

SILVER PEAK / 1983

U.S. BUR. OF MINES, WFOC
SPokane, WA.

BIBLIOGRAPHY

(19)
Item 23
2 of 21

Albers, J. Geology and Mineral Deposits of Esmeralda County, Nevada.
Nevada BuMines and Geol. Bull 78, 1972.

Albers, J. Preliminary Geologic Map of Esmeralda County, Nevada. U.S.
Geol. Surv. Map M-F 298, 1965.

Baker, A. Forecasts for the Future--Minerals. Nevada BuMines and Geol.
Bull. 82, 1972.

Barrett, W. T. Recovery of Lithium from Saline Brines Using Solar
Evaporation. 3rd Salt Symposium, v. 2, The Northern Ohio Geol. Soc.,
Inc., Cleveland, OH, 1970, pp. 47-50.

Berthold, C. E. Process Technology for Recovering Geothermal Brine Minerals,
BuMines OFR 35-75, 1975.

Bureau of Land Mangement. Claim Records, 1983.

_____. Air Photos, 1983.

_____. Surface Management Status, Surface-Mnerals Management Status Maps,
Gold Field Quadrangle, Nevada. 1978.

Chemical Engineering News. Nevada Brine Supports a Big New Lithium Plant.
Aug. 15, 1966.

_____. New Plant Pulls Lithium from Nevada Brines. V. 44, No. 32, 1966,
p. 38.

Chemical Week. Sizing up Lithium Process. Sept. 3, 1966.

Davis, J. R. Stratigraphic and Tectonic Setting of the Lithium Brine Field,
Clayton Valley, Nevada. RMAA, ^{USA} 1979 Basin and Range Symposium.
G G

Dole, R. B. Exploration of Salines in Silver Peak Marsh Nevada. U.S.
Geol. Surv. Bull. 530, 1913.

Engineering and Mining Journal. Silver Peak Gives Bright Look to Foote
Minerals Company Lithium Picture. V. 171, No. 4, April 1970.

Environmental Protection Agency. Reno, Nevada Office Files, 1983.

Industrial Minerals Magazine. Jan. 1983.

Kesler, T. Raw Lithium Supplies. Min. Eng., Mar. 1978, pp. 283-284.

Kunasz, I. A. Geology and Geochemistry of the Lithium Deposit in Clayton
Valley, Esmeralda County, Nevada. PA State Univ. Ph.D., 128 pp., 1970.

_____. Lithium Raw Materials, Industrial Minerals and Rocks. AIME Book,
1975, pp. 791-803.

- Lee, J. Recovery of Lithium from Brines. U.S. Pat. 4,159,311, June 1979.
- Nell, J. R., and I. E. Arthur, Jr. Recovery of Lithium from Bitterns. U.S. Pat. 3,537,813, Nov. 1970.
- Norton J. Lithium, Cesium, and Rubidium--the Rare Alkali Metals. U.S. Geol. Surv. Prof. Paper 820, 1973, p. 365.
- Olson, R. A Survey of Industrial Mineral Possibilities in Nevada. Nevada BuMines Rep. 13, Pt. B, 1966, p. 25.
- Pantea, M. P. Lithologic Log and Lithium content of Sediments Drilled in Clayton Valley, Nevada. U.S. Geol. Surv. OFR 82-0415, 1982.
- Pantea, M. P. Lithology and Lithium Content of Sediments in Basins Surrounding Clayton Valley, Nevada. U.S. Geol. Surv. OFR 81-0962, 1981.
- Papke, K. Evaporites and Brines in Nevada Playas. Nevada BuMines and Geol. Bull. 87, 1976, pp. 29-31.
- Pressler, J. Lime Commodity Specialist, BuMines. Personal communication, 1983.
- Robinson, P. Cenozoic Volcanism and Sedimentation, Silver Peak Region, Western Nevada and Adjacent California. Geol. Soc. of America Memoir 116, 1968.

Schreck, A. E. Lithium, a Materials Survey. BuMines IC 8053, 1961.

Searls, J. P. Lithium Mineral Facts and Problems. BuMines B 671, 1980, p. 521.

Singleton, R. Lithium. BuMines Mineral Commodity Profile, 1979.

REVIEW
Skillings' Mining Preview. Foote Mineral Company's Lithium Operation in Nevada. Jan. 20, 1968

Spurr, J. Ore Deposits of the Silver Peak Quadrangle, Nevada. U.S. Geol. Surv. Prof. Paper 55, 1906.

Vine J. Lithium Resources and Requirements by the Year 2000. U.S. Geol. Surv. 1005, 1976.

↑ PROF. PAPER

_____. Lithium in Sediments and Brines--How, Why, and Where to Search. J. of Research of the U.S. Geol. Surv., v. 3, No. 4, 1975, p. 479.

U.S. Bureau of Mines. Silver Peak Lithium Deposit. Mine Map File, WFOC, Spokane, Washington.

Wilson, C. W. Bouguer Gravity Map of Clayton Valley, Nevada. U.S. Geol. Surv. OFR 75-333, 1975.

typed from confidential on-site.

September 23, 1982

701
Item 23
3 of 21

Visit to Foote Mineral Company, Silver Peak, Nevada Lithium Operation

George Gale and Otto Schumacher

Foote personnel: George Kazonich, Operations Manager
Diane Schaaf, Geologist
John "Cliff" Ludich, Playa Superintendent
Frank Wiswell, Plant Superintendent
Allen Ruberry, Playa Supervisor.

Foote Mineral is a subsidiary of Newmont Mining Company. George explained that the company is very particular about giving any information which would allow someone to accurately determine their costs, reserves, and production capabilities. He will give me a name at their headquarters office to contact for this purpose.

Their well development technique has evolved from simple water well-type development to very sophisticated oil field drilling techniques. This was necessary to prevent subsidence which is a big problem, to prevent losing holes, and to prevent destroying source beds. George ^{would} ~~could~~ not provide us with a diagram showing the layout of the operation; however, a map on his wall showed most of the well development to be in a strip along the southwest edge of the valley. The ponds are located in the central portion of the valley. They do not like to drill beneath the ponds for fear of causing subsidence and thereby leakage of the pond areas. They have 49 active wells at the moment. The diagram appeared to show approximately three times that many of dormant or defunct wells. They have 12 operating ponds covering 4000 acres. Their work is seasonal; from April through September they do what they call liming, that is, they add deadburned lime to cause magnesium to precipitate out. At this time, they draw the ponds way down and fill up what they call a storage pond which is the only lined pond in the operation. It is lined with PVC and several feet of clay over that. This pond is quite deep with a small

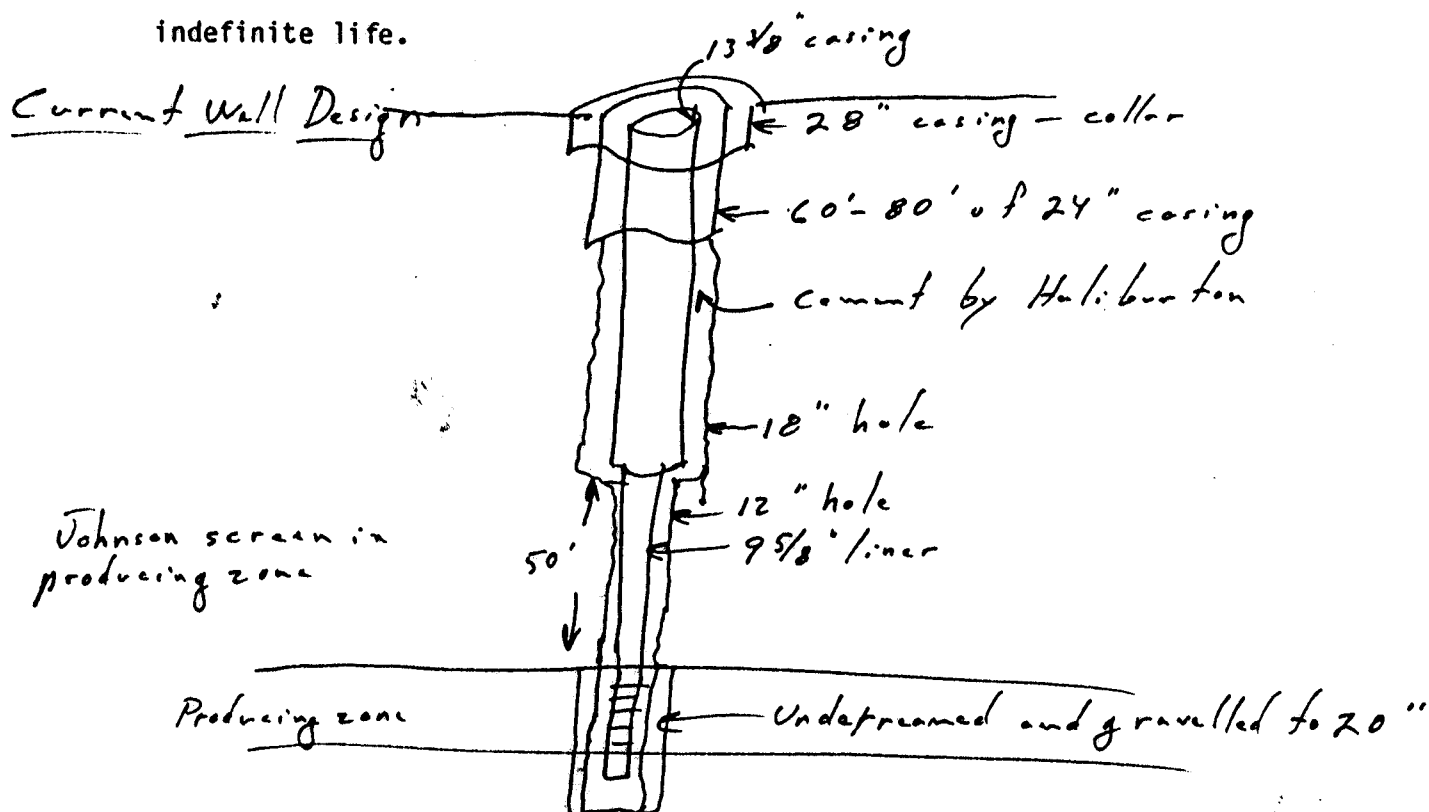
evaporative area in proportion to volume. Rainwater, therefore, ~~also~~ has minimal effect. This pond is used to help provide feed for the plant during the winter months when evaporation and brine production is lower. During the winter months, October through April, the liming crew becomes a dredge operating crew and ponds ^{are} cleaned out at that time. Not all ponds are cleaned out, however. In some cases, they simply raise the dikes, particularly in those ponds where precipitation is extremely high. In late winter, therefore, pond depth is at its maximum.

The personnel operating the ponds consists, in addition to Cliff, of 13 production personnel, 4 maintenance personnel, 1 pond supervisor, 1 maintenance supervisor, 1 geologist, and 1 engineering technician.

According to Cliff, their production rate has been fairly constant over the last ten years.

Electric power is an extremely large problem to them. They have two substations for the operation. Power distribution around the playa to all of the pumps is a big problem. Their system is somewhat overloaded at the moment. They may need larger lines and a new substation. They buy power ~~power~~ from Sierra Pacific and are at such an extreme location that power outages and surges are common. Their power costs run 6.2 to 6.8 cents/kW. The 6.8 cent figure apparently is for domestic consumption. Their average pump bowl depth is about 500 feet. The actual pumping level varies with each well depending on power of the pump, aquifer recharge, etc. The static level average may be something like 200 feet of depth. The average well depth in the southern portion is 350 to 600 feet; in the eastern portion it is something over 800 feet. The drilling is done by contractor and the amount varies each year. They typically drill every three years. One typical well, including drilling, cementing, casing, pumps, roads, and power connection, will cost between

\$175,000 to \$250,000 with about a \$200,000 average. In 1977, they began drilling very complex costly holes. All of the wells that have been drilled since that time are still functioning and they expect that these have an indefinite life.



An 18 inch gathering line collects brine from the wells. The brine at natural concentrations is not as corrosive as one might think. An ordinary steel pipe is used; corrosion does take place, and this pipe does require replacement. Where concentrations are higher, transite pipe made of asbestos concrete by Johns-Manville Corporation is used.

Upon completion of a well, a diesel-gear test pump is installed which very carefully begins pumping the well. The well is cleaned out. The slow pumping stabilizes the aquifer. If it is pumped too fast at first, the aquifer may move and seal itself off. Upon completion of this test, a pump is selected which best fits the hole. Some of these pumps are submersible

pumps but most are aligned pumps with motors at the collar and impellers down on the average about 500 feet. On Cliff's wall was a diagram of a Layne Well Line pump. The pumping rate is controlled by the size of the motor and the number of impeller stages. Pumps are largely 8 to 10 inch pumps. These pumps are 50 to 100 hp and require 440 volts.

It takes about 18 months from the wellhead to the finished product for any particular portion of brine.

Little consideration is being given to any artificial recharge partly because of a lack of a water source.

Source of the brines are considered to be lithium from rhyolitic volcanic ash material in the surrounding mountains. Approximately 40 million years of accumulation is considered to have taken place to build up the playa sediments. Diane did not seem to feel there was any significant lithium in the solid state in these sediments because of the high solubility of lithium. She did mention at another point that the head office was doing some limited work in the area of in-place leaching. Recharge into the basin is fresh water, which is not coming in as fast as the pumps are pulling water out. The operation is therefore facing continued drop in concentration, and also drop in volume.

Not all of the wells are producing high concentration lithium. Some of the lower concentration brines are used to purge salted up pumps and lines, etc.

Apparently, no other products other than lithium are currently being produced. However, waste salts are being stockpiled on the playa in separate stockpiles; one pile being high potassium salts and the other pile being higher sodium salts. I also noticed in the plant one partial pallet of sacks labeled Morton Solar Salt. One problem hindering production of any other salts is the 75 mile haul to the railhead at Mina. Cliff also mentioned something about their three year cycle during production of these other salts.

(Probably not
prod-spec
on site)

Lime for the playa operation comes from two sources: 1) 50 miles north of Las Vegas, and 2) 60 to 70 miles south of Bishop, California. The operation receives 40 tons per day from one of these sources and 50 tons per day from the other, 7 days per week for the 5 1/2 month liming season. I also noticed palletted, sacked lime at the warehouse near the plant.

Equipment for the playa operation consists of two pump pulling rigs, one old cable tool drilling rig, two water trucks, one boom truck, 21 pickup trucks, and three small front-end loaders. A great deal of work is done on the dikes and roads by a contractor. One thing he does is excavate deep trenches in the dikes and goes through a process to provide an impermeable core to the dike to prevent seepage from one pond to another. There are 35 miles of roadwork on the playa. I do not know the extent of this contractor's involvement but I noticed a dragline, three dump trucks, and some other equipment belonging to him on the site. This contractor has been involved with the operation since its inception and carries on many routine functions for the company.

At the lime plant all of the brine from the last strong pond is passed through a couple of mixing tanks where lime is added. It is agitated and then discharged into a pond where a delta of magnesium salts develops right at the discharge point. ~~For some reason,~~ Lithium carbonate precipitation proceeds at a much greater pace as soon as these magnesium carbonates are removed from the brine.

Some small test ponds were nearby which were being used to test the possibility of producing another lithium product.

*Ihor Kunasz of Foster's home office in
Exton, PA*
George Kazonich mentioned a consultant by the name of Ehor(?) Kunas.

This man writes the lithium section for Engineering and Mining Journal each year. I also told George I would find out about Larry Schultze's work on lithium extraction at our Reno laboratory and send him that along with anything else I could find on lithium. He already had received a copy of a paper by somebody named Wozinki(?) from Denver. Schultze's work involves an ion exchange procedure.

Visit to the Plant with Frank Wiswell

Frank was moderately secretive about certain reagents used and volumes of fluids, brines, production, etc. One of the items Frank would not tell us was what is used for binder material in making the pellets. He told us one item was cornstarch. I noticed at the pelletizing bin feedpoint there were bags of a Dow Chemical product called Methocell and Melojel. The plant produces both crystalline or granular lithium carbonate and pelletized or prilled lithium carbonate. Frank noted that the prilled material was used in the aluminum potlines by throwing bag and all into the pots to prevent dust. The settling tanks are old thickeners from the previous silver operation. There appeared to be two tanks about 35 feet by 35 feet to which soda ash in warm liquid form is added and precipitation takes place in a batch process. Actually, there were three settling tanks. The brine is not heated at this point. Soda ash is prepared in one tank about 40 feet by 40 feet which is heated and then it is transferred to another similar tank for storage. At a point very early in the process, calcium is made to precipitate in some unknown manner. Shriver filter presses are used to remove impurities. The brine is then heated with oil which comes from Tonopah. It is mixed with dry soda ash in three 8 x 15 foot tanks which are agitated. Temperature appeared to about

120 degrees. It is then passed through four cyclones, a fifth cyclone was there for some purpose. After dewatering in the cyclones, the residue is washed on a belt filter and further dewatered on this belt filter. The granular material is then dried in a propane dryer which appeared to be about 5 feet in diameter and 20 feet long. Propane is used here because they can not get any oil residues in the material. Pellets are made with the rest of the material in a Sprout-Waldron pelletizer. These pellets are then fired in another 5 by 20 feet dryer to make them hard. The crystalline material has color specifications so is screened to remove colored impurities. The crystalline material goes to a bin for bulk load-out into trucks which haul it to Mina for either bulk shipment, bagging, or packing in drums. The pelletized material goes into containers which are forklifted onto flat-bed trucks for hauling to Mina. Most of the pelletized material is bagged at Mina. The plant utilizes 40 to 52 hourly employees total; they are low right now. ^{There} ~~They~~ are no shift foremen. Frank seems to be the only boss. The plant operates three shifts.

Ihor Kneasz - for reserve information
also

VP Production George Kneasz

Foot Minerals

Rt 100

Exton, PA 19341

215-363-6500

Foote Mineral Company

	1982	1981
Sales	\$124,813,000	\$185,297,000
Net income (loss)	\$ (3,730,000)	\$ 9,556,000
Preferred dividends paid	None	\$ 953,000
Common dividends paid	None	\$ 2,520,000
Dividends received by Newmont		
from preferred stock	None	\$ 485,000
from common stock	None	\$ 2,242,000

Foote's ferroalloy division operated at a loss, and the lithium division operated at reduced profits in 1982 due to reduced sales volume.

Ferroalloy sales declined 42 percent, reflecting recessionary conditions in the foundry, steel and aluminum industries. All of Foote's ferroalloy plants operated at curtailed levels. Lithium sales declined 16 percent in 1982 primarily due to reduced demand for lithium carbonate by the aluminum industry. The King's Mountain, North Carolina, lithium processing plant was closed for the final five months of 1982 after producing 7,900,000 pounds of lithium carbonate, compared with 14,870,000 pounds in 1981.

During 1982, a pilot plant was constructed to produce electrolytic manganese dioxide at the New Johnsonville, Tennessee, electrolytic manganese metal plant. Plant operation testing of the process will extend into early 1983.

In 1982, Sociedad Chilena de Litio Ltda. (SCL) began construction of solar evaporation ponds to produce lithium from a brine deposit in northern Chile. Construction of treatment facilities, designed to produce 14,000,000 pounds of lithium carbonate annually, began in late 1982. The most recent estimate of the project cost for this facility is \$55 million versus earlier estimates totaling \$61 million due to more favorable estimated exchange rates. SCL has arranged for project financing of \$30 million from a consortium of banks, with the remaining funds to be supplied by SCL. SCL is a limited partnership owned 55 percent by Foote and 45 percent by the Chilean government's development company, Corporacion de Fomento de la Produccion.

Highveld Steel and Vanadium Corporation Limited

	6 Mo. Ended Dec. 31, 1982*	12 Mo. Ended June 30, 1982	12 Mo. Ended June 30, 1981
Production of principal metals, short tons			
Iron	401,236	879,912	861,505
Steel	430,325	927,642	923,476
Rolled product	328,266	760,221	748,111
Ferroalloys	42,105	165,150	144,500
Financial			
Net income, S.A. rands	R17,523,000	R51,522,000	R48,704,000
Total dividends declared	—	R18,403,000	R21,780,000
Dividends received by Newmont	R 1,127,229	R 2,324,910	R 2,113,554

*Calculated by subtraction of unaudited data through June 30, 1982, from data covering eighteen months through December 31, 1982.

Average exchange rate was \$0.88 per rand for the six-month period July 1, 1982, through December 31, 1982, \$1.01 per rand in fiscal year 1982 and \$1.29 per rand in fiscal year 1981.

During the year, Highveld changed from a June 30 fiscal year to a calendar year accounting basis. Production and financial results for 1982 have, therefore, been shown for the 12-month period ended

June 30, 1982, and a six-month period ended December 31, 1982. In February 1983, Highveld declared a dividend of R14,991,000, payable April 29, 1983, from profits of the six-month period ended December 31, 1982. Newmont's share of the dividend will be R1,559,064.

During the latter half of 1982, the recession affecting Highveld's overseas markets and the downturn in the South African economy led to a significant reduction in the demand for the Highveld group's products. While results during the first 12 months of the reporting period were actually better than in fiscal 1981, the decline in demand and prices in late 1982 resulted in a significant reduction in earnings in the second half. Two of Highveld's submerged arc ironmaking furnaces were taken out of operation in November effectively reducing iron and steel capacity to 67 percent. Vanadium production was reduced to similar levels, and further reductions for all three product areas may be necessary in 1983.

At December 31, 1982, Highveld's capital expenditure commitments were reduced to R47,628,000, compared with R116,852,000 at June 30, 1981. The construction of the first furnace and the first three kilns in the second iron plant is proceeding according to plan, but it probably will not be brought into production until 1984 due to current market conditions. A reversing hot strip steel mill was commissioned in November 1982 and will be in full operation by April 1983.

Atlantic Cement Company, Inc.

	1982	1981
Net sales	\$78,600,000	\$82,138,000
Net income (loss)	\$ (52,000)	\$ 1,413,000
Dividends received by Newmont	None	None

*After extraordinary charge of \$2.7 million, net of tax, in settlement of a lawsuit.

Atlantic registered a net loss for 1982 as the economic recession took a heavy toll on the construction industry throughout the U.S. The resultant oversupply of cement reduced prices below the already depressed levels of 1981. Atlantic's buildup of inventories forced a two-month shutdown of one of the two kilns at the Ravena plant early in the year. Investment tax credits of \$4,019,000 offset Atlantic's 1982 operating losses.

Construction of the Company's new slag cement plant at Sparrows Point, Maryland, was completed in the second quarter of the year with limited production of NewCem™ beginning in May, about two months behind schedule. The plant was declared operational for financial accounting purposes on December 1, 1982. The new product was well received, but shipments were below expectations because of the late start and the failure of one of four motors driving the two grinding mills, which restricted production rates. The new 18,000-ton ocean-going barge, designed to supplement the existing barge fleet in handling the added volume of NewCem™, was launched and went into service in August.

In December, Baltimore County, Maryland, sold \$14,000,000 of 20-year, 11 percent Industrial Development Revenue Bonds for the benefit of Atlantic Cement Company. The proceeds from the issue were used to finance the construction of certain port and related facilities for the NewCem™ plant.

406-8.5

Nº 267

Carson City, N.

2

三

Source of air contaminant

no serial no. or

of 22.68 metric

ditional period not

was controlled

三

[illegible]

Quality Regulations.

years after the date of issue.
 of the premises by the
 without prior notice.

[illegible]

100

OPERATING PERMIT

Issued toFoot Mineral Company

Silver Leaf Operation

LIBRARY OF THE
UNIVERSITY OF CHICAGO

who is granted a permit to operate the following source of air contaminant:
(Give name, description and location).

Fuller Draco pneumatic conveyor with no serial number or model number operating at a rated peak load of 1,200 metric (1.06 short) tons per hour with an operational period not to exceed 5,760 hours per year. Emissions controlled with a Fuller Draco Model #1 off baghouse, located south

end of Silver Post. Sec. 21. (15)

which shall operate in compliance with the Nevada Air Quality Regulations.
Date of issue: JUNE 13, 1977

This permit:

1. Is non-transferable.
2. Shall be posted conspicuously on or near the source.
3. Shall expire and be subject to renewal five (5) years after the date of issue.
4. Is issued on condition that the holder allows inspection of the premises by the control officer at any time during its hours of operation, without prior notice.

CONFIDENTIAL - OFFICIALS ONLY

My Dear Mr. [illegible]

Item 23
5 of 21

101



STATE OF NEVADA
DEPARTMENT OF CONSERVATION
AND NATURAL RESOURCES
CAPITOL COMPLEX
CARSON CITY, NEVADA 89710

Nº 690

AIR QUALITY OPERATING PERMIT

Issued to Foote Mineral Company
Silver Peak, Nevada 89047

Location Section 21, T2S, R38E, MDB&M (HA 143)
is granted a permit to operate the following source of air contaminant:

Davenport rotary dryer, serial #MD 716, with a
peak load of 1.5 metric (1.65 short) tons per hour,
using propane as fuel, with emissions controlled
by a Schutte and Koerting Type 4010 wet scrubber,

which shall operate in compliance with the Nevada Air Quality Regulations.

Restrictions

1. Source must not operate in excess of 4,160 hours per year.
2. Yearly production must be submitted to the Air Quality Officer by April 15 annually to verify compliance with the maximum input and hours of operation of this source.

This permit:

1. Is non-transferable.
2. Shall be posted conspicuously on or near the source.
3. Shall expire and be subject to renewal five (5) years after the date of issue.
4. Is issued on condition that the holder allows inspection of the premises by the representatives of the department at any time during its hours of operation, without prior notice.

DIRECTOR'S OFFICE

OP 690 amended
by letter dated
Oct. 7, 1982

Signature *[Signature]*
Issued by Dick Serdoz
Phone 885-4670 Date June 13, 1982

6771

FOOTE MINERALS

SILVER PEAK

FUEL COMBUSTION INFORMATION

Combustion Sources	Fuel Rate Ave. Max.	Fuel Type	% Sul.	% Ash	Heat Content
02 0.1142	111 135 (64K/102)	RESIDUAL FUEL	1.2	0.2	150,000 BTU/GAL
03 0.0152	520 530 (517/44)	PROPANE	0	0	2300 BTU/CT ³

CONTROL EQUIPMENT INFORMATION

Type of Control	Efficiency		VEO
	Design	Operating	
a. FABRIC FILTER - MED TEMP		99.99%	< 52
b. NONE			< 52
c. WET SCRUBBER - MED EFF		99.02	< 52
d. _____			
e. _____			
f. _____			

EMISSION MEASUREMENT RELIABILITY

a. EMISSION FACTOR	
b. EMISSION FACTOR	
c. EMISSION FACTOR	
d. _____	
e. _____	
f. _____	

1. PROCESS EQUIPMENT OBSERVATIONS

PROCESS EQUIPMENT APPEARED TO BE IN GOOD REPAIR
AND PROPERLY MAINTAINED. THE AUTOMATIC TEMPERATURE
CONTROL ON THE GAS FIRED DRYER WAS OUT OF SERVICE.
THE TEMPERATURE CONTROL WAS BEING MAINTAINED MANUALLY

2. CONTROL EQUIPMENT OBSERVATIONS

THE WET SCRUBBER CONTROLLING THE GAS FIRED DRYER WAS
OPERATING SATISFACTORILY DURING THE INSPECTION. THE SCRUBBER
CONTROLLING THE PNEUMATIC CONVEYOR WAS HAD A RECENT
ADDITION IN ORDER TO HANDLE AN INCREASED LOAD. IT
WAS OBSERVED IN OPERATION AND HAD NO VISIBLE EMISSIONS

Signature

K. B. Ruck

Date of Report 11 FEBRUARY 23, 1977

EQUIPMENT LIST

Company FOOTE MINERAL COMPANY

Inspection Date NOVEMBER 3, 1977

APCD
Permit No.

Unit

Specifications

269	FULLER PLATE PNEUMATIC CONVEYOR	1.62 TON/LR	5760 WPL/HR
270	SWENSON DIVISION ROTARY DRIER	1.34 Y 10 ⁶ BTU/LR	5760 WPL/HR
271	DIXON BOILER (C) #WW-10 S.N. N-80-N 1470	25.1 Y 10 ⁶ BTU/LR	5760 WPL/HR

LIST ATTACHMENTS ON REVERSE SIDE

PROCESS DESCRIPTION

LITHIUM CARBONATE (Li_2CO_3) IS PRODUCED FROM LITHIUM CHLORIDE BRINE (LiCl) IN THE PROCESS

THE LiCl BRINE IS PUMPED TO EVAPORATION BOWLS. LIME IS ADDED. THE BRINE IS COCONCENTRATED BY EVAPORATED A SECOND TIME AND PUMPED TO A BATCH TANK IN THE PLANT. THE BRINE IS TREATED WITH LIME AND SODA ASH AND SENT TO A THICKENER. THE BRINE IS STORED IN LARGE OPEN VATS FROM THE STORAGE VATS THE BRINE & SLUDGE IS FILTERED, PREHEATED, HEATED AND SENT THE PREHEATED REACTORS. EXCESS SODA ASH IS ADDED TO CAUSE THE REACTION $2\text{LiCl} + \text{Na}_2\text{CO}_3 \rightarrow \text{Li}_2\text{CO}_3 + 2\text{NaCl}$. FROM THE REACTORS THE PRECIPITATED LITHIUM CARBONATE PASSES TO A CYCLONE WHERE THE PRECIPITATE IS SEPARATED FROM THE SOLUTION. THE SALT IS THEN DEWATERED ON A DEC-CHUTE (DEWATER FILTER) AND DRIED IN A PROpane FIRED ROTARY DRIER. THE DRIED PRODUCT IS AIR CONVEYED TO A COLLECTING BAGHOUSE AND DROPPED INTO A STORAGE HOPPER. AFTER DETERMINING THE PRODUCT IS BAGGED AND SHIPPED TO STORAGE.

Surveillance & Analysis Division
Environmental Protection Agency
Region IX
STATIONARY SOURCE INSPECTION NOTES

1. GENERAL INFORMATION

Company FOOTE MINERAL COMPANY
Address APCD
State NEVADA County CLARK 18
(include codes)
AOCR 147 City SILVER PEAK
NEDS Plant ID No. 001 CDS Source No.
Inspector KURT B. RUCH Date 11-3-77 Phone (702) 445-5560

2. PROCESS EMISSION INFORMATION

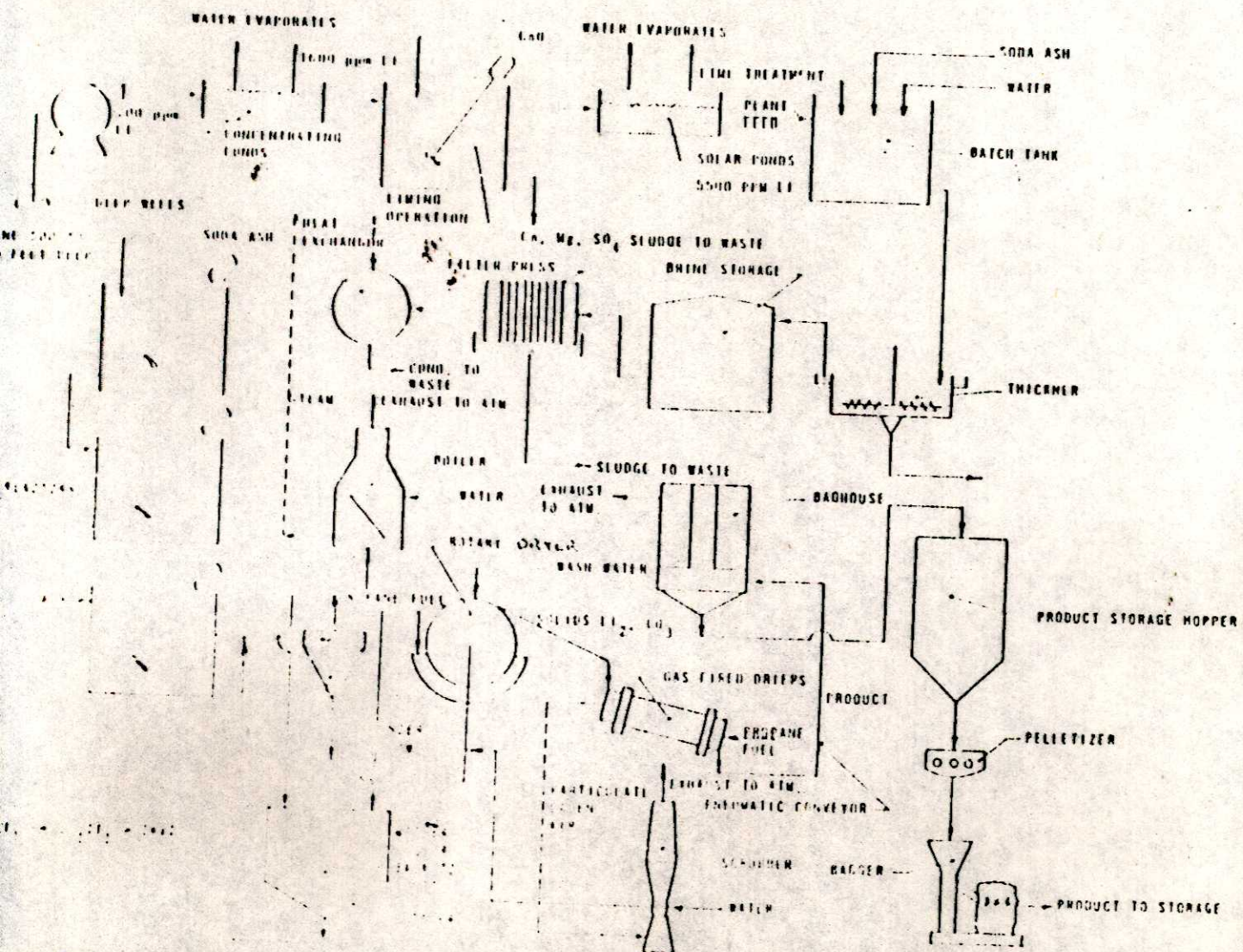
SCC Code (1st 6 digits) 3-05-700 Confidential File

Plant Type LITHIUM CHLORIDE (1.00) MINE AND MILL

Process	Point SCC ID IV (2 digits ea.)	Operating Schedule (hrs/day), (hrs/year)
a. <u>PNEUMATIC CONVEYOR</u>	<u>99</u>	<u>24 hr/day 5760 hr/yr</u>
b. <u>BOILER</u>	<u>99</u>	<u>24 hr/day 5760 hr/yr</u>
c. <u>ROTARY DRYER</u>	<u>99</u>	<u>24 hr/day 5760 hr/yr</u>
d. <u> </u>	<u> </u>	<u> </u>
e. <u> </u>	<u> </u>	<u> </u>

Control Equipment	Emissions (lbs/hr-tons/yr-Poll)	Method Of Calculation
a. <u>FULLER</u> <u>WALKER BAGHOUSE MODEL BLUE</u>	<u>3.25</u> <u>0.37</u>	<u>APCD</u>
b. <u>NONE</u>	<u>0.002</u> <u>0.005</u>	<u>APCD</u>
c. <u>WW SLY CO. 100% IMPUR</u>	<u>0.48</u> <u>1.37</u>	<u>APCD</u>
d. <u> </u>	<u> </u>	<u> </u>
e. <u> </u>	<u> </u>	<u> </u>

NESHAPS Source NO NSPS Source NO NSR Source NO
SPCC Plan NO Toxic Chemicals NO



LITHIUM IN SEDIMENTS AND BRINES—HOW, WHY, AND WHERE TO SEARCH

By JAMES D. VINE, Denver, Colo.

Abstract.—The possibility of using lithium in batteries to power electric vehicles and as fuel for thermonuclear power has focused attention on the limited resources of lithium other than in pegmatite minerals. The Clayton Valley, Nev., subsurface lithium brine has been the major source of lithium carbonate since about 1967, but the life of this brine field is probably limited to several more decades at the present rate of production. Lithium is so highly soluble during weathering and in sedimentary environments that no lithium-rich sedimentary minerals other than clays have been identified to date. The known deposits of lithium, such as the clay mineral hectorite and the lithium-rich brines, occur in closed desert basins of the Southwest in association with nonmarine evaporites. However, the ultimate source for the lithium in these deposits may be from hydrothermal solutions. The search for previously unreported deposits of nonpegmatitic lithium should consider its probable association, not only with nonmarine evaporite minerals, but also with recent volcanic and tectonic activity, as well as with deposits of boron, beryllium, fluorine, manganese, and possibly phosphate.

A revised estimate of the lithium resources in brine at Clayton Valley, near Silver Peak, Nev. (Kunasz, 1975), represents a significant reduction from previous estimates and hence requires a reappraisal of the total resources in the United States as reported by Norton (1973, p. 372). Although the total resources of lithium in brine are probably large, the amount that can be regarded as proved as well as probable recoverable reserves may be only about one-tenth of the total United States reserves of lithium. The remaining resources of brine would come under the categories of submarginal or undiscovered and therefore would not be regarded as economic at present. The major reserves of lithium in the United States occur in spodumene-bearing pegmatites at Kings Mountain, N.C., which have been estimated to contain about 440 million kilograms of lithium (Norton, 1973, p. 372). Spodumene is a silicate mineral, which is ideally suited for the ceramic industry but costly to reduce to other commodities such as lithium carbonate. The Clayton Valley brine has been the principal source of lithium carbonate in the United States since about 1967. The discovery of additional large brine fields or bedded lithium deposits

will be required if the United States is to use lithium batteries for load leveling of off-peak power, or to sustain an automobile industry based on lithium batteries as a source of power, or to construct a thermonuclear power industry based on lithium fuel. This report is intended to further explain the need to search for new deposits of nonpegmatite lithium, to review the geological occurrence and geochemical distribution of lithium in sedimentary environments, and to speculate on the prospects for finding new deposits.

PRODUCTION AND USE

The use and production of lithium minerals and chemicals have increased steadily since the first lithium minerals were produced more than 75 years ago. Prior to 1938, lithium was obtained almost exclusively by handpicking large lithium-bearing crystals from granite pegmatites, where it occurs in both silicate and phosphate minerals. The principal, commercial lithium-bearing mineral, spodumene ($\text{LiAlSi}_2\text{O}_6$), is purified and used directly in making glass and ceramics where its value is related to both the strength and the thermal expansion of the product. Beginning in 1938, lithium phosphate has been produced from the brine at Searles Lake, Calif., where it is a minor by-product recovered during the production of trona, sulfate minerals, potash, and borates. Lithium carbonate has been produced as a primary product from subsurface brine at a desert playa in Clayton Valley, Nev., since about 1967. The estimated total production of lithium from pegmatite minerals and lithium salts derived from brine amounted to about $2\frac{1}{4}$ million kilograms of lithium¹ in 1968 and was valued at slightly more than \$5 million (Cummings, 1970). Although exact production figures have not been published, it seems reasonable to assume that the Clayton Valley brine field accounted for nearly half of this amount.

¹In comparing production data for lithium it is essential to specify the basis for calculation, as different sources will report Li_2O , Li_2CO_3 , LiCl , or LiOH . The most convenient basis for calculation, which is used throughout this report, is elemental (metallic) lithium (Li) to which all the others can be converted; for example the amount reported for Li_2O multiplied by 0.464 gives the amount of lithium.

In addition to its uses in the glass and ceramic industries, lithium is used in multiple-purpose greases and in a great variety of industrial chemicals, including salts, the hydroxide, organic compounds, and as metallic lithium. The administration of lithium carbonate in the treatment of various mental illnesses has led to the speculation that trace quantities of lithium may be desirable in human nutrition. An increasing amount of lithium is used each year in primary lithium batteries of the dry-cell type (Grady, 1974), and one industry authority has indicated that this use alone will consume half a million kilograms annually by 1977 and a rapidly increasing amount thereafter.

Several potential new uses for lithium may completely alter the resource and demand outlook in the near future. The Argonne National Laboratory and others are currently working on the design of lithium batteries for the storage of off-peak power and to power electric vehicles of various sorts as an alternative to the pollution-producing internal combustion engine. One design model intended for an automobile would require a total of about 45 kg of lithium in the electrolyte and electrodes. The manufacture of 50,000 electric vehicles requiring 45 kg of lithium in each vehicle battery would take an entire year's production of lithium at the 1968 rate of production. The number of vehicles required to ameliorate the smog problem in our major cities would probably be several times 50,000 vehicles each year for a number of years.

Thermonuclear powerplants now being designed will require lithium to produce tritium, a primary fuel for the reaction. Different reactor designs will require more or less lithium, depending on the relative amounts of lithium and beryllium used in the neutron-absorbing blanket. One design would require 2.8 kg of lithium per megawatt of electrical power, MW(e), whereas another might require 920 kg/MW(e). For an ultimate capacity of perhaps 500,000 MW(e) by the year 2020 A.D., the first would require 1,400 t of lithium; the second would require 920,000 t of lithium (Locke Bogart, written commun., 1974).

LITHIUM INDUSTRY

Can industry increase the production of lithium at the rate necessary to meet the growing demand? The answer to this question requires a careful look at the industry and the technical problems associated with the extraction of lithium from known deposits and potential future resources.

Three companies in the United States account for all the domestic lithium production. The Foote Mineral Co. of Exton, Pa., is the largest producer of lithium minerals and chemicals. It produces spodumene

($\text{LiAlSi}_2\text{O}_6$) from pegmatite mines at Kings Mountain, N.C., and lithium carbonate from lithium-bearing brines that are pumped from the subsurface at Clayton Valley, near Silver Peak, Nev. Kerr-McGee Chemical Corp. (formerly American Potash and Chemical Corp.) recovers lithium phosphate as a byproduct of solar evaporation for other saline minerals at Searles Lake near Trona, Calif. Lithium Corp. of America, Inc., a subsidiary of Gulf Resources and Chemical Corp., produces lithium minerals from pegmatites in North Carolina. Several years ago they announced plans to extract lithium as a byproduct of solar evaporation from Great Salt Lake, Utah, but the plan was canceled, apparently because they could not get a firm contract for the sale of magnesium, which would have to be precipitated before the lithium could be produced. Several other companies, including NL Industries, have indicated an interest in the byproduct recovery of lithium from Great Salt Lake but to date this has not been accomplished.

Lithium-bearing pegmatite minerals such as spodumene will probably continue to be the source of much of the lithium used in the glass and ceramic industries. Although the Kings Mountain area, North Carolina, supplies most of the U.S. requirement for lithium-bearing pegmatite minerals, Canada and Rhodesia also have large reserves and resources of lithium in pegmatites (Norton, 1973, p. 372), but only South America is known to have even potential resources of lithium in brine. Lithium carbonate produced from brines will probably be the most satisfactory source for metallic lithium and lithium salts required in vehicle batteries and for lithium uses in industries other than ceramics.

ESTIMATES OF LITHIUM-BEARING BRINE RESERVES

When the Clayton Valley, Nev., brine field was being developed in the middle 1960's there were no data from which to estimate the quantity of brine that might ultimately be recovered. Reserve estimates were based on the average geochemical abundance of lithium-bearing sediment calculated from a few core holes and extrapolated to 1,000-ft depth and for the entire floor of the valley, some 32 mi² in area. Although these estimates made no allowance for recoverability of the brine, they seemed reasonable enough to be accepted and quoted in several reports of the U.S. Geological Survey and the U.S. Bureau of Mines as recently as 1974. After more than 8 yr of development and production history with the brine field at Clayton Valley, the Foote Mineral Co. has calculated and released a new estimate of lithium resources (Kunasz, 1975). Although this new estimate represents a significant reduction from previously published figures, the added

statement that only part of the total lithium resource can ever be recovered may have equal or greater significance.¹ Analysis of the available data indicates why this may be true.

The nature and distribution of the brine-bearing permeable strata in alluvium in Clayton Valley have not been described. Close analogies with other brine fields such as Searles Lake, Calif., where the brine is pumped from permeable salt beds (W. C. Smith, 1966; G. I. Smith, oral commun., February 1974), and Bonneville Salt Flat, Utah, where brine is derived from shallow clay fractures (Turk and others, 1973), have been denied by Ihor Kunasz (oral commun., May 1974). It follows that permeability in the Clayton Valley sediments is probably associated with the fine-grained detrital sediments that characterize the bulk of the sediments in the playa. The technique of drilling wells to a depth of as much as 600 ft implies recovery of brine throughout a section of alluvium as much as 600 ft thick. Consideration of the 10-mi² area of the brine field and the 600-ft depth of the producing wells suggest that the total volume of sediment from which lithium-bearing brine is pumped is about 5 km³. If an average permeability of 3 percent is assumed, the volume of lithium-bearing water can be estimated to be about 150 million cubic metres. If the density of the water is about 1.1 this would be equivalent to about 165 million tons of brine. Published data indicate an average concentration of about 300 ppm lithium in the brine, for a total quantity of about 50 million kilograms of lithium.

Recharge to the brine aquifer is by ground- and surface-water flow from the surrounding mountains and pediment gravels and to a much lesser extent from precipitation on the playa surface. The ground-water flow, in particular, may bring with it a moderate amount of dissolved mineral matter including a minor amount of lithium. If the spring waters along the margin of the playa are representative of recharge from ground-water sources, they may carry a few tens of parts per million of lithium into the aquifer. The life of the deposit will be a function of the rate of production of the original 50 million kilograms of lithium plus lithium added from ground-water recharge until the concentration of lithium is reduced to a level that is no longer economic to pump. This may be two-thirds or three-fourths of the total, but production will cease before all the lithium is depleted because the price of the finished product must be balanced against the cost of pumping, maintenance of the evaporating ponds, precipitation, and drying of the lithium carbonate.

¹After this report was in page proof, I. A. Kunasz (oral commun., 1975) submitted a revised estimate of 44,500 tons for the recoverable reserves of lithium at Clayton Valley, Nev.

OCCURRENCE OF LITHIUM

Lithium is associated chiefly with the clay fraction of sedimentary rocks (Horstman, 1957; Tardy and others, 1972), and it is known to occur in anomalously high concentrations primarily in the arid regions of the Western United States. Lithium is an essential constituent of a bentonitic clay from the Mojave Desert near the railroad stop of Hector (fig. 1, loc. 1), about 56 km east of Barstow, Calif. (Foshag and Woodford, 1936; Ross and Hendricks, 1945). The unusual properties of this clay attracted interest among the clay mineralogists who have given it the name hectorite and speculated as to its origin and the source of the 0.5 percent lithium and 4.75 percent fluorine that it contains (Ames and others, 1958). Hectorite is a trioctahedral montmorillonite belonging to the high magnesium (saponite) end of the smectite group. These minerals are low in aluminum and can be distinguished from the more common dioctahedral smectites by the position of the 060 reflection near 62° 2 θ on the X-ray diffraction pattern. Table 1 and figure 1 list the localities where hectorite or a clay mineral similar to hectorite have been reported. All are in nonmarine Cenozoic rocks or sediments, most occurring in the late Cenozoic.

GEOCHEMISTRY

The geochemical behavior and mineralogy of lithium in pegmatites is well documented (Heier and Adams, 1964; Heier and Billings, 1972), but its behavior and mineralogy in the sedimentary cycle is less thoroughly documented. Lithium is the lightest of all metals and a member of the alkali group of metals. It is a minor element, having a crustal abundance of about 20 ppm, similar to such elements as lead, gallium, and lanthanum. In minerals, univalent lithium can substitute to some extent for divalent magnesium and iron, but its smaller ionic size does not permit its substitution to any significant extent for the chemically related more abundant alkalies, sodium and potassium. All the common cations are able to dislodge Li⁺ from base-exchange material, hence base-exchange reactions tend to bring lithium into solution (Hem, 1959, p. 134). Moreover, the simple salts of lithium are highly soluble, so there is little opportunity for their precipitation, except possibly under the most arid climatic conditions. Lithium tends to remain in the residual brine during evaporation of seawater and is not generally concentrated in marine halite. The lithium released from the primary minerals as the Li⁺ cation is readily transported to sea where it becomes dispersed in the fine-grained argillaceous sediments in amounts generally less than 100 ppm. Locally higher concentra-

TABLE 1. *Hectorite localities in the United States*

Locality (fig. 1)	Name	Location	Rock unit	Reference
1	Hector	San Bernardino, Calif. (sec. 35, T. 18 N., R. 5 E.).	Unnamed (Pliocene?)	Foshag and Woodford (1930), Ross and Hendricks (1945), Ames and others (1958).
2	Kramer borate	Kern, Calif. (secs. 13, 14, and 24, T. 11 N., R. 8 W.).	Tropico Group (Oligocene? and Miocene).	Dibblee (1967), Morgan and Erd (1969).
3	Unnamed (25 km NE. of Amboy).	San Bernardino, Calif. (not known).	Unknown	Foshag and Woodford (1930).
4	Spor Mountain (road-side claims).	Junb, Utah (sec. 8, T. 13 S., R. 12 W.).	Unnamed (Pliocene?)	Shawe, Mountjoy, and Duke (1964), Starkey and Mountjoy (1973).
5	Lyles lithium deposit	Yavapai, Ariz. (sec. 12, T. 13 N., R. 6 W.).	Unnamed (upper Cenozoic).	Norton (1965).
6	Peoples Valley	Yavapai, Ariz. (NE ¼, T. 11 N., R. 4 W.).	Unknown	Norton (1969).
7	Shadow Mountain	Teton, Wyo. (sec. 1, T. 43 N., R. 115 W.).	Teewinot Formation (Pliocene).	J. D. Love (written commun., 1973).
8	Roan Cliffs, (Uinta Basin).	Duchesne, Utah (sec. 12, T. 11 S., R. 10 E.; sec. 27, T. 6 S., R. 8 W.).	Green River Formation (Eocene).	Dyni (1973).
9	Clayton Valley	Esmeralda, Nev. (sec. 35, T. 1 S., R. 40 E., unsurveyed).	Alluvium (Quaternary).	Kunasz (1970).

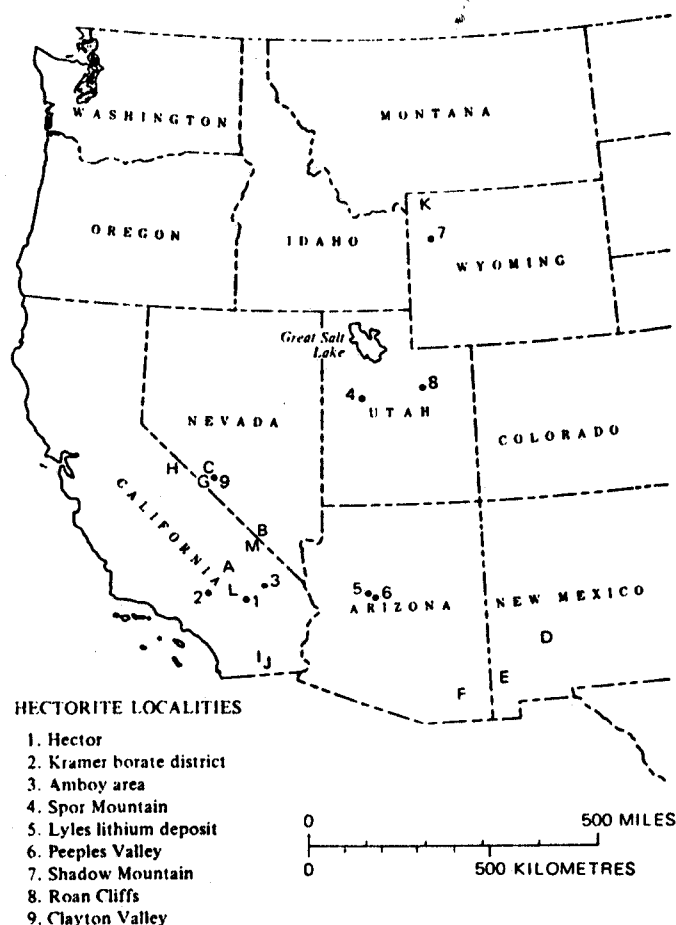


FIGURE 1.—Index map showing hectorite localities in the United States. Other localities mentioned in text: A, Searles Lake; B, Amargosa Desert; C, Columbus Salt Marsh; D, Truth or Consequences; E, South Alkali Flat; F, Willcox Playa; G, Nivloc mine; H, Mono Lake; I, Salton Sea; J, Imperial Valley; K, Yellowstone National Park; L, Mojave Desert; and M, Death Valley.

tions are associated with nonmarine sediments, especially in arid climates and in oil-field brines where several tens of parts per million are known. In humid climates, lithium tends to become concentrated in kaolinitic clays associated with bauxite, where as much as 340 ppm lithium has been reported (Ronov and others, 1970). Magnesian silicates, such as sepiolites, stevensites, and hectorites that have formed authigenically during arid periods in lagoonal environments, and the associated limestones, dolomites, and detrital rocks, yield the largest amounts of lithium, ranging from 400 to 6,000 ppm (Tardy and others, 1972). Natural lithium salts are not known to exist; however, if they do exist, recognition might be difficult especially if they are fine grained and mixed with other fine-grained minerals. Lithium substitution for Mg^{+2} or Fe^{+2} might not be recognized in carbonates and other salts.

Anomalous concentrations of lithium have been reported in various plants, waters, and soils collected from desert regions of the Western United States. Sievers and Cannon (1974) expressed concern for the health problem of Pima Indians living on the Gila River Indian Reservation in central Arizona because of the anomalously high lithium content in water and in certain of their homegrown foods. Cannon (unpub. data, 1974) identified the Amargosa Desert area along the border between Nevada and California as another area of anomalously high lithium. Papke (1972) reported on the occurrence of sepiolite derived from saponite clay near Ash Meadows in this same area, and I have found as much as 500 ppm lithium in clay at the abandoned claypits at Clay City, Nev., also in the same area.

Other areas of anomalously high lithium are as follows: Alluvial sediments associated with an old borate mine at the south end of Columbus Salt Marsh, Esmeralda County, Nev.; a deposit of limonite and quartz resulting from the alteration of limestone at Geronimo Hot Spring, near the center of Truth or Consequences, N. Mex.; alluvial sediment from the surface of several dry lakes in San Bernardino County, Calif.; Sevier Lake in Millard County, Utah; South Alkali Flat in Hidalgo County, N. Mex.; Willcox Playa in Cochise County, Ariz.; and a quartz-calcite vein sample from the Nivloc mine, near Silver Peak, Nev.

The lithium content of natural waters is highly variable and bears only a slight relation to the content of sodium or total dissolved solids (Bradford, 1963). Table 2 lists the content of lithium and sodium and the lithium-sodium ratio for some selected natural waters. The average content of lithium in seawater is shown to be less than that of the freshwater of Lake Tanganyika in Africa. Moreover, the ratio of lithium to sodium in seawater is only about one-tenth that of the ratio of these elements in the Earth's crust. White, Hem, and Waring (1963, p. F10-F11, and tables 19 and 29) suggested that the highest lithium-sodium ratio probably occurs in acid sulfate-chloride spring waters associated with active or recent volcanism. They further suggested that a high ratio may reflect a high content of lithium in certain volcanic emanations. Recent stable isotope studies of hydrothermal minerals and fluid inclusions such as those from Tonopah and Goldfield, Nev., provide evidence of the quantitative importance of meteoric water relative to primary magmatic water in epithermal gold-silver mineralization (Taylor, 1974). The igneous intrusion serves as a source of heat energy to power a convective circulation of meteoric water in permeable country rock. In such a system, lithium might be leached from the country rock and concentrated in adjacent playa basins. The same mechanism might help to explain the difference in chemical composition of brines in adjacent basins within the same geologic province.

PROSPECTING FOR LITHIUM

Because concentrations of lithium have not as yet been reported from marine sediments, including marine evaporites, authors commonly state that lithium is dispersed among the clay minerals during marine sedimentation. The fate of lithium during deposition of marine evaporites is certainly not obvious. If lithium is concentrated in the residual brine and the brine becomes buried with the sediment, there should be a chance of finding such a lithium-rich brine among the ancient sediments. Saline minerals generally form impervious rocks as a result of deep burial so any residual brine originally buried with the evaporites is probably pressed out into the surrounding more permeable clastic sediments where equilibrium reactions may greatly alter the composition of the brine. Whether or not lithium may enter into such reactions is unknown. Perhaps the Michigan basin brine from the Sylvania Sandstone listed in table 2 is such a residual brine.

Nonmarine environments appear more favorable for the concentration of lithium brine during evaporation and precipitation of saline minerals because of the examples, such as Clayton Valley, where this has occurred. However, there is no adequate explanation yet as to why the brine at Clayton Valley should contain so much more lithium than do brines in other valleys of the same region. An explanation possibly lies in the answers to the following questions for which data are not now available: Is there a source for an unusually abundant supply of lithium within rocks that crop out in the drainage area of Clayton Valley? Is there a source of lithium at depth from the residual liquid of a cooling magma chamber? Is lithium that is extracted from country rock by meteoric waters kept in circulation by a deep-seated source of heat? Is there something unique or distinctive about the structure and geomorphic history of this basin, the type of volcanic activity and lithology of the volcanic rocks, the chemistry and mineralogy of the weathering products within the basin, or the hydrologic character of the basin?

TABLE 2.—Lithium and sodium content of natural waters

Water source	Lithium (ppm)	Sodium (ppm)	Li: Na ratio	Reference
Seawater	0.17	10,500	0.00001	Goldberg (1963).
Great Salt Lake, Utah	56	92,200	.0006	Cohenour (1966, p. 211).
Lake Tanganyika, Africa (700 m depth)	.8	64.2	.012	Livingstone (1963, table 84).
Laguna Escudado, Peru	7.6	694	.011	Do.
Mono Lake, Calif	8.5	21,400	.0004	Do.
Salton Sea, Calif	1.9	6,249	.0003	Do.
Searles Lake, Calif. (brine from upper salt)	81	110,000	.0007	White, Hem, and Waring (1963, table 84).
Clayton Valley, Nev. (subsurface brine)	300	66,200	.0045	Kunasz (1970, p. 114).
Michigan basin (brine from Sylvania Sandstone)	70	22,500	.003	White, Hem, and Waring (1963, table 13).
Niland well, Imperial Valley, Calif	18	7,280	.0025	White, Hem, and Waring (1963, table 18).
Norris Basin, Yellowstone National Park, Wyo	8.4	439	.019	White, Hem, and Waring (1963, table 17).

The existence in pegmatites of several lithium phosphate minerals, including Li_3PO_4 , plus several more complex compounds of iron, aluminum, and manganese, suggests the possibility that some sedimentary phosphates might also contain significant amounts of lithium. Those phosphates formed in closed basins might be the most favorable.

Lithium is also known to occur in manganese oxide minerals such as lithiophorite (Fleischer and Faust, 1963), which can be distinguished from psilomelane or wad by a characteristic X-ray powder pattern. Lithiophorite is probably a common mineral and has been reported from both hydrothermal and supergene deposits. It occurs in the weathering products of magnesium-rich ultramafic rocks and as black stains and encrustations on quartz, sandstone, and chert.

A maximum of 200 ppm lithium from iron-rich sedimentary rocks was reported by James (1966, table 32), but this value did not include lithium in manganese nodules from the sea floor because no such data were available.

Lithium in sedimentary environments is associated with a characteristic suite of other minor elements. One of these associations is that with boron in the borate deposits of the Mojave Desert and Death Valley areas. Another association is with fluorine, beryllium, and manganese at Spor Mountain, Utah. These same suites of minor elements are also associated with lithium in pegmatites and in lithium-bearing greisen, both of which form from crystallizing magma at relatively high temperatures. The occurrence of the same suites of elements in both high-temperature and low-temperature environments is rather unusual and therefore deserving of an explanation. One possibility is that the sedimentary lithium deposits include a significant contribution from solutions derived from the residual fluids of a differentiated magma. Such a contribution could be derived from thermal springs associated with igneous intrusion or volcanism, especially acid volcanic rocks, which may be the end products of a differentiated magma. This possibility is also consistent with the suggestion for a hydrothermal origin for the hectorite in the Mojave Desert (Ames and others, 1958), the lithium-bearing brine at Clayton Valley (Kunasz, 1970), and the lithium-bearing beryllium deposits at Spor Mountain, Utah (Shawe and others, 1964; Lindsey and others, 1973).

The desert region of the Southwest includes the largest number of known concentrations of lithium in the form of hectorite deposits, lithium-rich brines, and anomalous concentrations of lithium in rocks and sediments. This area may be regarded as a lithium-rich province that is nearly coincident with the Basin and

Range structural province. Clearly the desert climate affords the greatest opportunity for concentration of lithium at or near the surface where it may be observed because of an excess of evaporation over precipitation. However, the association of lithium with the Basin and Range structural province may have genetic significance for other reasons as well. For example, the deep-seated faults may provide pathways for the deep circulation of ground water; the volcanic activity provides a source of heat energy to drive ground-water convection cells; and the block faulting interrupts the drainage, forming local basins that serve as hydrologic sinks from which the soluble constituents of surface and ground water cannot escape. Together these features serve to concentrate and trap the lithium in near-surface sedimentary environments where any deposits are most easily discovered. The potential role of lithium-rich source rocks such as alkali-rich volcanics has yet to be evaluated. So also has the role of different clay minerals formed during weathering in causing the concentration or dispersal of lithium in the associated sediments and ground waters.

The prospects for discovering previously unreported deposits of nonpegmatite lithium in any given area can be evaluated empirically by assigning appropriate weight to a list of factors such as the following:

- Anomalous concentrations of lithium in surficial materials
- Desert climate
- Evaporite minerals
- Topographic closure
- Structural closure
- Basin and Range faults
- Types of igneous rocks
- Volcanic activity
- Intrusive activity
- Hydrothermal alteration
- High Li:Na in water
- Thermal springs
- Late Cenozoic tectonism
- Base or precious metal mineralization
- Deposits of boron, beryllium, fluorine, tin, strontium, or tungsten
- Deposits of manganese or phosphate
- Noncarbonate aquifers
- Proportions of clays and zeolites in weathered rocks

More experience in searching for nonpegmatite lithium deposits will be required before the relative importance of these various factors can be determined. Meanwhile, any search for nonpegmatite lithium deposits should be conducted with these factors in mind and an effort should be made to rank their relative importance.

REFERENCES CITED

- Ames, L. L., Sand, L. B., and Goldich, S. S., 1958, A contribution on the Hector, California, bentonite deposit: *Econ. Geology*, v. 53, p. 22-37.

- Bradford, G. R., 1963, Lithium survey of California's water resources: *Soil Sci.*, v. 96, no. 2, p. 77-81.
- Cohenour, R. E., 1966, Great Salt Lake, Utah, and its environment, in 2d symposium on salt—Volume 1, *Geology geochemistry, mining*: Cleveland, Northern Ohio Geol. Soc., p. 201-214.
- Cummings, A. M., 1970, Lithium, in *Mineral facts and problems*: U.S. Bur. Mines Bull. 650, p. 1073-1081.
- Dibblee, T. W., Jr., 1967, Areal geology of the western Mojave Desert, California: U.S. Geol. Survey Prof. Paper 522, 153 p.
- Dyni, J. R., 1973, Trioctahedral smectite in the Green River Formation, Duchesne County, Utah: U.S. Geol. Survey open-file rept., 25 p.
- Fleischer, Michael, and Faust, G. T., 1963, Studies on manganese oxide minerals—[Pt.] 7, Lithiophorite: *Schweizer. Mineralog. u. Petrog. Mitt.*, v. 43, no. 1, p. 197-216.
- Footo Mineral Company, 1967, Is there enough lithium?: *Footo Prints*, v. 36, p. 22-23.
- Foshag, W. F., and Woodford, A. O., 1936, Bentonitic magnesian clay-mineral from California: *Am. Mineralogist*, v. 21, no. 4, p. 238-244.
- Goldberg, E. D., 1963, Composition of sea water, in Hill, M. N., ed., *New York, Interscience Publishers*, v. 2, p. 3-25.
- Grady, H. R., 1974, The lithium battery moves center stage: *Footo Prints*, v. 41, no. 2, p. 2-12.
- Heier, K. S., and Adams, J. A. S., 1964, The geochemistry of the alkali metals, in Ahrens, L. H., and others, eds., *Physics and chemistry of the earth*: New York, Macmillan Co., v. 5, p. 253-381.
- Heier, K. S., and Billings, G. K., 1969, Lithium, Chap. 3 [sec. B-0], in Wedepohl, K. H., ed., *Handbook of geochemistry*: New York, Springer-Verlag, v. 2, no. 1.
- Hem, J. D., 1959, Study and interpretation of the chemical characteristics of natural water: U.S. Geol. Survey Water-Supply Paper 1473, 269 p.
- Horstman, E. L., 1957, The distribution of lithium, rubidium, and caesium in igneous and sedimentary rocks: *Geochim. et Cosmochim. Acta*, v. 12, nos. 1-2, p. 1-28.
- James, H. L., 1966, Chemistry of the iron-rich sedimentary rocks: U.S. Geol. Survey Prof. Paper 440-W, 61 p.
- Kunasz, I. A., 1970, Geology and geochemistry of the lithium deposit in Clayton Valley, Esmeralda County, Nevada: Pennsylvania State Univ. Ph.D. thesis (thesis 71-16, 629, available from University Microfilms, Ann Arbor, Mich.), 113 p.
- 1975, Lithium raw materials, in *Industrial minerals and rocks (1975 revision)*: Am. Inst. Mining, Metall., and Petroleum Engineers, p. 791-803.
- Lindsey, D. A., Ganow, Harold, and Mountjoy, Wayne, 1973, Hydrothermal alteration associated with beryllium deposits at Spor Mountain, Utah: U.S. Geol. Survey Prof. Paper 818-A, 20 p.
- Livingstone, D. A., 1963, Chemical composition of rivers and lakes: U.S. Geol. Survey Prof. Paper 440-G, 64 p.
- Morgan, Vincent, and Erd, R. C., 1969, Minerals of the Kramer borate district, California: California Div. Mines and Geology Mineral Inf. Service, pt. 1, v. 22, no. 9, p. 143-153; pt. 2, 22, no. 10, p. 165-172.
- Norton, J. J., 1965, Lithium-bearing bentonite deposit, Yavapai County, Arizona, in *Geological Survey research 1965*: U.S. Geol. Survey Prof. Paper 525-D, p. D163-D166.
- 1969, Lithium, in *Mineral and water resources of Arizona*: U.S. 90th Cong., 2d sess., Senate Comm. Interior and Insular Affairs, Comm. Print (also Arizona Bur. Mines Bull. 180), p. 206-211.
- Norton, J. J., 1973, Lithium, cesium, and rubidium—the rare alkali metals, in Brobst, D. A., and Pratt, W. P., eds., *United States mineral resources*: U.S. Geol. Survey Prof. Paper 820, p. 365-378.
- Papke, K. G., 1972, A sepiolite-rich playa deposit in southern Nevada: *Clays and Clay Minerals*, v. 20, no. 4, p. 211-215.
- Ronov, A. B., Migdisov, A. A., Voskresenskaya, N. T., and Korzhina, G. A., 1970, Geochemistry of lithium in the sedimentary cycle: *Geochemistry Internat.*, v. 7, p. 75-102.
- Ross, C. S., and Hendricks, S. B., 1945, Minerals of the montmorillonite group, their origin and relation to soils and clays: U.S. Geol. Survey Prof. Paper 205-B, 77 p.
- Shawe, D. R., Mountjoy, Wayne, and Duke, Walter, 1964, Lithium associated with beryllium in rhyolitic tuff at Spor Mountain, western Juab County, Utah, in *Geological Survey research 1964*: U.S. Geol. Survey Prof. Paper 501-C, p. C86-C87.
- Sievers, M. L., and Cannon, H. L., 1974, Disease patterns of Pima Indians of the Gila Indian Reservation of Arizona in relation to the geochemical environment, in Hemphill, D. D., ed., *Univ. Missouri Symposium on Trace Elements in Environmental Health*: v. 7, p. 57-61.
- Smith, W. C., 1966, Borax and other boron compounds, in *Mineral and water resources of California*, pt. 1: U.S. 89th Cong., 2d sess., Senate Comm. Interior and Insular Affairs, Comm. Print (also California Div. Mines and Geology Bull. 191), p. 104-111.
- Starkey, H. C., and Mountjoy, Wayne, 1973, Identification of a lithium-bearing smectite from Spor Mountain, Utah: U.S. Geol. Survey Jour. Research, v. 1, no. 4, p. 415-419.
- Tardy, Yves, Krempf, Gérard, and Trauth, Norbert, 1972, Le lithium dans les minéraux argileux des sédiments et des sols: *Geochim. et Cosmochim. Acta*, v. 36, no. 4, p. 397-412.
- Taylor, H. P., Jr., 1974, The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition: *Econ. Geology*, v. 69, no. 6, p. 843-883.
- Turk, L. J., Davis, S. N., and Bingham, C. P., 1973, Hydrogeology of lacustrine sediments, Bonneville Salt Flats, Utah: *Econ. Geology*, v. 68, p. 65-78.
- White, D. E., Hem, J. D., and Waring, G. A., 1963, Chemical composition of subsurface waters: U.S. Geol. Survey Prof. Paper 440-F, 67 p.

To: OTTO SHUMACHER (439 5350)
WFOP (SPOKANE) Date. 1968

101
Ted Evans Item 23
Silver Peak, 12/21

SENDING 6 PAGES

LITHIUM FROM NEVADA BRINE

1966-1968

By: Ned Gadsby

45

Yote Mineral Company has been engaged in exploration and development of a lithium-bearing brine deposit near Silver Peak, Nevada since 1964. Located about forty miles southwest of Tonopah, Nevada, Silver Peak lies in Clayton Valley, a closed basin lying east of the effective rain barrier provided by the Sierra Nevada and White Mountain ranges.

The Clayton Valley plays which contain lithium-bearing sediments covers an area about four miles wide by eight miles long, and averages about 1500 feet in depth. It appears that the ancient lake which formed the plays was not connected with the extensive Lake Lahontan, nor did it have any overflow out of the valley. Our geologists tell us that the origin of the Silver Peak deposit is apparently related to the Pleistocene volcanic activity typical of this area. Hot springs, cinder cones, and lava deposits remain on the periphery of the valley as reminders of this era. It has probably taken tens of thousands of years to accumulate and concentrate the brine. Preliminary calculations indicate reserves in the order of ten-billion pounds of lithium chloride.

Sediments in the lithium-bearing area are mainly composed of gypsum beds, clays, and salt layers, with no coarse layers to form good aquifers. The brine saturating these sediments is extracted with deep-well turbine pumps from drilled wells ranging from 300 to 800 feet in depth. Because of the lack of aquifers, well placement is important to avoid having wells depress the output of neighboring wells.

Brine brought to the surface has the following typical analysis, compared with other lithium-bearing brine deposits.

	Ocean	Dead Sea	Great Salt Lake	Bonneville	Salton Sea	Silver Peak
	%	%	%	%	%	%
Na	1.05	3.0	7.0	9.4	5.71	6.2
K	0.038	0.6	0.4	0.6	1.42	0.8
Mg	0.123	4.0	0.8	0.4	0.028	0.04
Li	0.0001	0.002	0.006	0.007	0.022	0.04
Ca	0.040	0.3	0.03	0.12	2.62	0.05
SO ₄	0.25	0.05	1.5	0.5	0.00	0.71 x
Cl	1.90	16.0	14.0	16.0	15.06	10.05
Br	0.0065	0.4	0.0	0.0	0.0	0.0
Li/Mg	1/12720	1/2000	1/135	1/60	1/1.3	1/1
Li/K	1/3800	1/300	1/70	1/90	1/71	1/20

TELETYPE TRANSMITTED

SENT BY

RECD BY

DATE 9/15 9:15

The two major advantages of the Silver Peak brine are the high lithium content and the low Li/Mg ratio. These features allow economic recovery of lithium without the necessity of any other concomitant commercial extraction.

Once the brine is at the surface, additional characteristics of Clayton Valley critical to economic recovery of the lithium become evident. There is ample flat space available in present and potential well fields for evaporation ponds having a bottom slope of only one to two feet per mile. There are located within the valley several deposits of impervious gravel-clay mixtures to provide cheap dike material for pond construction. By far the most important is the climate which, were it not favorable, would relegate the other features to geological curiosities.

In order to process economically the brine for lithium recovery, it is necessary to concentrate from 0.25 percent LiCl to about 4.0 percent LiCl, or sixteenfold. The cost using commercial fuels would be prohibitive. Solar evaporation, therefore, is a requisite, and Clayton Valley has quite adequate climatic conditions for such an operation. Normally, annual water evaporation exceeds 50 inches with precipitation of less than three inches.

To recover five to ten-million pounds of lithium carbonate annually, Foote currently has thirty wells pumping into the first of several evaporating ponds of generally decreasing size, totalling about 1600 acres. This has required construction of 14 miles of dikes, 17 miles of access roads, and 10 miles of power lines.

Since about 90 percent of evaporation occurs during a five-month period, careful pond control is necessary for stabilization of production. During the period of high evaporation, millions of gallons of concentrating brine must be moved forward in the pond system according to strength in order to provide a stable feed to the processing plant both during the evaporating season and the winter months. Complicating control are daily variations in evaporation, varying pond depths which affect evaporation rate and concentration effect, varying pond leakage rates, and changes in input. Optimum operation for maximum overall evaporation while achieving and maintaining pond-balance also requires a great deal of attention.

With the foregoing variables under firm control, it now becomes a simple

matter to move the brine forward through the evaporation ponds, decreasing in size from 600 to 10 acres, then into the storage ponds which are maintained at sufficient depth to minimize the effect of evaporation. As the brine approaches 0.4 percent lithium chloride concentration, sodium chloride begins to precipitate; at about two percent lithium chloride, a mixture of sodium and potassium chlorides (sylvinites) precipitates, forming the basis for future potash recovery.

Magnesium contained in the brine is precipitated as the hydroxide from brine containing one to two percent lithium chloride. Pebble lime is slaked in water and mixed with the brine to accomplish this precipitation. Liming in this concentration range appears to reduce the sulfate in the brine to acceptable levels through precipitation of gypsum. The slurry resulting from this treatment is clarified by settling in a reserved pond large enough to permit clear magnesium-free brine to move forward at a rate consistent with overall pond requirements.

Concentrated, treated, clear brine from the storage ponds is pumped to the processing plant, about a mile and one half from the evaporating pond area. This brine is treated with lime and soda ash to remove the last traces of magnesium and calcium. Following the clarification required by this treatment, the brine is stored for continuous feed through filter presses into the extraction system.

The overall process from this point on is simple. Filtered brine is heated on its way to the cascading reaction system where it is joined by hot wash and makeup waters and dry soda ash. Preheating is used to combat the inverse solubility of lithium carbonate, which is about 1 1/2 percent in cold brine versus about half that in hot brine. Water is added to hold in solution the sodium chloride which is formed by the reaction of soda ash with lithium chloride, since the influent brine is already saturated with salt. Control of the reaction system is accomplished through flow and temperature instrumentation and periodic analyses of the reaction slurry.

Initial thickening of the reactor effluent is accomplished in a bank of cyclones. The clear mother liquor overflow containing soluble lithium carbonate is returned to the evaporation ponds for reconcentration. Thickened

underflow feeds a continuous vacuum belt filter which extracts most of the remaining mother liquor, washes the resulting cake and feeds it to a rotary steam tube dryer. Dry product is air conveyed to a bin from which bulk or packaged shipments may be drawn as required. Quality of the finished product is typically a 99.5 percent assay with the major impurities being sulfate, sodium and potassium along with smaller amounts of calcium, magnesium and moisture. Physically the product is a white, granular, free-flowing 20-mesh by down solid.

Lithium carbonate is one of two chemicals from which all other lithium compounds are made, the other being lithium hydroxide. Currently all of Silver Peak's output is going directly to users thanks to a much wider market than was anticipated three years ago. About eighty percent of present ¹⁹⁶⁸ lithium carbonate usage is confined to the ceramic and glass industries. To these products it imparts resistance to thermal shock, lower firing temperatures and shorter firing cycles, lower thermal expansion, lower viscosity, higher electrical resistance, and decreased brittleness. Lithium carbonate is further used to impart a chemical temper to high-strength plate glass. To ceramic glazes it imparts chemical stability, acid-alkali resistance, and it allows the use of thinner base metals. 2

The balance of the lithium carbonate goes into welding rod coatings and other fluxes or is used by the purchaser as a raw material. One rather exotic application recently reported upon finds it being used with some success in treating manic depression. A recently-granted patent covers the use of lithium carbonate as a lithium metal cell feed.

There are myriad uses for other lithium compounds as well as for lithium metal. These compounds find wide use in such diverse applications as greases, absorption air conditioners, very light alloys used in space vehicles, scavenging for gases in high-purity metals, production of thermonuclear weapons, radiation shields, lift-support systems, bleaches, and catalysts in organic syntheses such as those used in preparing stereospecific rubbers, vitamin A, and oral contraceptives.

While it is already demonstrated that extraction of lithium carbonate alone from the Clayton Valley brine is economical, there is other mineral

wealth available. Of primary interest now is recovery of fertilizer-grade potash. Foote expects to market potash from Silver Peak by 1969 to 1971, probably from the mechanical harvesting and flotation separation of sylvite, although an evaporation process is still being considered. Interest by outsiders has been expressed in the precipitated sodium chloride as well as the magnesium hydroxide precipitated in the initial brine purification. Recovery of boron compounds and rubidium have distinct commercial possibilities once their concentrations have been improved through the recycle of process mother liquors. Sodium sulfate and caustic-chlorine plants could be constructed at Silver Peak in the future, but much groundwork remains to be accomplished in these areas. Greater development of western markets for lithium and its compounds will surely see the development of lithium chemical complex in Clayton Valley.

So far only established markets for lithium and its compounds have been discussed. While these markets are important and are expected to enjoy continued growth, it should be remembered that most of them have been developed within the past twenty years. There are now two ~~exciting~~ new prospects for lithium usage, either one of which could eclipse the existing markets.

Aluminum
The first of these uses involves lithium carbonate addition to aluminum potlines. It has long been known that such an addition can increase the current efficiency of an aluminum cell by as much as 20 percent. The price reduction for lithium carbonate initiated by Foote following startup of this Silver Peak Operations, rekindled the interest of the aluminum industry in this process, and as further operating economics are realized and further expected price reductions made, there is little doubt that this tremendous potential market can become a reality.

Perhaps further in the future but of no less interest and potential lies the lithium battery. With the increase of awareness of air pollution problems has come considerable speculation concerning replacement of internal combustion engines in automobiles with electric motors. One of the major objections has been the bulk, weight, and short life of the requisite battery systems. One of the best solutions could well be the lithium battery. Potential advantages of the lithium battery start with a theoretical production of more

than 1,000 watt hours per pound, compared with 115 for the conventional lead-acid battery. Investigators so far report up to 230 watt hours per pound in lithium batteries, compared with the practical rating of 12 for lead-acid batteries. 3 to 3.5 volts per cell are observed for lithium batteries, about twice that of other battery systems. In addition, they are found to have very high current densities, well over 20 times those of the lead-acid type.

It is not intended to say there are no problems associated with lithium battery development. For one, lithium's great chemical reactivity has made difficult the locating of suitable materials for the case, the spacers, and any internal insulators. Even more difficult has been the search for a suitable solvent since water cannot be used. Some have been found, however, in the form of fused salts and certain organic liquids. At current prices for lithium metal, the lithium battery would be quite expensive, but for a mass market such as automobiles represent, there is every reason to expect that it could become competitive.

In the three years we have been working with the Clayton Valley brine, we have learned much about well designs, pond construction and operation, brine chemistry, and lithium carbonate recovery. The prospects for lithium as well as for other valuable materials in the brine do not as yet appear to be limited. We are confident that the Silver Peak Operation has established lithium as a moderately-priced industrial commodity of ready availability.

United States Patent [19]

Lee et al.

[11]

4,159,311

[45]

Jun. 26, 1979

[54] RECOVERY OF LITHIUM FROM BRINES

[56]

References Cited

U.S. PATENT DOCUMENTS

[75] Inventors: John M. Lee; William C. Bauman,
both of Lake Jackson, Tex.

2,683,124	7/1954	D'Alelio	252/426
2,839,569	6/1958	Kramer	252/426
2,980,497	4/1961	Goodenough et al.	423/179.5
3,578,609	5/1971	Haage	252/430
3,755,393	8/1973	Kniese et al.	252/426

[73] Assignee: The Dow Chemical Company,
Midland, Mich.

[21] Appl. No.: 939,546

Primary Examiner—O. R. Vertiz
Assistant Examiner—Wayne A. Langel
Attorney, Agent, or Firm—W. J. Lee

[22] Filed: Sep. 5, 1978

[57] ABSTRACT

Related U.S. Application Data

[62] Division of Ser. No. 812,543, Jul. 5, 1977, Pat. No. 4,116,858.

Lithium is preferentially extracted from brine containing Li salts along with salts of other metals, e.g. Na, Ca, Mg, K, and/or B, by contacting the brine with a particulate anion exchange resin having suspended therein a microcrystalline form of $\text{LiX} \cdot 2\text{Al}(\text{OH})_3$, where X = halide.

[51] Int. Cl. ² C01D 15/00
[52] U.S. Cl. 423/179.5; 423/181
[58] Field of Search 423/179.5, 181

5 Claims, No Drawings

BUREAU OF MINES
WESTERN FIELD OPERATION CENTER

MAY 4 1983

SPOKANE, WASH.

Bob -
Here is the patent
for extracting
Li by an
anion exchange
resin
Dan

DEPARTMENT OF INTERIOR
BUREAU OF MINES
RECEIVED

79 OCT 9 A10:35

RENO, NEVADA

MATERIAL LOGGED	<input checked="" type="checkbox"/>
REPLY REQUIRED	<input type="checkbox"/>
ROUTE TO:	INITIAL/DATE
CHIEF	<input type="checkbox"/>
ASSISTANT	<input type="checkbox"/>
BR. ES	<input type="checkbox"/>
<input checked="" type="checkbox"/> BR. MAS	BRW, 5/4
BR. MLA	<input type="checkbox"/>
ADMIN.	<input type="checkbox"/>
Schumacher	5/5
Gale	<input type="checkbox"/>
CENTRAL FILES	<input type="checkbox"/>

RECOVERY OF LITHIUM FROM BRINES

CROSS-REFERENCE TO CO-FILED APPLICATION

This is a divisional application of Ser. No. 812,543 filed July 5, 1977 now U.S. Pat. No. 4,116,858.

A related invention is disclosed in our application Ser. No. 812,534, filed July 5, 1977 now U.S. Pat. No. 4,116,856.

BACKGROUND OF THE INVENTION

Various brines exist which contain Li salts. At times, it is desired to preferentially remove and/or recover the Li ion from the brine. In some brines, such as geothermal brines or such as Smackover brines, it is often desirable to remove Li values therefrom, either because one wants the Li values in substantially pure or concentrated form or because one wants the brine to be substantially free of Li.

There are various published articles and patents dealing with Li extraction from brines.

In *Israel J. Chem.* Vol. 1, 1963 (pp. 115-120) there is an article by D. Kaplan titled "Process For The Extraction of Lithium From Dead Sea Solutions." There it is taught that Li is precipitated as lithium aluminate from Dead Sea brines by adding an aluminum salt and an alkali thereto.

There is a U.S. Government Publication, PB 245,686, prepared by Hazen Research, Inc. for the U.S. Department of Interior, Bureau of Mines dated June 12, 1975 and distributed by National Technical Information Service, U.S. Department of Commerce, which is titled "The Recovery and Separation of Mineral Values From Geothermal Brines." The article teaches among other things, the use of aluminum hydroxide as a precipitant for extracting Li from brine. The article also refers to U.S. Pat. Nos. 3,307,922; 3,306,712; 3,537,813; 2,964,381; and 3,306,700.

U.S. Pat. No. 3,307,922 teaches the use of an immiscible monoalkanol or ketone along with ammonia to separate lithium salts from calcium salts in a brine solution.

U.S. Pat. No. 3,306,712 is similar to 3,307,922 above except that it teaches the use of a complexing agent, e.g. urea, to form soluble complexes with the calcium in the brine.

U.S. Pat. No. 3,537,813 involves the use of a metal halide (e.g., iron, cobalt, nickel) to react with lithium in brines, adding acid to avoid hydrolysis of the metal halide, and extraction of the lithium-containing compounds into a water-insoluble organic solvent.

U.S. Pat. No. 2,964,381 teaches to separate lithium values from an aqueous solution which contains alkaline earth metal salts, by adding a soluble aluminum salt to precipitate the lithium as a lithium aluminate complex.

U.S. Pat. No. 3,306,700 enlarges on, and improves, the lithium aluminate complex process of U.S. Pat. No. 2,964,381 above.

Other patents which also help establish the state of the art of extracting lithium values from brines are, e.g., U.S. Pat. Nos. 2,980,497; 2,980,498; 2,980,499; 3,295,920; and 3,268,290.

U.S. Pat. No. 2,980,497 discloses a method of recovering the lithium from a lithium aluminate complex formed, e.g., in the process of U.S. Pat. No. 2,964,381. The method involves heating the complex in water to at least 75° C. to decompose it and then using a strongly acidic cation exchange resin to bind the soluble lithium

compound and impurities, subsequently treating the resin with a caustic solution to form soluble lithium hydroxide and insoluble impurities and recovering the lithium hydroxide.

U.S. Pat. No. 2,980,498 shows recovering of lithium values from ores (spodumene, lepidolite, and the like) by using a strongly acidic cation exchange resin in the acid form to obtain an ion exchange of the lithium from the ore. The Li-containing resin is separated from the ore material and the Li is recovered from the resin by e.g., eluting with caustic to get lithium hydroxide. The resin may then be regenerated with an acid to revert back to the acid form.

U.S. Pat. No. 2,980,499 shows improvement over U.S. Pat. No. 2,980,498 above, by contacting the ore with the strongly acidic cation exchange resin at a temperature between 95° C. and 150° C.

U.S. Pat. No. 3,295,920 shows improvement over U.S. Pat. No. 2,980,499 above by contacting the ore and the ion exchange resin in the presence of an aqueous solution containing about 10 to 80% of acetic or propionic acid.

U.S. Pat. No. 3,268,290 shows recovering Li values from sludge which comes from certain electrolytic processes for magnesium production. The lithium recovery involves the use of a short-chain aliphatic monohydric alcohol, heat and agitation to dissolve the Li away from the other components of the sludge, then evaporating the alcohol to obtain LiCl.

It can be seen, then, that there is a recognized need for methods of recovering Li from brines or other aqueous mixtures and solutions which contain metal values other than Li.

The art teaching the formation of lithium aluminate complexes and the use of cation exchange resins to remove Li values from aqueous brines is believed to be the art most pertinent to the present invention.

It is an object of the present invention to provide an ion exchange method of preferentially removing Li values from brines wherein the ion exchange material is long-lived and does not require acid treatment to revert it to the acid form.

Another object is to provide an ion exchange method for preferentially recovering Li values from brines which also contain other metal values.

A further object is to provide an ion exchange resin having incorporated therein $\text{LiX} \cdot 2\text{Al}(\text{OH})_3$ which, after having LiX partially removed and then contacted with brines containing Li salt and other metal salts, will preferentially form a complex with the Li salt while substantially excluding the other metal salts.

Yet another object is to incorporate $\text{LiX} \cdot 2\text{Al}(\text{OH})_3$ in an anion exchange resin in such fashion that Li^+ may be cyclically removed from brine by the resin and then eluted from the resin, the cycle being performed numerous times before encountering appreciable loss of exchange capacity.

SUMMARY OF THE INVENTION

An anion exchange resin is treated with AlCl_3 , then with ammonia to change the AlCl_3 to $\text{Al}(\text{OH})_3$. The resin, containing the $\text{Al}(\text{OH})_3$ dispersed in it, is treated with aqueous LiX (where X is halide) and heated for a time sufficient to create a microcrystalline form $\text{LiX} \cdot 2\text{Al}(\text{OH})_3$ dispersed in the resin. This novel form of resin is useful in preferentially recovering Li^+ from brines, including brines which contain MG^{++} . The resin may be cycled numerous times before encounter-

ing appreciable loss of exchange capacity. As used herein, the term "microcrystalline" is used to indicate small crystals formed in small pores, voids, and spaces in the resin which are detectable by X-ray diffraction, if not by a microscope.

DETAILED DESCRIPTION OF THE INVENTION

In general, the novel composition disclosed here is an anion exchange resin containing $\text{LiX} \cdot 2\text{Al}(\text{OH})_3$ dispersed or suspended within the resin particles. Throughout this disclosure, LiX refers to lithium halides, especially LiCl. The expression "suspended therein" when referring to compounds dispersed in the resin, means that the compounds are dispersed within the polymer matrices, not merely clinging to the external surfaces of the polymers.

The novel process disclosed here comprises contacting the anion exchange resin, containing $\text{Al}(\text{OH})_3$ dispersed within the resin particles, with a Li^+ -containing (but Mg^{++} -free) brine and heating it thereby forming a microcrystalline form of $\text{LiX} \cdot 2\text{Al}(\text{OH})_3$ dispersed in the resin particle, and eluting a portion of the LiX out of the resin with water containing a small amount of LiX. The resin containing the $\text{LiX} \cdot 2\text{Al}(\text{OH})_3$, with a portion of the LiX removed, is usable to remove more Li^+ from brines, including brines which contain Mg^{++} .

The anion exchange resin with which one starts, may be any particulate water-insoluble polymeric resin which contains basic amine groups attached to the polymeric resin. Macroporous anion exchange resins are preferred over the gel-type resins.

By "macroporous," as the term is commonly used in the resin art, it is generally meant that the pores, voids, or reticules are substantially within the range of about 200 to about 2000 Å. Another term, meaning the same thing is "macroreticular."

Of particular interest are macroporous anion exchange resins sold as DOWEX (a trademark of The Dow Chemical Company) MWA-1 as the chloride form of a particulate polystyrene highly crosslinked with divinylbenzene having $-\text{CH}_2\text{N}(\text{CH}_3)_2$ groups attached to the benzene rings. These resins have a particle size, generally, of about 20-50 mesh (U.S. Standard Sieve size) and about 30-40% porosity with an internal surface area of about 30-50 m^2/gm . Thus, each particle is a reticular solid containing pores of about 200-800 Å in size. The base capacity is about 4.2-4.3 meq./gm. of dry resin in its basic (or free amine) form. The base strength, as measured by a glass electrode in 26% NaCl, is $\text{pK}_b = 4 \times 10^{-7}$ (mid-point in acid-base titration curve is $\text{pH} = 7.6$).

Other resins of particular interest are, e.g., those similar to DOWEX MWA-1, with the amine group being $-\text{CH}_2\text{NRR}'$ where R and R' may be, individually, a hydrogen or alkyl group of 1-4 carbon atoms. Also, resins containing other amines or amino groups (tertiary, primary, secondary, cyclic) are within the purview of the present invention.

Other exchange resins which may be employed may be any anion exchange resins with a base strength greater than $\text{pK}_b = 1 \times 10^{-7}$, with macroporous resins being preferred, e.g. Amberlyst A-21.

The Kirk-Othmer Encyclopedia of Chemical Technology, vol. 11, pp. 871-899 on the subject of "Ion Exchange," including discussions of commercially available anion exchange resins, is a helpful reference. Another helpful reference is a book titled "Ion Ex-

change" by Friedrich Helfferich published by McGraw-Hill, 1962.

Detailed information about pore sizes of "gel-type," "microreticular," and "macroreticular" ion exchange resins may be found in *Ion Exchange in The Process Industries* published in 1970 by The Society of Chemical Industry, 14 Belgrave Square, London, S.W.1, England.

Among the macroporous anion exchange resins, which are within the purview of the present invention are: strongbase resins containing quaternary ammonium groups fixed to a poly(styrene-divinylbenzene); poly(vinyltoluene) which has been side-chain chlorinated and reacted with a tertiary amine to form a quaternary ammonium salt; or any of the water-insoluble, but water-swellaable aromatic polymers containing quaternary ammonium groups such as those named in the market place as Dowex MSA-1. Other macroporous strong-base resins are, e.g., AMBERLYST A-26 and 27.

Also gel-type anion exchange resins which contain primary, secondary, tertiary amine and quaternary ammonium groups are operable, such as Amberlite IRA-400, Amberlite IRA-401, Amberlite IRA-402, Amberlite IRA-900, Duolite A-101-D, Duolite ES-111, Dowex 1, Dowex 11, Dowex 21K, Ionac A540, Dowex 44, Duolite A-7, Ionac A-260 and Amberlite IRA-68. Such commercial resins are discussed and described in the literature, such as in the Kirk-Othmer Encyclopedia of Technology and product brochures.

In determining the efficacy of an exchange resin for use in the present invention, particulate macroporous resins which have a porosity of at least about 15%, an internal surface area of at least about 10 m^2/gm and a base capacity of at least about 2.0 meq./gm. (dry, basic form) are preferred.

Such resins, if obtained in the base form, are preferably converted to the chloride-form prior to being contacted with the aq. AlCl_3 . This is conveniently done by treating the amine-form, under reduced pressure, with an excess of aqueous HCl, then filtering, washing and draining off the water. A pressure differential across the filter may be employed to speed the draining process, if desired.

The AlCl_3 which is used in treating the chloride-form of the resin is conveniently, and preferably, a saturated aqueous solution containing about 31% to about 32% AlCl_3 though weaker concentrations are operable, giving less capacity. Hydrates of AlCl_3 , such as $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, are useful in preparing the aqueous solutions.

Outlining the overall preferred steps, generally, used in preparing the $\text{LiX} \cdot 2\text{Al}(\text{OH})_3$ -containing resin and employing it to recover Li^+ values from brine:

1. Impregnate an anion exchange resin with aqueous AlCl_3 ;
2. Treat the AlCl_3 -impregnated resin with aqueous NH_3 to convert the AlCl_3 to $\text{Al}(\text{OH})_3$;
3. Treat the resulting $\text{Al}(\text{OH})_3$ -containing resin with aqueous Li halide to provide halolithium aluminate or lithium aluminate dispersed in the resin;
4. Heat the resin, containing the so-formed aluminate, at a temperature and for a time sufficient to form microcrystalline $\text{LiX} \cdot 2\text{Al}(\text{OH})_3$ dispersed in the resin and adjust the pH, if needed, to within the range of about 6.0 to 7.5 in saturated NaCl brine;
5. Elute a portion of the Li^+ values from the resin by employing a weak solution of LiX;
6. Contact the resin, containing the partially LiX-depleted microcrystalline $\text{LiX} \cdot 2\text{Al}(\text{OH})_3$ dispersed therein,

with a Li⁺-containing brine to selectively remove the Li⁺ from the brine;

7. Repeat steps 5 and 6, sequentially, a plurality of times.

Ordinarily, a cubic foot of resin prepared by the present invention, will contain about 3 to about 12 pounds of microcrystalline LiX.2Al(OH)₃, or stated another way, about 50 to about 200 gms./liter of resin.

The above steps are described in greater detail by the following generalized embodiments:

STEP I

The anion exchange resin with which one starts may be impregnated as is with aqueous AlCl₃ or may be first converted to its chloride form by being treated with aqueous HCl. The anion exchange resin may be of the "weak base" or "strong base" type, normally containing pendant amine, or quaternary ammonium groups attached to a polymeric structure. If it is desired to convert the basic form of the resin to the chloride form, this may be done, e.g., by contacting the resin with aqueous HCl (of, say, 5-10% concentration). Ambient temperature may be used for the HCl treatment, though slightly increased temperature may also be used. In order to completely "soak" the resin, a reduced pressure is usually helpful during the HCl treatment. An aqueous solution of AlCl₃ is impregnated into the resin, whether the resin is in its basic form or its chloride form. The aqueous AlCl₃ is preferably concentrated, with a saturated solution of about 31-32% AlCl₃ being most preferred. The amount of aq. AlCl₃ used should be enough to substantially replace all the liquid which was already in the resin and still have enough to completely flood the resin. The excess aq. AlCl₃ is then drained, leaving a resin which is moist; the remaining moisture may be removed, e.g., by blowing hot, dry inert gas or air through the resin, but this is not necessary. Ambient temperature is operable for this step, though increased temperature may be used to speed the process.

An alternative method of impregnating the resin with AlCl₃ is to add AlCl₃ to a resin/water mixture, but it is generally preferred to flow concentrated aq. AlCl₃ through a column bed of resin, thereby replacing the liquid in the resin with the aq. AlCl₃.

STEP II

The AlCl₃-containing resin is then treated with ammonia, preferably aqueous ammonia, NH₄OH, to convert the AlCl₃ to Al(OH)₃ within the resin particles. Ambient temperature is operable, though increased temperature may be used to speed the process. Generally, it is best to employ an excess of NH₄OH to be assured of rapid and complete conversion of the AlCl₃ to Al(OH)₃. The excess NH₄OH may be drained off and it is generally best to flush with enough H₂O or NaCl brine to substantially remove the NH₄OH, NH₄Cl and any Al(OH)₃ which may have formed outside the resin particles.

NH₄OH is preferred over the use of NaOH or KOH or other strong alkali because the strong alkalis tend to form water-soluble alkali aluminates, such as sodium aluminate, and these soluble aluminates would then be more easily washed from the resin than the Al(OH)₃ precipitated by using NH₄OH. The quantity of NH₄OH to be used is equivalent to the AlCl₃ according to the equation



plus the amount required to convert the resin to its basic form (assuming that all the resin was converted to the chloride form in Step 1.) The preferred amount is a several-fold excess of concentrated aq. NH₄OH over the above minimum amount. The volume of the NH₄OH should be as much as is needed to achieve uniform wetting of the resin particles throughout. Preferably at least about 0.5-1.0 part by weight of conc. NH₄OH solution (e.g. about 30% NH₃) is used per part of AlCl₃-containing resin. The Al(OH)₃ so-obtained is an "active" Al(OH)₃ which will readily absorb LiX from brine solutions; X-ray diffraction pattern analysis indicates this Al(OH)₃ has little or no crystallinity.

An alternate, but not preferred, method of converting the AlCl₃ to Al(OH)₃ is to treat the thoroughly wetted AlCl₃-containing resin with NH₃ gas or NH₃ diluted with air or other inert gas.

STEP III

The active Al(OH)₃-containing resin from Step 2 is then treated, at pH 6.0 or higher, with an aqueous solution of lithium halide, especially LiCl. The aqueous solution may be a Li⁺-containing brine which is Mg⁺⁺-free. The Li halide combines with the Al(OH)₃ to give a halolithium aluminate or lithium aluminate which, by X-ray diffraction, is found to have little or no crystallinity. If the lithium aluminate-resin mixture is employed, without the heat treatment described below, to remove Li⁺ from brines, it must be reconstructed after one cycle, the residual non-active Al(OH)₃ removed, re-impregnated with AlCl₃ and then again treated with NH₃ to regain the active Al(OH)₃ form. It is preferred that the amount of LiX be an amount in excess of that required to complex with the Al(OH)₃ to form the structure LiX.2Al(OH)₃ in Step IV.

STEP IV

According to the present invention the lithium aluminate-resin, or halolithium aluminate-resin, is heated at an elevated temperature for a time sufficient to convert the aluminate compound to a microcrystalline form having the formula LiX.2Al(OH)₃, where X=halide, the crystal structure of which is found to exhibit essentially the same X-ray diffraction pattern as the aluminates prepared according to Goodenough and by Lejus et al.

Formation of a crystalline chlorolithium aluminate is reported by Goodenough and confirmed by X-ray (U.S. Pat. No. 2,964,381). X-ray studies of such compounds are reported by Anne Marie Lejus et al in e.g. *Compt. Rend.* vol. 254 (1962) and in *Rev. Hautes Temper. et Refract.* t. I, 1964, pp. 53-95.

Preferably the elevated temperature is from at least about 50° C. up to the reflux temperature of the mixture, there being enough water present to provide a refluxing portion while maintaining the resin thoroughly wetted during the heating. Ordinarily the time of heating for the temperature range of 50°- reflux will be about one hour to about 16 hours. Insufficient heating or insufficient time of heating may result in having some of the aluminate compound not converted to the microcrystalline form, thereby reducing the cyclable capacity of the resin.

If not enough LiX has been employed in Step III to complex with all the active Al(OH)₃ then some crystalline Al(OH)₃ may be formed during this Step IV heating step and not form the desired LiX.2Al(OH)₃. Such

crystalline $\text{Al}(\text{OH})_3$, e.g. Bayerite, Gibbsite, Norstrandite, or mixtures of these, are not effective in absorbing LiX from brine in the present invention. Thus, it is preferred that substantially all the active (freshly prepared) $\text{Al}(\text{OH})_3$ be complexed with excess LiX and then heated to form microcrystalline $\text{LiX} \cdot 2\text{Al}(\text{OH})_3$ in order to attain or approach the maximum cyclable capacity. A 26% NaCl brine containing at least about 300–1000 mg/l Li^+ is suggested for use in this step.

STEP V

A portion of the Li^+ values are eluted from the resin using an aqueous wash, preferably containing a small amount of lithium halide, e.g., LiCl . The concentration of lithium halide in the elution liquor is preferably in the range of about 300 to about 1500 ppm. An aqueous elution liquor may be employed which does not contain lithium halide if the elution is done batchwise with only enough water to remove a portion of the LiX from the resin composition, but is not preferred since this may reduce the amount of LiX in a given crystal to less than the amount required to maintain the crystal integrity (crystals may change to Norstrandite and/or Bayerite). It is best, then, to employ at least a small amount of lithium halide in the eluting liquor especially in column operation, to assure that not all, preferably not more than half, the lithium halide in the microcrystalline $\text{LiX} \cdot 2\text{Al}(\text{OH})_3$ is removed. The elution step is best done at elevated temperatures above about 40°C ., preferably about 50°C . to reflux temperature.

STEP VI

This step is done, e.g., by contacting the Li^+ -containing brine with the partially eluted $\text{LiX} \cdot 2\text{Al}(\text{OH})_3$ -containing resin from Step V in a column bed by flowing the brine through until the Li^+ conc. in the effluent approx. equals the Li^+ conc. in the influent. Loading rate is enhanced if the temperature of the brine is above about 40°C ., preferably about 50°C . to reflux, most preferably about 80° – 108° . Higher temperatures, requiring superatmospheric pressures, require equipment capable of withstanding the pressure.

STEP VII

Steps V and VI are repeated, sequentially, a plurality of times.

The resin, containing the microcrystalline $\text{LiX} \cdot 2\text{Al}(\text{OH})_3$ is re-usable numerous times in a cycling process where Li^+ -containing brine, even brine containing Mg^{++} , is contacted with the resin to recover Li^+ from the brine, then the Li^+ values are eluted from the resin using a weak concentration of aq. lithium halide.

EXAMPLE 1

(Preparing the resin/ $\text{LiCl} \cdot 2\text{Al}(\text{OH})_3$)

The product is prepared in the following way: 40.0 gms of Dowex MWA-1 (in dry chloride form) is poured into a solution of 12.0 gms. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in 60 gms. H_2O . With hand stirring, using a spatula, uniformly damp particles result. This product is dried at room temperature in a stream of dry air to a weight of 52.67 gms. This free-flowing product is poured into a solution of 55 ml. NH_4OH of 8.2% NH_3 conc. and mixed as before to uniformly damp particles. Five minutes later it is mixed with 500 ml of 7.0 pH Mg^{++} -free Smackover brine containing 15.8% NaCl , 9.1% CaCl_2 , and 305 mg/liter Li^+ and warmed to 56°C . for 45 minutes. The brine is filtered off and found to contain 55 mg/l Li^+ . Product

is mixed with 500 or more ml of fresh brine and warmed to 70°C . over a period of 45 minutes and filtered, with filtrate analyzing 215 mg/liter Li^+ . An additional 500 ml of brine is mixed with the product and refluxed for 16 hours. The final filtrate contains 280 mg/liter Li^+ . Thus, the "sucked" dry product contains 182.5 mg Li^+ . The bulk or settled volume of product is 136 ml. The pore volume is estimated to be 36 ml, which would be filled with final filtrate containing 10.1 mg Li^+ . Hence, the resin particles contain 172.4 $\text{mg Li}^+ = 0.025$ mols Li^+ . 12.0 gms $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ is equivalent to 0.050 mols $\text{Al}(\text{OH})_3$. Hence, the final product contains 1 mol $\text{Li}/2$ mol Al . The crystallinity of the compound, denoted here as $\text{LiCl} \cdot 2\text{Al}(\text{OH})_3$ is confirmed by X-ray diffraction analysis.

EXAMPLE 2

(Recover Li^+ from brine)

The use of the product of Example 1 above is shown here for recovering Li^+ from brine:

116 ml of Product from Ex. 1 is put in a water jacketed burette column to produce a resin bed 73 cm in depth. Product is made is saturated with Li^+ , so it is transferred into the column in 7.0 pH Mg -free Smackover brine (containing 305 mg/liter Li^+). Each cycle then consists of elution followed by brine resaturation. 8 cycles are run with downflow of 6.4 ml/min. on water and brine, and all at 85° – 90°C . water jacket temperature. When idle (e.g., 5 days between Cycle 5 and 6) the column is left in the brine saturated state and allowed to cool to room temperature. Excessive water washing of earlier products had resulted in inactivation of the $\text{LiCl} \cdot 2\text{Al}(\text{OH})_3$, so a limited quantity of water is used (250 ml on Cycles 1–5, inclusive and 200 ml on 6–8, inclusive) and a small quantity of LiCl is added to the water to limit further the reduction in Li^+ content of the resin (0.15% LiCl in Cycles 1 and 2, 0.06% LiCl in Cycles 3–8, inclusive). In each cycle 400 ml of brine follows the water elution. This is about 125 ml more than required for Li^+ saturation. The first 5 cycles were Mg^{++} -free Smackover brine having 305 mg/liter Li^+ at pH 7.0. The remaining cycles were with Smackover brine containing 305 mg/liter Li^+ and 0.31% Mg^{++} at pH 6.0. In the 6th cycle the effluent is caught in a series of 18 receivers: 25 ml in cuts 1–12, inclusive, and 50 ml in cuts 13–18, inclusive. These cuts are then analyzed for Li^+ content by flame photometry. The analyses for Cycle 6 are:

Cut No.	mg/l Li^+	Cut No.	mg/l Li^+
1	280	10	145
2	287	11	85
3	380	12	0
4	1220	13	5
5	700	14	20
6	345	15	35
7	245	16	210
8	195	17	285
9	165	18	305

Integration of the results shows Li^+ removal and recovery of 57.9 mg, which is 39.5% of the Li^+ on the resin. Had the brine feed been limited to 275 ml, as required for Li^+ saturation, the recovery of Li^+ is 69% from the brine. The average Li^+ content of the water eluant is 430.7 $\text{mg Li/liter} = 0.26\%$ LiCl . The peak Li^+ observed in the product (1220 mg/l) is 4 times the brine

feed concentration. The performance shown in Cycle 6 remained substantially the same through the 8 cycles run: Cycles 1-5, inclusive, using Mg-free brine and Cycles 6, 7 and 8 using untreated brine (with Mg^{++} present).

EXAMPLE 3

A macroporous anion exchange resin (Dowex MWA-1) is converted to the chloride form by treatment with aqueous HCl. The resin is drained, washed with water, and drained again. The drained resin still contains about 59.73% water.

Approximately 135 parts of the drained resin is treated with an excess of 31% aq. $AlCl_3$ and the excess liquid is drained off. In effect, the aq. $AlCl_3$ replaces the water (80.64 parts) in the resin. After draining off the excess aq. $AlCl_3$, the resin is found to weigh about 159.37 parts and by analysis, is found to contain about 39.66 parts $AlCl_3$. Thus, by computation, the resin mixture contained, at this point about 54.36 parts of resin, 20 about 39.66 parts $AlCl_3$ and about 65.35 parts water.

The resin mixture is then treated with about 89.5 parts of 30% NH_4OH aq. solution; this constituted about 28% excess NH_3 over that required, theoretically, to convert the $AlCl_3$ to $Al(OH)_3$ and the resin to the basic form. 25 The resin is washed and drained.

EXAMPLE 4

The above resin, containing the $Al(OH)_3$, is treated with an aqueous solution of LiCl in an amount to flood the resin and to provide more than enough LiCl to complex with most, if not all, of the $Al(OH)_3$ according to the formula $LiCl \cdot 2Al(OH)_3$. The mixture is heated at reflux temperature for about 2 hours or more. After this time X-ray diffraction patterns indicate the formation of 35 microcrystalline $LiCl \cdot 2Al(OH)_3$ dispersed in the resin structure.

The resin is then used to preferentially separate Li^+ from a brine containing about 15.8% NaCl, about 9.1% $CaCl_2$ and about 305 mg/liter Li^+ . This is done by passing the brine through a column-bed of the resin. 40 After that, the Li^+ values are eluted from the resin by using a weak solution of aq. LiCl. The cycles of brine flow and elution are repeated numerous times without encountering a substantial loss of capacity in the ex- 45 change resin.

The time cycles for the brine flow and elution are established for a given resin by determining the resin capacity, the concentration of Li^+ in the brine, and the elution factors. Once these have been established for a 50 given resin and a given brine, the process may be automatically cycled using conventional methods and techniques known in ion exchange technology.

EXAMPLE 5

To 350 gms. of dry DOWEX MWA-1 (base form) is added 480 gms. $AlCl_3 \cdot 6H_2O$ dissolved in 410 gms. H_2O . The mixture is prepared, with stirring, and then substantially dried by air-blowing at ambient temperature. The "dried" mixture is found to still contain about 60 25.9% H_2O .

To the mixture is added, with stirring, a solution prepared by diluting 430 ml. of 30% NH_3 aqueous solution with 100 ml H_2O . The resulting exotherm brings the mixture to about 67° C. After standing for about 1.5 65 hours during which time the temperature drops to about 48° C., the mixture is washed with 3 portions of 1000 ml. each of a saturated NaCl solution to elute excess

NH_4OH and also NH_4Cl and $Al(OH)_3$ formed outside the resin particles. After each washing step, the NaCl brine is decanted. By analysis, it is found that 3.9% of Al^{3+} is removed by the washings.

5 The resin, still moist with NaCl brine, is added to enough NaCl brine to bring the total volume to 3 liters. Then there is added 85 Gms. of dry LiCl, which dissolves, and a small amount of NH_3 is added to assure that the mixture is not too far on the acid side. The pH, 10 as measured by a glass electrode with a KCl bridge, is found to be 8.3. This addition of NH_3 is optional and is not needed if the pH is known to be above about 6.5.

The mixture is then heated in a large beaker for 15 minutes during which time the temperature increases to 15 about 63° C. and the pH drops to about 7.06. A small amount of NH_3 is added, bringing the pH to 7.5 but NH_3 comes out and the pH quickly drops to about 7.0-7.1.

The mixture is transferred to a round-bottom flask equipped with a reflux condenser and heated at reflux for about 2.5 hours. The resin mixture is filtered out on a glass frit using a Buchner funnel. The still-moist solids are rinsed twice with 600 ml. distilled water. Analysis indicates there is about 41.7 gms. LiCl in the filtrate, and about 8.73 gms. in the wash water, thus there is a net deposit in the resin particles of about 34.56 gms. LiCl.

In an effort to assure high loading, the resin, after drying to a water content of about 11.2% and a weight of about 569.3 gms., is treated with a solution prepared by dissolving 280 gms. $AlCl_3 \cdot 6H_2O$ in 240 gms. H_2O , stirred well, then air-dried overnight down to about 804 gms. To this is added 250 ml. of 30% NH_3 with 50 ml. H_2O added to it, and stirred; it exotherms to about 83° C. Then mix with 1800 ml. NaCl brine and decant. Analysis shows that 8.04 gms. of the $AlCl_3 \cdot 6H_2O$ does not stay with the resin. 41.7 gms of LiCl in the above filtrate is enriched by adding 8 gms of LiCl to it and is then mixed with the drained resin. At this point the total volume is about 3700 ml. with pH 7.78. The mixture is heated in a beaker to 54° C. with intermittent stirring and the pH drops to 7.34.

The mixture is transferred back to the reflux pot and heated up to reflux within an hour and refluxed for about 80 minutes and allowed to stand and cool overnight, then filtered. Analysis for Al and Li in the filtrate and calculations based thereon determines that the resin contains 1.37 moles Li^+ and 3.05 moles Al^{3+} . This is 0.449 Li^+ per Al^{3+} which is 89.8% of theoretical amount of $Li:Al$ in the formula $LiCl \cdot 2Al(OH)_3$. X-ray diffraction pattern indicates presence of crystalline $LiCl \cdot 2Al(OH)_3$.

The resin is transferred to a jacketed, heated exchange column, and flooded with NaCl brine (actually it is the filtrate from above and containing a small amount of Li^+). Then alternate cycles of wash water (containing about 50 ppm Li^+) and Smackover brine (pH 5.6) at a pump rate of 13 ml/min. for about 70 minutes while heating at about 90° C. The wash cycles are at 13 mls./min. for 27 minutes and are at ambient temperature but become heated by the column heated at 90° C. The results of the fourth full wash cycle, taken in 25 ml cuts, is shown below:

Cut No.	Li^+ mg/liter*	Remarks**	Cut No.	Li^+ mg/liter*	Remarks**
1	400	Start wash	10	500	
2	430	brine	11	470	

-continued

Cut No.	Li ⁺ mg/liter*	Remarks**	Cut No.	Li ⁺ mg/liter*	Remarks**
		coming out			
3	460		12	370	
4	1560		13	333	
5	1540		14	310	
6	1130		15	280	start brine
7	880		16	250	
8	700		17	65	wash coming out
9	580		18	80	

*not adjusted for Sr⁺⁺ values which interfere with Li⁺ analysis, but stay in the brine.

**About 75 ml. hold-up in the column.

EXAMPLE 6

Large particles of spodumene ore, roasted at 900°-1000° C., are ground up and screened to 35-100 mesh (U.S. Standard Sieve Size). 41.7 gms. (44.5 cc) of the screened ore is placed in the bottom of a column with a cross-sectional area of 1.59 cm² to a depth of 28 cm. On top of that is placed 71.5 ml. of a resin/LiCl·2Al(OH)₃ exchange agent prepared in accordance with the present disclosure. The bed depth of the resin/LiCl·2Al(OH)₃ is about 45 cm.

Brine (26% NaCl and containing 140 mg/liter Li⁺) is circulated downwardly at a pump rate of about 3.2 ml/min. of flow. The column holds about 60 ml. of the brine and a hold-up (inventory) pot holds about 40 ml., with the re-cycle lines and pump lines holding about 25 ml. After circulating for 15 min. with column heated at about 95° C., the brine in the inventory pot is found, by analysis, to contain about 500 mg/liter Li⁺. The system is allowed to cool overnight.

The column is re-heated to 95° C. and circulation of the inventory brine is resumed. After 15 min. analysis shows 395 mg/liter Li⁺; after 30 min., 430 mg/liter Li⁺; after 75 min., 630 mg/liter Li⁺; after 105 min., 710 mg/liter Li⁺; and after 125 min., 730 mg/liter Li⁺.

After 130 min., 25 ml. of Smackover brine is added, bringing the total brine in the circulating system to about 150 ml. After 185 min. analysis shows 775 mg/liter Li⁺; after 220 min., analysis shows 785 mg/liter Li⁺.

At this point 75 ml. of the circulating brine is removed and replaced with 75 ml. of Smackover brine and circulation is resumed. After 10 min., analysis shows 905 mg/liter Li⁺ and after 30 min., 890 mg/liter Li⁺ (Li⁺ analysis is affected by Sr⁺ in the brine). The system is apparently at, or near equilibrium at this point, so all the inventory is removed, except that held in the column and a wash cycle of water (containing about 180 mg/liter Li⁺) is flushed downwardly through the column at 95° C. and a pump rate of 3.2 ml/min. At start of the wash cycle 15 ml. samples are taken of the effluent. After 135 ml. of wash water is added, switch to 26% NaCl brine wash for 90 ml. 15 samples of 15 ml. each analyze for Li⁺ (mg/liter) as follows:

Sample	Li ⁺	Sample	Li ⁺	Sample	Li ⁺
1	610	6	1750	11	430
2	575	7	1700	12	375
3	580	8	1000	13	365
4	670	9	670	14	480
5	840	10	520	15	340

Recycling the 26% effluent back as influent, after 45 min. the effluent is 160 mg/liter Li⁺; after 60 min., 160 mg/liter Li⁺. Shut down for 2 days and start up again; effluent still coming out 160 mg/liter Li⁺. After 5 hours more of recirculation, effluent is 280 mg/liter Li⁺. Run terminated.

Synthetic or natural brines containing Li⁺ values are within the purview of the present invention and include such natural brines as Smackover brines (such as found at Magnolia, Ark.), Ludington brine (such as found at Ludington, Mich.), Monroe brine (such as found near Midland, Mich.), and other Li-rich brines such as found at Silver Peak, Nev., Great Salt Lake, Searles Lake (California), Dead Sea, and many others. Li⁺-containing brines also exist in many other parts of the world, e.g., in South America.

The foregoing examples are to illustrate embodiments of the invention, but the invention is limited only by the following claims.

We claim:

1. A process for removing Li⁺ from aqueous brines, said process comprising, in sequence, the steps of:
 - a. contacting a Li⁺-containing brine with an anion exchange resin having suspended therein a microcrystalline form of LiX·2Al(OH)₃, where X is halogen;
 - b. eluting Li⁺ values from the resin by contacting it with an aqueous wash liquor; and
 - c. repeating steps (a) and (b), sequentially, a plurality of times by using the resin from step (b) as the resin in step (a).
2. The process of claim 1 wherein the anion exchange resin is macroporous.
3. The process of claim 4 wherein the amount of lithium halide dissolved in the wash liquor is about 50 to about 200 mg. per liter, as Li⁺.
4. The process of claim 1 wherein the aqueous wash liquor contains a small amount of lithium halide dissolved therein.
5. A process for recovering Li⁺ values from Li⁺-containing ores, said process comprising:
 - a. providing the ore in particulate form and leaching water-solubles from the ore using an aqueous brine wash, thereby forming an aqueous brine solution containing Li⁺ values,
 - b. contacting the so-formed Li⁺-containing aqueous brine solution with an anion exchange resin having suspended therein a microcrystalline form of LiX·2Al(OH)₃, where X is halogen,
 - c. eluting Li⁺ values from said exchange resin, by using an aqueous wash, and
 - d. recovering Li⁺ values from said aqueous wash.

* * * * *

Nov. 3, 1970

J. R. NELLI ETAL

3,537,813

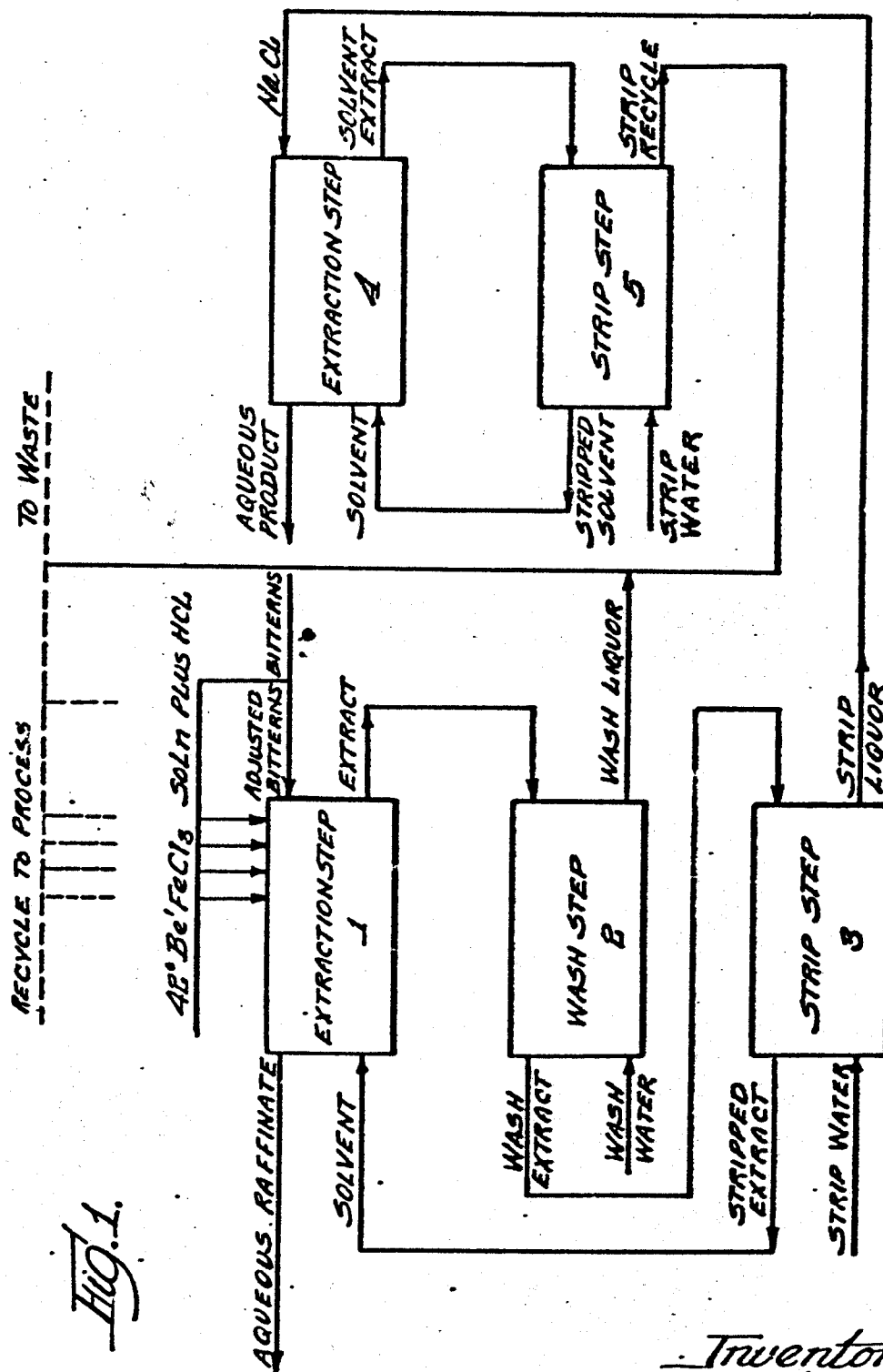
Item 23

16 of 21

RECOVERY OF LITHIUM FROM BITTERNS

Filed April 25, 1968

3 Sheets-Sheet 1



Inventors
Joseph R. Nelli
Theodore E. Arthur, Jr.
By: Wallenstein, Spangenberg, Hatten & Strumpf

Nov. 3, 1970

J. R. NELLI ETAL

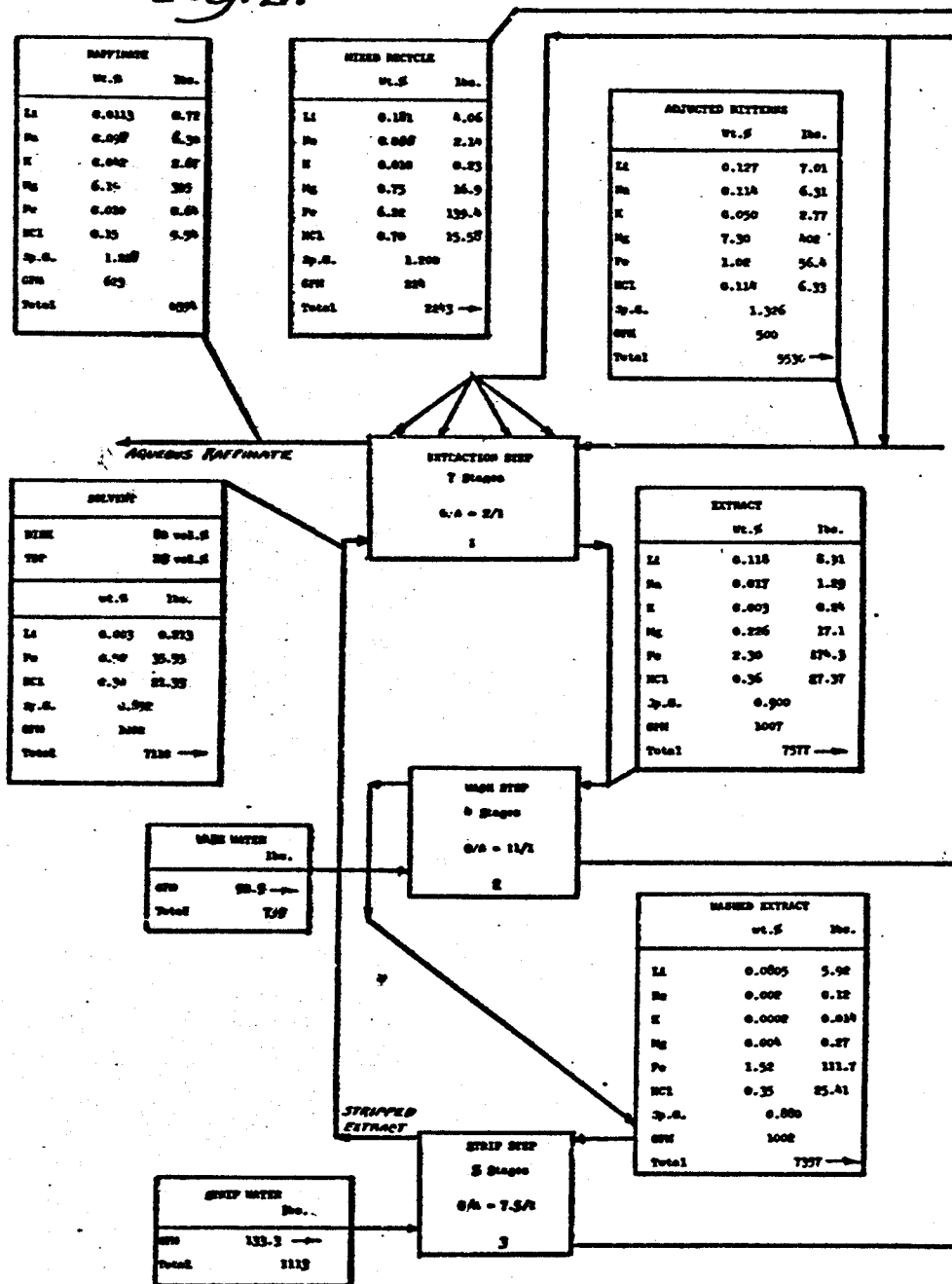
3,537,813

RECOVERY OF LITHIUM FROM BITTERNS

Filed April 25, 1962

3 Sheets-Sheet 2

Fig. 2.



Inventors
 Joseph R. Nelli
 Theodore E. Arthur, Jr.
 By: Wallmutter, Spangenberg, Hathi & Strunkel attys.

Nov. 3, 1970

J. R. NELLI ETAL

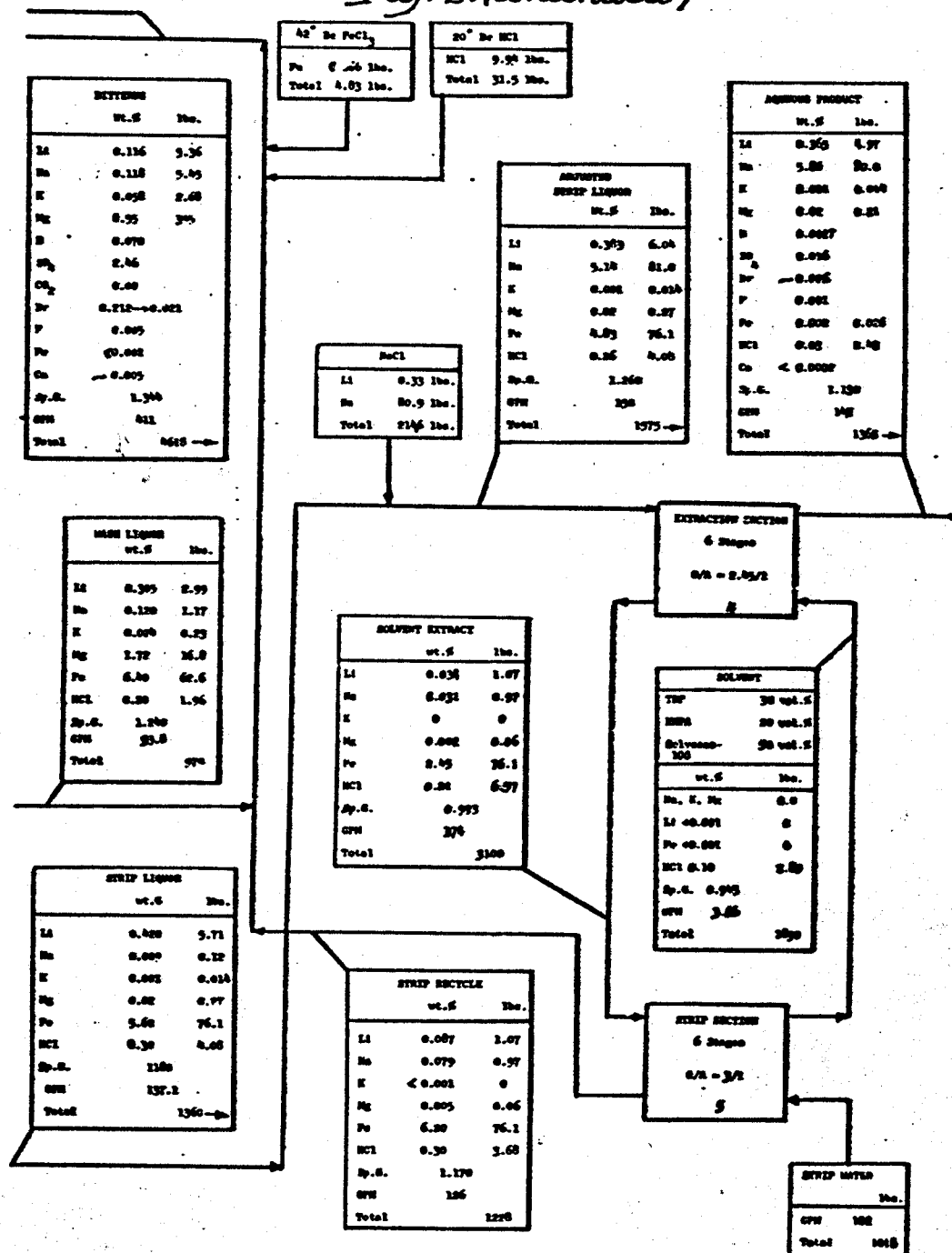
3,537,813

RECOVERY OF LITHIUM FROM BITTERNS

Filed April 25, 1968

3 Sheets-Sheet 3

Fig. 2. (continued)



Inventors
 Joseph R. Nelli
 Theodore E. Arthur, Jr.
 By: Wallenstein, Spangenberg, Hattis & Strampel, Inc.

United States Patent Office

3,537,813

Patented Nov. 3, 1970

1

2

3,537,813

RECOVERY OF LITHIUM FROM BITTERNS

Joseph R. Nelli and Theodore E. Arthur, Jr., Gastonia, N.C., assignors to Lithium Corporation of America, New York, N.Y., a corporation of Delaware
Continuation-in-part of application Ser. No. 570,192, Aug. 4, 1966. This application Apr. 25, 1968, Ser. No. 724,295

U.S. Cl. 23-89

Int. Cl. C01d 11/02

17 Claims

ABSTRACT OF THE DISCLOSURE

A process for recovering certain mineral, especially lithium, values from liquids obtained from brines or sea water, after removing the major content of sodium chloride and reducing the content of other salts in said brines or sea water. A metal halide which is reactive with lithium to form a lithium-containing compound, particularly ferric chloride, is added to the liquid, together with an acid, such as hydrochloric acid, to inhibit hydrolysis of the metal halide, and the lithium values are recovered by extraction with a water-insoluble organic solvent, phase separation, and washing of said separated organic solvent extract phase with water.

CROSS-REFERENCE TO RELATED DISCLOSURE

This application is a continuation-in-part of application Ser. No. 570,192, filed Aug. 4, 1966, now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a process for recovering certain residual mineral values, particularly lithium, from waste liquids or bitterns resulting from the extraction of various salts from brine or sea water.

Description of the prior art

It is well recognized that the waste liquids resulting from the processing of brines or sea water contain important mineral values. Among these are lithium salts, particularly lithium chloride, which is present in the waste liquid in small, but commercially significant, quantities along with various percentages of other salts principally including those of magnesium, sodium and potassium. Considerable research and effort have been directed toward the development of processes for recovering the lithium values from such waste liquid. While a number of processes have evolved from work in this area, generally speaking, they are unsatisfactory due to their complexity and the excessive costs involved in the ultimate recovery of the desired values. As a consequence, there are essentially no large commercial operations in use wherein the recovery of such values is carried out separately or as a part of an overall process for recovering mineral values generally from brines or sea water. The present invention provides a simple, inexpensive procedure for recovering lithium values from waste liquids of the type mentioned.

SUMMARY OF THE INVENTION

In accordance with the present invention, it has been discovered that a high percentage of the lithium values contained in waste liquids or bitterns resulting from the processing of brines or sea water can be recovered by adding a metallic, and especially an iron, salt to the liquid under conditions to inhibit hydrolyzation of the salt, whereby the salt reacts with the lithium salts, e.g. lithium chloride, present in the liquid to form a compound which then can be extracted from the liquid with a suitable

organic solvent. The lithium is then separated from the compound and the metallic salt and the organic solvent is recycled in the process. The extraction of the compound formed by the reaction of the metallic salt with the lithium is carried out with an organic solvent which is essentially insoluble, or difficultly soluble, in water. Reextraction of the compound from the organic solvent is achieved with ordinary tap water. The reaction involving the lithium present in the waste liquid or bitterns takes place substantially independently of other mineral values present. While the process of the present invention is uniquely suitable for the recovery of lithium values, it can be used to advantage in recovering or extracting and/or separating other mineral values in waste liquids or bitterns. Thus, other alkali metal salts (other than sodium), and other metal salts, for example, magnesium salts, commonly present in such liquids, can be recovered along with, or separately from, the lithium values present without requiring any substantial departure from the basic processing steps outlined herein. It should be understood that no claim is made to any novelty in the concept broadly of extracting iron from iron-containing hydrochloric or perchloric acid solutions, or from acid solutions containing iron and other salts such as lithium chloride, calcium chloride, magnesium chloride or aluminum chloride by means of organic solvents of various types.

BRIEF DESCRIPTION OF THE DRAWING

The accompanying drawing FIG. 1 is a diagrammatic or schematic form of equipment arrangement for carrying out the process of the present invention.

FIG. 2 represents an arrangement similar to that of FIG. 1 but includes thereon references to compositions of the starting bitterns and material balances in the compositions of at the various stages of the process in a typical illustrative example in carrying out the extractions, washes and stripping operations in multiple stages.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The metallic salts having utility in the practice of the present invention are characterized in that they are capable, in solution, of forming a stable compound with lithium, and/or magnesium, if such be the case, which can be extracted with a suitable organic solvent and then recovered, as by simple extraction, from the solvent. As indicated, the metallic salt is added to the waste liquid or bitterns under conditions such that the salt will not be hydrolyzed to any appreciable extent. To this end, the metallic salt advantageously, and further, is characterized in that it is capable of forming, with an acid, a dissociable acid salt or complex which, in solution, resists hydrolyzation but readily undergoes a replacement reaction with, for instance, a lithium salt to yield the desired extractable compound.

While there are a number of metallic salts having properties which satisfy the foregoing criteria, the objectives of the present invention are most advantageously met by utilizing metal halides, particularly the chlorides and bromides of ferric iron, cobalt and nickel. Of this group, ferric chloride, especially in a hydrated form such as ferric chloride hexahydrate, is preferred and the dissociable acid salt or complex which is formed is soluble lithium tetrahaloferrate. The metal halide can be added to the waste liquid or bitterns as an acid solution or can be added to a suitably acidified waste liquid or bitterns. The concentration of the metal halide solutions employed in the practice of the present invention is somewhat variable. In utilizing ferric chloride, for example, as the metallic salt, good results can be attained with solutions comprising, by weight, from about 30 to 50% ferric

chloride, with particularly satisfactory results being obtained with solutions in which the weight percent of ferric chloride ranges from about 38 to 45%, for instance, a 42° Baumé solution which contains about 40% ferric chloride.

The process of the present invention can be carried out in both chloride and bromide systems. The acid employed, therefore, should be one which is compatible with such a system. Further, in this same connection, the acid used in the process advantageously is one that is capable of forming an acid salt or complex with the metallic salt which, in solution, will not only substantially prevent hydrolyzation of the metallic salt but will dissociate to provide an anion for reacting with the desired metal cation values present in the waste liquid or biterms. In a chloride system, utilizing ferric chloride as the metal halide to recover lithium values, for example, from the system, the preferred acids are chlorine-containing acids such as hydrochloric or perchloric acid. In such a system, the hydrochloric acid or perchloric acid desirably is employed in the form of aqueous solutions of strength of from about 20% to 30%, usually about 25%. Sulfuric acid can also be employed but it is particularly preferred to use hydrochloric acid.

The quantity of the metallic salt that is added to the waste liquid or biterms can vary within appreciable limits. Thus, by way of illustration, in recovering lithium values from a chloride system utilizing ferric chloride as the metallic salt, the generally optimum objectives of the invention are attained when the ferric chloride is introduced in an amount sufficient to provide a ferric-to-lithium gram-ion ratio of the order of from about 0.5:1 to about 1.5:1, especially desirably a gram-ion ratio of about 1:1.

The acid, whether added as part of the metallic salt solution or separately, should be present in the waste liquid or biterms in an amount such that the acid concentration is sufficiently high to prevent hydrolysis of the metallic salt. To this end, the acid should be used in an amount sufficient to provide an acid concentration in the waste liquid or biterms in the range of from about 0.02 N to 0.3 N, usually 0.04 N to 0.1 N.

The organic solvents employed in the process of the present invention for extracting the desired compound formed in the waste liquid or biterms, apart from having good extraction properties with respect to said compound, are characterized in that they are insoluble, or difficultly soluble, in water, and thus are readily separable from the aqueous phase of the solutions by decantation or other such conventional separation techniques. Of a variety of solvents satisfying these criteria, certain oxygen-containing solvents are particularly suitable for the purposes of this invention. Exemplary of such solvents are esters such as n-butyl acetate, ethyl acetate, amyl acetate and isopentyl acetate; ketones exemplified by distilled cyclohexanone, diisobutyl ketone and isobutyl methyl ketone; ethers such as diisopropyl ethers; 1-ethoxybutane and 1-ethoxyhexane; alcohols such as 3-methyl pentanol and 2-hexanol; and the like, and compatible mixtures thereof. Of this group, diisobutyl ketone is especially preferred due to its low solubility in water, its general availability, its good extraction properties, and its good chemical stability.

It is especially desirable to use, in conjunction with the aforementioned solvents, certain neutral or acidic phosphorus esters such as are described below, and particularly satisfactory is tributyl phosphate. Such phosphorus esters are used in minor proportions in the mixture of solvents. They tend to enhance the extraction of the desired compound and they tend to reduce the possibility of formation of undesirable emulsion conditions. In general, such phosphorus esters, where used will usually constitute from 15 to 25%, by volume, of the total solvent mixture. An illustrative, and highly desir-

able, solvent mixture is about 80% diisobutyl ketone and about 20% tributyl phosphate.

The quantity of organic solvent utilized in the extraction step of the process can vary within appreciable limits. From the standpoint of practical considerations, however, it is desirable to employ only so much of the solvent as is necessary to effect extraction of the compound resulting from the reaction of the anion furnished by the dissociable metallic salt-acid salt or complex with the metal cation value, or values, present in the waste liquid or biterms. Generally speaking, the objectives of this invention can be attained at the extraction step of the process with organic solvent-to-aqueous solution volume ratios ranging from about 0.5:1 to about 3:1, especially desirably with a ratio of about 1 to 2 of the organic solvent to 1 of the aqueous solution. At the wash step, following extraction with the organic solvent, the organic solvent-to-aqueous ratios advantageously should range from about 8:1 to about 15:1, preferably from about 10 or 11 volumes of the organic solvent to 1 of aqueous solution. The higher organic solvent-to-aqueous ratio employed at this step in the process tends to limit the drive of the desired metal value-containing compound into the aqueous phase. At the strip step of the process, on the other hand, recovery of the desired metal values is favored by organic solvent-to-aqueous ratios substantially lower than those utilized at the wash step. Generally speaking, organic solvent-to-aqueous ratios at this step will range from about 3:1 to about 10:1, usually about 3 to 7 volumes of the solvent to 1 of the aqueous solution.

Referring, now, to FIG. 1 of the accompanying drawings, in which there is illustrated in diagrammatic or schematic form an arrangement for carrying out the process of the present invention for the recovery of lithium values from biterms by a continuous counter-current single stage or multi-stage mixer-settler operation, at extraction step 1, a biterms solution, to which an aqueous ferric chloride-hydrochloric acid solution has been added, forming soluble lithium tetrahaloferrate is contacted with an organic solvent stream. The adjusted biterms solution and solvent are thoroughly mixed, and phase separation is then allowed to take place. The aqueous raffinate phase from step 1 is discarded and the organic phase is passed to a wash step 2 where it is mixed with a stream of fresh water. Following phase separation at step 2, the washed extract is passed to a strip step 3. Here the washed extract is contacted with another stream of water. The solvent-rich stripped extract from step 3 is recycled to step 1 while the strip liquor is passed to a second extraction step 4. Prior to entering step 4, the chloride ion content of the strip liquor from step 3 is adjusted by the addition thereto of a chlorine-containing salt such, for example, as sodium chloride or potassium chloride. The quantity of the chlorine-containing salt added at this step in the process should be sufficient to provide a chloride ion concentration in the strip liquor of at least 2 M, and preferably higher. The increased chloride ion concentration in the strip liquor tends to drive the ferric iron into the organic phase resulting from the addition, at step 4, of a solvent to the strip liquor. The solvent added at this step advantageously should favor extraction of the ferric iron present in the strip liquor to the exclusion of the lithium values contained therein. Exemplary of a solvent having good selectivity as well as extraction capabilities for this purpose is a mixed solvent comprising a combination of a neutral phosphorus ester, an acidic phosphorus ester and a diluent, such that the physical and chemical properties of the individual components of the combination complement each other. The neutral phosphorus esters employed in the combination can be characterized in that the substituents on the phosphoryl group, $P=O$, may be alkoxy, RO, a combination of alkoxy and alkyl, or alkyl, wherein the alkyl substituent or substituents, may be represented by the general

formula C_nH_{2n+1} . Generally speaking, the order of increasing extraction power of the neutral phosphorus ester, based on substitution of the phosphoryl group, will be phosphate, phosphonate, phosphinate and phosphinic oxide. The acid phosphorus ester component used in the mixed solvent can be characterized in that the substituents on the divalent phosphino group, $:POOH$, thereof may be dialkoxy or dialkyl, while the substituents on the monovalent phosphonon group, $:PO(OH)_2$, where such is the case, may be monoalkoxy or monoalkyl. The diluent utilized in the mixed solvent most advantageously is a non-polar aromatic hydrocarbon exemplified by benzene, toluene, and xylene, or commercially available aromatic diluents such as those sold under the trade designations "Amsco Solv D" (American Oil Co.) and "Solvesso 100" (Esso). An illustrative example of a mixed solvent having the properties desired is one containing tri-n-butyl phosphate and di(2-ethyl hexyl)phosphoric acid, in a mole ratio of about 1:1, with benzene as the diluent.

The solvent extract from step 4 is passed to a strip step 5 where it is contacted with a stream of water. The stripped solvent from this step is recycled to step 4 and the strip liquor, containing the recovered ferric chloride, is recycled through the process. The aqueous product from step 4 contains the desired lithium values in the form of lithium chloride. The aqueous solution is evaporated to effect precipitation of the chloride-containing salt added to the strip liquor obtained from step 3. Following separation of the precipitated salt from the aqueous product, which salt may be recycled to step 4, the resulting solution may be evaporated to obtain anhydrous lithium chloride, or the lithium values present therein can be recovered by chemical means as by addition of sodium carbonate to effect precipitation of the lithium as lithium carbonate.

By far the major proportion of the lithium values is extracted at step 1 of the process, but, from an economic standpoint, in multiple stages. The raffinate from step 1 may be discarded or treated, if desired, to recover lithium and other mineral values therefrom. In those instances where lithium and magnesium are present in the bitterns and the magnesium may interfere with the extraction of the lithium values, it is possible, in accordance with the practice of this invention, to control the extent of magnesium interference by proper adjustment of the organic solvent phase-to-aqueous phase ratios at the wash step. Since the aqueous phase has a greater affinity for the magnesium salt values, by utilizing a limited quantity of water at the wash step to thereby increase the organic solvent phase-to-aqueous phase ratio, a concentration of magnesium salt values is obtained which is sufficient to suppress the re-extraction of the lithium values.

Variations in the ratios of values, particularly with

tion does not increase lithium value extraction but does increase magnesium extraction; and (2) increasing the acid concentration decreases the extraction of both lithium and magnesium values but produces lower magnesium-to-lithium value ratios.

The process of the present invention, in its optimum aspects, enables the recovery of greater than 80% of the lithium values from waste liquids or bitterns having a magnesium-to-lithium ratio of about 160:1. The economics of the process are extremely good both from the standpoint of the relatively few processing steps involved and in view of the fact that both the metallic salt and the solvent utilized can be readily recovered for recycle through the process.

In FIG. 2, the material balances are shown, in the case of an illustrative example, in relation to the various steps of the process. The following abbreviations apply: g.p.m. is gallons per minute; IBK is diisobutyl ketone; TBP is tributyl phosphate; EHPA is di-2-ethylhexyl phosphoric acid; and O/A is organic to aqueous volume ratio.

The following examples are illustrative of the practice of the present invention. While the examples primarily involve a multistage continuous countercurrent mixer-settler, batch type operation, it should be understood, as indicated, hereinabove, that a distinctly major percentage of the desired lithium values can be extracted in a single stage.

EXAMPLE I

Extraction step—3,000 mls. of a synthetic bitterns (a saturated aqueous chloride solution containing about 0.076% Li, 7.80% Mg, 0.22% Na, 0.20% K and 2.0% SO_4^{--}) were adjusted with 127.6 mls. of 42° BÉ. $FeCl_3$ solution and 10 mls. of 25% HCl solution, thereby forming soluble lithium tetrahaloferrate. This adjusted bitterns had a gm.-ion ratio of Li to Fe of about 1 to 1, and a HCl concentration of about 0.07% to prevent hydrolysis of the $FeCl_3$. In a batch simulation of a seven-stage continuous, countercurrent mixer-settler operation, 300 mls. of adjusted bitterns were contacted with 200 mls. of diisobutyl ketone (DIBK). 9, 7, 5½ and 4 mls. of 42° BÉ. $FeCl_3$ solution were added to the aqueous phases leaving stages 7, 6, 5 and 4, respectively.

Wash step—In a batch simulation of a four-stage continuous countercurrent mixer-settler operation, 350 mls. of extract from the above step were contacted with 35 mls. of wash water.

Strip step—In a batch simulation of a five-stage continuous countercurrent mixer-settler operation, 300 mls. of washed extract from the above step were contacted with 60 mls. of strip water.

The following table is illustrative of the composition of the entering and exiting streams in each of the foregoing steps.

TABLE I

Process step	Process stream	Stream analysis, wt. percent			Weight ratio	
		Li	Mg	Fe	Li/Mg	Li/Fe
Extraction—Organic to aqueous Volume ratio—3½	Adjusted bitterns	0.0725	7.43	0.898	1/102	1/8.26
	Aqueous raffinate	0.011	0.209	0.209	1/19.0	
	Diisobutyl ketone	0	0	0		
	Extract	0.125	0.170	2.14	1/1.36	1/23.1
Wash—Organic to aqueous volume ratio—10/1	Extract	0.125	0.170	2.14	1/1.36	1/23.1
	Washed extract	0.005	<0.002	1.43	>47/1	1/15.0
	Wash water	0	0	0		
	Wash liquor	0.309	1.04	9.65	1/3.0	1/48.1
Strip—Organic to aqueous volume ratio—5/1	Washed extract	0.005	<0.002	1.43	>47/1	1/15.0
	Stripped extract	<0.0005	0	0.0014		
	Strip water	0	0	0		
	Strip liquor	0.371	<0.002	8.41	>185/1	1/14.6

reference to lithium and magnesium value ratios, obtained by the practice of the process of this invention, can be controlled by changing the concentration of either the metallic salt or the acid, or both. In this connection, the following generalizations can be made (1) increasing the metallic salt concentration at constant acid concentra-

EXAMPLE II

Extraction step—3000 mls. of an actual bitterns (a saturated aqueous chloride solution containing about 0.182% Li, 8.65% Mg, 0.17% Na, 0.085% K, 3.03% SO_4^{--} , and trace amount of impurities) were adjusted with 372 mls. of 42° BÉ. $FeCl_3$ solution and 20 mls. of

25% HCl solution, thereby forming soluble lithium tetrahaloferrate. The adjusted biterms had a gm.-ion ratio of Li to Fe of about 1 to 1, and a HCl concentration of about 0.12% to prevent hydrolysis of FeCl_3 . In a batch simulation of a seven-stage continuous countercurrent mixer-settler operation, 90 mls. of adjusted biterms were contacted with 135 mls. of diisobutyl ketone. 3, 2.5, 2 and 1.5 mls. of 42° B ϕ . FeCl_3 solution were added to the aqueous phase leaving stages 7, 6, 5 and 4, respectively.

Wash step—In a batch simulation of a four-stage continuous countercurrent mixer-settler operation, 150 mls. of extract from the above step were contacted with 15 mls. of water.

Strip step—In a batch simulation of a four-stage continuous countercurrent mixer-settler operation, 150 mls. of washed extract from the above step were contacted with 30 mls. of water.

EXAMPLE IV

Iron recovery process

Extraction step—1500 mls. of a synthetic strip liquor, (an aqueous chloride solution containing about 0.410% Li and 3.84% Fe) was adjusted with about 263 gms. of NaCl to give an adjusted strip liquor about 3 M in NaCl. In a batch simulation of a six-stage continuous countercurrent mixer-settler operation, 40 mls. of adjusted strip liquor were contacted with 50 mls. of solvent comprised of 32 parts tri-n-butyl phosphate, 18 parts di-2-ethylhexyl phosphoric acid, and 50 parts of benzene, by volume.

Strip step—In a batch simulation of a four-stage continuous countercurrent mixer-settler operation, 60 mls. of the solvent extract from the above step were contacted with 20 mls. of water. Illustrative stream analyses are given in the following table.

TABLE IV

Process step	Process stream	Stream analyses, wt. percent		Weight ratio, Li/Fe
		Li	Fe	
Extraction—Organic to aqueous volume ratio—1.24/1	Adjusted strip liquor	0.254	0.22	1/9.4
	Aqueous product	0.205	0.011	35/1
	Solvent	0	0	—
	Solvent extract	0.021	0.04	1/1.9
Strip—Organic to aqueous volume ratio—3/1	do.	0.021	0.04	1/1.9
	Stripped solvent	<0.0005	0.01	—
	Strip water	0	0	—
	Strip recycle	0.023	0.11	1/4.8

¹ Tri-n-butyl phosphate plus di-2-ethylhexyl phosphoric acid in benzene.

Illustrative stream analyses are presented in the following table.

What is claimed is:

1. A process for recovering lithium values from liquid

TABLE II

Process step	Process stream	Stream analyses, wt. percent					Weight ratio			
		Li	Mg	Fe	Na	K	Li/Mg	Li/Fe	Na/Mg	K/Mg
Extraction—Organic to aqueous volume ratio—3/2	Adjusted biterms	0.100	1.00	1.34	0.155	0.074	1/47.5	1/3.26	1/48.0	1/108
	Aqueous raffinate	0.0088	—	0.113	0.0065	0.0046	—	1/100	—	—
	Diisobutyl ketone	0	0	0	0	0	—	—	—	—
	Extract	0.177	0.201	2.97	0.157	0.072	1/1.13	1/14.8	1/1.26	1/2.70
Wash—Organic to aqueous volume ratio—10/1	Extract	0.177	0.201	2.97	0.157	0.072	1/1.13	1/14.8	1/1.26	1/2.70
	Washed extract	0.120	<0.001	1.25	—	—	>120/1	1/10.4	—	—
	Wash water	0	0	0	—	—	—	—	—	—
	Wash liquor	0.200	1.04	0.15	—	—	1/2.7	1/24.1	—	—
Strip—Organic to aqueous volume ratio—5/1	Washed extract	0.120	<0.001	1.25	—	—	>120/1	1/10.4	—	—
	Stripped extract	<0.0005	—	0.0005	—	—	—	—	—	—
	Strip water	0	0	0	—	—	—	—	—	—
	Strip liquor	0.413	<0.001	4.21	0.148	0.100	>110/1	1/10.3	>140/1	>100/1

EXAMPLE III

Extraction step—3000 mls. of an actual biterms (a saturated aqueous chloride solution containing about 0.0854% Li, 7.28% Mg, 0.53% Na, 0.78% K, 3% SO_4^{2-} , and small amounts of impurities) were adjusted with 143 mls. of 42° B ϕ . FeCl_3 solution and 34 mls. of concentrated HCl solution, thereby forming soluble lithium tetrahaloferrate. The adjusted biterms had a gm.-ion ratio of Li to Fe of about 1 to 1, and an HCl concentration of about 0.06% to prevent hydrolysis of FeCl_3 . In a batch simulation of a seven-stage continuous countercurrent mixer-settler operation, 120 mls. of adjusted biterms were contacted with 120 mls. of diisobutyl ketone. 2, 1.6, 1.3, and 1.0 mls. of 42° B ϕ . FeCl_3 solution were added to the aqueous phases leaving stages 7, 6, 5 and 4, respectively. In addition, 0.1 ml. of concentrated HCl solution was added to the aqueous phases leaving stages 5 and 4. Illustrative stream analyses are presented in the following table.

TABLE III

Process step	Process stream	Stream analyses, wt. percent					Weight ratio			
		Li	Mg	Na	K	Fe	Li/Mg	Na/Mg	K/Mg	Li/Fe
Extraction—Organic to aqueous volume ratio—1/1	Adjusted biterms	0.0605	0.96	0.50	0.74	0.053	1/8.5	1/12.7	1/8.8	1/8.23
	Aqueous raffinate	0.012	—	—	—	0.002	—	—	—	1/2
	Diisobutyl ketone	0	0	0	0	0	—	—	—	—
	Extract	0.064	0.029	0.22	0.26	1.00	2.2/1	1.6/1	12.1/11	1/21

obtained from brines or sea water, said liquid resulting from initially removing the major content of sodium chloride and reducing the content of other salts in said brines or sea water, comprising adding a chloride or bromide of a metal selected from the group of ferric iron, cobalt and nickel to said liquid under acidic conditions to inhibit hydrolyzation of the said metal chloride or bromide, allowing the said metal chloride or bromide to react with the lithium ion present in said liquid to form a soluble compound containing said lithium, extracting said soluble compound containing said lithium by means of a substantially water-insoluble organic solvent in which said soluble compound containing said lithium is soluble, and recovering the lithium values, in the form of lithium chloride or bromide, from said organic solvent extract containing the soluble compound containing said lithium.

2. A process as claimed in claim 1, wherein hydrolyzation of the metal chloride or bromide is inhibited by the addition of a chlorine- or bromine-containing acid.

3. A process as claimed in claim 2, wherein the organic solvent is an oxygen-containing solvent.

4. A process as claimed in claim 2, wherein the organic solvent is diisobutyl ketone.

5. A process as claimed in claim 2, wherein the organic solvent is a mixture of diisobutyl ketone with a minor amount of tributyl phosphate.

6. A process as claimed in claim 2, wherein the metal chloride is ferric chloride.

7. A process as claimed in claim 6 wherein hydrolyzation of the ferric chloride is inhibited by addition of hydrochloric or perchloric acid.

8. A process for recovering lithium values from a liquid obtained from brines or sea water, said liquid resulting from initially removing the major content of sodium chloride and reducing the content of other salts in said brines or sea water, comprising adding ferric halide selected from the group of ferric chloride and ferric bromide to said liquid under acidic conditions to inhibit hydrolyzation of the ferric halide, allowing said ferric halide to react with the lithium present in said liquid to form soluble lithium tetrahaloferrate, adding a substantially water-insoluble oxygen-containing organic solvent to the liquid to extract the lithium tetrahaloferrate therefrom, separating the organic solvent from the liquid and adding water to the solvent to extract the lithium tetrahaloferrate therefrom, adding sodium or potassium chloride to the water extract to increase the chloride ion concentration thereof, adding a ferric-ion selective organic solvent to the water extract to recover said ferric halide therefrom, separating said ferric-ion selective organic solvent solution from the water extract, adding water to the solvent to extract said ferric halide therefrom, and recovering the lithium values as lithium chloride or bromide from the water extract containing the same.

9. A process as claimed in claim 8, wherein the ferric chloride is a ferric chloride hydrate.

10. A process as claimed in claim 8, wherein the oxygen-containing organic solvent is a substantially water-insoluble alcohol, ether, ester or ketone.

11. A process as claimed in claim 8, wherein the ferric halide is recycled in the process.

12. A process as claimed in claim 8, wherein a chlorine- or bromine-containing acid is added to the liquid to inhibit hydrolyzation of the ferric halide.

13. A process as claimed in 12, wherein the acid is hydrochloric or perchloric acid.

14. A process as claimed in claim 8, wherein the ferric-ion selective organic solvent is a mixed solvent comprising a neutral phosphorus ester, an acidic phosphorus ester and a non-polar aromatic hydrocarbon diluent.

15. A process as claimed in claim 14, wherein the mixed solvent comprises a mixture of tributyl phosphate and di(2-ethyl hexyl)phosphoric acid in benzene.

16. A process for recovering lithium values from waste liquids resulting from the processing of brines or sea water, comprising adding a soluble complex-forming metal chloride or bromide selected from the group of ferric iron, cobalt and nickel to said waste liquid under acidic conditions to inhibit hydrolysis of said chloride or bromide, allowing said added metal chloride or bromide to react with the lithium ion of the lithium salt to be recovered to form a complex therewith which is soluble, extracting said complex by means of a substantially water-insoluble organic solvent in which said complex is soluble, and recovering the lithium values, in the form of lithium chloride or bromide, from said organic solvent extract containing said complex.

17. A process as claimed in claim 16, in which the organic solvent is a mixture of diisobutyl ketone with a minor amount of tributyl phosphate.

References Cited

UNITED STATES PATENTS

2,564,241	8/1951	Warf	23-32 X
2,808,313	10/1957	Fleischmann	23-32
3,144,304	8/1964	Nagumo et al.	23-140
3,154,500	10/1964	Jansen et al.	
3,306,712	2/1967	Goodenough et al.	23-89 X

OTHER REFERENCES

Clark: Nucl. Sci. Abstr. vol. 16, No. 11, Abstr. No. 13128, June 12, 1962.

OSCAR R. VERTIZ, Primary Examiner

G. T. OZAK, Assistant Examiner

U.S. Cl. X.R.

23-39, 51

STRATIGRAPHIC AND TECTONIC SETTING OF THE LITHIUM BRINE FIELD, CLAYTON VALLEY, NEVADA

J. R. DAVIS¹ and J. D. VINE²

ABSTRACT

Lithium is extracted from a sodium chloride brine pumped from an air-fall-tuff aquifer beneath the playa in Clayton Valley, Nevada. During pluvial periods of the Pleistocene, a lake about 200 ft (60 m) deep existed in Clayton Valley. Lacustrine conditions during pluvial periods favored deposition of calcareous mud in the central portion of the basin, while fluvial and detritic sand and silt were deposited near the margins. Evaporation from the lake surface may have concentrated the lake water several hundred times during pluvial periods. With the onset of interpluvial conditions, the lake receded, concentrating the water until gypsum and halite precipitated. As the dry trend continued, eolian and fluvial processes reworked the salt, mud and marginal sediments, and the central portion of the basin became an ephemeral lake or playa, being flooded only during wet seasons.

Evaporative concentration and evaporite precipitation led to the chemical evolution of a lithium-enriched residual brine, which saturated the central salt and mud facies of the playa. Subsidence due to normal faulting caused rapid sedimentation, burying the saturated sediments. The normal faults also served as conduits to allow the brine to percolate downward and reach an air-fall-tuff aquifer. Authigenesis of zeolites and clays at the surface or silicate diagenesis in the subsurface led to further evolution of the brine, with the resulting lithium-enriched, sodium chloride brine being compositionally quite different from the apparent source waters.

HISTORY OF THE DEPOSIT

In the first part of this century, demand for sodium chloride, sodium carbonate, borates, and potash salts led to an extensive reconnaissance of playa lakes throughout the western United States. The playa in Clayton Valley near Silverpeak, Nevada, was first studied by Dole (1912), who found high concentrations of sodium chloride in near-surface brines but made no mention of lithium. The lithium deposit at Silverpeak remained undiscovered until the late 1950's, when the Leprechaun Mining Company of Las Vegas, Nevada, while searching for potassium brines, discovered high concentrations of lithium in the subsurface brines of the playa. In 1964, Foote Mineral Company acquired the property to develop the brine as a primary source of lithium.

Foote Mineral Company pumps brine from depths of about 300 to 800 ft (100 to 250 m) into a series of evaporating ponds (Barrett and O'Neill, 1970). Solar evaporation results in the precipitation of sodium chloride and the concentration of lithium. Brines that initially contain about 300 ppm Li are thus concentrated to as much as 5,000 ppm Li. After precipitation of most of the sodium chloride, lithium carbonate is precipitated in a processing plant. Production of Li_2CO_3 from the Clayton Valley brine field began in 1967 and has continued to the present. The reported annual capacity of about 14 million tons (6350

metric tons) of Li_2CO_3 represents about one-third of the present U.S. requirements.

GEOLOGIC SETTING

Clayton Valley is one of a group of intermediate sized valleys in west central Nevada. It has a playa floor of about 40 mi² (100 km²) that receives surface drainage from an area of about 500 mi² (1,300 km²). Figures 1 and 2 show the location of the important physiographic features in the vicinity. The playa floor is surrounded by alluvial fan slopes and these, in turn, by mountain ranges, including the Silver Peak Range on the west and the Palmetto Mountains and Montezuma Range on the south and southeast. The Weepah Hills and Paymaster Ridge form mountain barriers on the north and the east respectively. Altitudes range from 4,265 ft (1,300 m) on the playa floor to 9,450 ft (2,880 m) at Piper Peak in the Silver Peak Range.

TECTONIC SETTING

Clayton Valley lies within the Basin and Range Province, a structural and physiographic region of generally linear mountain ranges and valleys. Since mid-Tertiary time, one dominant Basin and Range structural element has been horst and graben normal faulting related to regional extension. However, it has been noted that this type of deformation could coexist with lateral shear stresses, and most recent regional tectonic syntheses have used large-scale topographic features to infer the location of shear

¹U.S. Geological Survey, Menlo Park, California

²U.S. Geological Survey, Denver, Colorado

(101)
Item 23
18 of 21
Check
Bib to
see if
you have
this reference

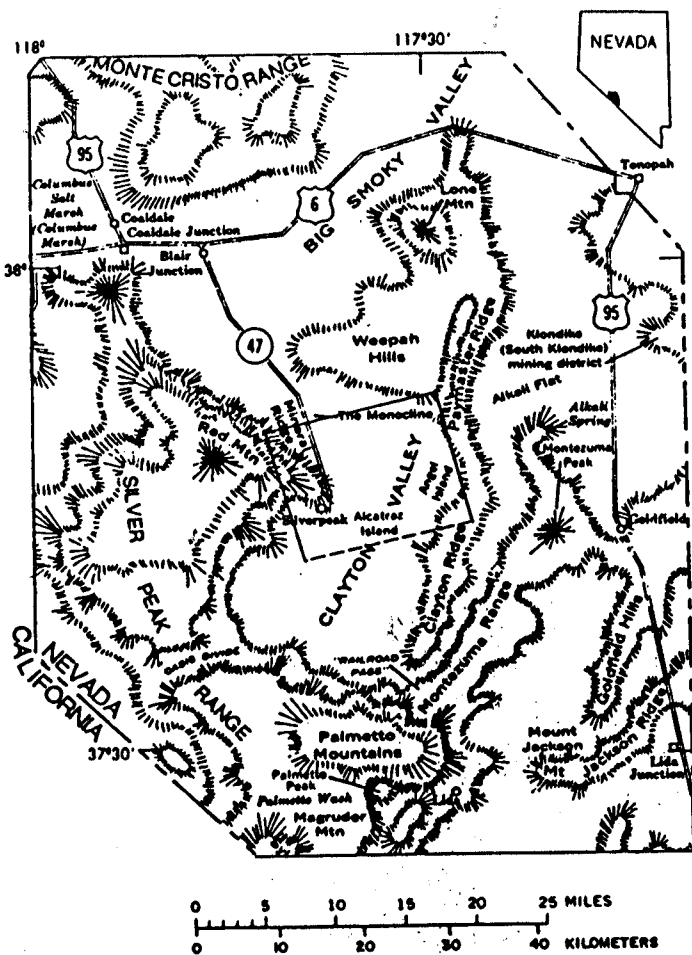


Figure 1.—Index map of Clayton Valley, Nevada, showing physiographic features and major roads. Outlined square in the central portion of the valley shows location of fig. 2. (After Albers and Stewart, 1972).

zones (Shawe, 1965; Stewart, 1967, Ekren and others 1976). The Walker lane (Fig. 3), a zone of disrupted topography (Locke and others, 1940) perhaps related to right-lateral shearing (Stewart, 1967), may pass within a few kilometers of the northern and eastern boundaries of Clayton Valley. The Walker lane is not well defined in this area and may be disrupted by the east-trending Warm Springs lineament (Ekren and others, 1976), which could be a left-lateral fault conjugate to the Walker lane (Shawe, 1965). To the west of Clayton Valley, the Death Valley-Furnace Creek fault zone is a right-lateral fault zone that may die out against the Walker lane northwest of Clayton Valley (Ekren and others, 1976). South of Clayton Valley, the arcuate form of the Palmetto Mountains may be a result of tectonic bending called oroflexural bending by Albers (1967). Albers (1967) believes this tectonic bending is a mechanism for taking up movement in shear zones at the end of major right-lateral faults.

Although the regional tectonic arguments suggest that lateral shear zones may surround Clayton Valley, there is no published evidence that is suggestive of lateral displace-

ment along faults within the valley. In the mountains bordering Clayton Valley on both east and west, faults in the Tertiary rocks generally trend about N. 20° - 40° E. Near the margins of the playa surface, fault scarps having two distinct trends have been studied in detail (Davis, 1979). At the eastern margin, a set of moderately dissected scarps in alluvial gravels of Quaternary age strikes about N. 20°E. South of the northeastern arm of the playa, a more highly dissected set of scarps in alluvium and upper Tertiary lacustrine sediments strikes about N. 65°E. If the modification of these fault scarps is similar to fault-scarp modification elsewhere in Nevada and Utah (Wallace, 1977; Bucknam and Anderson, 1979) the most recent movement on the N. 20°E. set of scarps probably occurred less than 10,000 years ago, while the last movement on the N. 65°E set is probably closer to 20,000 years in age.

PRE-TERTIARY STRATIGRAPHY

The pre-Tertiary rocks exposed in the area include Precambrian metamorphic and sedimentary rocks, Paleozoic marine sedimentary rocks, and Mesozoic intrusive rocks. The oldest rocks in the area consist of the upper Precambrian Wyman Formation, Reed Dolomite, Deep Spring Formation, and the Precambrian and Lower Cambrian Andrews Mountain Member of the Campito Formation. Conformably overlying these rocks are about 8000 ft (2400 m) of Cambrian and Ordovician strata, which include the Lower Cambrian Montenegro Member of the Campito Formation, Poleta Formation, Harkless Formation, and Mule Spring Limestone; the Middle and Upper Cambrian Emigrant Formation; and the Ordovician Palmetto Formation. The siltstone, black shale, chert, limestone, and dolomite that make up this sequence of rock are the deep-water facies equivalents of the Paleozoic shelf carbonates of central and eastern Nevada.

Bodies of plutonic rock intrude the Precambrian and Paleozoic strata at Lone Mountain, Weepah Hills, the Palmetto Mountains, and Mineral Ridge (Fig. 3). The rocks are generally gray, coarse- to medium-grained quartz monzonites. Radiometric ages for these plutons range from Jurassic to Tertiary (Albers and Stewart, 1972).

TERTIARY VOLCANIC ROCKS

There is no evidence of anomalous lithium in pre-Tertiary rocks. The Tertiary volcanic rocks however, are considered likely to be involved in the origin of the lithium deposit, although they generally contain only 20 - 100 ppm Li, because volcanism could have provided the heat energy and hydrothermal activity required to mobilize lithium from glass and other relatively unstable minerals. There were two major volcanic centers in the Clayton Valley area during late Tertiary time. West of Clayton Valley the Silver Peak volcanic center was active from 6.0 to 4.8 m.y. ago (Robinson, 1972). East of Clayton Valley a volcanic center in the vicinity of Montezuma Peak may have been active up to 11 m.y. earlier.

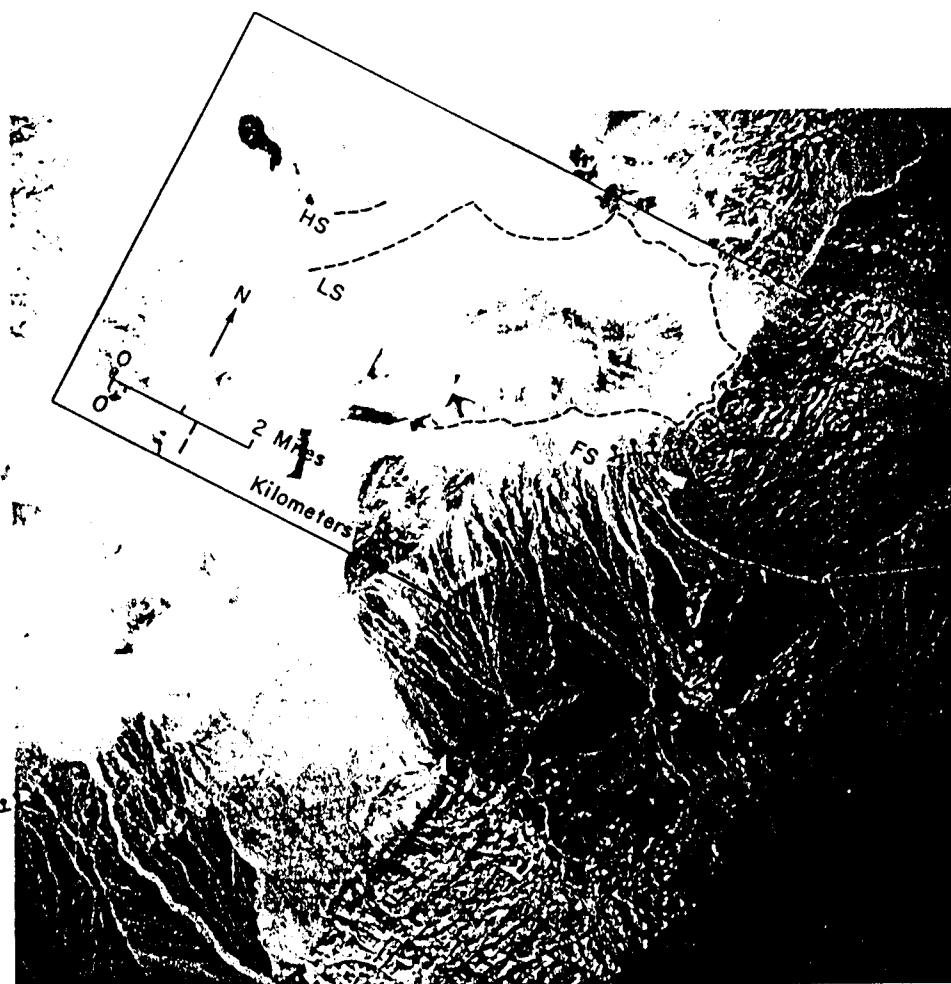


Figure 2.—High-altitude vertical aerial photograph of Clayton Valley, Nevada showing the fault scarp trends in the alluvium (FS). The prominent low shoreline (LS) and the high strandline (HS). Outlined rectangle shows location of fig. 4. NASA photo #27-0048, August 1973.

The approximately 25 mi³ (100 km³) of lava erupted from the Silver Peak Center is 60 percent latitic or quartz latitic in composition, 28 percent rhyolitic, and 12 percent trachyandesitic (Robinson, 1972). Analyses of these rocks indicate that they are part of a potassium-rich alkali-calcic suite, probably produced by crystal fractionation of a trachyandesitic parent magma in a relatively shallow magma chamber (Robinson, 1972; Keith, 1977). A relatively small volume of trachybasalt in the Silver Peak Range and adjacent areas was extruded 4.8 ± 0.6 m.y. ago, and may represent eruptions from a separate parent magma (Robinson, 1972).

East of Clayton Valley, more than 25 mi³ (100 km³) of Tertiary ash-flow and air-fall tuff is exposed at Clayton Ridge and as far east as Montezuma Peak. These predominately flat lying, pumiceous rocks are interbedded with tuffaceous sediments between Clayton Ridge and Montezuma Peak; but at Montezuma Peak, these rocks are considerably altered and dip at angles as much as 30°. In the Montezuma Range, they are unconformably overlain by rhyolitic agglomerates. The source of these tuff sheets

may have been a volcanic center to the east near Montezuma Peak or to the south in the Montezuma Range, the Palmetto Mountains, or Mount Jackson. Preliminary analyses show very little differentiation in these Tertiary ash-flow and air-fall tuffs; they are generally rhyolitic in composition and are not as enriched in sodium and potassium as the rocks from the Silver Peak volcanic center. The age of these volcanic rocks is unknown, but inferred to be Miocene.

TERTIARY SEDIMENTARY ROCKS

Tertiary sedimentary rocks are exposed in the Silver Peak Range, in the Weepah Hills, and in the low hills east of the Clayton Valley playa. These rocks are all included in the Esmeralda Formation of Turner (1900). The Esmeralda Formation consists of sandstone, shale, marl, breccia, and conglomerate, and is intercalated with volcanic rocks, although Turner excluded the major ash-flow units and other volcanic rocks from the formation. The rocks of the Esmeralda Formation in and around Clayton Valley apparently represent sedimentation in several discrete Mio-

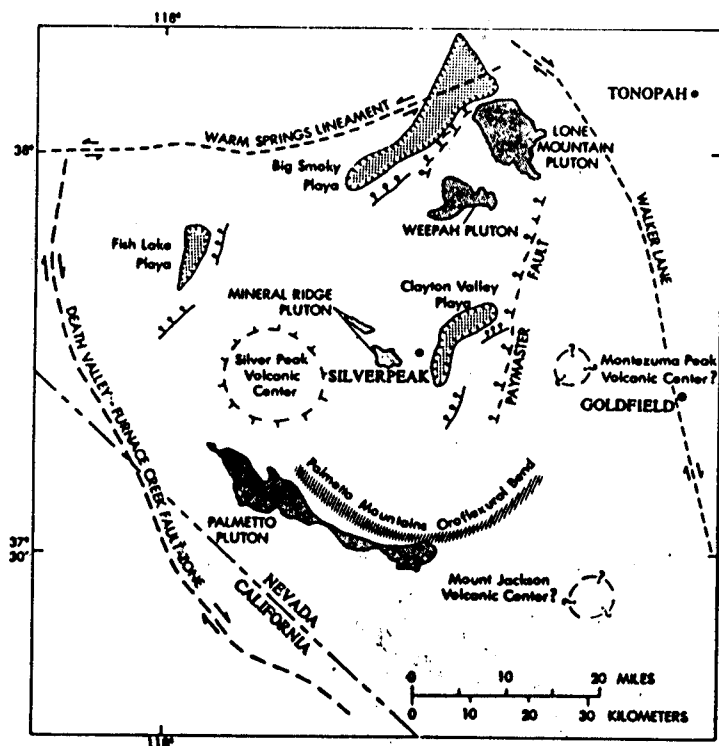


Figure 3.—Generalized diagram of regional structural and geologic features in the vicinity of Clayton Valley, Nevada. Light stipple, playas and dry lakes. Dark stipple, Mesozoic and Tertiary plutons. Normal faults shown with bar and ball on downthrown side.

cene basins. The age of the lower portion of the Esmeralda Formation in Clayton Valley is not known, but an air-fall tuff in the uppermost unit of the Esmeralda Formation has a K-Ar age of 6.9 ± 0.3 m.y. (Robinson and others, 1968).

Extensive diagenetic alteration of vitric material has taken place in the tuffaceous sandstone and shale of the Esmeralda Formation, and anomalously high lithium concentrations locally accompany the alteration. Robinson (1966) noted several distinct assemblages of authigenic minerals in vertical zones, but the stratigraphic framework was not adequate for lateral correlation and facies analysis of the assemblages at that time. Our research confirms the existence of opal-cristobalite, clinoptilolite, heulandite-celandonite, phillipsite-celandonite, and smectite assemblages in tuffaceous zones of unit G of Robinson and others (1968, p. 586) exposed at The Monocline and at new localities east of the playa. Moreover, lithium concentrations in these rocks are not anomalous (10–100 ppm), except where smectite is present. One sample of tuffaceous mudstone, from an exposure east of the playa that contains celandonite, heulandite, and smectite has 1300 ppm lithium, but a sample from the overlying mudstone, which contains only celandonite and heulandite as authigenic phases, has less than 100 ppm lithium.

The high lithium concentration associated with smectite occurrence is confined to the Esmeralda Formation exposed east of the playa. Kunasz (1974) identified the lithium smectite, hectorite, both in the sediments of the

Esmeralda Formation and in altered tuffs lying in a narrow zone near the projected trace of the Paymaster fault (Fig. 3). We believe that the high lithium concentrations in these rocks occur in hectorite or other diagenetic lithium silicate phases. Furthermore, this alteration was probably separate from that responsible for the formation of zeolites and other non-detrital clay minerals, and may have been related to hydrothermal alteration along the numerous northeast-trending fault zones east of the playa.

GEOLOGY OF THE BASIN FILL

In mapping the Quaternary deposits of Clayton Valley, the playa surface, the surrounding alluvial fans and slopes, and the sand dunes are easily distinguished. A large portion of the playa surface has been changed by the construction of roads and evaporating ponds, but prior to this construction the northeastern part of the playa was characterized by a central zone of soft, moist silt and salt, an intermediate zone of silt and sand, and a marginal zone of either travertine or vegetated mounds of soft, puffy silt (Motts and Matz, 1970). The southwestern part of the playa is higher and dryer than the central zone of the northeastern part, and is similar to the marginal vegetated zone there. Alluvial fans are highly dissected and deeply entrenched in the southeastern portion of the valley and less dissected elsewhere. Fan surfaces of at least two different ages can be distinguished in many parts of the valley. Sand dunes are in the southern portion of the valley and are partially stabilized by vegetation.

SUBSURFACE STRATIGRAPHY

The subsurface stratigraphy of the basin fill is known from numerous wells drilled in the playa and adjacent alluvial slopes by Foote Mineral Company between 1964 and 1978, and by the U.S. Geological Survey in 1912 and 1977. Poor sample recovery, contamination of cuttings, and the highly faulted nature of the playa sediments inhibited a clear understanding of the stratigraphy until Foote Mineral Company initiated an exploratory drilling program in 1976 using rotary drilling with reverse circulation and careful logging of the cuttings by well-site geologists. Much of the data collected since that time is still proprietary, but data from several wells are available (Figs. 4 and 5), making the following summary possible.

The facies model used to interpret the subsurface data for this study is similar to that used by G. I. Smith (in press) in a study of the subsurface stratigraphy at Searles Lake, California. Essential to this model is the concept of fluctuating pluvial and interpluvial periods throughout the Pleistocene. The model predicts that during pluvial periods deep-water to shallow-water lacustrine conditions favored deposition of mud in the central portion of the valley, merging laterally with fluvial and deltaic sands and muds and well-sorted beach sands and gravels. In the margin of the valley, there would be a sharp transition between the lacustrine facies and the poorly sorted alluvial gravels.

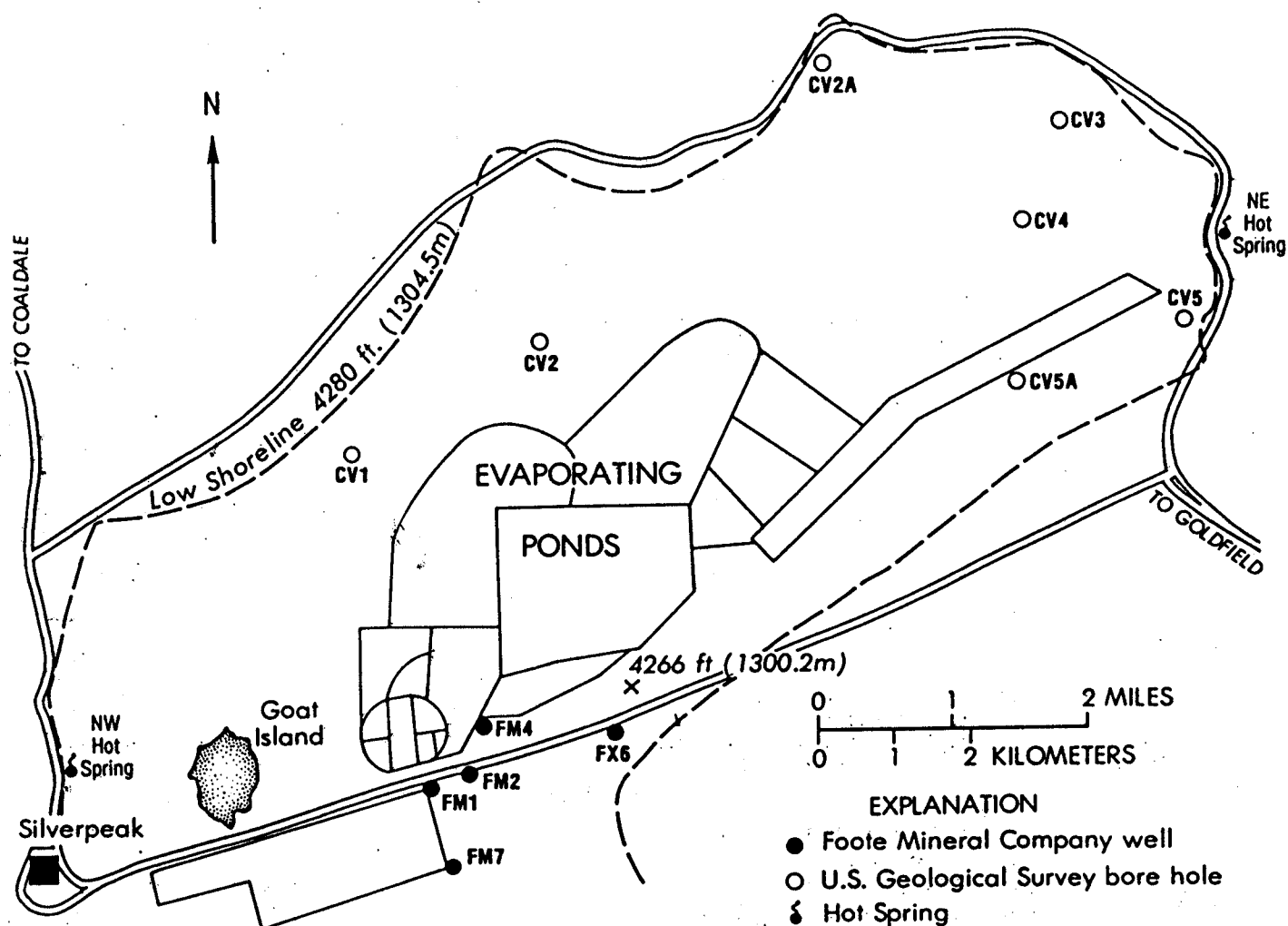


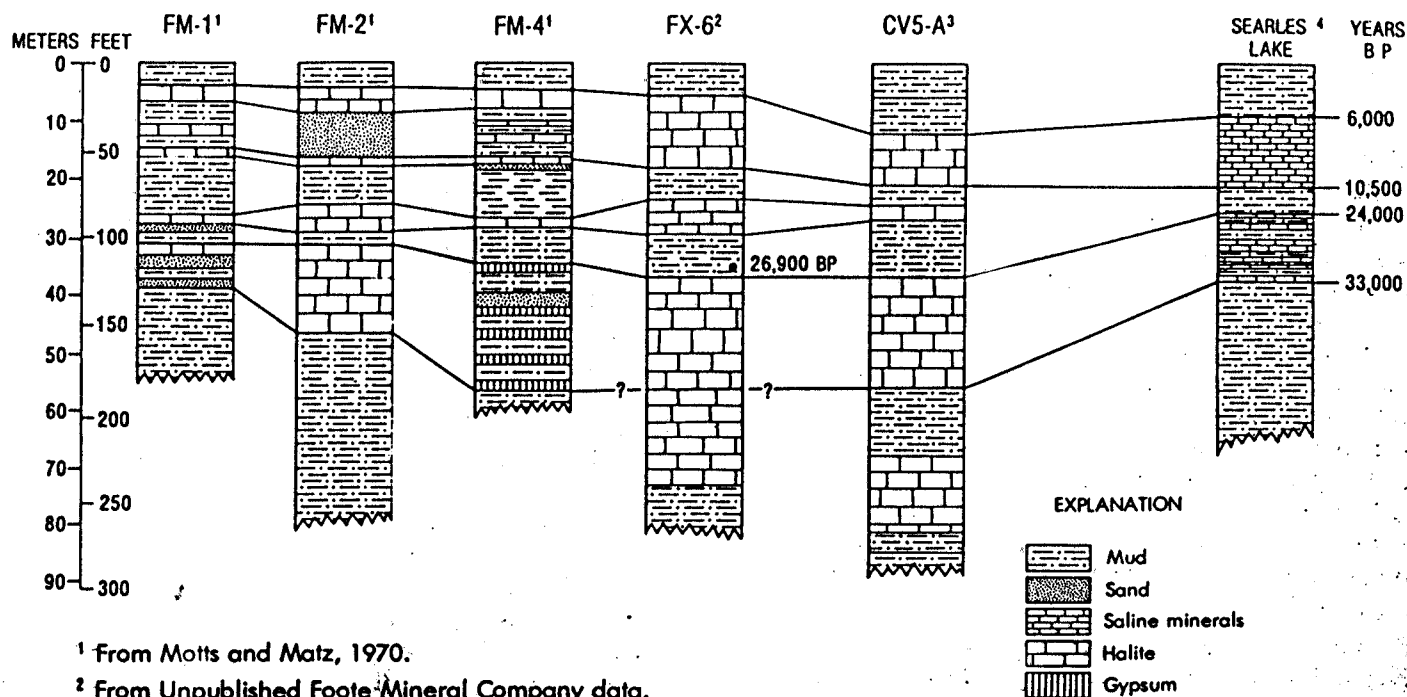
Figure 4.—Map of the northeastern arm of the playa, Clayton Valley, Nevada, showing the location of wells drilled by Foote Mineral Company and U.S. Geological Survey.

During interpluvial periods, shallow-water lacustrine to ephemeral lacustrine conditions favored deposition of muds, silt, sand, and evaporite minerals in the central portion, grading laterally to alluvial deposits. The gravity data (Wilson, 1975) and subsurface stratigraphic correlations (Fig. 5) independently suggest that the center of deposition and subsidence in Clayton Valley was apparently in the northeastern arm of the playa throughout late Quaternary time. This center of deposition is bounded on the south and east by steeply dipping normal faults that parallel the two fault scarp trends in alluvial gravels (Fig. 2). The thickest clastic and chemical sedimentation was confined to the downdropped area north and west of these faults. Where present on the upthrown side of the faults, lacustrine sediments grade into alluvial fan gravel within a few hundred meters; on the downthrown side of the fault, the central lacustrine facies merge into their coarse-grained lateral equivalents over a distance of several kilometers.

The lacustrine sediment that was deposited near the center of pluvial lakes in Clayton Valley generally is green to black calcareous mud. About half of the mud, by weight,

is smectite and illite, which occur in roughly equal amounts. Calcium carbonate generally makes up 10% to 20% of the mud, and kaolinite, chlorite, sand- and silt-sized volcanoclastic detritus, traces of woody organic material, and diatoms compose the rest. Pumice lapilli and other vitric material are thought to represent air-fall deposition into a lacustrine environment and are partially altered to clays, to opal or cristobalite, and to zeolites. These lacustrine muds grade laterally into tuffaceous and calcareous sand and silt of probably fluvial and deltaic origin and into well-sorted sand and gravel associated with beach deposition. Finally, these sedimentary facies grade abruptly into poorly sorted alluvial gravels.

In the northeastern arm of the playa, thick layers of evaporite minerals are interbedded with lacustrine muds. These evaporite minerals were probably precipitated as the lake dried up during interpluvial periods. A lateral sequence from calcite to gypsum to halite occurs from playa margin to center. The calcite and gypsum horizons are generally indurated, but the halite beds are an extremely friable framework of euhedral halite crystals



¹ From Motts and Matz, 1970.

² From Unpublished Foote Mineral Company data.

³ From Unpublished U.S. Geological Survey data.

⁴ From G.I. Smith, 1976a.

Figure 5.—Well logs from Clayton Valley, Nevada, and correlation with Searles Valley, California.

and generally contain a green mud matrix or are interbedded with mud. The period of salt deposition coincident with the drying of the lake was probably fairly short; as the dry trend continued, the central portion of Clayton Valley became an ephemeral lake or playa. The existence of a playa is inferred from the occurrence of salt and tan silt in the center of the valley and with coarser-grained sediments near the margins. Eolian deposition and reworking of sand and/or fluvial deposition of sands may have taken place at this time, as indicated by the locally thick lenses of sand, some of which extend toward the center of the valley.

Most of the fine-grained facies of both the lacustrine and playa sediments have anomalous (greater than 300 ppm Li) lithium concentrations, although values range from less than 100 ppm to more than 1,000 ppm. High lithium concentrations commonly correspond with increased amounts of smectite in the sediment (Kunasz, 1970), probably because of presence of hectorite. Kunasz (1974) identified hectorite in several samples from the playa and suggested that the mineral was detrital. However, the amount of hectorite contributed to the playa by weathering does not seem adequate to account for the high lithium concentrations in the playa sediments. The Esmeralda Formation and altered tuffs east of the playa provide the only source of hectorite; clay fractions of present-day fluvial sediment from other major drainages in the valley do not contain anomalous lithium concentrations and generally contain

more illite than smectite. Nevertheless, some playa sediments have lithium concentrations as high as those in the proposed source rocks of the Esmeralda Formation. Considering this evidence, we believe that the hectorite in the playa sediments is authigenic rather than detrital.

PLUVIAL LAKES IN CLAYTON VALLEY

Many valleys of the Great Basin that now have dry playa surfaces or small lakes contained large lakes as deep as 650 ft (200 m) during pluvial periods (Meinzer, 1922; Snyder and others, 1964). However, there is no evidence for such a large lake in Clayton Valley during late Quaternary time; the prominent lower strandline (LS, Fig. 2) marks the maximum extent of the most recent lake in Clayton Valley. This strandline occurs at an approximate elevation of 4270 ft (1301.5 m), or about 4 ft (1.2 m) above the lowest surveyed location on the playa surface. There is also some evidence for a higher strandline (HS, Fig. 2) at an approximate elevation of 4350 ft (1326 m). This evidence consists of truncated patches of heavily weathered Quaternary alluvium, scattered deposits of lithoid tuff on bedrock, and slight slope changes and changes in drainage patterns on alluvial surfaces.

The correlation between the only radiometric date from the subsurface of Clayton Valley (Fig. 5) to nearby wells suggests that it may be possible to correlate the pluvial stratigraphy in Clayton Valley with that in Searles Valley, California (G. I. Smith, 1976a) and Lake Lahontan.

Nevada (Benson, 1978). Apparently the response of the hydrologic budget to Pleistocene climatic fluctuations in Clayton Valley was similar to the response in the other valleys even though the drainage basin of Clayton Valley is much smaller. Although local lithologies differ, lacustrine conditions during pluvial periods favored deposition of a central facies of green and black clayey marl or marly clay, while interpluvial conditions favored precipitation of various saline minerals and reworking and mixing of the marginal sediments with the central salt and mud facies.

If the correlation of these salt and mud cycles is correct, the upper salt bed in well CV5A was deposited since the last pluvial period ended about 10,500 years B.P. The underlying mud and salt sequence was deposited during the last pluvial period from 24,000 to 10,500 B.P. (Fig. 5). The low strandline (LS, Fig. 2) probably correlates with a Holocene (probably post-5000 B.P.) period of slightly increased precipitation, and the high strandline with the last pluvial period, from 11,000 to 13,500 B.P. (Fig. 5).

The strandline elevations and subsurface data were used to develop estimates of the lake depths and volumes (Fig. 6). The upper Quaternary section in well CV5A (Fig. 5) may be unusually thick near the normal faults that bound the northeastern arm of the playa, owing to faulting and subsidence, but away from the faults, the stratigraphy is apparently unaffected. The average depth to the base of the interpluvial salt beds in wells FM 1 and FM 4 (Fig. 5) was used to determine the depths of the two pluvial lakes, and lake areas were measured on topographic maps with a polar planimeter.

The formation and maintenance of pluvial lakes in Clayton Valley required certain changes in the hydrologic budget relative to today. Outflow of water from the valley takes place by evapotranspiration, while inflow is contributed by surface runoff and ground-water discharge. Present-day inflow appears to be much less than outflow, which suggests some ground-water recharge is derived from outside the Clayton Valley drainage basin, probably from Big Smoky Valley and Alkali Spring Valley (Rush, 1968). The formation of a pluvial lake would require inflow to exceed outflow. This might be accomplished through a combination of increased runoff and decreased evaporation (Snyder and Langbein, 1962; Brakenridge, 1978), or through increased ground-water recharge from outside the valley.

BRINE EVOLUTION

The most saline, lithium-enriched brine is in the down-faulted northeastern arm of the playa. Brine is produced primarily from a SE-dipping air-fall tuff bed or "ash aquifer." Although some brine was previously produced from the permeable salt beds overlying the ash aquifer, the practice was abandoned due to dissolution of the salt and collapse around the wells. The highest salinities and lithium concentrations are found where the tuff bed abuts the faults, which may be due to percolation of brine down the faults from the overlying strata. The sample collected from well CV5A represents the brine which saturates the ash aquifer; other playa brines and thermal waters sampled from the overlying strata also show anomalous lithium concentrations (Fig. 7).

The halite and gypsum beds in the playa sediments give direct evidence of high salinity levels during interpluvial periods. The most likely explanation for halite precipitation is evaporative concentration of pluvial lake water. Even if the cooler pluvial climate reduced the current pan evaporation rate of 9 ft (2.7 m) per year (National Oceanographic and Atmospheric Administration, 1974) by as much as 45% (Brackenridge, 1978) evaporation from a pluvial lake in Clayton Valley would have exceeded 0.05 mi³ (0.23 km³/yr), requiring that the total lake volume be replaced by inflow every 26 years. Thus, during the pluvial period from 13,500 B.P. to 11,500 B.P., the lake water might have been concentrated more than 100 times. During the onset of interpluvial conditions, the water would have been further concentrated as the lake receded. For example, drying the lake until it was only 20 ft (6 m) deep and the size of the present playa would yield a volume about one-tenth of the pluvial lake, for a final concentration factor of more than 1000 times.

When water is concentrated by evaporative processes, reactions at the sediment-water interface can change the composition of the evolving brine. After halite (NaCl) and gypsum (CaSO₄·2H₂O) precipitation, the proportions of sodium, chloride, calcium, and sulfate relative to the other ions in solution are decreased. The suggested authigenic formation of hectorite, Na₂(Mg, Li)₃Si₄O₁₀(F,OH)₂, in the playa sediments of Clayton Valley would reduce proportionately the constituent elements of hectorite in the residual fluid. These processes could cause the residual brine to have ionic ratios significantly different from those of the inflow. Li/Cl ratios have previously been used to assess the hypothetical potential of dilute waters as brine sources (C. L. Smith, 1976; White and others, 1976). It has been suggested that the water which was concentrated to form the brine pumped for lithium production in Clayton Valley had an original Li/Cl ratio near 0.01 (White and others, 1976). To date, the only analyzed waters having Li/Cl ratios in this range are dilute hot springs waters from Big Smoky or Alkali Spring Valleys (Fig. 7) and a sample of surface runoff from an exposure of the Esmeralda For-

Figure 6.—Pluvial lake dimensions, Clayton Valley, Nevada.

Age of Lake	Shoreline elevation	Depth	Area	Volume
Holocene (5000 B.P.)	4270 ft (1301.5 m)	35 ft (10.6 m)	39 mi ² (100 Km ²)	0.26 mi ³ (1.1 Km ³)
Late Wisconsin (13,500-11,000 B.P.)	4350 ft (1325.9 m)	190 ft (57.9 m)	74 mi ² (190 Km ²)	1.5 mi ³ (6.4 Km ³)

Figure 7.—Analyses of cold brines, thermal waters, and regional hot springs, Clayton Valley, Nevada.

[Locations shown on figure 4]

Well or Spring	Depth ft (m)	Temp. °C	pH	Conductivity (μmh cm ⁻¹)	mg/l										SO ₄	HCO ₃	F	Li/Cl
					Ca	Mg	Na	K	Li	SiO ₂	Cl							
A. COLD BRINES																		
CV1 ¹	137 (41.7)	18.0	7.7	28,000	420	190	6,500	400	23	60	11,000	460	930	0.8	.0021			
CV1 ¹	315 (96.0)	22.0	7.8	31,000	450	180	7,200	520	27	64	12,000	500	710	1.5	.0022			
CV2 ¹	173 (52.7)	21.0	8.0	29,500	170	100	7,200	720	29	74	11,000	570	1,040	2.6	.0026			
CV2 ¹	195 (59.4)	21.0	8.0	29,100	150	92	7,200	730	27	78	11,000	590	1,000	2.7	.0025			
CV4 ¹	415 (126.5)	22.0	7.7	99,000	660	240	31,000	3100	140	24	50,000	290	550	2.9	.0028			
CV5 ¹	235 (71.6)	22.0	8.0	27,500	120	41	6,000	490	26	34	10,000	550	580	1.8	.0026			
CV5A ¹	715 (217.9)	19.5	7.1	260,000	710	360	93,000	8000	320	11	150,000	6,600	650	0.5	.0021			
FM7 ²	700 (213.4)	19.4	7.3	75,500	840	400	20,000	2100	89	55	37,000	160	151	0.4	.0024			
B. THERMAL WATERS																		
CV2A ¹	195 (59.4)	38	8.0	37,500	240	30	8,400	850	38	53	15,000	510	320	4.9	.0025			
CV3 ¹	255 (77.7)	24	8.0	42,600	210	150	10,000	1000	43	59	16,000	840	660	1.9	.0027			
CV3 ¹	415 (126.5)	33	8.0	42,500	320	87	10,000	920	44	71	16,000	860	660	2.9	.0028			
CV4 ¹	575 (175.3)	28	7.9	52,000	330	88	13,000	1400	58	80	23,000	1,100	640	4.0	.0025			
CV4 ¹	795 (242.3)	36	7.8	51,000	270	78	13,000	1300	58	86	21,000	1,200	640	1.7	.0028			
Hot spring ₃ NW plays	—	—	—	—	443	64	9,220	934	38	—	13,700	500	—	—	.0024			
Hot spring ₂ NE plays	—	36.5	7.3	37,400	300	37	8,800	850	34	46	14,000	590	609	4.2	.0028			
C. REGIONAL HOT SPRINGS																		
Alkali Spring ⁴	—	32	—	1,700	—	—	305	—	2	—	100	—	—	—	.021			
Darrough ⁴	—	83	9.3	470	320	1.40	28	2.1	.37	140	40	—	—	8.0	.0093			

¹ Analyzed in the Denver laboratory of the U. S. Geological Survey, Water Resources Division.² Hans Claassen, 1974, (written communication).³ Data from Kunasz (1970, p. 114).⁴ Analyses by J. Crock and V. Merritt, U.S. Geological Survey, Denver, Colorado.

mation on the west side of the Silver Peak Range, which contained 1.4 ppm Li and an Li/Cl ratio of 0.03. Formation of a connate brine from any of these waters would require from several hundred to several thousand times concentration of the original water, which would leave large excesses of silica, lithium, magnesium, sodium and fluoride available for the formation of hectorite or other silicate phases (last line, Fig 8).

SUMMARY

The lithium-enriched brine in Clayton Valley is associated with late Cenozoic basin-filling sediments deposited during alternating lacustrine and sub-aerial conditions. Significant evaporative concentration of the lake waters

may have taken place both during the high stands of pluvial lakes, and during interpluvial lake recession. The ionic ratios of the brine were altered by evaporite precipitation and by silicate diagenesis or authigenesis so that the residual brine is significantly different from the apparent source waters. Regional thermal waters or surface runoff from tuffaceous Tertiary rocks may have provided these source waters. Although tuffaceous Tertiary volcanic and sedimentary rocks may have provided a source for the lithium, it is possible that no single outcrop area or volcanic unit contains high enough concentrations of lithium to account for the deposit by itself. The air-fall tuff bed that serves as the major aquifer for the brine is significant only as a unit with good reservoir characteristics and not as a lithium source. Late Cenozoic Basin and Range faulting

Figure 8.—Comparison of the brine from borehole CV5A with a hypothetical 3750x concentration of water from Darrough Hot Spring.

	Mg/L								
	Ca	Mg	Na	K	Li	SiO ₂	Cl	F	Li/Cl
Darrough hot spring ^{1/}	3.2	1.4	28	2.1	.37	140	40	8	.0093
Darrough hot spring X 3750	12,00	5,250	105,000	7,875	1,387	525,000	150,000	30,000	.0093
Borehole CV5A, 715 ft ^{1/}	<u>710</u>	<u>360</u>	<u>93,000</u>	<u>8,000</u>	<u>320</u>	<u>11</u>	<u>150,000</u>	<u>.05</u>	<u>.0021</u>
Difference	+11,290	+4,890	+12,000	-125	+1,067	+524,984	0	+30,000.00	+0.0072

^{1/}Data from Fig. 7.

has influenced the nature of the deposit because subsidence has caused high sedimentation rates in a local area of the playa, because the normal faults near the playa allowed brine to percolate downward to an adequate aquifer, and perhaps because major faults have served as conduits for regional thermal waters.

ACKNOWLEDGMENTS

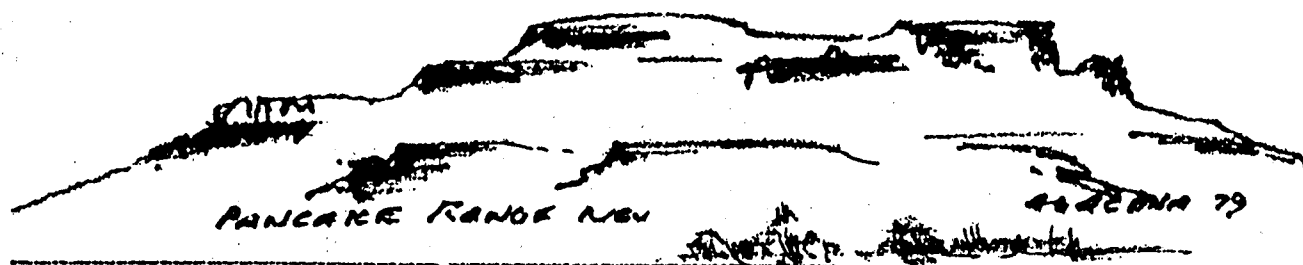
Geologic studies in the Clayton Valley area and U.S.

Geological Survey drilling projects in Clayton Valley were done with the permission and cooperation of Foote Mineral Company. Drilling was done under the terms of a cooperative agreement with the Division of Energy Storage Systems and the Division of Uranium Resources and Enrichment of the U.S. Department of Energy. In addition to the authors, R. K. Glanzman, R. G. Bohannon, E. F. Brenner-Tourtelot, H. D. Downey, and A. R. Wanek, all of the U.S. Geological Survey, assisted in data collection in Clayton Valley and adjacent areas.

REFERENCES CITED

- Albers, J. P., 1967, Belt of sigmoidal bending and right-lateral faulting in the western Great Basin: *Geol. Soc. America Bull.*; v. 78, p. 143-156.
- Albers, J. P., and Stewart, J. H., 1972, Geology and mineral deposits of Esmeralda County, Nevada: Nevada Bur. Mines and Geology Bull. v. 78, 80 p.
- Barrett, W. T., and O'Neill, B. J., Jr., 1970, Recovery of lithium from saline brines using solar evaporation, in Rau, J. L., and Dellwig, L. E., eds., Third symposium on salt: Northern Ohio Geol. Soc., v. 2, p. 47-50.
- Benson, L. V., 1978, Fluctuation in the level of pluvial Lake Lahontan during the last 40,000 years: *Quaternary Research* v. 9, p. 300-318.
- Brakenridge, G. R., 1978, Evidence for a cold, dry full-glacial climate in the American Southwest: *Quaternary Research*, v. 9, p. 22-40.
- Bucknam, R. C., and Anderson, R. E., 1979, Estimation of fault-scarp ages from a scarp-height-slope-angle relationship. *Geology*, v. 7, p. 11-14.
- Davis, J. R., 1979, Quaternary faulting in Clayton and Big Smoky Valleys, Nevada: (abs) *Geol. Soc. America Abstracts with Programs, Cordilleran Section*, v. 11, p. 74.
- Dole, R. B., 1912, Exploration of salines in Silver Peak Marsh, Nevada: *U.S. Geol. Survey Bull.* 530-R, p. 1-18.
- Ekren, E. B., Bucknam, R. C., Carr, W. J., Dixon, G. L., and Quintivan, W. D., 1976, East-trending structural lineaments in central Nevada: *U.S. Geol. Survey Prof. Paper* 986, p. 16.
- Keith, W. J., 1977, Geology of the Red Mountain Mining District Esmeralda County, Nevada: *U.S. Geol. Survey Bull.* 1423, p. 45.
- Kunasz, I. A., 1970, Geology and geochemistry of the lithium deposit in Clayton Valley, Esmeralda County, Nevada: Unpublished Ph. D. dissertation, Pennsylvania State University.
- , 1974, Lithium occurrence in the brines of Clayton Valley, Esmeralda County, Nevada in Coogan, A. H., ed., Fourth symposium on salt: Northern Ohio Geol. Soc., v. 1, p. 57-66.
- Locke, Augustus, Billingsley, P. R., and Mayo, E. B., 1940, Sierra Nevada tectonic patterns: *Geol. Soc. America Bull.*, v. 51, p. 513-540.

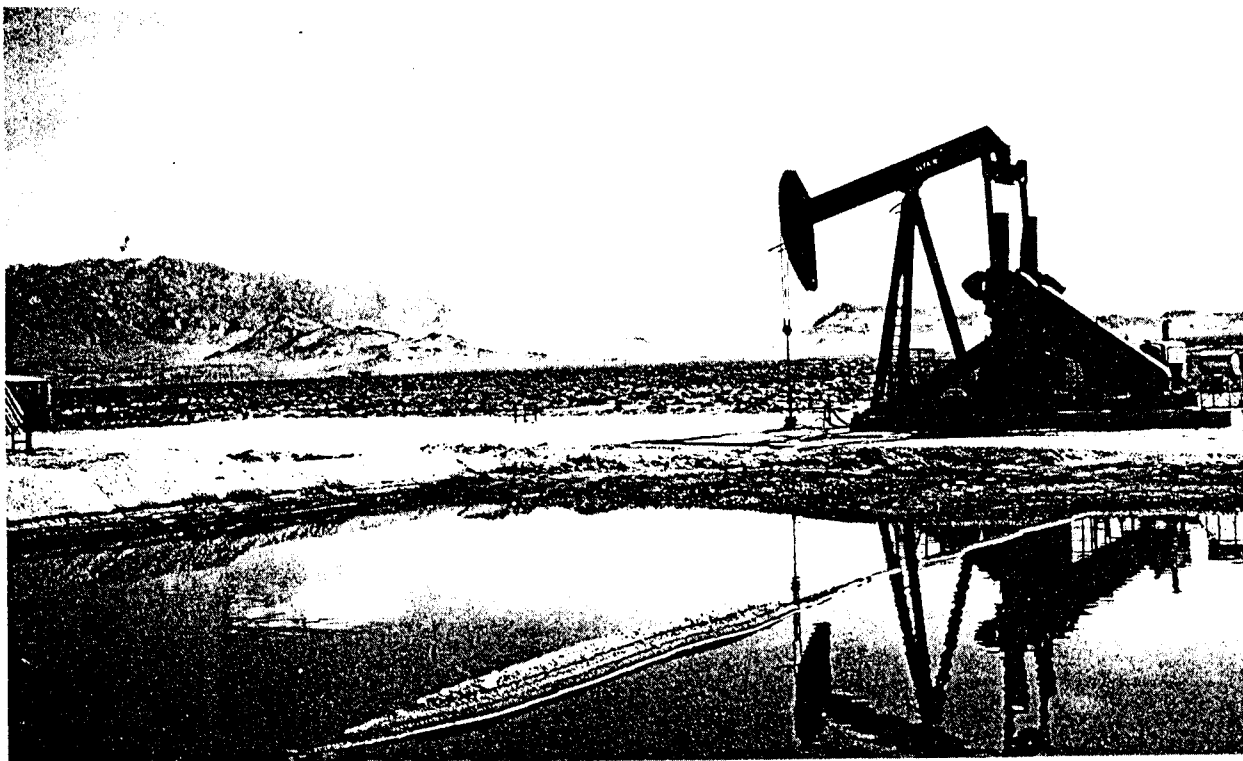
- Motts, W. S., and Matz, D. B., 1970, Reconnaissance geology of Clayton Playa, Nevada, Chapter 6, in Motts, W. S., ed. *Geology and hydrology of selected playas in the western United States*: U.S. Air Force Cambridge Research Laboratories, Hanscom Field, Bedford, Mass., Final report, Contract No. AFL 19 (628)-2486, p. 214-236.
- National Oceanic and Atmospheric Administration, 1974, *Climatological Data for Nevada, 1974*, v. 89, n. 1-13.
- Robinson, P. T., 1966, Zeolitic diagenesis of Mio-Pliocene rocks of the Silver Peak Range, Esmeralda County, Nevada: *Jour. Sed. Petrology*, v. 36, p. 1007-1015.
- , 1972, Petrology of the potassic Silver Peak Volcanic center, Western Nevada: *Geol. Soc. America Bull.* v. 83, p. 1693-1708.
- Robinson, P. T., McKee, E. H., and Moiola, R. J., 1968, Cenozoic volcanism and sedimentation, Silver Peak region, western Nevada and adjacent California: *Geol. Soc. America Mem.* 116, p. 577-611.
- Rush, F. E., 1968, Water-resources appraisal of Clayton Valley, Stonewall Flat area, Nevada and California: Nevada Department of Conservation and Natural Resources Water Resources Reconnaissance Series Report 45, 54 p.
- Shawe, D. R., 1965, Strike-slip control of Basin-Range structure indicated by historical faults in western Nevada: *Geol. Soc. of America Bull.* v. 76, p. 1361-1378.
- Smith, C. L., 1976, Use of lithium and chloride concentrations in ground water for lithium exploration: U.S. Geol. Survey Prof. Paper 1005, p. 103-105.
- , 1976a, Paleoclimatic record in the upper Quaternary sediments of Searles Lake, California, U.S.A., in Horie, S., ed., *Paleolimnology of Lake Biwa and the Japanese Pleistocene*, v. 4, p. 577-604.
- , 1976b, Origin of lithium and other components in the Searles Lake evaporites, California: U.S. Geol. Survey Prof. Paper 1005, p. 93-103.
- Snyder, C. T., Hardman, George, and Zdenek, F. F., 1964, Pleistocene lakes in the Great Basin: U.S. Geol. Survey Misc. Geol. Inv. Map 1-416.
- Snyder, C. T., and Langbein, W. B., 1962, The Pleistocene lake in Spring Valley, Nevada, and its climatic implications: *Jour. of Geophys. Research*, v. 67, p. 2385-2394.
- Stewart, J. H., 1967, Possible large right-lateral displacement along fault and shear zones in the Death Valley area, California and Nevada: *Geol. Soc. America Bull.* v. 78, p. 131-142.
- Turner, H. W., 1900, The Esmeralda Formation, a fresh water lake deposit: U.S. Geol. Survey Ann. Report 21, part 2, p. 191-208.
- Wallace, R. E., 1977, Profiles and ages of young fault scarps, north its climatic implications: *Jour. of Geophys. Research*, v. 67, p. 2385-2394.
- White, D. E., Thompson, J. M., and Fournier, R. O., Lithium content of thermal waters: U.S. Geol. Survey Prof. Paper 1005, p. 58-60.
- Wilson, C. W., 1975, Bouguer gravity map of Clayton Valley, Nevada: U.S. Geol. Survey Open-File Report 75-333.



557.473
B2.92

BASIN AND RANGE SYMPOSIUM

AND GREAT BASIN FIELD CONFERENCE



Northwest Exploration = 1 Currant, Nye County, Nevada. View is northeast toward the town of Currant. The mountain at the left is the ridge of Paleozoics which includes White Pine Peak, Currant Mountain, and Duckwater Peak, and is part of the Grant Range. Photo by Jack Rathbone.

GARY W. NEWMAN

HARRY D. GOODE

Editors

ROCKY MOUNTAIN ASSOCIATION
OF GEOLOGISTS
1615 California Street
Denver, Colorado 80202

UTAH GEOLOGICAL
ASSOCIATION
P.O. Box 11334
Salt Lake City, Utah 84147

1979

25.14.53.14.0774 127 13 121 13 121 13 121

HAZEN RESEARCH, INC.

Property of Library
Bureau of Mines
Albany, Oregon

U. S. BUREAU OF MINES
Western Field Operations Center
East 360 3rd Ave.
Spokane, Washington 99201

Item 23

19 of 21

4601 INDIANA STREET
GOLDEN, COLORADO • 80401
TELEPHONE 303/270-4501

HRI Project 1370
Copy No. 32

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

February 4, 1975

Prepared by:

C. E. Berthold

C. E. Berthold
Senior Research Engineer

Pablo Hadzeriga

Pablo Hadzeriga
Senior Research Engineer

David H. Christopher

David H. Christopher
Senior Analytical Chemist

Thomas A. Applegate

Thomas A. Applegate
Research Engineer

Daniel M. Gillespie

Daniel M. Gillespie
Research Engineer

Approved by:

F. M. Stephens, Jr.

F. M. Stephens, Jr.
Vice President

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

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

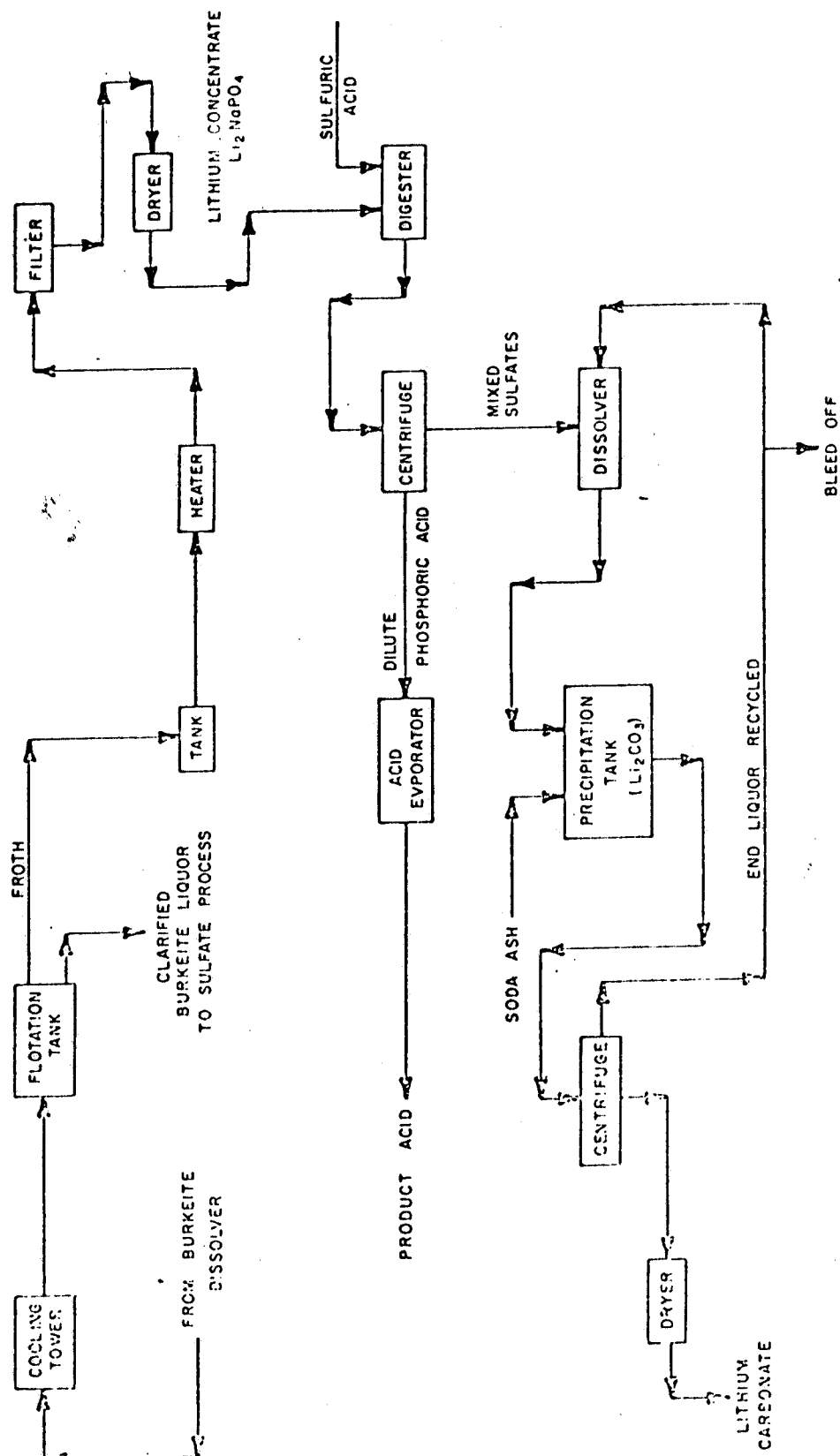


FIGURE 33
hri

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.

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.

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	<u>0.007%</u>
	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

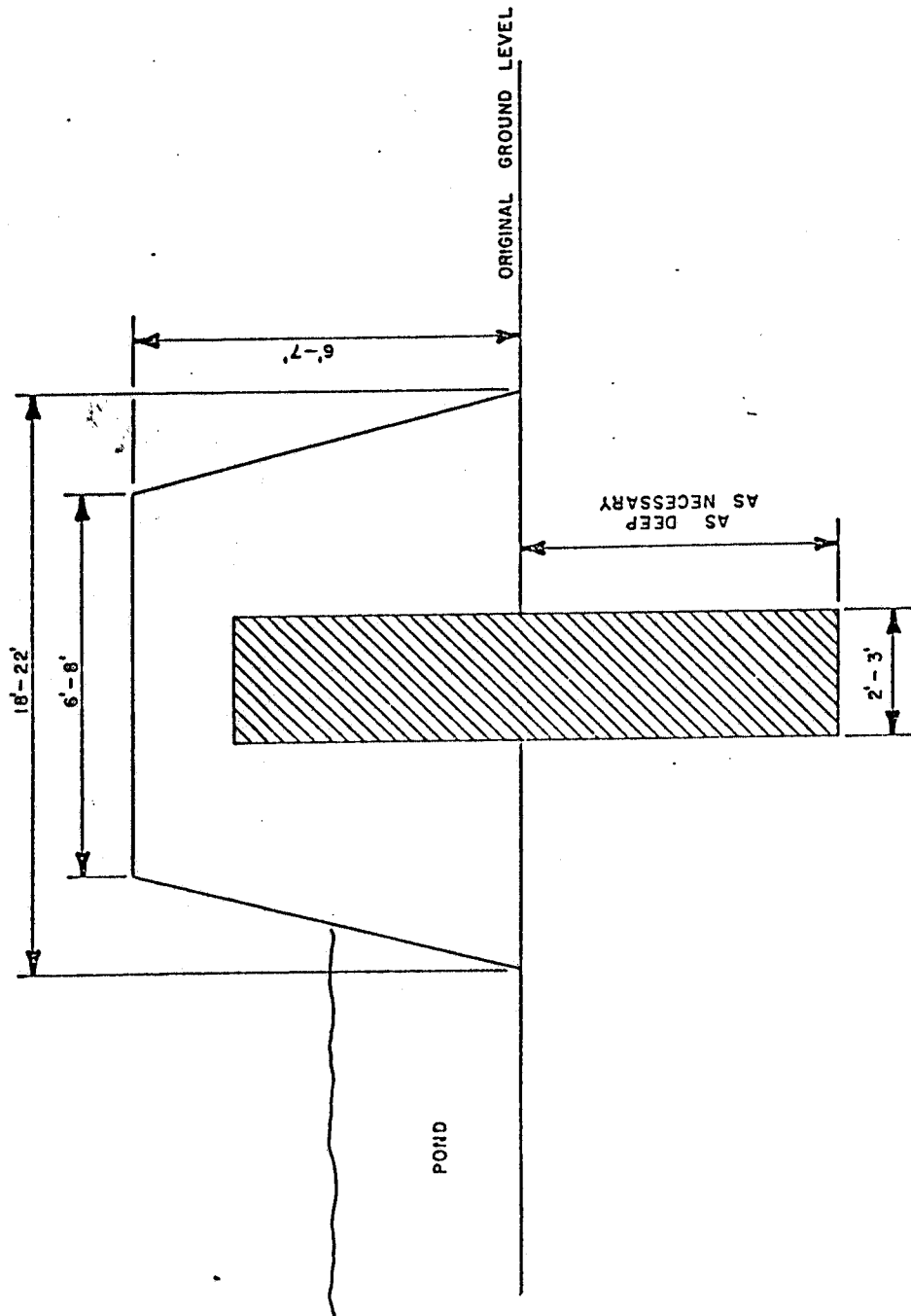


FIGURE 2
hri

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

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 ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), 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.

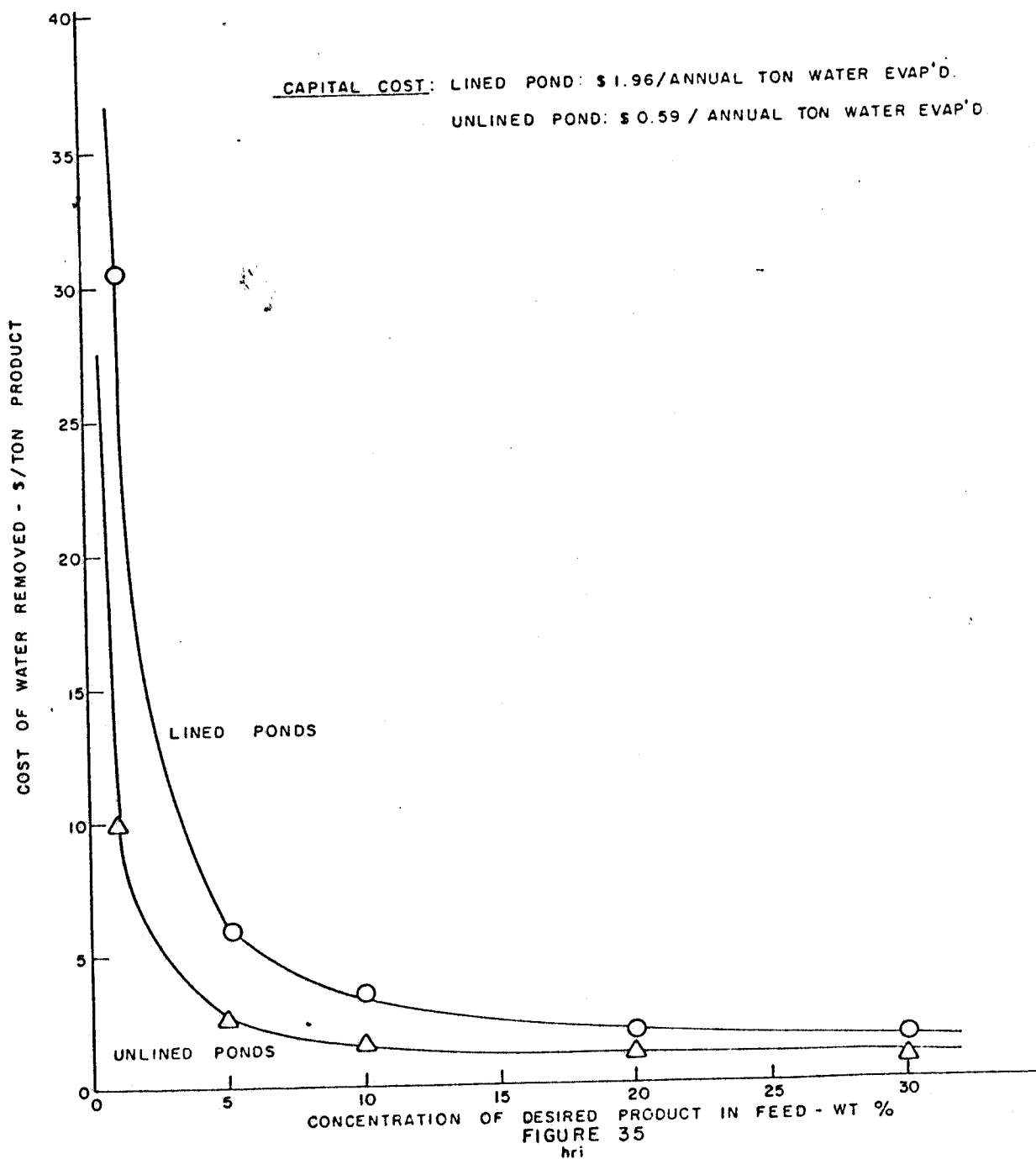
In order to quantify the costs involved in removing water by these two methods, we have postulated an evaporation system capable of removing 15×10^6 tons/year of water (3600×10^6 gal/year) from geothermal fluids and calculated the cost of water removed per ton of desired product as a function of the 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. Lof 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.

1972 COSTS

SOLAR POND EVAPORATION COSTS



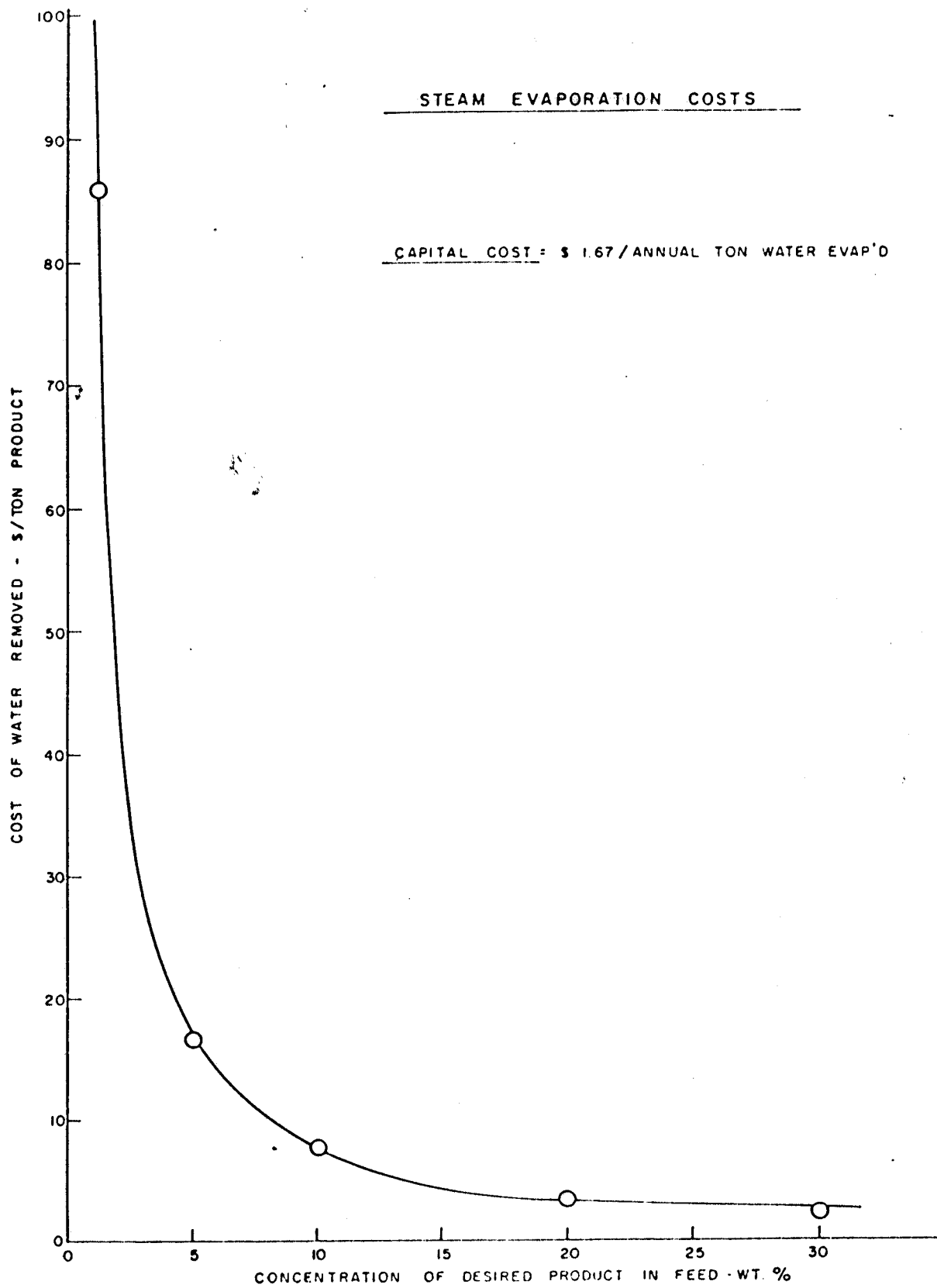


FIGURE 34
hrl

SUMMARY OF BRINE EVAPORATION COSTS

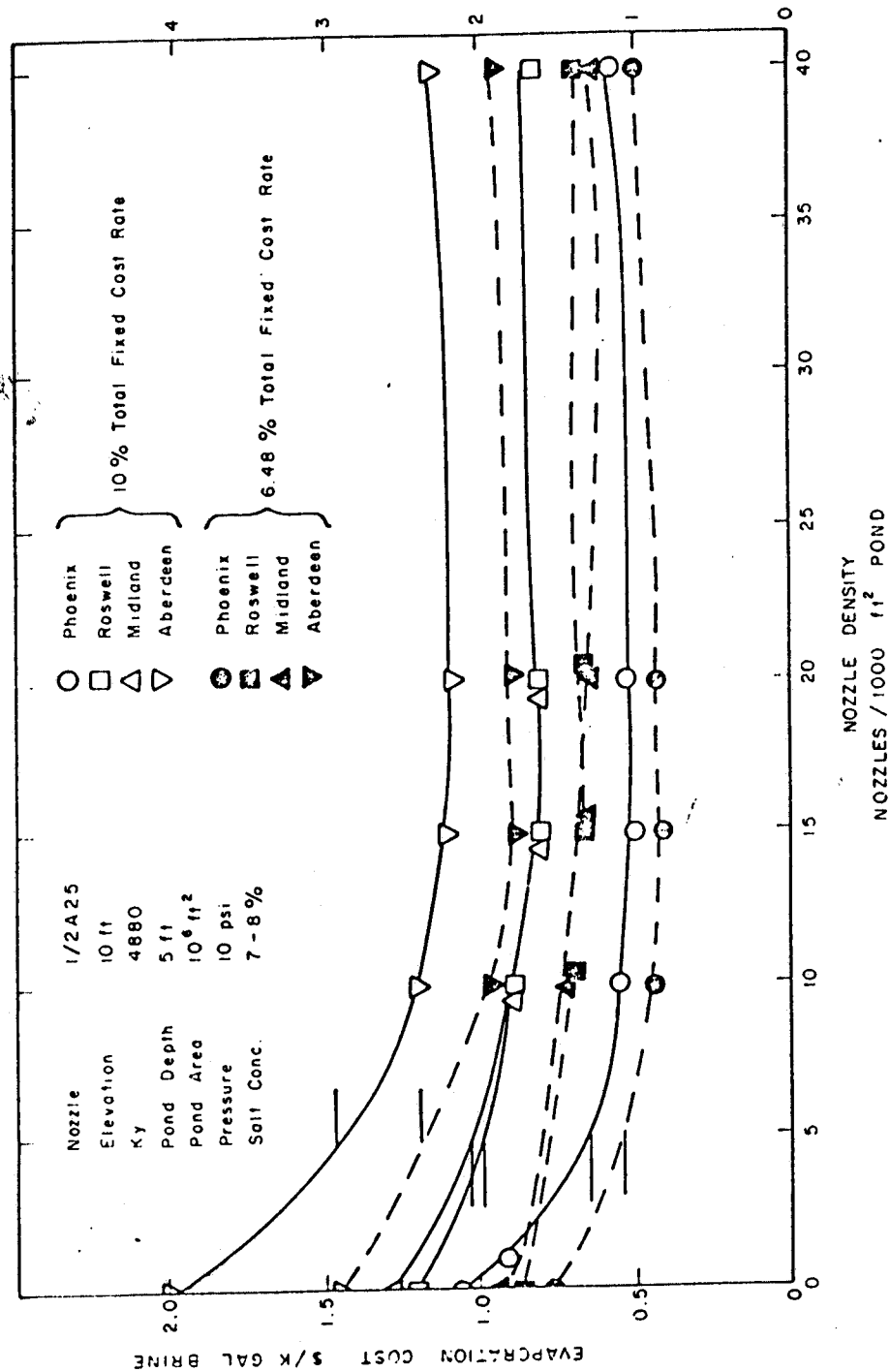


FIGURE 36
hri

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 captured 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.

SOLAR EVAPORATION COSTSBasis:

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 = \$1.96, lined ponds
of water evaporated = \$0.59, unlined ponds

Operating Costs: Basis, 330 days/year operation

	<u>Cost/day</u>	<u>Cost/year</u>
<u>Labor:</u> 1 man/day @ \$5.50/hr x 8 hr/day	\$ 45.00	\$ 14,500
<u>Supervision:</u> 30% of labor	15.00	4,950
<u>Fringes:</u>	18.00	5,940
Sub Total	\$ 78.00	\$ 25,390
<u>Overheads:</u> 50% of above	\$ 39.00	\$ 12,700
	\$ 117.00	\$ 38,090
<u>Operating Supplies:</u>	\$ 10.00	\$ 3,300
<u>Utilities:</u>		
Power costs, assumed pumping costs	\$ 151.50	\$ 50,000
<u>Maintenance</u>		
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	<u>\$ 534</u>	<u>\$ 176,200</u>

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	<u>\$ 2,670</u>	<u>\$ 881,000</u>

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

LITHIUM RECOVERY FROM GEOTHERMAL FLUIDS¹

By C. E. BERTHOLD, HAZEN RESEARCH, INC., GOLDEN, CO, and
D. H. BAKER, JR., U.S. BUREAU OF MINES, BOULDER CITY, NV

ABSTRACT

The lithium resource of the Imperial Valley, Salton Sea KGRA (Known Geothermal Resource Area), in southern California, appears to be of significant size, comparable to the Clayton Valley, Nevada, lithium reserve in quantity of contained lithium.

Lithium occurs, presumably as lithium chloride, in amounts of about 200 ppm (as Li) in the geothermal fluids obtained from depths of 5,000 feet or more (as typified by Sinclair No. 4 fluid).

Recovery of lithium from this resource can be achieved by chemical concentration (precipitation) techniques and ion-exchange methods, both liquid and solid, among others.

The paper will discuss in general terms the studies undertaken and preliminary results obtained in attempting to recover lithium from this resource.

INTRODUCTION

Geothermal fluids from various sources in the Western United States contain quantities of lithium ranging from the low parts per million level to concentrations of hundreds of parts per million (ppm). Some of these geothermal resources can be considered to be significant, if not major, resources or reserves of lithium.

In some studies on recovery of mineral values from geothermal fluids for the U.S. Bureau of Mines, a sampling survey was made of several hot springs and geothermal sites in the Western United States. Table 22 presents a summary of the lithium content found in some of these geothermal fluids and hot springs waters. As can be seen, the geothermal fluids of the Salton Sea Known Geothermal Resource Area (KGRA), Imperial

County, Calif., contain significant concentrations of lithium. Lithium reserves within this KGRA site have been compared in quantity with those of the Clayton Valley, Nevada, area, that is, approximately 40,000 tonnes of contained lithium (Kunasz, 1975).

The lithium content of the Salton Sea geothermal fluids appears to vary, both with respect to location within the reservoir and depth of the producing zone. As an example, Magmamax No. 1 well produces brine from the 2400-foot level and has a lithium content of about 150 ppm with a total salinity of approximately 180,000 ppm. Contrasted to this geothermal fluid are those of Sinclair No. 4 brine (well located one mile south of Magmamax No. 1) at 5400-foot depth, with over 200 ppm lithium and a total salinity of nearly 300,000 ppm. Figure 22 shows the locations of these geothermal wells in the Imperial Valley area.

Lithium occurs in the Salton Sea KGRA fluids, presumably as lithium chloride, since the predominant anion is chloride, with small amounts of bromide, fluoride, and sulfate also present. The major cations present in these geothermal fluids are sodium, calcium, potassium, and ammonia, with minor amounts of magnesium, rubidium, and cesium also present. Table 23 presents a partial analysis for Mesa, Sinclair, and Magmamax geothermal fluids, together with a comparison of lithium-sodium and lithium-calcium ratios for these geothermal fluids with other naturally occurring saline brines.

It appears that brine from Mesa L-6-1 well at the southern fringe of the Salton Sea KGRA is considerably higher in Li/Ca ratio as compared to other geothermal fluids found in this KGRA. Whether this implies a different source for this fluid or a different subsurface rock matrix that supplies the lithium for this fluid is not known. In any event, recovery of lithium from Mesa L-6-1 fluid would appear to be somewhat easier than from either Sinclair No. 4 or Magmamax No. 1, owing to the relatively higher lithium level with respect to the other salines present.

Recovery of lithium from such naturally occurring geothermal fluids is complicated by several factors: (1) relatively low concentration in the fluid, (2) high temperature of the fluid, and (3) presence of relatively large amounts of other potentially valuable minerals such as iron, manganese, silica, zinc, lead, barium, strontium, and magnesium. In general, geothermal fluids from the

TABLE 22.—Lithium contents of selected geothermal fluids and hot spring waters¹

Location	Lithium concentration (ppm Li)
Mesa L-6-1, Imperial County, Calif., pre-flash, 8,000-ft depth	55
Magmamax No. 1, Imperial County, Calif., pre-flash, 2,400-ft depth	145
Sinclair No. 4, Imperial County, Calif., post-flash, 5,400-ft depth	258
Coso Hot Spring, Inyo County, Calif., average of published analyses	Trace to 0.1
Darrrough Hot Springs, Nye County, Nev., post-flash	0.06
Gokunda Hot Springs, Humboldt County, Nev., No. 1	0.45
No. 2	1.0
Beowawe Steam Well, Eureka County, Nev., post-flash	3.3

¹From work performed by C. E. Berthold and others, June 1973 for the U.S. Bureau of Mines under contract No. SO 133084, Process Technology for recovering geothermal brine minerals.

²The data and results presented herein were obtained during the performance of work for the U.S. Bureau of Mines under contracts SO 133084 and HO 144104. The views and conclusions presented herein should not be interpreted as necessarily representing the official policies or recommendations of the Interior Department, Bureau of Mines, or of the U.S. Government.

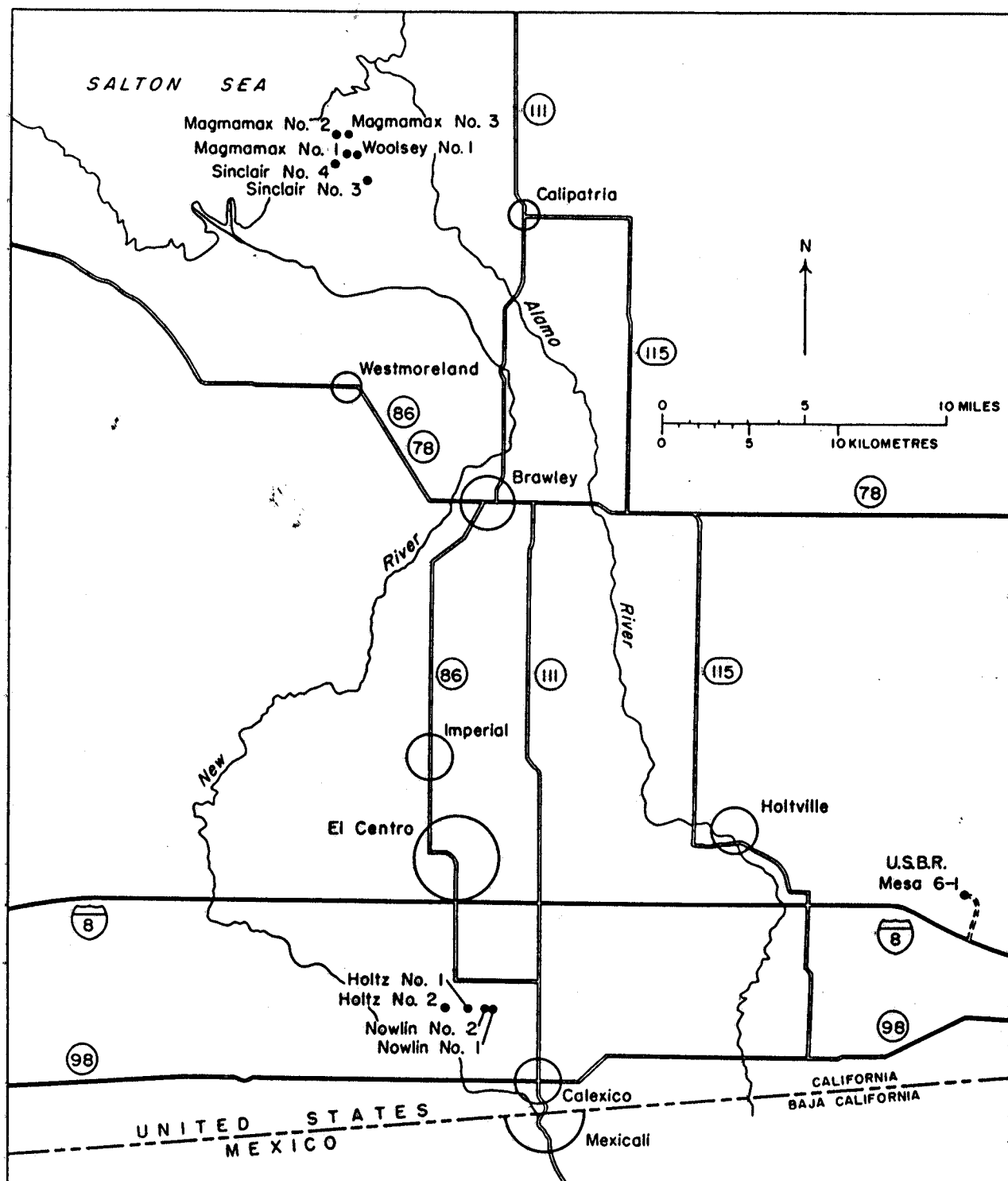


FIGURE 22.—Imperial Valley geothermal area showing location of geothermal wells, highways, and cities.

Salton Sea KGRA require clean-up, or removal and perhaps recovery, of the silica, iron, manganese, lead, zinc, and magnesium therefrom prior to recovery of the lithium values.

RECOVERY METHOD

Recovery methods for lithium contained in solution can be broadly categorized into two general schemes: (1)

TABLE 23.—Analyses, in ppm, of geothermal fluids

Sample	Br	Cl	Na	Ca	K	Mg	NH ₄	Li	F	SO ₄	Li/Na	Li/Ca
Mesa 1-6-1	35	18,000	11,000	1,370	1,430	22	39	55	1.5	16	0.005	0.04
Sinclair No. 4	162	186,000	71,000	35,000	18,000	152	611	238	5.8	42	.003	.007
MagmaMax No. 1	109	102,000	44,000	21,000	8,500	100	504	143	4.6	50	.003	.007
Clayton Valley, Nev.0045	.6
Searles Lake, Calif.007	No Ca present

direct recovery from the brine via liquid (Baniel and Blumberg, 1963; Fletcher and Wilson, 1961; Grinstead and Davis, 1970; Morris and Short, 1963; Morrison and Freiser, 1962; various patents² and written communications³) or solid ion exchange (Kennedy, 1961) and (2) removal of the lithium by precipitation as an insoluble compound or double salt.

In discussing methods of lithium recovery from geothermal fluids, it should be kept in mind that such recovery processes are secondary to the original intent behind the development of geothermal resources, namely power generation and production of freshwater.

Whatever method or methods are used to recover lithium from such resources must be adaptable to the constraints imposed upon geothermal wells. These are:

1. The almost universally accepted belief that waste geothermal fluids must be reinjected back into the producing structure to maintain hydraulic balance and prevent ground surface subsidence. Alternatively, fresh or brackish water, if available, could be used as a substitute fluid, thus allowing some concentration of the geothermal fluid, if this would aid in recovering some of the constituents from the geothermal fluid.
2. Whatever methods or means used for lithium recovery must be compatible with the need for geothermal fluid reinjection. That is, no material should be present that might precipitate out in the subsurface structure, thereby leading to plugging-off of the aquifer(s). The presence of organic compounds, such as might result from liquid ion-exchange methods of lithium recovery, constitutes yet another unknown if reinjected back into the producing zone.

Keeping these constraints in mind, a series of laboratory studies on lithium recovery was started, using Sinclair No. 4 geothermal fluid as the raw material.

Post-flash Sinclair No. 4 geothermal fluid required a "clean up" treatment to remove soluble silica, iron,

manganese, zinc, and lead prior to lithium removal. This was achieved by adjusting pH to a nominal value of 7.5 to 8.0 and removing the precipitated hydroxides, together with adsorbed zinc and lead values. At this point, the purified Sinclair No. 4 fluid can be used directly for lithium recovery or else concentrated (using steam evaporation or solar evaporation), if such concentration is deemed necessary and/or desirable.

Our studies utilized both types of Sinclair No. 4 geothermal fluid, post-flash and concentrated. Figure 22A illustrates the behavior of lithium in post-flash Sinclair No. 4 fluid, during the course of concentration by simulated solar evaporation. Using magnesium as a tracer element to follow the course of evaporation, it appears that no lithium is lost from solution up to a concentration ratio in excess of 5.

The limiting factor in degree of solution concentration becomes saturation with respect to the calcium chloride content of the geothermal fluid. Further concentration of Sinclair No. 4 fluid results in crystallization of large quantities of calcium chloride hexahydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) which entrains significant quantities of the valuable, concentrated, lithium-bearing fluid.

While much has been published in the literature and in the patent files regarding recovery of lithium values from solution, our studies have indicated that precipitation of lithium values as the aluminate complex to be the most effective.

Organic solvents such as butyl and amyl alcohols, have been used to selectively dissolve away lithium chloride from mixtures of alkali metal chlorides (Lindal, 1970; Morrison and Freiser, 1962). Alcohol-ketone mixtures have been used to extract lithium from brines, but urea or ammonia additions are required to prevent calcium interference⁴. Lithium Corporation of America has patented a process⁵ where lithium is extracted as a complex lithium tetrachloroferrate, but this scheme requires pretreatment of the lithium-containing fluid with both hydrochloric acid and ferric chloride to establish proper operating conditions.

In addition, the application of liquid or solid ion-exchange techniques to such hot saline fluids ($T \geq 110^\circ\text{C}$)

¹Israel patent 16017, and U.S. patents numbered 3,307,922; 2,964,381; 3,306,700, U.S. Department of Commerce, Patent and Trademark Office, Washington, D.C.

²C. Hanson, 1970 written commun., "Extraction of magnesium chloride from brines using mixed ionic extractants," University of Bradford, Bradford, York. W. C. Keder, 1970, written commun., from Kedder and others, "Separation of alkali metals by solvent extraction with mixtures of organic-soluble acids and phenols," Battelle Pacific Northwest Laboratory, Richland, Washington. R. L. Focht and others, 1961, oral commun., "Separation of lithium aluminate" paper presented at the Pittsburgh Conference on analytical chemistry, Pittsburgh, Penn., 1961.

⁴U.S. patent, 3,307,922, U.S. Department of Commerce, Patent and Trademark Office, Washington, D.C.

⁵U.S. patent, 3,537,813, U.S. Department of Commerce, Patent and Trademark Office, Washington, D.C.

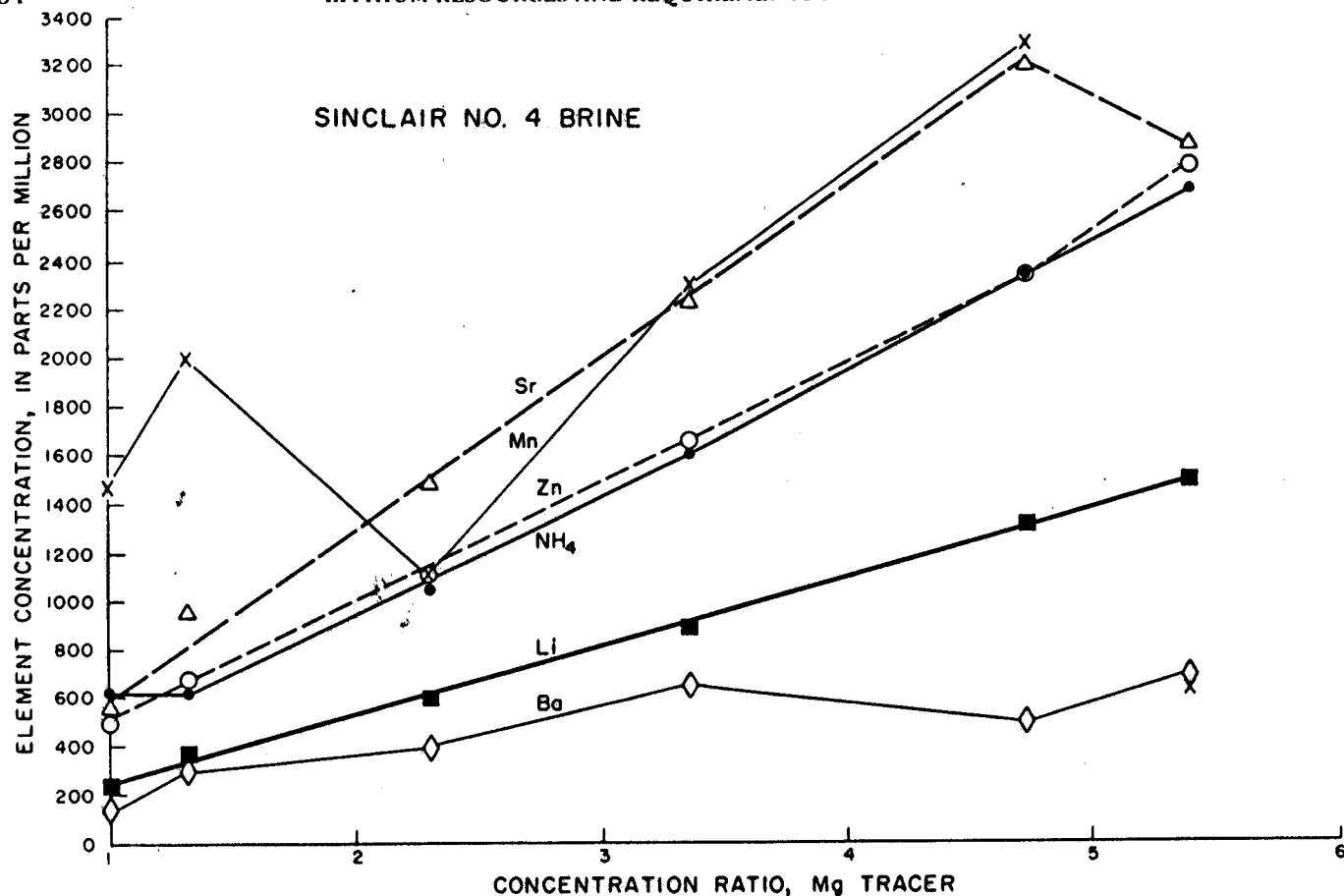


FIGURE 22A.—Behavior of lithium and other elements during concentration by evaporation.

leads to problems regarding solvent degradation and losses due to evaporation of the carrier solvent, while ion-exchange resins are subject to dehydration and shrink-swelling fracturing with consequent destruction of the resin beads.

The preferred method for lithium recovery from Sinclair No. 4 geothermal fluid is the precipitation as a complex lithium aluminate using either freshly precipitated aluminum hydroxide or in-situ precipitation of aluminum hydroxide via aluminum chloride with pH control.

Ratios of concentration in excess of 150 have been obtained by this method with lithium recoveries in excess of 98 percent. Figure 23 presents data on lithium recovery versus mole ratio of aluminum to lithium used to effect the precipitation. Apparently the optimum Al/Li ratio for 98+ percent lithium recovery is about 2.75/1. Precipitation temperature for these results was in the 75°C–85°C range.

Control of pH is critical to achieve maximum lithium recovery, with a range of 5.5 to 8.2 appearing to be optimum for Sinclair No. 4 brine as shown in figure 24. This pH range is somewhat different than that called for in the literature and is probably dependent to some

degree on the composition of the fluid used. For example, R. L. Focht (1961, oral commun.) recommends a pH range of 10 to 12.5 as being optimum for maximum lithium extraction.

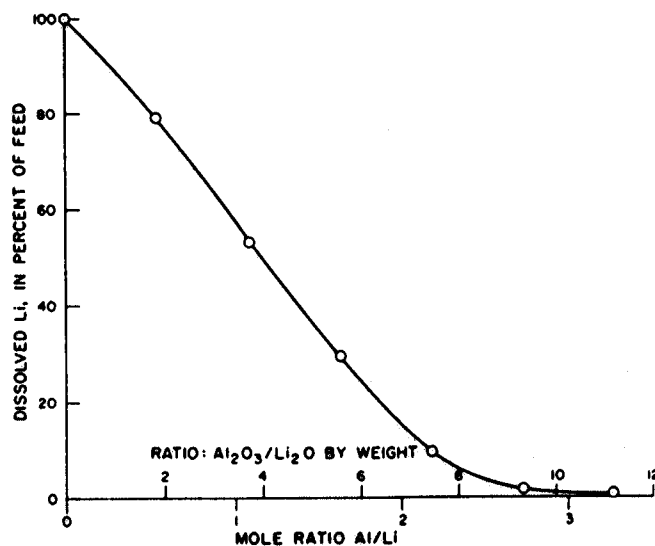


FIGURE 23.—Effect of Al:Li ratios on lithium recovery.

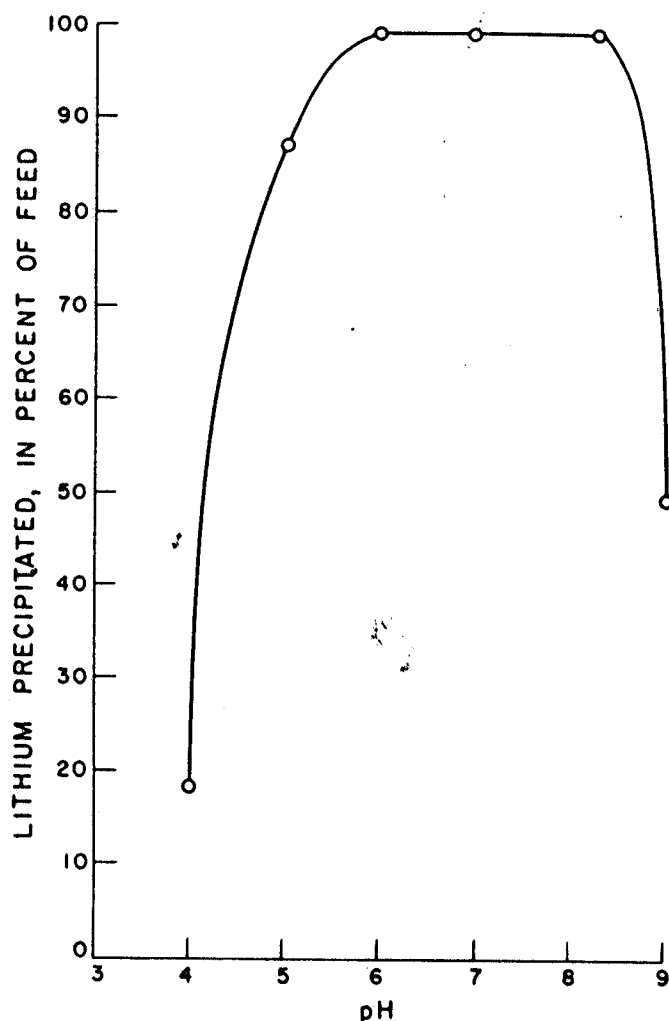


FIGURE 24.—Effect of pH on precipitation of lithium with aluminum hydroxide.

A major difficulty associated with the aluminate method of lithium recovery is the gelatinous nature of the precipitate formed. This is probably due to the high mole ratio of aluminum to lithium used in previous work. In addition, pH of precipitation exerts a profound effect on the settling characteristics of the precipitate as shown in figure 25.

Optimum pH of precipitation for maximum settling rate appears to be about 8.3, using an Al/Li ratio of 4/1. However, a pH of 8.3 is just outside the optimum pH range for maximum lithium recovery.

Using an aluminum to lithium ratio of 3/1 and a precipitation pH of 7.5 resulted in both maximum lithium recovery and a reasonably rapid settling precipitate as shown in figure 26.

In conclusion, it should be noted that the conditions outlined for maximum lithium recovery from Sinclair No. 4 geothermal fluid may not be optimum for other

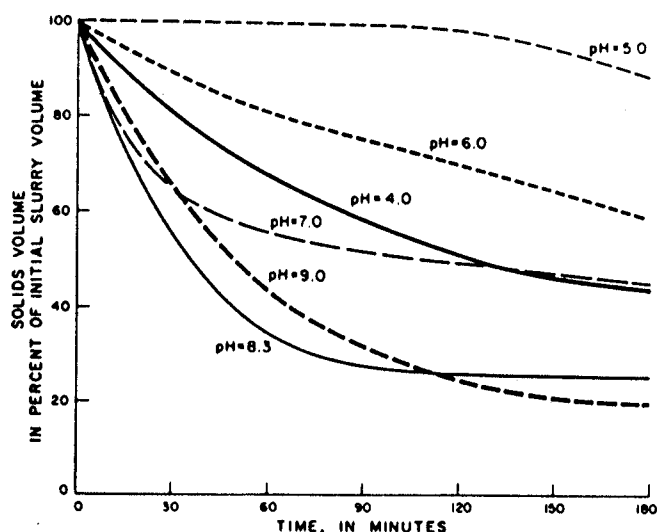


FIGURE 25.—Settling data for aluminum (lithium) hydroxides.

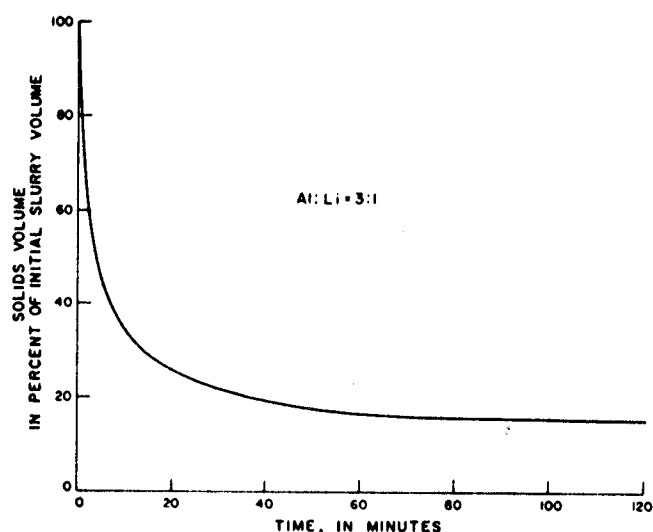


FIGURE 26.—Settling curve—aluminum (lithium) hydroxide at pH=7.5.

geothermal fluids. A properly planned experimental program should enable one to determine optimum lithium recovery conditions for each type of lithium-containing fluid.

REFERENCES CITED

- Baniel, A., and Blumberg, R., 1963, Concentration of aqueous solutions by liquid-liquid extraction: London Indust. Chem., v. 39, p. 460.
- Fletcher, A. W., and Wilson, J. C., 1960-61, Naphthenic acid as a liquid-liquid extraction reagent for metals: Inst. Mining and Metallurgy Trans., v. 70, p. 355.
- Grinstead, R. R., and Davis, J. C., 1970, Extraction by phase separation with mixed ionic solvents: Indust. Eng. Chem., v. 9, no. 1, p. 66.
- Kennedy, A. M., 1961, The recovery of lithium and other minerals