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Recovering Lithium Chloride From a Geothermal Brine

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UNITED STATES DEPARTMENT OF THE INTERIOR

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CONTENTS

ILLUSTRATIONS

TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree celsius	mg	milligram
d	day	mg/L	milligram per liter
ft	foot	min	minute
g	gram	mL	milliliter
g/L	gram per liter	MW	megawatt
gal	gallon	pct	percent
gpd	gallon per day	ppm	part per million
h	hour	tpd	ton per day
L	liter	tpy	ton per year
lb/h	pound per hour	yr	year

RECOVERING LITHIUM CHLORIDE FROM A GEOTHERMAL BRINE

By L. E. Schultze[1] and D. J. Bauer[2]

ABSTRACT

The Bureau of Mines has devised techniques to recover lithium from geothermal brines as the chloride. More than 99 pct of the lithium was precipitated from a brine containing 170 mg/L Li by adding a solution of $AlCl_3$ and increasing the pH to 7.5 with lime slurry. The Li-Al precipitate was dissolved in HCl and sparged with gaseous HCl to recover the $AlCl_3$; this resulted in a solution containing LiCl and $CaCl_2$. The solution was evaporated at 100° C to obtain a mixture of the chlorides from which 97 pct of the lithium was recovered and 90 pct of the calcium was rejected by leaching with tetrahydrofuran. The LiCl recovered by evaporation of the tetrahydrofuran was purified by dissolution in water and treatment with oxalic acid. The final LiCl solution contained 89 pct of the lithium originally present in the brine and had a purity of 99.9 pct.

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INTRODUCTION

A potentially large, new industry based on using geothermal brines as an energy source is emerging. Extensive research has been carried out during the last decade to develop techniques for using geothermal brines for heating, drying, and generating electricity. Published research deals with specific industrial problems, such as reservoir assessment, scaling, and corrosion, and includes Bureau of Mines studies of corrosion in high-salinity brines (1-2).[3]

Since some of the high-salinity geothermal reservoirs represented a potential source for byproduct metals recovery, Bureau of Mines in-house and contract studies were initiated to evaluate the potential of the resource and to devise techniques for recovering contained metal values. The studies utilized geothermal brines from the Imperial Valley of California because the reservoirs represented the highest metal contents of the resources under development. One of the contract studies suggested a total-use concept that proposed making high-value products on site from lower value materials recovered from the brine (3). The concept was incompatible with energy recovery systems being developed and was not pursued. Another contract study suggested techniques for precipitating Fe, Mn, Pb, and Zn from the brines as hydroxides (4). An engineering study was done to design a demonstration plant (5), and a mineral recovery unit (MRU) was assembled and operated (6). Increasing the pH of the brine from 5.5 to 8.5 by adding 20 pct lime slurry precipitated 95 pct of the Fe, Mn, Pb, and Zn. The precipitated hydrous oxides were recovered by thickening and filtration. Bench-scale evaluations of the precipitates showed that they contained 55 to 60 pct water, 20 to 25 pct soluble salts, and 15 to 20 pct hydrous metal oxides.

Another metal having potential value is lithium, which is used by the aluminum, air conditioning, ceramics, grease, specialty glass, synthetic rubber, thermoplastic, and primary battery industries. The United States is the world's primary producer and consumer of lithium minerals and chemicals and supplies three-fourths of the demand of nonproducing countries (7). Increasing demand for lithium is evidenced by the fact that one of the two domestic producers recently entered into a partnership to develop a lithium resource in Chile.

Geothermal brines from the Niland and South Brawley reservoirs of the Imperial Valley contain from 150 to 400 ppm Li. Since a 100-MW powerplant, after steam recovery, would generate an estimated 7.5 million lb/h of brine, between 5,750 and 15,000 tpy Li could be produced based on 90-pct recovery and 300 24-h days of operation. The resource is capable of supporting between 1,600 and 5,200 MW of power generation by the year 2000 (8). Two 20-MW demonstration plants are operational, and a 50-MW plant is under construction.

A method for precipitating lithium from the brines was provided by one of the contract studies (9). The method employed addition of aqueous $AlCl_3$ and pH adjustment to precipitate mixed Li-Al hydrous oxides. The contract was limited to lithium precipitation and did not treat the precipitated lithium. A study of lithium recovery from Dead Sea brines also used aqueous $AlCl_3$ addition to precipitate lithium and solvent extraction with alcohols to recover the lithium (10). Since the alcohol solvent extraction method used for Dead Sea brines was inefficient owing to low distribution coefficients and high aqueous solubility of the extractants, a study was initiated to devise improved methods for recovering a LiCl product. This report presents the results of the study and a suggested flowsheet for lithium recovery from a geothermal brine.

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

EQUIPMENT, MATERIALS, AND PROCEDURES

Lithium precipitation studies used brine being sent to the injection well of a power generation test facility in the Imperial Valley. The production well was located near the southern end of the Salton Sea (fig. 1) and drew brine from the Niland Reservoir. The brine was concentrated by removing 25 to 33 pct of its mass as steam in the power generation facility and had the analysis shown in table 1. All other cations were present at concentrations of less than 50 mg/L.

Table 1. - Concentrations of selected components in a typical brine, mg/L

Na	58,000	SiO_2	230
Ca	25,000	Fe	190
K	12,000	Li	170
Mn	680	Ba	115
Sr	520	Mg	84
Zn	270	Pb	49
B	250		

Precipitation tests were performed with standard bench-scale equipment and reagent-grade chemicals. Brine samples were treated with lime at pH 8.5 and filtered to remove Fe, Mn, Pb, and Zn before lithium precipitation. Solutions were analyzed by atomic absorption (AA) or inductively coupled plasma (ICP). Analyses by both methods agreed, although ICP gave lower detection limits. Precipitates were analyzed by dissolution in an excess of HCl. The final volumes were measured, and the solutions were analyzed by AA or ICP. Acid-insoluble residues were filtered, washed, dried, and weighed. Emission spectroscopy showed that the residues were silica.

Large-scale precipitation tests were performed at the well site. The equipment and operating procedures are discussed under "Results and Discussion." The tests used commercial lime and aluminum chloride hexahydrate (ACH), which was precipitated by sparging with gaseous HCl and washed with concentrated HCl. Test samples, including portions of the Li-Al precipitate, were shipped to the Bureau's Reno Research Center for analysis. Part of the study on Ca-Li separation used synthetic mixtures prepared from reagent-grade chlorides. Analyses of salts dissolved in tetrahydrofuran (THF) were accomplished by diluting the solution with an equal volume of water, evaporating to the original volume, and analyzing the aqueous solutions.

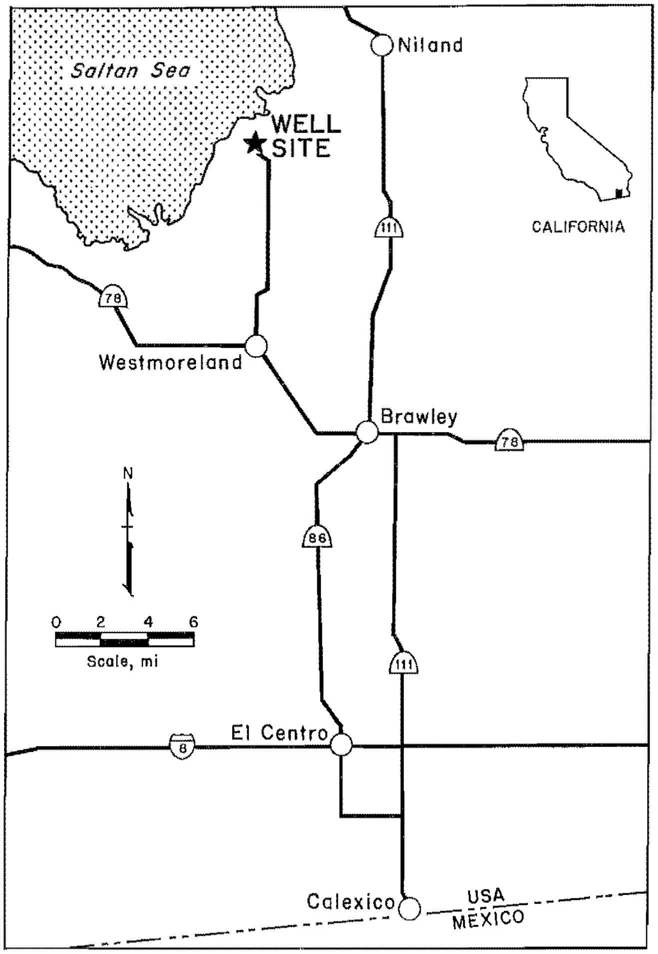

FIGURE 1. - Location map of well site.

RESULTS AND DISCUSSION

PRECIPITATION

A contract study outlined conditions for precipitation of lithium with aqueous $AlCl_3$ (9). Data from the study showed the effect of Al:Li ratio on precipitation of lithium at pH 7.5 (fig. 2) and the effect of pH at an Al:Li mole ratio of 4 (fig. 3). The data for both figures were obtained at 75° C. More than 95 pct of the lithium was precipitated when the Al:Li mole ratio was at least 2.5 and at pH of 6 to 8. Bench-scale tests verified that these conditions precipitated at least 95 pct of the lithium from the brine.

An interesting phenomenon encountered during the preliminary bench-scale tests was an aging effect. When an aged, pretreated brine was used in lithium precipitation tests, a decrease in lithium recovery was observed. In one test using brine treated with lime 5 months before lithium precipitation, recovery was 56 pct. When the brine was pretreated with lime within a few days of lithium precipitation, more than 95 pct of the lithium was precipitated. The causes of aging were not investigated because the lithium recovery flow scheme employed lime pretreatment immediately before lithium precipitation and aging was not a factor.

A large-scale lithium precipitation test was carried out during the operation of the MRU for lime precipitation of Fe, Mn, Pb, and Zn (6). The equipment used for lime precipitation was employed to precipitate lithium (fig. 4). Lime slurry was added to the first train of four 90-gal reactors, and conditions developed during lime precipitation studies were used. The precipitated hydroxides and silica were thickened and removed by filtration in a 1- by 1-ft filter press. After 24 h of operation, lithium precipitation in the second train of four 90-gal reactors was begun by treating the

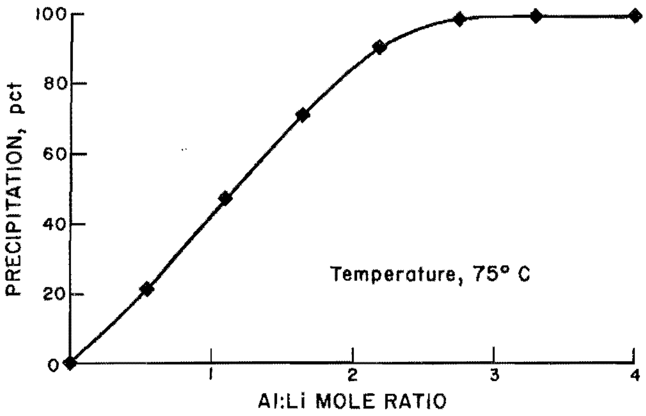

FIGURE 2. - Effect of Al:Li ratios on lithium precipitation.

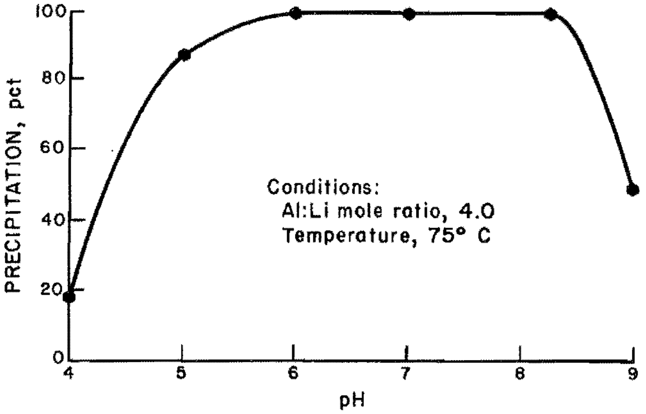

FIGURE 3. - Effect of pH on precipitation of lithium with aluminum hydroxide.

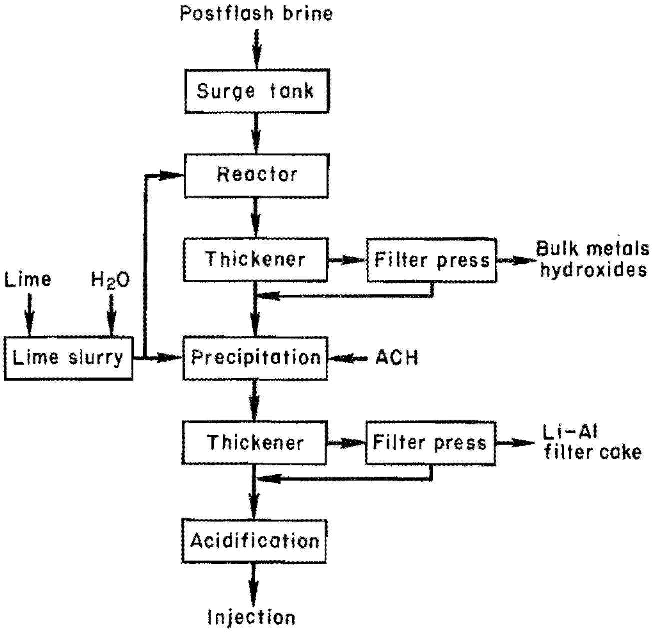

FIGURE 4. - Flowsheet for lithium precipitation.

overflow from the thickener with a solution of $AlCl_3$. An Al:Li mole ratio of 2.6 was maintained. The pH was maintained at 7.5 by the addition of a 20-pct lime slurry. The mixed Li-Al precipitate was thickened in a rake thickener and filtered in a 2- by 2-ft filter press. The filtrate was combined with the overflow from the thickener, acidified with HCl to pH 5.5, and returned to the injection well.

Samples of the filtrate from the first filter press showed that more than 99 pct of the Fe, Mn, Pb, and Zn was precipitated after 18.5 h of operation. Samples of filtrates from the second filter press indicated that 89 pct of the lithium was precipitated 2 h after the ACH addition was begun. Precipitation of lithium increased to more than 99 pct at 9.5 h and decreased to 91 pct at 24 h. Precipitation of lithium returned to more than 99 pct at 38 h. Inspection of the operating logs indicated that the pH in the lithium reactor train had decreased from 7.5-8.0 to 2.8 at 9 h. The pH gradually increased to 8.5 at 33 h and remained at 7.8-8.9 through the remainder of the test. Figure 5 presents profiles for pH in the lithium reactor and percent precipitation of lithium determined by analysis of filtrates from the second filter press versus time. Time zero was the time at which addition of ACH was begun. Inspection of the data, allowing for a delay in response of the dynamic system, shows that lithium was effectively precipitated when the pH was maintained at 7.5 to 8.9.

Evaluation of the two thickener circuits indicated poor efficiency in solids removal. This was expected because the thickeners were designed for a different application. Solids removal was erratic and ranged from 50 to 90 pct. As a consequence, lithium filter cakes were contaminated with Fe, Mg, Mn, Pb, and Zn hydroxides. During portions of the test the contamination was high, but a number of filter cakes were obtained that contained small amounts of contaminants. The least contaminated filter cakes were used in the bench-scale studies for recovering Li and Al. Analyses of the less contaminated filter cakes are shown in table 2.

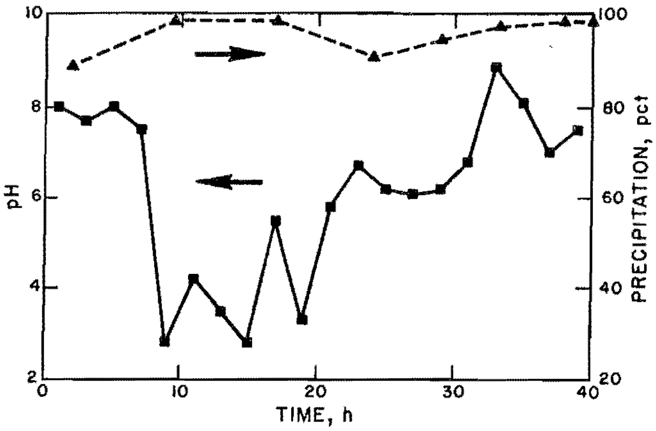

FIGURE 5. - Profiles for pH and percent precipitation of lithium during mineral recovery unit operation.

Alternative methods of precipitating lithium, such as precipitation of lithium phosphate or lithium metal phosphate, were considered. Precipitation of lithium carbonate was not used because of the high calcium content of the brine. The lithium content of the brine was measured before and after additions of increasing amounts of sodium phosphate up to 10 times the stoichiometric requirement for precipitation. There was no detectable decrease in the lithium analysis. Tests were made with ACH and sodium phosphate in an attempt to form an Al-Li phosphate.

TABLE 2. - Analyses of Li-Al precipitates, percent

Time from start of ACH addition, h	Al	Li	H_2O	Fe	Mn	Pb	SiO_2	Zn
3.5...............	11.7	1.1	38	0.02	0.6	0.1	1.6	0.1
65................	13.7	.7	30	.2	.1	.2	2.7	ND
71.5..............	12.3	.8	32	.1	.5	.3	2.5	.1

ND Not detected.

No decrease was detected in the lithium content of the brine. Two inorganic ion exchangers were investigated for lithium removal. One, a zirconium phosphate, was not successful. The other was prepared by drying a portion of Li-Al precipitate and stirring the dried material with a sample of the brine. The technique decreased the lithium content of the brine from 0.19 to 0.07 g/L. Since the precipitate was noncrystalline, no satisfactory method for large-scale brine treatment was available. Research on recovering lithium from brine has been reported on methods using a similar precipitate incorporated in an organic resin (11) and using MnO_2 as a mole sieve-ion exchanger (12). Neither method has been demonstrated as being suitable for a continuous unit operation.

Since the alternative lithium precipitation methods were not effective, research on recovering lithium from mixed Li-Al precipitates was pursued.

FILTRATION

Since initial bench-scale studies at ambient temperatures suggested difficulties in filtration of the precipitates, a series of experiments was undertaken to evaluate flocculants and filter aids. The criteria used for evaluation were percent moisture of the filter cake and filtration rate. The tests were run at 95° C and included tests with no additive for comparison. The results are shown in table 3. One-liter samples of the brine at pH 6.5 were treated with 18 g ACH. The slurries were filtered in Buchner filters. No improvement in filtration rate or percent solids was observed with the flocculants except for SF-214, which gave an increased filtration rate. Since filtration presented no problems during the large-scale precipitation tests, flocculants were not used in subsequent research.

TABLE 3. - Effect of flocculants on filtration

Flocculant	Filtration time, min	Filtrate, mL	Solids in filter cake, pct
None...	6.5	880	75.7
None...	6.5	860	74.2
MG-500[1]	6.5	870	72.3
SF-214.	4.0	875	72.7
SF-1301	7.0	830	29.1
SF-1303	14	815	73.7

[1] Reference to specific trade names does not imply endorsement by the Bureau of Mines.

ALUMINUM RECOVERY

Since a large quantity of ACH was required for precipitating lithium from the brine, the first priority was to devise a method for separating lithium from aluminum so that the aluminum could be recycled to the precipitation step. Methods available in the technical literature employ solvent extraction of lithium after dissolution of the Li-Al precipitate in HCl (10). The extractants have either low loading factors or high aqueous solubility, which render them inefficient as unit processes. An alternative method based on Bureau research on recovering alumina from domestic resources was available (13). The method involved acidification of a solution of $AlCl_3$ with gaseous HCl. When the acidity was increased, the solubility of ACH decreased.

Preliminary experiments using a chloride solution containing 124 g/L Al and 6.6 g/L Li verified that 99.7 pct of the aluminum and 0.2 pct of the lithium were precipitated at an acid normality of 11.3. Experiments using precipitates obtained during operation of the MRU were conducted to determine the effect of final normality on the Li-Al separation. The precipitates were put into solution by dissolving 250-g portions in 100 mL of concentrated HCl. The solutions were sparged with HCl for different lengths of time to obtain the final normalities. The results are presented in table 4. More than 99 pct of the lithium remained in solution at normalities greater than 8. High recovery of aluminum required sparging to a normality of at least 10. At a normality of 10.8, 99.7 pct of the lithium and 0.7 pct of the aluminum remained in solution, and the aluminum precipitated as ACH was suitable for recycle.

TABLE 4. - Effect of HCl normality on Li-Al separation

Normality	Metal remaining in solution, pct	
	Li	Al
8.0...........	99.6	8.0
9.6...........	99.6	4.0
9.9...........	99.6	3.0
10.8..........	99.7	.7

Alternatives to sparging were also investigated. A portion of dried Li-Al precipitate was leached with 36 pct HCl. The leached precipitate was washed with 36 pct HCl. The washed filter cake contained 78 pct of the Al, 26 pct of the Ca, and 27 pct of the Li.

Fractional crystallization was evaluated by dissolving portions of the Li-Al precipitate in HCl and evaporating fractions of the solution. Crystals were filtered and washed with 36 pct HCl. At 50-pct volume decrease, 25 pct of the Al, 4 pct of the Li, and 1 pct of the Ca were crystallized from the solution. At 63-pct volume decrease, the solution became very viscous and filtration was difficult. The crystals contained 82 pct of the Al, 5 pct of the Li, and 5 pct of the Ca.

Since none of the alternative methods were as effective as sparging for separating aluminum from lithium, research on sparged lithium solution was emphasized.

DISTILLATION OF HYDROCHLORIC ACID

While the sparging step was an effective means for separating and recovering aluminum from the process stream, a highly acidic solution containing the lithium and impurities was obtained. Neutralizing the solution would consume large quantities of base and result in the loss of the HCl. A more efficient approach was to recover the HCl. Recovery of a gas suitable for recycle to the sparging step can be accomplished by distillation of the acidic solution. An evaluation of the lithium recovery flowsheet estimated that 96.3 pct of the HCl could be recovered (14). Actual recovery would have to be optimized for a commercial plant by balancing equipment and operating costs for distillation against losses of HCl.

LITHIUM-CALCIUM SEPARATION

While calcium was beneficial in improving precipitation of ACH and recovering gaseous HCl by distillation, the need to separate calcium from lithium prompted investigations into calcium rejection at different steps in the treatment sequence. The first method employed washing of the Li-Al precipitate to remove entrained brine prior to sparging. Even with two reslurry water washes of the precipitate, only 65 pct of the calcium was removed and a solution containing 5 g/L Ca was produced for the sparging step.

Another approach was to leach Li-Al precipitate with sulfuric acid solution at pH 2. The leached filter cake was subjected to two repulp water washes. The leaching solution and the two wash solutions were combined prior to analysis. The combined solutions contained 98 pct of the Li, 88 pct of the Al, and 38 pct of the Ca. $CaSO_4$ solubility was approximately the same as in water containing no chlorides.

Since the methods were not satisfactory for rejecting calcium, another purification step was required to separate calcium and remaining impurities from the lithium.

The initial method considered was to selectively precipitate calcium by adding Na_2CO_3 to a solution of the distillation residue. While this approach would probably be successful, it was not investigated because of the excessive consumption of Na_2CO_3. Instead, a separation technique based on the low-percent-ionic character exhibited by LiCl was devised.

Experiments were carried out with a mixture of reagent-grade hydrates of LiCl and $CaCl_2$. The mixture had a Ca:Li weight ratio of 6. The first set of experiments was designed to select classes of organic compounds for detailed study. The salt mixture was dried at 100° C for 12 h, and 20-g charges were contacted with 100 mL of the test solvent for 3 h. The slurries were filtered, and the insoluble residues were dissolved in water and analyzed. The metal concentrations in the organic phases were calculated based on a mass balance. The results of the series of tests are shown in table 5.

TABLE 5. - Calcium and lithium chloride dissolved by representative organic solvents[1]

Solvent	Element in solution, g/L	
	Ca	Li
Acetonitrile.......	0	0
Xylene.............	0	.2
Hexane.............	0	.2
Tetrahydrofuran....	2.0	4.8
Methyl isobutyl ketone...........	3.0	0
Decanol............	4.0	4.9
Ethylene glycol....	42	7.1
Dimethyl sulfoxide.	36	6.3

[1] Conditions: 20 g mixed chlorides, 100 mL organic solvent, 3-h contact time, ambient temperature.

Of the organic compounds tested, only the alcohol and ether provided separation of lithium and calcium. Since ethers are health and safety hazards, alcohols were evaluated as the primary source. A series of alcohols was tested under the same conditions except that 10-g charges of the dried salts were contacted with 50 mL of the test solvent. The results are shown in table 6. While the alcohols exhibited good solvent characteristics for LiCl, all except decanol were also good solvents for $CaCl_2$. The viscosity and high boiling point for decanol make it difficult to use on a large scale.

TABLE 6. - Calcium and lithium chloride dissolved by alcohols[1]

Alcohol	Element in solution, g/L	
	Ca	Li
Decanol.........	3.0	4.0
2-propanol......	11	4.4
2-propanol (dewatered)....	12	3.6
Sec-butanol (dewatered)....	23	4.2
2-octanol.......	24	4.3
1-heptanol......	25	4.2
Hexanol.........	25	4.5
Sec-butanol.....	26	2.4

[1] Conditions: 10 g mixed chlorides, 50 mL alcohol, 3-h contact time, ambient temperature.

A similar series of experiments was also conducted to evaluate ethers. The results are shown in table 7. None of the alkyl ethers exhibited good solvent characteristics for LiCl. Tetrahydrofuran (THF) was the most promising, and a set of experiments was initiated to evaluate compounds having structural similarities to THF. Table 8 shows the results of these tests. THF was the most selective solvent for the LiCl. While the reasons for the specificity of THF were not clear, research was continued to define the use of THF for separating LiCl from $CaCl_2$. Samples of reagent-grade $CaCl_2 \cdot 2H_2O$ and $LiCl \cdot H_2O$ were dried at 200° C to dehydrate the salts. Portions of the dried salts were contacted with THF to determine solubility limits. Lithium chloride was soluble to 53.8 g/L, while $CaCl_2$ was soluble to 0.2 g/L. In tests with mixtures of the two salts, from 3 to 10 g $CaCl_2$ per liter of THF contaminated the leached LiCl.

TABLE 7. - Calcium and lithium chloride dissolved by ethers[1]

Ether	Element in solution, g/L	
	Ca	Li
Isopropyl ether.....	0	0.1
t-butyl methyl ether	0	0
Tetrahdyrofuran.....	2.0	2.9
Diethyl ether.......	4.0	.8

[1] Conditions: 10 g mixed chlorides, 100 mL ether, 3-h contact time, ambient temperature.

TABLE 8. - Calcium and lithium chloride dissolved by selected solvents[1]

Compound	Element in solution, g/L	
	Ca	Li
Tetrahydrofuran....	1.0	4.1
Tetrahydropyran....	1.0	.6
Furfuryl alcohol...	5.0	3.5
Tetrahydro furfuryl alcohol..........	19	4.0

[1] Conditions: 10 g mixed chlorides, 100 mL test solvent, 3-h contact time, ambient temperature.

A portion of the Li-Al precipitates obtained during operation of the MRU was dissolved in HCl, sparged, evaporated, and dried at 200° C, resulting in 138 g of fused mixed chlorides. The chlorides went through a molten phase during the drying step and had to be pulverized prior to leaching with THF. Pulverizing was best accomplished with a mortar and pestle immediately after drying. Mechanical techniques caused the fused chlorides to become sticky, owing to either mechanical heating or sorption of water. After grinding to minus 35 mesh, the salt mixture was contacted with 1 L THF. The salt mixture, the insoluble residue, and the THF solution were analyzed by ICP. The results are shown in table 9. The product LiCl contained large amounts of Ca, Mg. Mn, and Zn. Other impurities, such as potassium and boron, were rejected. Efficient solid-liquid separation during lime treatment of the brine would eliminate Mg, Mn, and Zn. Only calcium would present a problem in the LiCl product.

TABLE 9. - Weight distribution of metals in tetrahydrofuran, milligrams

Metal	Salt	THF	Residue
Al.............	210	<10	270
B..............	350	<3	380
Ba.............	180	<.5	180
Ca.............	30,000	2,300	27,000
Fe.............	770	18	760
K..............	5,500	46	5,900
Li.............	3,200	3,100	220
Mg.............	1,300	180	1,200
Mn.............	2,000	1,700	490
Na.............	480	21	490
Pb.............	88	21	85
Sr.............	260	6	250
Zn.............	830	700	190

A differential thermal analysis (DTA) was obtained on the synthetic $LiCl-CaCl_2$ mixture (fig. 6). The analysis showed endothermic reactions at 32°, 80°, 140°, and 460° C and indicated gas evolution between 175° and 210° C. Only the peak at 460° C occurred in the cooling portion of the curve, indicating that 460° C is the melting point of the mixture. The other peaks are due to dehydration of the chloride salts. Literature values for hydrates of LiCl and $CaCl_2$ show that $CaCl_2 \cdot 2H_2O$ loses water at 30° and 200° C and $LiCl \cdot H_2O$ loses water at greater than 98° C (15), which is consistent with the analysis.

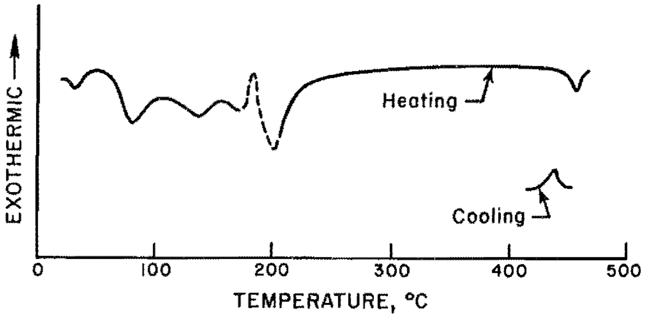

FIGURE 6. - Differential thermal analysis results for mixed calcium-lithium chlorides.

Experiments were performed to determine the effect of drying temperature on Li-Ca separation. Mixtures of $LiCl \cdot H_2O$ and $CaCl_2 \cdot 2H_2O$ were dried at different temperatures in a drying oven or spray dryer. Spray drying had the advantage of producing a powder product rather than fused chlorides. The dried chlorides were leached with THF that had been stored on mole sieves to eliminate water. The results are shown in table 10. Since drying at temperatures greater than 100° C was not advantageous, a test was run with mixed $LiCl \cdot H_2O$ and $CaCl_2 \cdot 2H_2O$ with no drying. The THF contained 5.1 g Li and 2.7 g Ca per liter.

TABLE 10. - Effect of drying temperature on separation of LiCl from $CaCl_2$

Drying method	Temp, °C		Metals in THF, g/L	
	In	Out	Li	Ca
Oven.......	105	105	5.2	4.2
	210	210	5.7	4.4
	250	250	5.7	5.0
Spray dryer	210	132	4.6	2.1
	182	115	4.4	1.7

The presence of calcium in the THF was puzzling because solubility tests had shown low solubility for $CaCl_2$. Plotting the concentration of lithium in THF versus the concentration of calcium for all the tests (fig. 7) indicated that a solubility relationship existed. The possibility that the solvation characteristics of THF were altered by loading with LiCl was investigated. A portion of THF was contacted with an excess of $LiCl \cdot H_2O$ and loaded to 4 g/L Li. The loaded THF was contacted with $CaCl_2 \cdot 2H_2O$ and analyzed. The THF contained 3.6 g Li and 1.3 g Ca per liter. The results of the test show that $CaCl_2$, which has low solubility in THF, is soluble in THF when lithium is present.

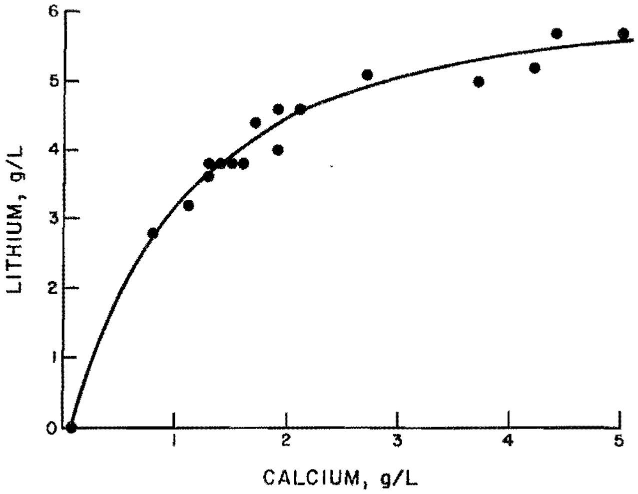

FIGURE 7. - Concentration of calcium versus lithium in tetrahydrofuran.

Methods were investigated to suppress $CaCl_2$ solubility in the lithium-loaded THF. Tests in which CO_2 was bubbled into the THF during leaching of a $LiCl\text{-}CaCl_2$ mixture and calcium precipitants, such as Na_2CO_3, oxalic acid, and ammonium oxalate, were added to the mixed chlorides were not successful. Attempts to modify the solvation characteristics of THF by adding a less polar solvent, such as hexane, were also unsuccessful because both LiCl and $CaCl_2$ solubilities were suppressed.

Since no method increased the selectivity of THF for LiCl compared to $CaCl_2$, a purification step was added. Aqueous solutions of LiCl and $CaCl_2$ were prepared that were representative of the mixture remaining after removal of the bulk of the calcium by leaching with THF. The solutions were treated at ambient temperature and with oxalic acid to precipitate the remaining calcium. By treating a solution containing 60 g Li and 34 g Ca per liter with increasing amounts of oxalic acid up to 2.5 times the stoichiometric requirement for calcium, 90 pct of the calcium was precipitated. This was not satisfactory because the solubility for calcium oxalate indicated that calcium can be decreased to 0.001 g/L. Precipitation of calcium from the chloride solution will result in generation of HCl, which must be removed to obtain calcium concentrations approaching the solubility limit. Since HCl is very insoluble in a hot saturated LiCl solution, a test was made at 90° C. At an oxalic acid addition of 1.2 times the stoichiometric amount needed to precipitate the calcium, 99.7 pct of the calcium was removed from solution. The precipitated calcium oxalate was washed with water, and the filtrate and wash solution were analyzed. Evaporation of the combined filtrate and wash solutions resulted in 99.6-pct recovery of LiCl containing 0.08 pct $CaCl_2$. Additions of oxalic acid up to 1.9 times the stoichiometric requirement did not improve calcium precipitation.

LITHIUM RECOVERY FLOWSHEET

A flowsheet containing the treatment steps shown in figure 8 was devised. Brine returning to the injection well of a power generation facility is treated with lime to remove Fe, Mg, Mn, Pb, and Zn. The lithium is precipitated by adding ACH and lime slurry. After solid-liquid separation, the brine is acidified to its original pH and returned to the injection line. The Li-Al precipitate is dissolved in HCl and sparged to separate the aluminum as ACH, which would be returned to the lithium precipitation step. The aluminum-free lithium solution is distilled to recover gaseous HCl for recycle to sparging. The distillation residue is dried and leached with THF to remove the bulk of the calcium and reject other impurities, such as boron and potassium. LiCl, recovered by evaporating the THF, is dissolved in water and treated with oxalic acid to remove remaining calcium. The purified lithium chloride solution would contain 330 g/L LiCl and would be 99.9 pct Li.

Each unit operation resulted in at least 95-pct lithium recovery. The overall recovery from the brine was 89 pct. Exit streams, other than LiCl and lithium-depleted brine, are the bulk metal hydroxides, $CaCl_2$, and calcium oxalate. Reagents consumed are HCl, lime, and oxalic acid. A preliminary cost evaluation (16) showed that the cost of recovering LiCl was $2.99 per pound, including capital and operating costs. A selling price of $3.70 would be needed to realize a 15-pct return on investment. Major cost items were $1.30 for HCl and $0.63 for fuel oil for spray drying.

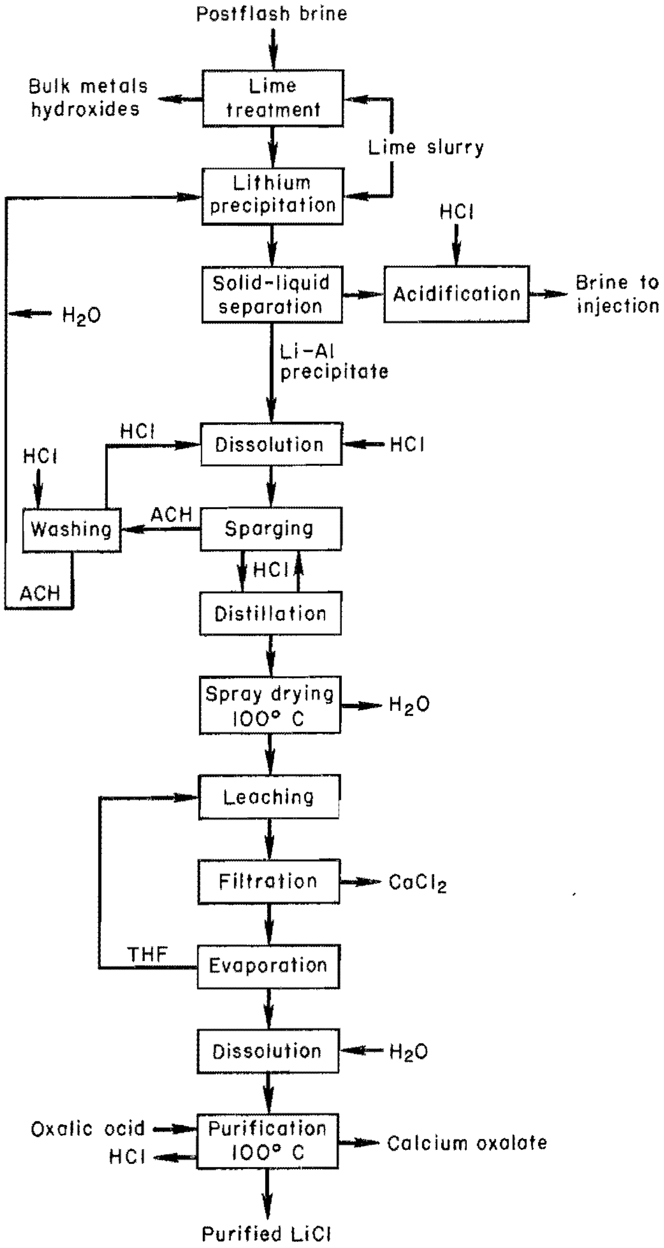

FIGURE 8. - Flowsheet for lithium chloride recovery.

The largest cost factor in LiCl recovery is consumption of HCl during dissolution of the Li-Al precipitate. Since the ratio of aluminum to lithium is large, the quantity of HCl required per pound of LiCl is large. Figure 2 shows that a 25-pct decrease in $AlCl_3$ addition results in a 10-pct decrease in lithium precipitation. The smaller quantity of aluminum would decrease the amount of HCl needed for dissolution. Calculations of the resultant change in reagent requirements show that the cost of recovering LiCl would be decreased by $0.20 per pound. A larger savings could be realized if the recycled ACH could be partially decomposed to a water-soluble hydroxy-chloride. The decomposition would produce HCl, which could be recycled to dissolution of the Li-Al precipitate. Water-soluble hydroxy-chloride having a composition of $5AlCl_3:8Al(OH)_3:37.5H_2O$ has been obtained during leaching of kaolinitic clays, but it is not known whether this specie can be formed from ACH.

The next largest cost factor is fuel oil for spray drying. Other drying techniques, such as multiple-effect evaporation, might decrease the cost, but a final spray drying step would be needed to eliminate pulverization of the solid mixed chlorides. Part of the heat requirements for evaporation may be obtained from steam available from a power generation plant after the steam exits the turbine. The low-grade steam could extract part of the heat from the exothermic sparging step and be used to evaporate part of the water. An energy balance should be combined with data from power generation test facilities. Another benefit of combining costs for LiCl recovery with those for power generation is the water balance. Steam used to generate electricity is presently condensed and returned to the injection well to maintain reservoir pressure. Since the condensed steam is potable water, minimizing the amount returned to injection would provide a valuable byproduct. Treatment of the spent brine at a 50-MW powerplant for lithium recovery increases the mass from 42,000 to 43,948 tpd. Of the increase, 1,721 tpd is water added with the reagents. The remaining 227 tpd is due to added reagents and the chemical reactions taking place. This 227 tpd represents 54,500 gpd of potable water, which would not need to be injected.

SUMMARY AND CONCLUSIONS

A lithium recovery system in which brine returning to an injection well from a power generation facility may be treated to recover a lithium chloride product was devised. Each unit operation was studied and gave at least 95-pct lithium recovery. Overall lithium recovery was 89 pct. The lithium product contained 330 g/L LiCl, was 99.9 pct pure, and could be used "as is" or dried to anhydrous LiCl.

The cost of recovering LiCl is approximately equal to the present market price but could be decreased by combining lithium recovery with some of the operations used in power generation instead of treating it as an isolated process.

REFERENCES

1. Carter, J. P., F. X. McCawley, S. D. Cramer, and P. B. Needham, Jr. Corrosion Studies in Brines of the Salton Sea Geothermal Field. BuMines RI 8350, 1979, 35 pp.

2. Cramer, S. D., and J. P. Carter. Laboratory Corrosion Studies in Low- and High-Salinity Geobrines of the Imperial Valley, Calif. BuMines RI 8415, 1980, 30 pp.

3. Urbanek, M. W., C. D. Hornberg, and B. Lindal. Research on a Geothermal Mineral Extraction Complex. Phase 1. Preliminary Technical and Economic Assessment (contract J0275010, DSS Engineering, Inc.). BuMines OFR 51-79, 1979, 194 pp.

4. Berthold, C. E., P. Hadzeriga, D. H. Christopher, T. A. Applegate, and D. M. Gillespie. Process Technology For Recovering Geothermal Brine Minerals (contract S0133084, Hazen Research, Inc.) BuMines OFR 35-75, 1975, 255 pp.; NTIS, PB 241 867/AS.

5. Berthold, C. E., and F. M. Stephens. Magmamax No. 1 Geothermal Brine Bulk Solids Precipitation Plant--Engineering Design (contract J0265057, Hazen Research, Inc.). BuMines OFR 127-78, 1978, 84 pp.

6. Schultze, L. E., and D. J. Bauer. Operation of a Mineral Recovery Unit on Brine From the Salton Sea Known Geothermal Resource Area. BuMines RI 8680, 1982, 12 pp.

7. Ferrell, J. E., and J. P. Searls. Lithium. Ch. in BuMines Minerals Yearbook 1981, v. 1, pp. 551-556.

8. Cassel, T. A. V., G. T. Shimato, C. B. Amudsen, and P. O. Blair. Geothermal Electric Power Forecast in the United States and the Impact of R & D Advancements: 1982-2000. Geothermal Resource Council, Trans., v. 6, 1982, pp. 331-335.

9. Berthold, C. E., and F. M. Stephens. The Recovery and Separation of Mineral Values From Geothermal Brines (contract H0144104, Hazen Research, Inc.). BuMines OFR 81-75, 1975, 39 pp; NTIS, PB 245 686.

10. Epstein, J. E., E. Feist, J. Zmora, and Y. Marcus. Extraction of Lithium From the Dead Sea. Hydrometallurgy, v. 6, 1981, pp. 269-275.

11. Lee, J. M., and W. C. Banman. Recovery of Lithium From Brines. U.S. Pat. 4,159,311, 1979, 7 pp.

12. Shen Xiangmu and Wang Xueyuan. Lithium Recovery From Aqueous Solution By Ionic Sieve Method. Huaxue Xuebao (Acta Chimica Sinica), v. 39, No. 8, 1981, 7 pp.

13. Shanks, D. E., J. A. Eisele, and D. J. Bauer. Hydrogen Chloride Sparging Crystallization of Aluminum Chloride Hexahydrate. BuMines RI 8593, 1981, 15 pp.

14. Maysilles, J. (Bureau of Mines). Private communications, 1982; available upon request from L. E. Schultze, BuMines, Reno, NV.

15. Weast, R. C. (ed.). Handbook of Chemistry and Physics. CRC Press Inc., Cleveland, OH, 55th ed., 1974-75, pp B-77 and B-103.

16. Henn, John J. Preliminary Economic Evaluation of a Process To Recover Lithium Chloride From Geothermal Brines. BuMines internal report, Sept. 1983, 22 pp.; available upon request from L. E. Schultze, BuMines, Reno, NV.