation Kaiser Chemicals Division	Gramercy, Louisiana	199
Linden Chlorine Products, Inc.	Linden, New Jersey	167
Monsanto Company Monsanto Industrial Chemicals Company	Sauget, Illinois	90
Northwest Industries, Inc. Velsicol Chemical Corporation, subsid.	Memphis, Tennessee	25.7

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)	Annual capacity (thousands of metric tons)
<u>Sodium hydroxide (cont'd)</u>		
Occidental Petroleum Corporation		
Hooker Chemical Corporation, subsid.		
Hooker Chemicals & Plastics Corporation, subsid.	Montague, Michigan)	
Electrochemical & Specialty Chemicals Division	Niagara Falls, New York)	955
	Tacoma, Washington)	
	Taft, Louisiana)	
Olin Corporation		
Designed Products Division	Charleston, Tennessee)	
Industrial Products and Services Division	Augusta, Georgia)	596
	McIntosh, Alabama)	
	Niagara Falls, New York)	
Pennwalt Corporation		
Chemical Division	Calvert City, Kentucky)	
	Portland, Oregon)	306
	Tacoma, Washington)	
	Wyandotte, Michigan)	
PPG Industries, Inc.		
Chemical Division		
Industrial Chemical Division	Barberton, Ohio)	
	Corpus Christi, Texas)	1,198
	Lake Charles, Louisiana)	
	Natrium, West Virginia)	
PPG Industries (Caribe)	Guayanilla, P.R.)	

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)	Annual capacity (thousands of metric tons)
<u>Sodium hydroxide (cont'd)</u>		
Richardson-Merrell, Inc.		
J. T. Baker Chemical Company, subsid.	Phillipsburg, New Jersey	n.a.
Shell Chemical Company Base Chemicals	Deer Park, Texas	135
Sobin Chemicals, Inc.	Ashtabula, Ohio Orrington, Maine	37 74
Stauffer Chemical Company Industrial Chemical Division	Henderson, Nevada) Le Moyne, Alabama) St. Gabriel, Louisiana)	353
K. A. Steel Chemicals, Inc.		
Steelco Chemical Corporation, subsid.	Lemont, Illinois	n.a.
Texaco, Inc.		
Jefferson Chemical Company, Inc., subsid.	Port Neches, Texas	56
Vulcan Materials Company Chemicals Division	Denver City, Texas) Wichita, Kansas)	102
Weyerhaeuser Company	Longview, Washington	139

Table C-1 (Continued). COMPANY/PRODUCT LIST

<u>Company name</u>	<u>Location of operation (city and state)</u>	<u>Annual capacity (thousands of metric tons)</u>
<u>Sodium iodide - NaI</u>		
Allied Chemical Corporation Specialty Chemicals Division	Marcus Hook, Pennsylvania	
Deepwater Chemical Company, Ltd.	Carson, California	
Kewanee Oil Company Harshaw Chemical Company, division Crystal & Electronic Products Dept.	Solon, Ohio	
Mallinckrodt Chemical Works Industrial Chemicals Division	St. Louis, Missouri	
Richardson-Merrell, Inc. J. T. Baker Chemical Company, subsid.	Phillipsburg, New Jersey	
<u>Sodium sulfate (salt cake) - Na₂SO₄</u>		
Akzona, Inc. American Enka Company, division	Enka, North Carolina) Lowland, Tennessee)	55
Allied Chemical Corporation Industrial Chemicals Division Specialty Chemicals Division	Baltimore, Maryland Marcus Hook, Pa.	40
American Cyanamid Company Industrial Chemicals & Plastics Division	Fort Worth, Texas	13

Table C-1 (Continued). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)	Annual capacity (thousands of metric tons)
<u>Sodium sulfate (cont'd)</u>		
Climax Chemical Company	Monument, New Mexico	32
Courtaulds North America, Inc.	Le Moyne, Alabama	55
El Paso Natural Gas Company Beaunit Corporation, subsid. Beaunit Fibers Division	Elizabethton, Tennessee	5
FMC Corporation Chemical Group Fiber Division	Front Royal, Virginia) Nitro, West Virginia) Fredericksburg, Virginia) Marcus Hook Pa.)	220
Film and Packaging Division		
Green Bay Packaging, Inc.	Green Bay, Wisconsin	n.a.
Gulf Resources & Chemical Corporation Great Salt Lake Minerals & Chemicals Corporation, subsid. Lithium Corporation of America, Inc., subsid.	Ogden, Utah Bessemer City, N. C.	136 16
Hercules, Inc. Coatings & Specialty Products Department	Hopewell, Virginia	22
Kerr-McGee Corporation Kerr-McGee Chemical Corporation, subsid.	Trona, California) West End, California)	225

Table C-1 (Continued). COMPANY/PRODUCT LIST

<u>Company name</u>	<u>Location of operation (city and state)</u>	<u>Annual capacity (thousands of metric tons)</u>
<u>Sodium sulfate (cont'd)</u>		
Koppers Company, Inc. Organic Materials Division	Petrolia, Pa.	13
Mallinckrodt, Inc. Industrial Chemicals Division	St. Louis, Missouri	n.a.
Morton-Norwich Products, Inc. Morton Chemical Company, division	Weeks Island, Louisiana	110
Nalco Chemical Company Industrial Division	Chicago, Illinois	9
Occidental Petroleum Corporation Hooker Chemical Corporation, subsid. Searles Lake Chemical Company, subsid.	Trona, California	n.a.
Pennwalt Corporation Ozark-Mahoning Company, subsid.	Brownfield, Texas) Monahans, Texas) Seagraves, Texas)	140
Pratt Sodium Company	Casper, Wyoming	n.a.
Stauffer Chemical Company Industrial Chemical Division	San Francisco, Calif.	188
U. S. Borax & Chemical Corporation	Boron California) Wilmington, California)	54

Table C-1 (Concluded). COMPANY/PRODUCT LIST

Company name	Location of operation (city and state)
Sodium tetraborates	
Sodium borate decahydrate (borax)	- $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
Sodium borate pentahydrate	- $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$
Anhydrous borax	- $\text{Na}_2\text{B}_4\text{O}_7$
Kerr-McGee Corporation	
Kerr-McGee Chemical Corporation, subsid.	Trona, California
Stauffer Chemical Company	
Industrial Chemicals Division	West End, California
U. S. Borax & Chemical Corporation	Boron, California

^aCompanies producing each of the products shown in Appendix B, either for sale or captive use, are listed here under the product name. Various forms of the same product are listed here under the generic product name in cases where information sources make no distinction between the product forms produced.

Locations listed are those of the production facilities involved.

^bPublished lists of HCl producers do not reveal the identity of the operations used. To avoid omissions, the following list includes operations at locations where HCl may be produced as a byproduct of another industry. The list excludes locations where it is known with reasonable confidence that the HCl is produced as a byproduct of another industry.

An asterisk (*) has been used to identify the companies and the locations known to produce HCl as an end product of the Brine and Evaporite Chemical Industry.

TECHNICAL REPORT DATA (Please read instructions on the reverse before completing)			
1. REPORT NO. EPA-600/2-77-0230		3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE Industrial Process Profiles for Environmental Use: Chapter 15. Brine and Evaporite Chemicals Industry		5. REPORT DATE February 1977	
7. AUTHOR(S) P.E. Muehlberg, B.P. Shepherd, J.T. Redding, and H.C. Behrens (Dow Chemical) Terry Parsons, Editor		6. PERFORMING ORGANIZATION CODE	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Radian Corporation 8500 Shoal Creek Boulevard P.O. Box 9948 Austin, Texas 78766		8. PERFORMING ORGANIZATION REPORT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS Industrial Environmental Research Laboratory Office of Research and Development U.S. ENVIRONMENTAL PROTECTION AGENCY Cincinnati, Ohio 45268		10. PROGRAM ELEMENT NO. 1AB015	
		11. CONTRACT/GRANT NO. 68-02-1319, Task 34	
		13. TYPE OF REPORT AND PERIOD COVERED Initial: 8/75-11/76	
		14. SPONSORING AGENCY CODE EPA/600/12	
15. SUPPLEMENTARY NOTES			
16. ABSTRACT The catalog of Industrial Process Profiles for Environmental Use was developed as an aid in defining the environmental impacts of industrial activity in the United States. Entries for each industry are in consistent format and form separate chapters of the study. The Brine and Evaporite Chemicals Industry encompasses all first-level inorganic compounds derived from subterranean brines, from existing or historic salt lakes, and from sea water. Certain second-level inorganic compounds derived from these sources are included when produced in the same facility as the parent compound. The industry is discussed in six segments: (1) Borax and Boric Acid, (2) Chlorine-Caustic, (3) Lithium Chemicals, (4) Magnesium Metal, (5) Potash and (6) Sodium Metal. One chemical tree, twenty-two process flow sheets, and sixty-seven process descriptions have been prepared to characterize the industry. Within each process description available data have been presented on input materials, operating parameters, utility requirements and waste streams. Data relating to the subject matter, including company, product and raw material data, are included as appendices.			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Chlorine-Caustic	Air Pollution Control	07B
Brine	Lithium Chemicals	Water Pollution Control	13B
Evaporites	Magnesium Metal	Solid Waste Control	
Inorganic Compounds	Potash	Stationary Sources	
Salt	Sodium Metal	Inorganic Chemicals	
Sea Water	Process Description		
Borax			
Boric Acid			
19. DISTRIBUTION STATEMENT Release to Public		19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 324
		20. SECURITY CLASS (This page) Unclassified	22. PRICE