BuMines OFR 35-75

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HRI Project 1370

PROCESS TECHNOLOGY FOR RECOVERING GEOTHERMAL BRINE MINERALS

for

U. S. Bureau of Mines
Department of the Interior
Branch of Contracts and Grants
Interior Building
Washington, D. C. 20240

Bureau of Mines Open File Report 35-75

February 4, 1975

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Geothermal fluids and hot springs waters from California and Nevada were sampled and analyzed to provide a basis for process development and economic studies on the potential for recovering valuable minerals from these fluids. In general, bulk precipitation methods were utilized to remove the valuable constituents from the geothermal fluids, followed by separation of the constituents from this bulk precipitate. Concentration of geothermal fluids to recover soluble saline constituents such as sodium chloride and calcium chloride does not appear practical, owing primarily to the probable need for reinjecting such fluids back into the production zone.

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U. S. Bureau of Mines

During the course of the subject study, on geothermal resources and recovery of minerals therefrom, a great number of persons contributed valuable assistance in providing guidance, background information, access to geothermal sites, and procurement of samples for laboratory studies.

As in every listing of this sort, there are the inevitable omissions and our apologies are offered in advance for such unintentional oversights.

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i.e., permission to visit Brady's and
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Members of the Darrough family
i.e., permission to sample Darrough Hot
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ABSTRACT

Geothermal fluids and hot springs waters from California and Nevada were sampled and analyzed by Hazen Research personnel and others to provide a basis for process development and economic studies on the potential for recovering valuable minerals from these fluids.

Specific objectives were: (1) determine types and amounts of components present in these fluids; (2) survey existing processing routes presently used for recovering similar commodities to determine what, if any, technology transfer could be effected; (3) survey existing unit operations used in (2) to determine if such unit operations could be utilized for effecting recovery of valuable minerals from these fluids; (4) determine marketability and economic potential of valuable minerals that might be recovered from geothermal fluids; (5) attempt to find potential use areas for those constituents present in geothermal fluids which might not be economically recoverable at the present state of the art; (6) define process areas requiring additional definition and work effort.

An in-depth study of existing commercial operations, foreign and domestic, for production of sodium chloride (salt), potassium chloride (potash), sodium carbonate (soda ash), magnesium and calcium chlorides, borax, bromine, iodine and lithium salts was carried out.

Methods were developed for evaluating and assessing recoverability of mineral components in geothermal fluids and hot springs waters.

Processes were developed and existing technology evaluated for recovering valuable commodities from geothermal fluids and methods outlined for assessing the economic viability of mineral recovery from geothermal fluids and hot spring waters.

In general, bulk precipitation methods were utilized to remove the valuable constituents from the geothermal fluids, followed by separation of the constituents from this bulk precipitate.

Concentration of geothermal fluids to recover soluble saline constituents such as sodium chloride and calcium chloride does not appear practical, due primarily to the probable need for reinjecting such fluids back into the production zone.

Should it prove possible to forego reinjection of geothermal fluids, consideration of salines recovery will depend on location of resource in relation to the market and cost of shipping the product. Cost figures have been developed for concentration of such fluids, via multiple-effect steam evaporation and also for solar evaporation, to be used if desired.

INTRODUCTION AND GENERAL OUTLINE

The earth as a whole is an extensive reservoir of thermal energy, albeit, of relatively low grade due to its location at extreme depths or being too diffuse to warrant exploitation.

However, some locations on the earth's land mass appear to have a higher-than-"Normal" geothermal gradient, i.e., temperature change with depth, or are considered to be hot spring areas with emanations of hot or superheated water or saline solutions. A "Normal" geothermal gradient is referred to as having a temperature increase of from 1°C to 2°C per 100 feet of depth. Values in excess of this are usually taken to indicate potential sites for geothermal energy recovery.

Possibly the first commercial utilization of geothermal energy took place early in this century at Lardarello, Italy, with the generation of electric power from the "dry" geothermal steam resources of that area.

Iceland has used their bountiful supply of hot springs for home heating in and around Reykjavik, the capital city. Additionally, several power plants have been or are in the process of being installed which will operate on geothermal steam.

New Zealand and Japan have also been long-time developers and utilizers of geothermal energy to provide low-cost electric power to their respective countries.

Steam wells or geothermal steam wells in the United States were probably first "discovered," as contrasted to naturally occurring steam emanations such as Yellowstone Hot Springs, in the Imperial County area of California in the mid-1920's while drilling carbon dioxide gas wells.

The first commercial utilization of geothermal steam for power generation in the United States occurred in the early 1960's when Pacific Gas and Electric Company installed turbines and generating equipment at The Geysers in Sononia County, California. Since that time additional turbines and generators have been installed until there is presently about 350,000 kw(e) capacity at this location.

To date, this is the only commercialized geothermal resource in the United States, even though other such resources exist in great numbers in this country, particularly in the western portions.

The United States Government, under the auspices of the Department of the Interior, has cataloged such geothermal resource reserves under the heading of Known Geothermal Resources Areas (KGRA). Table 1 presents a listing of such KGRA's, while Figures 1A and 1B depict the location of these geothermal resources.

To date, the geothermal resources of the world that have been placed into commercial operation have either been of the "dry" steam type, such as at Lardarello, Italy, and The Geysers, California, or else have been of the relatively innocuous "wet" steam variety, such as at Wairakei, New Zealand, Reykjavik, Iceland, and various localities in Japan.

By "innocuous" is meant that the mixture of water and steam (hence the term "wet") is relatively non-saline, non-fouling, and non-mineral laden. The water phase that accompanies the steam is essentially free of minerals and does not cause any significant fouling of the well bore or steam piping.

A number of other potential "wet" geothermal steam locations, such as those of the Imperial Valley area of California, however, contain varying quantities of dissolved salts and metal compounds. These geothermal saline

Table 1

Known Geothermal Resources Areas

(Detailed land descriptions of these areas have been published in the Federal Register, v. 36, p. 5626, March 25, 1971; v. 36, p. 6118, April 2, 1971; v. 36, p. 6441, April 3, 1971; v. 36, p. 7319, April 17, 1971; and v. 36, p. 7759, April 24, 1971.)

No. on figure 1A, 1B, or 1C	Name
ALASKA	
1	Pilgrim Springs
2	Geyser Spring Basin and Okmok Caldera
CALIFORNIA	
1	The Geysers
2	Salton Sea
3	Mono-Long Valley
4	Calistoga
5	Lake City
6	Wendel-Amedee
7	Coso Hot Springs
8	Lassen
9	Glass Mountain
10	Sespe Hot Springs
11	Heber
12	Brawley-Holtville
13	Dunes
14	Glamis
IDAHO	
1	Yellowstone
2	Frazier
MONTANA	
1	Yellowstone
WASHINGTON	
1	Mount St. Helens
NEVADA	
1	Beowawe
2	Fly Ranch
3	Leach Hot Springs
4	Steamboat Springs
5	Brady Hot Springs
6	Stillwater-Soda Lake
7	Darrough Hot Springs
8	Gerlach
9	Moana Springs
10	Double Hot Springs
11	Wabuska
12	Monte Neva
13	Elko Hot Springs
NEW MEXICO	
1	Baca Location No. 1
OREGON	
1	Breitenbush Hot Springs
2	Crump Geyser
3	Vale Hot Springs
4	Mount Hood
5	Lakeview
6	Carey Hot Springs
7	Klamath Falls
UTAH	
1	Crater Springs
2	Roosevelt

FROM: Bu MINES DRAFT ENVIRONMENTAL IMPACT STUDY,
1971

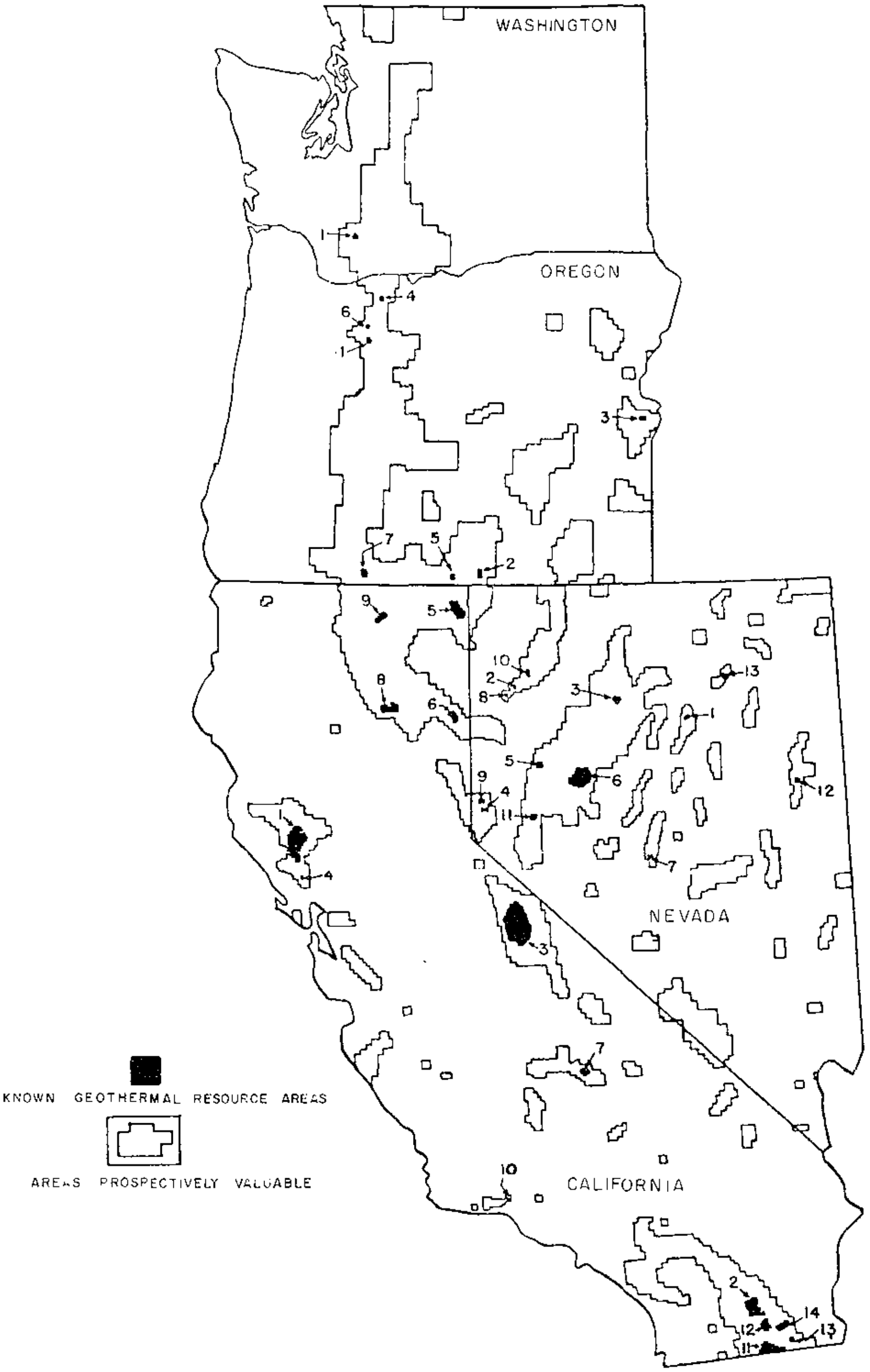
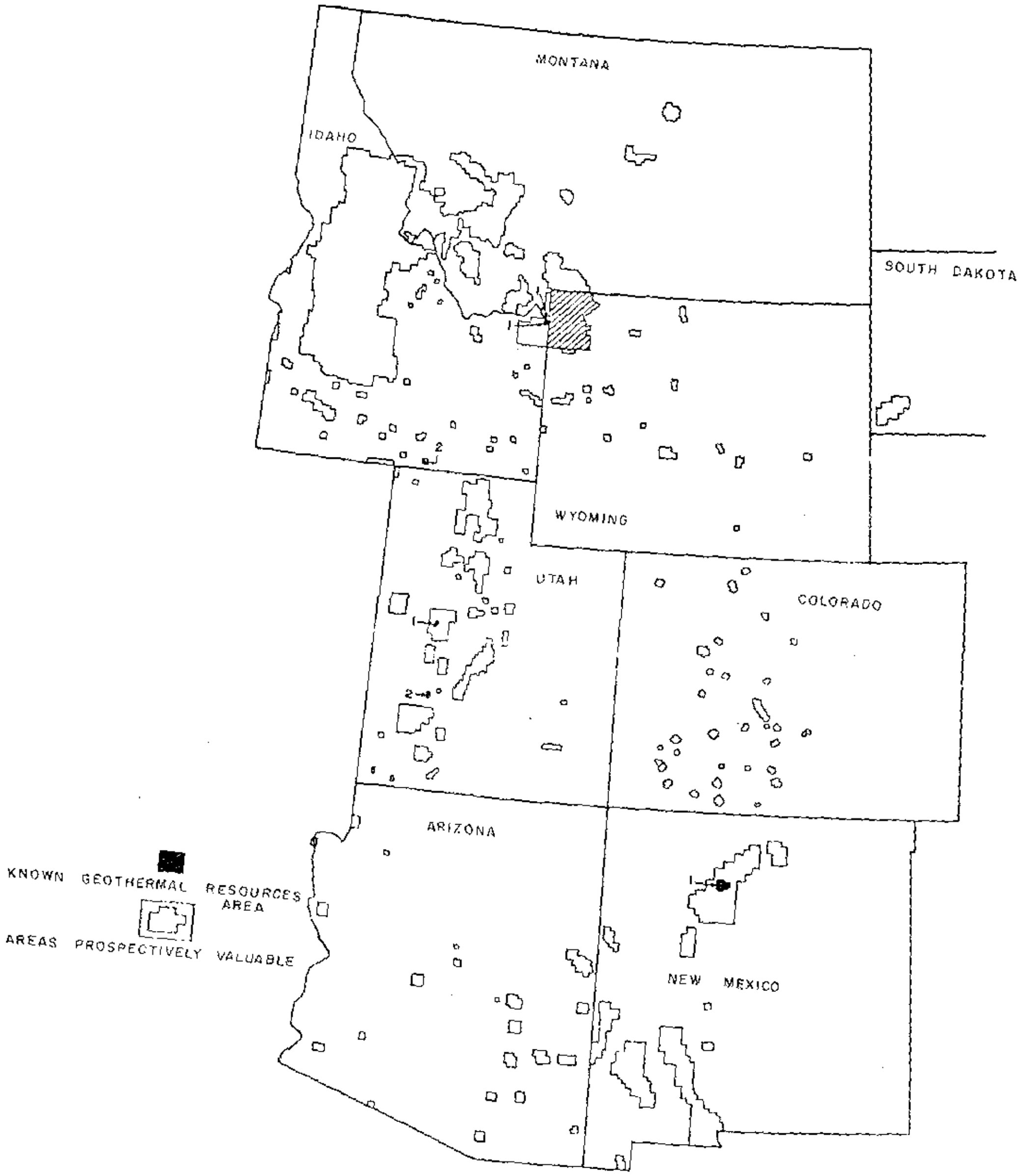


FIGURE 1A



DEC. 24, 1970

FIGURE 18

solutions contain a wide range of elements in trace amounts, with silica (SiO_2), iron (Fe), manganese (Mn), barium (Ba), strontium (Sr), lithium (Li), zinc (Zn), and boron (B) predominating. The major components, dissolved in these geothermal saline solutions, are chlorides of sodium, calcium, and potassium.

Power generation from such "wet" geothermal resources has been slow to be realized, due to the presence of these above-mentioned dissolved salts. The high salinity, i.e., concentration of sodium, calcium, and potassium chlorides, coupled with the low pH of these fluids, results in a very corrosive environment, both in the geothermal well bore and in external equipment such as steam-brine flash tanks or steam separators.

In addition, the presence of silica and other minerals in trace quantities in the geothermal fluids gives rise to solids precipitation and deposition, i.e., scale formation on fluid piping, with eventual plugging of the process piping and vessels. Such solids precipitation and scaling problems are usually present in every "wet" geothermal resource and vary only in degree, depending upon the concentration of such dissolved, scale-forming compounds present in the geothermal fluid.

For example, the geothermal bore (well) fluid (post-flash) at Wairakei, New Zealand, contains only about 4200 ppm dissolved salts, while geothermal fluids (post-flash) of the Imperial Valley area of California contain in excess of 250,000 ppm dissolved salts.

The "wet" geothermal resource at Wairakei, New Zealand, is presently being utilized, with about 300,000 kw(e) generating capacity installed.

Conversely, while there have been several attempts to produce electrical energy from the "wet" geothermal resource of the Imperial County area, to date none have been successful, due primarily to the high content

OBJECTIVES OF STUDY

The objectives of the subject study on geothermal fluids and hot springs waters are presented below, in the order that the project effort was expended.

1. Locate suitable types of geothermal fluids and hot springs waters for consideration and obtain samples for analysis and possible laboratory study.
2. Carry out a literature search and process evaluation study on present and available methods for recovering the valuable minerals components of geothermal fluids and hot springs waters.
3. Develop potential sales and process economics details for the valuable constituents in these fluids and waters.
4. Attempt to develop additional and/or new uses for some of the components of these fluids that would otherwise be valueless.
5. Develop potential processing routes, in conjunction with laboratory studies, for the recovery of valuable constituents from such geothermal fluids and hot springs waters.
6. Identify and attempt to quantify problem areas that exist in the recovery of valuable constituents from geothermal fluids or hot springs waters.

After the study was underway and various geothermal fluids had been sampled and analyzed, it became evident that many such fluids did not contain sufficient quantities of valuable minerals or other commodities to warrant the expenditure of much effort in their evaluation of mineral potential. Hence, most of our efforts have been directed toward the more saline geothermal fluids, such as those of the Imperial Valley area of

California, with the thought that process conception and scope developed for these fluids could then be adapted, with use of appropriate scale factors, to other fluids of lower salinity.

In addition, most, if not all, operators of geothermal resource areas expressed great concern if sizeable amounts of the geothermal fluids were to be removed from the resources zone, i.e., not reinjected into the producing subsurface structure, such as would be the case if the fluids were evaporated to dryness to recover the valuable minerals.

These two constraints, lack of valuable constituents in the geothermal fluids and the apparent requirement for reinjection of the geothermal fluids back into the producing zone to maintain some degree of hydraulic balance, therefore, provided additional guidelines for this study.

SUMMARY OF WORK DONE

A total of four geothermal sites were visited in California and five in Nevada. Samples of geothermal fluid were obtained from three of the California locations:

Name	Location
Mesa L-6-1	Holtville, California
Sinclair No. 4	Calipatria, California
Magmamax No. 1	Calipatria, California

Coso Hot Springs, near Darwin, California, was visited but the steam well had been shut in and no samples could be obtained.

Locations in Nevada that were sampled are:

Name	Location
Darrough Hot Springs	Big Smokey Valley, Nevada
Golconda Hot Springs	Golconda, Nevada
Beowawe Hot Springs	Beowawe, Nevada

In addition, a former lithium-containing hot spring in Clayton Valley, near Silver Peak, Nevada, was visited but found to be dry. Brady's Hot Spring geothermal site was also visited but all the hot springs were dry and the steam wells shut in, so no samples could be obtained from this location.

Complete chemical analyses were done on Mesa, Sinclair, and Magmamax geothermal fluids, as well as mass spectrographic analyses on the solids from dehydration of Sinclair and Magmamax fluids.

Since the hot springs waters contained very little dissolved salts, all of these waters were evaporated to dryness and the residues analyzed chemically, spectrographically, and also by mass spectrography to determine trace metals concentrations.

Portions of Mesa, Sinclair, and Magmamax geothermal fluids were concentrated by simulated solar evaporation techniques and the concentration path of most of the fluid components followed by means of chemical tracers.

Yield data was obtained for those components that crystallized out or precipitated out during the course of concentration. Purity of saline minerals that crystallized out was determined and a process developed for separating sodium and potassium chlorides from a mixture of these salts.

A laboratory study was carried out to explore methods for recovering the valuable constituents from such geothermal fluids utilizing Sinclair No. 4 fluid for the work. Based on commodity survey data of the Bureau of Mines and Geological Survey, it was decided that manganese, zinc, lead, iron, lithium, strontium, and barium constituted valuable minerals. Saline minerals, particularly sodium and calcium chloride are valuable only if located close to a consuming area,or else in close proximity to low cost transportation. Potassium chloride could find a ready market,but it is doubtful if this product alone could bear the total recovery cost,via either steam or solar evaporation.

Processes were developed that enabled recovery of essentially all of the iron, manganese, zinc, lead, and lithium from Sinclair No. 4-type chloride fluids. Recovery of barium as barium sulfate was also achieved, but some contamination with coprecipitated strontium sulfate resulted.

In order to obtain a significant recovery of strontium, as a precipitate of strontium sulfate, it was necessary to concentrate Sinclair No. 4 geothermal fluid approximately fourfold. Apparently the concentration of strontium sulfate in these brines is the equilibrium solubility value for such high chloride brines. Addition of sulfate ion results in precipitation of the least soluble member of the alkaline earth metal sulfate family, barium sulfate. Lithium was recovered from Sinclair No. 4 brine by precipitation as lithium aluminate and by solvent extraction of the lithium ferric chloride complex, formed in the brine by addition of ferric chloride.

Broad-scope process economic studies were undertaken to determine the economic value of several of the subject geothermal brines. Following this study, the costs for removing water from such saline fluids by steam evaporation, solar evaporation, reverse osmosis, and electrodialysis were calculated to allow determination of an economically compatible flowsheet for minerals recovery.

Reverse osmosis, electrodialysis, and freezing techniques were eliminated from consideration due to such potential problem areas of limited concentration range, susceptibility of fouling by precipitates, cost, and/or energy conservation.

Ultimately, the process route(s) chosen for consideration appeared to be the most economic, consistant with the inherent value of the fluid and external constraints, such as availability of steam, land for solar evaporation ponds, environmental considerations and the apparent necessity for reinjecting geothermal fluids back into the production zone.

In cases where hot springs waters or geothermal fluids of low dissolved solids content are involved, none of the conventional approaches, i.e., evaporation, precipitation, ion exchange, solvent extraction, etc., would seem to have any economic viability.

One approach that would appear to have merit and be worth further study and experimental verification is the use of a hydrous metal oxide such as ferrous or ferric hydroxide, generated in situ by addition of such iron salts in solution, or by utilizing bacterial conversion of iron compounds in solution to hydrous ferrous or ferric oxides. The bacterial systems utilized would have to be capable of withstanding the relatively high temperatures involved (50°C+). Brierley, et al, at New Mexico Tech. have published several interesting papers regarding such high temperature organisms and their applicability to aqueous metal systems.

RECOMMENDATIONS FOR ADDITIONAL WORK

The process development work carried out under this contract was of necessity limited in nature and scope. Its purpose was to define the path and delineate several of the process parameters so that some confidence could be placed in the proposed process routes described herein.

We believe that additional work in the following areas would be justified:

a. Use of high temperature bacterial organisms to produce hydrous metal oxides which can act as scavenging agents to collect or coprecipitate various heavy metals such as tungsten, molybdenum, etc.

   Such a coprecipitated mixture of hydrous oxides could be looked upon as a "synthetic ore," suitable for further processing.

b. Further definition of the capability of hydrous metal oxides to act as coprecipitants for many of the metals found in geothermal fluids, such as lead, zinc, copper, silver, etc. In this regard, the use of organic precipitants such as tannin should be studied also.

c. Investigation of solvent extraction systems for selective removal of elements such as lithium, strontium, barium, etc., from geothermal fluids. This might include the preparation and evaluation of new and different organic chelating and solvating systems.

d. A laboratory study of methods for converting lithium aluminate compounds into other lithium chemicals, and recovering and reusing the aluminum values for precipitation of additional lithium.

e. Construct and operate a small pilot scale demonstration plant, at a suitable geothermal site, to verify process concepts and quantify equipment requirements and sizing. Such a facility would also enable one to more accurately follow the course and dispostion of the many trace elements present in such geothermal fluids.

f. Carry out laboratory studies on new and potential uses for the relatively nonvaluable, saline constituents, of geothermal fluids; i.e., sodium chloride, potassium chloride, and calcium chloride in combination.

The entire field of heavy metal chloride chemistry and the winning of metals from chloride systems is a relatively new field of metallurgy, where formerly, sulfate systems were most common.

PRESENTATION OF RESULTS

GEOTHERMAL RESOURCES VISITED AND ANALYSES

As mentioned earlier, a total of four geothermal sites were visited in California and five sites in Nevada. Samples of geothermal fluids or hot springs waters were taken for a total of six of the areas and the results are presented below.

It was believed necessary to visit these sites and collect on-the-spot samples of recent origin rather than rely upon old analytical results or in some cases nonexistant results.

In addition most, if not all, of the available analyses were incomplete as regards trace elements, type and quantity present.

California

Description

1. Mesa L-6-1, near Holtville, California
   U.S. Bureau of Reclamation Well

   Total depth to producing zone, 7,000 feet
   Sample obtained by condensing total flow

2. Sinclair No. 4 near Calipatria, California.

   Joint lessees: Southern California Edison Company
   Southern Pacific Land Company
   Phillips Petroleum Company

   Total depth to producing zone, 5,400 feet
   Sample obtained after flashing at inlet to pond

3. Magmamax No. 1, near Calipatria, California.

   Leaseholder: Magma Power Company

   Total depth to producing zone, 2,400 feet
   Sample obtained by condensing total flow

Analytical data for each of the three geothermal fluids are shown in Table 2.

In addition, samples of Sinclair No. 4 and Magmamax No. 1 geothermal fluids were evaporated to dryness and the solids analyzed mass spectrographically to determine trace elements present. Tables 3 and 4 present these results for Sinclair No. 4 and Magmamax No. 1 geothermal fluids, respectively.

While no samples could be obtained from the Coso Hot Springs geothermal site due to its being shut in, a number of analyses, both old and relatively recent, were obtained from one of the Naval Weapons Center Publications TP4878, and are included for the sake of interest.

Tables 5 and 6 present these analytical results on a number of samples from the Coso Hot Springs area for various sample times, i.e., 1876, 1910, 1943, and 1963-1967.

One item worth mentioning, is the apparent disappearance of mercury which used to be present in waters from this hot spring area, and resulted in deposition of significant quantities of cinnabar (Hg S) in and on the silicious sinter and calcarious tufa of the area.

The following hot springs and geothermal fluids were sampled in Nevada.

Nevada

Description

4. Darrough Hot Springs, near Big Smokey Valley, Nevada

   Owner: Darrough Ranch

   Total depth to producing zone, unknown
   Sample obtained from pool surrounding geyser

Table 2

Analyses of Geothermal Fluids

Sample Description	Br ppm	Total Cl, %	Na %	K %	Pa %	Mg %	Fe %	Mn %	Pb ppm	Zn ppm	Cu ppm	Li ppm	Ba ppm	Sr ppm	NH_4 ppm	SO_4 ppm	F ppm	SiO_2 ppm	Rb ppm	Cs ppm	B ppm	Ag ppm
Mesa L-6-1	35	1.80	1.10	0.143	0.137	0.0022	0.18 ppm	0.9 ppm	0.26	0.02	0.05	55	58	226	39	16	1.5	101	1.7	4.0	27	0.04
Sinclair No. 4	162	18.6	7.10	1.80	3.50	0.0152	0.087	0.147	141	492	0.69	238	118	570	611	42	5.8	44	17	32	344	0.77
Magmamax No. 1	109	10.2	4.40	0.83	2.10	0.010	0.015	0.068	29	293	0.49	143	33	368	504	50	4.6	71	5.3	16	192	0.39

Table 3

Mass Spectrographic Analysis
Sinclair No. 4

Concentration in ppm Weight							
Element	Conc	Element	Conc	Element	Conc	Element	Conc
Uranium		Terbium		Ruthenium		Vanadium	0.80
Thorium		Gadolinium		Molybdenum	28	Titanium	6.8
Bismuth	<0.20	Europium		Niobium	0.23	Scandium	
Lead	150	Samarium		Zirconium	24	Calcium	Maj
Thallium	4.9	Neodymium		Yttrium		Potassium	Maj
Mercury		Praseodymium		Strontium	1200	Chlorine	Maj
Gold		Cerium		Rubidium	97	Sulphur	380
Platinum		Lanthanum		Bromine	790	Phosphorus	1.3
Iridium		Barium	73	Selenium	7.0	Silicon	100
Osmium		Cesium	10	Arsenic		Aluminum	1.5
Rhenium		Iodine	1.1	Germanium	3.8	Magnesium	≈1600
Tungsten		Tellurium		Gallium	1.3	Sodium	Maj
Tantalum	17	Antimony		Zinc	460	Fluorine	54
Hafnium		Tin		Copper	0.35	Oxygen	NR
Lutecium		Indium		Nickel	1.7	Nitrogen	NR
Ytterbium		Cadmium	2.4	Cobalt		Carbon	NR
Thulium		Silver	0.18	Iron	2000	Boron	1500
Erbium		Palladium		Manganese	≈1.0%	Beryllium	<0.20
Holmium		Rhodium		Chromium	5.7	Lithium	≈0.36%
Dysprosium						Hydrogen	

All other < 0.3 ppm
NR-Not Reported

Table 4

Mass Spectrographic Analysis
Magmamax No. 1

Concentration in ppm Weight							
Element	Conc	Element	Conc	Element	Conc	Element	Conc
Uranium		Terbium		Ruthenium		Vanadium	0.49
Thorium		Gadolinium		Molybdenum	12	Titanium	9.9
Bismuth	0.54	Europium		Niobium	0.15	Scandium	
Lead	54	Samarium		Zirconium	5.7	Calcium	Maj
Thallium	3.1	Neodymium		Yttrium		Potassium	Maj
Mercury		Praseodymium		Strontium	600	Chlorine	Maj
Gold		Cerium		Rubidium	61	Sulphur	240
Platinum		Lanthanum		Bromine	990	Phosphorus	0.81
Iridium		Barium	140	Selenium	4.4	Silicon	60
Osmium		Cesium	13	Arsenic		Aluminum	0.38
Rhenium		Iodine	0.68	Germanium	2.3	Magnesium	780
Tungsten		Tellurium		Gallium	1.1	Sodium	Maj
Tantalum	11	Antimony		Zinc	220	Fluorine	34
Hafnium		Tin		Copper	1.7	Oxygen	NR
Lutecium		Indium		Nickel	0.80	Nitrogen	NR
Ytterbium		Cadmium	2.0	Cobal		Carbon	NR
Thulium		Silver	0.14	Iron	410	Boron	840
Erbium		Palladium		Manganese	2200	Beryllium	<0.20
Holmium		Rhodium		Chromium	3.1	Lithium	≈0.15%
Dysprosium						Hydrogen	

All others <0.3 ppm
NR-Not Reported

Table 5 (1 of 2 pages)

Analysis of Waters in the Coso Thermal Area (1943)

	Location and Water Appearance									
	Main Spring ppm		Main Spring Area, Estimated % Residue						Mud Bath Pit, Estimated % Residue	
Analysis	1876	1910	Main Spring, Clear	Small Stream East of Shelter, Clear	Concrete Pier, Iron-stained	Stone Cribbed Well, Clear	Stone Cribbed Well, East of Shelter, Red	Edge of Pond Deep Red	Spring North End, Milk White	South End, Clear
Constituent:										
Na	49	81	0.1-1	1	1	0.1-1	0.1-1	0.1-1	0.1	0.1-1
K	11	12	1	0.1-1	0.1-1	0.1-1	0.1-1	0.1-1	0.1-1	0.1-1
Li	trace	-	-	-	-	-	-	-	-	-
NH_4	trace	-	-	-	-	-	-	-	-	-
Ca	45	59	10	10	10	10	10	10	10	10
Mg	2.4	34	1-10	1-10	1-10	1	1	1	1	1-10
Fe	122	83	1	1-10	1-10	1	1	1	1	1-10
Al	201	56	10	1-10	1	1	1	1	1-10	1-10
Hg	16	12	-	-	-	-	-	-	-	-
SO_4	2308	1400	-	-	-	-	-	-	-	-
NO_3	trace	0	-	-	-	-	-	-	-	-
Cl	trace	40	-	-	-	-	-	-	-	-
CO_3	0	0	-	-	-	-	-	-	-	-
BO_2	-	0	-	-	-	-	-	-	-	-
PO_4	trace	trace	-	-	-	-	-	-	-	-
SiO_4	-	411	-	-	-	-	-	-	-	-
Si	-	-	1-10	10	10	1-10	1	1-10	1	1-10
Mn	-	-	0.1	0.1	0.1	0.1	0.01-0.1	0.01-0.1	0.01	0.1
Sr	-	-	0.1	0.1	0.1	0.1	0.1	0.1	0.01-0.1	0.1
Cu	-	-	0.01-0.1	0.01-0.1	0.01-0.1	0.01	0.01	0.01-0.1	0.01-0.1	0.01-0.1

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Table 5

(2 of 2 pages)

			Location and Water Appearance							
	Main Spring ppm		Main Spring Area, Estimated % Residue						Mud Bath Pit, Estimated % Residue	
Analysis	1876	1910	Main Spring, Clear	Small Stream East of Shelter, Clear	Concrete Pier, Iron-stained	Stone Cribbed Well, Clear	Stone Cribbed Well, East of Shelter, Red	Edge of Pond Deep Red	Spring North End, Milk White	South End, Clear
Constituent:										
Zn	-	-	0.01-1	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ba	-	-	0.01	0.01	0.01-0.1	0.1	0.01-0.1	0.01	0.001-0.01	0.01
B	-	-	0.01-0.1	0.01-0.1	0.01	0.01	0.01	0.001-0.01	0.01	0.001-0.01
Pb	-	-	0.01	0.01	0.01	0.01	0.001-0.01	0.001-0.01	0.001-0.01	0.01
Sn	-	-	0.01	0.01	0.001-0.01	0.001-0.01	0.001	0.001	0.001-0.01	0.001-0.01
V	-	-	0.01	0.001	0.001	0.001-0.01	0.001-0.01	0.001	0.001	0.001
Ti	-	-	0.01	0.001-0.01	0.001-0.01	0.001-0.01	0.001-0.01	0.001-0.01	0.001-0.01	0.001-0.01
Ni	-	-	0.01	0.001	0.001	0.001	0.001	0.001	0.001-0.01	0.001
Cr	-	-	0.001-0.01	0.001	0.001-0.01	0.001	0.001-0.01	0.001-0.01	0.001-0.01	0.001-0.01
Bi	-	-	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Ga	-	-	0.001	-	-	-	-	-	-	-
Be Be	-	-	trace	trace	trace	trace	-	-	trace	trace
Ag	-	-	0.0001-0.001	0.0001	0.0001-0.001	0.0001	0.0001	0.0001	0.0001	0.0001
Total dissolved solids, ppm	2754.4	2188	7000	2300	4100	3700	3600	4300	6900	10,000

Note: From NWC Tech. Pub. 4878

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Table 6

Recent Analysis of Waters at Coso Thermal Area (1963)

Analysis	Location and Date					
	22/39-7J1 Spring, 1960	22/39-4K5 Well, 1961	22/39-4K4 Well, 1961	22/39-4K3 Condensed Steam From Well, 1960	22/39-4K2 Spring, 1960	Coso No. 1 Drilled Well at 375 ft 1967
Constituent, ppm:						
SiO_2	326	306	326	203	202	50
Fe	28	9.0	5.5	0.06	0.09	0.15
Al	44	3.8	2.3	0.11	1.4	-
Ca	18	44	28	17	98	72.8
Mg	81	19	12	6.2	25	0.5
Na	14	36	30	25	81	1,764
K	28	9.2	8.8	8.6	23	154
HCO_3	-	-	-	-	-	134.2
CO_3	-	-	-	-	-	84
SO_4	1,450	1,270	947	133	528	38
Cl	-	375	275	1	6.5	2,790
F	0.9	0.6	0.4	0.2	0.8	3.70
NO_3	3.0	0.6	0.5	0.1	8.1	7.1
B	0.6	-	0.11	-	-	48
Mn	1.7	-	0.8	-	-	0.0
Li	0.1	-	0	-	-	-
PO_4	-	0	0.10	-	-	0.4
Br	-	1.8	3.4	-	-	-
As	-	0	0	-	-	-
Mo	-	0.004	0.004	-	-	-
I	-	0.003	0.006	-	-	-
Cu	-	-	-	-	-	0.0
Total dissolved Solids, ppm	2,260	2,060	1,070	443	1,030	5,744
pH	2.2	1.2	2.1	4.5	4.0	8.9
Temp, °F	206	115	173	201	78	240

Note: From NWC Tech. Pub. 4878.

5. Golconda Hot Springs-No. 1 Sample)
No. 2 Sample) Golconda, Nevada

Owner: Unknown

Samples obtained from two pools in the general hot springs area.

6. Beowawe Steam Well, near Beowawe, Nevada

Owner: Unknown

Total depth to producing zone, unknown.
Sample obtained from runoff at wellhead; well top works had been reportedly blown off by vandals.

Tables 7 through 14 present the data obtained for each hot springs water and geothermal well. In general, approximately five gallons of water or fluid was evaporated to complete dryness and the residual solids analyzed chemically, by arc emission spectrograph and by mass spectrograph.

Total dissolved solids present in these waters ranged from 450 to 1,430 parts per million, generally too low to warrant consideration of minerals recovery by any method, except where a specific heavy metal, such as tungsten, might be recoverable by using a hydrous iron oxide as a coprecipitant or collecting agent.

Based on the samples of geothermal fluids and hot springs waters analyzed, it was decided to concentrate efforts on the most highly mineralized fluids, namely, those from the Imperial County area of California.

Table 7

Darrough Hot Springs

Total Volume: 19.310 liters = 19,310 g

Weight of Residue: 8.7 g; %TDS = 0.0450%

Analysis of Residue				
Wet Chemical		Emission Spectroscopy		Mass Spectrographic
Cl	3.70%	Na	Major	See Table 8
		SiO_2	Major	
CO_3	15.77%	Ca	190	
		K	–	
Br	<0.05%	Al	10%	
		Mg	0.1%	
		Fe	0.2%	
		B	0.1%	
		Mn	0.01%	
		Mo	0.05%	
		Sr	–	
		Ba	–	
		Ti	0.01%	
		Cr	0.01%	
		Cu	0.002%	

Table 8

Mass Spectrographic Analysis
Darrough Hot Springs

Concentration in ppm Weight							
Element	Conc	Element	Conc	Element	Conc	Element	Conc
Uranium	3.1	Terbium	<0.27	Ruthenium		Vanadium	1.0
Thorium	2.0	Gadolinium	<0.67	Molybdenum	110	Titanium	46
Bismuth	<0.88	Europium	<0.80	Niobium	0.98	Scandium	
Lead	8.6	Samarium	<2.1	Zirconium	1.1	Calcium	≈0.38%
Thallium	0.21	Neodymium	<6.3	Yttrium	1.2	Potassium	880
Mercury		Praseodymium	<0.50	Strontium	150	Chlorine	Maj
Gold		Cerium	7.0	Rubidium	5.3	Sulphur	≈8.0%
Platinum		Lanthanum	0.08	Bromine	45	Phosphorus	63
Iridium		Barium	100	Selenium	8.2	Silicon	≈7.0%
Osmium		Cesium	23	Arsenic	54	Aluminum	510
Rhenium		Iodine	18	Germanium	8.6	Magnesium	≈0.18%
Tungsten	49	Tellurium	0.04	Gallium	8.2	Sodium	Maj
Tantalum	0.80	Antimony	7.0	Zinc	26	Fluorine	≈3.1%
Hafnium	<0.33	Tin	0.81	Copper	2.1	Oxygen	NR
Lutecium	<0.36	Indium		Nickel	0.52	Nitrogen	NR
Ytterbium	<2.1	Cadmium	0.41	Cobalt	0.10	Carbon	NR
Thulium	<0.15	Silver	0.18	Iron	820	Boron	310
Erbium	<0.60	Palladium		Manganese	17	Beryllium	0.37
Holmium	<0.35	Rhodium		Chromium	19	Lithium	130
Dysprosium	<4.5					Hydrogen	

NR-Not Reported

Table 9

Golconda Hot Springs Sample No. 1

Total Volume:	18.15 liters = 18,150 g
Weight of Residue:	10.8 g; % TDS = 0.0595%

Analysis of Residue				
Wet Chemical		Emission Spectroscopy		Mass Spectrographic
Cl	4.25%	Na	Major	See Table 10
		SiO_2	10%	
CO_3	32.34%	Ca	5%	
		K	3%	
Br	$<0.05\%$	Al	1%	
		Mg	1%	
		Fe	0.1%	
		B	0.5%	
		Mn	0.1%	
		Mo	–	
		Sr	0.05%	
		Ba	0.01%	
		Ti	–	
		Cr	0.003%	
		Cu	–	

Table 10

Mass Spectrographic Analysis
Golconda Hot Springs No. 1

Concentration in ppm Weight							
Element	Conc	Element	Conc	Element	Conc	Element	Conc
Uranium	<0.58	Terbium	<0.27	Ruthenium		Vanadium	0.02
Thorium	<0.80	Gadolinium	<0.67	Molybdenum	20	Titanium	0.40
Bismuth	<0.88	Europium	<0.80	Niobium	0.18	Scandium	
Lead	8.1	Samarium	<2.1	Zirconium	0.08	Calcium	≊2.0%
Thallium	<0.17	Neodymium	<6.3	Yttrium	<0.27	Potassium	≊0.38%
Mercury		Praseodymium	<0.50	Strontium	360	Chlorine	Maj
Gold		Cerium	0.28	Rubidium	180	Sulphur	≊2.1%
Platinum		Lanthanum	0.04	Bromine	21	Phosphorus	8.5
Iridium		Barium	270	Selenium	1.3	Silicon	3.3
Osmium		Cesium	65	Arsenic	14	Aluminum	160
Rhenium		Iodine	40	Germanium	<0.10	Magnesium	2.9%
Tungsten	40	Tellurium	0.06	Gallium	0.08	Sodium	Maj
Tantalum	0.75	Antimony	46	Zinc	4.0	Fluorine	≊0.32%
Hafnium	<0.33	Tin	0.29	Copper	0.46	Oxygen	NR
Lutecium	<0.36	Indium		Nickel	0.74	Nitrogen	NR
Ytterbium	<2.1	Cadmium	0.19	Cobalt	0.07	Carbon	NR
Thulium	<0.15	Silver	0.22	Iron	180	Boron	810
Erbium	<0.60	Palladium		Manganese	50	Beryllium	0.27
Holmium	<0.35	Rhodium		Chromium	4.7	Lithium	750
Dysprosium	<4.5					Hydrogen	

NR-Not Reported

Table 11

Golconda Hot Springs No. 2 Sample

Total Value: 19.125 liters = 19,125 g

Weight of Residue: 11.7 g; % TDS = 0.0612%

Analysis of Residue				
Wet Chemical		Emission Spectroscopy		Mass Spectrographic
Cl	3.43%	Na	Major	See Table 12
		SiO_2	10+%	
CO_3	29.07%	Ca	5%	
		K	3%	
Br	<0.05%	Al	1%	
		Mg	1%	
		Fe	0.5%	
		B	0.5%	
		Mn	0.2%	
		Mo	–	
		Sr	0.07%	
		Ba	0.01%	
		Ti	–	
		Cr	0.001%	
		Cu	0.001%	

Table 12

Mass Spectrographic Analysis
Golconda Hot Springs No. 2

Concentration in ppm Weight							
Element	Conc	Element	Conc	Element	Conc	Element	Conc
Uranium	3.1	Terbium	<0.27	Ruthenium		Vanadium	0.13
Thorium	<0.80	Gadolinium	<0.67	Molybdenum	21	Titanium	5.7
Bismuth	1.1	Europium	<0.80	Niobium	0.10	Scandium	
Lead	1.8	Samarium	<2.1	Zirconium	1.1*	Calcium	≊16%
Thallium	0.15	Neodymium	<6.3	Yttrium	1.2	Potassium	≊0.21%
Mercury		Praseodymium	<0.50	Strontium	≊0.18%	Chlorine	≊1.3%
Gold		Cerium	0.35	Rubidium	19	Sulphur	≊6.9%
Platinum		Lanthanum	<0.10	Bromine	23	Phosphorus	≊0.12%
Iridium		Barium	160	Selenium	0.82	Silicon	≊13%
Osmium		Cesium	29	Arsenic	25	Aluminum	39
Rhenium		Iodine	18	Germanium	8.6	Magnesium	1.8
Tungsten	49	Tellurium	0.05	Gallium	0.18	Sodium	Maj
Tantalum	0.80	Antimony	90	Zinc	2.6	Fluorine	≊1.1%
Hafnium	<0.33	Tin	0.81	Copper	4.9	Oxygen	NR
Lutecium	<0.36	Indium		Nickel	0.52	Nitrogen	NR
Ytterbium	<2.1	Cadmium	0.21	Cobalt	0.22	Carbon	NR
Thulium	<0.15	Silver	0.14	Iron	≊0.33%	Boron	860
Erbium	<0.60	Palladium		Manganese	100	Beryllium	<0.30
Holmium	<0.35	Rhodium		Chromium	3.3	Lithium	≊0.16%
Dysprosium	<4.5					Hydrogen	

NR-Not Reported

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*Heterogeneous

Table 13

Beowawe Steam Well

Total Volume: 18.9 liters = 18,900 g

Weight of Residue: 27 g; %TDS = 0.143%

Analysis of Residue				
Wet Chemical		Emission Spectroscopy		Mass Spectrographic
Cl	4.53%	Na	Major	See Table 14
		SiO_2	Major	
CO_3	13.01%	Ca	0.01%	
		K	2%	
Br	$< 0.05\%$	Al	5%	
		Mg	0.01%	
		Fe	0.1%	
		B	0.2%	
		Mn	0.001%	
		Mo	0.01%	
		Sr	-	
		Ba	-	
		Ti	0.01%	
		Cr	0.001%	
		Cu	-	

Table 14

Mass Spectrographic Analysis
Beowawe Steam Well

Concentration in ppm Weight							
Element	Conc	Element	Conc	Element	Conc	Element	Conc
Uranium	<0.58	Terbium	<0.27	Ruthenium		Vanadium	3.0
Thorium	<0.80	Gadolinium	<0.67	Molybdenum	24	Titanium	24
Bismuth	2.4	Europium	<0.80	Niobium	0.18	Scandium	
Lead	0.97	Samarium	<2.1	Zirconium	1.1	Calcium	730
Thallium	0.20	Neodymium	11	Yttrium	0.20	Potassium	≊0.58%
Mercury		Praseodymium	3.0	Strontium	9.7	Chlorine	Maj
Gold		Cerium	39	Rubidium	140	Sulphur	≊9.5%
Platinum		Lanthanum	0.09	Bromine	38	Phosphorus	10
Iridium		Barium	16	Selenium	0.80	Silicon	≊15%
Osmium		Cesium	30	Arsenic	14	Aluminum	120
Rhenium		Iodine	9.7	Germanium	≈0.10	Magnesium	42
Tungsten	120	Tellurium	0.12	Gallium	2.3	Sodium	Maj
Tantalum	0.90	Antimony	3.3	Zinc	15	Fluorine	≊1.0%
Hafnium	<0.33	Tin	0.32	Copper	0.21	Oxygen	NR
Lutecium	<0.36	Indium		Nickel	1.7	Nitrogen	NR
Ytterbium	<2.1	Cadmium	<0.12	Cobalt	0.08	Carbon	NR
Thulium	<0.15	Silver	0.16	Iron	270	Boron	810
Erbium	<0.60	Palladium		Manganese	1.8	Beryllium	0.31
Holmium	<0.35	Rhodium		Chromium	1.1	Lithium	≊0.23%
Dysprosium	<4.5					Hydrogen	

NR-Not Reported

REVIEW OF EXISTING PROCESS TECHNOLOGY FOR MINERALS RECOVERY

This portion of the study presents a survey of existing commercial operations, both foreign and domestic, that produce salt, potash, soda ash, magnesium, and calcium chlorides, borax, bromine, iodine, and lithium salts.

In order to effectively present this wide range of individually non-related material, we have subdivided the material on each commodity into separate sections and have provided a table of contents for ease in locating a particular subject of interest.

In addition, references pertaining to a particular commodity are listed following that commodity, rather than in the general bibliography section at the back of the report.

We have presented material herein covering production of a particular commodity in the United States and foreign countries and have emphasized those operations which are of interest to the subject study or have unusual or special characteristics worth noting.

It should be noted that a great deal of process information and presentation of practical applications of Chemical Engineering Unit Operations has been included in with descriptions of commercial processes. Hence, the following section, "Survey of Process Technology," will rely to a great extent upon the material discussed herein rather than repeat this information.

General references to be read in conjunction with this section are:

> Mineral Facts and Problems, Bulletin 650, 1970 Edition, prepared by staff of U. S. Bureau of Mines
>
> United States Mineral Resources, Geol. Survey Prof. Paper 820, edited by D. A. Brobst and W. P. Pratt, 1973

I. SALT

INTRODUCTION

The most important methods for the production of sodium chloride are: mining, solar evaporation of sea water and natural brines, artificial evaporation of brines obtained from various sources, and as by-product from potash production.

GENERAL PROCESSES

Mining

In most cases, rock salt obtained by mining surface or underground deposits is pure enough to meet specifications in a variety of uses. Thus in general, the processing of mined rock consists only of crushing, grinding, and screening to produce a series of salt products differing mainly in grain size.[1/]

SOLAR EVAPORATION OF SEA WATER AND NATURAL BRINES

Solar salt was produced for many centuries B. C. and even today contributes a considerable proportion of the total production. This is especially true in those countries having sea shores with high evaporation rates.

Sea water has many elements in solution, but few may be considered major constituents. The hypothetical composition of average sea water may be expressed, in percent by weight, as follows:

NaCl	2.74%
$MgCl_2$	0.34%
$MgSO_4$	0.23%
$CaSO_4$	0.13%
KCl	0.07%
$Ca(HCO_3)_2$	0.012%
$MgBr_2$	0.007%
	3.529%

The production of sodium chloride from sea water by solar evaporation consists essentially of three major steps: intake of sea water to the solar ponds, concentration by evaporation of water crystallizing salts, and withdrawing the final bittern. However, the success of a solar evaporation operation depends on many factors which are briefly reviewed here.

The solar evaporation process is conducted on a topographically selected piece of flat land. A preferred location would permit the intake of sea water during high tide to minimize pumping. The land must be as naturally impervious as possible to assure minimum leakage.

Pond layout depends on the terrain selected. In general, the pond system consists of a series of small ponds, usually with an area between 100 and 500 acres, which allow the segregation of sea water at different stages of concentration. If possible, the direction of sea water flow through the pond system should be perpendicular to the prevailing winds in the area in order to minimize wave action.

Dike and wall construction varies from one operation to another. In most cases, a trench is made deep enough to reach an impervious clay layer, refilled with clay or mud, and wall is then built on top as shown in Figure 2.

Strategically located pumps and weirs are used to transfer the brines from one pond to the next. Final bitterns returned to the sea should be discarded at a sufficient distance to avoid short circuiting.

The rate at which sea water is concentrated by solar evaporation depends on several factors: temperature and humidity of the air during day and night, wind mean velocity and frequency, and size of fluvial precipitation. Operating water depth in the ponds varies between 6 and 18 inches. Evaporation rate becomes slower as sea water becomes more concentrated in saline content. In several parts of the world, a green dye (naphthol green B) is used to improve solar energy absorption and thus increase evaporation rates in concentrate brines.

TYPICAL DIKE CONSTRUCTION FOR A POND SYSTEM

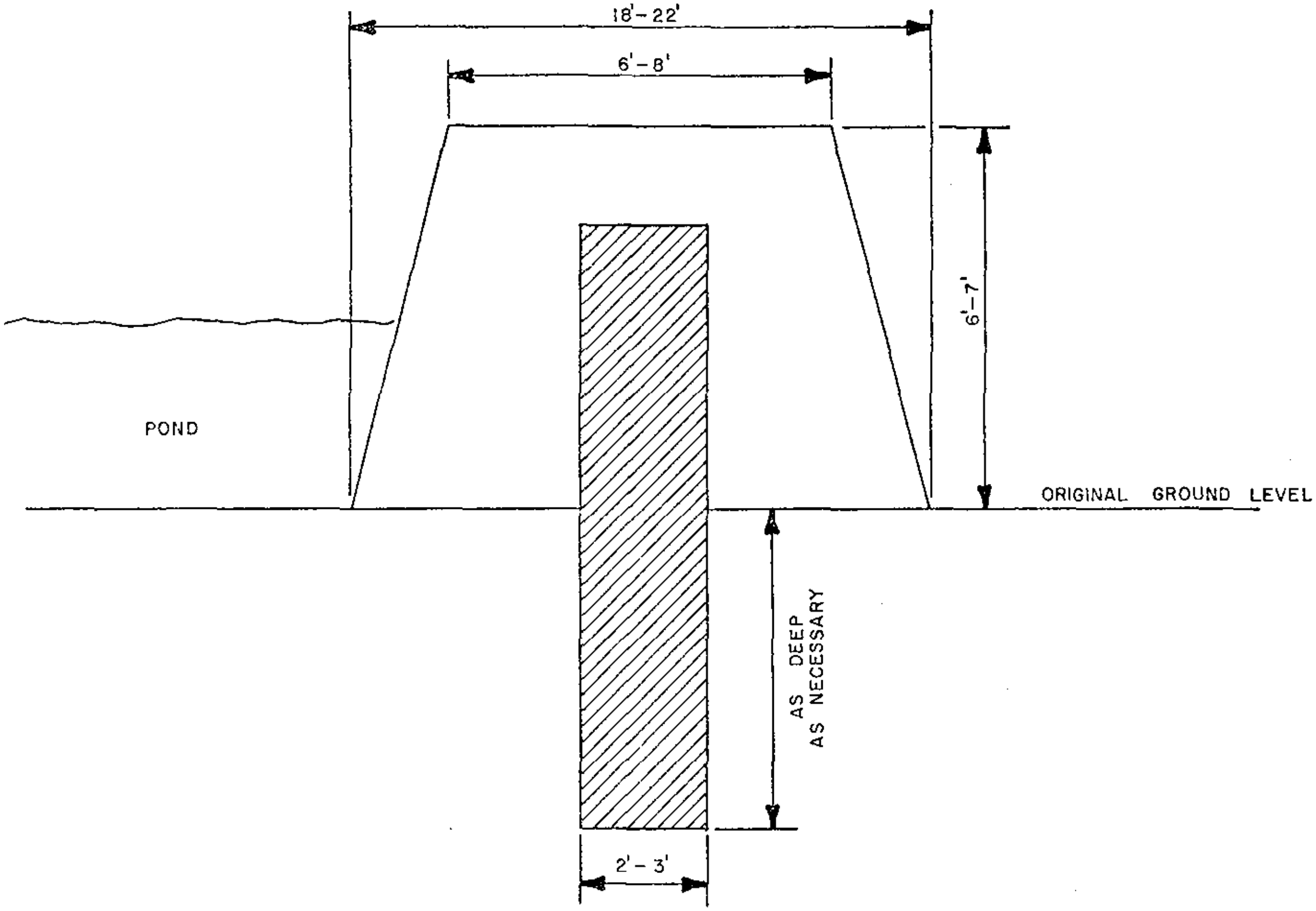

FIGURE 2
hri

Table 14 shows the sequence of major occurrences during evaporation of sea water up to the point of withdrawal of the final bittern which should take place when the sodium chloride begins to be impurified by other crystallizing salts. During the crystallization of sodium chloride (specific gravities 1.214 to 1.250), some gypsum or anhydrite is crystallized out but the relative amount is very minor. The average salt in the pond contains 97-98% NaCl which, with a simple wash, can be upgraded to 99.5% NaCl. 2/

Table 14

Sequence of Solar Evaporation of Sea Water

Specific Gravity	°Be	% of Original Volume	Precipitation
1.024	3.4	100	
1.051	7.0	46.3	Fe oxide, $CaCO_3$
1.098	12.9	23.2	Gypsum - $CaCO_3$
1.206	24.8	10.0	Gypsum - Saturation w/NaCl
1.214	25.6	8.0	Gypsum - Sodium chloride
1.250	29.0	3.8	Gypsum - Sodium chloride

Natural brines are found in many parts of the world. Most of them are of sea water origin but because isolated long ago, they may be several times more concentrated than sea water. Sometimes the brine has undergone chemical change which results in a different relative composition from sea water. However, in practically all cases these natural brines contain sodium chloride which can be recovered by solar evaporation if the weather conditions permit.

Artificial Evaporation

Artificial evaporation of sodium chloride solutions is widely used, especially in the United States. The feed brine to the evaporator may be obtained in different ways:

1. By dissolving an underground rock salt deposit which is then brought to the surface using a well;
2. By dissolving rock salt which has been mined but should be purified by recrystallization;
3. By pumping natural underground brine to the surface.

Surface brine containing sodium chloride in solution may also be processed by artificial evaporation.

There are several general types of equipment which may be used to perform artificial evaporation. Limited use of the Grainer process of evaporation continues because of its unique crystal growth (hopper crystals of sodium chloride) which has special applications in industry. Vacuum evaporation, by far the most commonly used system, produces cubic crystals which can be controlled in size by the way the multiple effect evaporators are operated.

By-product Salt Production

Sodium chloride is produced as a by-product in many industries. Perhaps the major by-product is from potash production since these salts usually occur together. If either flotation or crystallization is used to recover potash, common salt will constitute the tailing from either process.

COMMERCIAL OPERATIONS IN THE UNITED STATES

Production of sodium chloride by solar evaporation accounts for 3-4% of the total produced in this country. Sea water feed operations are restricted to the state of California. The Leslie Salt Co., the major California operation, has 30,000 acres of salt marsh area covering the southern end of the San Francisco bay in the Alameda, Santa Clara and San Mateo counties. Other producers in the state include the Metropolitan Water District of Southern California, the Standard Salt Co., the Pacific Salt and Chemical Co., and the Western Salt Company.

The only other solar evaporation operations in the United States are in the state of Utah. Here the brines of the Great Salt Lake are used. The brines differ slightly from sea water in the relative concentration of constituents. The major difference is that sea water has 3.5% dissolved solids and the Great Salt Lake brine has from 20 and 26% dissolved solids. 3/ Table 15 compares the composition of major components of the Great Salt Lake brine and sea water on a dry basis. 4/

Table 15

Major Constituents in Great Salt Lake and Sea Water on Dry Basis

Component	Great Salt Lake	Sea Water
Cl^-	55.7%	55.3%
Na^+	33.4%	30.6%
$SO_4^=$	6.6%	7.7%
Mg^{++}	2.3%	3.7%
K^+	1.7%	1.1%
Ca^{++}	0.3%	1.2%
$CO_3^=$	Trace	0.2%
Br^-	Trace	0.2%
	100.0%	100.0%
Ratios		
$SO_4^=/Mg^{++}$	2.9	2.1
Mg^{++}/K^+	1.35	3.36
$SO_4^=/K^+$	3.9	7.0

The solar salt operations on the shores of the Great Salt Lake are similar to those in California with an important difference. The solar salt operations in California, with a slightly lesser rate of evaporation, produce about 35 to 40 tons of salt per acre of pond area. The Great Salt Lake operations produce between 300 and 350 tons of sodium chloride per acre of pond area.

The importance of the geographical location of a salt producer and distance from markets for salt is shown in the Bonneville operation of Kaiser Chemical Corporation at Wendover, Utah. The Bonneville operation produces potash by a solar evaporation-flotation process. During the evaporation of brine, which is different in composition from that at the Great Salt Lake, about 1.2 million tons of sodium chloride are crystallized out in the ponds every year. However, only a limited amount of this salt (around 50,000 tons a year) is harvested and sold by an independent company (Utah Salt Co.). This is also true in the potash producing area of Carlsbad, New Mexico. After potash has been produced by flotation, millions of tons of sodium chloride tailings are discarded because of the distance to the consumer market.

FOREIGN COMMERCIAL OPERATIONS

World production of salt by solar evaporation of sea water or brines amounted to 20% of the total during 1970. However, solar salt constitutes the major source of salt in Latin American, Australia, and many countries of Asia and Africa.

The world's largest single producer of salt by solar evaporation of sea water is the Exportadora de sal, S.A. at Guerrero Negro, Baja California Sur, Mexico. The company produced close to five million tons of salt during 1972, all of which was exported.

Other large producers of solar salt from sea water are located in Australia, especially in South Australia, Victoria, and Western Australia. The solar salt works of Texada Mining Pty., Ltd. at Lake McLead, about 40 miles north of Carnarvon in Western Australia, uses a five times concentrated sea water found underneath the dry lake. This operation may produce three million tons of salt per year.

In many parts of Europe by-product sodium chloride from potash plants reaches the market because of the consumer's proximity.

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II. POTASH

INTRODUCTION

Potash, the common name for potassium chloride, is produced mainly by mining underground deposits. Several potash ores are mined but the great majority of deposits are composed of sylvinite, a crystalline mixture of halite and sylvite. Some exploited deposits in Europe contain carnallite ($KCl.MgCl_2.6H_2O$) and halite; others contain kainite ($KCl.MgSO_4.3H_2O$), carnallite, and sylvinite; and still other mines contain a mixture of sylvinite and kieserite ($MgSO_4.H_2O$).

There are a few operations in the world where natural occurring brines are used for potash production. Most of these are located in the United States, one is in Israel, and one is in Australia. The latter is in the startup stage.

A relatively small quantity of potash is also produced as a by-product of other industries.

In the beneficiation processes used, the presence of a relatively high percentage of slimes in the ore causes problems in the operation. Thus, desliming at the beginning of the flowsheet is a common feature of all processes with these ores.

GENERAL PROCESSES

Processing Mined Sylvinite by Flotation

The most common method for the treatment of mined sylvinite is by flotation. Mined sylvinite usually contains between 25 and 45% KCl and the balance is predominantly NaCl. Two possibilities exist for the flotation separation of these two salts: to float the KCl away from NaCl or the reverse. At the present the first process is most commonly used. The process is shown Schematically in Figure 3.

A dry crushing, grinding, and classification may precede the wet grinding shown in Figure 3. Size reduction to the liberation level results in separation of the individual crystals of halite and sylvite. For some ores, liberation may occur at 4-mesh; other ores are ground to 14-mesh or finer. The latter is true for some sylvinite mined in Europe. Since both components of sylvinite are soluble in water, the circuit uses an ore saturated brine. Flotation is performed at pulp densities between 20 and 35%. The common collectors for potash flotation are aliphatic amines generally of C_{12} to C_{18}. The amines are converted to their hydrochloric or acetate salts to render them soluble in water. There are many factors affecting the amount of collector needed to float one ton of potash. The presence of large amounts of clay in the ore can be harmful since clay adsorbs the collector. Relatively small amounts of clay can be controlled

SIMPLIFIED FLOWSHEET FOR THE RECOVERY OF POTASH FROM SYLVINITE BY FLOTATION

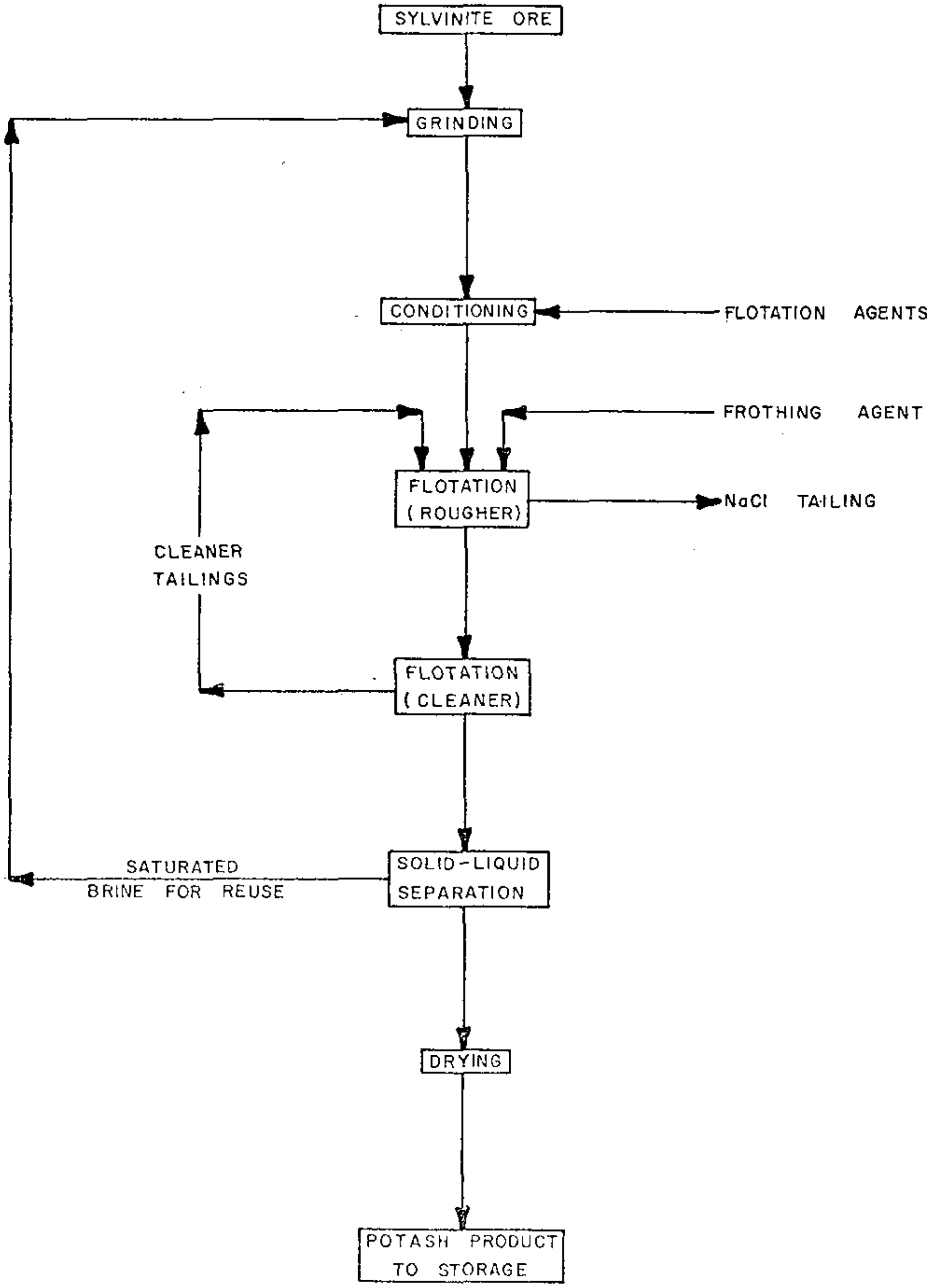

FIGURE 3

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by using reagents which are less expensive than the collectors. Among them are some protective colloids as Guar Gum, starch, dextrines, etc. Frothers such as cresylic acid, pine oil, or alcohols are usually added before the slurry enters the flotation machine.

Although most of the sylvite is present in the feed is floated, the rougher flotation concentrate is of relatively low grade (85-92% KCl). Thus, this material is subject to a cleaning flotation step which upgrades it to 95-97% KCl. The tailing from the cleaner flotation step is returned to the rougher circuit.

A solid-liquid separation step yields the potash product and the brine for reuse.

Processing Mined Sylvinite by Crystallization

The separation of sodium chloride from potassium chloride by crystallization was the usual procedure used by the industry until the development of the flotation method in the mid-thirties.

Figure 4 shows the solubility of KCl-NaCl in water at 20° and 80°C. The invariable point b, saturated with both salts, at 20°C contains 14.8 parts of KCl and 30.4 parts of NaCl per 100 parts of H_2O. If this solution is heated to 80°C and contacted with a sufficient amount of solid sylvinite, the composition of the liquid phase will be located at point e. This point contains 30.0 parts of KCl and 27.7 parts of NaCl per 100 parts of water. Thus in this process 2.7 parts of NaCl

SOLUBILITY OF KCl AND NaCl IN WATER

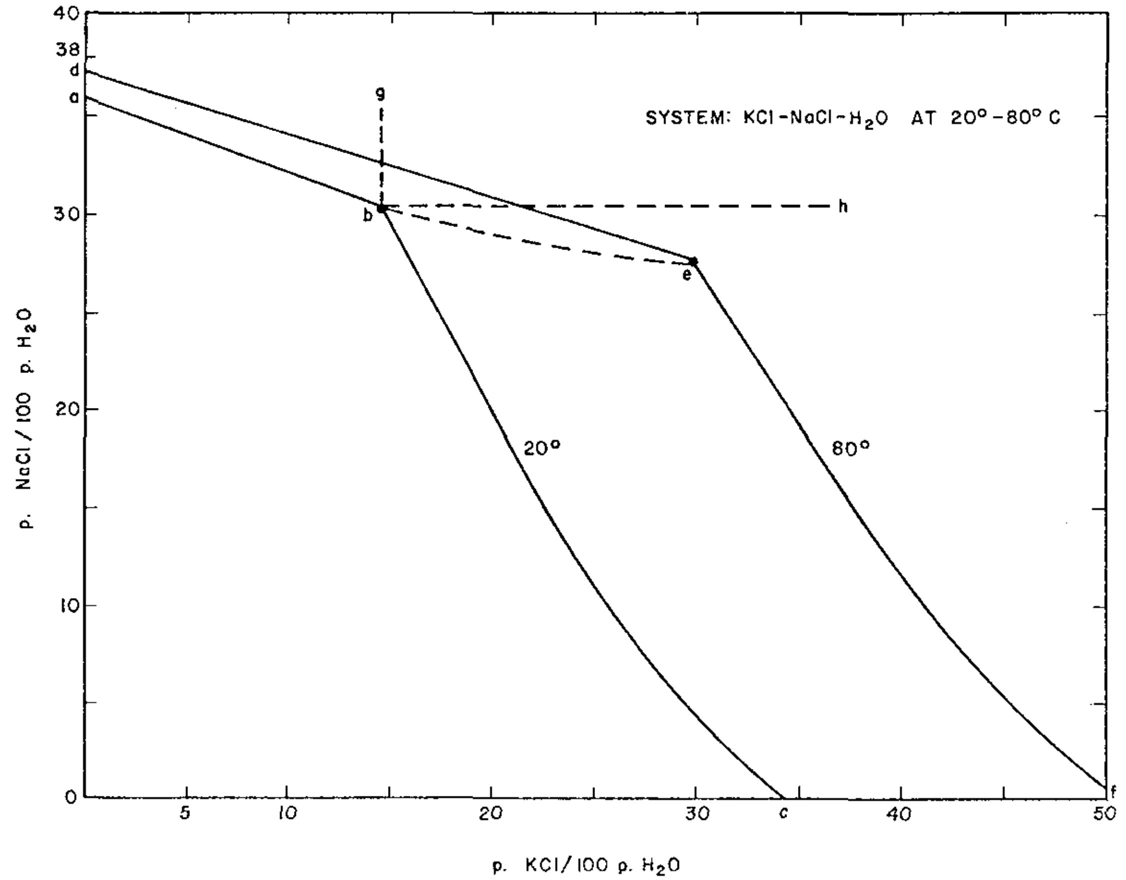

FIGURE 4

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has been crystallized out and 15.2 parts of KCl has been dissolved per 100 parts of water. If the solids are now removed from the liquid phase, the latter by cooling to 20°C, only KCl will crystallize. After separation of the solid potash, the brine is recycled. In essence, this is the basic physical chemistry of the separation of potassium and sodium chloride by crystallization. A simplified flow diagram[1/] for this process is presented in Figure 5.

A common impurity in many sylvinite ores is carnallite ($KCl.MgCl_2.6H_2O$), which is dissolved during the leach. In this case, the $MgCl_2$ content in the brine is controlled by bleeding brine from the system. Figure 6 illustrates that a higher $MgCl_2$ level causes decreased solubility of both NaCl and KCl. The higher the concentration of $MgCl_2$ in the brine, the more difficult the crystallization process becomes. However, the higher $MgCl_2$ content in the bleeding brine results in smaller losses of potash.

SIMPLIFIED FLOWSHEET FOR THE RECOVERY OF POTASH FROM SYLVINITE BY CRYSTALLIZATION

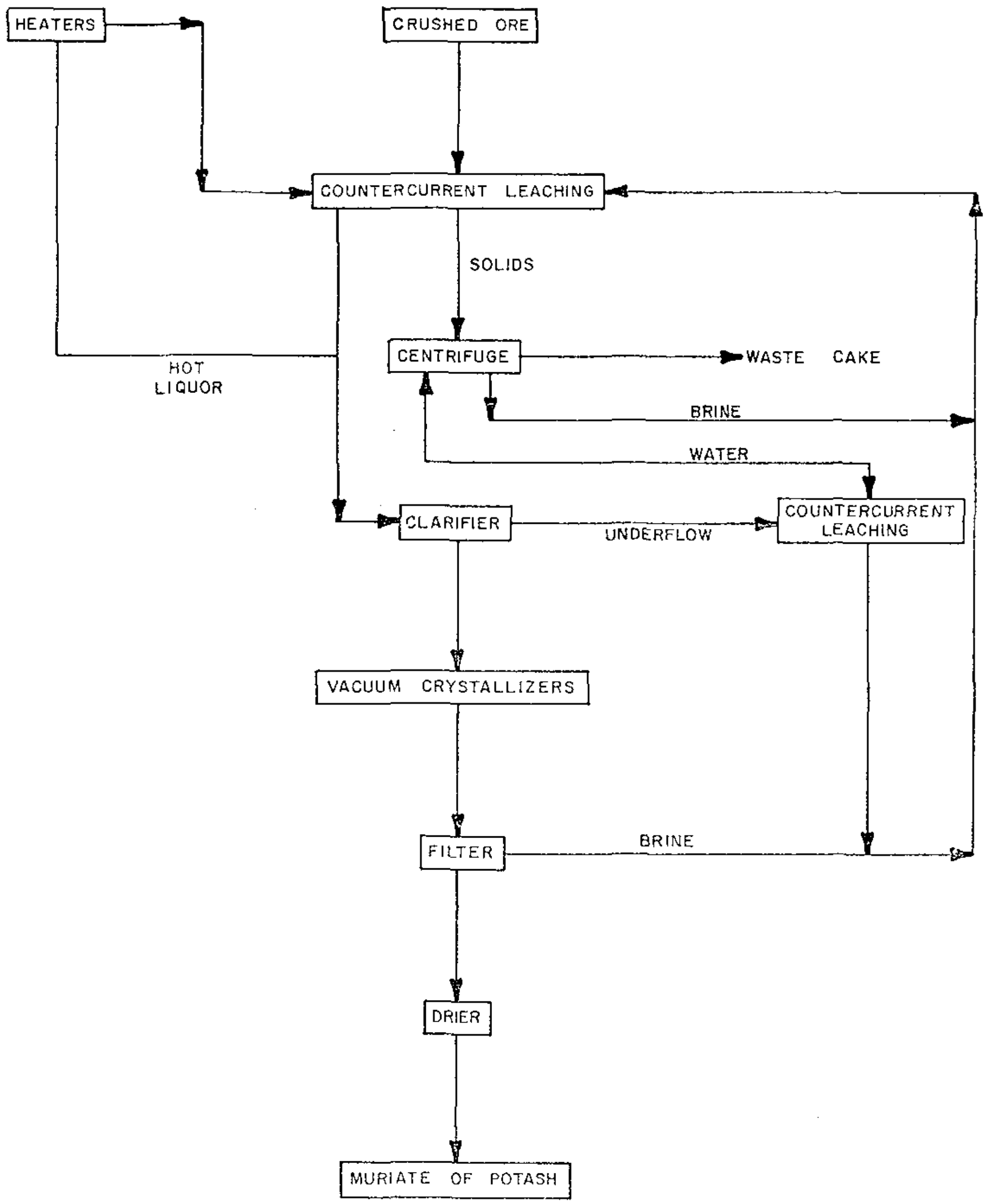

FIGURE 5

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THE SOLUBILITY OF BOTH NaCl AND KCl AT SEVERAL LEVELS OF $MgCl_2$ CONCENTRATION (ALL DATA SHOWN ARE IN PARTS OF SALT PER 100 PARTS OF WATER)

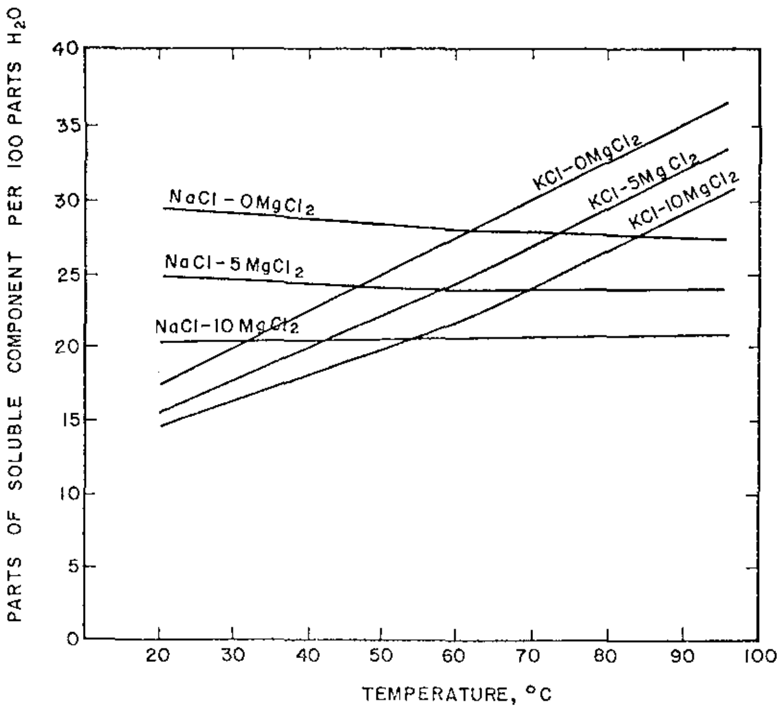

FIGURE 6

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Processing Carnallite

There are two major ways of processing carnallite. In one, flotation is involved and in the other crystallization only. The choice of method depends, among other factors, upon the composition of the ore.

Carnallite may be leached with the proper amount of brine saturated with respect to NaCl and KCl but unsaturated with respect to $MgCl_2$. After a solid-liquid separation, the residue, consisting mainly of NaCl-KCl, is separated by standard aliphatic amine flotation of the potash.

The crystallization process flowsheet may vary considerably depending on the ore. However, it consists essentially of decomposing the carnallite ore with the correct amount of a brine which is unsaturated with respect to magnesium chloride. After nearly all of the latter salt has been dissolved, the brine and insolubles are separated. The solids, again a mixture of NaCl and KCl, are leached hot with a recycle brine saturated with respect to sodium chloride but unsaturated with respect to potassium chloride. Following solid-liquid separation, the liquid phase is fed to a vacuum crystallizer. Potash crystallized out when cooled.

These general procedures for the recovery of potash from carnallite are modified depending upon the presence in the ore of minerals other than carnallite and halite.

Commercial Operations in the United States

Over 80% of the potash produced in the United States comes from mines in the Carlsbad area in New Mexico. Sylvinite and langbeinite are the only two potash containing ores which are mined in the country. Mined sylvinite is processed by froth flotation in all U. S. plants with the exception of operations by the Kermac Potash Co. and by United States Potash and Chemical Co., both in the Carlsbad area, where crystallization methods are used. International Minerals and Chemical Corp. and Duval Corp. are the only companies mining langbeinite (also in the Carlsbad area) which results in the production of potassium sulfate and a mixture of the latter and magnesium sulfate.

The operation of Texas Gulf Sulphur at Moab, Utah is unique among potash producers from sylvinite. After several years of difficulties in mining the ore, the company decided to flood the mine with water, pump the NaCl-KCl solution to the surface, and solar evaporate to obtain a recrystallized sylvinite. After harvesting, the sylvinite is subjected to froth flotation of the potash.

Kerr-McGee Chemical Corp. plant (ex-American Potash and Chemical Corp.) at Trona, California, processes underground brine mainly through a solubility relationship to obtain several chemicals including potash. The brine feed to the plant has a complex composition[2/] as shown in Table 16.

Table 16

Average Brine Composition Feed to Kerr-McGee's Plant at Trona, California*

(% by weight)

NaCl	16.35	As_2O_3	0.019
Na_2SO_4	6.96	CaO	0.0022
KCl	4.75	$Fe_2O_3 + Al_2O_3$	0.0020
Na_2CO_3	4.74	NH_3	0.0018
$Na_2B_4O_7$	1.51	NaI	0.0014
Na_3PO_4	0.155	Sb_2O_3	0.0006
NaBr	0.109	Organic matter	0.006
LiCl	0.021		
Na_2S	0.020	pH	9.5

* In addition, bicarbonate, metaborate, monohydrogen phosphate, and fluoride ions are present.

The potash recovery section is relatively simple as shown in Figure 7. The brine is pumped from under dried Searles Lake to the plant where it is subjected to triple effect evaporation. In the process the concentration of KCl is increased to about 20% and NaCl and burkeite ($2Na_2SO_4 \cdot Na_2CO_3$) are crystallized out. After separation of the solids, the brine is fed to a vacuum crystallizer to crystallize potash. The solid-liquid separation then removes the crystals from the brine. This brine and the NaCl-burkeite are advanced in the flowsheet for further processing to recover other chemicals.

SIMPLIFIED FLOWSHEET FOR THE RECOVERY OF POTASH AT KERR-McGee's TRONA PLANT

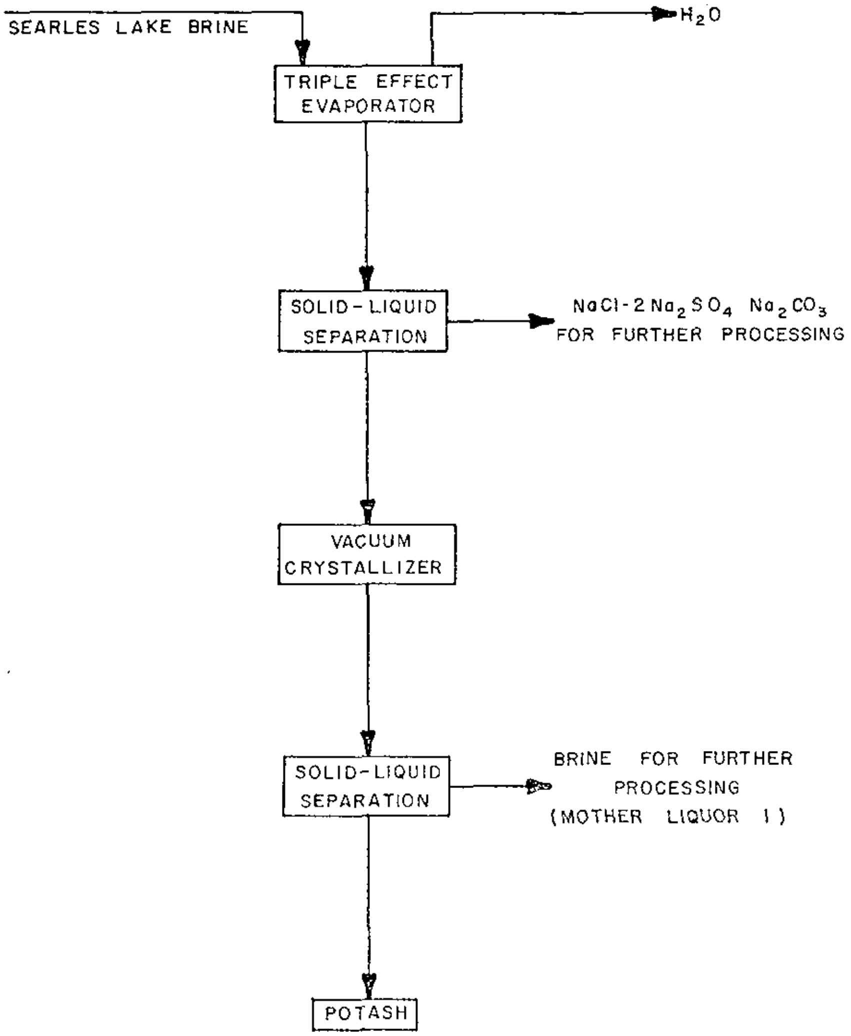

FIGURE 7

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The operation of Bonneville Division of Kaiser Aluminum and Chemical Corp. at Wendover, Utah, uses a brine found just underneath the Great Salt Lake desert. The brine is collected by a network of 16-20 feet deep ditches. Approximately 67 miles of ditches extend into the desert in different directions covering an area of about 90 square miles. Including the solar evaporation ponds, the operation covers about 100 square miles. A diagrammatic sketch of the operation is shown in Figure 8. The brine collected in the ditches is pumped at strategic points into the solar evaporation ponds. Total pond area is about 5,000 acres. As evaporation takes place, halite crystallizes out with some gypsum while the concentration of the remaining salts increases. When the concentration of KCl reaches between 7.0 and 8.0% by weight (depending on the brine temperature), sylvinite starts to crystallize and the brine is moved to the "harvest pond". This sylvinite is hauled to a flotation mill where primary aliphatic amine flotation is performed to yield agricultural grade potash. Additional potash values are recovered by washing the crystalline mixture of NaCl and double potassium-magnesium salts which are crystallized after sylvinite by further solar evaporation. The final brine is nearly saturated with respect to all components including bischofite ($MgCl_2 \cdot 6H_2O$)[3/]. Table 17 shows the variation in composition of the brine during the solar evaporation process at the different stages of crystallization.

POTASH RECOVERY BY SOLAR EVAPORATION - FLOTATION AT BONNEVILLE'S OPERATION AT WENDOVER, UTAH

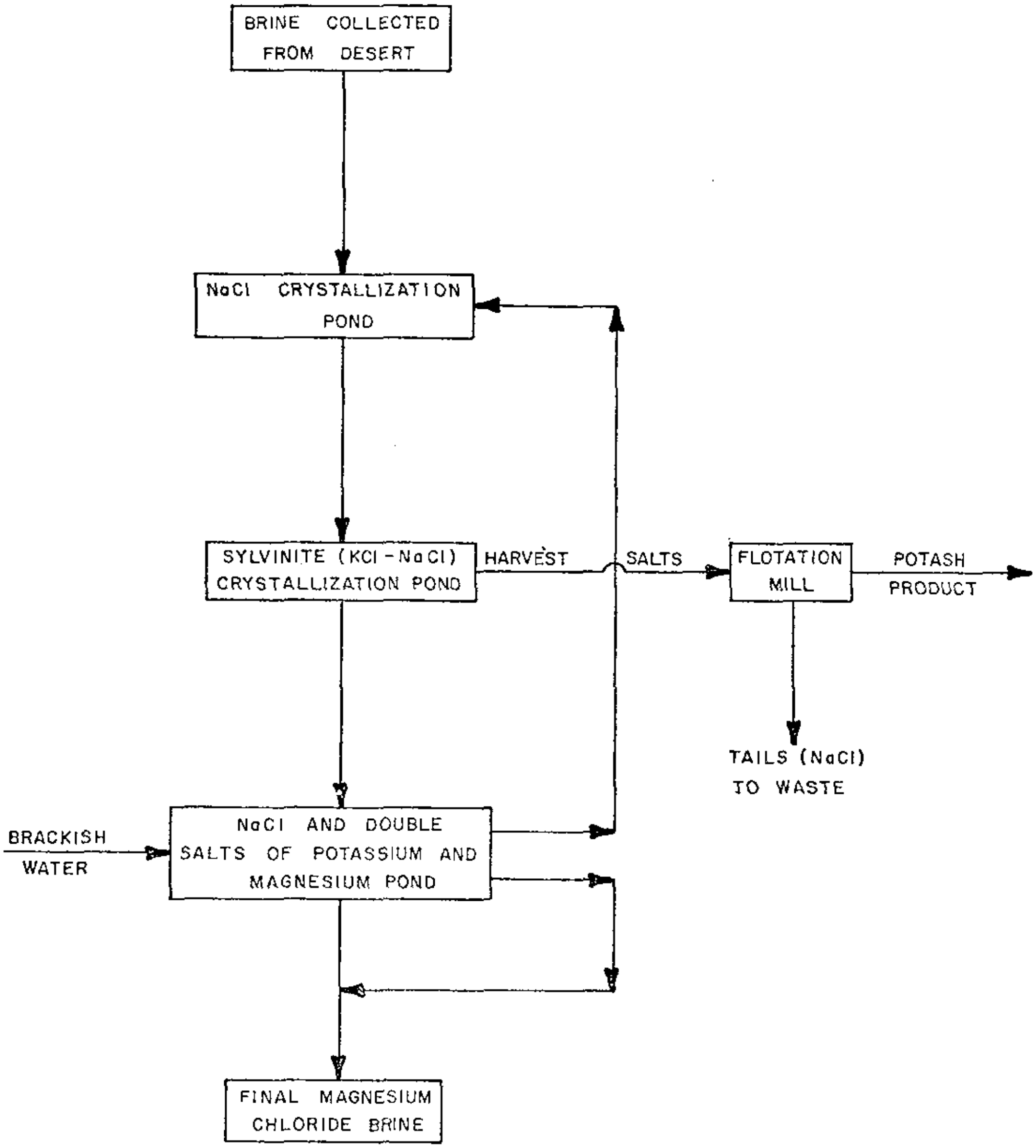

FIGURE 8
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Table 17

Composition (% by weight) of Bonneville's Brine at Different Stages of Crystallization by Solar Evaporation

Original Brine		To Harvest Pond	
$NaCl$	18.0 - 24.0	$NaCl$	12.5 - 13.5
KCl	0.8 - 1.2	KCl	7.0 - 8.0
$MgCl_2$	0.9 - 1.2	$MgCl_2$	7.5 - 8.0
$MgSO_4$	0.2 - 0.3	$MgSO_4$	1.2 - 1.8
$CaSO_4$	0.3 - 0.4	$CaSO_4$	0.10 - 0.12
$LiCl$	0.03 - 0.04	$LiCl$	0.19 - 0.25

To Carnallite Area		To Magnesium Chloride Pond	
$NaCl$	2.4 - 3.5	$NaCl$	0.5 - 1.5
KCl	3.0 - 4.5	KCl	0.5 - 2.0
$MgCl_2$	18.5 - 21.0	$MgCl_2$	28.0 - 30.0
$MgSO_4$	3.8 - 4.2	$MgSO_4$	2.3 - 3.3
$CaSO_4$	0.07 - 0.09	$CaSO_4$	0.03 - 0.05
$LiCl$	0.4 - 0.5	$LiCl$	0.5 - 0.6

There are two new additional solar evaporation operations in the United States which may be related to potash production, both located on the shores of the Great Salt Lake in Utah. One is operated by the Great Salt Lake Minerals and Chemical Co. (a wholly owned subsidiary of Gulf Resources and Chemical Corp.) which has a solar evaporation complex and processing plant on the central-east shore of the lake. The other is the Magnesium Division of NL Industries, Inc. with an operation on the southwest side of the lake. At the present, the concentration of salts in the Great Salt Lake brines varies because the lake is divided by the

Southern Pacific Railroad east-west causeway which makes the northern arm of the lake more concentrated than the southern arm. However, the relative ratios of the different components of the brine are approximately the same. The maximum concentration compositions of the major constituents are presented in Table 18. Data for this table were taken and recalculated from Stokes' work.[4/] Flowsheets of the two operations only are outlined at the present time.

Table 18

Average Composition of the Great Salt Lake Brine
(Maximum concentration, major components only, % by weight)

	Northern Arm	Southern Arm
Cl^-	12.7	12.2
Na^+	7.0	7.1
$SO_4^=$	2.2	2.0
Mg^{++}	1.10	0.93
K^+	0.63	0.55
Ca^{++}	0.026	0.028
Li^+	0.005	0.005
Total dissolved solids	24.2	23.5
Density	1.223	1.218

In the sequence of crystallization by solar evaporation, the GSL Mineral and Chemical Co. operation first produces sodium chloride. After about 65% of the latter has been crystallized, a potassium containing salt begins to crystallize. This salt is schonite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$) mixed with epsomite ($MgSO_4 \cdot 7H_2O$) and NaCl. The brine is then adjusted with recycled final mother liquor to crystallize kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$) which is followed by crystallization of carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$). The carnallite crop of crystals is harvested and treated with mother liquor from the kainite crystallization to produce an additional amount of kainite crystals. Production of potassium sulfate product is attained by converting the kainite to schonite using the first harvested crop of salts (schonite-epsomite) and then decomposing the schonite with water. The operation produces sodium sulfate as a by-product. Figures 9 and 10 show diagrammatically the operation of the GSL Mineral and Chemical Co.[5/] [6/]

The National Lead Magnesium Division operation involves artificial precipitation of some sulfate content in the brine and solar evaporation to produce, after the initial crystallization of NaCl, the crystallization of carnallite. After harvesting carnallite may be processed easily to make potash. However, the major goal of the company is to make magnesium metal using the residual brine from the solar pond evaporation process.[7/] [8/] [9/]

CRUDE SALTS AND CONCENTRATED BITTERNS FROM THE POND SYSTEM ARE PROCESSED IN A PLANT BY GREAT SALT LAKE MINERAL & CHEMICAL CO.

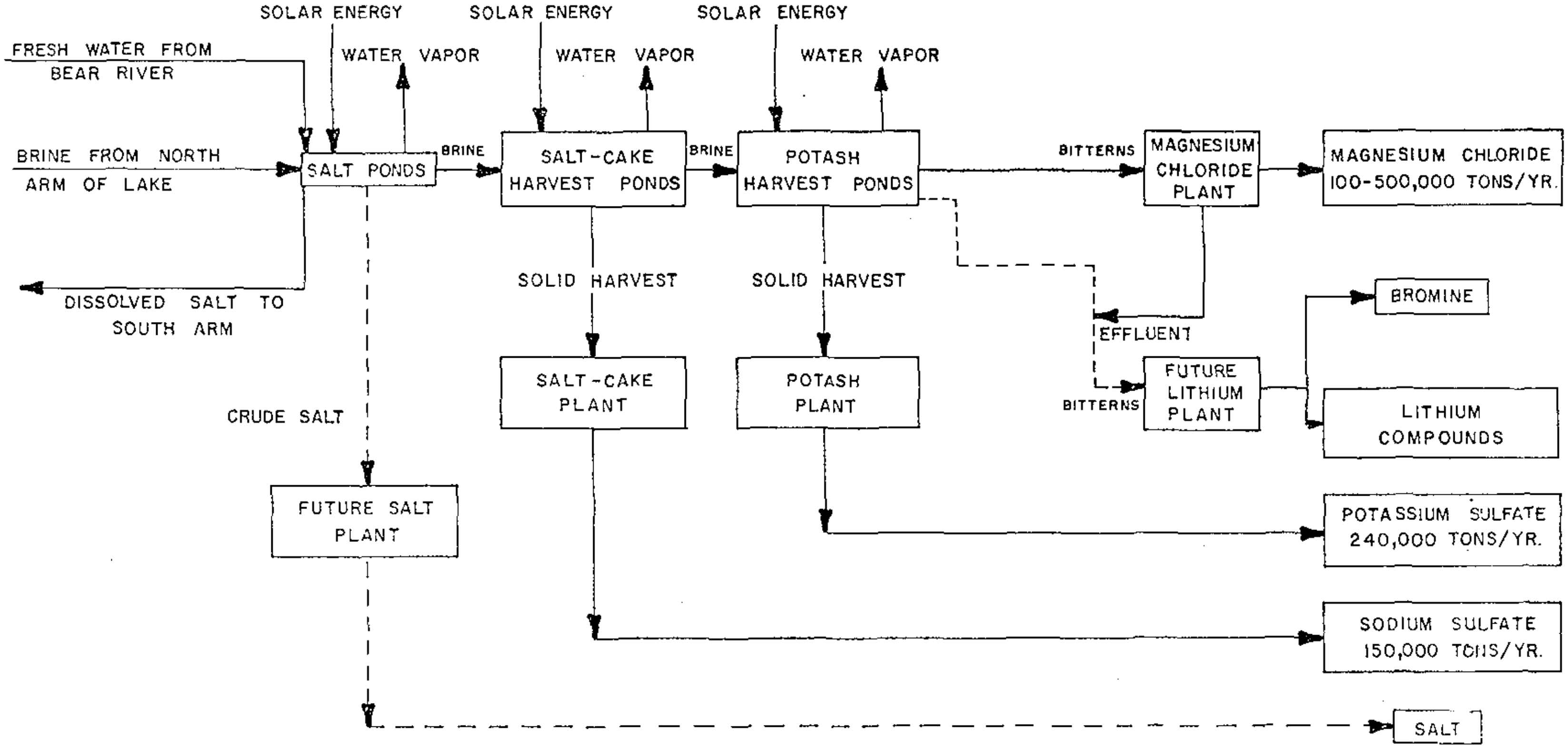

FIGURE 9
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THE SOLAR POND SYSTEM OF THE GSL MINERAL
AND CHEMICAL CO. NEAR OGDEN, UTAH
COVERING SOME 12,800 ACRES

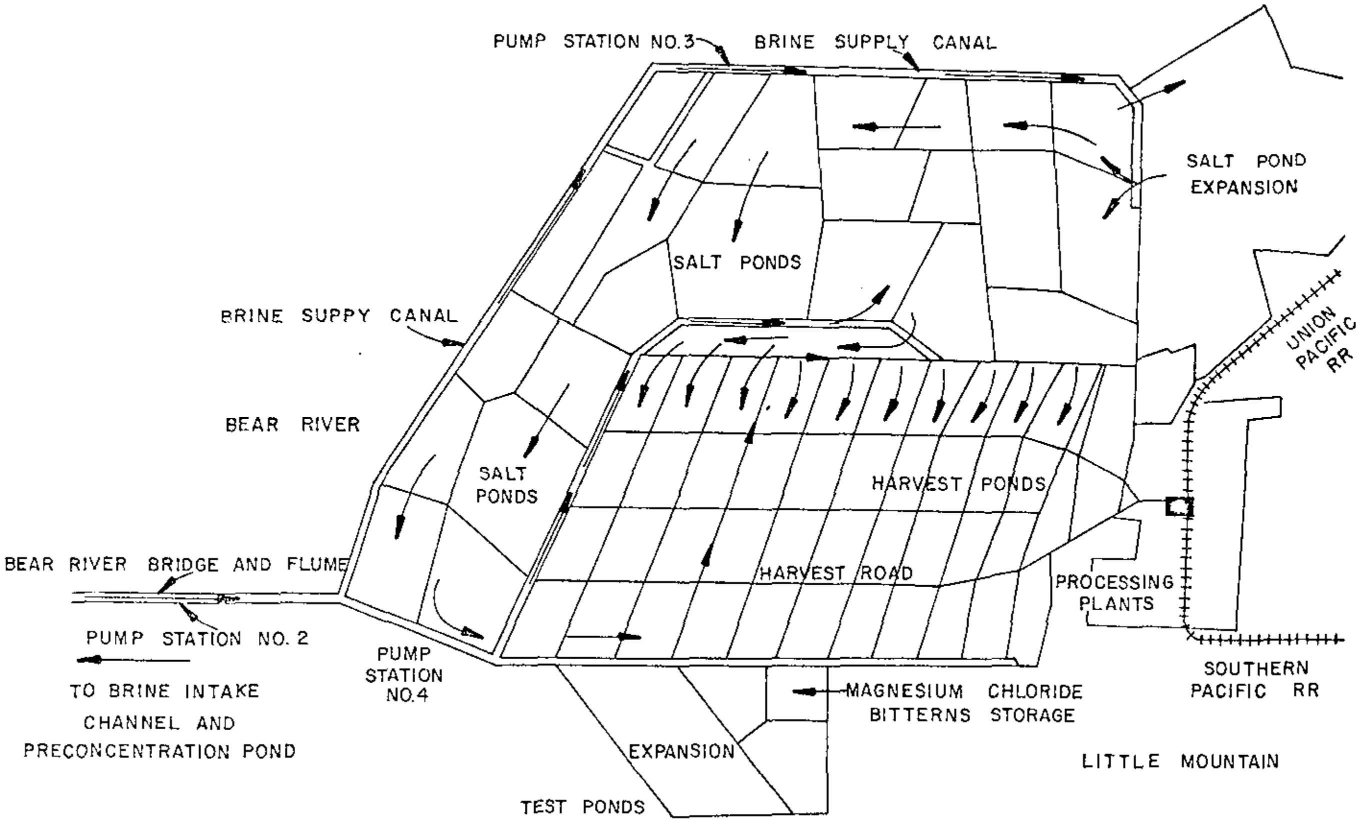

FIGURE 10
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Also, minor production of potash has been reported from underground brine in Michigan in an operation by Dow Chemical Co. at Midland.

Major Foreign Commercial Operations

In addition to the United States, the major potash producing countries are Canada, the Soviet Union, West and East Germany, France, Spain, Israel, and Italy.

CANADA

With one exception, all the potash producers in this country use standard flotation for conventionally mined sylvinite. The exceptional producer, and perhaps the most outstanding operation from a technical standpoint, is the one conducted by Kalium Chemical, Ltd., where solution mining is used to recover potash near Regina, Saskatchewan. The solution mining method was selected by Kalium in order to avoid the expensive shaft construction and to reach the sylvinite bed at a depth below approximately 3,500 feet which is the practical limitation for conventional shaft mining of the ore. By solution mining, Kalium is able to recover potash from an estimated depth of 5,200-5,300 feet. The process of solution mining consists essentially of injecting water through a well drilled to the sylvinite bed and withdrawing a NaCl-KCl saturated solution through another well. Once the brine is brought to the surface, 74

it is processed using crystallization techniques. Figure 11, taken from "Phosphorus and Potassium", No. 30, July-August, 1967, page 38, shows in simplified form the flowsheet that Kalium uses in its surface operation.

SOVIET UNION

Very little is known of the flowsheets used for potash recovery in the Soviet Union. However, most are known to process different ores mainly by flotation and, in some cases, by flotation followed by a crystallization step.

Two mines operate in West Ukraine: one at Kalush located 100 km south of the town of Lvov, and one at Stebnikov 70 km south of Lvov. The mines are in the region known as East Galicia, belonging to Poland until annexation by the Soviet Union after the second World War. The mined ore contains primarily sylvinite and kainite and is processed at the Novo Stebnikov plant. The ore also contains polyhalite, kieserite, langbeinite, and some clay. The ore is treated by flotation of the potassium-containing minerals away from the halite. Some of the magnesium-potassium sulfate is marketed as such, but a fraction is treated by crystallization with KCl to produce potassium sulfate and a residual magnesium chloride brine. Incidentally, this magnesium chloride brine is used for the production of magnesium metal.

SIMPLIFIED FLOW DIAGRAM OF THE SOLUTION MINING AND REFINING METHOD

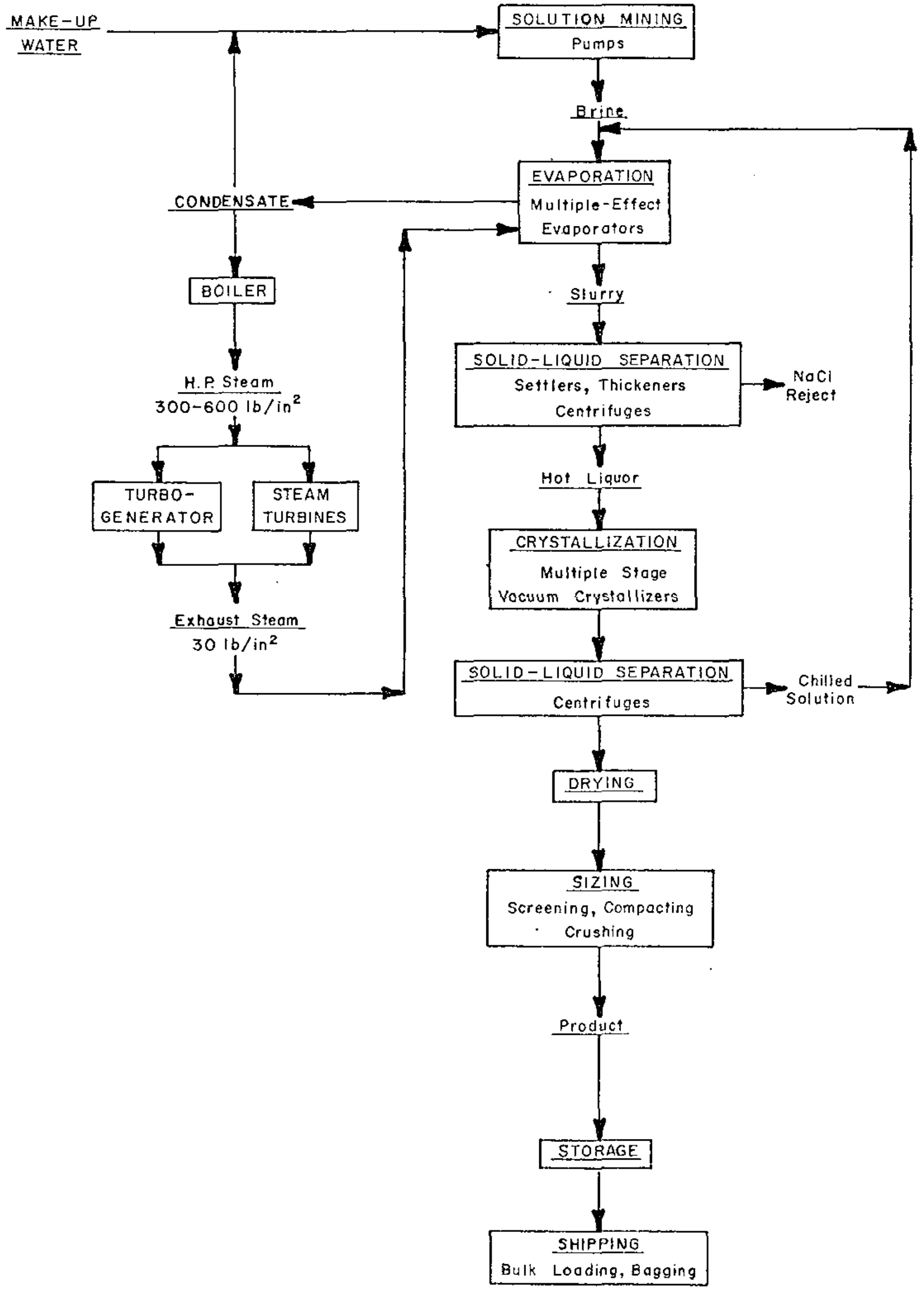

FIGURE 11
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The production of potash from mined sylvinite (which also contains small amounts of carnallite) in Byelorussia at the Soligorsk region is all processed by flotation. The same is true of the central Urals deposits of Solikamsk and Berezniki.

Perhaps the most interesting future project from the standpoint of brine processing for potash production in the Soviet Union is that at the Gulf of Kara Bogaz. Kara Bogaz is a shallow lake connected by a narrow channel to the east shore of the Caspian Sea. It is estimated that about 2.6 billion gallons of the Caspian Sea, which has a total dissolved solids of around 1.3%, flow into Kara Bogaz. Good solar evaporation conditions concentrate the salts and at the present the brine of Kara Bogaz is one of the largest and densest salt lakes in the world with 29% of total dissolved solids. The potassium content is 2.5% as KCl and a $MgCl_2$ concentration is in the range of 22-23% by weight. Studies on the recovery of potash from the deposited salts -- mainly carnallite and epsomite -- have been conducted in the Soviet Union for years. However, one of the disadvantages of the exploitation of this potash source is its distance from the consumers' markets. At the present only sodium sulfate is produced commercially from the brine.

References for potash in the Soviet Union are 10, 11, 12, 13 and 14.

WEST GERMANY

There are 14 active mines in West Germany and the potash ore is processed in 13 plants. At the present time, three plants use standard flotation techniques for the separation of potash from halite. Two other refineries use a combination of flotation and crystallization techniques. The other remaining plants use crystallization processes exclusively. Both the Wintershall and the Salzdetfurth groups (the latter recently acquired by the Kali-Chemie A.G., another West Germany potash producer) have facilities for the conversion of the potassium chloride by metathesis with kieserite to potassium sulfate and the production of a potassium-magnesium sulfate fertilizer product.

EAST GERMANY

The structure of the potash industry in East Germany is somewhat similar to that of West Germany. However, the underground deposits generally contain a higher percentage of magnesium salt as carnallite and kieserite than the West Germany deposits. Therefore, all beneficiation processes used for the recovery of potash are by crystallization methods.

FRANCE

The main potash producing center in France is in Alsace. All the potash ore is mined and processed in seven plants. Two of the plants use standard flotation and the others use a crystallization method for the production of potassium chloride.

SPAIN

The country has two major potash production centers. One is located in the Cataluna region (northeastern Spain) and the other is in the Navarra Province near Pamplona close to the Pyrenees Mountains. The potash ores are mined. Four processing plants are located in the Cataluna region: two use a combination of flotation and crystallization processes and two use crystallization exclusively. The operation near Pamplona by Potasas de Navarra S.A. mines both sylvinite (which is processed by flotation) and carnallite (which is processed separately by crystallization).

ISRAEL

The operation at Sodom in the southern end of the Dead Sea is the largest producer of potash by solar evaporation in the world. Production of potash started in 1932 on the northern end of the Dead Sea but the facilities were destroyed during the war in 1948. At the present there are three plants located at the southern end of the sea with a total capacity of one million tons of KCl per year. The original Dead Sea brine is solar evaporated in a pond system covering an area of approximately 150 km^2 (some 37,000 acres). This area is separated from the main body of the Dead Sea by dikes built into the shallow southern section. A schematic of the present pond system is shown in Figure 12. The processing plants are located close to the pond system east of the carnallite area.

THE SOLAR EVAPORATION POND SYSTEM AT THE DEAD SEA WORKS COVERING SOME 37,000 ACRES

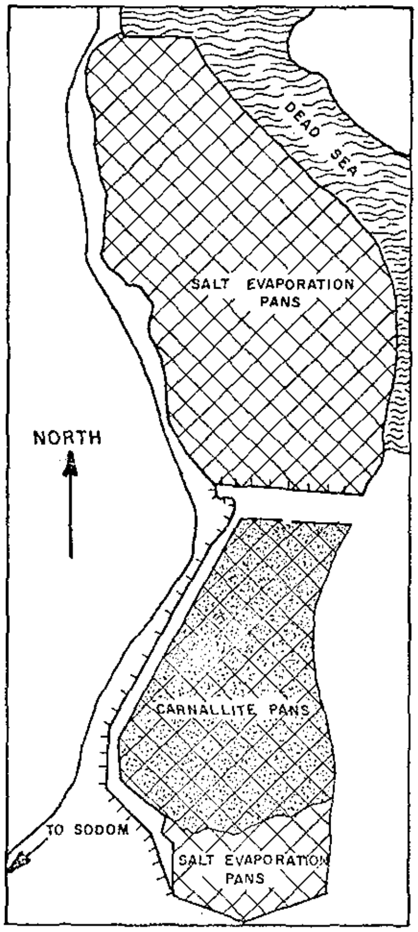

FIGURE 12
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The compositions of the average original Dead Sea brine (which varies according the depth and with the season) and the brines at the different stages of evaporations[16/] are presented in Table 19.

Table 19

Composition of the Dead Sea Brine at Different Solar Evaporation Stages (% by weight)

		Crystallization of Solid Phases		
	Original Brine	Beginning NaCl	Beginning Carnallite	Final Brine
$MgCl_2$	10.4-12.7	11.6	22.3	26.1
$CaCl_2$	3.3- 3.9	3.9	6.5	8.1
KCl	1.0- 1.2	1.2	2.1	0.4
NaCl	6.9- 8.4	8.5	1.5	0.5
$MgBr_2$	0.4- 0.5	*	0.8	1.0
Sp Gr	1.18-1.215	1.235	1.300	1.350

* Br^- expressed as chloride

The carnallite-halite crystallized in the carnallite pans is harvested as a 10-20% solids slurry using floating pumps called dredges. The slurry is thickened to 45-50% solids by weight, then filtered using pan filters producing solids with only 15-12% brine entrainment. The composition of the solids at this point on dry basis is as follows:

KCl	22.7%
$MgCl_2$	29.0%
NaCl	15.3%
H_2O (composition)	33.0%

These solids are treated in three different plants. The carnallite is decomposed to yield a mixture of KCl and NaCl. The separation of these halides is by crystallization in two plants, and by flotation in the third, the oldest installation. A simplified flowsheet of the whole operation is presented in Figure 13. Together, the two crystallization plants produced some 800,000 tons of potash annually using a similar flowsheet. This flowsheet is presented schematically in Figure 14.

As a by-product of the Dead Sea Works, quantities of bromine, magnesium oxide, and hydrochloric acid are produced.

ITALY

Commercial potash production in Italy is of recent history. The Sicilian deposits were discovered in 1951-1952. The deposits are located in the central and western central areas of the island. The principal mine is the San Cataldo, operated by Montecatini where a mixture of kainite-halite is mined. The ore is first processed by flotation to increase the grade of kainite. The kainite concentrate is transported by a cable railway to the main processing plant located 18 miles away. The kainite is converted to schonite and the schonite decomposed with water to make the potassium sulfate product. Montecatini also operates kainite mines at Campofranco and owns mining concessions close to San Cataldo, at Serradifalco, Palo and Rocalmuto. Other mines and processing facilities of kainite are owned by subsidiaries of Societa Edison.

OVERALL POTASH PRODUCTION OPERATION BY THE DEAD SEA WORKS AT SODOM

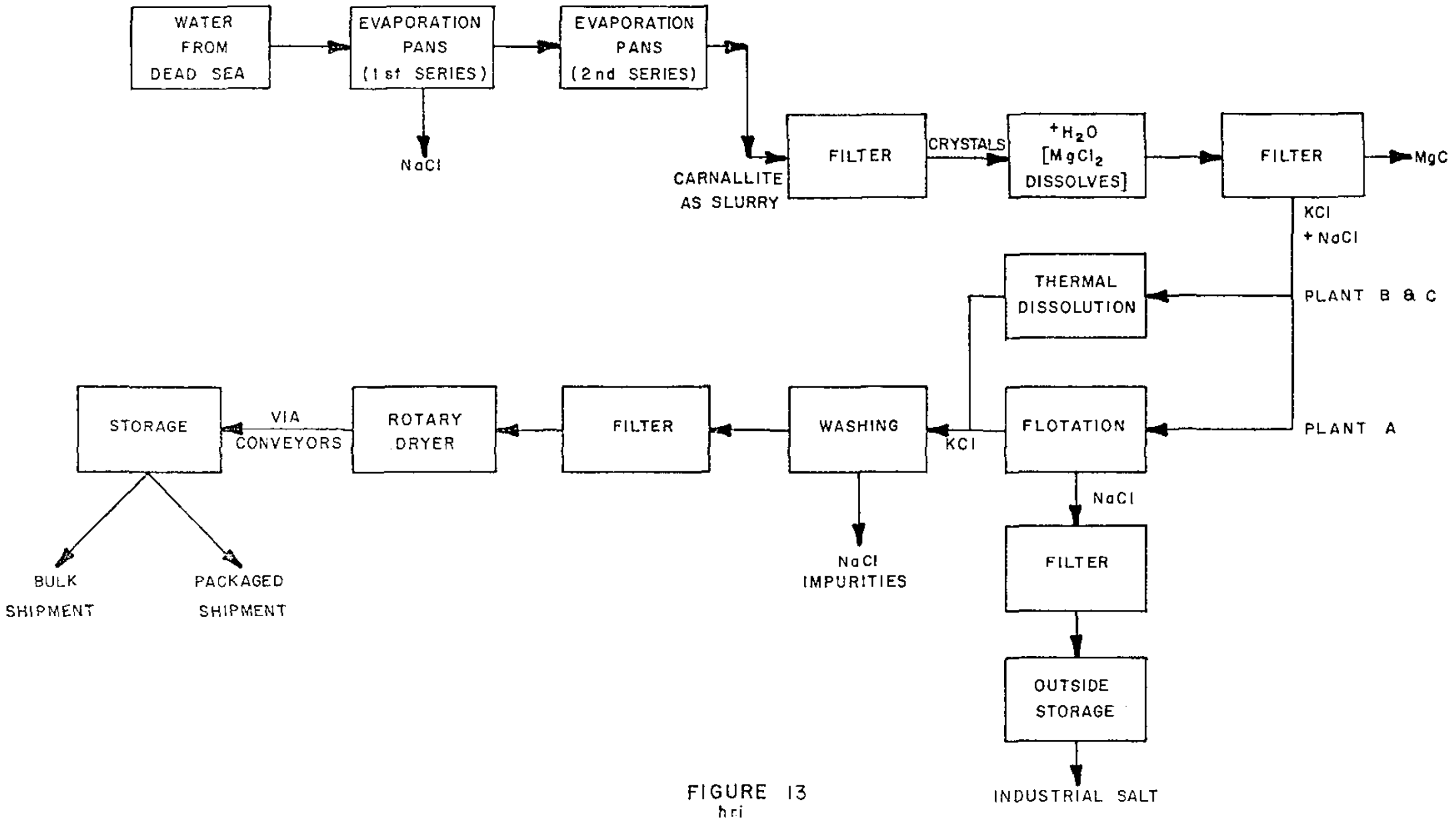

FIGURE 13
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FLOWSHEET FOR THE PRODUCTION OF POTASH FROM CARNALLITE BY THE DEAD SEA WORKS USING CRYSTALLIZATION PROCESS

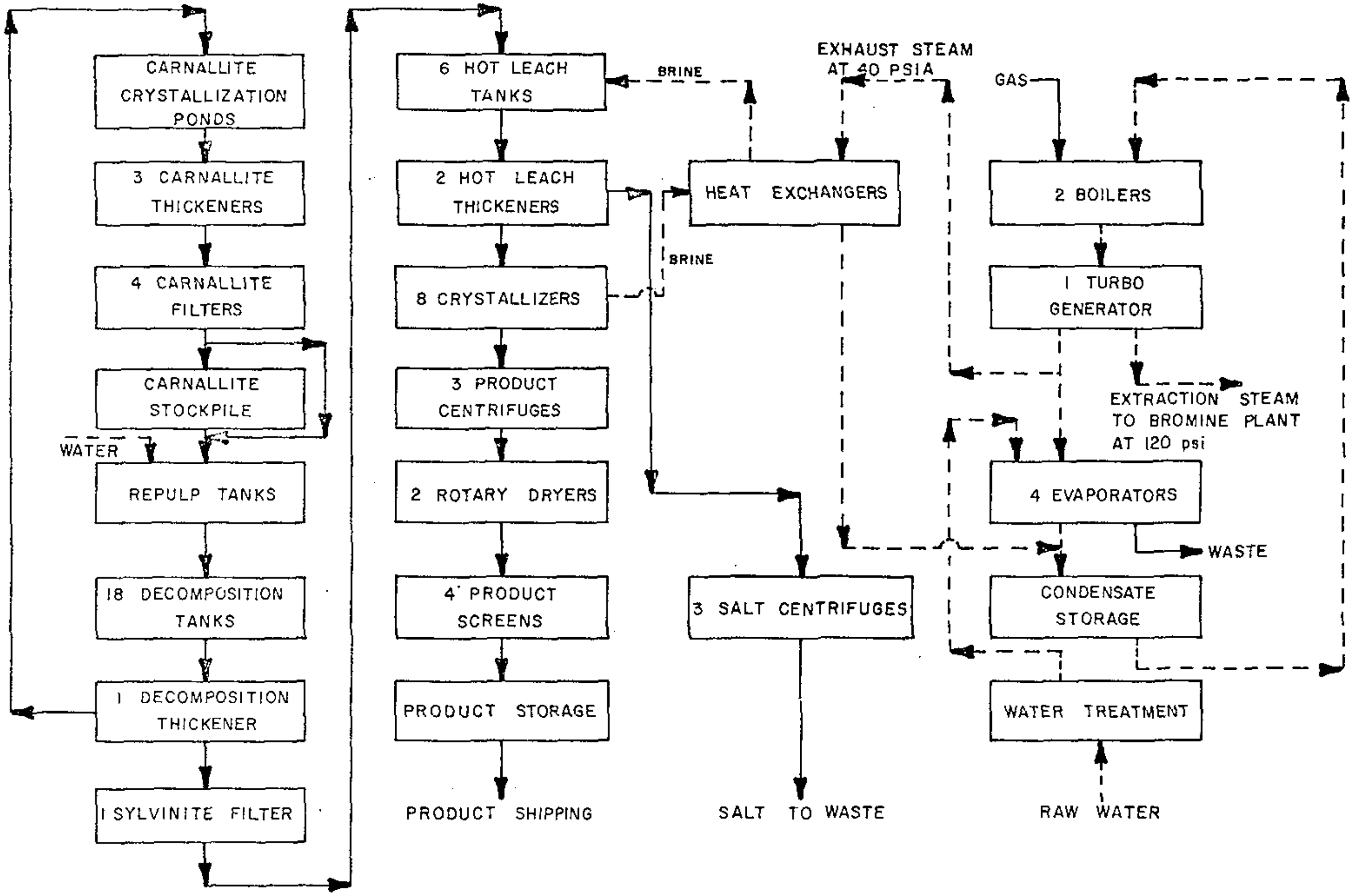

FIGURE 14
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III. SODA ASH

INTRODUCTION

There are three principal sources for the production of soda ash: natural occurring brines, underground deposits, and the Solvay process.

For economic reasons the trend in the United States in the last few years has been to increase production from the large underground trona ($Na_2CO_3.NaHCO_3.2H_2O$) deposits in Wyoming. Meanwhile, Solvay plants were reducing the rate of production or shutting down. Table 20 shows this trend.

Table 20

Soda Ash Production in the United States
(in 1,000 short tons of Na_2CO_3)

Year	Total	Solvay Process	Natural Sources	% of Total
1966	6,809	5,071	1,738	25.5
1968	6,639	4,596	2,043	30.8
1970	7,102	4,414	2,648	37.3
1972	7,461	4,050	3,411	45.7

However, in Europe and elsewhere the Solvay process is primarily used to produce sodium carbonate.

Some soda ash is made by bubbling carbon dioxide in sodium hydroxide produced by electrolysis of sodium chloride. Also, as in many other chemical commodities, soda ash is produced as a by-product from other industries.

Production of Soda Ash by the Solvay Process

Since much has been studied and written about the Solvay process,[1] [2] [3] it will be but briefly reviewed here.

The process essentially uses sodium chloride and calcium carbonate (limestone) to make soda ash and calcium chloride as a by-product. Ammonia is used as an intermediate. The reactions taking place in the different steps of the process are rather complicated but they can be summarized as follows:

$$CaCO_3 \rightarrow CaO + CO_2$$
$$CaO + H_2O \rightarrow Ca(OH)_2$$
$$NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3 + NH_4Cl$$
$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O$$
$$NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

An almost saturated and purified NaCl brine is ammoniated with recycled ammonia. The resulting solution goes to a carbonation tower where CO_2 is bubbled. The relative insoluble $NaHCO_3$ is precipitated and separated by filtration or centrifugation. The filtrate is treated with milk of lime to evolve NH_3 for recycling and produces calcium chloride as a by-product. Limestone is decomposed by heating to CO_2 and lime which are needed in the process. The solid $NaHCO_3$ is decomposed by heating in a kiln to make soda ash product and CO_2 for reuse. A schematic flowsheet of the process taken from Faith, Keyes and Clark[4] is presented in Figure 15.

SCHEMATIC FLOWSHEET FOR THE PRODUCTION OF SODA ASH BY THE SOLVAY PROCESS

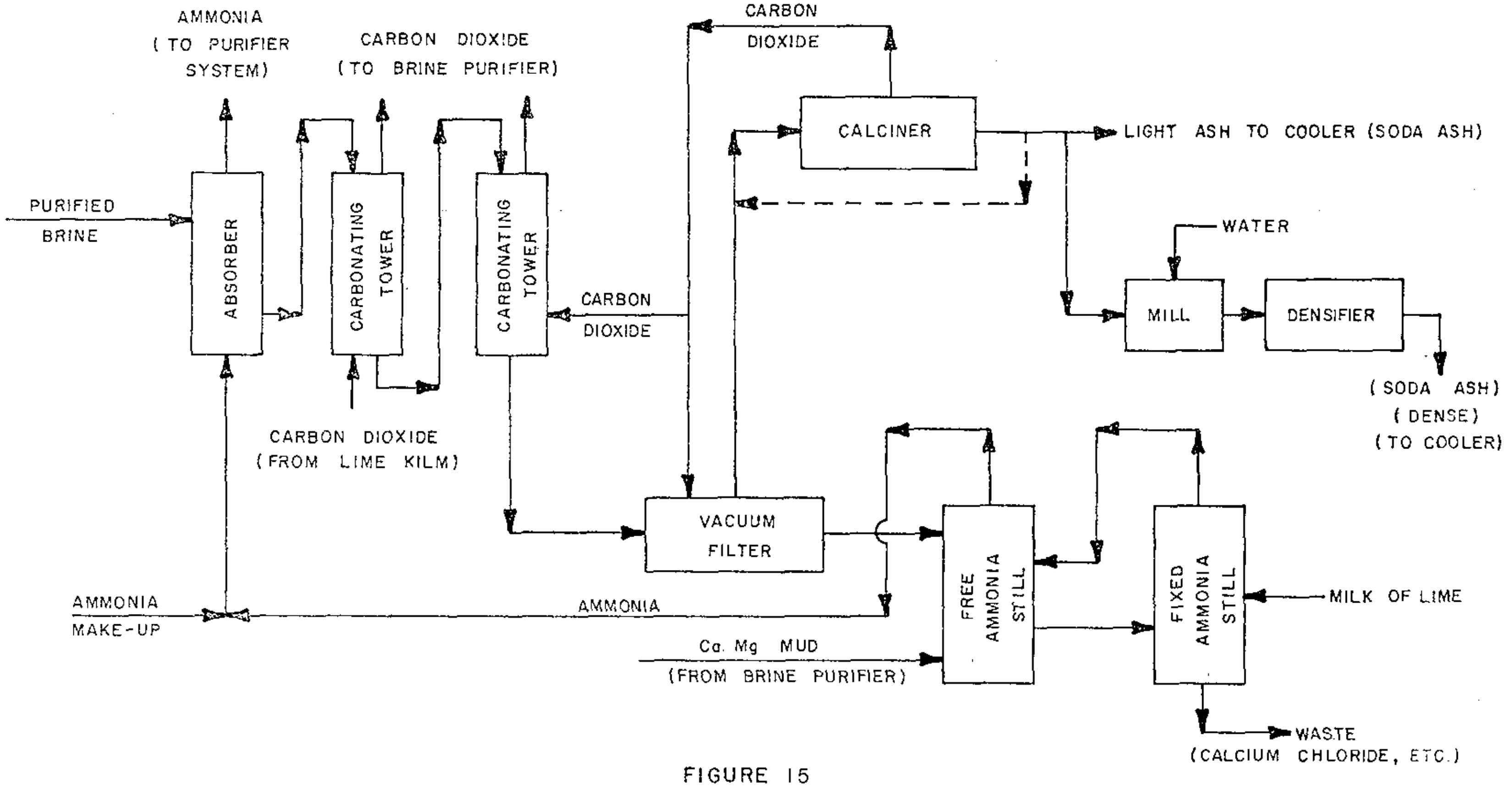

FIGURE 15
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Some ammonia is used to make up the relatively small losses, and coal is also burned to CO_2 for the same purpose.

Production of Soda Ash from Mined Trona

As previously mentioned, during 1972, the production of soda ash from natural sources in the United States amounted to 45.7% of the total. This share is expected to continue to grow in the years to come. A very large share of this soda ash production comes from the mined trona from the Green River, Wyoming, region.

The process used to produce soda ash from mined trona is simple: ore is crushed and dissolved in water; the insoluble mud is separated by thickening and filtration; the sesquicarbonate solution obtained is evaporated in vacuum crystallizers; solids are separated from the mother liquor which is recycled to the trona dissolution section; soda ash is produced by calcination of the solid sodium sesquicarbonate at about 240°C to drive off the water of crystallization and the CO_2.

Similar flowsheets are used by several producers in the Green River area. The one presented in Figure 10 is the FMC Corporation and was taken from an article published by the Chemical Engineering magazine[5].

FLOWSHEET FOR THE PRODUCTION OF SODA ASH FROM MINED TRONA

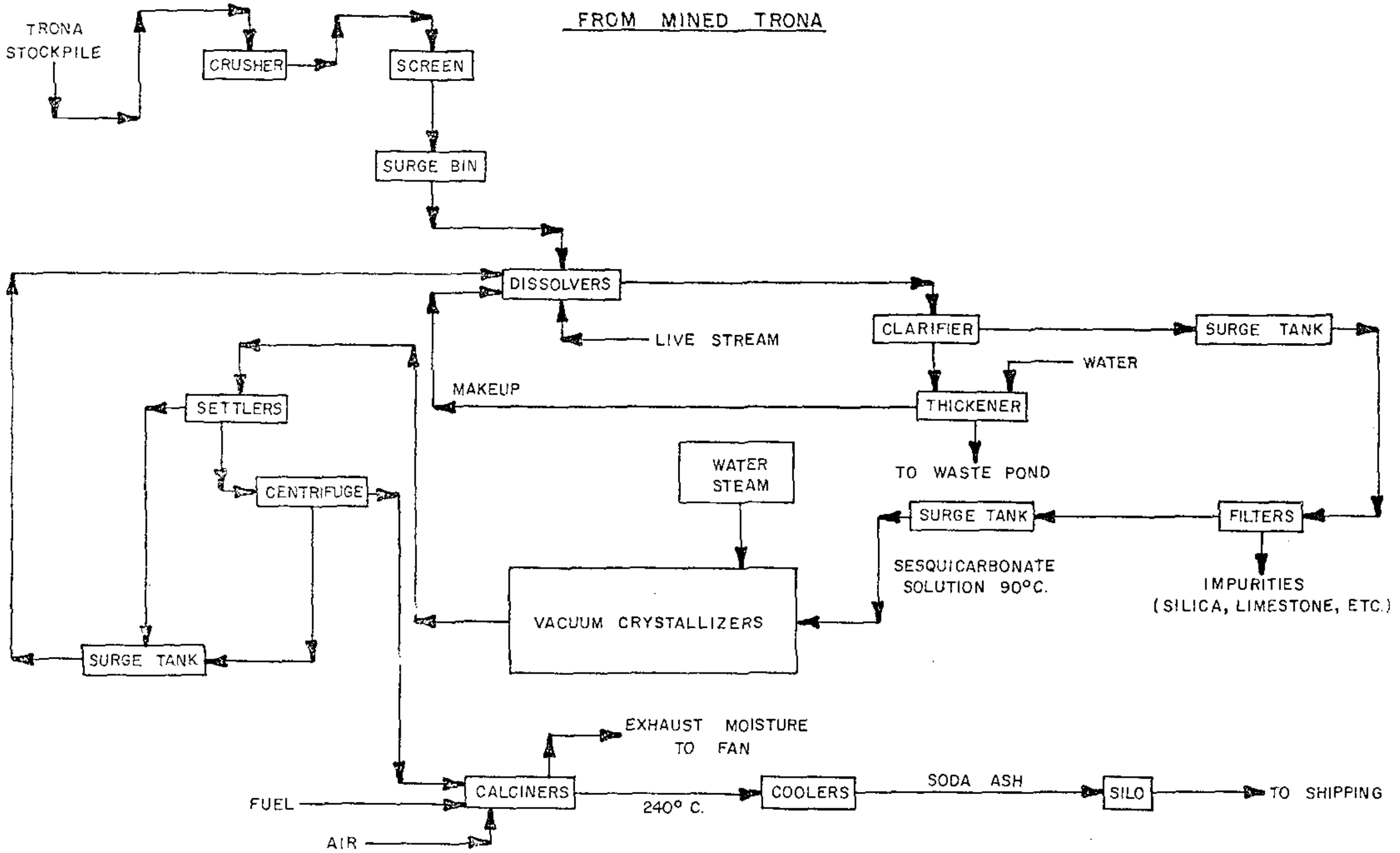

FIGURE 16
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Brief consideration should be given to the surface trona deposit at the southern end of Lake Magadi, Kenya[6] which is being exploited by the Magadi Soda Company. Estimated production[7] is in the range of 160-170 thousand tons of soda ash a year. The accumulation of trona by solar evaporation of hot spring brines has been estimated at three billion tons with a thickness varying from 7 to 40 meters deep[6]. Detailed process flowsheets of the Magadi Soda Company are not known but probably consist of solar evaporation of brines as well as harvesting the solid trona surface deposit followed by calcination. The average composition of the brine, contributing to the deposition of about 400,000 tons of trona a year by solar evaporation, is presented in Table 21.

Table 21

Average Brine Composition of the Southern end of Lake Magadi, Kenya[6]

(% by weight)

Total $CO_3^{=}$ as	Na_2CO_3	17.1%
	NaCl	13.7%
	$SO_4^{=}$	0.2%
	K^+	0.2%
	F^-	0.1%
	SiO_2	0.1%
	Br	0.03%
	B	0.01%

Production of Soda Ash from Brines

Many brines around the world contain sodium carbonate in solution. Usually, the brines also contain other soluble alkali metal salts; most common are the chlorides, sulfates, and borates. Depending on the relative quantities of these salts in solution, flowsheets may be selected based on phase chemistry relationships. At the present, the major commercial plants of the world which recover soda ash from naturally occurring brines are located in California. Fundamentally, two brine sources are used: the Owens Lake and the Searles Lake. Using different procedures, many companies have been involved in the production of soda ash since the latter part of the last century. However, only two are active now, both using brines from Searles Lake. One is the Kerr-McGee Chemical Corp. (formerly the American Potash and Chemical Corp.), and the other is the West End Chemical Co., a subsidiary of Stauffer Chemical Co. The average composition of the Searles Lake brine is given in Table 16 (Potash section, p 60).

The Kerr-McGee operation has two processes to produce soda ash from the Searles Lake brine. One uses the so-called low structure brine which is richer in carbonate than the upper structure brine. A simplified flowsheet, taken from Ver Planck[8/] is shown in Figure 17.

KERR-McGEE CARBONATION FLOWSHEET FOR THE PRODUCTION OF SODA ASH

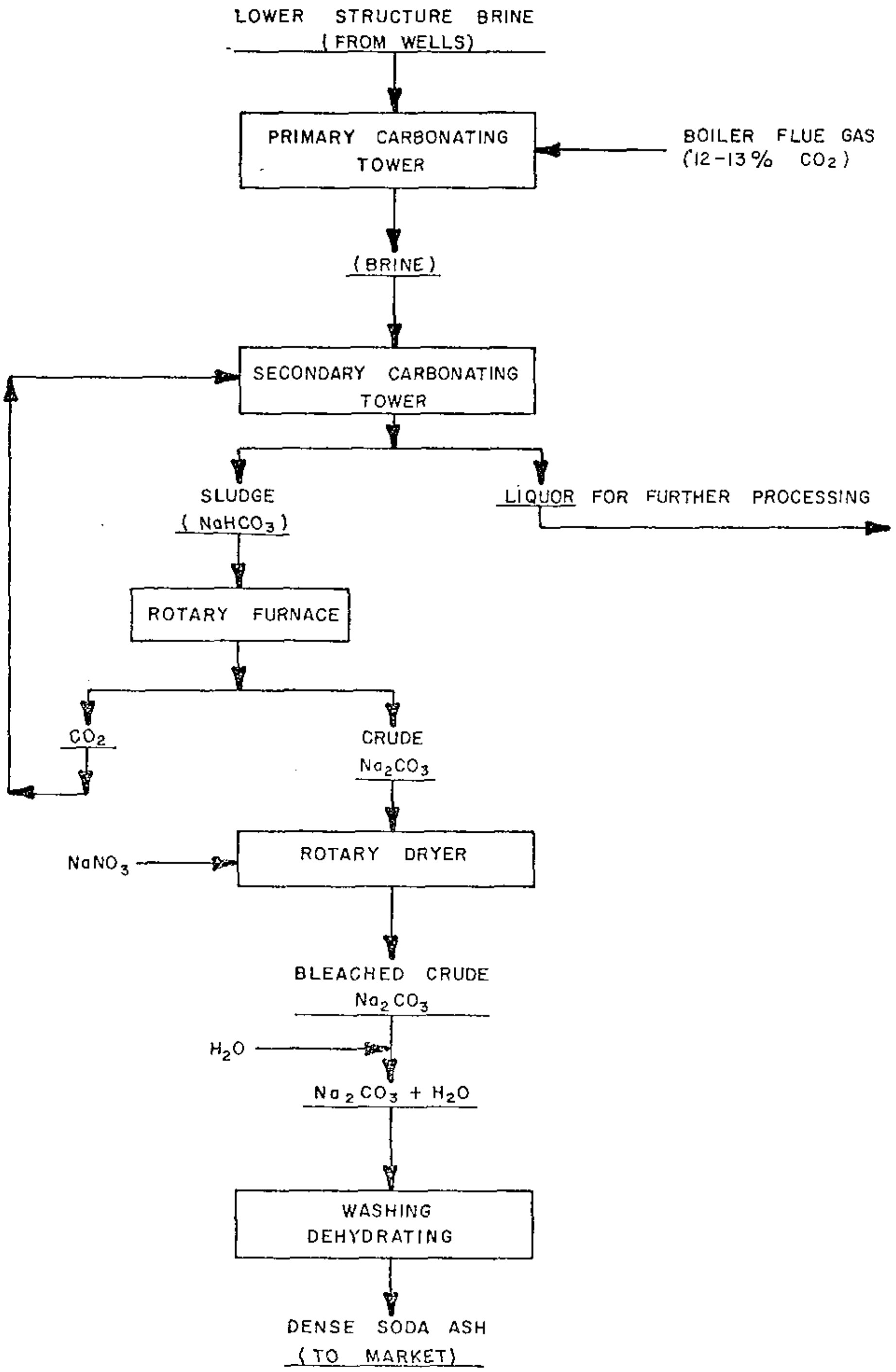

FIGURE 17
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In the other process, burkeite is crystallized during the multi-effect evaporation of the upper structure brine for the potash production shown in Figure 6 (Potash section, p. 57). The burkeite crystallizes with halite during evaporation. The mixed salts are processed in the simplified flowsheet shown in Figure 18 taken from Faith, Keyes and Clark[4/].

The Stauffer subsidiary, West End Chemical Company plant, produces sodium carbonate by carbonation of Searles brine using a somewhat similar flowsheet to that of Kerr-McGee as shown in Figure 19. This in simplified form is presented in Figure 19 which was taken from Ver Planck[8/].

Occidental Chemical Co. (a subsidiary of Occidental Petroleum Corporation) has been active in pilot plant testing with the Searles Lake brine. The process consists of solar evaporation of the brine and harvesting of three different crops of crystalline mixture. One of these mixtures will contain one-third burkeite which will then be processed to produce soda ash and sodium sulfate[9/].

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IV. MAGNESIUM CHLORIDE

INTRODUCTION

Magnesium chloride production methods are nearly all related to the production of magnesium metal or magnesium oxide. This is due to limited industrial use of the salt itself, such as in the manufacturing of special cements (Sorel's cement), sizing of paper, and in the ceramic industry.

Because cheap power is required in the production of magnesium metal, large quantities of magnesium chloride are available at different locations as a waste by-product either from sodium chloride production using sea water or from potash production using brines and ores. Hence, magnesium chloride is produced primarily as an intermediate chemical for the production of the metal or the oxide. Magnesium chloride is a by-product from the titanium metal production, but it is recycled to produce magnesium metal and chlorine.

A U.S. Bureau of Mines publication has been used extensively for the preparation of this review on magnesium chloride production.[1/]

GENERAL PROCESSES

Magnesium Chloride from Sea Water

Average sea water contains 0.51% by weight of magnesium expressed as $MgCl_2$. Two plants in the world (Dow Chemical Co. in the United States and Norsk-Hydro Electrisk in Norway) use sea water as raw material for the production of magnesium metal. In general, the method consists of precipitating $Mg(OH)_2$ using milk of lime and separating the precipitate by thickening and filtering. A thick slurry of the precipitate is reacted with hydrochloric acid (and a small amount of sulfuric acid to remove the calcium) to produce a concentrated $MgCl_2$ brine which is then dehydrated to 70-75% $MgCl_2$. This $MgCl_2$ product is then fed to the electrolytic cell. This process is schematically shown in Figure 20.[1/] The hydrochloric acid is produced from the chlorine made during the electrolysis of the molten bath of magnesium chloride.

Magnesium chloride may also be produced by using the final sea water bitterns from solar salt producers. This occurs in the Inorganic Division of FMC Corp. plant in San Diego county, California which reports production of $MgCl_2$ from the purchases salt-work bitterns[2/] [3/]. The company further evaporates the bittern using artificial evaporation. The additional salt and mixed potassium-magnesium salts are discarded. Further evaporation yields bischofite ($MgCl_2.6H_2O$) crystals[4/].

SCHEMATIC FLOWSHEET FOR THE PRODUCTION OF MAGNESIUM CHLORIDE FROM SEA WATER

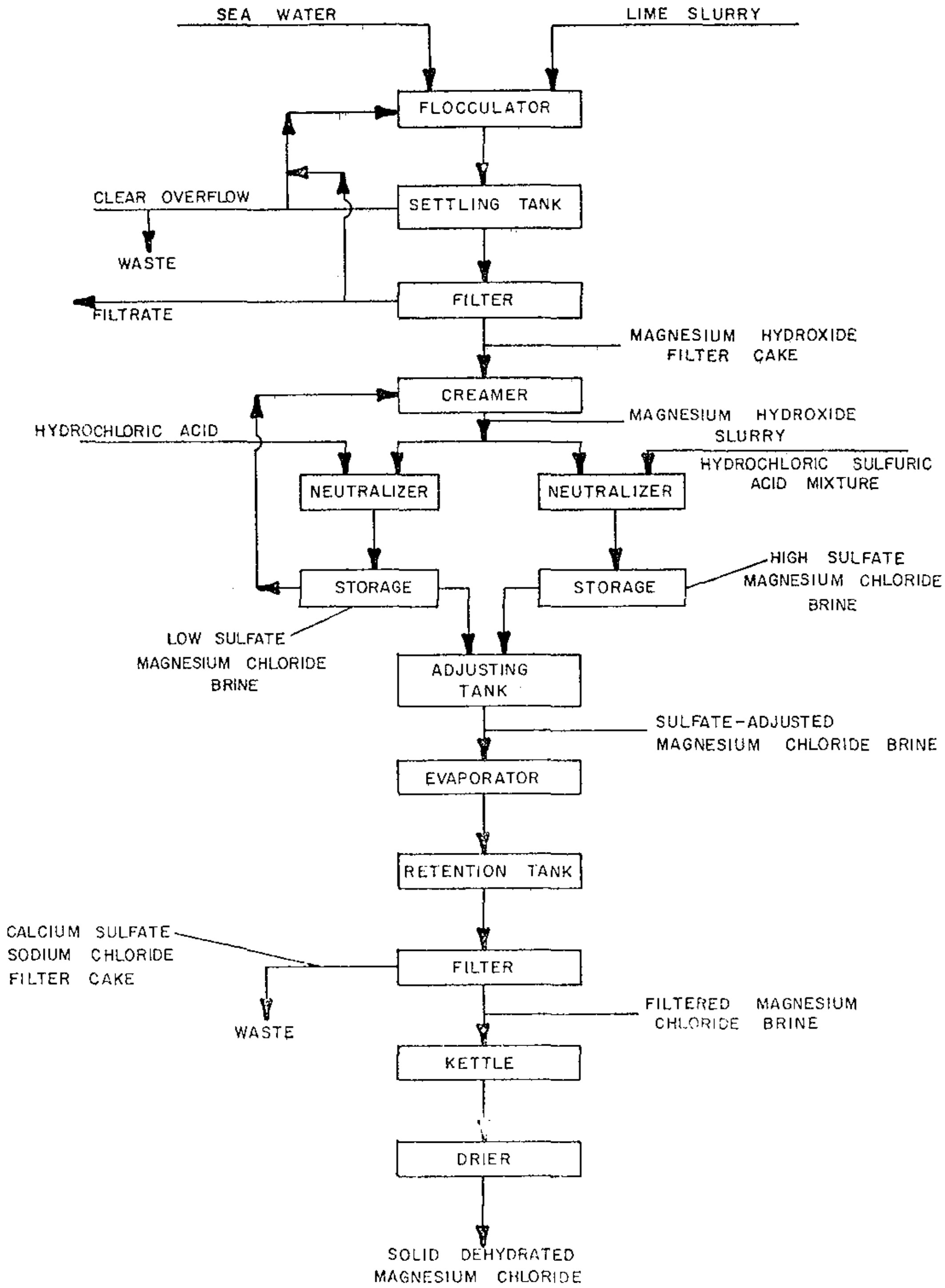

FIGURE 20
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Magnesium Chloride By-product from Potash Ore Processing

In several countries of Europe, carnallite ($KCl.MgCl_2.6H_2O$), kainite ($KCl.MgSO_4.3H_2O$), and other mixed sylvinite with magnesium salts are mined for the production of potash. These operations yield magnesium chloride as a by-product which sometimes is used but is more often a waste material. In the United States, the IMC Corp. and the Duval Corp. mine langbeinite ($2\ MgSO_4.K_2SO_4$) which, after processing, yields $MgCl_2$ brine as a by-product. At the present this $MgCl_2$ is wasted. Some years ago, IMC produced hydrochloric acid and MgO from the brine, but it is reported that the plant has been dismantled.

Magnesium Chloride From Naturally Occurring Brines

Brines containing magnesium chloride are formed throughout the world, both above and underground. In the potash section, the above-ground brine operation containing magnesium chloride was discussed (Bonneville and Great Salt Lake operations in Utah and the Dead Sea Works in Israel). Although different in final composition, all the brines are high in magnesium chloride content and are a potential source for making that salt. At present, of four operations described in that section, only one is using the residual brine. The NL Industries, Inc., at Great Salt Lake, will be using the magnesium chloride for making the metal. On several occasions, Dead Sea Works has made plans to produce magnesium oxide and hydrochloric acid. The latter would be used to react with phosphate rock found nearby to produce phosphoric acid. Apparently, these plans have not yet materialized.

Recovery of magnesium chloride from underground brines has been practiced for many years by the Dow Chemical Company at its facilities in Midland, Michigan. The underground brine contains chlorides (principally sodium, calcium, and magnesium) and about 0.15% of bromide. Chlorination is used to remove bromine and the brine is evaporated to crystallize NaCl. After separating this salt, the mother liquor is adjusted in composition so that on further evaporation, tachydrite ($2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$) is crystallized. Upon dissolution of the tachydrite crystals in hot water, bischofite ($MgCl_2 \cdot 6H_2O$) in a relatively pure state crystallizes. Washes and mother liquors at different stages are bled off or recirculated through the process. In addition to magnesium chloride, quantities of calcium chloride and bromine are produced[5/]. A schematic flowsheet is shown in Figure 22 in the calcium chloride section.

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V. CALCIUM CHLORIDE

INTRODUCTION

From an economic standpoint, the production of calcium chloride is similar to that of magnesium chloride. The market is restricted to few applications: major uses are to de-ice highways, lay dust on roads, refrigeration, additive in cement, and as a fill for tractor or big truck tires to improve traction. There are two sources of calcium chloride: as a by-product from soda ash production by the Solvay process and from naturally occurring brines.

GENERAL PROCESSES

Calcium Chloride as a By-product From Solvay's Plants

As was discussed in the soda ash section of this report, $CaCl_2$ is a by-product from its manufacture from salt and limestone. However, because of marketing difficulties, only a small fraction of this $CaCl_2$ is processed for a finished product and at present the remaining Solvay soda producers have a disposal problem of the waste $CaCl_2$ solution[1/].

The recovery of $CaCl_2$ from Solvay's plant is schematically shown[2/] in Figure 21. It is apparent that calcium chloride may be produced as the market may require in concentrated solution form, as flakes or solids (containing 72 to 80% $CaCl_2$), or anhydrous form.

Calcium Chloride From Naturally Occurring Brines

Natural occurring brines containing calcium chloride which is used for the production of this salt have been reported in Michigan, West Virginia, and California in the United States[2/3/].

CALCIUM CHLORIDE PRODUCTION AS BY-PRODUCT FROM SODA ASH, SOLVAY'S PLANTS

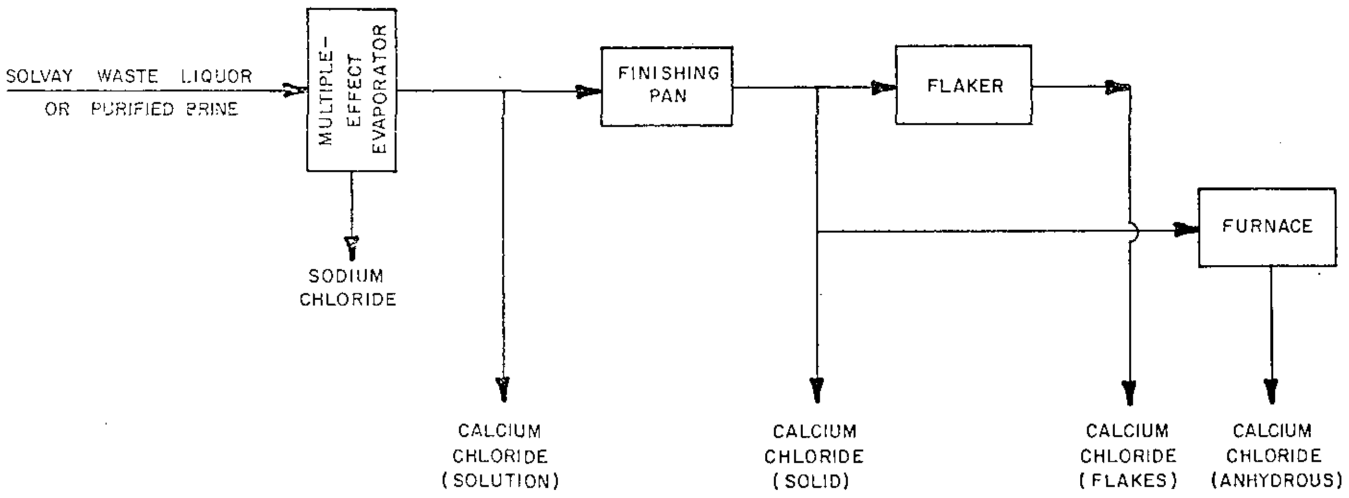

FIGURE 21
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The production by Dow Chemical Co. at Midland, Michigan, has been described briefly in the magnesium chloride section. The calcium chloride is probably obtained from the mother liquor after the decomposition of the tachydrite as shown in Figure 22, taken from U. S. Patent 1,796,920[4/].

Information about the production of calcium chloride from underground brine deposits in West Virginia is scarce. The composition of one such brine is given by Lefond and is presented in Table 22. The brine also contains small amounts of bromide, potassium, and strontium.

Table 22

Composition of One Underground Brine From West Virginia (Putman County)

(% by weight)

NaCl	12.7 %
$CaCl_2$	3.9 %
$MgCl_2$	1.2 %
$BaCl_2$	0.07%

The only commercial production of calcium chloride from brines occurs at Bristol Lake in southern California. Calcium chloride is produced from the brine that seeps into the excavations made during mining the uppermost bed of halite. The brine essentially contains only NaCl (14.6%) and $CaCl_2$ (12.0%) with trace quantities of potassium, magnesium, and strontium[5/]. The brine is partially concentrated in the ditches through the surface, and additional evaporation is attained in solar evaporation ponds. The sodium chloride which crystallized out during this process

FLOWSHEET FOR THE RECOVERY OF VALUES FROM MIDLAND, MICHIGAN BRINES

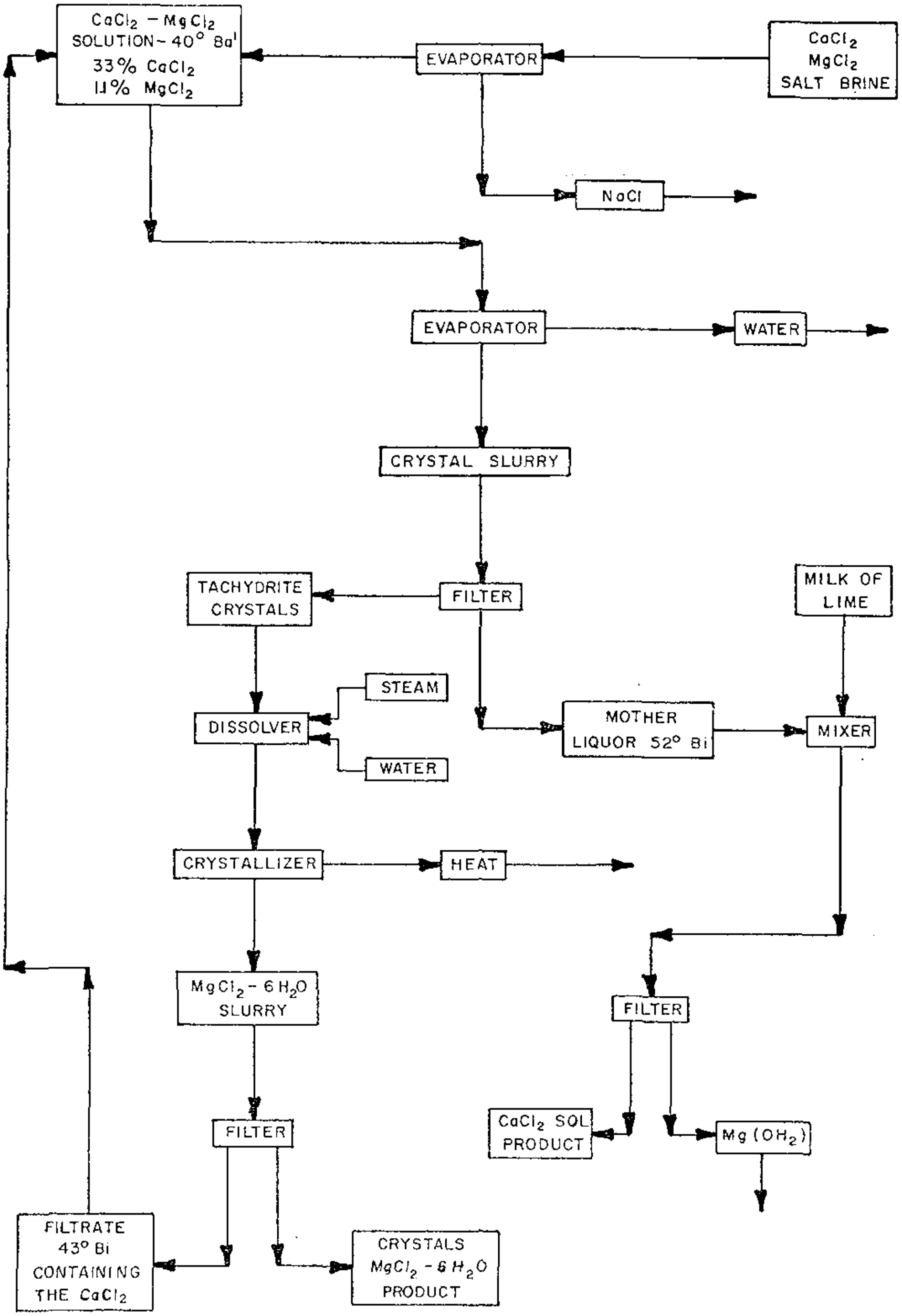

FIGURE 22

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is wasted. Artificial evaporation results in a flake calcium chloride product. The major steps of the process[5/] are shown in Figure 23.

FLOWSHEET FOR THE RECOVERY OF CALCIUM CHLORIDE USING THE BRINES FROM BRISTOL LAKE, CALIFORNIA

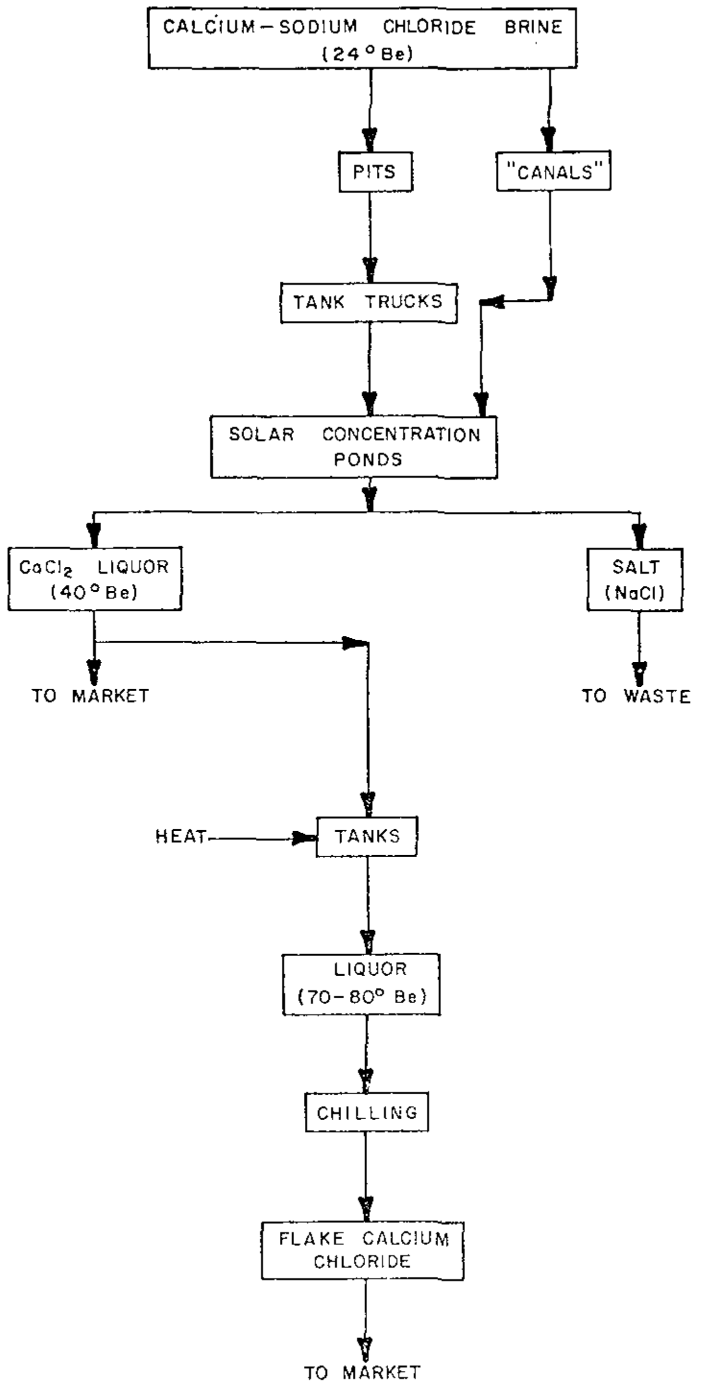

FIGURE 23

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VI. BORAX

INTRODUCTION

The United States has the largest known boron mineral deposits, all located in Southern California. Deposits which are commercially exploited are also found in Turkey, U.S.S.R., Argentina, Chile, and other countries. Most of the boron ore is exploited by mining and only two operations -- both in Searles Lake, California -- recover boron values from natural brines.

GENERAL PROCESSES

Mining and Processing Boron Minerals

Borax ($Na_2B_4O_7 . 10H_2O$) and kernite ($Na_2B_4O_7 . 4H_2O$) are the main boron minerals which are mined and processed near Boron, California, by the U. S. Borax and Chemical Corporation. The ore is open pit mined, crushed, and dissolved in hot water or weak borax mother liquor. After clarification, the mother liquor is fed to different crystallizer units where, under controlled temperature, borax or the pentahydrate are obtained as products. Part of the borax is used to make other marketable products such as anhydrous borax and boric acid[1/2/].

Processing Brines Containing Boron Values

There are two commercial plants in the world where borax is recovered from brines, both plants using the Searles Lake brine as feed material. The two operations are Kerr-McGee Chemical Corp. and the Stauffer Chemical Co., already referred to in the soda ash section. Soda ash is a co-product of the borax recovery.

The Kerr-McGee plant recovers borax with two types of feed material resulting from the use of two different initial brines: lower and upper structure. One is the mother liquor separated from the potash crystallizer, called Mother Liquor 1, as indicated in Figure 6 (Potash Section, p. 57). The other is $NaHCO_3$ impurified borax slurry separated from the cooling of the mother liquor from the $NaHCO_3$ crystallization shown in Figure 17 (Soda Ash Section, p. 90). The overall flowsheet of this section of the Kerr-McGee complex, taken from Bixler and Sawyer[2/], is presented in Figure 24. It may be of interest to mention here that by mixing these two flows, an improvement in borax recovery is accomplished. During the evaporation process to crystallize potash, some tetraborate reacts with the sodium carbonate in solution producing metaborate which is much more soluble than the tetraborate:

$$Na_2B_4O_7 + Na_2CO_3 \rightarrow 4NaBO_2 + CO_2.$$

When this ML-1 is mixed with the impure borax obtained from the carbonation process, the metaborate is converted back to the tetraborate by reaction with $NaHCO_3$:

$$4NaBO_2 + 2NaHCO_3 \rightarrow Na_2B_4O_7 + 2Na_2CO_3 + H_2O.$$

Fine crystals are recycled to improve the kinetics of the pentahydrate $Na_2B_4O_7$ crystallization. Crude borax is recrystallized to increase the purity of the product.

The Kerr-McGee plant also recovers additional amounts of boron values by solvent extraction techniques from dilute solution which are not

BORAX RECOVERY FLOWSHEET AT THE KERR-McGEE COMPLEX, TRONA, CALIFORNIA

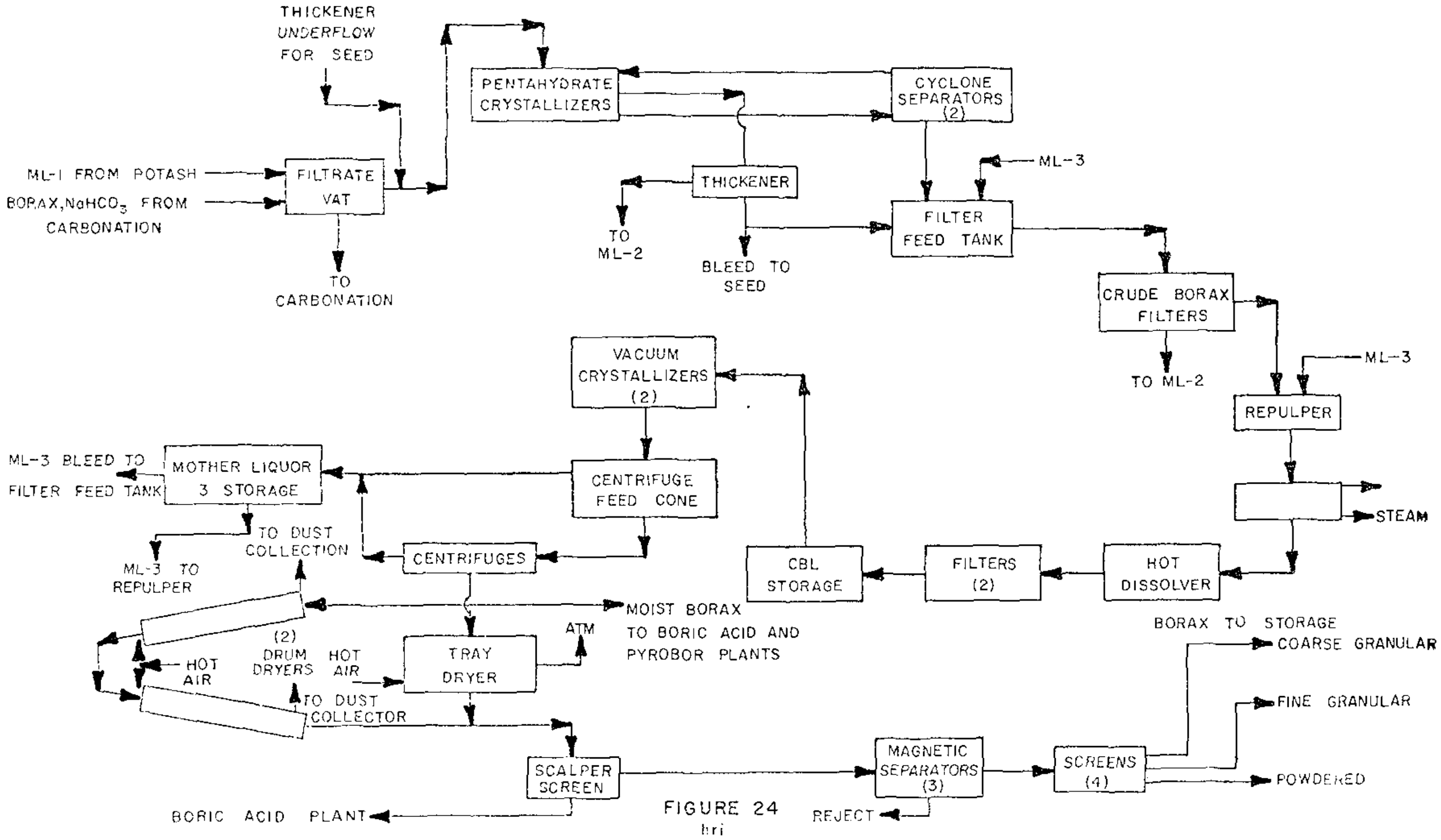

FIGURE 24

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amenable for economic recovery by a conventional crystallization process. Specific extractants for boron were developed[3/][4/] which can be dissolved in an inert, insoluble-in-water liquid such as kerosene. A series of aromatic or aliphatic polyols are used to extract the boron values from the dilute solutions. The specific extractant selected for the commercial operation has not been revealed, but preference has been indicated[4/] for the use of 2-chloro-4 (1,1,3,3, tetramethylbutyl)-6-methyolphenol. The extraction is performed in a single stage. The boron loaded organic phase is then stripped in a countercurrent fashion using four stages. Dilute sulfuric acid is used as stripping agent. Because of the natural alkalinity of the feed, the acid strip yields a solution of boric acid and alkali sulfate. High purity boric acid is made by fractional crystallization[5/][6/][7/]. Figure 25, taken from Havighorst[6/], schematically shows the steps of this novel process.

Borax is produced by Stauffer using the filtrate from the sodium bicarbonate cake shown in Figure 17 (Soda Ash Section, p. 89). This filtrate is mixed with some additional brine from the wells and refrigerated in the presence of borax seed crystals. After a solid-liquid separation, the borax is processed as diagrammatically shown in Figure 26 (taken from Ver Planck[8/]).

RECOVERY OF BORON VALUES BY SOLVENT EXTRACTION AT KERR-McGEE'S PLANT, TRONA, CALIFORNIA

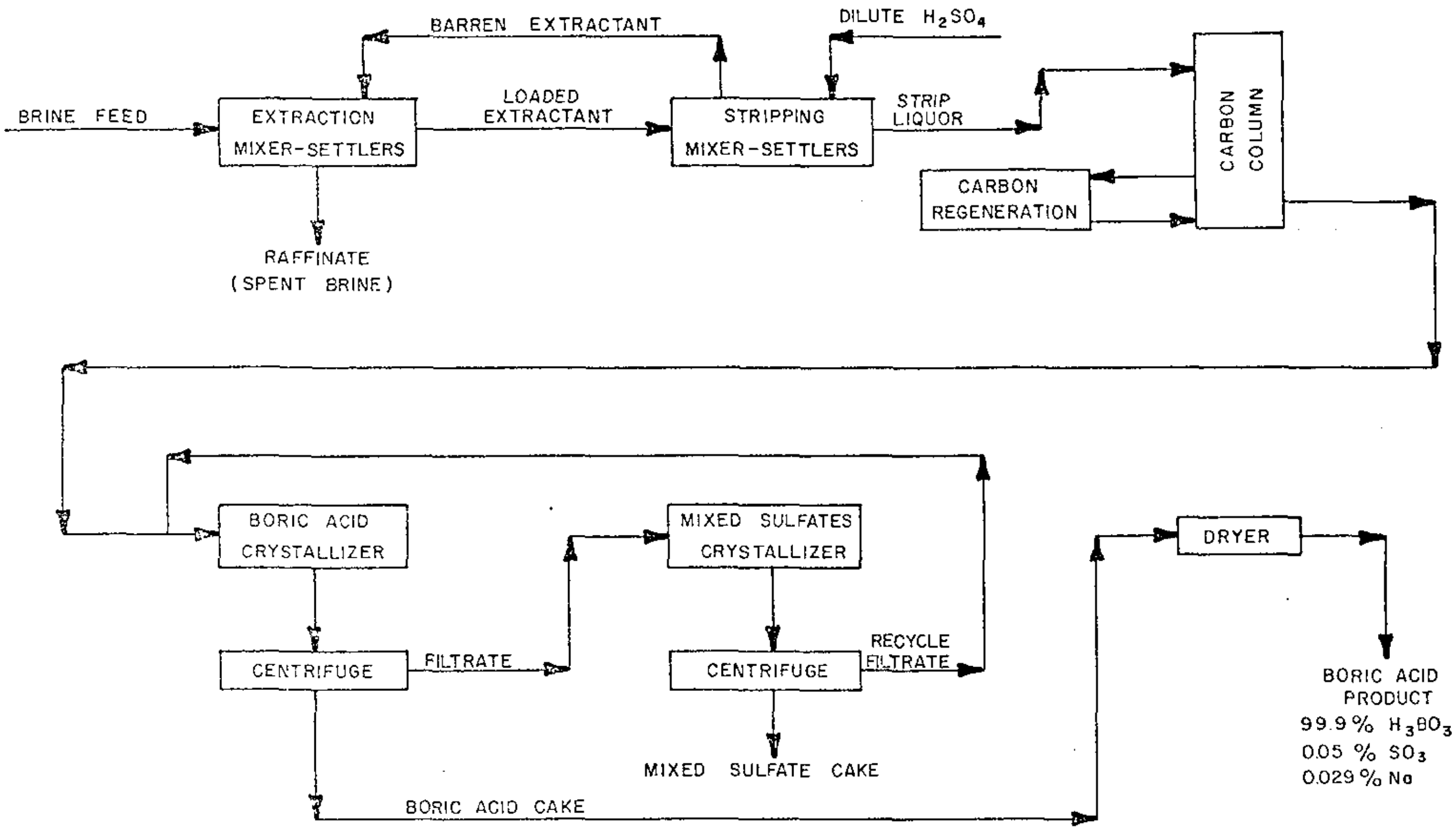

FIGURE 25
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VII. BROMINE

INTRODUCTION

Historically, bromine production has been associated with sea water, naturally occurring brines, and as a by-product from potash production by crystallization methods. Therefore, it has been available to nearly every country in the world. However, few countries are producing bromine commercially. The principal producer is the United States which produces and consumes about three-fourths of the total world production.

In all the bromine resources mentioned, the element occurs as a soluble bromide salt. Therefore, most commercial processes used both in the past and the present involve an initial common step. This is the oxidation of bromide to bromine by the use of chlorine gas:

$$2Br^- + Cl_2 \rightarrow Br_2 + 2Cl^-$$

This first step is followed by driving off the liberated bromine from the solution, condensation or fixation, and final purification.

GENERAL PROCESSES

Bromine From Sea Water

Bromine content of sea water averages about 67 mg per liter. Therefore, at 100% recovery, to produce one pound of bromine requires the treatment of 1,789 gallons of sea water. Potentially, sea water is by far the major reserve of bromine of the world. However, production of bromine directly from sea water in the United States ceased in 1969[1/], but it continues to be the only source in other major bromine producing countries such as Japan.

The so-called "blowing-out" process is well adapted for bromine production from sea water[2/]. Sea water is acidified with sulfuric acid to a pH of 3.5 to neutralize the bicarbonates present and also to avoid losses of chlorine and bromine by hydrolysis. Chlorine gas and acidified sea water are contacted in a blowing-out tower. From there, the liberated bromine is removed by injecting an air stream countercurrently. The air stream carrying the excess chlorine and bromine is then absorbed chemically in another tower. There are several variations of this process:

1. A solution of Na_2CO_3 is used in the following reactions:

   $3Na_2CO_3 + 3Br_2 \rightarrow 5NaBr + NaBrO_3 + 3CO_2$

   $6Na_2CO_3 + 5Cl_2 + Br_2 \rightarrow 10NaCl + 2NaBrO_3 + 6CO_2$

   Then crude bromine is produced by sulfuric acid acidification:

   $5NaBr + NaBr_2O_3 + 3H_2SO_4 \rightarrow 3Br_2 + 3Na_2SO_4 + 3H_2O$

2. The air stream is absorbed with SO_2 and water:

   $Br_2 + SO_2 + 2H_2O \rightarrow 2HBr + H_2SO_4$

   $Cl_2 + SO_2 + 2H_2O \rightarrow 2HCl + H_2SO_4$

The solution obtained is again chlorinated and crude bromine is produced:

$2HBr + Cl_2 \rightarrow Br_2 + 2HCl$

In both flowsheets, the crude bromine may be further purified by distillation.

BORAX PRODUCTS FLOWSHEET FROM SEARLES LAKE BRINE AT STAUFFER CHEMICAL CO.

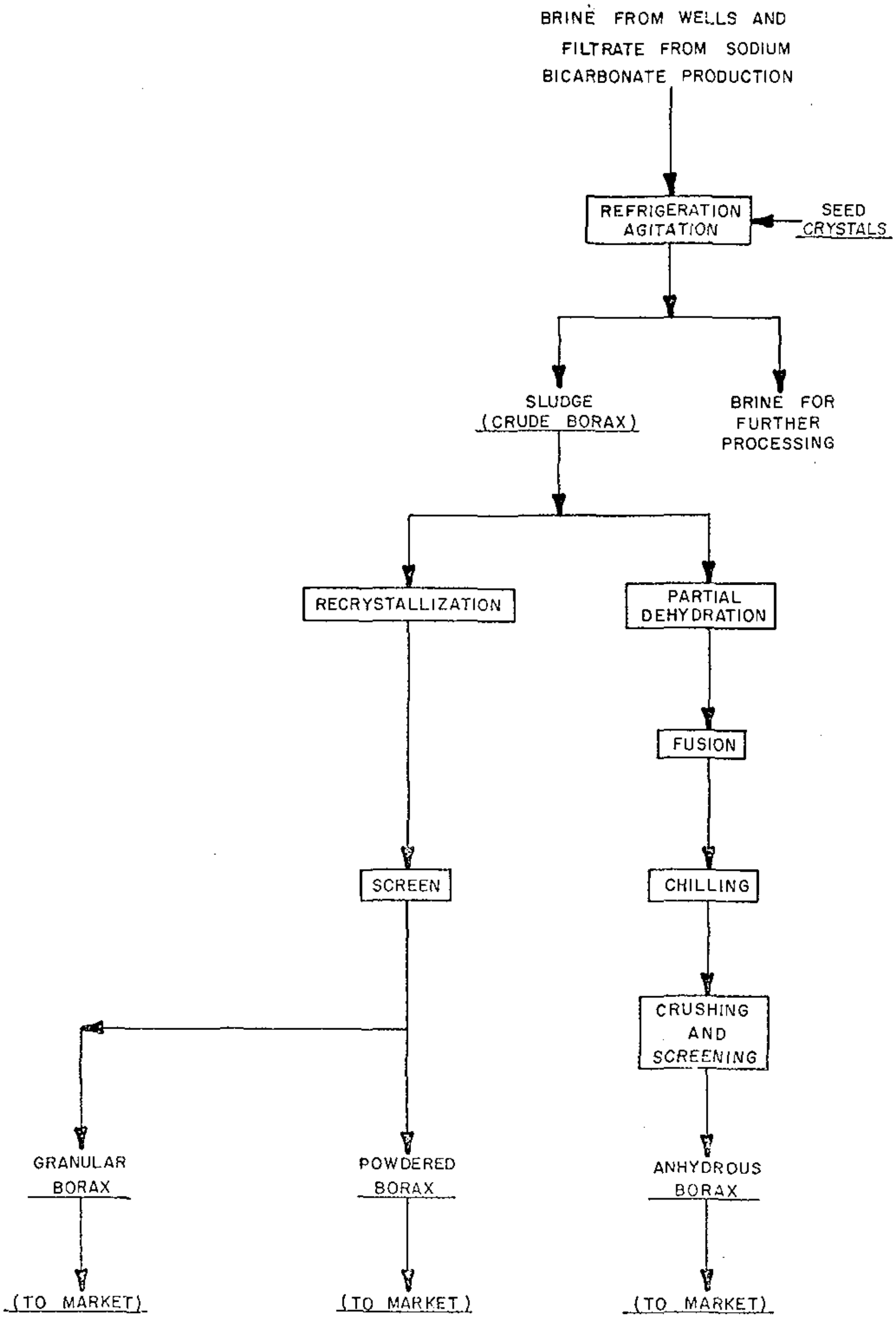

FIGURE 26

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A simplified flowsheet of bromine recovery from sea water by the SO_2 absorption method is shown in Figure 27, taken from Faith, W.L., et al[3/].

Bromine from Naturally Occurring Brines

In many cases, the bromine content of natural brines is higher than in sea water and its recovery can be justified.

In recovery of bromine from natural brines, the usual method is the so-called "steam-out" process, which is more satisfactory than the "blowing-out" procedure used for sea water. The basic principle of chlorination is the same but instead of air, the preheated brine is treated with steam to remove the liberated bromine. Instead of dealing with air-halogen for the second step of the recovery process, the method uses a steam-halogen stream. Therefore, there are variations in the "steam-out" route in the performance of this second step.

The most common procedure is to condense the steam-halogen stream and subject the condensate to distillation. A simplified flowsheet of this method is presented in Figure 28[4/].

Another method of processing the steam-halogen stream is to condense it and separate the bromine and water solution by gravity. The bromine present in the water layer can be recovered by blowing with air and the resulting vapor passed through an absorbing tower filled with wet iron filings. Thus the bromine will combine with the iron:

$$Br_2 + Fe \rightarrow FeBr_2$$

PRODUCTION OF BROMINE FROM SEA WATER

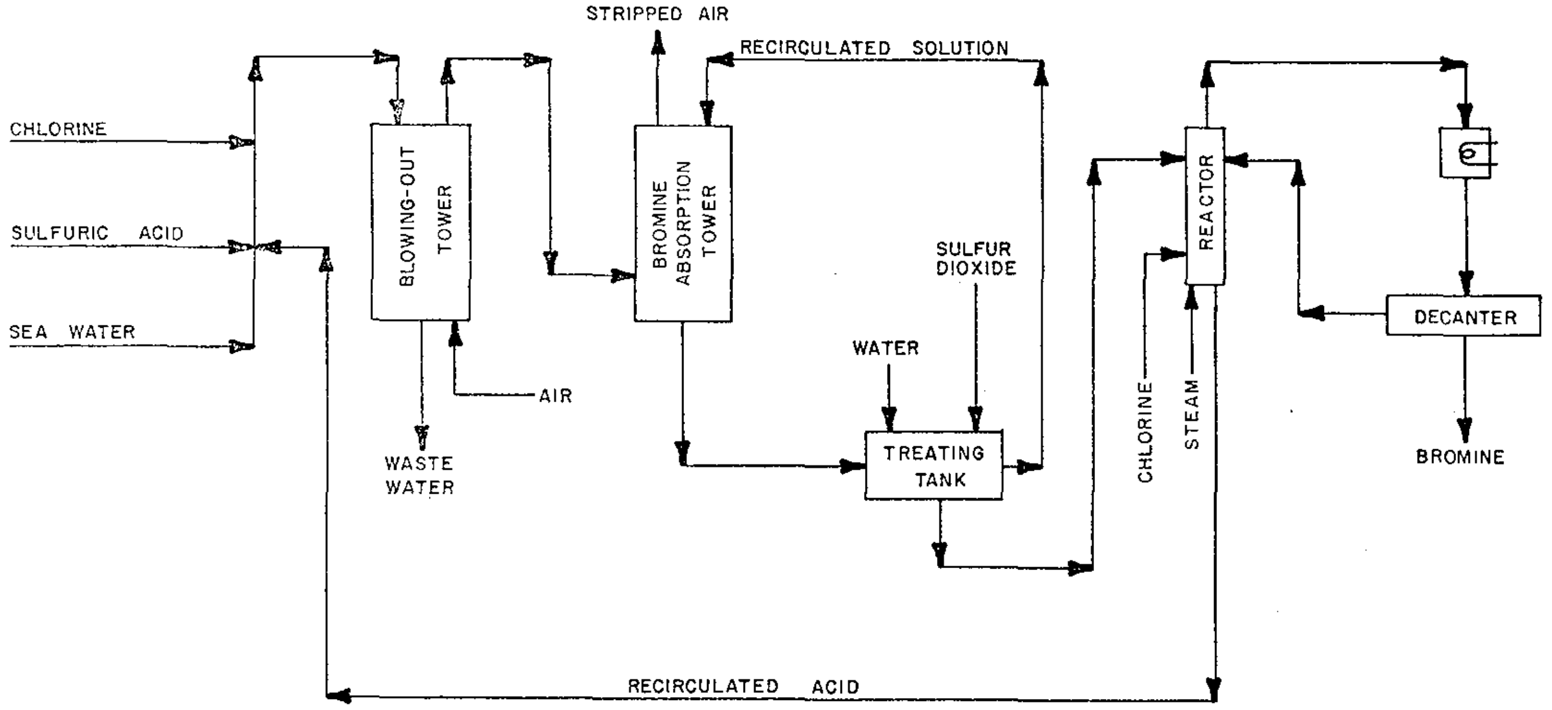

FIGURE 27
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STEAM-OUT AND CONDENSATION PROCESS FOR BROMINE RECOVERY FROM BRINES

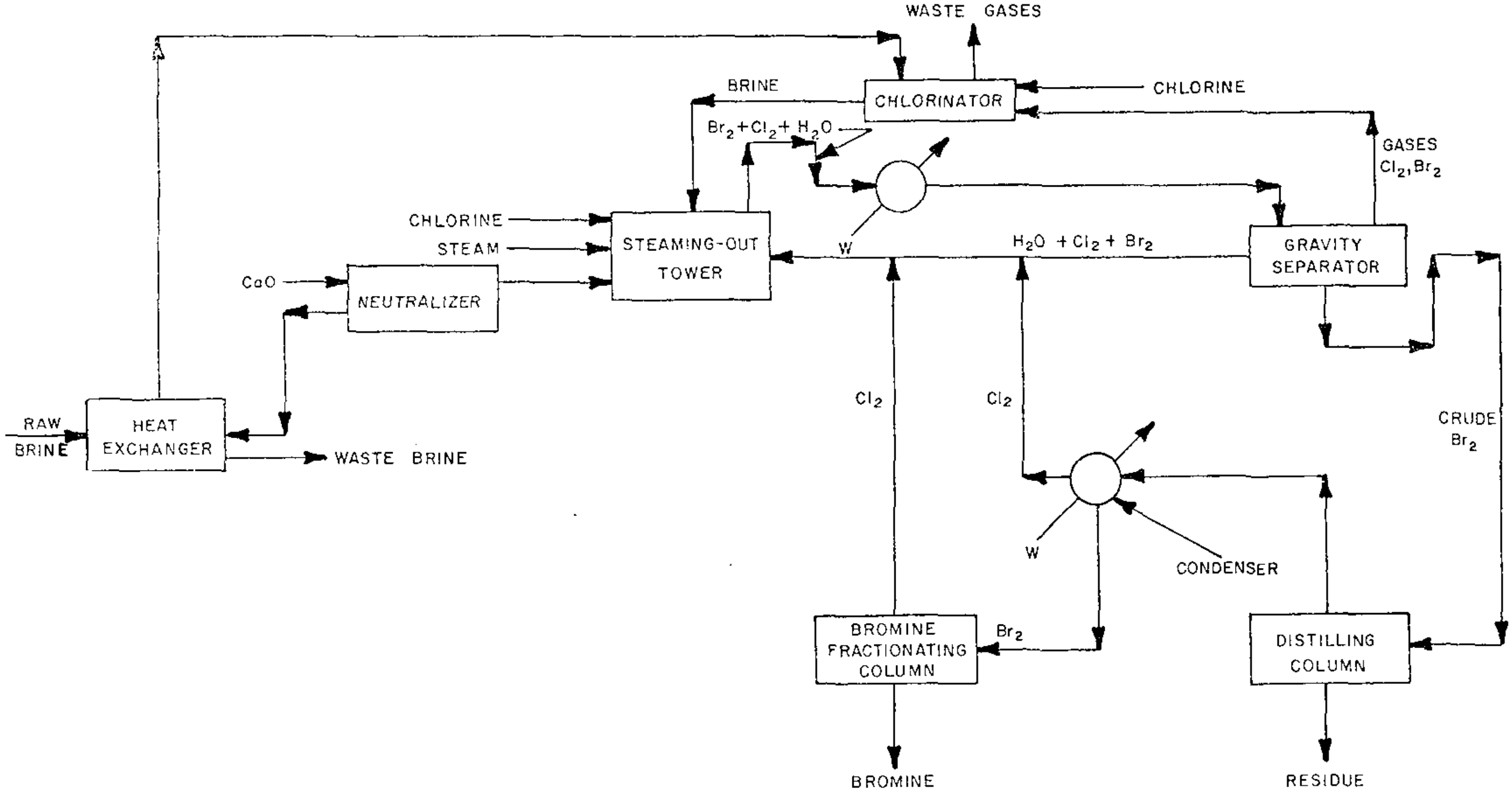

FIGURE 28
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The concentrated solution of the ferrous bromide is treated with chlorine:

$$FeBr_2 + Cl_2 \rightarrow FeCl_2 + Br_2$$

Since the bromine is only slightly soluble in the ferrous chloride solution, it settles and is separated. A schematic flowsheet is shown in Figure 29[3/].

Another method was adopted by the Dead Sea Bromine Co. in December, 1956, in a new plant to produce 1,250 tons a year of bromine using the clarified $MgCl_2$ brine from the potash plant[5/]. However, in this flowsheet the liberated bromine is "blown-out" with air instead of steam. The air-halogen passes through a glass chip-packed dechlorination tower in contra-current with a raw brine stream. The dechlorinated air-bromine stream is then absorbed in another column by a solution of about 350 g/l NaBr which has been cooled to about -18°C. The bromine saturated NaBr solution obtained contains about 35% by weight of bromine. This solution is heated and the water-bromine condensed and separated in a decanter. The hot NaBr solution is refrigerated and recycled. Figure 30 shows this process schematically[5/]. Bromine recovery is about 90% and the process requires less energy and chemicals than other processes.

Bromine is also recovered as a by-product from potash operations in Europe. The potassium bromide-rich solutions are treated by methods already described for the production of bromine.

STEAM-OUT, CONDENSATION, AND IRON TREATMENT PROCESS FOR THE RECOVERY OF BROMINE FROM BRINES

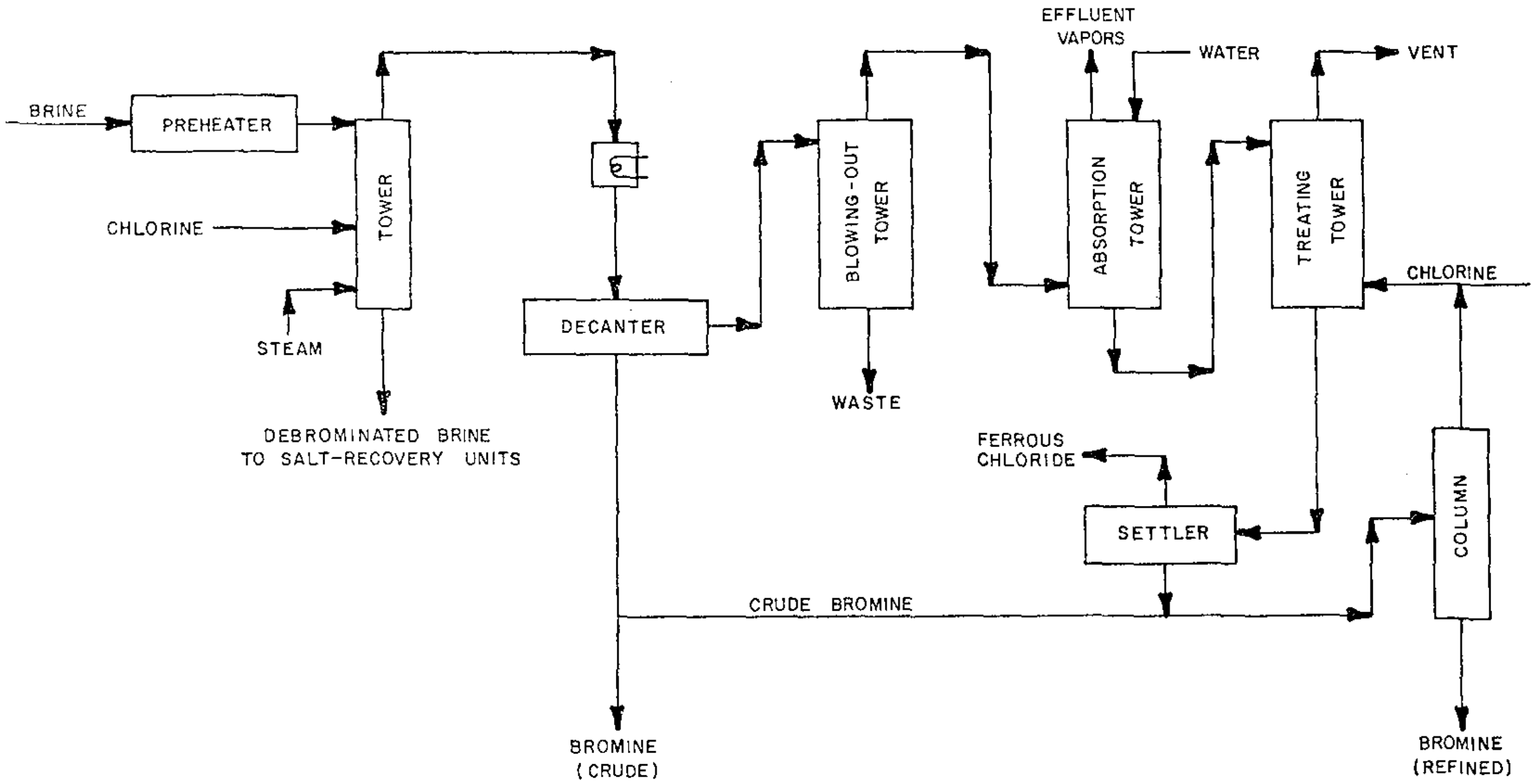

FIGURE 29
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RECOVERY OF BROMINE FROM DEAD SEA POTASH WORKS IN ISRAEL

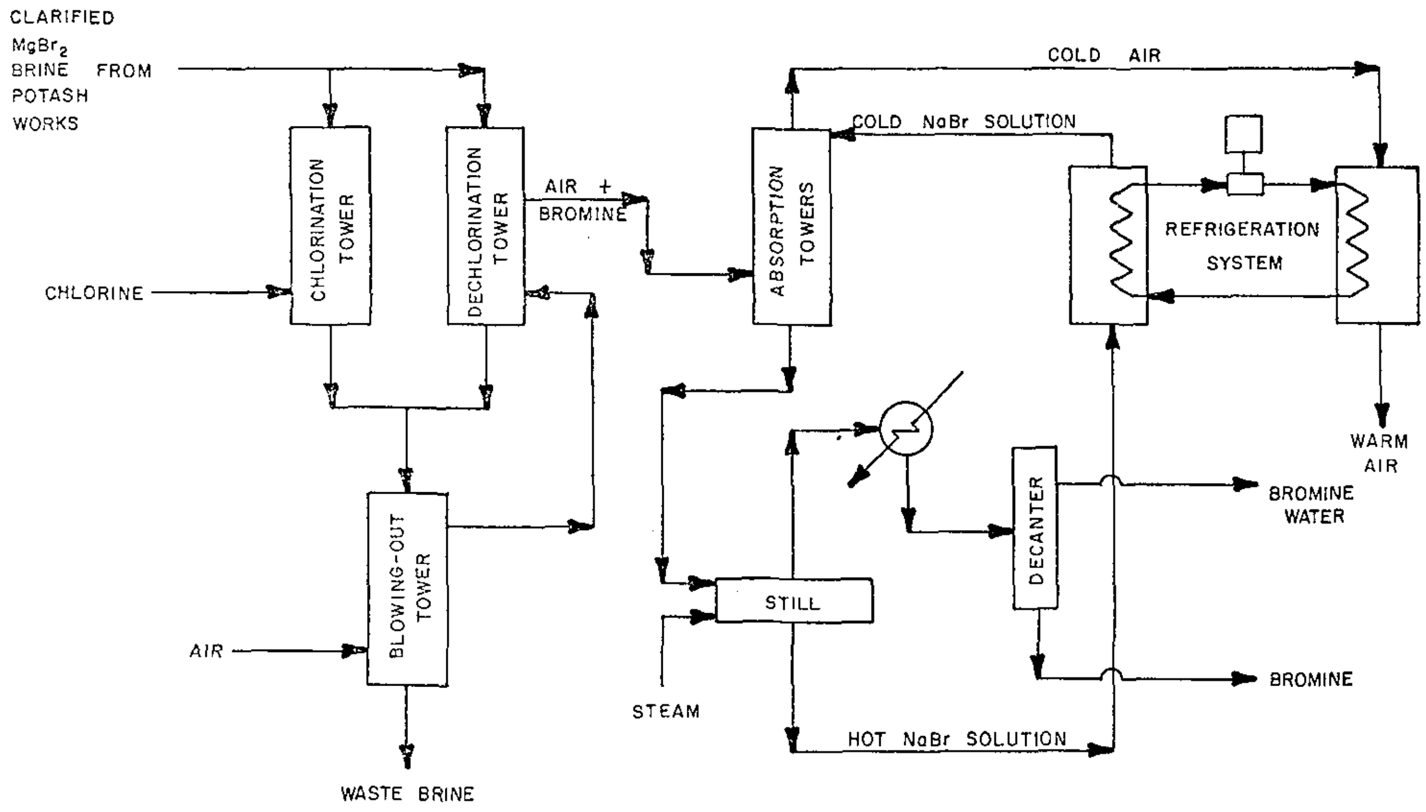

FIGURE 30

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VIII. IODINE

INTRODUCTION

World resources of iodine include: the nitrate deposits of Chile, oil well brines, seaweed, and naturally occurring brines. Therefore, the technology for iodine recovery varies according to the source. From the standpoint of production, the recovery of iodine from oil well brines (Japan) and by-products from the caliche ore (Chile) are by far the most important. During the last few years, Japan and Chile produced over 90% of the total iodine of the world. In the United States iodine is produced from oil well brine and from the underground brines of Michigan.

GENERAL PROCESSES

Production of Iodine From Oil Well Brines and Other Brines

Several methods are used for the recovery of iodine from this source. One is similar to that used in the recovery of bromine from sea water. The soluble iodade is oxidized to iodine using chlorine, followed by a "blow-out" with air. The air-halogen stream is absorbed in SO_2-H_2O in a HI-H_2SO_4 liquor. Iodine is obtained by treating the solution with chlorine. The chemical reactions involved are similar to those described for bromine recovery:

$$2I^- + Cl_2 \rightarrow I_2 + 2Cl^-$$

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4$$

$$2HI + Cl_2 \rightarrow I_2 + 2HCl$$

Figure 31 schematically shows the flowsheet of this process[1/] which is used for oil well brine as well as the underground brines of Michigan. In

RECOVERY OF IODINE FROM BRINES

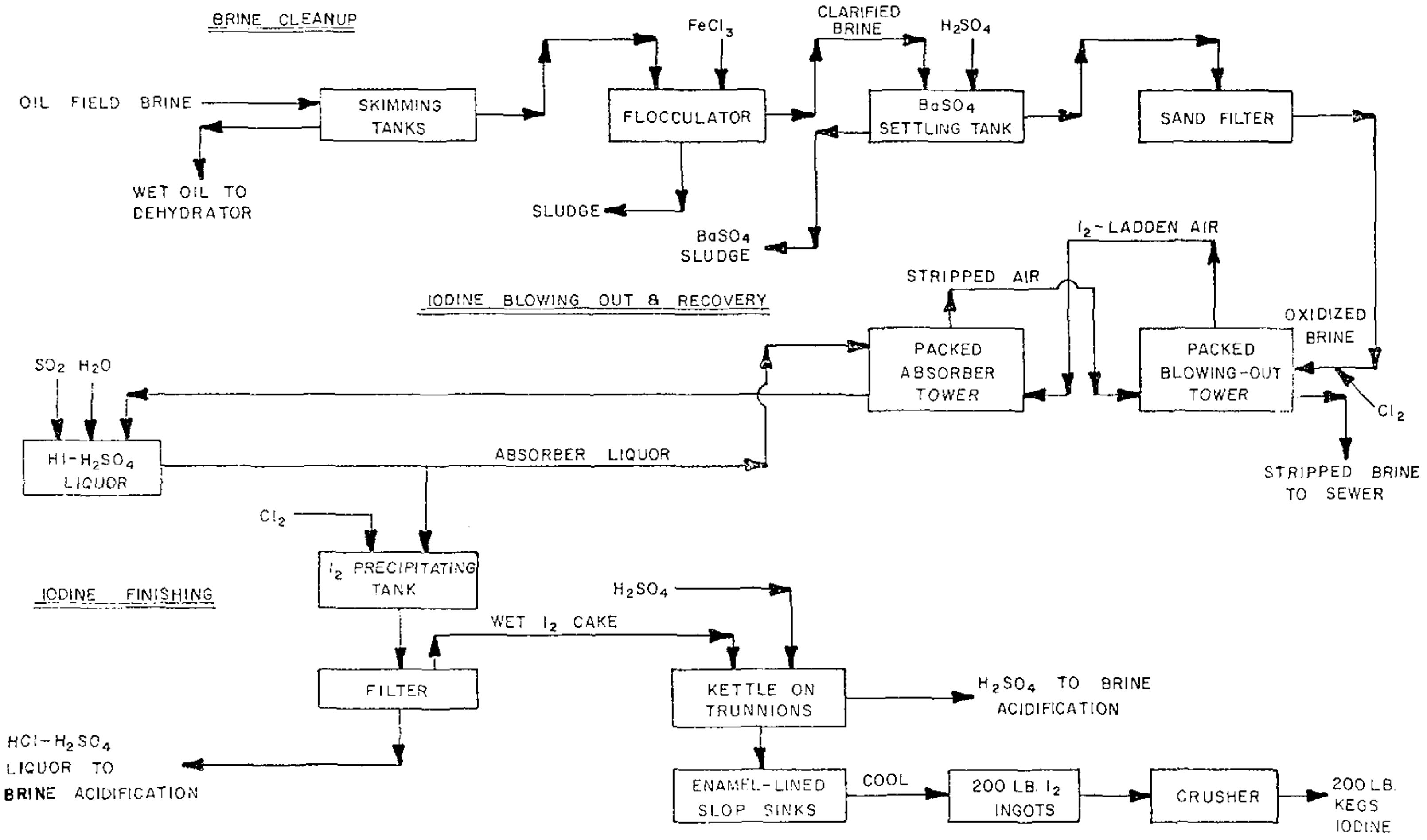

FIGURE 31

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the latter case, the brine cleanup section is not necessary.

Other processes differ in the way the iodine liberated by oxidation with chlorine is absorbed and purified. One method uses activated carbon which then is eluted with caustic soda and the purified iodine is obtained by another chlorination step. Another method is to react the iodine with copper to produce insoluble cuprous iodide. This salt is then treated with chlorine to recover iodine.

Production of Iodine From Chilean Caliche

The processes used are unique in the world because the nitrate deposit contains iodine in the form of the iodate minerals, primarily $Ca(IO_3)_2$-lautarite and $Ca_2(IO_3)_2(CrO_4)$-dietzeite. The mother liquor from the nitrate refineries contain between 6 and 12 g/l iodine in iodate form.

In one process the mother liquor is mixed with sufficient sodium bisulfite to convert the iodate to iodide:

$$2IO_3^- + 6NaHSO_3 \rightarrow 3I_2 + 6HO^-$$

The iodine is filtered and purified by sublimation.

In the other process, sulfur dioxide made by burning sulfur is contacted countercurrently with the iodate mother liquor and iodine is produced[2/] by the following reaction:

$$2NaIO_3 + 4H_2O + 5SO_2 \rightarrow Na_2SO_4 + 4H_2SO_4 + I_2$$

A schematic flowsheet of this process, taken from Shreve[2/], is shown in Figure 32.

IODINE FROM CHILEAN NITRATE MOTHER LIQUOR

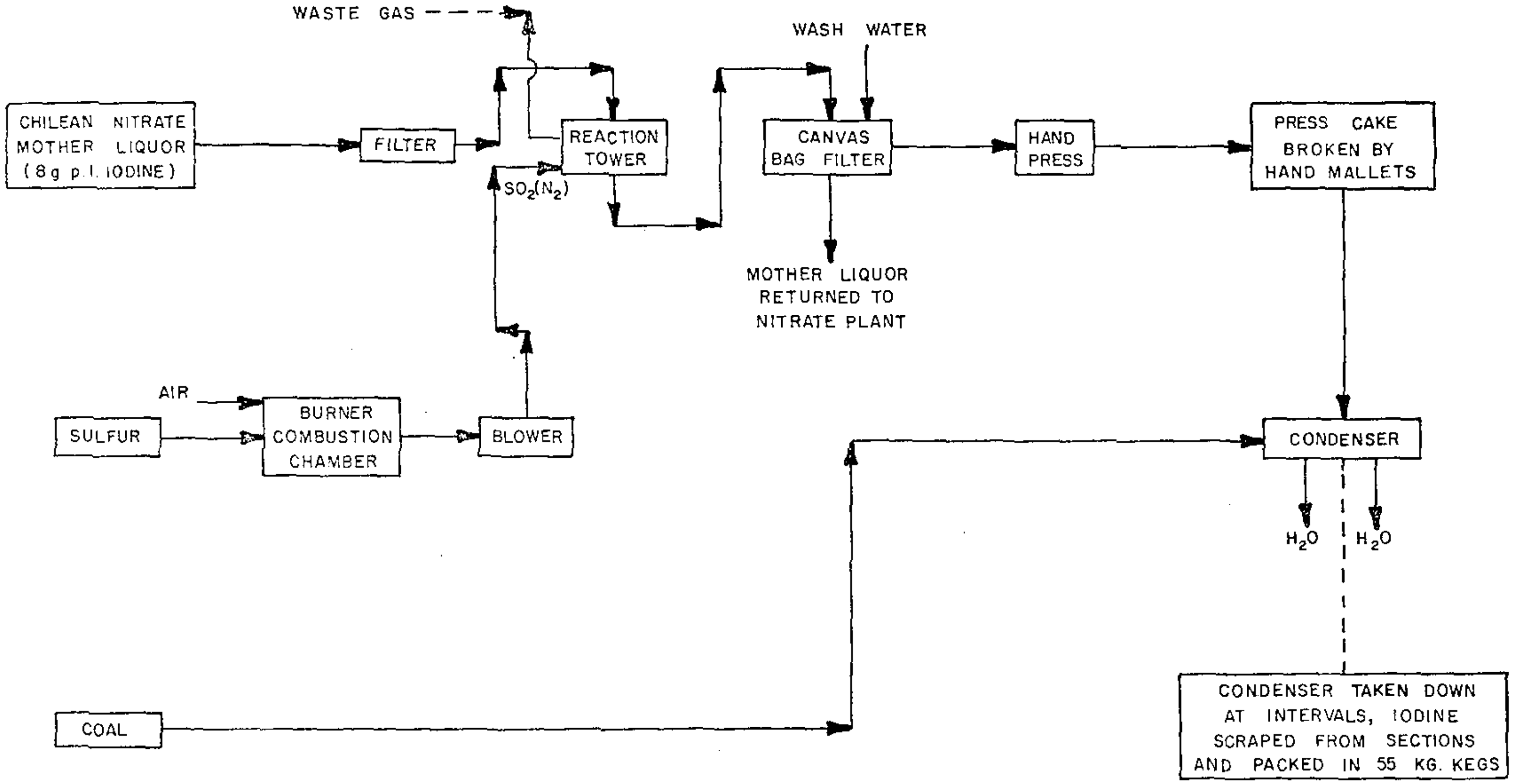

FIGURE 32

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IODINE BIBLIOGRAPHY

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IX. LITHIUM
INTRODUCTION

Lithium and lithium compounds are most frequently produced by treatment of lithium ores obtained by open-pit or underground mining. Spodumene and lepidolite are the most common lithium minerals in use. The processing of these or other ores will not be discussed here. Rather, this discussion will be limited to a description of the only two operations in the world which use brine as a commercial source of lithium. Both are located in the United States: Kerr-McGee Chemical Co. (former American Potash & Chemical Corp.) at Trona, California, and Foote Mineral Co. at Silver Peak, Nevada. Also mentioned is the potential future operation of Great Salt Lake Chemical Co. which may produce lithium compounds from their operation in Utah.

Lithium from Trona Brines

The Kerr-McGee operation in Trona, California, produces lithium carbonate as a co-product from the complex brine processing of the feed brine. The lithium values are recovered from processing of crude burkeite obtained after the artificial evaporation of the original brine (see Figure 18, page 91). The burkeite dissolution yields a solution in which the dilithium-sodium phosphate is in suspension. Fatty acid soap is added to float the lithium salt in specially designed flotation tanks working in parallel (four of them with 10,000-gallon capacity each). The floated salt is dried and treated with sulfuric acid in a digester tank. The sludge of lithium and sodium sulfate is separated from the phosphoric acid by centrifugation. The solid mixed sulfates are dissolved and the lithium is recovered as lithium carbonate by addition of soda ash. A diagrammatic flowsheet for this plant taken from Schreck[1/] is presented in Figure 33 The concentration of lithium in the original brine is 0.021% as LiCl (see Table 16 in the Potash section, page 61).

Lithium From Silver Peak, Nevada

The Silver Peak, Nevada, operation by Foote Mineral Company contributes over 25% of the domestic supply of lithium[2/]. It is a unique operation because it is the only commercial operation in the world where lithium is recovered from brines by solar evaporation followed by chemical treatment. The original brine is obtained from 200 to 800-foot deep wells by pumping. This brine contains 0.24% lithium expressed as LiCl. The total composition, assuming a hypothetical combination of the ions, is tabulated in Table 23.

Table 23

Composition of Well Brine at Silver Peak, Nevada
(% by weight)

NaCl	14.9 %
KCl	1.53%
Na_2SO_4	0.87%
LiCl	0.24%
$CaSO_4$	0.17%
$MgCl_2$	0.16%
Total dissolved solids	17.87%

RECOVERY OF LITHIUM AT KERR-McGEE PLANT, TRONA, CALIFORNIA

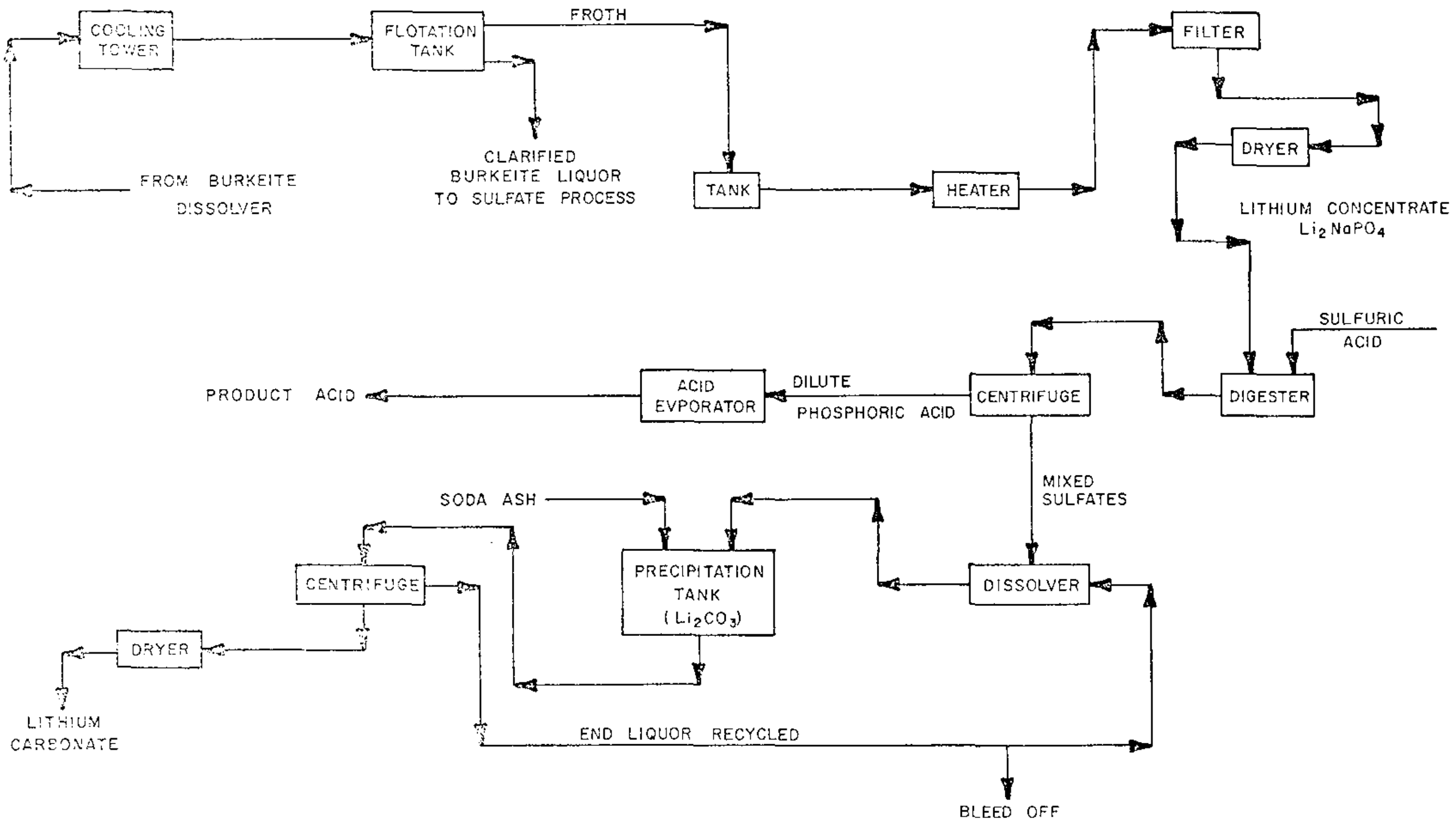

FIGURE 33
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The operation has about 1,600 acres of solar ponds divided into nine sections. As solar evaporation progresses, the brine becomes richer in lithium content. The sequence of crystallization as given by Barrett[2/] is shown in Table 24. Precipitation of $Mg(OH)_2$ and gypsum in Pond 5 is due to the addition of slaked lime to the brine at this point.

Table 24

Crystallization Sequence During the Solar Evaporation of Silver Peak Brine

Pond No.	Area (Acres)	Li Concentration (ppm)	Solid Phases
1	760	680	None
2	520	780	NaCl
3	90	930	NaCl
4	86	1200	NaCl
5	46	1400	NaCl, gypsum, $Mg(OH)_2$
6	41	1900	NaCl, $CaCO_3$
7	17	2400	NaCl, Glaserite
8	13	3100	NaCl, Glaserite, KCl
9	14	5000	NaCl, Glaserite, KCl

The final brine is pumped to a nearby chemical precipitation plant where Li_2CO_3 is recovered after soda ash addition.

Lithium From the Great Salt Lake, Utah

As shown in the flowsheet of Figure 10(Potash Section, page 68), the Great Salt Lake Minerals and Chemical Co. is planning to recover the lithium values from the final bitterns obtained by solar evaporation of the Great Salt Lake brine. This bittern contains approximately 0.70% lithium as LiCl. Another major constituent is magnesium in a concentration of about 30 to 33% as $MgCl_2$. The process to be used is not known at present, but it may be the one described in U. S. Patent 3,537,813[3/]. The proposed process is based on complexing the lithium present in the bittern preferentially with added $FeCl_3$ to form a lithium tetrahaloferrate. The complex is then solvent extracted with diisobutyl ketone or a mixture of tributyl phosphate and di-2-ethyl-hexyl phosphoric acid diluted in benzene. The extracted lithium can be stripped with either water or weak salt solution.

Lithium Bibliography

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SURVEY OF PROCESS TECHNOLOGY AND IDENTIFICATION OF PROBLEMS PRESENT IN MINERALS RECOVERY FROM GEOTHERMAL FLUIDS

In dealing with water solutions containing desired components, compounds, etc., there are two broad avenues of approach to the problem of recovering the desired component. These are:

1. Remove the water from the system, thereby recovering the desired material.
2. Remove the desired material directly from the system.

Geothermal fluids contain components whose concentrations range from parts per million to many parts per hundred. Therefore, it might appear that both avenues of approach might have merit.

Further elaboration of these two avenues into specific methodology for achieving the desired goal is as follows:

A. Water removal methods
    1. Steam evaporation
    2. Solar evaporation
    3. Hydrate formation with inorganic compounds
    4. Reverse osmosis
    5. Electrodialysis

Of the various water removal methods available, only the first two listed appear to have applicability to geothermal fluids.

Both reverse osmosis and electrodialysis are efficient producers of fresh water from brackish water, but are limited in the degree of concentration possible. This is of no consequence when dealing with brackish water of 1000 to 4000 ppm dissolved solids and concentrating this brackish water some tenfold, up to 40,000 ppm maximum dissolved solids.

However, most geothermal fluids that have sufficient mineral content to be worth recovering already have from 30,000 ppm (3%) up to 300,000 ppm (30%) dissolved solids. Thus neither reverse osmosis nor electrodialysis can be considered for this application.

In addition, most geothermal fluids contain dissolved silica, usually in supersaturation, together with iron and manganese salts that tend to precipitate and plug the pores of the reverse osmosis and electrodialysis membranes, thereby rendering them ineffective.

Hydrate formation, as a means of removing water, is difficult in chloride systems unless they are very concentrated, i.e., in excess of 40 wt % $CaCl_2$ or $MgCl_2$. At and above these concentration levels, it is possible to crystallize out the hexahydrate salt ($CaCl_2 \cdot 6H_2O$ or $MgCl_2 \cdot 6H_2O$), thereby removing about one part of water from the system for every one part of $CaCl_2$ or $MgCl_2$ removed.

However, this is not a very suitable method for consideration in this study since, at most, the $CaCl_2$ concentration of the geothermal brines considered is only 10 wt %. Some other method must be used to increase the $CaCl_2$ concentration some fourfold.

This leaves only the various evaporation routes to consider; steam evaporation and solar evaporation.

If one has large areas of low cost land containing a clayey-silt layer many feet thick just below the surface, and an evaporation rate that exceeds annual rainfall by at least 20 inches per year, then solar evaporation is normally the route to follow, even though it is a cyclical method of water removal; i.e., most of the evaporation occurs in four to six months of the year.

If such suitable land area is not available, then other means of water removal must be considered, such as steam evaporation. Normally, a geothermal resource will provide all the steam required for evaporating water, but at a cost, in terms of reduction in the quantity of electrical generating capacity.

This loss of electrical generating capacity would have to be balanced against the value of the commodities being recovered from the geothermal fluid.

In order to quantify the costs involved in removing water by these two mtehods, we have postulated an evaporation system capable of removing 15 x 10^6 tons/year of water (3600 x 10^6 gal/year) from geothermal fluids and calculated the cost of water removed per ton of desired product as a function of the concentration of the desired product (calculation details are given in the Appendix). Figures 34 and 35 present these data graphically and indicate that steam evaporation is relatively expensive unless the concentration of desired component exceeds 10 wt % (considering a component such as potash, KCl, for example).

Solar evaporation ponds afford a considerable savings over steam evaporation, providing that suitable land and climatic conditions are available.

An additional savings in solar evaporation costs can be achieved by using spray nozzles to increase the available solar pond or evaporation surface area available. Löf has compared such costs on the basis of quantity of nozzles utilized per 1000 ft^2 of pond area. Figure 36 depicts this relationship for various types of brine wastes resulting from operation of desalination plants.

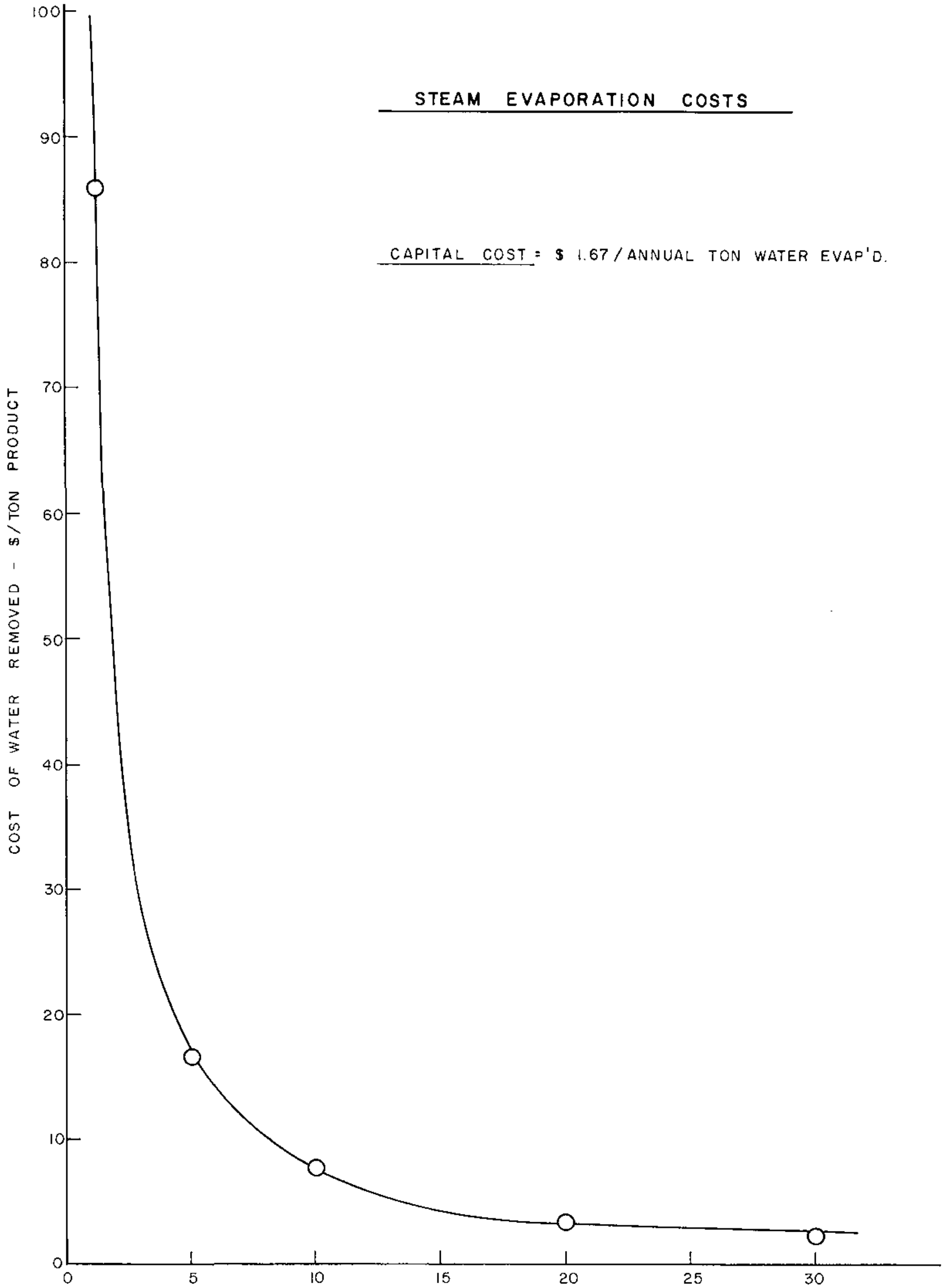

FIGURE 34

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SOLAR POND EVAPORATION COSTS

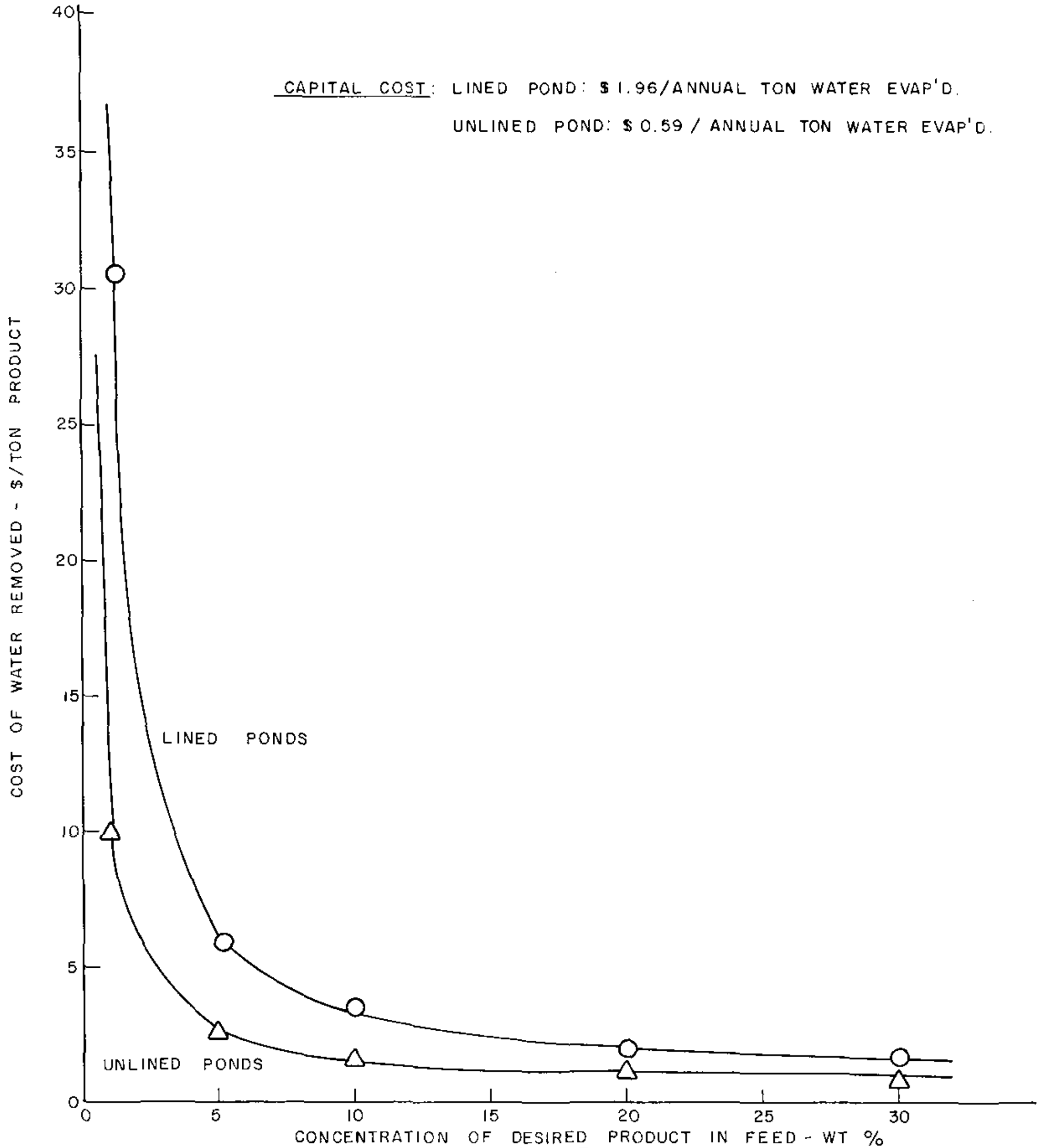
CAPITAL COST: LINED POND: $ 1.96/ANNUAL TON WATER EVAP'D.
UNLINED POND: $ 0.59 / ANNUAL TON WATER EVAP'D.

FIGURE 35

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SUMMARY OF BRINE EVAPORATION COSTS

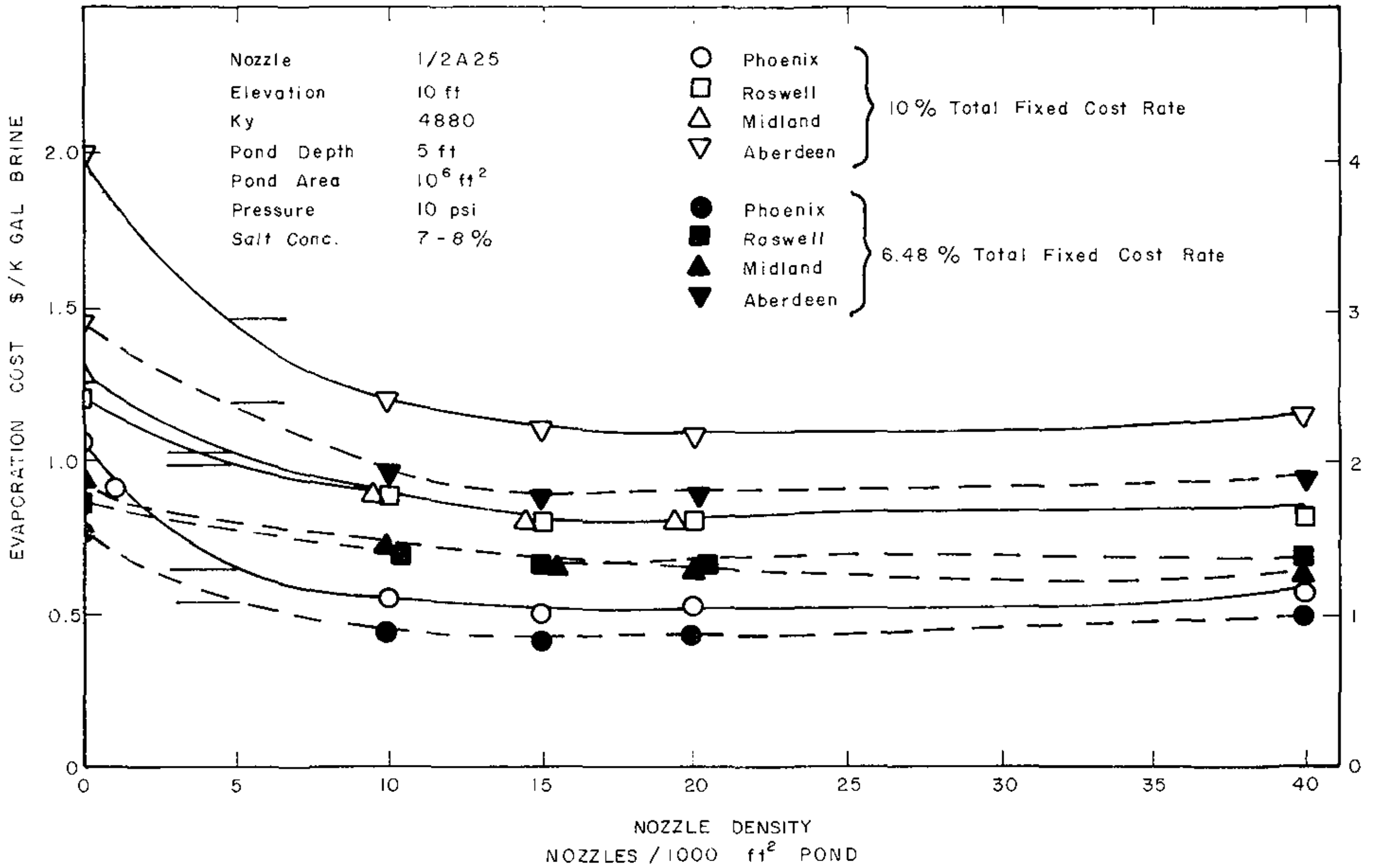

FIGURE 36
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One penalty that accrues to the use of spray nozzles is the increase in spray drift or windage loss. Such loss may not be significant in a large solar pond complex where the drift fallout would be caputured in other surrounding solar evaporation ponds, providing the use of sprays was restricted to the inner solar ponds of the system.

However, in an agricultural area such drift loss might be intolerable, spreading saline mist over a wide area and contaminating crop-bearing land. Figure 37 presents the experimentally determined drift loss as a function of spray nozzle pressure for two types of spray nozzles.

It is apparent that neither route is feasible when the concentration of desired component is in the range of 0.5 wt % or less, such as the iron, manganese, zinc, lead, lithium, etc., concentrations of Sinclair No. 4 geothermal brines.

Therefore, the case for directly removing the desired component from the geothermal fluid and the methods for doing so should be evaluated. These approaches are:

B. Specific material removal methods
   1. Ion exchange or exclusion
   2. Solvent extraction
   3. Selective precipitation
   4. Selective crystallization

The use of ion exchange resins for geothermal fluids faces a number of problems, the major one being temperature. Most ion exchange resins suffer rapid degradation at temperatures above 50°C due to the swelling and shrinking that takes place upon loading and unloading the resin with the desired cation.

VARIATION OF DRIFT LOSS WITH NOZZLE PRESSURE

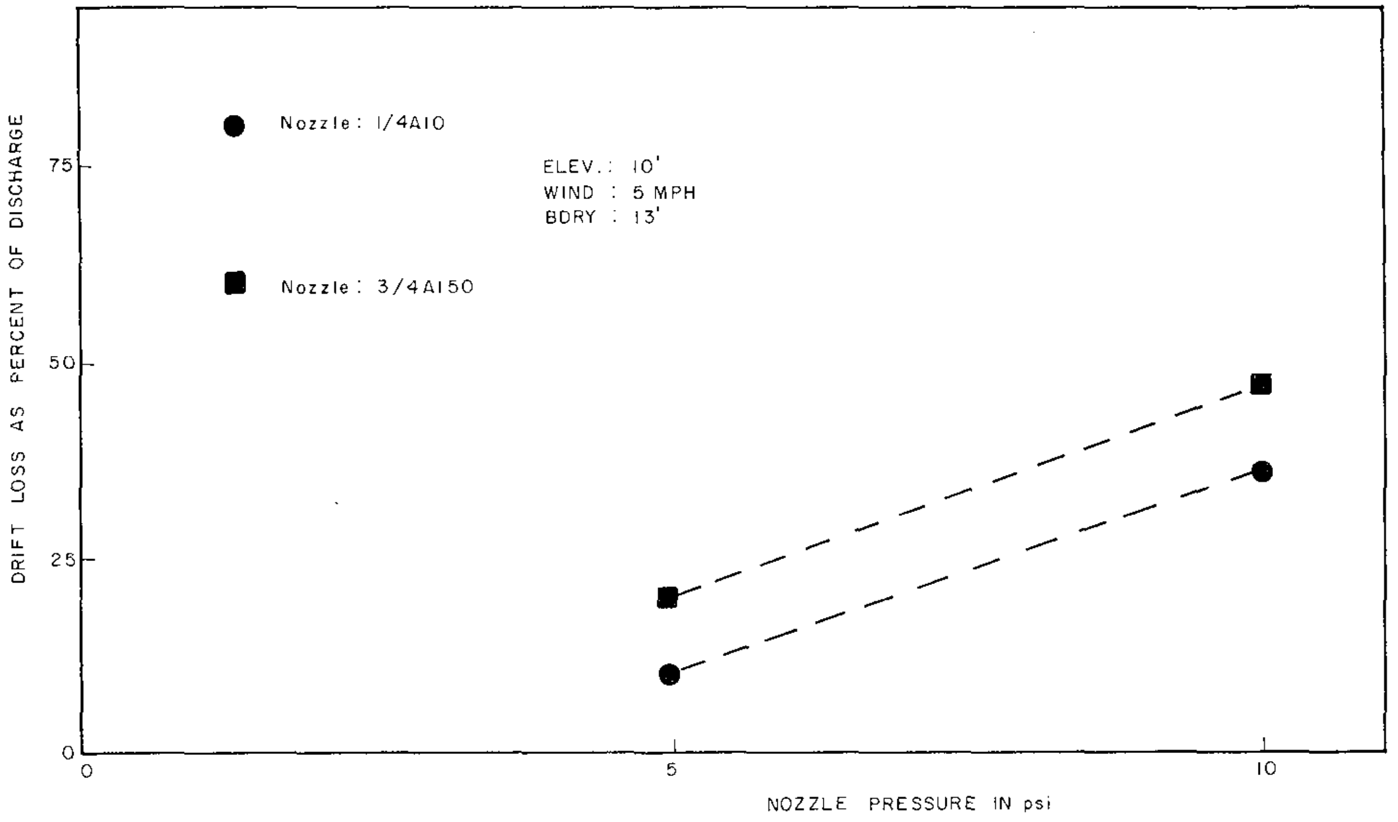

FIGURE 37

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Since most, if not all, geothermal fluids are at 100°C or above after flash-down, it does not appear that ion exchange resins can be utilized unless some form of cooling of the geothermal fluid is utilized. Such cooling, unless one can use solar evaporation ponds would appear to be quite energy intensive, thereby reducing the quantity of exportable electrical energy available from a given geothermal resource.

A potential use for ion-exchange technology would be its application to solar concentrated geothermal fluids where the fluid temperature has been lowered to the range of 40°C, through heat exchange to the atmosphere and evaporation of water.

The recovery of some of the heavy metal values, such as manganese, lead, and zinc, might be possible, providing that the high concentrations of sodium, potassium, and calcium chlorides do not cause interferences. It is probable that both the lead and zinc would be present as an anionic chlorocomplex in such a high chloride level environment and thus anion exchange resins might be suitable for loading these two metals.

However, the application of ion exchange technology to minerals recovery from geothermal fluids would require the correct set of circumstances; i.e., the availability of solar pond area to cool and partially concentrate the geothermal fluid, prior to the ion-exchange step.

In general, Perry (Chem. Engrs. Handbook, 4th Ed) states that the cost of removing dissolved solids is greater with ion exchange than with chemical precipitation. However, there may be some geothermal fluids, containing relatively high levels of valuable heavy metals, that may be advantageously handled by ion-exchange techniques.

The value of contained lead and zinc (per gallon of fluid) in the three Imperial County geothermal fluids is as follows:

Sinclair No. 4	\$0.0024/gal
Magmamax No. 1	0.0013/gal
Mesa L-6-1	Zero

It would appear that some form of concentration of the contained heavy metals values of these fluids should be considered prior to considering the application of ion exchange processes.

Consideration of solvent extraction techniques for recovering the valuable constituents of geothermal brines faces the same sort of constraints as does ion exchange, namely, sensitivity to high temperatures, leading to rapid alteration and degradation of the solvent system or chelating agent.

Again, if geothermal fluids can be cooled and partially concentrated in, say, a solar evaporation pond, solvent extraction processes may find some application.

In general, solvent extraction processes have been applied to solutions containing compounds valued in excess of \$0.01 per gallon. Uranium mills, where solvent extraction processes are extensively used, normally have uranium-containing leach solutions valued at \$0.14 per gallon or greater (with U_3O_8 priced at \$8.00/lb).

The lowest valued solution presently being treated by solvent extraction techniques appears to be the Kerr-McGee Chemical Company boric acid plant at Trona, California, and described in the previous section. The value of the extracted components in this process is of the order of \$0.01 per gallon of brine treated.

Here again, some form of concentrating process would appear necessary before solvent extraction techniques could be profitably employed with geothermal fluids.

Selective precipitation methods involve the stagewise, selective removal of desired components from a solution by addition of adsorbants, change in solution pH, change in oxidation state, decreasing the solubility of the component in the solution, or combinations of the above.

In view of the intrinsically low monetary value of the geothermal fluids examined in this study, this process route appeared to be the most attractive and was further explored and developed in laboratory studies utilizing geothermal fluids.

It was found possible to selectively remove the iron and manganese contents of geothermal fluids as hydrous oxides. Providing the hydrous metal oxides were maintained in the reduced, or ferrous-manganous state, these hydrous oxides acted as a collector or coprecipitant for the lead and zinc values contained in the geothermal fluids, thereby also removing them from the fluid.

The resulting precipitate of hydrous metal oxides with zinc and lead values could be considered as a high grade concentrate suitable for further processing and separation steps.

It was found possible to also selectively precipitate the lithium values present in geothermal fluids of the Sinclair No. 4 type, as a complex lithium aluminate compound, thereby recovering this element in a more concentrated form.

Barium could be precipitated as barium sulfate from Sinclair No. 4 geothermal brine, with some coprecipitation of strontium sulfate values. Recovery of strontium values from Sinclair No. 4 geothermal fluids appears to require concentration of the fluid to increase the strontium level whereby it can then be precipitated as the sulfate salt.

Selective crystallization techniques for recovering products from solution have widespread application in the chemical industry. This type of process requires removal of water from the solution so as to exceed the saturation concentration of the desired compound or compounds.

This removal of water can be achieved, as discussed earlier, most easily by steam or solar evaporation of a geothermal fluid.

However, any process step involving removing water from a geothermal fluid presupposes the fact that fluid reinjection into the producing zone is not necessary to maintain production and/or prevent land subsidence, or that other fluids of lesser intrinsic value (i.e., brackish water) are available for reinjection purposes.

In determining the economic viability of processes for valuable minerals recovery from geothermal fluids, we have not considered the economic impact of the saline components, sodium chloride, potassium chloride, and calcium chloride since recovery of these components requires removal of water from the geothermal fluid, leading to the water balance problem referred to above. However, sufficient process data and information is included herein to enable one to design a process for recovering these saline minerals should economic and geothermal reservoir factors dictate its feasibility.

IDENTIFICATION OF PROBLEMS PRESENT IN MINERALS RECOVERY FROM GEOTHERMAL FLUIDS

The major problem areas to be faced in exploiting a geothermal resource are as follows:

1. Separation of clean steam from a saline fluid, so that long-term operation of turbines can be assured.
2. Prevention of, or reduction in the rate of scale deposition from the geothermal fluid upon flashing and cooling, enroute to further processing.

3. Elimination of, or reduction in rate of corrosive attack on well system and process piping caused by the geothermal fluid and/or gases.
4. Disposal of residual geothermal fluid or bittern following recovery of valuable minerals.

Problem area No. 1, while a very real one to producers of geothermal steam and power, is not within the scope of our study on minerals recovery from geothermal fluids and hence, will not be discussed further.

Most geothermal systems of the "wet" variety contain fluids that are in substantial equilibrium with the host rock structure at the depth of the producing zone. Since most geothermal reservoirs range in depth from 2500 to 10,000 feet and the fluid in such reservoirs is hydrostatically balanced by the liquid column above it, the bottom hole temperatures of such reservoirs can range upwards of 300°C.

Water at such temperatures is an excellent solvent for most rock-forming minerals, particularly silica, and the presence of other dissolved salts, particularly saline minerals, appears to increase the solvent power of the geothermal fluid for silica.

Cooling of the geothermal fluid such as by flashing down to lower pressure as the fluid rises in the well bore, heat exchange with other cooler fluids, flash-down in separator vessels to separate steam for power generation, etc., results in supersaturation of the remaining fluid with silica. This supersaturation condition results in the gradual precipitation of hydrous silica ($SiO_2 \cdot XH_2O$), which coats, deposits, etc., on any surface in close proximity to the cooling fluid.

This is the "scale" that is commonly referred to as one of the major problems in the commercial utilization of "wet" geothermal resources.

The hydrous silica coating that forms this scale is apparently a good collector or scavenger for other heavy metal compounds in the geothermal fluid. "Scale" samples from well casings and downstream piping on wells in the Salton Sea geothermal field have contained, in addition to silica, such elements as iron, manganese, copper, silver, and calcium.

Table 25 presents an analysis of one such scale sampled from Well IID No. 1 in the Salton Sea field by Skinner, et al.

Table 25

Nominal Composition of Scale from IID No. 1 Well

Component	%
Silica (SiO_2)	28
Aluminum (Al)	0.1
Iron (Fe)	20
Copper (Cu)	0.4
Potassium (K)	10
Calcium (Ca)	1.0
Magnesium (Mg)	0.07
Manganese (Mn)	0.4
Beryllium (Be)	Trace
Boron (B)	0.04
Lead (Pb)	Trace
Gallium (Ga)	Trace
Bismuth (Bi)	Trace
Lithium (Li)	Trace
Silver (Ag)	0.02
Sodium (Na)	1.0
Zinc (Zn)	Trace

Control of such "scale," and where it will form, is one of the major problems facing operators of "wet" geothermal steam wells. Unless such scaling can be controlled or minimized so as to ensure a reasonable term of well operations prior to clean-out, the well field operator must provide almost a one-for-one redundency in geothermal steam wells.

Control of deposition of such "scale" can be handled in several ways. One method is to frequently clean out the steam brine piping by reaming or "pigging" the lines.

Another approach is to minimize surface roughness of all conveying piping and vessels which contact the steam-brine mixture, either by electropolishing or surface machining or by coating with some type of smooth surfaced polymer, such as Teflon®. However, these approaches only serve to reduce the rate of "scale" deposition, since once such "scale" begins to coat such a surface on a pipe or vessel, such surface is no longer smooth.

One approach that may not have had much application in this area is to treat the problem as one of crystallization and attempt to control the driving force, i.e., supersaturation, that causes silica precipitation, and also provide an alternative surface for the silica to deposit or grow upon.

The implementation of this approach would require control of the amount of flashing taking place in well bore by control of flow rate from each well, and the addition of silica seed crystals to the geothermal fluid prior to the multistage flash-down to generate process steam.

Corrosive attack by geothermal fluids and gases from "wet" geothermal wells can vary widely in extent, location, and severity, depending on the composition of the fluids and gases and the pH of the fluid.

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Geothermal resources containing fluids with low dissolved solids content, pH levels in the range of 6 to 8, and low or zero concentration of ammonia, hydrogen sulfide, and carbon dioxide in the gas phase will normally not be a severe corrosion situation. Areas of concern would be crevice corrosion occurring behind scale that had deposited on the piping, potential corrosion by wet carbon dioxide or hydrogen sulfide gases, which might require use of high nickel alloys, effects of wet ammonia gas on any copper, nickel or monel alloy in the system such as might be found on instrument air lines, etc.

High salinity geothermal fluids, such as those of the Salton Sea area ,pose a much more severe corrosion situation. The presence of high chloride ion concentrations, at high temperatures, constitutes an extremely aggressive corrosive environment, with both pitting and stress cracking types of corrosion possible. In addition, due to the scaling tendencies of this geothermal fluid, crevice-type corrosion can occur at discontinuities in "scale" coating.

The non-condensable gases from these geothermal resources contain mainly nitrogen, carbon dioxide, and hydrogen sulfide. Vessels and piping contacting these wet gases will have to be of suitable nickel alloy or stainless steel to withstand the potential corrosive attack.

As a general rule, the proper evaluation of degree of corrosivity of a system can only be determined by actual "coupon" corrosion testing where specimens ("coupons") of various types of metals, in both stressed and unstressed condition,and with and without weldments (to test for weld area sensitivity to the corrosive environment), are exposed to the fluid and gas phases present. These tests can be simulated in laboratory studies or the corrosion testing can be done at the actual well site if the well is flowing. Actual field testing, under flowing conditions, is to be preferred as it most closely simulates actual operating conditions.

Once corrosion testing is completed, the proper materials of construction can be selected to deliver maximum service life in the particular environment to be encountered.

Disposal of residual geothermal fluids or bitterns and control of toxic elements contained in the fluid are interrelated problems.

We would consider, for the purposes of this study, that the following elements found in the geothermal fluids sampled by us might be toxic, either to human and animal life or to plant life.

Barium
Boron
Copper
Lead
Zinc

Other elements such as mercury, antimony, arsenic, chromium, vanadium, selenium, and thallium, which are potentially toxic also, were found in hydrous iron oxide precipitates removed from Sinclair No. 4 brine during simulated solar evaporation studies.

The process approach developed by Hazen Research, Inc., during the course of this study effectively removes such heavy metals as lead and zinc as well as iron and manganese from geothermal fluids of the Sinclair No. 4 type. It is highly probable that this procedure of coprecipitation or scavenging of heavy metals in solution by means of hydrous iron oxides removes other heavy metals present in trace amounts in geothermal fluids.

However, no intensive study was made of this disposition and ultimate destination of the many trace elements found in geothermal fluids. Such a study would best be made during pilot plant size minerals removal studies where both sufficient material is available and nominal equilibrium conditions could be attained in a continuous flow reactor system.

Removal of boron from geothermal fluids is expected to pose a problem. Both ion exchange and solvent extraction techniques have had limited success due to the high dissolved salt content and presence of divalent ions such as calcium or magnesium.

It is anticipated that if the boron removal problem becomes one of sufficient magnitude and importance as regards geothermal fluid or bittern disposal, a "tailor-made" solvent extraction system, similar to that used by Kerr-McGee Chemical Corporation (described earlier in the previous section) could be developed.

Ultimate disposal of geothermal fluids or bitterns, following flash-down to generate process steam, appears to be of two types; (1) evaporate the liquids to dryness and dispose of the solids as land fill, or (2) reinject the flashed-down geothermal fluid back into the producing zone via a reinjection well.

The first approach, that of evaporating the fluid to dryness, can only be considered if solar evaporation ponds are useable. This implies the proper climatic conditions for a significant evaporation rate (i.e., in excess of 20 inches/year), plus the availability of suitable, low cost land on which to locate the solar ponds.

Use of multiple effect steam evaporation to convert geothermal fluids to dryness would be extremely costly, from an operating standpoint, since essentially all of the geothermal steam produced from such a resource would be used to convert the fluid or bittern into a dry solid. If the fresh water produced from such a multiple-effect evaporator system had a significant value and was required for use rather than the electric power derived from geothermal steam, then this evaporation concept might become viable.

Most, if not all, operators of geothermal resources believe that it is almost mandatory to recharge the producing zone and reservoir system of a geothermal resource, to maintain hydraulic equilibrium by reinjecting the geothermal fluid back into the structure, via an injection well located some distance from the producing well.

Reinjection immediately solves the problem of geothermal fluid or bittern disposal, providing this fluid is compatible with the structure chosen for the reinjection zone.

As discussed earlier, most geothermal fluids contain varying quantities of dissolved silica, plus some iron and manganese compounds. The contained silica is normally supersaturated in the flashed-down geothermal fluid, and precipitates out and forms "scale" throughout the system.

Reinjection of such a silica precipitate-laden fluid back into the structure could lead to plugging-off of the producing structure, thereby potentially shutting down producing wells and injection wells. Reportedly, reinjecting such a silica-laden fluid into a well in the Salton Sea geothermal area resulted in a continually increasing back pressure from the injection well until the injection piping failed.

Therefore, it appears necessary to clean up or remove the potentially precipitable materials from a geothermal fluid prior to reinjecting it for disposal.

This requirement enhances the potential for economic recovery of valuable minerals from geothermal fluids.

The process scoping and economics studies carried out by Hazen Research, Inc., for this contract have been aimed to achieve this goal.

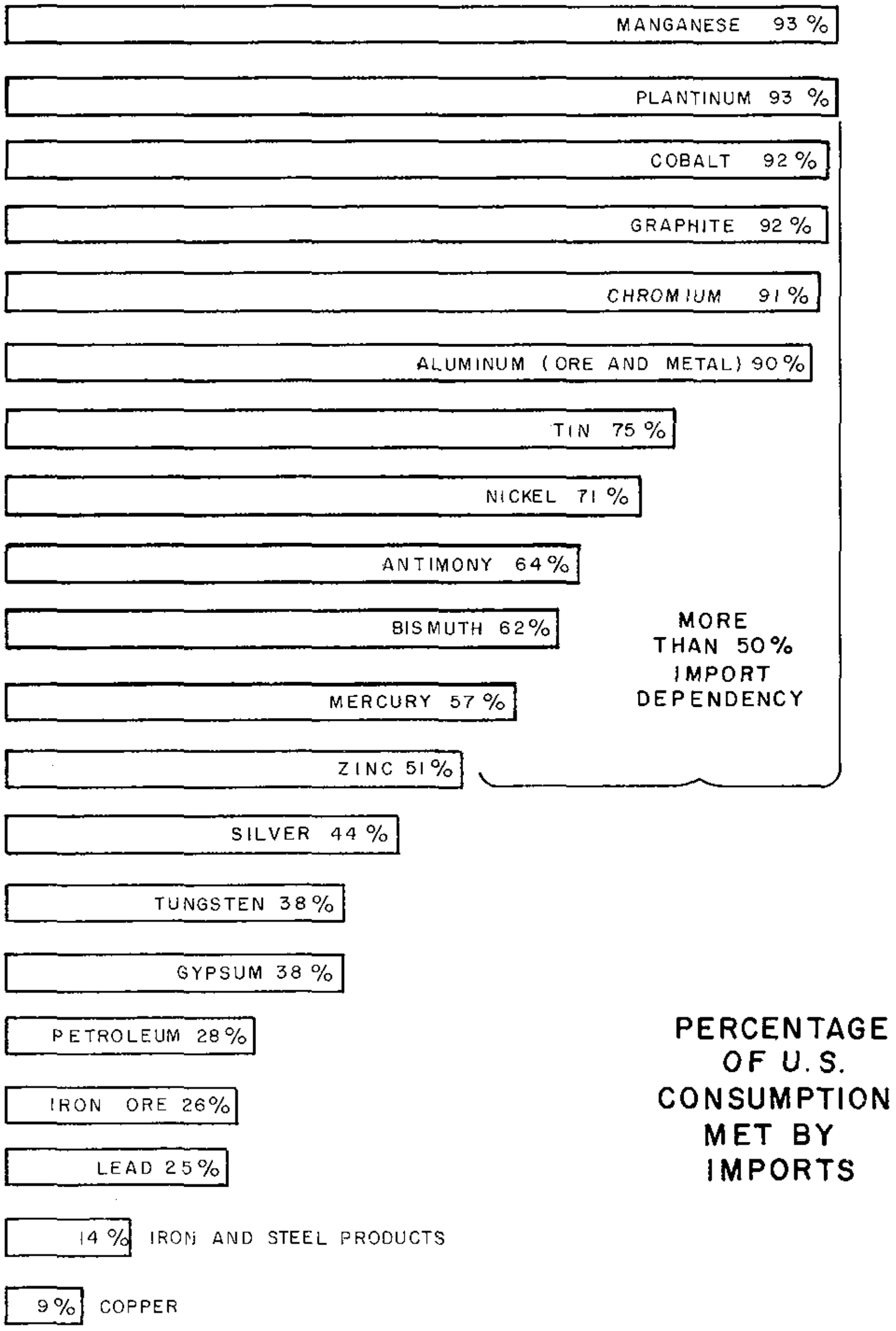
MARKET DEMAND FOR PRODUCTS DERIVED FROM GEOTHERMAL BRINES

The major products that appear to be recoverable from geothermal fluids are salines, such as sodium chloride, potassium chloride, calcium, and magnesium chloride, and heavy metal compounds of iron, manganese, lead, zinc,with trace amounts of other heavies such as copper and silver. In addition, some geothermal fluids also contain significant quantities of lithium, barium, and strontium.

Consideration of methods for the recovery of valuable minerals from geothermal fluids initially requires a definition of the term "valuable." This term, "valuable minerals," as applied to geothermal fluids is subject to different interpretations, depending upon the domestic and worldwide demand for commodities and their relative availability.

Based upon data published by the U. S. Bureau of Mines and U. S. Geological Survey (listed in the bibliography) regarding domestic production and imports of various mineral commodities (see Figure 38 for data on imports), it was decided to initially consider only the iron, manganese, lead, zinc, strontium, barium, lithium, bromine, and ammonia as "valuable constituents," with possible consideration of sodium, potassium, and calcium chloride production as an option, should marketing and transportation considerations make such production attractive.

We have summarized below the supply-demand picture for the salines, sodium, and potassium chloride, together with our estimate of the probable marketing picture for some of the other commodities listed above. Our presentation is slanted somewhat toward production from geothermal resources in the southwestern United States and is based on the commodity assemblage that could be expected from Sinclair No. 4 type geothermal fluids.



PERCENTAGE OF U.S. CONSUMPTION MET BY IMPORTS

FIGURE 38
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Sodium Chloride (Salt)

Data obtained from the 1971 issue of Mineral Facts and Problems, U. S. Bureau of Mines, indicate that demand for this very basic commodity follows the national and world GNP. Figure 39 presents these data in graphical form.

Projected U. S. consumption by year 1977 should be 55 x 10^6 tons/year with U.S. production lagging by some 4 x 10^6 tons/year. However, this short fall in U.S. production may best be met by foreign imports rather than by increasing U.S. production.

This is due to the low unit value of this commodity, coupled with ever-increasing rail freight rates, which, in general, make it uneconomic to ship this commodity more than 200 to 500 miles from the producing area.

It would appear that the greatest potential sales area for salt derived from geothermal brines in the western U.S. would be the Far East.

Slurry pipelining salt is estimated to cost between $0.50/ton and $1.00/ton per 100 miles, while unit trains would cost from $1.00 to $2.00 per ton, depending upon availability of a back haul for the same distance. Ocean freight to Japan from the West Coast in bulk carriers of 50,000 tons or greater capacity would cost from $5.00 to $9.00 per ton, depending on the negotiated rate one could obtain.

Potential competition in the salt market exists from the solar salt works at Exportadora de Sal, in Baja, California Sur, and at Lake McLeod, Western Australia, both of which have production capacities in excess of 5 x 10^6 tons/year. Other solar salt operations in the Bahamas and Netherland Antilles are also potential competition.

The most reasonable use for salt derived from this resource would be to convert it to soda ash via the Solvay process, or caustic soda and chlorine via electrolysis.

ESTIMATED SALT PRODUCTION AND CONSUMPTION

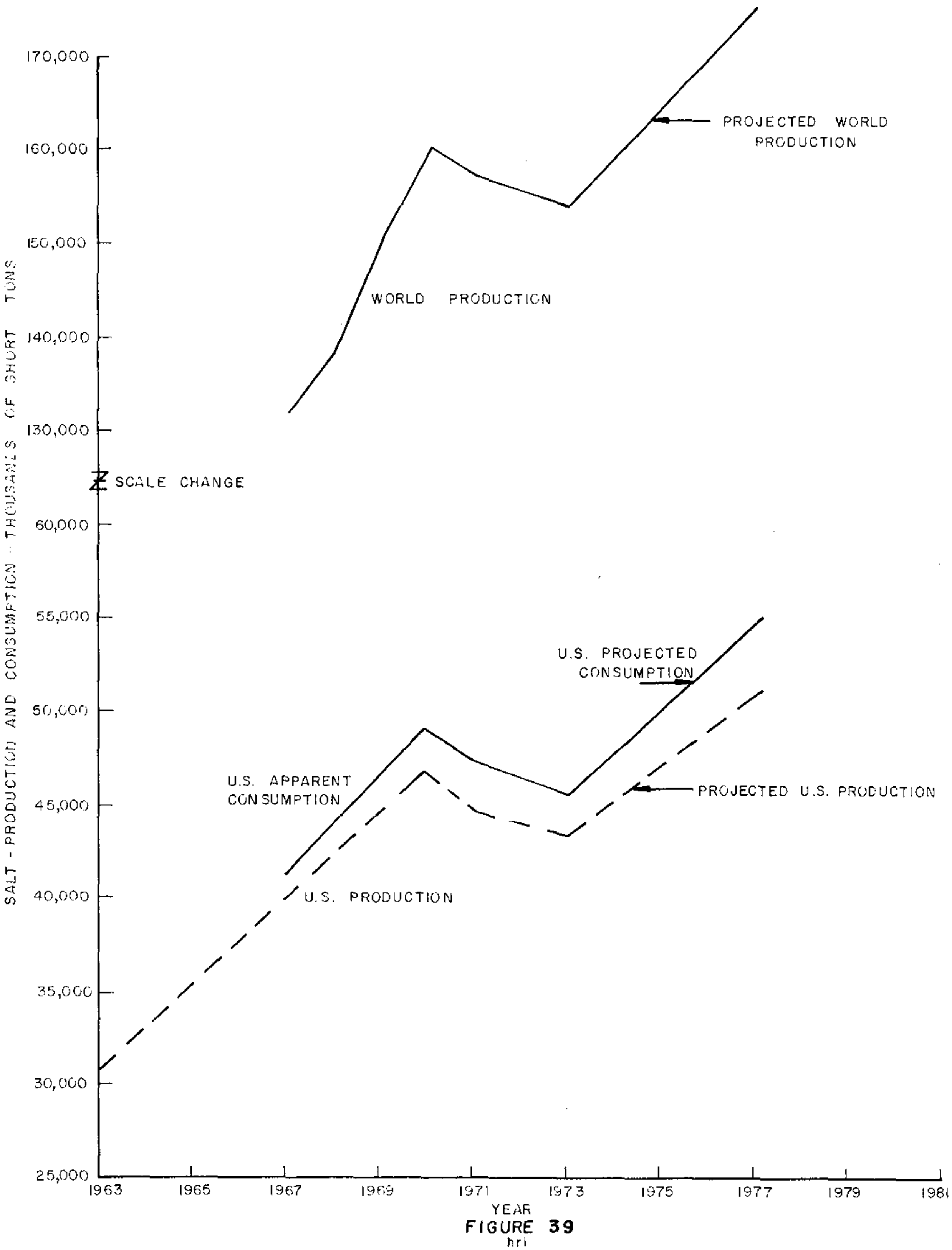

FIGURE 39

hri

Figure 40 depicts the domestic demand for alkali, both soda ash and caustic soda, through 1975. By 1975 the demand for caustic soda appears to have doubled over that for 1965; up to 12.5 x 10^6 tons/year.

Domestic soda ash production is due to increase rapidly with TGS at Green River, Wyoming, going on stream in 1975 with 1 x 10^6 tons/year, FMC at Green River adding another 1 x 10^6 tons/year capacity, and Kerr-McGee announcing an increase of 1 x 10^6 tons/year in soda ash production due on stream by 1977.

Apparently, the data shown in Figure 40 are understated, since by 1977 there will be approximately 10 x 10^6 tons/year of soda ash production capacity. Presently, soda ash is on allocation and commands prices in excess of $50 per ton, if and when available.

It would appear that conversion of salt to caustic soda-chlorine would be the most profitable route to follow.

Potassium Chloride (Potash)

Potash is used as a crop fertilizer in nearly every corner of the globe, and the U.S. is heavily dependent upon imports, primarily from Canada, to supply the growing U.S. demand for potash. Figure 41 presents the potash production and consumption figures.

By 1977 nearly one-half of the projected U.S. consumption of potash will be met by imported material. Therefore, the potential market for potash produced domestically should be excellent.

In the western U.S. potential competition exists from the Kerr-McGee operations at Trona, California, and the Canadian producers in Saskatchewan.

Kerr-McGee is limited to about 230,000-300,000 tons/year of potash production while the Canadian producers have a surplus of 1 x 10^6 tons/year available.

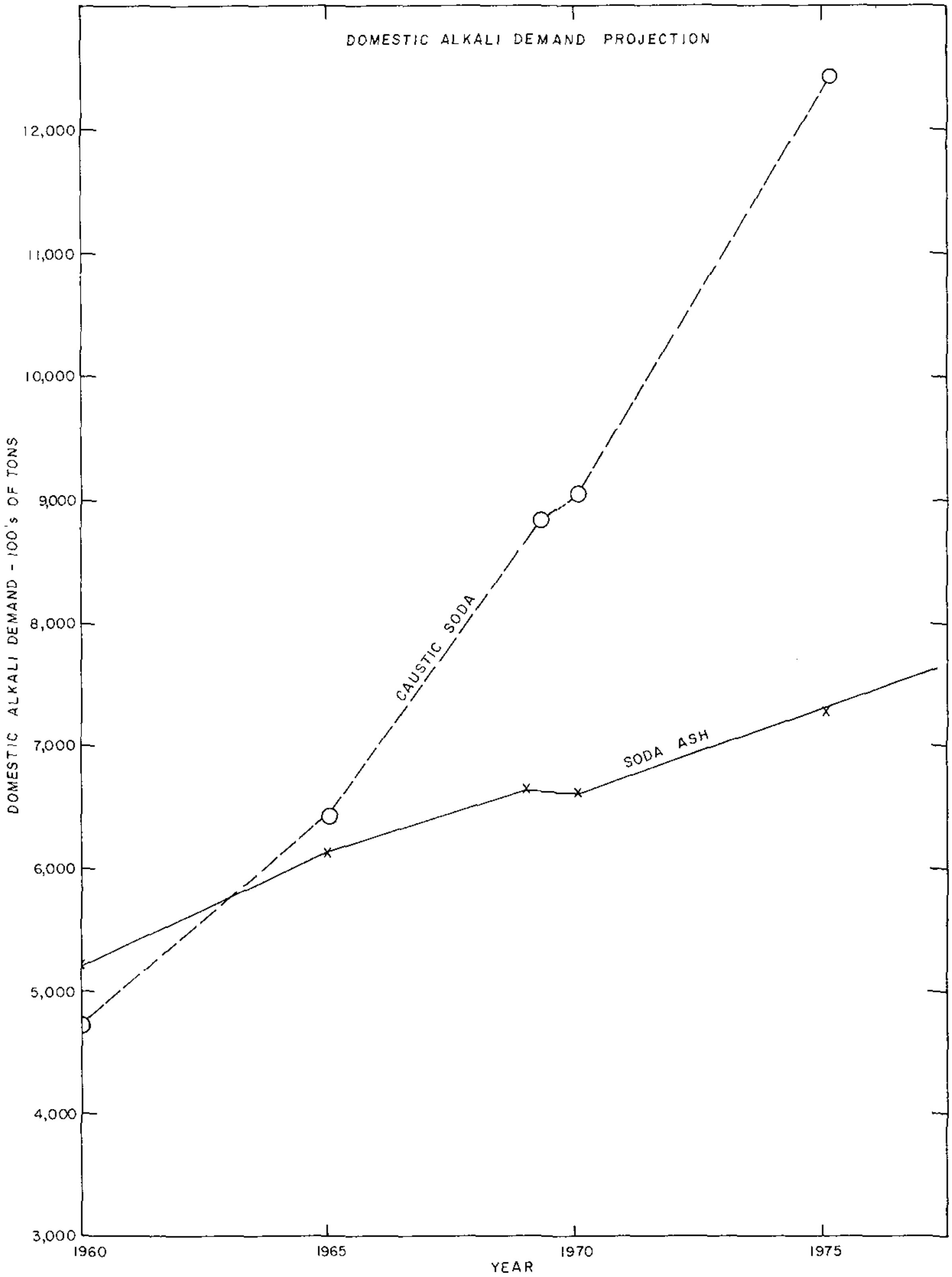

FIGURE 40 hri

ESTIMATED POTASH PRODUCTION AND CONSUMPTION

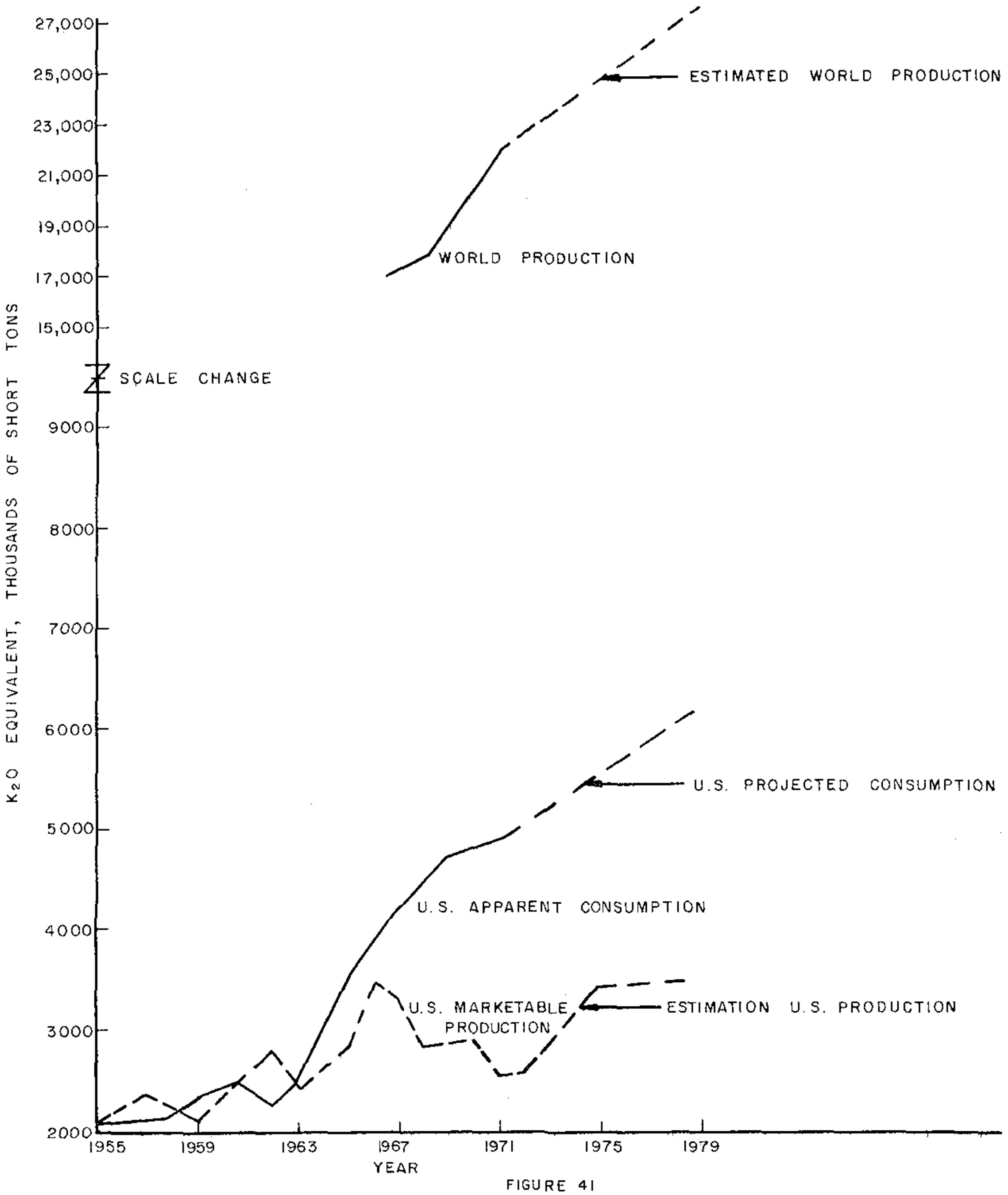

FIGURE 41

However, a regional producer of 50,000 to 100,000 tons/year capacity could be expected to capture a portion of the U. S. market plus some export business in South America, Australia, and the Far East.

Lithium

The geothermal fluids of the Salton Sea geothermal resource contain varying amounts of lithium and have the potential of becoming the largest lithium reserve in the United States.

Major producers of lithium chemicals are Foote Mineral Company at Sunbright, Virginia, and Silver Peak, Nevada; Kerr-McGee Chemical Corporation at Trona, California, and Lithium Corporation of America, Bessemer City, North Carolina. It is estimated that total production capacity, as lithium carbonate, is about 50-60 tons/day.

Since the United States is already self-sufficient in lithium resources, producing lithium from geothermal fluids can only be feasible or justified on the basis of producing at lower cost than present producers. Therefore, in our economic assessment of minerals recovery from geothermal fluids, we have assumed a very low selling price of $0.20/lb of lithium carbonate for this commodity.

Manganese

As far as is known, there is but one domestic producer of manganese ore as of this date. Essentially all the U.S. requirement of manganese is imported from Brazil, Gabon, the African Gold Coast, and South Africa.

Domestic consumption of manganese ores containing 35+% Mn are estimated to be in excess of 2.5×10^6 tons/year.

Projected manganese oxides derived from Sinclair No. 4 type geothermal brines should all be saleable on the domestic market.

Barium

Projected production of barium as barium sulfate from the brine derived from geothermal wells should all be saleable. As this should be premium quality barium sulfate, there should be no problem in selling it as drilling mud grade barite, at $50/ton.

It may be possible to obtain a premium price for the material or convert it to barium carbonate for sale at $180/ton. However, these options have not been included in the valuation of this product.

Strontium

The U.S. is presently completely dependent on foreign imports for the raw material, celestite ($SrSO_4$) or strontianite ($SrCO_3$), to produce strontium chemicals.

Presently, the domestic requirement for strontium carbonate stands at about 60 tons/day, with production derived from CPC, Cartersville, Georgia, and FMC Corp. at Modesto, California. Raw material is celestite ore obtained in Mexico, while some strontianite ore ($SrCO_3$) is obtained from Cumberland, England, for direct conversion to strontium nitrate, used in safety flares to impart their red color.

The production of $SrCO_3$ from Sinclair No. 4 type geothermal brines should capture a portion of the U.S. market, since the present two or three producers are dependent upon foreign imports of raw material, with a continually escalating price structure.

The present major uses for strontium carbonate are in the manufacture of TV tube glass for color TV's (imparts true color rendition and suppresses X-ray generation) and in the manufacture of high permeability ferrite magnets. Both of these uses are expected to continue to increase as color TV becomes more widespread and as the need for small, high field strength magnets increases.

Lead and Zinc

Domestic production of lead and zinc lags the demand because of shutdowns of old and obsolete smelters caused by enforcement of EPA emission controls. Replacement of these older units awaits a general price increase in both metals, which has begun to take place.

Quoted prices for smelter lead now exceed $0.20 per pound while prime slab zinc has risen to $0.40 per pound.

Marketing of both of these metals, as derived from Imperial County geothermal brines, in the western U.S. should realize the quoted prices.

Bromine

Production of bromine in the United States has shown a moderate rate of growth over the past decade, approximately doubling the quantity produced during this period, as shown in Figure 42.

Bromine is consumed primarily by conversion to compound, rather than as the element itself. Major areas of use are in conversion to ethylene dibromide for use in automobile antiknock fluid and as organic bromides used as agricultural fumigants and flame retardants for polymers.

The projected outlook for bromine sales hinges primarily on the outlook for the sale of antiknock fluid (tetraethyl lead). In 1973 approximately 70% of domestic bromine production was converted to ethylene dibromide, most of which was used in antiknock fluid.

If lead-based antiknock fluids are removed from gasolines, then the domestic bromine industry will face considerable over capacity.

Bromine is one of the components of the geothermal fluids analyzed during the course of this study and we have assumed it might be recovered.

However, if the market for bromine is nonexistent at such time as production would be contemplated from geothermal fluids, that portion of the processing complex need not be installed.

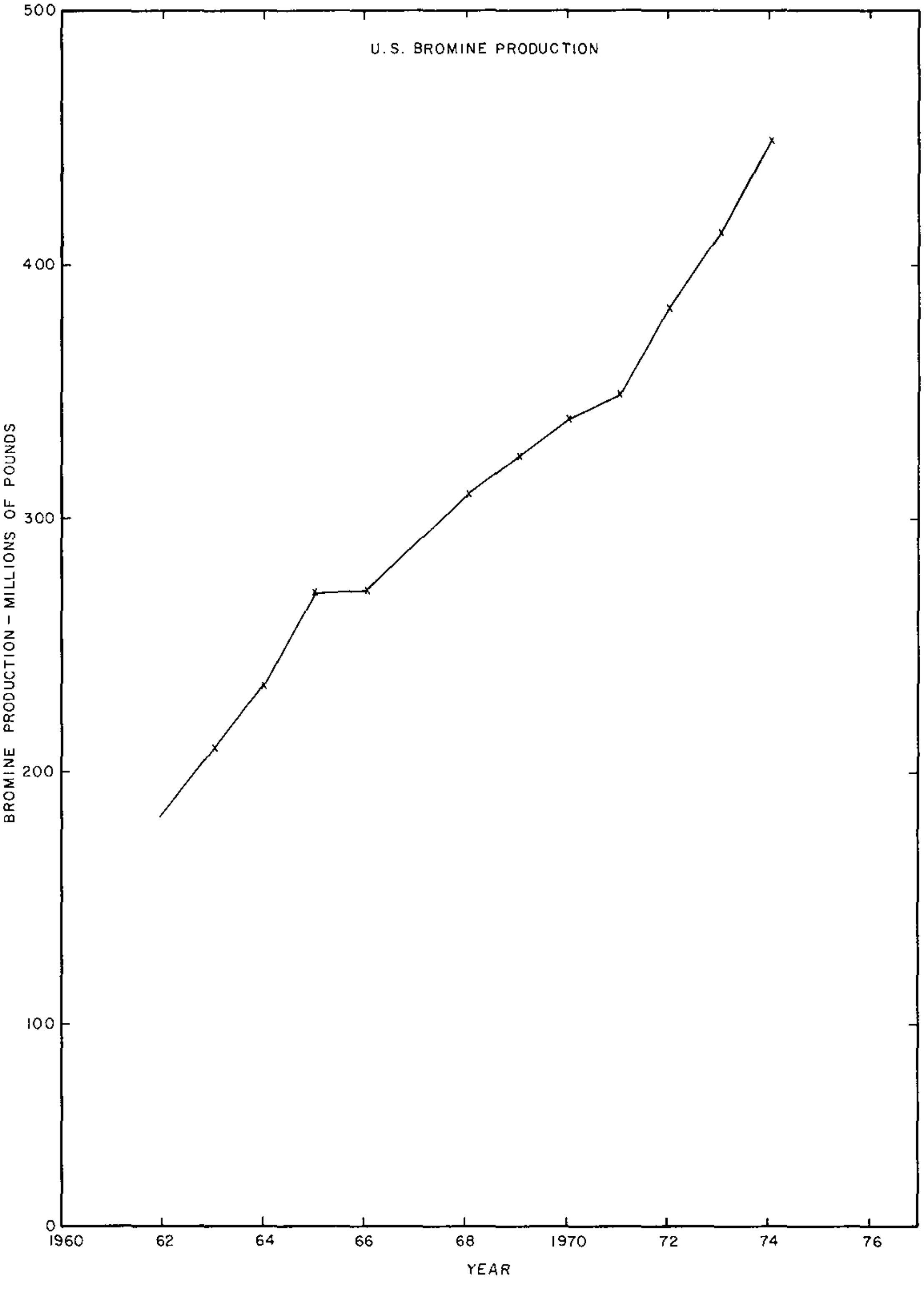
U.S. BROMINE PRODUCTION
BROMINE PRODUCTION - MILLIONS OF POUNDS
500
400
300
200
100
0
1960
62
64
66
68
1970
72
74
76
YEAR

FIGURE 42

ECONOMIC POTENTIAL OF MINERALS RECOVERY FROM GEOTHERMAL FLUIDS

This presentation of economic data on values of geothermal fluids will necessarily be general in nature due to the wide variations in composition of these fluids.

We have undertaken to present a methodology for evaluation of the economic feasibility of recovering valuable components from geothermal fluids which might serve as a guide for possible general application.

Processes for recovery of the valuable minerals from geothermal fluids are constrained by two major factors:

1. Reinjection of post-flash geothermal fluids back into the producing structure is believed to be necessary to maintain reservoir hydraulic balance and prevent general ground subsidence in the vicinity of the geothermal resource.
2. The necessity of "cleaning up" or removing precipitate forming components from geothermal fluids prior to reinjection into the structure to prevent plugging of the structure.

With these constraints, it is very probable that production of saline minerals will not be possible. Recovery of salines would entail concentration of the geothermal fluid by removing water, thus reducing the quantity (volume-wise) of fluid available for reinjection or perhaps even eliminating it.

In our economic studies we have assumed that only iron, manganese, lead, zinc, lithium, barium, strontium, and ammonia are to be considered valuable minerals from the standpoint of recoverability. However, we have shown the methodology involved in winning saline minerals from geothermal fluids in the generalized minerals recovery flowsheet contained herein.

Figure 44 presents a block flow diagram outlining a process concept for possible recovery of the valuable constituents from geothermal fluids, including therein a step for possible recovery of the contained sodium, potassium, and calcium chlorides, as well as liquid bromine. Figure 45 presents a block flow diagram for production of pure sodium and potassium chlorides, utilizing the high temperature geothermal fluid as a leaching solution to effect a separation between the salts. Details on the phase rule chemistry of this process are given in Appendix A, together with pertinent solubility information.

We have chosen two geothermal fluids to quantify the methodology of evaluating the economic potential of minerals recovery from such fluids. Sinclair No. 4 geothermal fluid was chosen because of its very high minerals content. At the other end of the scale, Mesa L-6-1 fluid was selected as an example of a geothermal fluid that is marginal, at best, for consideration of minerals recovery.

Table 26 presents a tabulation of the mineral values contained in Sinclair No. 4 geothermal brine, after flashing off steam, based on a daily flow of $10x10^6$ gal/day (6950 gpm). The components have been expressed as the most common form sold in the marketplace, and the capital costs presented hereafter reflect conversion costs to yield the component listed.

It should be noted that we have included silver as one of the commodities that contribute to the valuation of this geothermal fluid, even though it is present at a concentration of less than one part per million. However, with the very large flows involved, such trace elements, if sufficiently highly valued, could contribute significantly to the overall economic viability of minerals recovery.

POSSIBLE FLOWSHEET GEOTHERMAL BRINE PROCESSING

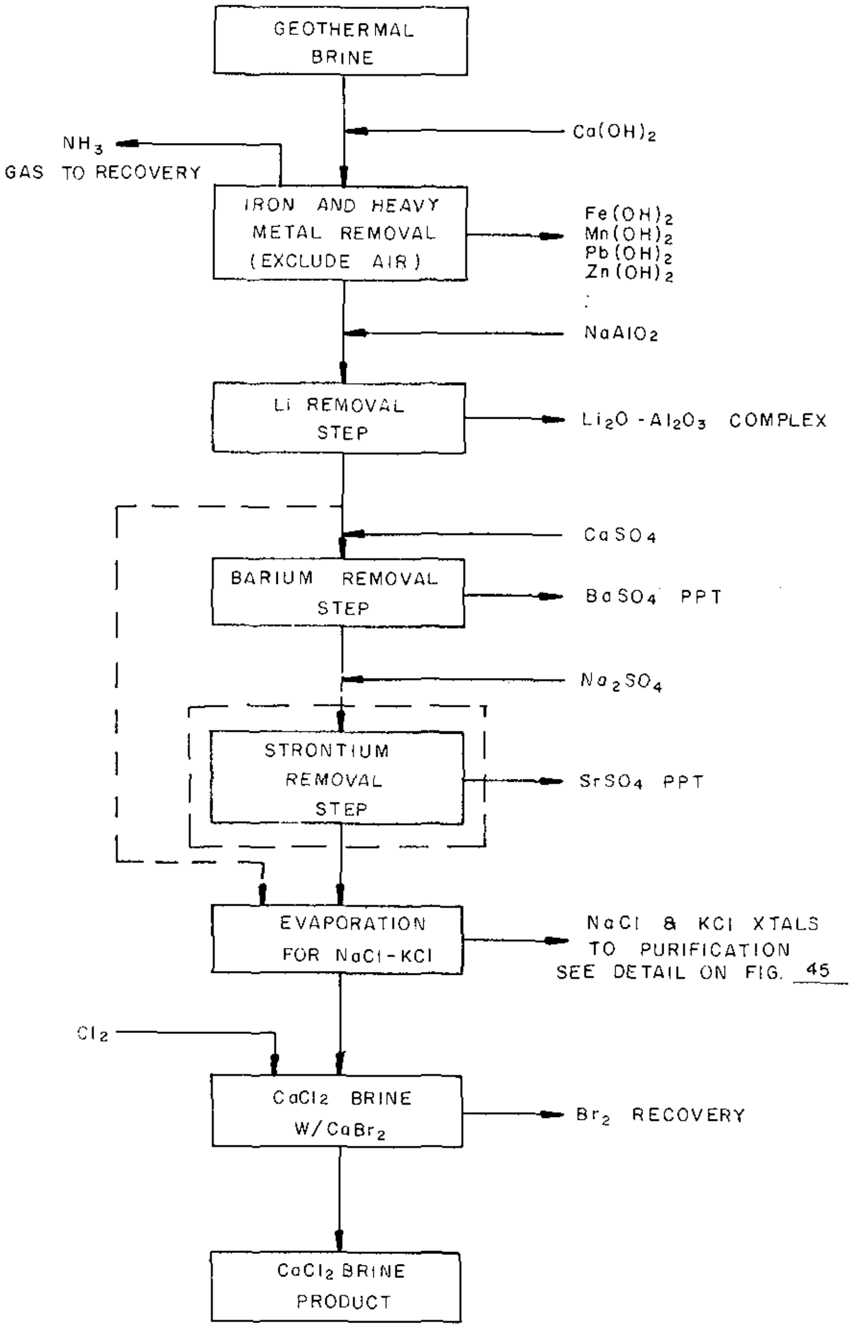

FIGURE 44
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PRODUCTION OF PURE KCl FROM GEOTHERMAL BRINES OF MAGMAMAX – SINCLAIR TYPE

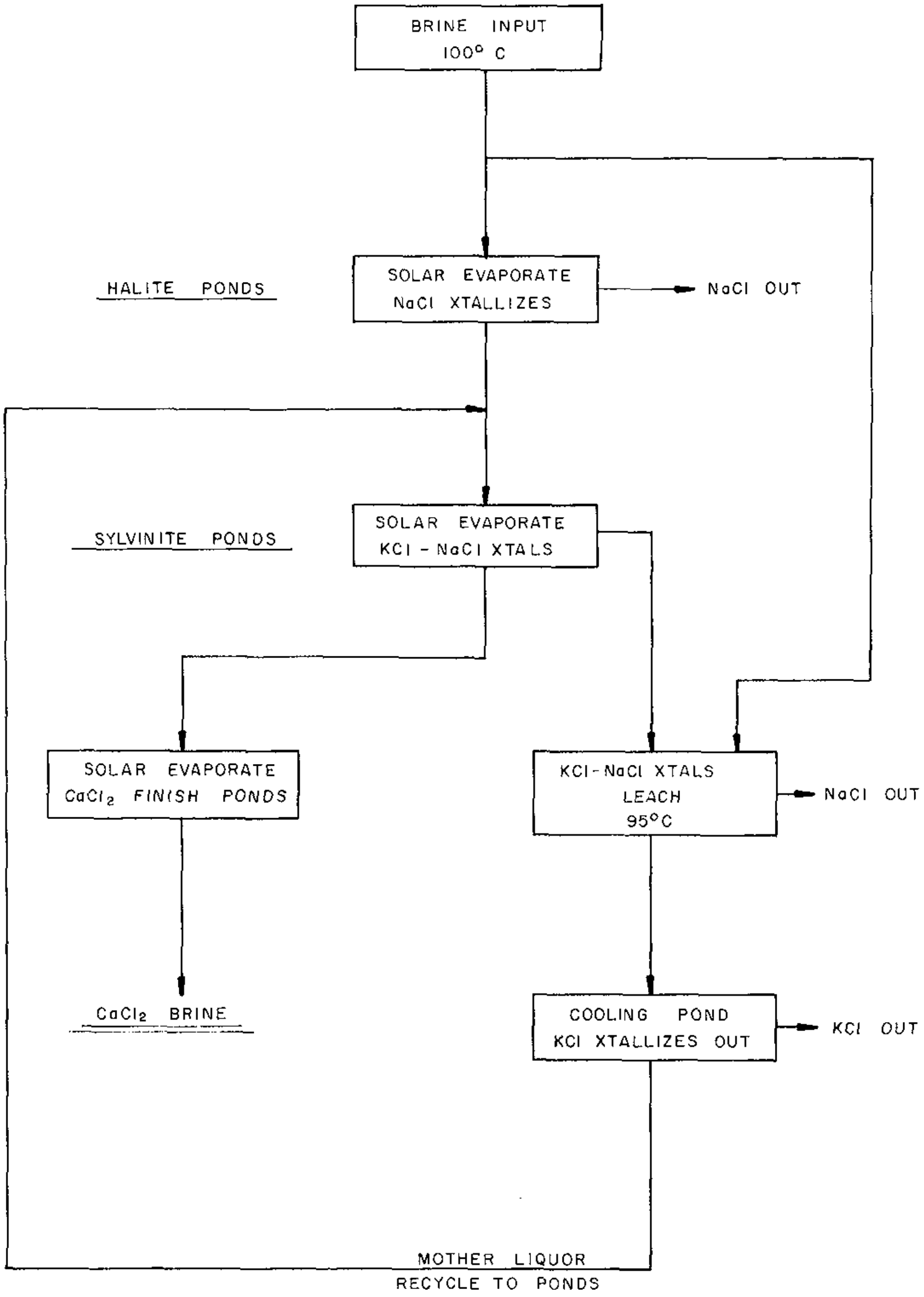

FIGURE 45
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Table 26

Mineral Values Contained in Sinclair No. 4 Brine

Basis: Post-flash flow of 10×10^6 gal/day and 330 days/year operation.

Component	Concentration in Brine, %	Quantity Tons/day	Unit Value Cost	Potential Gross Income	
				Cost/day	Cost/year
Bromine (Br_2)	0.016	8.7	$400	$3,480	$1,148,000
Ammonia (NH_3)	0.061	30.5	110	3,355	1,107,000
Barium sulfate ($BaSO_4$)	0.02	10	50	500	165,000
Borax ($Na_2B_4O_2 \cdot 10H_2O$)	0.30	150	70	10,500	3,465,000
Calcium chloride ($CaCl_2$)	9.7	4,850 anhydrous 12,125 as 40% brine	16.50 as 40%	200,062	66,020,600
Iron oxide (Fe_2O_3)	0.124	62	15	930	306,900
Lithium carbonate (Li_2CO_3)	0.126	63	400	25,200	8,316,000
Lead (Pb)	0.014	7	400	2,800	924,000
Manganese dioxide (MnO_2)	0.233	116.5	130	15,145	4,997,800
Potassium chloride (KCl)	3.43	1715	40	68,600	22,638,000
Sodium chloride (NaCl)	18.0	9000	6	54,000	17,820,000
Strontium carbonate ($SrCO_3$)	0.096	48	300	14,400	4,752,000
Zinc (Zn)	0.049	24.5	800	19,600	6,468,000
Silver (Ag)	0.000077	77 lb/day	48/lb	3,780	1,200,000
			Total		$139,328,300

Based on the consideration of recovering only 80% of the contained ammonia, iron, manganese, barium sulfate, lead, lithium, and zinc, plus 50% of the strontium carbonate, the gross annual sales income is $20,203,760.

Such an annual income would support a capital investment of between $\$20 \times 10^6$ and $\$40 \times 10^6$, based on the turnover ratio experienced by the chemical industry for such heavy chemicals. The turnover ratio is defined as the ratio of annual sales income to capital investment. Table 27 illustrates some typical turnover ratios for various chemicals.

Table 27

Turnover Ratios, Various Chemicals

Alumina from bauxite	0.74
Hydrochloric acid from salt	0.56
Cement	1.00
Soda ash from Trona ore	0.80
Phosphoric acid	1.70
Lime	1.80

The block flow diagram, Figure 44, presented earlier, was assumed to be useable on Sinclair No. 4 type brine, with the elimination of the steps for recovery of saline minerals and bromine.

Capital costs were estimated for such a recovery plant and the data presented in Table 28. Total fixed capital requirements are presented in Table 29 and are estimated to be $\$30 \times 10^6$ for a battery limits plant to recover minerals from geothermal fluids.

At this point, it should be emphasized that a large portion of the flowsheet has been assumed to be operable and that some processing steps remain to be defined.

Table 28

Equipment List and Cost, Sinclair No. 4 Brine

Assume: Battery limits plant, feed brine delivered by pipeline to process

		Cost
A.	Brine cleanup, iron and silica removal, pelletize and sinter iron oxides	$ 810,000
B.	Manganese precipitation and oxidation	710,000
C.	Lithium precipitation and conversion to lithium carbonate with recycle of aluminum	1,100,000
D.	Lead and zinc recovery, and electrolytic recovery	1,300,000
E.	Barium recovery	625,000
F.	Strontium recovery and conversion to carbonate	1,100,000
G.	Ammonia recovery	235,000
	Total estimated equipment cost	$5,880,000

Table 29

Estimated Fixed Capital Cost, Sinclair No. 4 Brine

Purchased equipment (P.E.)	$ 5,880,000
Installation @ 50% of P.E.	2,940,000
Piping @ 40% of P.E.	2,350,000
Instrumentation @ 20% of P.E.	1,175,000
Insulation @ 20% of P.E.	1,175,000
Electrical @ 30% of P.E.	1,770,000
Buildings @ 20% of P.E.	1,175,000
Land and yard @ 20% of P.E.	1,175,000
Utilities @ 10% of P.E.	587,500
Physical Plant Cost (P.P.C.)	$18,227,500
Engineering and construction @ 30% of P.P.C.	5,500,000
Direct Plant Cost (D.P.C.)	$23,727,500
Contractor's fee @ 7.5% of D.P.C.	1,780,000
Contingency @ 20% of D.P.C.	4,746,000
Total fixed capital	$30,253,500
say	$\$30 \times 10^6$

Ratio: $\frac{\text{Fixed Capital}}{\text{Purchased Equipment Cost}} = \frac{\$30 \times 10^6}{\$5.88 \times 10^6} = 5.1$ installed cost factor

Sufficient laboratory test work was done to delineate process concepts only,and no attempt was made to optimize process options. A complete discussion of the laboratory test work is presented in a later section.

Table 30 presents a listing of the production costs estimated for such a minerals recovery plant operating on a geothermal brine of the Sinclair No. 4 type.

Overall return on investment and cash flow statement is presented in Table 31.

We have assumed that a geothermal resource is considered to be a depletable reserve having a finite life and hence qualifies for depletion allowance. Precedent is available as regards geothermal steam and it has been assumed that this also holds for geothermal fluids and minerals recovered therefrom.

A discounted cash flow rate of return on investment has been calculated for the study on minerals recovery from Sinclair No. 4 type brines. Table 32 presents the calculation details.

No allowance was made for investment tax credit which would have increased the year one cash flow by several millions of dollars. It is understood that either the percentage of investment allowed or the number of years it is available are presently being changed by the United States Congress.

Therefore, the DCF return of 15% as shown in Table 32 is probably conservative.

Undoubtedly, considerable finessing could be done to the process outline to optimize investment for each portion of the flowsheet. However, the presentation in Table 32 was intended as a general study on the procedure for assessing economic viability of minerals recovery from geothermal fluids. The results presented indicate that Sinclair No. 4 type geothermal brines are worth further study regarding optimization of process routes for minerals recovery.

Table 30 (1 of 2 pages)

Estimated Operating Costs
Minerals Recovery Plant
Sinclair No. 4 Type Brine

Basis

1. Raw material (brine) cost is zero.
2. Plant fixed capital investment is $\$30 \times 10^6$.
3. Plant sized to process 10×10^6 gal/day of brine.
4. Steam is assumed to be available at $\$0.50/10^6$ Btu.
5. Electrical energy is assumed to be available at $0.005/kwhr.
6. Plant operation is taken to be 330 days per year.

Raw Materials

	Unit Cost Per Ton	Ton/day	Cost/day	Cost/year
Brine	-0-	50,000	-0-	-0-
Lime	$40.00	417	$16,700	$5,500,000
Al_2O_3 (10% makeup)	60.00	7	420	139,000
$CaSO_4$	10.00	15.5	155	51,100
Na_2SO_4	30.00	39	1,170	386,000
Na_2CO_3	55.00	30	1,650	545,000
Total Raw Materials Cost			$30,095	$6,621,100
Operating Labor				
7 men/shift @ $5.00/hr			$ 840	$ 277,000
Supervision				
30% of direct labor			252	83,200
Total Labor and Supervision			$ 1,092	$ 360,200
Fringe Benefits				
25% of total labor and supervision			$ 273	$ 90,050

Table 30 (2 of 2 pages)

	Cost/day	Cost/year
Overheads		
@ 50% of total labor and supervision	$ 546	$ 180,100
Operating Supplies		
Estimated	200	66,000
Utilities		
Steam [60x10^6 Btu/day estimated] @ $0.50/$10^6$ Btu	30	9,900
Fuel [120x10^6 Btu/day estimated] @ $1.50/$10^6$ Btu	180	59,500
Electricity [25,000 kw/day estimated] @ $0.005/kwhr	300	99,000
Process water [50,000 GPD estimated] @ $0.95/1000 gal	75	24,800
Total Utilities	$ 585	$ 193,200
Maintenance		
@ 6% of Capital Investment at $30x$10^6$	$ 5,400	$1,800,000
Depreciation		
10 year, straight line, no salvage value	$ 9,100	$3,000,000
Taxes and Insurance		
@ 3% of Capital Investment	$ 2,700	$ 900,000
Total Operating Cost	$48,991	$13,210,650

Table 31

Cash Flow Statement

	Cost/year
Gross Sales	$20,203,760
Royalties @ 2.5%	505,000
Net Sales Income	$19,678,760
Manufacturing Cost	$13,210,650
Gross Margin	$ 6,488,110
General Sales and Administrative Costs @ 10% of sales	$ 2,020,000
Taxable Income Before Depletion	$ 4,468,110
Depletion Allowance @ 50% of taxable income before depletion	$ 2,234,055
Taxable Income	$ 2,234,055
Income Taxes @ 52%	$ 1,160,000
	$ 4,468,110 1,160,000
Net Income	$ 3,308,110
Add Back Depreciation	3,000,000
Gross Cash Flow	$ 6,308,110
say	6.3×10^6

Table 32

DCF Return on Investment

Fixed Capital	$\$30 \times 10^6$
Working Capital	3×10^6
Total Base Capitalization	$\$33 \times 10^6$
Gross Cash Flow	$\$6.3 \times 10^6$

Yearly Cash Flow

Year	15% Factor	Amount
1	0.929	$\$ 5.85 \times 10^6$
2	0.799	5.04×10^6
3	0.688	4.35×10^6
4	0.592	3.72×10^6
5	0.510	3.22×10^6
6	0.439	2.76×10^6
7	0.378	2.38×10^6
8	0.325	2.04×10^6
9	0.280	1.77×10^6
10	0.241	1.52×10^6
		$\$32.65 \times 10^6$

DCF Return = 15%

As an example of a much more dilute geothermal fluid, Mesa L-6-1 brine was considered to see what the economic mineral recovery potential would be.

Table 33 presents a tabulation of components present in this fluid in significant quantities, together with the potential gross yearly income, based on a post-flash brine flow of $10x10^6$ gal/year.

Table 33

Mineral Values Contained in Mesa L-6-1 Brine

Basis: Post-flash flow of $10x10^6$ gal/day and 330 days/year operation.

Component	Concentration in Brine, %	Quantity Tons/day	Unit Value Cost	Potential Gross Income	
				Cost/day	Cost/year
Bromine (Br_2)	0.0035	1.5	$400	$ 600	$ 198,000
Ammonia (NH_3)	0.0039	1.7	110	187	61,710
Calcium chloride ($CaCl_2$)	0.38	161.5 anhydrous 404 as 40% brine	16.50 as 40%	6,666	2,199,800
Lithium carbonate ($LiCO_3$)	0.029	12.5	400	5,000	1,650,000
Strontium carbonate ($SrCO_3$)	0.038	16	300	4,800	1,584,000
Borax ($Na_2B_4O_2 \cdot 10H_2O$)	0.023	9.8	20	686	226,380
			Total		$5,919,890

Based on a gross yearly income of about $\$6x10^6$, this fluid does not appear to hold much promise for yielding an economic operation as regards minerals recovery.

One possibility might be to consider selectively recovering only lithium and strontium compounds from this fluid. At 80% recovery of lithium carbonate and 50% recovery of strontium carbonate, the gross annual income would be $\$2.1x10^6$, and would appear to justify an investment of from $\$2x10^6$ to $\$4x10^6$, based on the turnover ratio described earlier in Table 27.

However, the bare plant equipment required to recover these two compounds would cost $\$2.2 \times 10^6$ (see Table 28, Items C and F) and on an installed plant basis would cost $\$11.25 \times 10^6$ ($\$2.2 \times 10^6 \times 5.1$ installed cost factor).

Therefore, it does not appear economically feasible to consider minerals recovery from such very dilute geothermal fluids as exemplified by Mesa L-6-1, unless some additional process studies might evolve some new recovery technology.

POTENTIAL NEW AREAS OF UTILIZATION FOR COMPONENTS OF GEOTHERMAL FLUIDS

The major constituents of most geothermal fluids are chlorides of the alkali metals; sodium, potassium, and lithium, together with the alkaline earth metals calcium and magnesium, also as chlorides.

Heavy metals present in trace and greater concentrations usually can be removed (such as described elsewhere in this report) and are of sufficient economic value to warrant it.

However, the economics of recovering salines, such as those mentioned above, are heavily dependent upon location of the source of these chloride salts in relation to the marketplace. In particular, this is true of sodium chloride, a commodity used worldwide, at yearly rates in excess of 150 million tons.

The economics of marketing salines depend upon either closeness to the marketplace or closeness to low cost transport, such as bulk carrier ocean vessels.

Lacking any of the above fortuitous conditions (most geothermal resource areas are located relatively far from the coast and harbor sites), at least two courses of action are available for a given geothermal resource. These are:

A. Concentrate the geothermal fluid (after removing those elements that can be easily precipitated or extracted) either by steam or solar evaporation, thereby recovering sodium chloride, potassium chloride, and calcium/magnesium chloride brine.

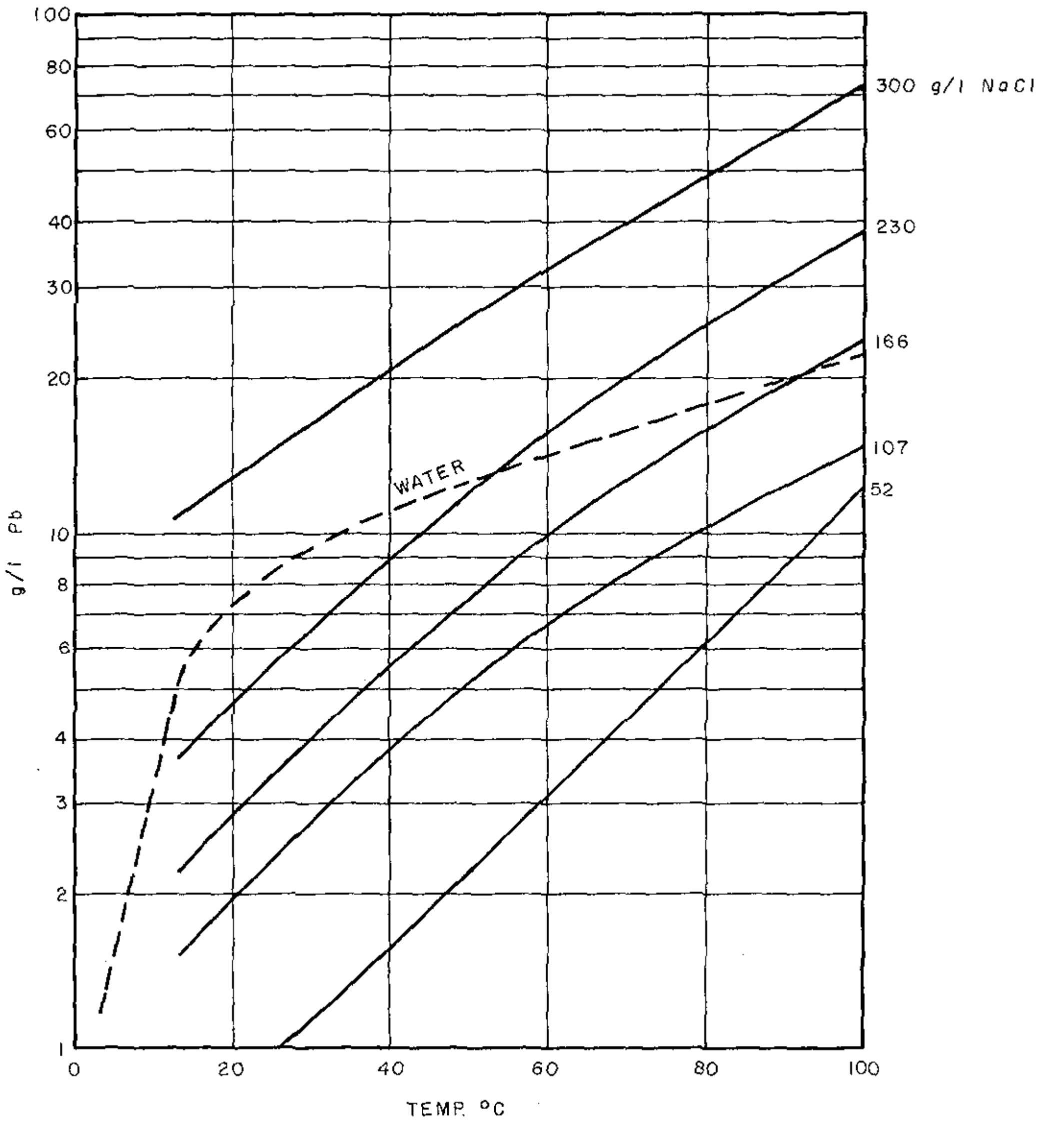
    1. Utilize the potassium chloride for a fertilizer product.
    2. Convert the sodium chloride to sodium hydroxide and chlorine which are more valuable; i.e., higher priced, and can thus bear more transportation cost to bring them to the consuming areas.
    3. Utilize the bittern or concentrated calcium/magnesium chloride brine either as a thawing agent for ice and freezing conditions or as a heavy media liquid for coal gravity separations.

       Such uses are not new and are well documented in the literature (Lessing and Belknap processes). Applicability depends entirely on the steam/power balance desired at any given geothermal site and the overall economics of the total package concept.

B. Utilize the saline geothermal fluid (either prior to removing those elements that can be easily precipitated or extracted, or after this step) as it is discharged from the steam separators as a hydrothermal leaching solution or as a metal complexing solution.

    1. Many heavy metal chlorides such as mercury, lead, silver, and copper have their solubilities markedly increased in the presence of high chloride concentrations. Figure 46

SOLUBILITY OF LEAD CHLORIDE IN AQUEOUS SOLUTIONS OF SODIUM CHLORIDE



DATA FROM SEIDELL
SOLUBILITIES OF
INORGANIC COMPOUNDS

FIGURE 46

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presents graphically the solubility of lead chloride in the presence of varying levels of sodium chloride.

Calcium chloride-magnesium chloride should be even more effective as higher chloride concentrations can be obtained and also higher operating temperatures, due to their greater boiling point rise.

2. Use of solutions of alkali and alkaline earth chlorides to promote or enhance the effectiveness of oxidative leaching solutions such as $CuCl_2$-$FeCl_3$ in leaching galena, chalcopyrite, and other heavy metal sulfide ores. Noranda Mines has been granted a patent on this type of concept.

   This type of leach condition promoting is apparently unique to the presence of chloride ion, as the corresponding sulfates are inactive. It would appear that the complexing ability of the Cl^- ion is part of the key in these applications.

3. The literature has reported (Tarabaev, S.I.) that alkali metal chlorides are effective in increasing the solubility product of basic heavy metal sulfides.

   Geothermal fluids of high salinity and at high temperatures (>100°C) should be ideal for this purpose.

4. Geothermal fluids of the Sinclair No. 4 type have been used by Hazen Research to decompose jarosite compounds such as plumbojarosite. While NaCl solutions were not very effective, Sinclair No. 4 type brine was extremely effective in decomposing such compounds, perhaps due to the combinations of NaCl, KCl, and $CaCl_2$.

5. Conversion of heavy metal sulfate solutions to their corresponding chloride salts can be achieved by highly saline geothermal fluids containing calcium chloride, together with other alkali metal chlorides. Calcium removes the sulfate ion as calcium sulfate while the remaining chlorides in solution serve to enhance the solubility of the heavy metal chlorides.
6. Use of geothermal fluids containing chlorides as the chlorine source for chloridizing roasting processes, whereby the heavy metals are volatilized as their respective chlorides, similar to the Kawa-Seiku process utilized in Japan.
7. High chloride ion concentrations, such as are found in geothermal fluids of the Sinclair No. 4 type, are reported to increase the hydrolysis of heavy metal ions such as divalent copper.

A large number of additional processes utilizing chloride chemistry for leaching and winning heavy metals, have been discussed by VanArsdale.

The Bureau of Mines has done considerable pioneering work in the area of electro-oxidation of heavy metal ores, utilizing sodium chloride brines. The use of geothermal fluids for such electro-oxidation would appear to be a logical substitution and might improve the process.

In addition, the Bureau has utilized sodium chloride brine as the carrier to electro-oxidize carbonaceous gold ores, thereby making such ores amenable to cyanide leaching for gold recovery. Substitution of geothermal fluids for sodium chloride brine should be possible for this application.

All of the foregoing discussion regarding new or additional use for geothermal fluids is predicated on the assumption that reinjection of the total geothermal fluid is not necessary to maintain hydraulic equilibrium, or that additional fluid or waters for reinjection can be found near the well site and will serve this purpose.

If reinjection of the geothermal fluid is necessary, then there will be no saline solution requiring utilization or disposal, and the only treatment required for such a fluid would be clarification and removal of precipitable components such as silica and iron which might otherwise plug the pores of the producing structure when reinjected. Recovery of heavy metal values and alkali metals such as lithium, would depend upon the relative economics of each individual situation.

BENCH SCALE STUDIES ON MINERALS RECOVERY FROM GEOTHERMAL BRINES

Following field trips to various geothermal resource sites to collect samples of fluids, these samples were analyzed to determine major and minor components present. These analytical results have been presented earlier in this section.

Of the seven geothermal fluid and hot springs water samples taken, only three appeared to contain sufficient dissolved constituents to warrant further exploratory process work; Mesa L-6-1, Sinclair No. 4, and Magmamax No. 1.

Initially, it was thought that evaporation of water might be economically feasible and that solar evaporation would result in the lowest cost per unit of water evaporated.

Therefore, simulated solar evaporation tests were started with all three geothermal fluids, using Teflon® lined pans to contain the fluids and

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infrared heat lamps providing the simulated solar radiation. A small room fan provided an air flow of about 5 mph over the surface of the evaporation pans to increase the rate of evaporation.

As the level of fluid dropped due to evaporation, additions of fresh feed were made to replenish the volume loss.

Samples of clear brine were periodically taken from each of the three evaporating fluids and analyzed, to follow the concentration path of those elements of interest. Chemical "tracers" were used to determine concentration ratio for each sample taken. Complete analytical data sheets are presented in Appendix B.

Chemical "tracers" are soluble compounds in a solution that will not precipitate out, crystallize out, or form mixed-crystals (isomorphous mixtures) with other salts that do crystallize. Since literature data on salts systems of the degree of complexity of these geothermal fluids is nonexistent, it was decided to utilize three tracer elements, lithium, calcium, and magnesium, to follow the course of concentration and serve as a check with each other.

Figures 47 and 48 present the concentration ratio data for Mesa L-6-1 geothermal fluid. Due to the very dilute nature of this fluid, it was necessary to concentrate up to a ratio of 100 to 1 to determine the disposition of the minor constituents. The only elements of interest that were concentrated without loss, due to precipitation or crystallization, were lithium, calcium, and apparently ammonia, although there may have been some loss as an ammonium chloride double salt with potassium chloride.

In general, it would appear that only lithium and perhaps ammonia and strontium values would be worth considering as recoverable components from this geothermal fluid, and then only if some concentration of the fluid could be achieved.

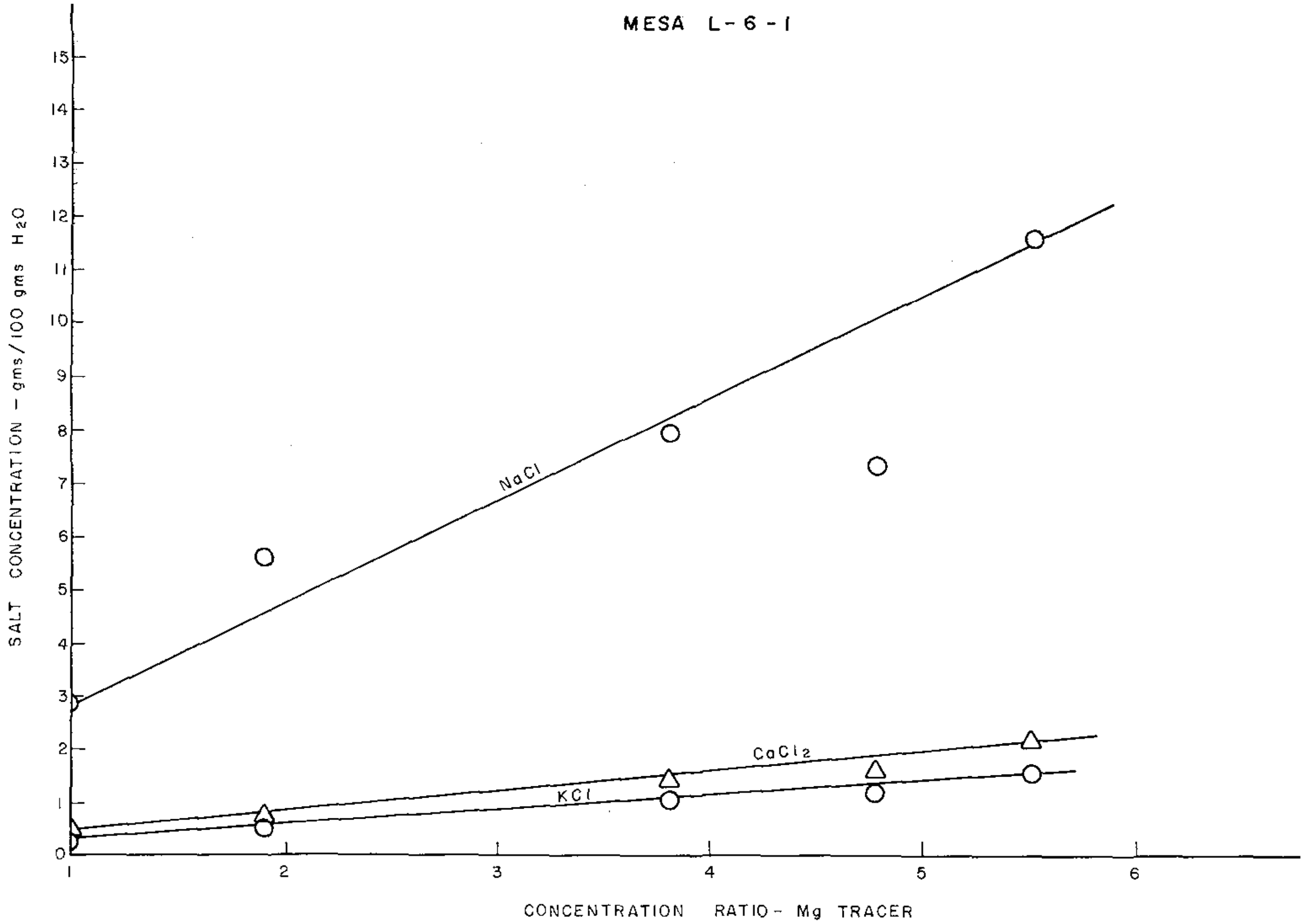

FIGURE 47
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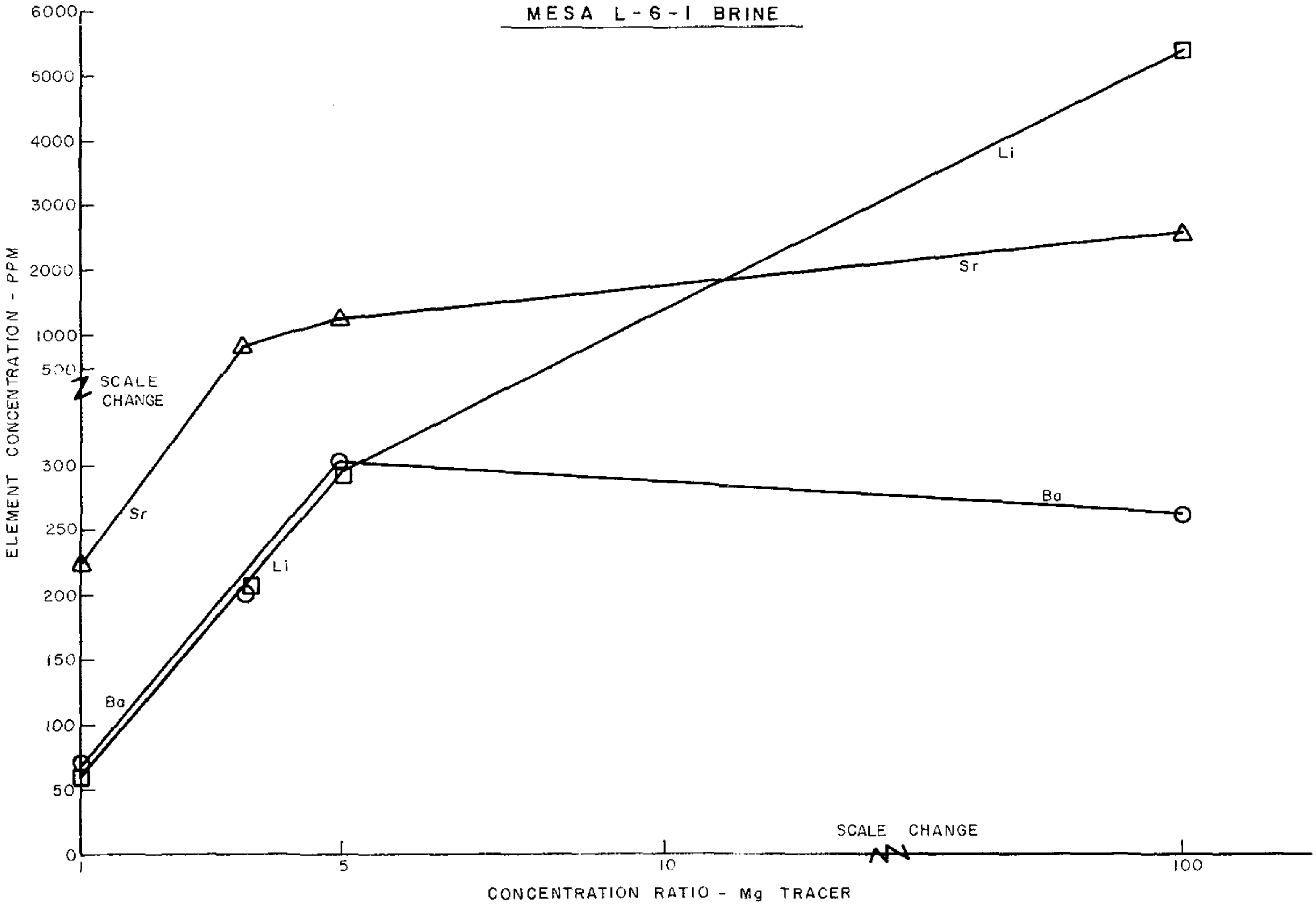

MESA L-6-I BRINE

FIGURE 48
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Figures 49 and 50 present data on the concentration paths of some of the components in Sinclair No. 4 geothermal fluid as a function of concentration ratio.

It is apparent that both sodium and potassium chloride crystallize out; sodium chloride commences to crystallize out almost immediately, while a concentration ratio of about 2.0 must be reached before potassium chloride begins to crystallize out. This indicates that a preliminary separation of a portion of the sodium chloride, free from contamination with potassium chloride is possible.

A more detailed phase rule study of the sodium, potassium, and calcium chloride system, which further elaborates on this portion of the evaporation work, is presented in Appendix A.

Most of the minor constituents present in the fluid seem to concentrate without loss, except for lead, manganese, iron, and barium. Lead appears to be either occluded, or coprecipitated, with the sodium chloride, almost quantitatively.

Iron present in Sinclair No. 4 fluid oxidized to some degree during the simulated solar evaporation tests and precipitated as ferric-ferrous hydroxide which collected at the bottom of the pan, together with the crystallized salts. Table 34 presents a mass spectrographic analysis of this iron hydroxide precipitate.

It can be seen that this iron hydroxide precipitate is a collector for many of the trace elements present in this geothermal fluid. Tungsten is at a 110 parts per million (ppm) concentration in this material, while arsenic is 35 ppm, copper at 14 ppm, and vanadium at 28 ppm. The original Sinclair No. 4 geothermal fluid only contained 0.7 ppm copper, so that the concentration ratio achieved by this iron hydroxide precipitate appears to

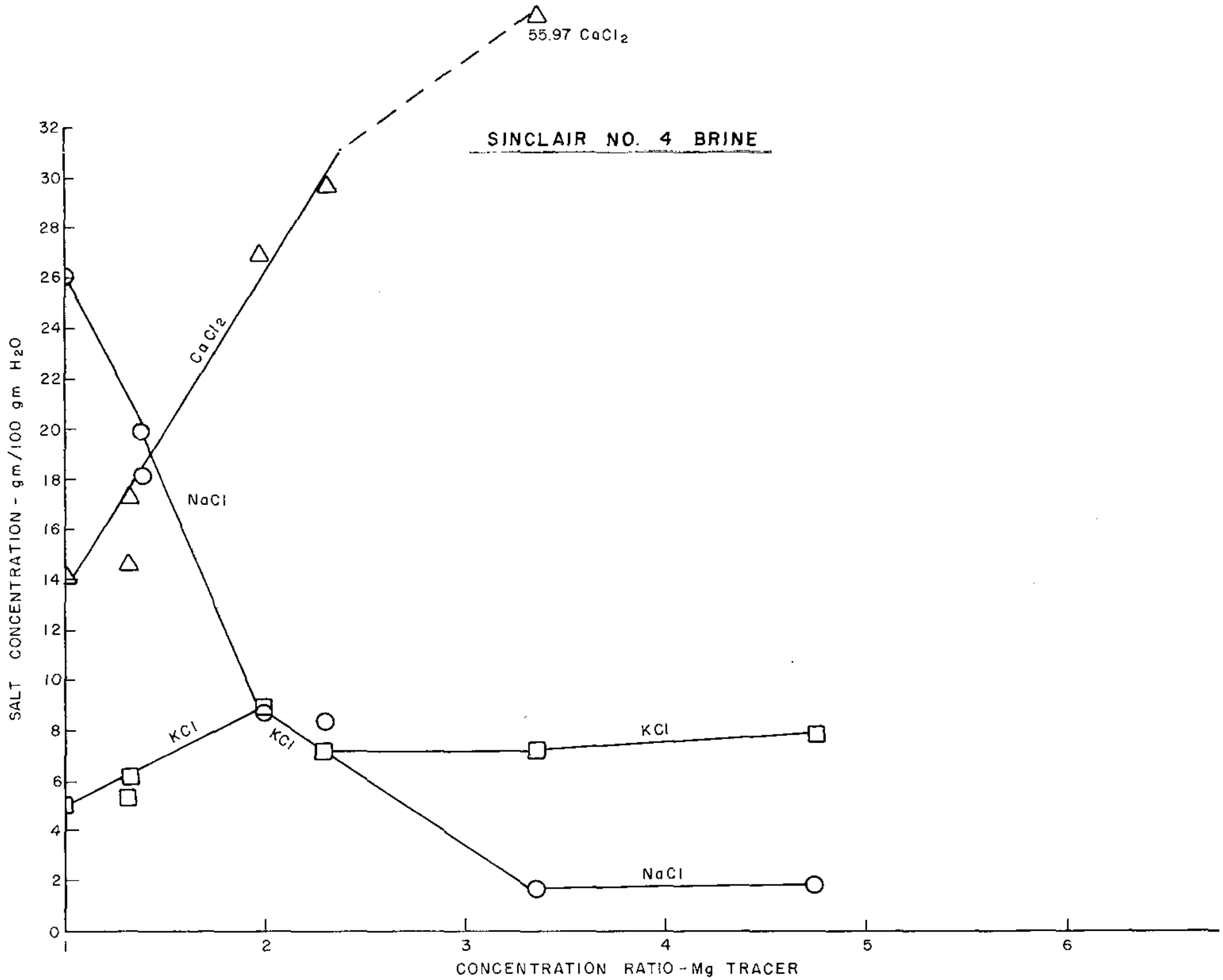

FIGURE 49

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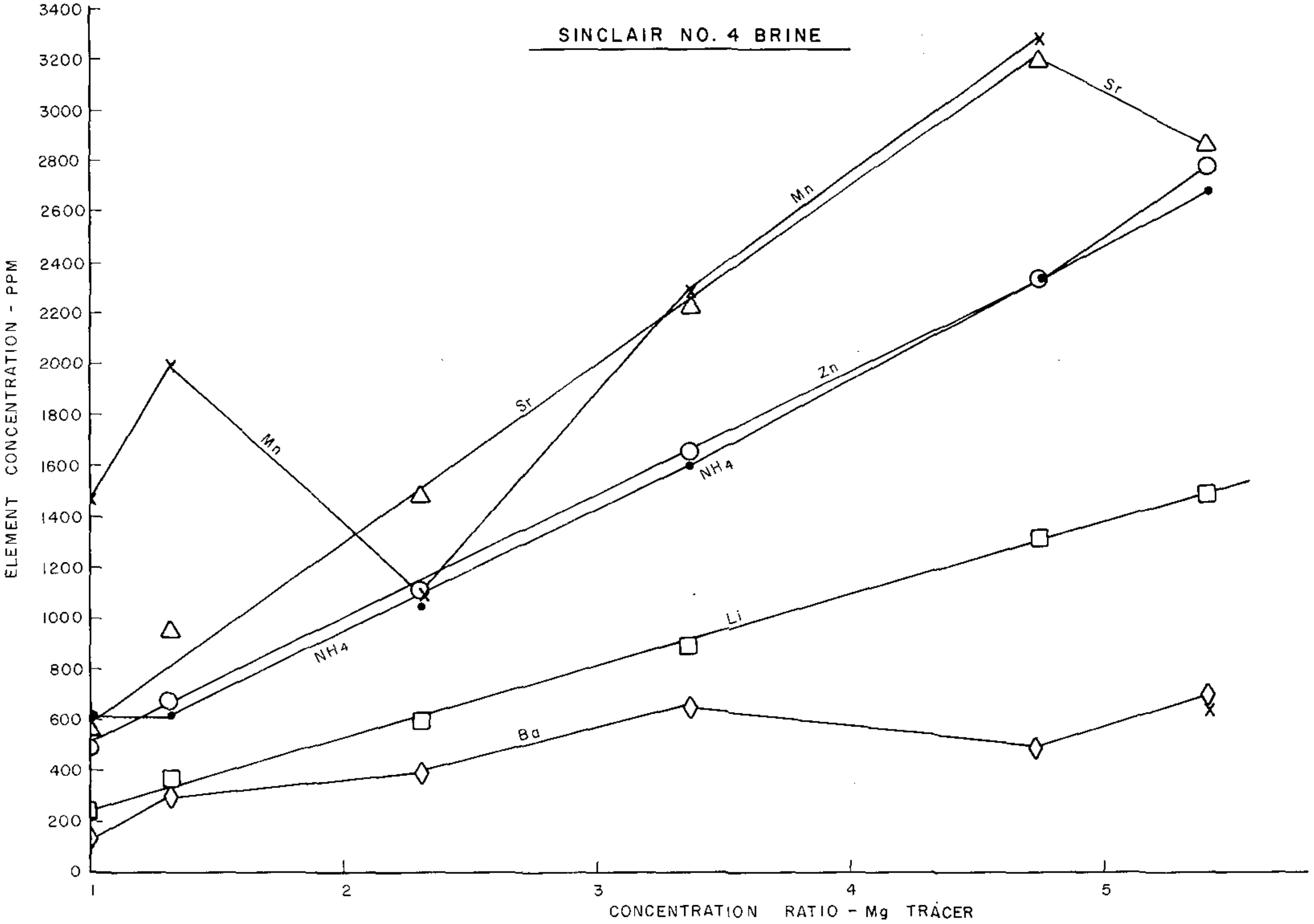

FIGURE 50

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Table 34

Ferric-ferrous Hydroxide Precipitate Removed
During Simulated Solar Evaporation of Sinclair No. 4 Brine

Concentration in ppm Weight

Element	Concentration	Element	Concentration	Element	Concentration	Element	Concentration
Uranium	<0.58	Terbium	<0.27	Ruthenium		Vanadium	28
Thorium	<0.80	Gadolinium	<0.67	Molybdenum	150	Titanium	62
Bismuth	<0.88	Europium	<0.80	Niobium	0.69	Scandium	
Lead	4.0	Samarium	<2.1	Zirconium	2.0	Calcium	≅0.38%
Thallium	0.11	Neodymium	<6.3	Yttrium	0.96	Potassium	820
Mercury		Praseodymium	0.35	Strontium	93	Chlorine	Maj
Gold		Cerium	6.5	Rubidium	25	Sulphur	≅4.2%
Platinum		Lanthanum	0.15	Bromine	7.9	Phosphorus	25
Iridium		Barium	98	Selenium	0.89	Silicon	4.9%
Osmium		Cesium	33	Arsenic	35	Aluminum	210
Rhenium		Iodine	12	Germanium	<0.10	Magnesium	≅0.13%
Tungsten	110	Tellurium	<0.13	Gallium	7.7	Sodium	Maj
Tantalum	0.28	Antimony	7.7	Zinc	24	Fluorine	≅1.3%
Hafnium	<0.33	Tin	0.41	Copper	14	Oxygen	NR
Lutecium	<0.36	Indium		Nickel	3.5	Nitrogen	NR
Ytterbium	<2.1	Cadmium	<0.17	Cobalt	<0.58	Carbon	NR
Thulium	<0.15	Silver	0.07	Iron	530	Boron	160
Erbium	<0.60	Palladium		Manganese	20	Beryllium	0.17
Holmium	<0.35	Rhodium		Chromium	8.8	Lithium	940
Dysprosium	<4.5					Hydrogen	

NR - Not reported.

be 50/1 for copper. The other elements mentioned in the starting fluid were not analyzed, so no concentration ratio figures are available for them. Based upon the apparently unique scavenging or collecting ability of the iron hydroxide precipitate, it was decided to explore this aspect in more detail. Details will be presented further on in this section.

Calculated yield figures for sodium and potassium chloride crystallized out from Sinclair No. 4 geothermal brine at a concentration ratio of 4.6/1 are as follows:

Sodium chloride	98.8%
Potassium chloride	74.3%
Lead	97% - equivalent to a level of <u>670</u> ppm on the combined sodium-potassium chloride salts. Starting lead level in the brine was 141 ppm (see Appendix B).

Figures 51 and 52 present similar concentration ratio data for Magmamax No. 1 geothermal fluid. As this fluid is very similar to Sinclair No. 4, with the exception of being more dilute, it reacts similarly to Sinclair No. 4 upon concentration.

Calculated yield of sodium and potassium chlorides at a concentration ratio of 4.3 is as follows:

Sodium chloride	92.5%
Potassium chloride	21.3%
Lead	68% - equivalent to a level of <u>186</u> ppm in the combined sodium-potassium chloride salts. Starting lead level in the brine was 29 ppm (see Appendix B).

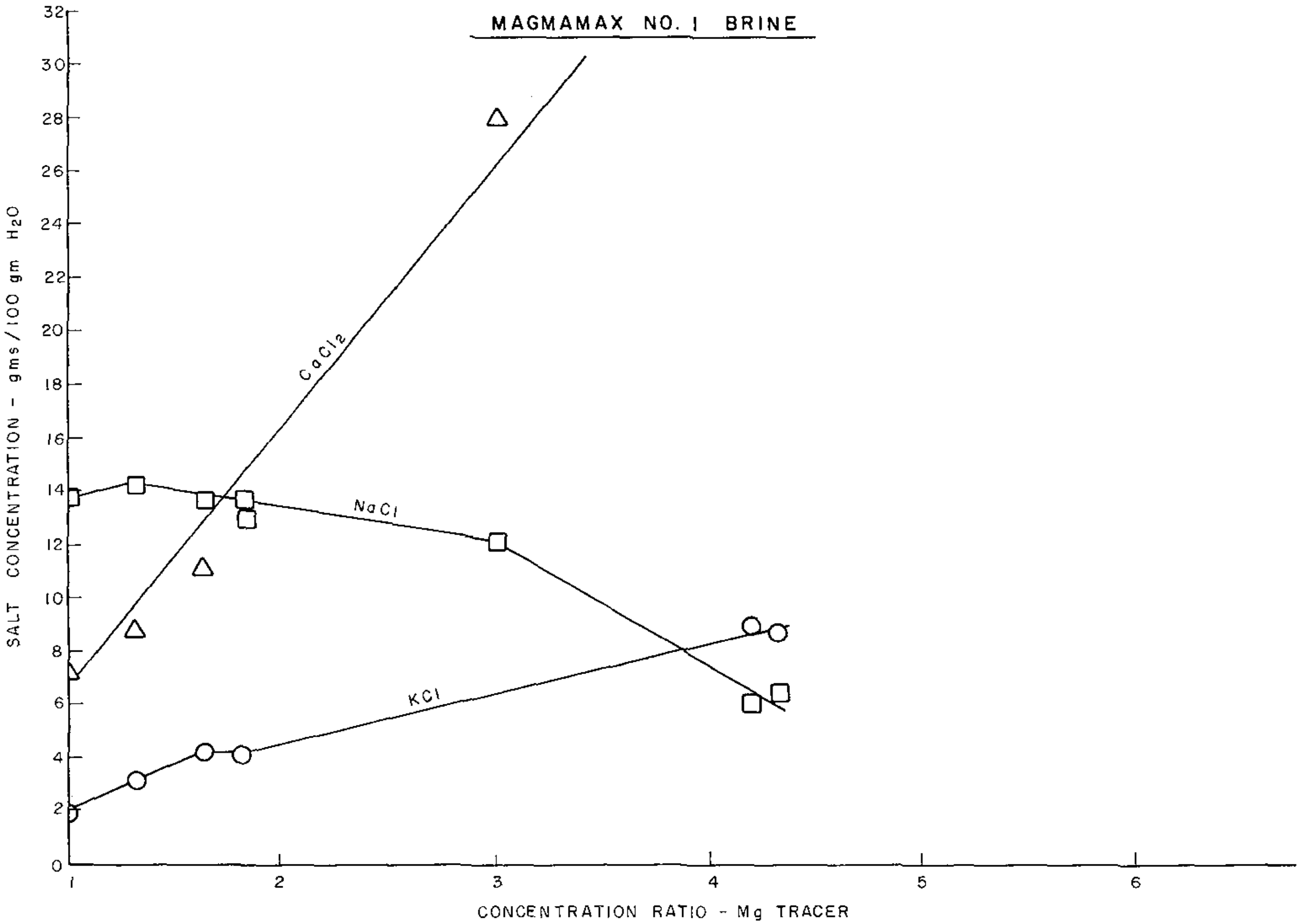

FIGURE 51
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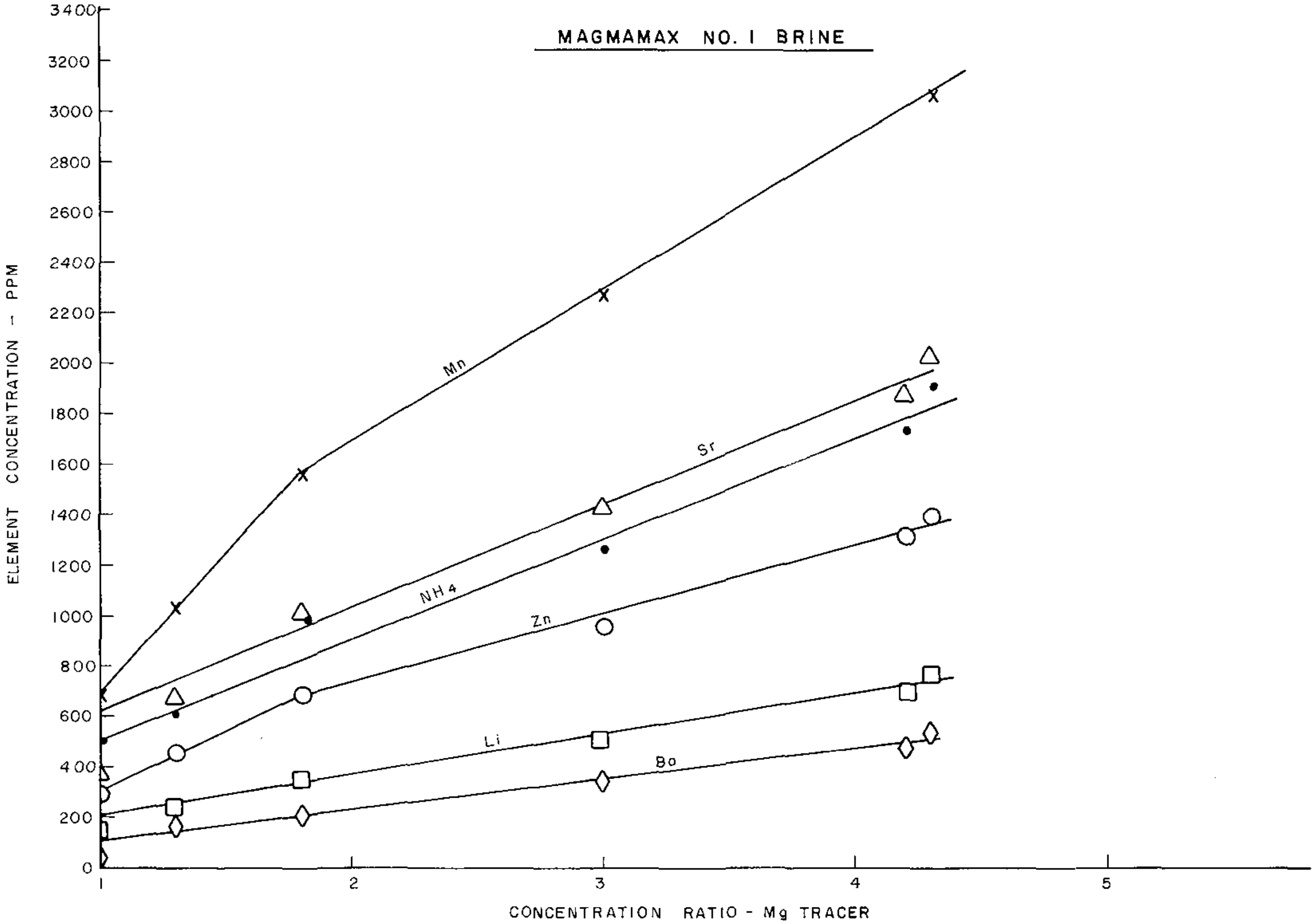

FIGURE 52

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Again, it is seen that any lead in these geothermal fluids appears to coprecipitate, or become occluded, with the sodium chloride. Since lead is an extremely deleterious impurity in sodium chloride, particularly where the sodium chloride is destined for animal or human consumption, its removal from geothermal fluids is mandatory if saleable sodium chloride is to be recovered.

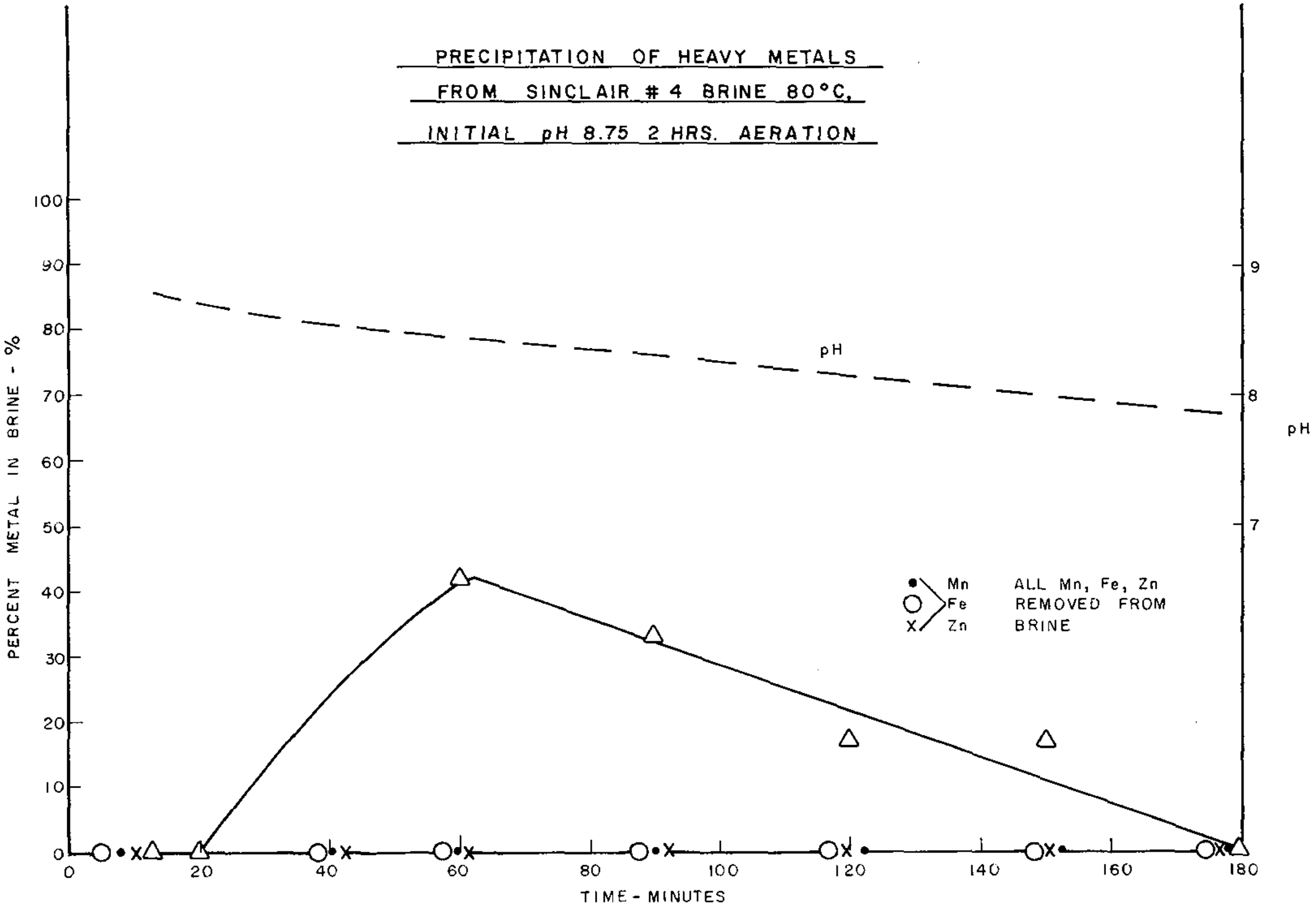
Following the geothermal fluid concentration tests described above, a series of brine purification studies was begun, utilizing the information developed above on the collecting capabilities of the iron hydroxides.

A series of precipitation studies was started, utilizing Sinclair No. 4 geothermal fluids since it had the highest level of minor constituents of any of the geothermal fluids analyzed.

The general work outline involved the adjustment of pH of the fluid, using calcium hydroxide, under both oxidizing and nonoxidizing conditions, to determine if ferrous or ferric iron, in conjunction with manganous or manganic oxides could remove the minor constituents present in the brine.

Figure 53 depicts the results obtained when Sinclair No. 4 brine at 80°C was adjusted to an initial pH of 8.75 with calcium hydroxide, and then aerated for two hours using an air sparge. As shown, all of the iron, manganese, and zinc were removed from the fluid and did not reappear in solution. Lead, initially, was also completely removed, but reappeared in solution as aeration (oxidation by air sparging the slurry) progressed.

As oxidation of the slurry progressed, the lead began to be removed from the solution again, until after three hours of aeration all of the lead had again been removed. A corresponding drop in the pH of the slurry from initial 8.75 down to 7.80 indicated that divalent iron and manganese were being oxidized to trivalent and quadrivalent states, respectively, with



PRECIPITATION OF HEAVY METALS FROM SINCLAIR # 4 BRINE 80°C, INITIAL pH 8.75 2 HRS. AERATION

FIGURE 53

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release of hydrogen ion, thereby consuming some of the calcium hydoxide.

Figure 54 depicts the results of a similar test carried out from initial pH 9.25 but with no aeration. No special provision was made for exclusion of air and after approximately 30 minutes the predominantly grey-green color of ferrous hydroxide began to turn color to the characteristic orange-brown color of ferric hydroxide. Correspondingly, when the ferrous iron began to convert to ferric,the lead, originally removed by adsorption or coprecipitation, began to reappear in the solution. A small portion of the zinc also appeared in solution.

To further investigate this facet of the brine purification study, a similar test was run where a constant nitrogen purge was maintained above the test slurry. Figure 55 presents the results of this test.

As shown, complete removal of iron, manganese, lead, and zinc was achieved for approximately one hour, after which time some oxidation took place, as evidenced by the change in color of the iron hydroxide precipitate from grey-green to a brown-orange color.

Apparently, ferrous iron hydroxide is the collector for the lead and zinc values present in the Sinclair No. 4 geothermal fluid. Ferric hydroxide, formed upon oxidation of the slurry, does not appear to have the ability to remove lead as efficiently as ferrous hydroxide, although zinc continues to be collected and held by the ferric hydroxide.

One further test was carried out to see if a selective precipitation of iron and manganese could be made, so as to obtain these two commodities, each in a relatively pure state.

Figure 56 presents data obtained by air oxidation of a slurry of Sinclair No. 4 brine, initially neutralized to a pH of 7.75, followed by aeration.

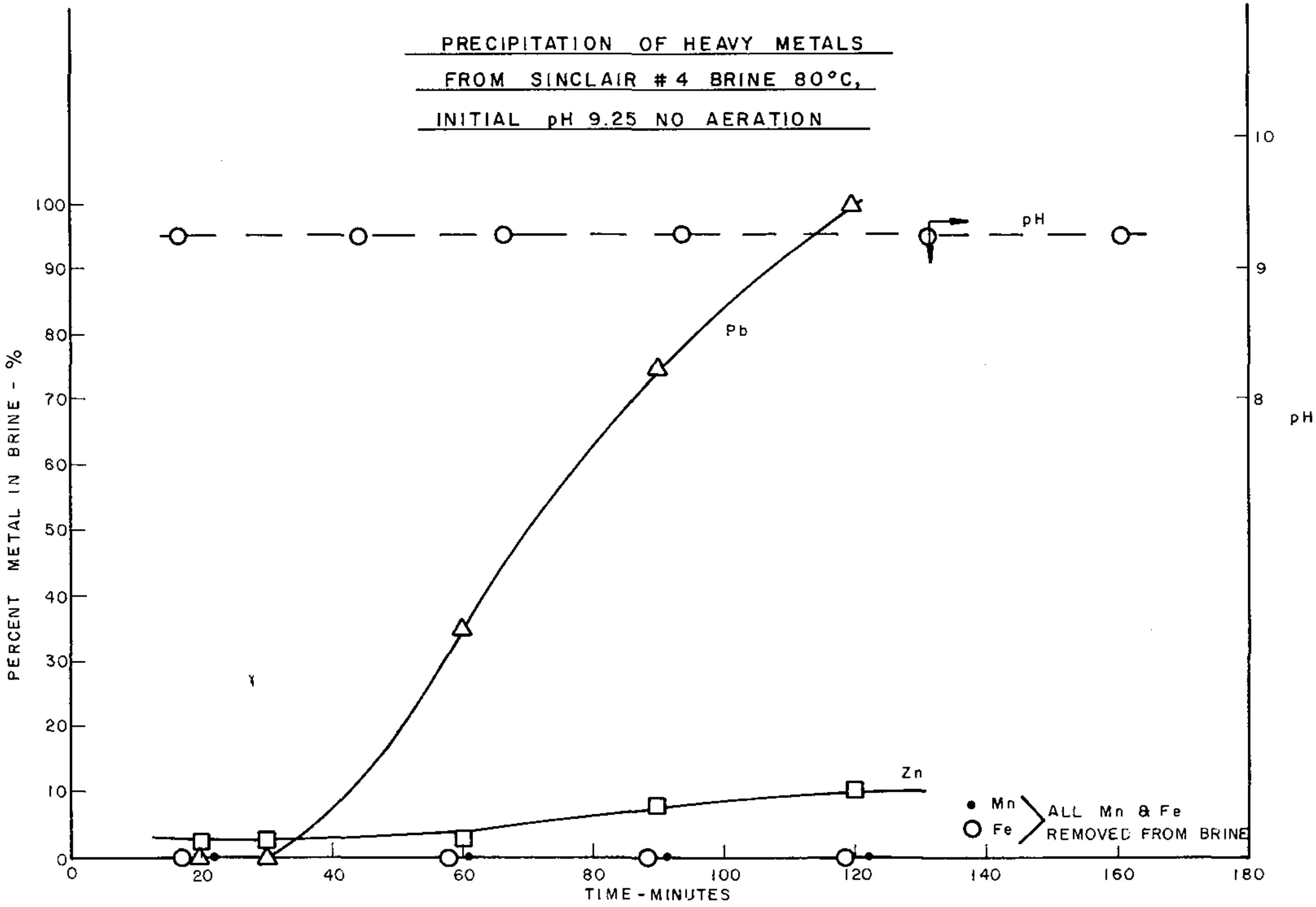

FIGURE 54
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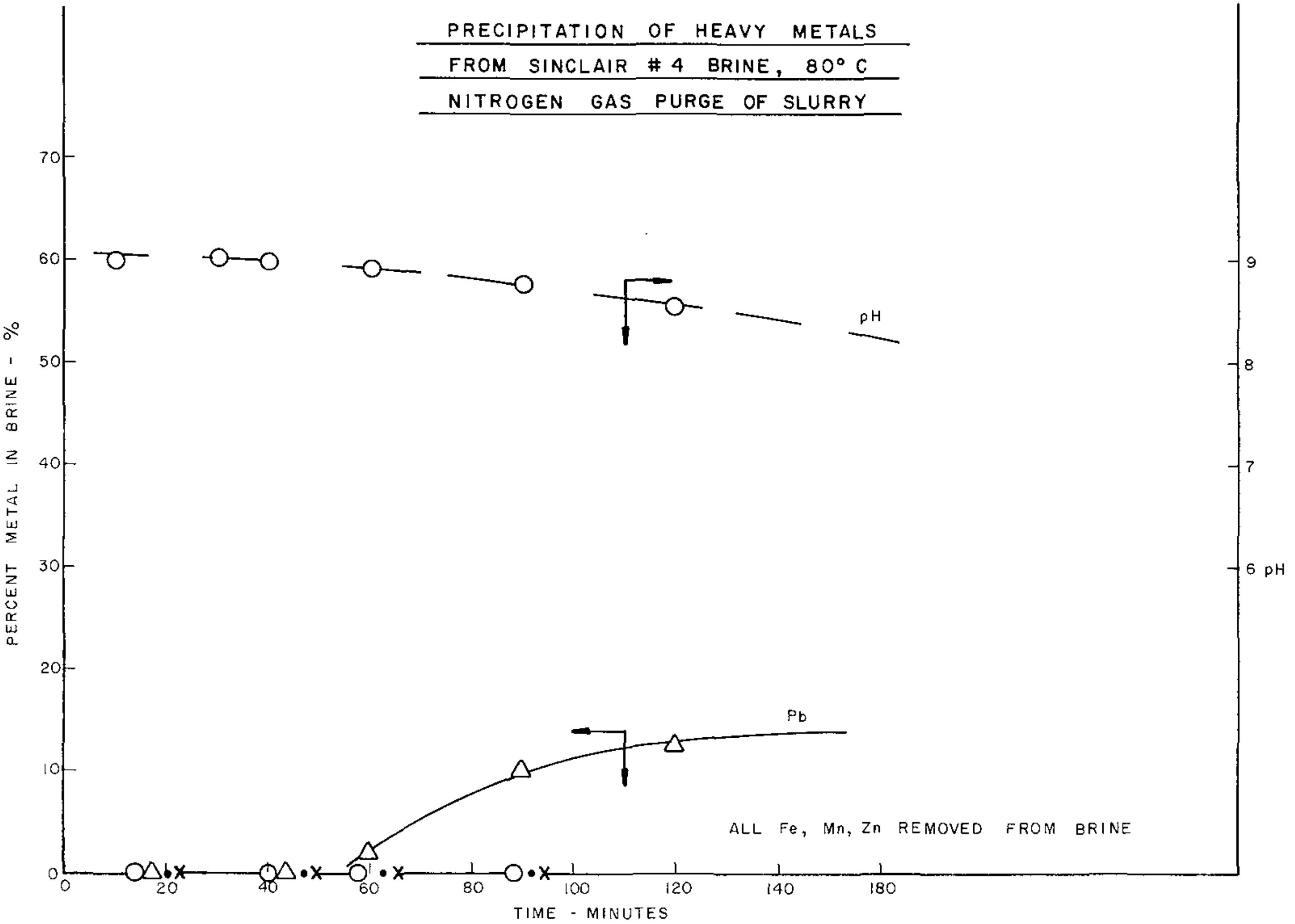
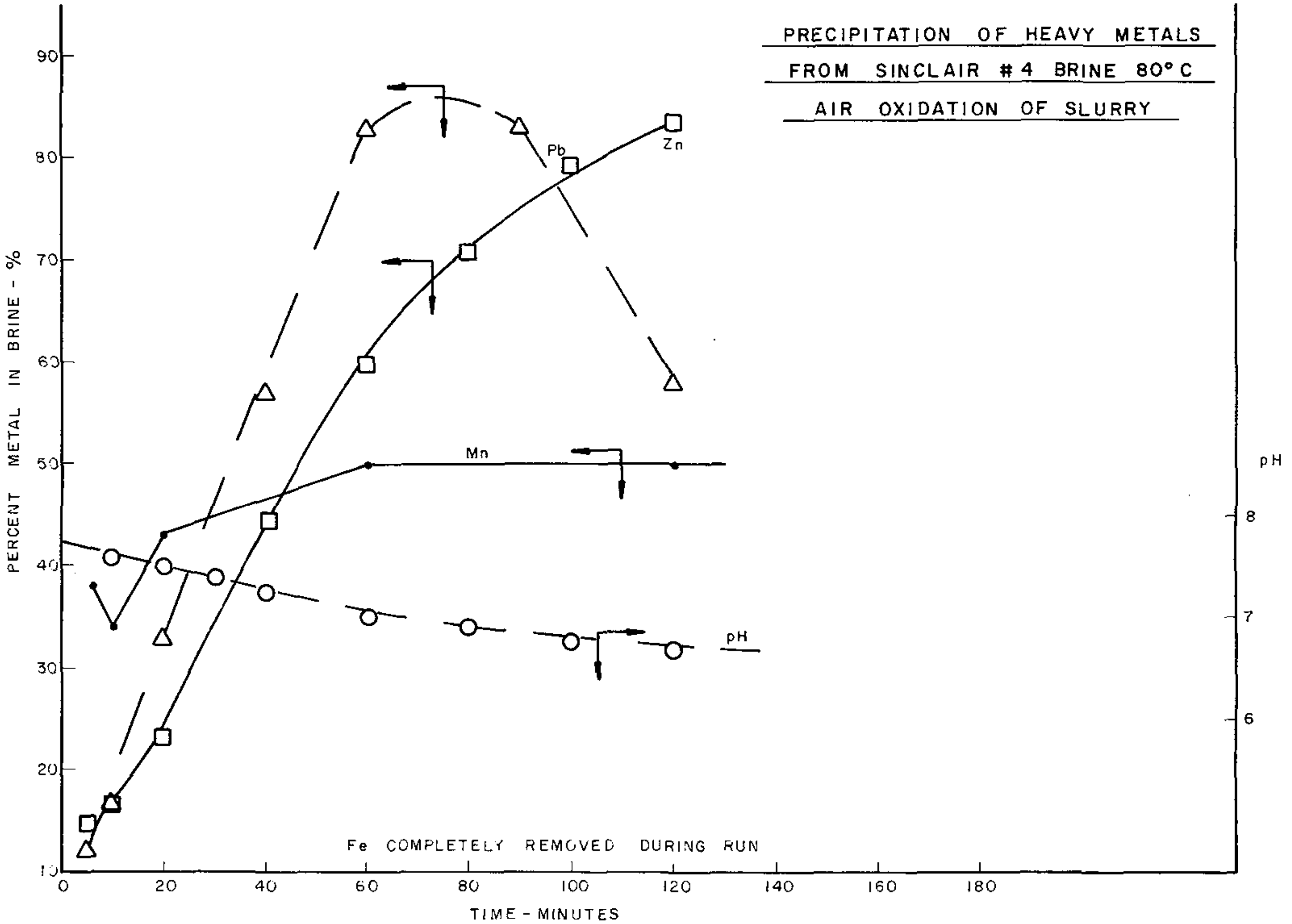


PRECIPITATION OF HEAVY METALS
FROM SINCLAIR # 4 BRINE, 80° C
NITROGEN GAS PURGE OF SLURRY

FIGURE 55
hri



PRECIPITATION OF HEAVY METALS

FROM SINCLAIR # 4 BRINE 80° C

AIR OXIDATION OF SLURRY

FIGURE 56
hri

Terminal pH was 6.70 and considerable (50%) of the manganese originally present remained in solution. Both lead and zinc were initially completely removed but reappeared in solution as oxidation of the slurry progressed.

Based upon the results of the scoping tests described above, the following tentative conclusions can be drawn:

1. Ferrous hydroxide is an effective collector of lead and zinc in solution, in conjunction with manganous hydroxide.
2. Some removal of lead and zinc from solution takes place, even when only ferrous hydroxide is precipitated, and some manganese is left in solution.
3. The possibility exists for a selective removal of zinc by collection on ferrous hydroxide and of lead by collection upon manganic oxide (manganese dioxide).

Additional studies were made on removing barium, strontium, and lithium from geothermal fluids.

Since it appears that the concentration of barium and strontium (as sulfates) in Sinclair No. 4 brine is the equilibrium solubility in solutions containing that concentration of alkali metal chlorides, two approaches were open to recover these components. One was the concentration of the geothermal fluid to remove water and increase the sulfate concentration, thereby precipitating the least soluble compound, barium sulfate (see Figure 50). Another approach would be to increase the sulfate ion concentration and thereby exceed the solubility product of either, or both, barium and strontium sulfates.

As discussed earlier, reinjection of all or part of the fluids derived from "wet" geothermal resources is believed to be a necessity; therefore, only a limited amount of concentration or water removal from such geothermal fluids can be considered.

The second approach, that of increasing the sulfate level in the geothermal fluid, seems to be a more feasible method for removing barium and strontium.

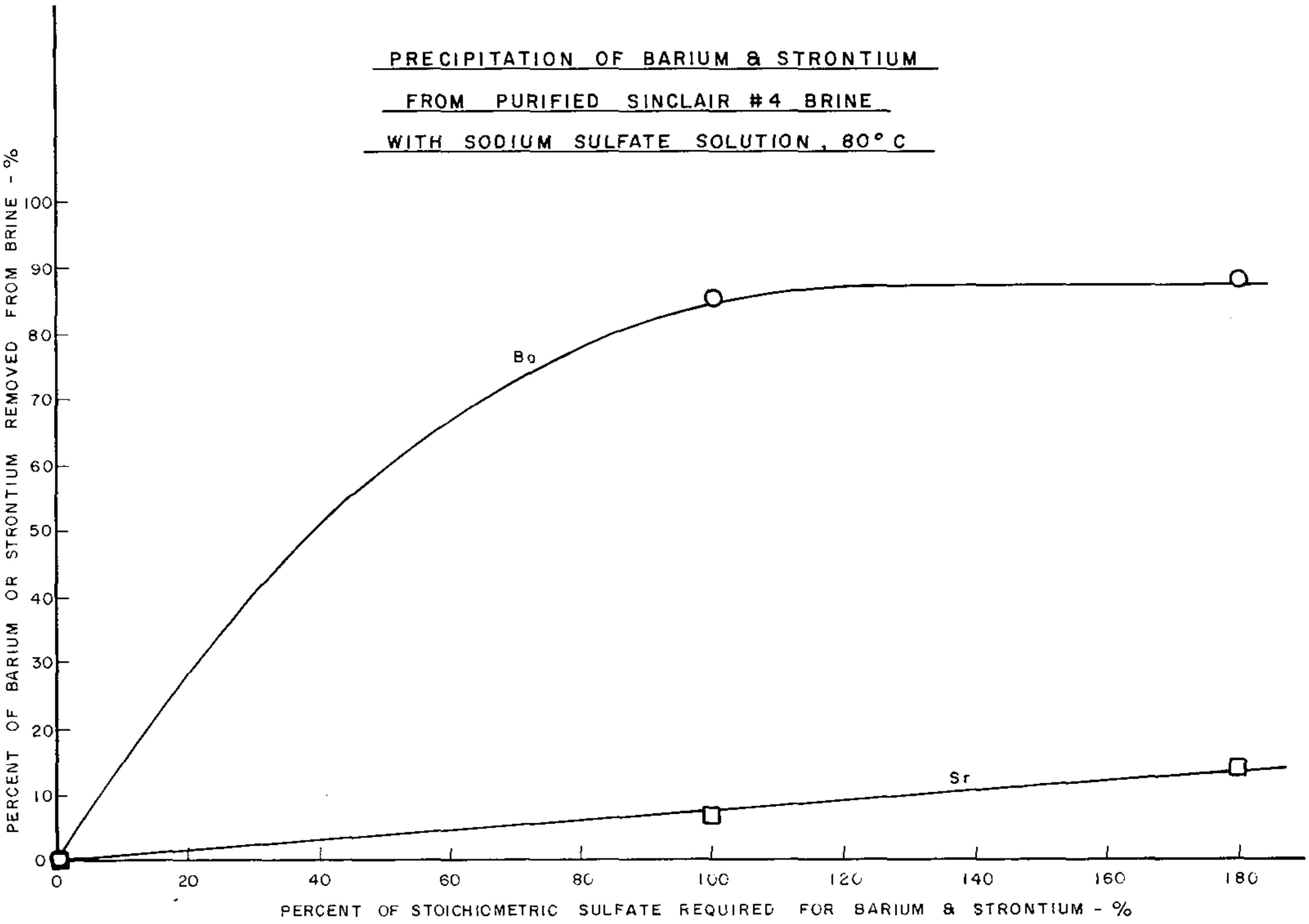
Figure 57 presents data obtained by saturating Sinclair No. 4 brine at 80°C with calcium sulfate, to increase the sulfate level of the fluid. Essentially no strontium is removed from the brine while 60 to 70% of the barium in solution is precipitated as barium sulfate.

An even greater yield of barium, as barium sulfate, from Sinclair No. 4 brines can be achieved by using a more soluble sulfate source, such as sodium sulfate. Figure 58 shows the percent recovery of barium and strontium from Sinclair No. 4 brine (at 80°C), as a function of the quantity of sulfate ion required to achieve stoichiometry.

Approximately 90% of the barium contained in Sinclair No. 4 brine can be removed, with only a 10% loss of strontium from the fluid, by use of this approach.

A follow-up area for study might be to consider removing barium in two stages, using calcium sulfate in the first stage and sodium sulfate in the second stage. Under these conditions, some recovery of strontium as the sulfate may be possible, even though the limited laboratory work to date indicates that some concentration of the geothermal fluid may be necessary to achieve reasonable strontium recovery.

As part of the geothermal brine purification studies carried out in this portion of the work, some of the purified Sinclair No. 4 brine, produced from the above test work was evaporated in a simulated solar evaporation pan to recover sodium and potassium chlorides. Figure 59 presents some of the physical data obtained during the course of the concentration cycle, while Table 35 presents the mass spectrographic analysis of the



PRECIPITATION OF BARIUM & STRONTIUM
FROM PURIFIED SINCLAIR #4 BRINE
WITH SODIUM SULFATE SOLUTION, 80° C

FIGURE 58
hri

SIMULATED SOLAR EVAPORATION

PURIFIED SINCLAIR #4 BRINE

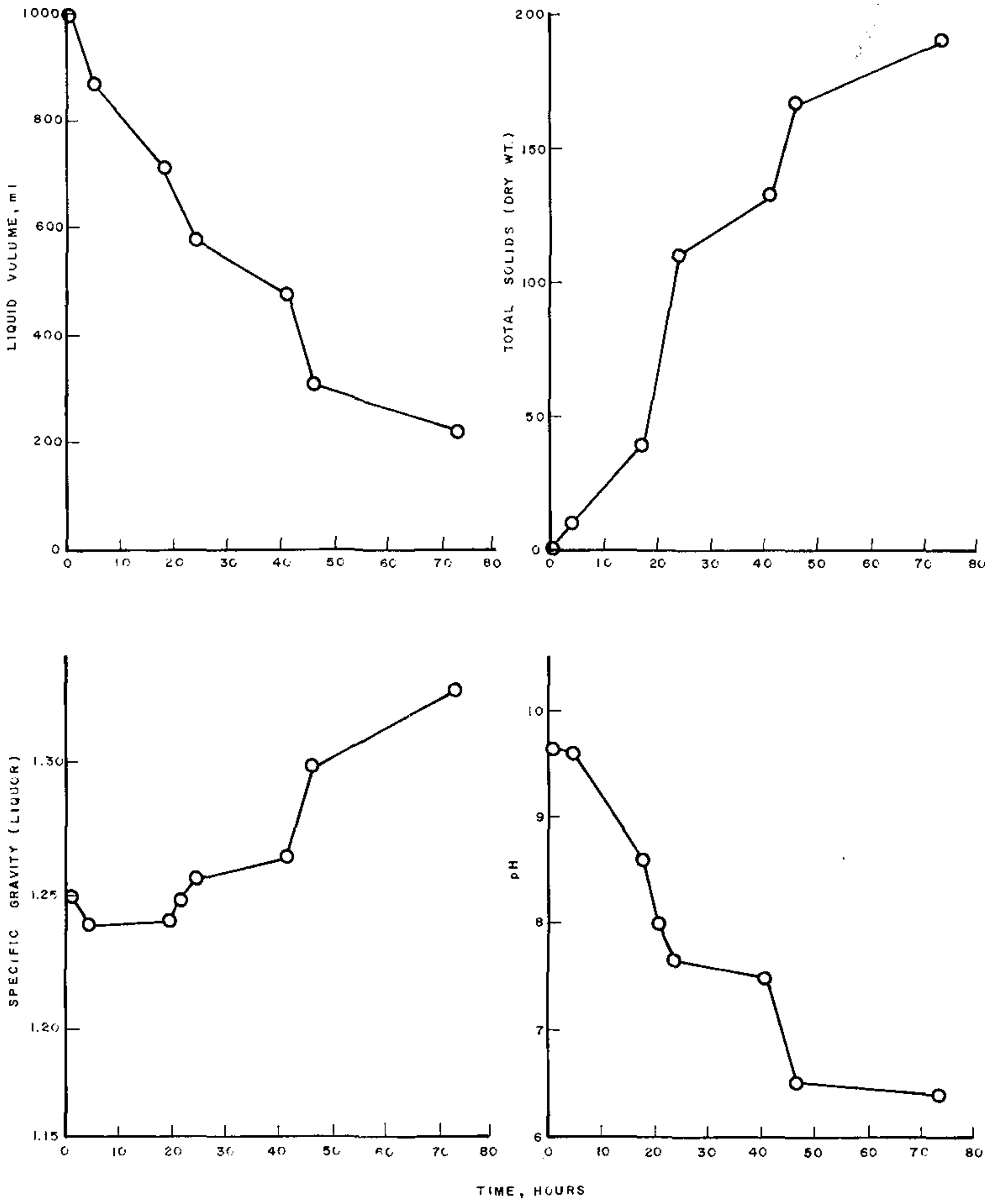


FIGURE 59
hri

Table 35

Salt Produced from Heavy-Metal-Free
Sinclair No. 4 Brine by Simulated Solar Evaporation

Concentration in ppm Weight

Element	Concentration	Element	Concentration	Element	Concentration	Element	Concentration
Uranium	<0.58	Terbium	<0.27	Ruthenium		Vanadium	<0.10
Thorium	<0.80	Gadolinium	<0.67	Molybdenum	4.0	Titanium	0.14
Bismuth	<0.88	Europium	<0.80	Niobium	0.16	Scandium	
Lead	0.35	Samarium	<2.1	Zirconium	0.05	Calcium	≅4.00
Thallium	0.42	Neodymium	<6.1	Yttrium	0.12	Potassium	≅8800
Mercury		Praseodymium	<0.50	Strontium	86	Chlorine	Maj
Gold		Cerium	0.23	Rubidium	40	Sulphur	17
Platinum		Lanthanum		Bromine	45	Phosphorus	0.12
Iridium		Barium	26	Selenium	0.38	Silicon	53
Osmium		Cesium	0.44	Arsenic	2.9	Aluminum	0.34
Rhenium		Iodine	1.6	Germanium	<0.10	Magnesium	<9.0
Tungsten	2.9	Tellurium	<0.10	Gallium	<0.10	Sodium	Maj
Tantalum	3.0	Antimony	<0.10	Zinc	<0.10	Fluorine	11
Hafnium	<0.33	Tin	0.19	Copper	0.37	Oxygen	NR
Lutecium	<0.36	Indium		Nickel	0.04	Nitrogen	NR
Ytterbium	<2.1	Cadmium	0.18	Cobalt	<0.10	Carbon	NR
Thulium	<0.15	Silver	0.07	Iron	7.7	Boron	22
Erbium	<0.60	Palladium		Manganese	0.02	Beryllium	<0.30
Holmium	<0.35	Rhodium		Chromium	0.57	Lithium	40
Dysprosium	<4.5					Hydrogen	

NY - Not reported

product sodium chloride. As can be seen, essentially all of the heavy metal impurities originally present in the brine have been removed so as to enable a pure sodium chloride product to be produced.

Additional scoping studies were carried out on methods for recovering lithium from Sinclair No. 4 brine.

Precipitation of lithium as the complex aluminate was achieved, with a 99.9% recovery of the contained lithium values from the brine or the concentrated bittern. However, aluminum consumption was excessive in that the lithium to aluminum ratio was inordinately high in order to achieve the high recovery of 99+% lithium. Table 36 presents a summary of the process results on lithium from Sinclair No. 4 brine.

Table 36

Lithium Recovery from Sinclair No. 4 Brine as Lithium Aluminate

Material	pH for Precipitation	Li/Al Ratio	Lithium in Solution ppm Before	Lithium in Solution ppm After	% of Li Precipitated
Purified brine	7-7.5	1/16.2	261	0.2	99.9
Purified bittern	6.5-7.0	1/26.5	788	0.4	99.9
Purified brine	3.2	1/8.6	261	201	23
Purified brine	9.0	1/8.6	261	209	20

Some test work was done on solvent extraction of lithium from Sinclair No. 4 brines (see U.S. Patent No. 3,537,813) but lithium recoveries were much lower than with the aluminate precipitation route.

In conclusion, the scoping laboratory study described above resulted in defining a process concept that would allow removal of the iron, manganese, lead, and zinc values from a geothermal fluid, similar to Sinclair No. 4 geothermal brine, and yield an iron-manganese oxide material containing typically 17% manganese, 11% iron, 6% zinc, and 1.5% lead. This material can be considered to be a synthetic "ore" suitable for further processing to recover separately the metal values contained therein.

PHASE RULE STUDY OF SALT AND POTASH CRYSTALLIZATION AND PURIFICATION

During the subject study, samples of several geothermal brines were collected to perform laboratory bench scale experiments simulating solar evaporation. These tests were mainly concerned with the concentration of trace elements present in the brines, results of which are discussed in a separate section. However, the presence of relatively high concentration of sodium, potassium, and calcium chlorides in two of the geothermal brines collected (Magmamax No. 1 and Sinclair No. 4) justified a brief theoretical examination of the phase chemistry of the quaternary system $NaCl$-KCl-$CaCl_2$-H_2O. This appendix report covers the results of this examination.

THE QUATERNARY SYSTEM NaCl-KCl-CaCl$_2$-H$_2$O

This system was studied using the data presented in Seidell's Fourth Edition of "Solubilities of Inorganic and Metal-Organic Compounds," Vol. I, p. 586. From practical considerations, the study was restricted to the isotherms at 18°C and 95°C.

THE SYSTEM AT 18°C

Data for this quaternary system at 18°C is presented in Table A1 and its graphical representation in triangular coordinates is shown in Figure A1.

The phase chemistry examinations that will follow may be considered of theoretical nature and valuable only to give an idea of the order of magnitude of salts crystallized out, grade and sequence of crystallization. In the case of using solar energy to perform water evaporation, these phase chemistry examinations do not consider either the temperature variations which naturally occur in a solar pond system or the supersaturation condition which is frequently found in this type of operation. It also must be recognized that isothermal data for 18°C which is used; is a relatively low temperature for most summers in desert areas, when brine temperature during the day may vary from 25°C to 40°C or more. As evaporation takes place, some components in relatively small amounts in the original brine may become more concentrated and in turn start influencing the shape of the phase diagram, hence changing saturation points and crystallization paths. These facts should be acknowledged in the following examinations.

Out of the several field samples taken, two brines were selected for this brief study. Those were the Magmamax No. 1 and Sinclair No. 4 whose composition (major components only, namely sodium, potassium,

Table A1

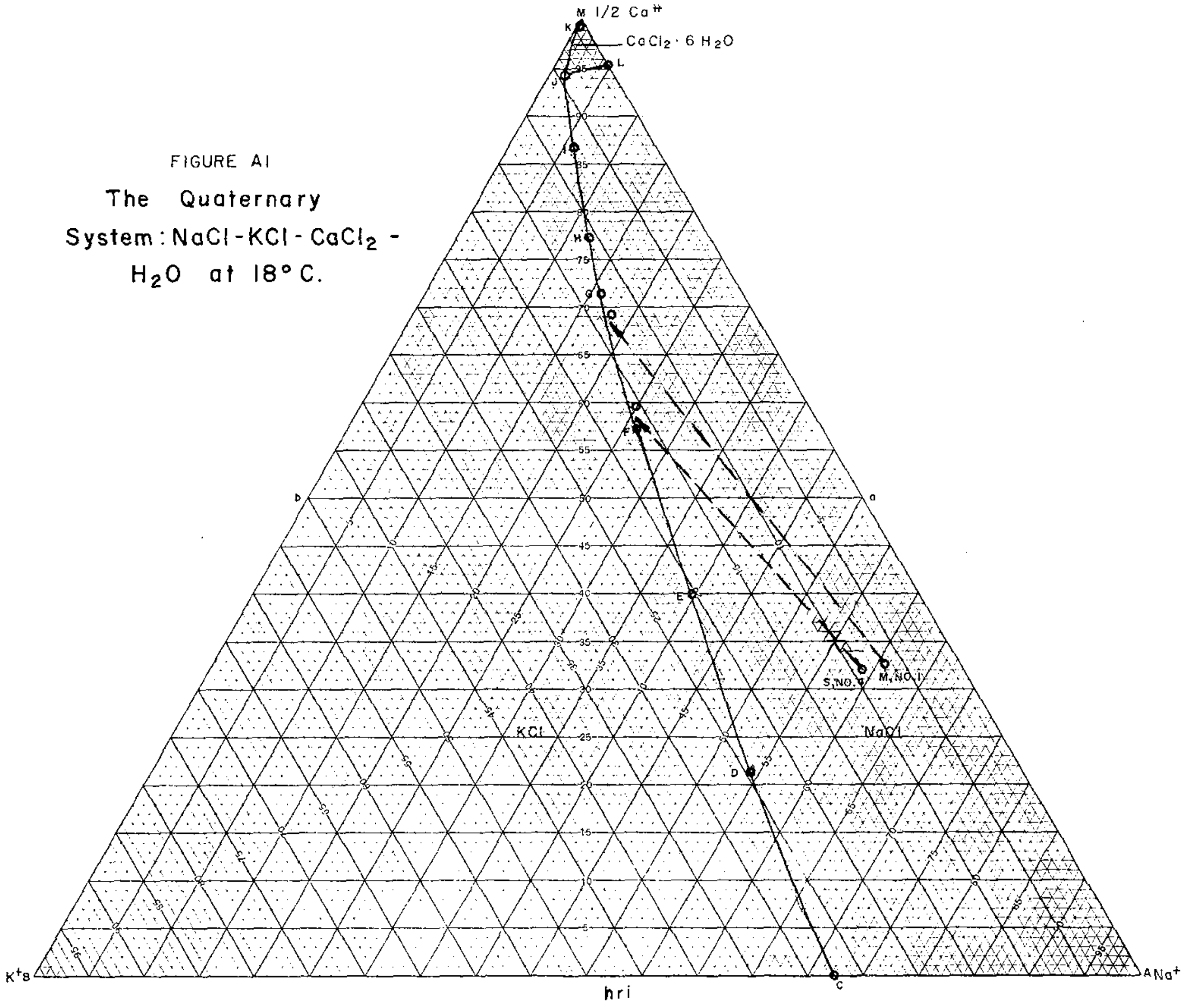
The System NaCl-KCl-$CaCl_2$-H_2O at 18°C

	Solid	% by Weight				p/100 p H_2O			Mol Eq/1000M H_2O			% Mol Eq		
Point	Phase*	NaCl	KCl	$CaCl_2$	H_2O	NaCl	KCl	$CaCl_2$	NaCl	KCl	1/2 $CaCl_2$	Na^+	K^+	1/2 Ca*
A	Na	26.5	-	-	73.5	36.1	-	-	111.3	-	-	100.0	-	-
B	K	-	25.1	-	74.9	-	33.5	-	-	80.9	-	-	100.0	-
C	Na+K	20.8	10.0	-	69.2	30.1	14.5	-	92.8	35.0	-	72.6	27.4	-
D	Na+K	16.0	9.3	6.0	68.7	23.3	13.5	8.7	71.8	32.6	28.2	54.1	24.6	21.3
E	Na+K	12.4	8.1	11.8	67.7	18.3	12.0	17.4	56.4	29.0	56.5	39.8	20.4	39.8
F	Na+K	8.4	6.8	17.6	67.2	12.5	10.1	26.2	38.5	24.4	85.1	26.0	16.5	57.5
G	Na+K	5.4	5.5	22.7	66.4	8.1	8.3	34.2	25.0	20.1	111.0	16.0	12.9	71.1
H	Na+K	4.0	4.8	25.3	65.9	6.1	7.3	38.4	18.8	17.6	124.6	11.7	10.9	77.4
I	Na+K	2.1	3.7	29.7	64.5	3.3	5.7	46.1	10.2	13.8	149.7	5.9	7.9	86.2
J	Na+K+Ca_6	0.45	2.65	40.8	56.1	0.80	4.72	72.7	2.5	11.4	236.0	1.0	4.6	94.4
K	Na+Ca_6	0.42	-	41.6	57.98	0.72	-	71.8	2.2	-	233.1	0.9	-	99.1
L	K+Ca_6	-	2.7	40.95	56.35	-	4.79	72.7	-	11.6	236.0	-	4.7	95.3
M	Ca_6	-	-	42.05	57.95	-	-	72.6	-	-	235.7	-	-	100.0

Na = NaCl
K = KCl
$Ca_6 = CaCl_2 \cdot 6H_2O$

FIGURE A1

The Quaternary System: NaCl - KCl - $CaCl_2$ - H_2O at 18° C.



and calcium chloride) are presented in Table A2. The % Molar Equivalent of these two brines are plotted in Figure A1. As it can be seen, both brines are located within the NaCl field, hence, both will first yield this salt when water is isothermally evaporated at 18°C. As this salt crystallizes out, the brine compositions will change, following the dotted line until they reach their respective points "a" on the boundary line of the NaCl-KCl fields (between points F and G in the diagram). From then on, evaporation will cause crystallization of sylvinite (a mixture of NaCl and KCl), while the brine composition will move toward point J, reaching the $CaCl_2 \cdot 6H_2O$ field and finally the crystallization end point of this system.

It is possible to calculate the composition of these two selected brines when they intersect the sylvinite crystallization path. Point "a" for the Magmamax No. 1 brine will have the following composition in percent by weight:

6.10% NaCl
5.83% KCl
21.49% $CaCl_2$

The equivalent point "a" for the Sinclair No. 4 brine will have the following composition, also in percent by weight:

7.52% NaCl
6.67% KCl
18.33% $CaCl_2$

Both brines will yield sylvinite upon further evaporation until point J is reached when the composition of both will be the same:

0.45% NaCl
2.65% KCl
40.8% $CaCl_2$

Table A2

Major Components of Magmamax No. 1 and Sinclair No. 4 Brines

Brine	% by Weight				p/100 p H_2O			Mol Eq/1000M H_2O			% Mol Eq		
	NaCl	KCl	$CaCl_2$	H_2O*	NaCl	KCl	$CaCl_2$	NaCl	KCl	1/2 $CaCl_2$	Na^+	K^+	1/2 Ca*
Magmamax No. 1	11.19	1.58	5.82	81.41	13.8	1.94	7.15	42.5	4.68	23.2	60.4	6.6	33.0
Sinclair No. 4	18.05	3.54	9.69	68.72	26.3	5.15	14.1	81.0	12.4	45.8	58.2	8.9	32.9

*By difference

A material balance then can be calculated for this process. The balance for the Magmamax No. 1 brine is presented in Table A3. It can be seen that theoretically the sylvinite grade is 43% KCl and the yield of KCl as sylvinite from the original brine can be calculated at 76%. The NaCl distribution from the original brine is 85.3% into the salt pond, 14.1% in the sylvinite pond and the remaining in the final concentrated $CaCl_2$ brine.

Table A3

Calculated Material Balance for the
Evaporation of Magmamax No. 1 Brine
Based on 1000 Parts of Original Feed
(All figures in parts by weight)

	H_2O Evaporated	Yield
Salt Pond	633.68	95.71 NaCl
Sylvinite Pond	100.20	15.84 NaCl + 11.99 KCl
Residual Brine		142.58

Some calculations were performed using the Sinclair No. 4 brine. The results are shown in Table A4. The sylvinite grade is 41% KCl and the recovery of KCl from the original brine as sylvinite can be calculated to be 82.1%. About 76.4% of the total NaCl present in the original brine will crystallize in the salt pond and 23% in the sylvinite pond.

The high grade sylvinite obtained in the two cases analyzed could be processed by standard amine flotation techniques to obtain fertilizer-grade potassium chloride.

Table A4

Calculated Material Balance for the
Evaporation of Sinclair No. 4 Brine
Based on 1000 Parts of Original Feed [1]

	H_2O Evaporated	Yield
Salt Pond	330.34	137.89 NaCl
Sylvinite Pond	223.34	41.60 NaCl + 28.95 KCl
Residual Brine		237.88

[1] Parts by weight.

THE SYSTEM AT 95°C

Solubility data for the quaternary system at 95°C is presented in Table A5. It is possible to notice several changes which occurred in the system at 95°C when compared with the one at 18°C. The equivalent crystallization path of sylvinite showed as the line C to J in Figure A1, has moved a considerable distance toward the K^+ corner, indicating a substantial increase in the concentration of KCl at 95°C. Also, it can be seen that a double salt has appeared in the diagram at 95°C, namely chlorocalcite $KCl \cdot CaCl_2$ which is formed at very high $CaCl_2$ concentrations. The $CaCl_2$ hexahydrate which was the stable phase at 18°C has been replaced by the dihydrate salt at 95°C.

Since the major interest in this study is the recovery of potassium chloride from the selected geothermal brines, Figure A2, presents the solubility of KCl and NaCl, when sylvinite is the stable saturating solid phase, at different $CaCl_2$ concentration at 95°C. To make a comparison, similar solubility data for 18°C also have been plotted in the figure. Points A, B, C, and D in the figure represent the point at which $CaCl_2$ joins sylvinite as stable solid phase. For the 18°C case, it is $CaCl_2 \cdot 6H_2O$ (points A and B) and for the 95°C case it is $KCl \cdot CaCl_2$ (points C and D).

A-9

Table A5

The System NaCl-KCl-$CaCl_2$-H_2O at 95°C

Point	Solid Phase*	% by Weight				p/100 p H_2O			Mol Eq/1000M H_2O			% Mol Eq		
		NaCl	KCl	$CaCl_2$	H_2O	NaCl	KCl	$CaCl_2$	NaCl	KCl	1/2 $CaCl_2$	Na^+	K^+	1/2 Ca*
A	Na	28.3	-	-	71.7	39.5	-	-	121.8	-	-	100.0	-	-
B	K	-	37.6	-	62.4	-	60.3	-	-	145.7	-	-	100.0	-
C	Na+K	17.0	21.0	-	62.0	27.4	33.9	-	84.5	81.9	-	50.8	49.2	-
D	Na+K	14.2	18.5	4.7	62.6	22.7	29.6	7.5	70.0	71.5	24.3	42.2	43.1	14.7
E	Na+K	13.3	15.3	9.7	61.7	21.6	24.8	15.7	66.6	59.0	51.0	37.5	33.8	28.7
F	Na+K	11.0	13.0	14.5	61.5	17.9	21.1	23.6	55.2	51.0	76.6	30.2	27.9	41.9
G	Na+K	8.2	10.6	19.4	61.8	13.3	17.2	31.4	41.0	41.6	101.9	22.2	22.6	55.2
H	Na+K	4.9	9.3	24.3	61.5	8.0	15.1	39.5	24.7	36.5	122.2	13.0	19.3	67.7
I	Na+K	2.3	8.4	33.8	55.5	4.1	15.1	60.9	12.6	36.5	197.7	5.1	14.8	80.1
J	Na+K	1.8	8.0	37.7	52.5	3.4	15.2	71.8	10.5	36.7	233.1	3.7	13.1	83.2
K	Na+K	1.6	8.0	41.4	49.0	3.3	16.3	84.5	10.2	39.4	274.3	3.1	12.2	84.7
L	Na+K	1.2	12.1	48.8	37.9	3.2	31.9	128.8	9.9	77.1	418.1	2.0	15.2	82.8
M	K+Na+KCa	1.1	12.5	49.4	37.0	3.0	33.8	133.5	9.2	81.7	433.4	1.7	15.6	82.7
N	Na+KCa	1.1	12.1	49.9	36.9	3.0	32.8	135.2	9.2	79.3	438.9	1.7	15.1	83.2
O	Na+KCa	1.1	11.4	50.3	37.2	3.0	30.7	135.2	9.2	74.2	438.9	1.8	14.2	84.0
P	Na+KCa	1.0	9.1	51.9	38.0	2.6	24.0	136.6	8.0	58.0	443.4	1.6	11.4	87.0
Q	Na+KCa	0.9	8.2	52.9	38.0	2.4	21.6	139.2	7.4	52.2	451.9	1.5	10.2	88.3
R	Na+KCa	0.9	7.4	53.6	38.1	2.4	19.4	140.7	7.4	46.9	456.8	1.4	9.2	89.4
S	Na+KCa	0.9	5.7	55.6	37.8	2.4	15.1	147.1	7.4	36.5	477.5	1.4	7.0	91.6
T	Na+KCa	0.9	4.6	57.4	37.1	2.4	12.4	154.7	7.4	30.0	502.2	1.4	5.5	93.1
U	Na+KCa	0.9	3.9	58.1	37.1	2.4	10.5	156.6	7.4	25.4	508.4	1.4	4.7	93.9
V	Na+KCa+Ca_2	0.9	3.2	58.8	37.1	2.4	8.6	158.5	7.4	20.8	514.5	1.4	3.8	94.8
W	KCa+Ca_2	-	2.9	59.6	37.5	-	7.7	158.9	-	18.6	515.8	-	3.5	96.5
X	Ca_2+Na	0.9	2.8	58.9	37.4	2.4	7.5	157.5	7.4	18.1	511.3	1.4	3.4	95.2
Y	Ca_2+Na	1.0	-	60.1	38.9	2.6	-	154.5	8.0	-	501.5	1.6	-	98.4
Z	Ca_2	-	-	60.2	39.8	-	-	151.3	-	-	491.1	-	-	100.0

*Na = NaCl
K = KCl
KCa = KCl·$CaCl_2$
Ca_2 = $CaCl_2 \cdot 2H_2O$

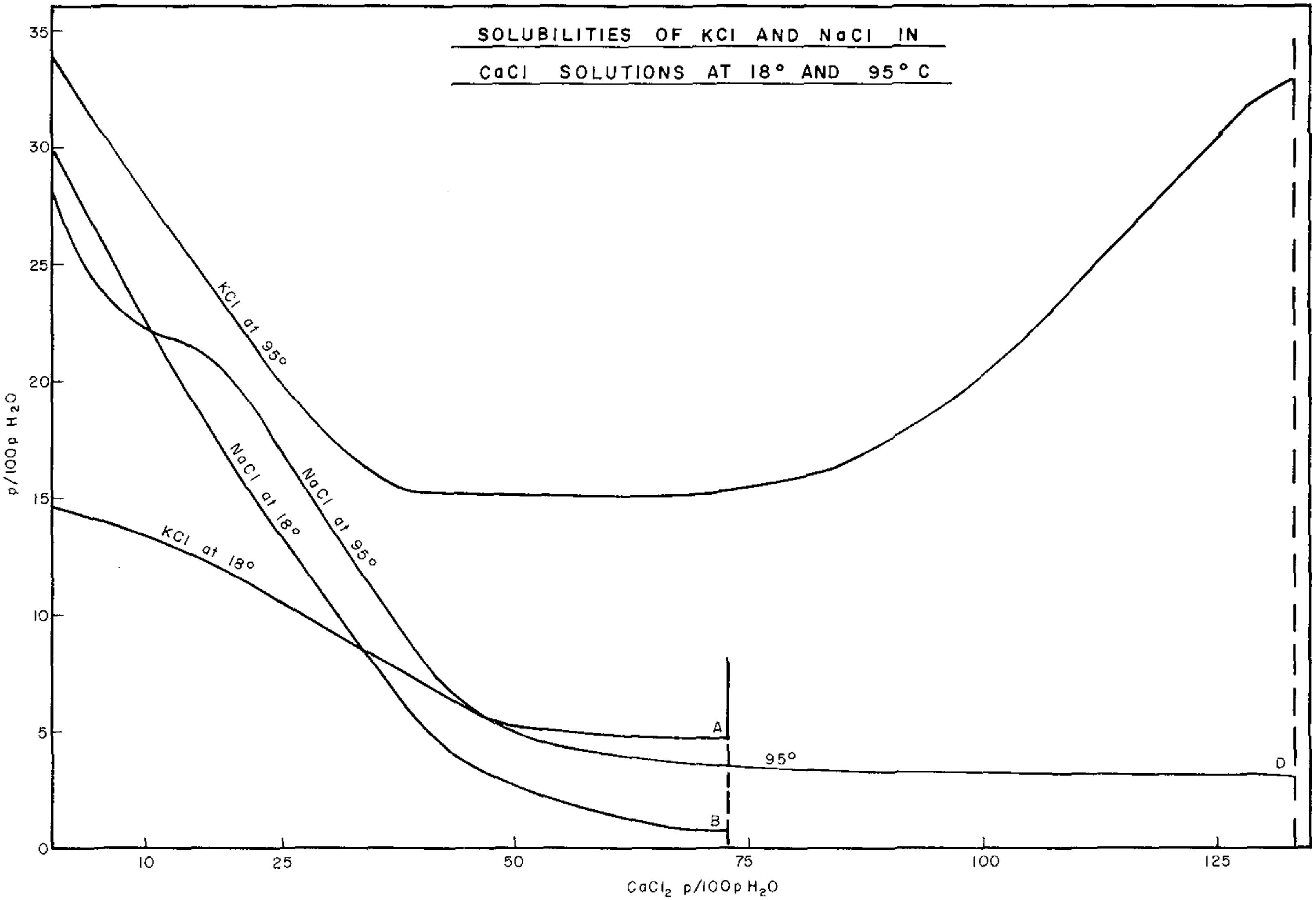

SOLUBILITIES OF KCl AND NaCl IN CaCl SOLUTIONS AT 18° AND 95° C

FIGURE A2

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Using the previously given composition for Magmamax No. 1 brine, several calculations were made, in order to obtain an idea of the potential flowsheets which could be used for the recovery of its contained potassium chloride.

Using the Magmamax No. 1 brine for one set of calculations, it was assumed that the brine will be evaporated isothermally at 95°C until it becomes saturated with respect to sylvinite. After removing the NaCl crystallized during the evaporation up to that point, the resulting brine was assumed to be cooled down to 18°C to crystallize sylvinite. The Magmamax brine reaches saturation with respect to sylvinite after evaporation of about 87% of the water present in the original brine and will have a composition as shown in Table A6 where it is compared with the equivalent point presented previously for the same brine, but evaporated at 18°C. As can be seen, a much higher concentration of KCl (and much lower concentration of NaCl) is attained at 95°C, before KCl starts to crystallize out. The composition of the brine at 95°C is inside the KCl field in the 18°C diagram, indicating that by cooling the solution, fertilizer grade KCl could be obtained. Using the 18°C equilibria data, it was calculated that by the process of cooling, sylvinite could be obtained with a 78.8% KCl grade and a recovery of 64.7% of the KCl originally present in the brine. This sylvinite will not meet fertilizer grade potash specifications which require a minimum of 95% KCl. Therefore, to meet this grade, the crystallized sylvinite should be further processed. Since the 95°C brine, upon cooling, will first crystallize out KCl, it is evident that NaCl will start crystallizing together with KCl at a temperature somewhat higher than the terminal 18°C assumed in these calculations. No attempts for interpolation were made to locate this point because it would only result in lower recoveries.

Table A6

Magmamax No. 1 Brine Composition When it Reaches Saturation in Respect to Sylvinite by Isothermal Evaporation at 18°C and 95°C 1/

18°C		95°C
6.10	NaCl	2.9
5.83	KCl	8.6
21.49	$CaCl_2$	31.7

1/ Figures are in % by weight.

During the previous calculation it was assumed that the cooling was done without evaporating any water. If cooling is done by flash evaporation, allowing some water to be evaporated, the recovery of KCl in the crystallized sylvinite is improved, but the grade becomes lower.

Since the brine originally will be hot (about 110-115°C), another route was considered to obtain pure KCl, taking advantage of the high temperature of the brine. This new flowsheet is diagramatically presented in Figure A3. The material balance data shown in the figure are based on 1000 parts by weight of the Magmamax No. 1 brine. The majority of the feed brine goes through solar evaporation to crystallize NaCl and when it reaches saturation with respect to KCl, the brine joins the mother liquor from the KCl crystallization step. Both are moved to a solar pond for the crystallization of sylvinite and produce a final $CaCl_2$ mother liquor. The sylvinite produced, having a grade of 39% KCl, is harvested and taken to leach tanks with hot Magmamax brine. The brine dissolves all the KCl but only 21% of the NaCl. The remaining solid phase NaCl is separated from the hot solution or mother liquor. This mother liquor is saturated with respect to KCl and NaCl. However, as it can be seen in Figure A2, upon

IDEAL MATERIAL BALANCE FOR THE PROCESSING OF MAGMAMAX NO. I BRINE

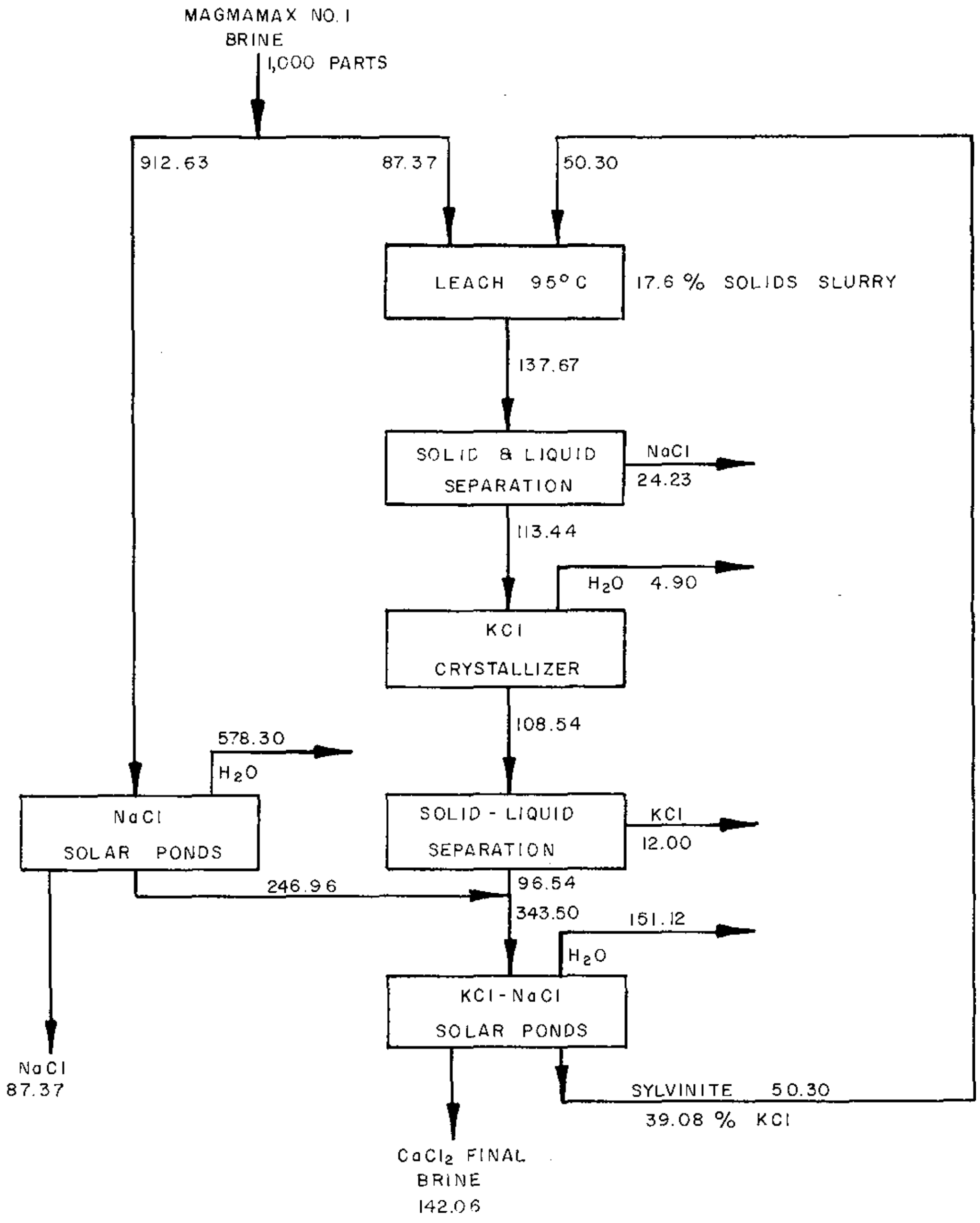

FIGURE A3

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cooling, the solubility of NaCl increases at this particular level of $CaCl_2$ concentration (7.15 p. of $CaCl_2$/100 p H_2O). Therefore, when the brine is cooled, only KCl will be crystallized out. After a solid liquid separation, pure KCl is obtained while the mother liquor joins the mother liquor from the pond and is channeled to the sylvinite solar ponds.

The KCl product obtained will have a purity more than sufficient to meet fertilizer grade specification. The overall recovery for this flowsheet is 76% of the KCl present in the original brine.

A similar flowsheet may be adapted for the Sinclair No. 4 brine, taking into account the higher initial $CaCl_2$ and KCl level of this brine. Sinclair No. 4 brine cannot dissolve as much KCl as can Magmamax No. 1 brine; hence the liquid-solids ratio in the 95°C leach step will be greater in order to dissolve all of the KCl from the sylvinite salt.

APPENDIX B

PROCESS CHEMISTRY
CONCENTRATION OF GEOTHERMAL FLUIDS

Table B-1

Mesa L-6-1
Pre-flash Brine Sample

Process chemistry, simulated solar concentration of geothermal fluids

	Initial Brine Sample	Conc Brine 1	Conc Brine 2	Conc Brine 3	Conc Brine 4	Terminal Bittern
Specific gravity	1.020	1.043	1.071	1.069	1.096	-
Br, ppm	35	-	-	-	-	1490
Total Cl, %	1.80	4.02	5.93	5.78	9.98	32.9
Na, %	1.10	2.08	2.82	2.63	3.98	0.090
K, %	0.143	0.28	0.52	0.58	0.71	2.43
Ca, %	0.137	0.26	0.48	0.53	0.68	14.4
Mg, %	0.0022	0.0040	0.0080	0.010	0.011	0.110
Fe, %	0.18	-	2.2	-	2.3	11.0
Mn, %	0.9	-	5.5	-	8.1	51
Pb, ppm	0.26	-	2.2	0	3.1	16
Zn, ppm	0.02	-	0.5	-	0.7	22
Cu, ppm	0.05	-	1.0	-	1.0	5.0
Li, ppm	55	-	205	-	295	5410
Ba, ppm	58	-	200	-	300	260
Sr, ppm	226	-	817	-	1210	2540
NH_4, ppm	38.8	-	113	-	129	3130
SO_4, ppm	16	-	74	-	39	170
F, ppm	1.5	-	-	-	-	124
SiO_2, ppm	101	-	215	-	120	33
Rb, ppm	1.7	-	-	-	-	510
Cs, ppm	4.0	-	-	-	-	240
B, ppm	27.4	-	194	-	0.8	2000
Mg, tracer conc ratio	1.0	1.8	3.6	4.5	5.0	50.0
Ca, tracer conc ratio	1.0	1.9	3.5	3.9	5.0	105
Li, tracer conc ratio	1.0	-	3.7	-	5.4	98

Table B-2

Sinclair No. 4
Post-flash Brine Sample

	Initial Brine Sample	Conc Brine 1	Conc Brine 2	Conc Brine 3	Conc Brine 4	Terminal Bittern
Specific gravity	1.220	1.248	1.296	-	-	-
Br, ppm	162	-	-	-	-	694
Total Cl, %	18.6	22.6	23.8	25.7	-	36.5
Na, %	7.10	5.07	2.27	0.44	0.39	0.146
K, %	1.80	2.06	2.56	2.26	2.08	2.55
Ca, %	3.50	4.41	7.36	12.2	15.8	17.6
Mg, %	0.0152	0.0200	0.0350	0.0510	0.0721	0.0833
Fe, %	0.087	0.118	0.097	0.180	0.23	0.0743
Mn, %	0.147	0.203	0.110	0.228	0.328	0.0650
Pb, ppm	141	87	54	20	19	108
Zn, ppm	492	677	1105	1652	2340	2790
Cu, ppm	0.69	3.9	3.9	4.0	6.0	5.1
Li, ppm	238	374	592	886	1300	1480
Ba, ppm	118	299	389	646	484	700
Sr, ppm	570	945	1487	2235	3200	2870
NH_4, ppm	611	606	1051	1591	-	2680
SO_4, ppm	42	39	58	43	-	106
F, ppm	5.8	-	-	-	-	55
SiO_2, ppm	44	71	39	158	-	36
Rb, ppm	17	-	-	-	-	320
Cs, ppm	32	-	-	-	-	97
B, ppm	344	496	712	1281	-	2590
Mg, tracer conc ratio	1.0	1.32	2.30	3.36	4.74	5.48
Ca, tracer conc ratio	1.0	1.26	2.10	3.48	4.51	5.03
Li, tracer conc ratio	1.0	1.57	2.49	3.72	5.40	6.22

Table B-3

Magmamax No. 1
Pre-flash Brine Sample

	Initial Brine Sample	Conc Brine 1	Conc Brine 2	Conc Brine 3	Conc Brine 4	Conc Brine 5	Terminal Bittern
Specific gravity	-	1.200	1.169	1.280	-	-	-
Br, ppm	109	-	-	-	-	-	808
Total Cl, %	10.2	15.0	13.2	23.9	24.1	23.0	36.6
Na, %	4.40	3.89	4.47	3.03	1.57	1.51	0.15
K, %	0.83	1.64	1.30	5.78	2.84	2.97	3.04
Ca, %	2.10	3.65	2.52	6.40	10.3	9.56	17.2
Mg, %	0.010	0.018	0.013	0.030	0.043	0.042	0.086
Fe, %	0.015	0.035	0.024	0.040	0.062	0.063	0.030
Mn, %	0.068	0.156	0.104	0.227	0.306	0.392	0.059
Pb, ppm	28.8	29	33	35	34	42	74
Zn, ppm	293	674	445	949	1395	1309	2810
Cu, ppm	0.49	2.0	2.0	4.0	2.8	3.0	2.6
Li, ppm	143	345	235	503	765	695	1470
Ba, ppm	33	210	170	330	539	467	680
Sr, ppm	368	1010	663	1427	2027	1876	3120
NH_4, ppm	504	985	600	1262	1914	1729	2970
SO_4, ppm	50	45	41	29	40	108	57
F, ppm	4.6	-	-	-	-	-	63
SiO_2, ppm	71	65	20	91	42	30	115
Rb, ppm	5.3	-	-	-	-	-	290
Cs, ppm	16	-	-	-	-	-	120
B, ppm	192	463	460	669	1413	1020	2760
Mg, tracer conc ratio	1.0	1.8	1.3	3.0	4.3	4.2	8.6
Ca, tracer conc ratio	1.0	1.7	1.2	3.0	4.9	4.6	8.2
Li, tracer conc ratio	1.0	2.4	1.6	3.5	5.4	4.9	10.3

STEAM EVAPORATION COSTS

Basis:

1. Water removal capacity = $15x10^6$ ton/year
2. Capital investment required = $\$25x10^6$
3. Capital cost per annual ton H_2O evaporated = $1.67
4. Assume the use of triple effect evaporators with a steam economy of 2.3 lb H_2O evaporated/one-lb steam.

Operating Costs: Basis 330 days/year operation

		Cost/day	Cost/year
Labor: 5 men/shift @ $5.50/hr x 3 shifts/day x 8 hr/shift		$ 660.00	$218,000
Supervision: 30% of labor		198.00	65,500
Fringes:		59.50	19,600
	Sub Total	$ 917.50	$303,100
Overheads: 50% of above		$ 458.75	$151,550
		$1,376.25	$454,650
Operating Supplies:		$ 200	$ 66,000
Utilities:			
Steam @ $0.50/1000 lb (for $41x10^6$ lb/day)		$20,500	$6,760,000
Power @ $0.005/kwhr		6,060	2,000,000
Maintenance: @ 7% of capital investment		5,300	1,750,000
Taxes and Insurance: @ 3% of capital investment		2,270	750,000
	Total Cash Costs	$35,706	$11,780,650
Depreciation:			
20 year straight line No salvage		$3,790	$ 1,250,000
	Total Operating Costs	$39,496	$13,030,650
	Cost/ton water evaporated		$0.87

SOLAR EVAPORATION COSTS

Basis:

1. Water removal rate = 15×10^6 tons/year
2. Capital investment required = $29,400,000, lined pond $10,000/acre @ 20 mil, PVC
   $8,810,000, unlined pond $3,000/acre
3. Evaporation rate, average = 45 inches/year or 5,100 tons/year/acre
4. Pond area required = 2,940 acres
   Basis: 5,100 tons/year/acre
5. Salt removal costs = $0.75/ton salts removed (pond clean-out)
6. Capital cost per annual ton of water evaporated = $1.96, lined ponds
   $0.59, unlined ponds

Operating Costs: Basis, 330 days/year operation

	Cost/day	Cost/year
Labor: 1 man/day @ $5.50/hr x 8 hr/day	$ 45.00	$ 14,500
Supervision: 30% of labor	15.00	4,950
Fringes:	18.00	5,940
Sub Total	$ 78.00	$ 25,390
Overheads: 50% of above	$ 39.00	$ 12,700
	$ 117.00	$ 38,090
Operating Supplies:	$ 10.00	$ 3,300
Utilities:		
Power costs, assumed pumping costs	$ 151.50	$ 50,000
Maintenance		
3% of capital investment		
Lined	$2,970.00	$ 980,000
Unlined	$ 802.00	$ 264,300

Taxes and Insurance:			
@ 2% of capital investment			
	Lined	$ 1,781	$ 588,000
	Unlined	$ 534	$ 176,200
Total Cash Costs			
	Lined	$ 5,029.50	$1,659,030
	Unlined	$ 1,614.50	$ 531,890
Depreciation:			
10 year straight line	Lined	$ 8,900	$2,940,000
No salvage value	Unlined	$ 2,670	$ 881,000
Total Operating Costs			
	Lined	$13,929.50	$4,599,030
	Unlined	$ 4,284.50	$1,412,870
Cost/ton Water Evaporated Exclusive of Pond Cleanout			
	Lined	$0.306	
	Unlined	$0.094	

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