Bulletin 691

Lithium and Its Recovery From Low-Grade Nevada Clays

By L. Crocker, R. H. Lien, and Others

UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

BUREAU OF MINES
David S. Brown, Acting Director

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering the wisest use of our land and water resources, protecting our fish and wildlife, preserving the environment and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to assure that their development is in the best interests of all our people. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.

Library of Congress Cataloging in Publication Data

Lithium and its recovery from low-grade Nevada clays.

(Bulletin/Bureau of Mines; 691)

Bibliography: p.

Supt. of Docs. no.: I 28.3:691.

1. Lithium—Metallurgy. 2. Leaching. 3. Roasting (Metallurgy). 4. Clay minerals—McDermitt Caldera Complex (Nev. and Or.). I. Crocker, Laird. II. Series: Bulletin (United States. Bureau of Mines) ; 691.

TN23.U43 [TN799.L57] 622 s [669'.725] 87-600197

CONTENTS

ILLUSTRATIONS

ILLUSTRATIONS—Continued

Material balance:

TABLES

TABLES—Continued

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Btu	British thermal unit	lb	pound
Btu/gal	British thermal unit per gallon	lb/ft^3	pound per cubic foot
°C	degree Celsius	lb/st	pound per short ton
cm^3/min	cubic centimeter per minute	Mgal	thousand gallon
d/yr	day per year	min	minute
ft^3	cubic foot	mL	milliliter
g	gram	mL/min	milliliter per minute
g/L	gram per liter	MM Btu	million British thermal unit
gal	gal	mm-diam	millimeter diameter
gal/d	gallon per day	pct	percent
h	hour	ppm	part per million
h/d	hour per day	psi	pound per square inch
in	inch	psig	pound per square inch, gauge
K	kelvin	st	short ton
kcal	kilocalorie	st/d	short ton per day
km	kilometer	vol pct	volume percent
kW·h	kilowatt hour	W	watt
L	liter	wt pct	weight percent
L/kg	liter per kilogram	yr	year
L/(m^2·h)	liter per square meter per hour		

LITHIUM AND ITS RECOVERY FROM LOW-GRADE NEVADA CLAYS

By L. Crocker,[1] R. H. Lien,[2] and Others

ABSTRACT

The Bureau of Mines investigated processes for recovering a marketable lithium product from the montmorillonite-type clays of the McDermitt caldera. The clay deposit, located on the Nevada-Oregon border, is estimated to contain over 3 million short tons of lithium.

Limestone-gypsum roasting and selective chlorination proved most successful for extracting lithium from the clays; 80-pct Li recovery was achieved using either technique. With both processes, lithium silicate in the clay was converted to a water-soluble compound—either lithium sulfate or lithium chloride. The lithium was then recovered as a carbonate by water leaching the calcine, concentrating the leach solution by evaporation, and precipitating the lithium with soda ash. The operating costs for the limestone-gypsum roast process were estimated at \$2.02/lb Li_2CO_3; selective chlorination operating costs were estimated at \$3.85/lb Li_2CO_3. The current selling price of Li_2CO_3 is about \$1.50/lb.

A detailed flowsheet, material balance, and process evaluation are presented for the limestone-gypsum roast process. In addition, lithium reserves and resources are discussed and the McDermitt clays are described.

---

[1] Chemical engineer (retired).
[2] Chemical engineer.
Bureau of Mines, Salt Lake City Research Center, Salt Lake City, UT.

OVERVIEW

Lithium is the most electrochemically reactive and has the lowest density of all the alkali metals. Because of these properties, lithium and lithium chemicals are used in many commercial applications including the production of aluminum and ceramics. Lithium's properties make it particularly attractive for energy applications such as lightweight batteries for use in electric automobiles and utility load-leveling purposes. Furthermore, lithium is being used in nuclear fusion research as a source of tritium and as a coolant and heat-transfer agent. In addition, aluminum-lithium aircraft alloys, which cut aircraft weight, resulting in considerable fuel savings, are being developed.

Currently, the United States supplies about 70 pct of the world's lithium needs from domestic pegmatites and subsurface brines (*1*).[3] At the present consumption rate, these reserves are sufficient to supply primary lithium demand for the foreseeable future. In contrast, in the 1970's, lithium shortages were predicted (*2-4*) because an oil embargo intensified interest in alternative energy sources such as lithium batteries. In the future, an oil shortage could again push lithium to the forefront as an alternative energy source. Thus, the development of technology to recover lithium from unconventional sources such as clays would expand the domestic reserve base of lithium and would help the Nation meet a sharp rise in lithium demand.

The lithium-bearing clays of the McDermitt caldera were identified by the U.S. Geological Survey (USGS) in the 1970's (*5*). These clays were estimated to contain over 3 million tons of lithium (*6*). The Bureau of Mines conducted extensive research to recover lithium from these clays. Of the many extraction techniques investigated, two showed promise for effective lithium recovery: selective chlorination (*7-9*), and limestone-gypsum roasting (*9-11*). A practical lithium extraction level of 70 pct was set for selective chlorination; 80 to 85 pct of the lithium was recovered using the limestone-gypsum roast procedure. Extensive research was conducted in a process research unit (PRU) to optimize the limestone-gypsum roast process.

The data generated by the PRU work were used to prepare an economic evaluation of the process in July 1987. For a plant treating 1,000 st clay per day, the estimated operating cost was $2.02/lb lithium carbonate (Li_2CO_3) produced. The current (July 1987) selling price for Li_2CO_3 is about $1.50/lb. Although the process is not currently economical, technology now exists for lithium recovery from McDermitt clays.

INTRODUCTION

The United States, the world's largest producer and consumer of lithium minerals and chemicals, is self-sufficient in lithium. Nearly all the Nation's lithium is recovered from spodumene deposits in North Carolina and subsurface brines in Nevada.

The largest end use for lithium is in aluminum potlines. In the aluminum cells, Li_2CO_3 is added to reduce electricity consumption and fluorine emissions. The ceramics, air conditioning, grease, synthetic rubber, and pharmaceutical industries also use lithium chemicals. Recently, lithium has gained importance in areas such as low-density aluminum-lithium aircraft alloys, lightweight batteries for use in electrical automobiles and utility load-leveling purposes, and nuclear fusion for use as a supply of tritium and as a coolant and heat transfer agent.

In the 1970's, several research and Government organizations discussed the possibility of domestic lithium shortages by the year 2000 (*2-4*). These predictions were based primarily on rapid expansion of the lithium batteries market, principally in the area of electric automobiles. The development of thermonuclear energy was expected to have an impact on lithium reserves after the year 2000.[4]

Forecasts of lithium shortages prompted the USGS, under a cooperative agreement with the Department of Energy, to search for alternative domestic lithium resources. The USGS identified a large deposit of lithium-bearing clay in the McDermitt caldera complex (*5*) on the Nevada-Oregon border (fig. 1). The caldera complex, one of the largest in the world, comprises five overlapping and nested calderas (circular volcanic depressions). The principal clay deposit area measures 30 miles (48 km) long by 22 miles (35 km) wide. The lithium-bearing clays are found primarily along the edge of the caldera in a crescent extending from the northeastern corner to the southwestern section.

The clay deposits can be considered a potential resource because of high lithium content (up to 0.65 wt pct) in beds having a cumulative thickness of several feet. These beds crop out for several miles and have little overburden. The lithium content in these clays is probably derived from volcanic material and was incorporated into the beds during alteration. The clays are estimated to contain over 3 million st of lithium (*6*). The Bureau investigated methods for recovering lithium from this unconventional resource to help ensure the availability of an adequate minerals base for the Nation's future economic and strategic needs.

This investigation began in cooperation with the USGS Lithium Resource Appraisal Group, which supplied clay samples from two areas of the McDermitt caldera. Samples from the northern area contained as much as 0.36 wt pct Li and were associated with clinoptilolite and feldspar. Samples from the southwestern section contained up to 0.64 wt pct Li and were associated with analcime and potassium feldspar. Exploratory lithium extraction tests were conducted on a representative sample from each area (*12*).

Laboratory testing showed that over 80 pct of the lithium in either clay sample could be extracted by sulfuric acid (H_2SO_4) pugging followed by water leaching; however, the acid requirement of over 1,000 lb H_2SO_4 per

---

[3] Italic numbers in parentheses refer to items in the list of references preceding the appendixes.

[4] Estimates of lithium demands have been revised because the lithium batteries market has not expanded as anticipated. In addition, fusion power programs have encountered technological as well as funding problems, which have further clouded the lithium demand picture. However, an oil shortage, such as that experienced in the 1970's, could increase the demand for lithium storage batteries. The development of aluminum-lithium aircraft alloys may also cause a substantial increase in lithium demand.

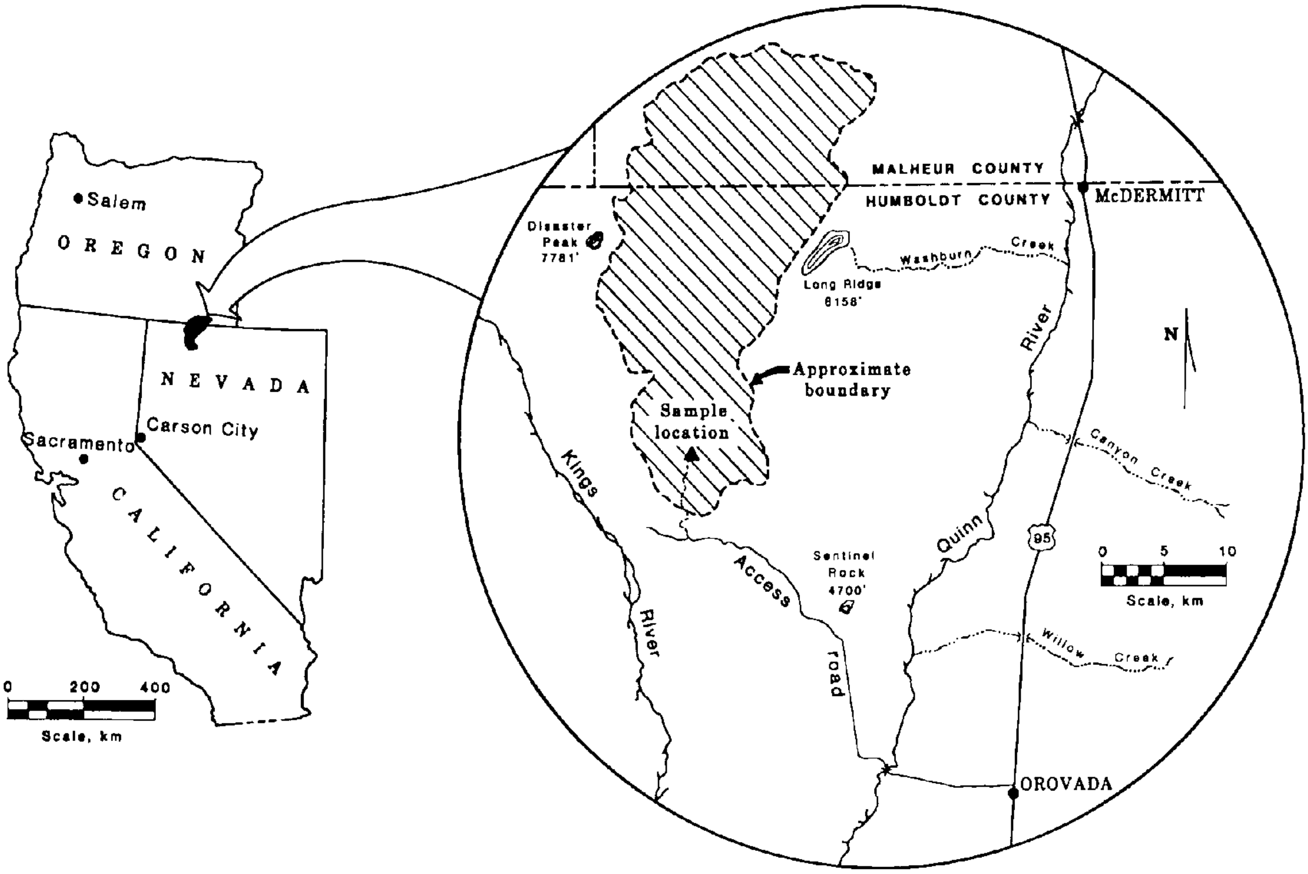

Figure 1.—Location of McDermitt caldera complex.

short ton of clay was excessive (*12*). Complex extraction procedures such as multiple-reagent roasting appeared more promising in the exploratory research (*12*).

To provide raw material for further testing, the Bureau obtained about 6,000 lb of clay from a discovery cut in the southwest section of the caldera (fig. 1). A typical sample contained 0.6 wt pct Li.

Bureau research concentrated on finding extraction techniques that would convert the lithium in the clay to a water-soluble product without converting major contaminating elements such as aluminum and magnesium to water-soluble compounds. Extensive laboratory testing resulted in two techniques that met this requirement: selective chlorination (*7-9*) and limestone-gypsum roasting (*9-11*).

The selective chlorination technique involves chlorinating a mixture of clay and limestone at 750° C using 20 wt pct hydrochloric acid (HCl). In the limestone-gypsum roast method, lithium in the clay is converted to lithium sulfate (Li_2SO_4) by roasting a mixture of clay, limestone, and gypsum at 900° C. Both methods are selective for alkali metals over alkaline earths.

At least 80 pct of the lithium in the clay can be extracted using either technique. However, a practical level of 70 pct was set for selective chlorination because HCl utilization and the lithium extraction rate decreased sharply at extraction levels above 70 pct. For example, 80-pct Li extraction required nearly twice as much HCl as 70-pct extraction. With both methods, lithium is recovered as a carbonate by water-leaching the roast product (calcine), concentrating the leach solution by evaporation, and precipitating lithium from the concentrated solution with soda ash.

A discussion of lithium uses and production is presented in chapter 1. Lithium reserves and resources are summarized in chapter 2. Chapter 3 describes the McDermitt clays and the preliminary lithium extraction studies. The selective chlorination process is discussed in detail in chapter 4. Chapter 5 presents the limestone-gypsum roast research. A material balance for the process is presented in appendix A, and a detailed economic evaluation is given in appendix B.

CHAPTER 1. — LITHIUM PROPERTIES, HISTORY, USES, AND PRODUCTION

By L. Crocker and R. H. Lien

PROPERTIES

Lithium is a silver-white metal with a specific gravity of 0.543 at 20° C. Its atomic weight is 6.94, the lowest of any solid element. The metal's density is 33.9 lb/ft^3, compared with 108.6 lb/ft^3 for magnesium and 168.6 lb/ft^3 for aluminum. The melting temperature of lithium is 180° C; it boils at 1,400° C. Because of its malleability and ductility, lithium can be rolled into thin plates and drawn into wire. Also, lithium is the most electrochemically reactive of all the alkali metals.

HISTORY

Lithium was first identified in 1817 by the Swedish geologist, Johann Auguste Arfredson, who, with Jons Jakob Berzelius, named it after the Greek word "lithos," meaning stone, to signify that it was mineral in origin. Sir Humphrey Davy in England was successful in preparing a small quantity of the metal in 1818. In 1855, Robert Bunsen and Augustus Mathiesen produced enough lithium for extensive laboratory study by the electrolysis of lithium chloride (LiCl). These researchers, using spectrographic techniques, found lithium in plant and animal tissues, thus disproving Berzelius' theory that the element occurred only in minerals from the earth's crust.

Lithium-bearing minerals were probably first mined in German Saxony and Bohemia about the middle of the 19th century. Lithium salts were first produced commercially in Germany by Dr. L. C. Marquart in 1854. In 1886, France became involved in the commercial mining of lithium minerals, principally amblygonite (*13*). Commercial mining of lithium minerals began in the United States about 1898 when 30 st of spodumene was produced in the Black Hills of South Dakota. Early production was mainly from the zoned pegmatites of that area (*14*).

In 1881, gem-quality, green-colored spodumene was found in Alexander County, NC, and named hiddenite. The extent of the lithium mineralization in North Carolina was not widely known until Hess suggested its importance in 1936 (*15*). Spodumene deposits near King's Mountain have been developed since, and now supply a large portion of the U.S. demand.

USES

Early uses of lithium and its compounds are not well documented; however, mineral waters containing lithium were taken internally as a tonic in the 19th century in both Europe and America, and this may represent the first use for the element. Another early use of lithium chemicals was in the manufacture of ceramic and glass products. In addition to the pharmaceutical and ceramics industry, lithium chemicals and metals are now used for a wide variety of purposes.

The largest end use for lithium is in aluminum potlines. In the aluminum cells, Li_2CO_3 is added to reduce power consumption and fluorine emissions. The benefits of using lithium additives in aluminum cells were first demonstrated on a commercial scale by Kaiser Aluminum and Chemical Corp. in 1958 (*16*).

The second major use of lithium is in the glass and ceramics industries. Several lithium minerals, including lepidolite, petalite, amblygonite, and low-iron spodumene, are consumed directly by the glass industry. Ceramic products that are lightweight, heat-shock resistant, and chemical resistant can be produced using lithium additives. The development of the lithium-containing ceramic material Pyroceram[5] by Corning Glass Co. has given rise to a variety of cookware, dishes, and stove tops (*13*).

The manufacture of lithium-based lubricants is the third leading use of lithium chemicals. Superior lubricants, based on lithium stearate, were developed during World War II by the U.S. Navy. Lithium-based greases are superior to sodium- and calcium-based greases in their resistance to moisture and temperature extremes. These greases are used extensively in military, industrial, automotive, aircraft, and marine applications (*1*).

In recent years, lithium has gained importance in energy-related areas such as batteries and nuclear fusion. Lithium batteries, which are used in a variety of portable electronic devices, are lightweight, work well under temperature extremes, and have a long shelf life. Lithium batteries are also used for military applications; the Air Force uses lithium battery systems in the Minuteman and Peacekeeper missile programs (*1*). The high electrochemical potential and low density of lithium make lithium batteries a leading contender for use in electric automobiles and energy storage systems.

In nuclear fusion power development, lithium is used as a heat-transfer medium and as a source of tritium, which is produced by bombarding lithium with neutrons. Nuclear fusion may provide a large-scale use for lithium; however, fusion-powered electric generators are not likely to become commercial before the year 2020 (*1*).

Another application for lithium is in aluminum-lithium alloys. Using a rapid solidification casting technology, Aluminum Co. of America, in conjunction with other aerospace contractors, has developed an aluminum-lithium alloy that is 30 pct lighter than titanium, has equal strength, and retains its shape under stress 100 times longer (*17*). The use of these alloys for aerospace structural components may become a major lithium end use by the year 2000 (*1*).

Other lithium end uses include (1) LiCl and LiBr (lithium bromide) in industrial air conditioning and drying systems, (2) lithium fluoride (LiF) in self-fluxing brazing alloys, (3) lithium hydroxide monohydrate ($LiOH \cdot H_2O$) in air purification systems, (4) lithium hypochlorite (LiOCl) as a sanitizing agent for swimming pools and commercial kitchens, and (5) butyllithium (C_4H_9Li) as a catalyst for synthetic rubber production. Lithium metal is used as a scavenger and degasser by smelters and refiners of high-conductivity copper and copper alloys.

---

[5] Reference to specific products does not imply endorsement by the Bureau of Mines.

WORLD CAPACITY AND PRODUCTION

Table 1 shows world lithium-production capacity for 1983 and 1984 as well as predicted capacities for 1990 (*1*). Also, the table gives production figures for 1983. The United States, the world's largest producer of lithium products, had over 60 pct of the estimated world capacity in 1984. The U.S.S.R. is probably the second largest producer of lithium chemical products, although published data are not available.

Since 1940, world lithium production has been subject to considerable fluctuation (*18*). A small production peak of about 600 st contained lithium occurred in 1944 because of U.S. Government purchasing programs during World War II. Similar purchasing programs for nuclear weaponry research accounted in large part for the production peak of about 6,600 st in 1957. The purchasing program ended in 1960, and world production bottomed out at about 2,200 st in 1962. Following 1962, production grew steadily until a peak of 6,800 st was reached in 1977. World production has since leveled off because of decreased lithium use by the aluminum industry and the effect of the worldwide recession of the early 1980's.

In 1984, Lithium Corp. and Foote Minerals Co. were the sole major producers of lithium in the United States. Lithium Corp. depends upon the pegmatites of North Carolina for raw materials. Foote Minerals Co. recovers lithium from North Carolina pegmatite deposits and from the brines of Silver Peak, NV. In 1984, Foote Minerals Co. began lithium production from a major new brine source in Chile called Salar de Atacama. This production is a joint venture by Foote Minerals Co. and the Chilean Government industrial development group (CORFO). This operation is expected to have an annual capacity of 1,300 st Li equivalent (*19*). Another emerging lithium producer is Australia. In 1982, Greenbushes Tin Ltd. opened a spodumene quarry adjacent to its tin-tantalite ore body southeast of Bunbury in Western Australia (*1*). Production from this source was 7,200 st of spodumene concentrate in 1984 (*20*).

TABLE 1.—World lithium production capacity

(Short tons of contained lithium)

	Production in 1983	Capacity		
		1983	1984	1990[1]
North America: United States	W	6,600	6,600	6,600
South America:				
Argentina[e]	5	10	10	10
Brazil[e]	60	100	100	100
Chile	0	0	1,300	1,300
Total[e]	65	110	1,410	1,410
Europe:[e]				
Portugal	10	20	20	20
U.S.S.R.[2]	1,400	1,500	1,500	1,500
Total	1,410	1,520	1,520	1,520
Africa:				
Namibia[e]	20	30	30	30
Zimbabwe	[e]150	300	300	300
Total[e]	170	330	330	330
Asia: China[2]	350	400	400	500
Oceania: Australia	[e]75	300	300	400
World total[e3]	W	9,300	10,600	10,800

[e] Estimated. W Withheld to avoid disclosing company proprietary data.

[1] Forecast.

[2] These estimates denote only an approximate order of magnitude; no basis for more exact estimates is available. Output by China and the U.S.S.R. has never been reported.

[3] Data may not add to totals shown because of independent rounding.

CHAPTER 2. — LITHIUM RESERVES AND RESOURCES

By L. Crocker and R. H. Lien

SOURCES OF LITHIUM

Lithium is not a rare element; however, it is widely disseminated in nature with trace amounts occurring in most rocks and soils and in many natural waters. The average lithium content of the earth's crust is estimated to be about 20 ppm; seawater contains about 0.18 ppm (*21*).

Over 40 lithium minerals have been named and described (*6*). Silicates and phosphates, the most common minerals, are generally classified as pegmatites; table 2 shows the principal minerals found in pegmatites (*1*). Although the theoretical lithium content of these minerals is 2 to 5 pct, the pegmatite-bearing ores that have been exploited generally contain less than 1 pct Li. Spodumene is the primary lithium mineral being mined.

Lithium is also present as LiCl in many natural brines and spring waters; the lithium content of several representative waters is shown in table 3. All of the waters listed, except the brines of Silver Peak, NV, and Salar de Atacama, Chile, are either too dilute or too contaminated with other salts to warrant recovery of lithium alone.

Relatively high concentrations of lithium also occur in sediments such as clays. Hectorite, a clay mineral, generally contains 0.3 to 0.6 pct Li. Flint clays and other high-alumina clays contain <0.01 to 0.5 pct Li.

EVALUATION OF LITHIUM RESERVES

Several estimates of lithium resources and reserves have been published in recent years (*1, 6, 18, 22*). Comparing these estimates is difficult because the authors differ in the description and classification of each resource. In 1980, the USGS and the Bureau of Mines developed a uniform method of classifying mineral reserves and resources (*23*). Table 4, which follows the format generally used by the Bureau, classifies lithium resources as reserves and reserve base (*1*). The reserve base includes demonstrated resources that are currently economic (reserves) or marginally economic (marginal reserves), and some of those that are currently subeconomic (subeconomic resources). The current market economy world lithium reserves total about 2 million st; the reserve base is approximately 9 million st of contained lithium. Although the U.S.S.R. and China are believed to have substantial lithium resources, no published figures are available.

Virtually all of the world's reserves and marginal reserves are in the form of lithium-bearing pegmatites and lithium-bearing brines. About 80 pct of the domestic reserves are accounted for in spodumene-rich pegmatites; over 80 pct of the world lithium reserve base is in the form of large subsurface brines. Subeconomic lithium sources with some potential commercial value include geothermal brines and lithium-bearing clays (*1*).

TABLE 2.—Lithium content of commercial minerals

Mineral source material	Chemical formula	Theoretical Li content, pct	Approximate range of Li in commercial mineral, pct
Amblygonite	$LiAl(PO_4)(F,OH)$	4.73	3.7-4.2
Lepidolite	$K_2Li_3Al_3(AlSi_30_{10})_2(O,OH,F)_4$	Variable	1.4-1.9
Petalite	$Li_2O \cdot Al_2O_3 \cdot 8SiO_2$	2.26	1.4-2.2
Spodumene	$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$	3.73	2.6-3.0

TABLE 3.—Lithium content of natural brines

Brine location	Li analysis, ppm
Sea water	0.18
Smackover oil field brine (Texas and Louisiana)	50- 500
Searles Lake, CA	81
Silver Peak, NV, brine	300
Imperial Valley CA (geothermal brine)	55- 238
Salar Atacama, Chile	130-1,570
Yellowstone mineral spring (Norris basin)	8.4
Michigan basin (Sylvania sandstone brine)	70
Great Salt Lake, UT (1966)	[1]56

[1] Fresh water dilution had reduced lithium concentration in the Great Salt Lake, as reported by the Utah Geological and Mineral Survey, to about 10.6 ppm in 1984, although the concentration varies with depth.

TABLE 4.—Lithium reserves and reserve base

(Thousand short tons of contained lithium)

	Reserves	Reserve base[1]
North America:		
Canada	None	400
United States	400	450
Total	400	850
South America:		
Argentina	4	NA
Bolivia	None	6,000
Brazil	1	NA
Chile	1,400	1,500
Total[2]	1,400	7,500
Europe:		
Portugal	Small	NA
U.S.S.R.	NA	NA
Total	NA	NA
Africa:		
Namibia	NA	NA
Rwanda	Small	NA
Zaire	None	350
Zimbabwe	25	30
Total	25	380
Asia: China	NA	NA
Oceania: Australia	300	350
World total[2]	2,100	9,100

NA Not available.

[1] The reserve base includes demonstrated resources that are currently economic (reserves), marginally economic (marginal reserves), and some of those that are currently subeconomic (subeconomic resources).

[2] Data may not add to totals shown because of independent rounding.

Geothermal brines and lithium-bearing clays are extensive resources. Economic methods for recovering lithium from these sources could dramatically increase the domestic reserve base. The Bureau has investigated lithium recovery from geothermal brines (*24*). Vine estimated this resource at over 1 million st contained lithium (*6*). Also, the Bureau has conducted extensive research on lithium recovery from clays. One of the largest lithium-bearing clay deposits is in the McDermitt caldera of northern Nevada. Vine estimated this resource at over 3 million st contained lithium (*6*). Chapter 3 describes the McDermitt deposit; proposed lithium extraction methods are described in later chapters.

CHAPTER 3. — DESCRIPTION AND PRELIMINARY TESTING OF McDERMITT CLAYS

By L. Crocker, R. H. Lien, J. T. May,[1] D. S. Witkowsky,[2] and D. C. Seidel[3]

DESCRIPTION OF McDERMITT CLAYS

In the 1970's, the USGS, under a cooperative agreement with the Department of Energy, conducted a search for alternative domestic lithium resources. A significant resource was identified in the McDermitt caldera complex (*5*) located on the Nevada-Oregon border (fig. 1). The caldera complex, one of the world's largest, measures about 22 miles (35 km) wide by 30 miles (48 km) long. The complex developed over a period of 5 million yr during which time five large-volume ash flow tuffs were vented. These volcanic eruptions produced five overlapping calderas, which later collapsed and are now considered a single caldera.

The major collapse of the caldera probably occurred about 16 million yr ago. The caldera has since filled with tuffaceous sediments because of erosion. Although several streams have cut deeply into the caldera's outside rim, most of the interior sediments have remained in place; thus, minerals leaching from the sides have remained in the sediments. Minerals such as uranium, thorium, mercury, and lithium have been enriched in hydrothermally active areas of the caldera.

Lithium is present in montmorillonite clays that are found in a rough crescent shape extending from the northeastern corner to the southwestern section of the caldera. The lithium occurs in the clay mineral hectorite $[Na_{0.33}(Mg, Li)Si_4O_{10}(F, OH)_2]$ and in a clay mineral similar to hectorite but containing more aluminum. Clays in the northern part of the caldera contain up to 0.36 pct Li and are associated with clinoptilolite and feldspar. In the southern area, clay deposits contain up to 0.65 pct Li and are associated with analcime and potassium feldspar. Mineralogical studies have shown that the lithium is evenly distributed throughout the clay.

The Lithium Resource Appraisal Group of the USGS supplied the Bureau with six samples from the caldera's northern section (designated McDermitt A) and three samples from the southwestern section (designated McDermitt B). Representative compositions of these samples are presented in table 5. Preliminary lithium recovery studies were conducted on both ore types (*12*). Detailed research was conducted on the higher grade McDermitt B ore (*7-11*). For the in-depth studies, the Bureau obtained about 6,000 lb of McDermitt B ore from a discovery cut in the southwestern section of the caldera (fig. 1).

TABLE 5.—Composition of McDermitt clays, percent

Element or compound	McDermitt A	McDermitt B	Element or compound	McDermitt A	McDermitt B
Al	1.50	4.0	Li	0.36	0.64
B	.003	.04	Mg	12	7.70
Ca	1.13	1.30	Na	.59	.18
Cl	.01	.01	Rb	.02	.09
CO_3	<.10	<.10	SiO_2	53.05	53.48
F	1.40	2.29	SO_4	.14	.08
Fe	.53	1.90	Sr	.01	.01
H_2O	9.10	5.74	U_3O_8	.001	.001
K	.17	4.70			

PRELIMINARY LITHIUM EXTRACTION TESTS

In the preliminary McDermitt clay studies, several lithium extraction methods were investigated. Water disaggregation, hydrothermal treatment, acid leach, alkaline roast-water leach, sulfate roast-water leach, and chloride roast-water leach were techniques used in the treatment of both McDermitt A and B clays (*12*). Only the higher grade McDermitt B clay was treated by the following methods: (1) multiple-reagent roast-water leach (*12*), (2) sulfur dioxide (SO_2) atmosphere roast-water leach, (3) HCl roast-water leach (*7-9*), and (4) limestone-gypsum roast-water leach (*9-11*).

Water Disaggregation (*12*)

Samples of both McDermitt clays were slurried with water to determine if the clay would disaggregate and form a lithium-rich fraction, and to determine the amount of water-soluble lithium in the clay. Clay samples of 25 g were slurried with 225 mL of water and agitated for 1 h. The slurry prepared with McDermitt A showed slight gelation; the McDermitt B slurry did not form a gel. The slurries were screened; analyses of the products showed that the clays did not disaggregate to form a lithium-rich fraction and that less than 1 pct of the lithium in each sample was soluble in water.

Hydrothermal Treatment (*12*)

Hydrothermal tests were conducted to determine if lithium in the clay could be solubilized under relatively

---

[1] Group supervisor (retired).

[2] Metallurgist (now supervisory physical scientist, Bureau of Mines, Denver, CO).

[3] Research supervisor.

Salt Lake City Research Center, Bureau of Mines, Salt Lake City, UT.

mild conditions of heat and pressure. In each test, 40 g of clay was mixed with 360 mL of water and heated to 200° C in an autoclave for 1 h; the steam pressure was 225 psig. Analyses of the solids and solutions showed that less than 1 pct Li was solubilized by this treatment.

Acid Leaching (*12*)

Both types of McDermitt clay were leached with H_2SO_4 solution at pH 1. Clay samples of 25 g were added to 225 mL of pH 1 acid, and the resulting slurry was stirred for 3 h; acid was added every 10 min to maintain pH 1.0. The amount of acid required to achieve the pH 1.0 acidity was designated the standard acid addition. The clays were also leached with multiples of the standard acid addition.

Test results, presented in table 6, show that lithium was extracted from McDermitt A clay by direct H_2SO_4 leaching; however, the acid requirement was excessive. For example, 1,125 lb H_2SO_4 per short ton clay was required for 89-pct extraction. In contrast, about 2 pct of the lithium was extracted from McDermitt B clay using 1,178 lb H_2SO_4 per short ton clay.

Acid Pug-Water Leach

Sulfuric acid pug-water leach tests were conducted on McDermitt A and B clays to determine the effect on lithium extraction. Finely ground clay samples were well mixed to achieve 40 to 50 pct moisture; 98 pct H_2SO_4 was added to make a thick paste. After standing 1 h, the McDermitt A paste was water-leached; McDermitt B paste was soaked overnight prior to leaching. Leaching was conducted at about 15 pct solids and ambient temperature for 1 h.

Test results, presented in table 7, show that lithium extraction for McDermitt A clay was slightly lower with the acid pug procedure than with the acid leach. For example, the acid pug method resulted in 81-pct Li extraction with 1,150 lb H_2SO_4 per short ton clay, whereas leaching with 1,125 lb H_2SO_4 per short ton clay extracted 89 pct of the lithium. Acid pugging of the McDermitt B clay dramatically improved lithium extraction over the diluted acid leach. For example, acid pugging with 1,325 lb H_2SO_4 per short ton clay extracted 98.5 pct of the lithium; leaching with 1,413 lb H_2SO_4 per short ton clay yielded 2.6-pct Li extraction.

Lithium was extracted from both types of McDermitt clay by the acid pug-water leach procedure. However, the procedure would not be commercially feasible because (1) the amount of H_2SO_4 required was excessive, and (2) the leach solution was grossly contaminated with magnesium, potassium, aluminum, and iron (table 8). In addition, leach slurries filtered slowly and were difficult to wash.

TABLE 6.—Sulfuric acid leach of McDermitt clays[1]

H_2SO_4 added, lb/st clay	*Li extraction, pct*	*H_2SO_4 added, lb/st clay*	*Li extraction, pct*
McDermitt A:		McDermitt B:	
[2]375	19	[2]226	0.7
750	67	451	1.1
1,125	89	1,178	2.3
		1,413	2.6

---

[1] 25 g clay, at 10 pct solids, for 3 h.
[2] Standard acid addition.

TABLE 7.—Sulfuric acid pug-water leach of McDermitt clays

98 pct H_2SO_4 used, lb/st clay	Moisture in clay, pct	Soak time, h	Temp, °C	Li extraction, pct
	McDERMITT A CLAY			
875	40	1	70	60
1,150	40	1	25	81
1,450	40	1	25	94
1,750	40	1	25	97
	McDERMITT B CLAY			
1,000	55	1	25	50
1,200	50	16	75	8.2
1,325	50	16	25	98.5
1,514	50	16	25	98.9
1,616	50	16	25	99.6

TABLE 8.—Sulfuric acid pug-water leach of McDermitt B clay, leach solution analysis[1]

Element	*Conc, g/L*	*Element*	*Conc, g/L*
Al	5.6	Li	0.93
Ca	.36	Mg	15.2
Fe	3.9	Na	1.14
K	4.3		

---

[1] 1,200 lb 98-pct H_2SO_4 used per short ton of clay.

Alkaline Roast-Water Leach (*12*)

The McDermitt clays were roasted with carbonates of sodium, potassium, and calcium, and hydroxides of sodium and potassium; the roasted calcines were leached with water. These tests were conducted to determine if the lithium in the clay could be converted to a water-soluble form by the alkaline roasting reactions.

Finely ground clay samples of 100 g were mixed with 20 to 40 g of potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), or calcium carbonate ($CaCO_3$); the mixtures were roasted at 1,000° C for 4 h. Less than 10 pct of the lithium in the clay volatilized during these roasts. Water leaching the finely ground calcines resulted in relatively low lithium extractions (less than 45 pct in all cases).

In the hydroxide roasts, 100-g samples of clay were mixed with 20 to 30 g of sodium hydroxide (NaOH) or potassium hydroxide (KOH). Roasting with NaOH at 1,000° C produced a fused mass that attacked the roasting crucible. Over 72 pct of the lithium in both clays volatilized as the oxide during this roast. Roasting with either NaOH or KOH at 500° C volatilized 5 to 8 pct of the lithium from McDermitt B calcine; no lithium was volatilized from the McDermitt A calcine. Water leaching these calcines extracted only 1 or 2 pct of the contained lithium.

Sulfate Roast-Water Leach (*12*)

McDermitt A and B clays were roasted with calcium sulfate ($CaSO_4$), sodium sulfate (Na_2SO_4), and potassium sulfate (K_2SO_4) to determine if water-soluble Li_2SO_4 could be formed. The results of the initial roasting tests with 54 g Na_2SO_4 or K_2SO_4 per 100 g clay showed that less than 50 pct of the lithium was extracted by water leaching the calcines. Results of $CaSO_4$ testing, presented in table 9, show that roasting at 1,000° C resulted in a 67-pct Li extraction from McDermitt A clay and a 72-pct Li extraction from McDermitt B clay. The total lithium extracted includes lithium in the leach solution as well as a small amount of lithium volatilized.

TABLE 9.—$CaSO_4$ roast-water leach of McDermitt clays[1]

Roast temp, °C	Li extraction, pct	
	McDermitt A	McDermitt B
800	3	6
900	(2)	41
950	(2)	44
1,000	67	72
1,050	(2)	68
1,100	(2)	55

[1] Roast: 100 g ore, 50 g $CaSO_4$, 4 h.
[2] Not tested.

Chloride Roast-Water Leach (*12*)

A chloride roast-water leach process has been reported by Peterson and Gloss (*25*) for extracting lithium from spodumene ores. In this process, 347 parts of potassium chloride (KCl) was roasted with 100 parts of spodumene containing 3.58 pct Li. The ratio of KCl to lithium in the ore was 89:1. When chloride roast-water leach techniques were investigated for extracting lithium from McDermitt B, the same weight ratio was used. This weight ratio was 57 g of KCl to 100 g of the clay. The same amount of KCl was used in the roasting tests with McDermitt A; in these tests, the weight ratio of KCl to lithium in the clay was 158:1.

The mixtures of clay and KCl were roasted at 1,000° C for 4 h. The calcines produced were leached with water to extract water-soluble LiCl. For McDermitt A, 27 pct of the lithium was volatilized during roasting, but no lithium was extracted from the calcine by water leaching; the total lithium extraction was 27 pct. For McDermitt B, 39 pct of the lithium was volatilized during roasting; 19 pct of the lithium was recovered by water leaching the calcine. The total lithium extraction was 58 pct.

Multiple-Reagent Roast-Water Leach (*12*)

The purpose of multiple-reagent roasts was to achieve greater lithium extraction by combining the effects of chloride roasting with those obtained by a roast-water leach treatment. The reagent combinations tested were KCl plus $CaCO_3$ and KCl plus $CaSO_4$. The tests were conducted with McDermitt B clay only. Roasting temperature and reagent additions were studied. Roasting time was 4 h, and the finely ground calcines were leached in water at 10 pct solids. Test results are shown in tables 10 and 11.

TABLE 10.—KCl-$CaCO_3$ roast-water leach of McDermitt B clay

Roast temp, °C	Reagent, g per 100 g clay		Li extraction, pct		
	KCl	$CaCO_3$	Volatilized	Leached	Total
800	57	40	86	3	89
1,000	57	40	3	21	24
	42	30	57	7	64
	28.5	20	44	3	47
	14	10	35	0	35

TABLE 11.—KCl-$CaSO_4$ roast-water leach of McDermitt B clay

Roast temp, °C	Reagent, g per 100 g clay		Li extraction, pct		
	KCl	$CaSO_4$	Volatilized	Leached	Total
800	57	50	14	67	81
1,000	57	50	0	24	24
	42	38	21	54	75
	28.5	25	10	53	63
	14	12	11	22	33

Best lithium extraction by the KCl-$CaCO_3$ roast-water leach procedure was 89 pct. Water leaching recovered 3 pct of the lithium; 86 pct of the lithium was volatilized and not recovered. The highest extraction obtained with the KCl-$CaSO_4$ procedure was 81 pct; 67 pct of the lithium was recovered in the leach, and 14 pct of the lithium was volatilized.

Overall, the test data indicate that multiple-reagent roasting improved lithium recovery over roasting with a single reagent.

Sulfur Dioxide Atmosphere Roast-Water Leach[4]

A series of roast tests was conducted in a 2-in-diam vertical tube furnace to determine if the lithium in McDermitt B clay could be sulfated directly using SO_2 gas. Variables investigated included roast temperature, SO_2 concentration, and SO_2 usage. Calcines were water-leached to determine the effectiveness of each set of operating conditions. Test data indicated 700° C and 20 pct SO_2 to be optimum. However, the most important variable was the amount of excess SO_2 used. At optimum operating conditions, 903 lb SO_2 per short ton clay was required for 85.8-pct Li extraction. Extraction decreased to 58 pct using 450 lb SO_2 per short ton clay at similar operating conditions.

Overall, the test results showed that lithium can be extracted from McDermitt B clay by direct sulfation; however, an excessive quantity of SO_2 was required. In addition, this roast procedure sulfated most of the magnesium and calcium in the clay, resulting in a highly contaminated leach solution.

Chlorinating Roast With Hydrochloric Acid

Extensive research was conducted to study lithium extraction from McDermitt B clay by roasting in an HCl-H_2O atmosphere. The research was prompted by several chloride roasting techniques described in the literature (*25-28*). For example, a method for chlorinating lithium by mixing lithium-bearing ore with carbon and roasting with chlorine was proposed by MacDougall (*29*). Another method involving the chlorination of lepidolite with HCl was investigated by Lof and Lewis (*30*), who found that lithium extraction increased with the chlorination temperature up to 950° C, whereupon the lepidolite began to melt and the reaction rate decreased rapidly. Above 900° C, a large part of the LiCl was recovered as a volatile product. Additions of water vapor or air to the HCl gas resulted in decreased lithium extraction.

Bureau research found that proper control of HCl-H_2O ratios and roast conditions minimized the extraction of impurities from chlorinated calcines. Also, data showed that the formation of soluble lithium was greatly enhanced when the McDermitt clay was mixed with $CaCO_3$ before chlorination. The research was reported by Davidson (*7*) and May (*9*), and a patent was granted on the chlorination roast procedure (*8*). Chapter 4 summarizes the chlorination research; capital and operating costs are also included.

---

[4] The authors acknowledge V. E. Edlund and C. F. Davidson of the Bureau of Mines Salt Lake City Research Center for the primary research in this subsection.

Limestone-Gypsum Roast-Water Leach

A limestone-gypsum roast-water leach process was studied in detail. The research was patterned after work conducted by Sternberg, Williams, and Hayes (*31-32*) involving lime-gypsum roasting to recover lithium from spodumene. In this process, lime combined with silica to form a calcium silicate; the lithium in the ore reacted with the gypsum to form water-soluble Li_2SO_4.

Bureau research showed that lithium could be effectively recovered from McDermitt clay by roasting a mixture of clay, limestone, and gypsum, followed by water leaching. A series of purification steps was developed to recover lithium from the leach solution. This work was reported by Edlund (*10*) and Lien (*11*). The research, as well as capital and operating costs, is summarized in chapter 5. A detailed cost evaluation for this lithium recovery technique is given in appendix B.

CHAPTER 4.—HYDROCHLORIC ACID CHLORINATION ROAST-WATER LEACH PROCESS

By L. Crocker, R. H. Lien, C. F. Davidson,[1] and J. T. May

Bureau researchers investigated two types of chlorination using HCl (7). Initially, anhydrous chlorination was studied to determine if HCl could be used to effectively extract lithium from McDermitt clay. Subsequently, selective chlorination using $HCl-H_2O$ mixtures was investigated to determine if the chlorination of major contaminating elements such as magnesium and calcium could be eliminated.

BENCH-SCALE TESTING (7)

Equipment and Procedure

Chlorination experiments were conducted in a 1-in-diam tube furnace using approximately 10-g samples contained in ceramic boats. The furnace tube was Vycor glass. A schematic of the furnace setup is given in figure 2. The setup consists of a chlorinating agent supply system, the reaction zone, and a scrubbing system for volatile products. Anhydrous HCl and nitrogen (N_2) were delivered to the furnace tube by metering through gas flowmeters. Mixtures of $HCl-H_2O$ were obtained by forcing an HCl solution from a flask into the furnace tube by pressuring the flask with N_2. The HCl solution, which was measured by the flowmeter, flowed through a capillary tube directly into the furnace hot zone.

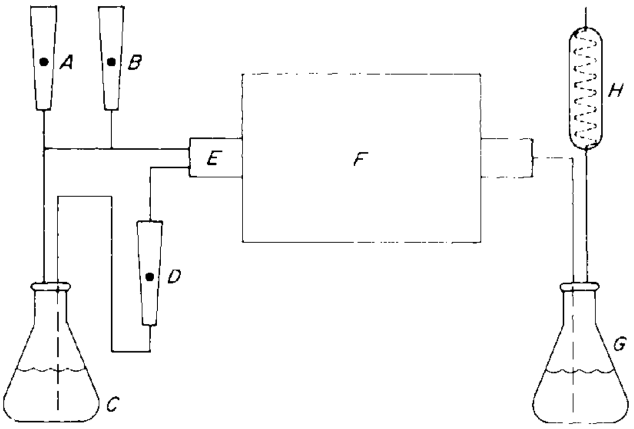

Figure 2.—Furnace schematic for small-scale HCl chlorination roast tests.

The furnace temperature was controlled by a Bristol on-off-type controller. A thermocouple was placed on the outside of the furnace tube directly over the sample. Any gaseous products flowed through a water scrubber and condenser system to collect the volatile products.

Samples were weighed into ceramic boats and placed in the furnace tube; then the system was purged with N_2. The furnace was heated under N_2 to 700° C and held for 15 min to dehydrate the clay and any other materials being reacted. After dehydration, the samples were brought to the desired reaction temperature and the chlorination was started. When the experiment was finished, the furnace was cooled under N_2 atmosphere.

After chlorination, the calcined sample was water-leached using 50 mL of water at 80° C. The leach solution, residue, and any volatile condensate were analyzed. A mass balance, computed between the input and output materials, accounted for all elements within ±5 pct.

Chlorination With Anhydrous HCl

The general effects of chlorination on lithium extraction from clays were measured by chlorinating McDermitt B clay samples with anhydrous HCl. The effect of temperature on lithium, calcium, and magnesium extraction is shown in figure 3. Clay samples were chlorinated for 30 min using 70 cm^3/min of anhydrous HCl. As the reaction temperature was increased, the extraction of all elements increased. However, the lithium and calcium extraction rates increased faster than did the magnesium extraction rate.

The lower extraction for magnesium, as compared with lithium, can be explained by the difference in the free

---

[1] Group supervisor, Salt Lake City Research Center, Bureau of Mines, Salt Lake City, UT.

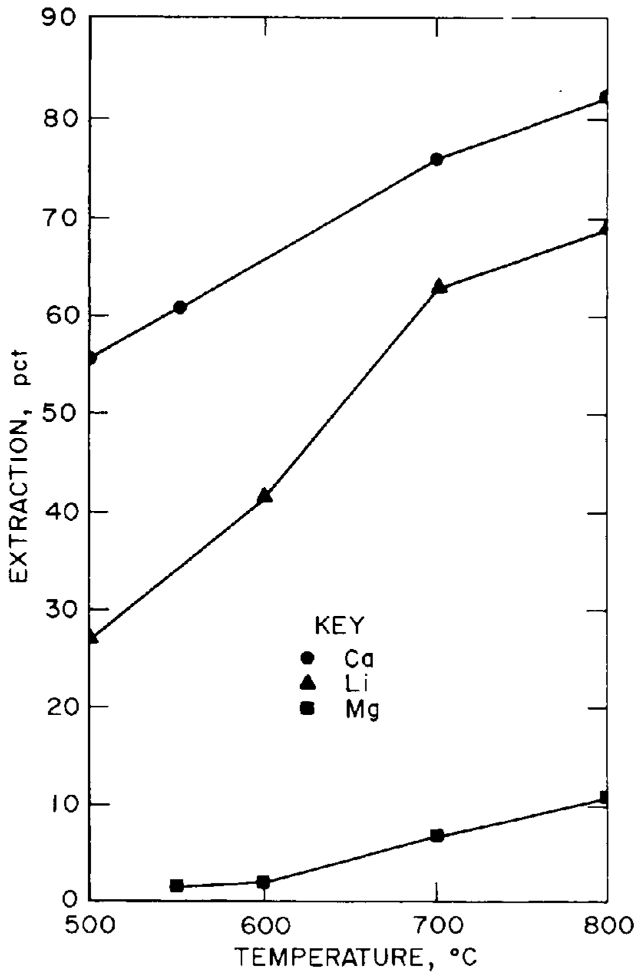

Figure 3.—Effect of chlorination roast temperature on water extraction of metals from McDermitt clay.

energies of chlorination. The Gibbs free-energy curves (*33-34*), plotted in figure 4, show that lithium, potassium, sodium, and calcium have negative free energies of chlorination. However, the free energy of chlorination for magnesium is positive; therefore, the extent of magnesium chlorination is relatively low.

The chlorination free-energy curves are based on the assumption that metallic ions are usually associated with silica in a clay material. Thus, chlorination of the clay should follow the general reaction 2M (silicate) + 2HCl = 2MCl + $2SiO_2$ + H_2O where M is a metallic cation.

The effect of reaction time on lithium, calcium, and magnesium extraction is shown in figure 5. McDermitt clay was chlorinated at 700° C with 70 cm^3/min anhydrous HCl; reaction times of 15, 30, and 60 min were investigated. Total extraction of each element increased with increased reaction time; however, the rate of extraction increased for magnesium while decreasing for lithium and calcium. Chlorination rates (as determined by extraction) may be estimated by the slope of each curve at any point. The increased extraction rate for magnesium was actually a function of the decreased rates of extraction for lithium and calcium, wherein more HCl was available to react with the magnesium as the lithium and calcium chlorination neared completion. Thus, as lithium extraction became complete, high magnesium extraction resulted. In addition, calcium extraction was greater than

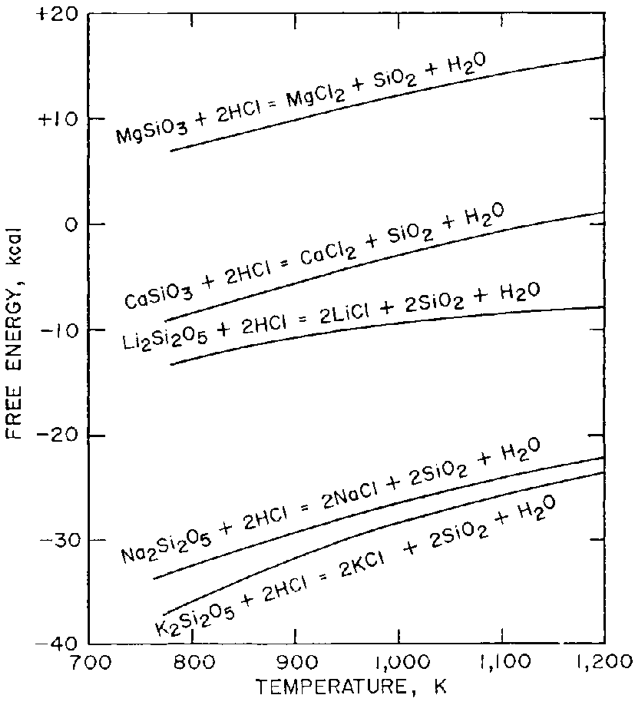

Figure 4.—Free energy for reaction of magnesium, calcium, lithium, sodium, and potassium silicates with gaseous HCl.

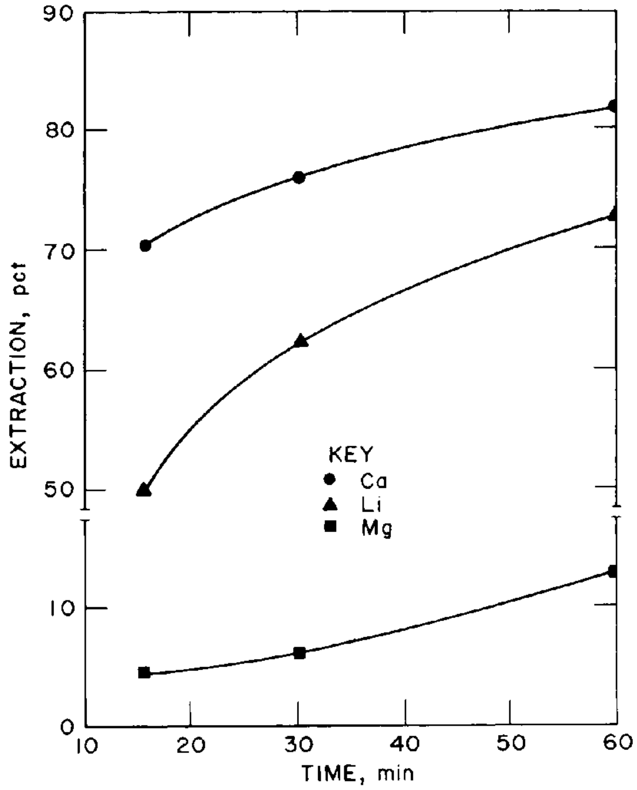

Figure 5.—Effect of reaction time on extraction of lithium, calcium, and magnesium from McDermitt clay after chlorination with anhydrous HCl at 700° C.

lithium extraction, resulting in a grossly contaminated leach solution. Therefore, continued research concentrated on developing a chlorination technique that would be selective for lithium or, if necessary, all of the alkali metals.

Selective Chlorination With HCl-H_2O Mixtures

The high magnesium content of the McDermitt clay and the relatively high percent extraction of calcium result in high consumption of HCl. Since HCl is an expensive reagent, selective chlorination of lithium in preference to the magnesium and calcium is desirable. The selective chlorination process is based on the greater stability of alkali metal chlorides versus other metal chlorides when they are exposed to an H_2O-HCl atmosphere. The chlorination of a particular cation can be prevented by maintaining a water concentration in the chlorinating gas that is greater than the equilibrium concentration.

A temperature-composition phase diagram relating the equilibrium H_2O-HCl ratio to the chloride-silicate phase boundary between 500° and 900° C is shown in figure 6. From this figure, the stable phase of each element at a given temperature and gas composition can be predicted. For example, to avoid the chlorination of magnesium silicate ($MgSiO_3$) and calcium silicate ($CaSiO_3$) when using an H_2O-HCl mole ratio of 8:1 (20 wt pct HCl), the reaction temperature must be above 615° C. If the H_2O-HCl mole ratio is decreased to 4:1 (33 wt pct HCl), the temperature must be increased to 700° C to avoid chlorination of $MgSiO_3$ or $CaSiO_3$. The trends predicted in figure 6 were investigated by chlorinating various silicate mixtures.

In the initial tests, finely ground $CaSiO_3$, $MgSiO_3$, and Li_2SiO_3 (lithium silicate) were mixed in equal weights and chlorinated. Test conditions were chosen to ensure lithium chlorination while preventing magnesium chlorination. The HCl concentrations used were 20 and 33 wt pct; the reaction temperature ranged from 550° to 850° C. Chlorinated samples were water-leached and analyzed for soluble chlorides.

Test results, presented in table 12, verify the trends predicted in figure 6. For the conditions tested, magnesium extraction was no greater than 0.01 pct, whereas lithium extraction ranged from 49 to 95 pct. Calcium extraction was most affected by the chlorination conditions. As predicted in figure 6, increased temperature caused dramatic decreases in calcium extraction. Overall, the test data confirmed that selective chlorination is dependent on reaction temperature and HCl concentration.

An extensive series of tests indicated that the selective chlorination of lithium in McDermitt clay was not as effective as anticipated. Several variables were investigated including (1) roast temperatures of 450° to 700° C, (2) HCl concentrations of 20 to 33 wt pct, and (3) reaction times of 30 to 120 min. The best lithium extraction of 22 pct was obtained at 500° C when chlorinating with 33 wt pct HCl for 30 min. The lower curve in figure 7 shows the results of 60-min chlorination tests conducted at 550° to 700° C using 20 wt pct HCl. The maximum lithium extraction was only 13 pct.

TABLE 12.—Extraction of lithium, calcium, and magnesium from pure silicate mixtures after chlorination[1] with HCl-H_2O

Test	Test conditions		Extraction, pct		
	Temp, °C	HCl, wt pct	Li	Ca	Mg
1	550	20	50	50	0.01
2	700	20	80	2	.01
3	750	33	95	10	.01
4	850	33	49	1	.01

[1] For 30 min.

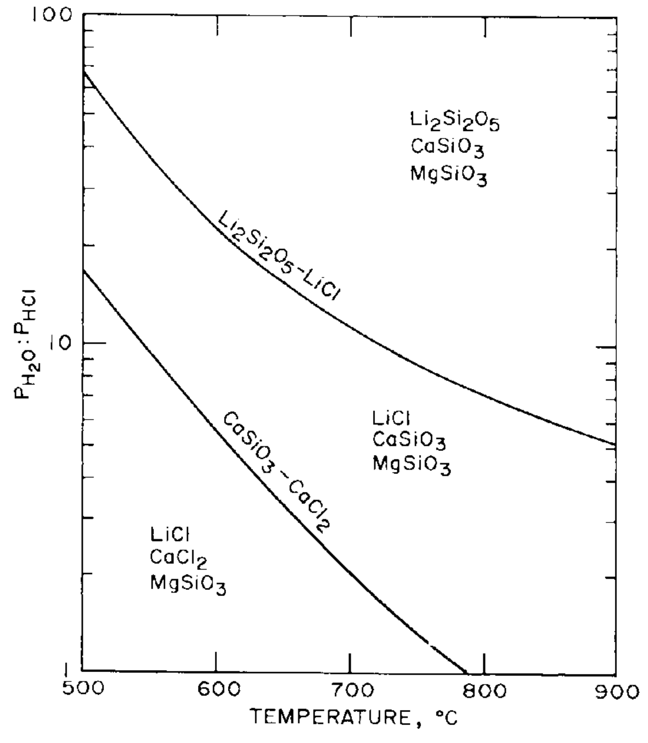

Figure 6.—Temperature versus HCl-H_2O stability diagram of the Li-Ca-Mg-Cl-SiO_2 system.

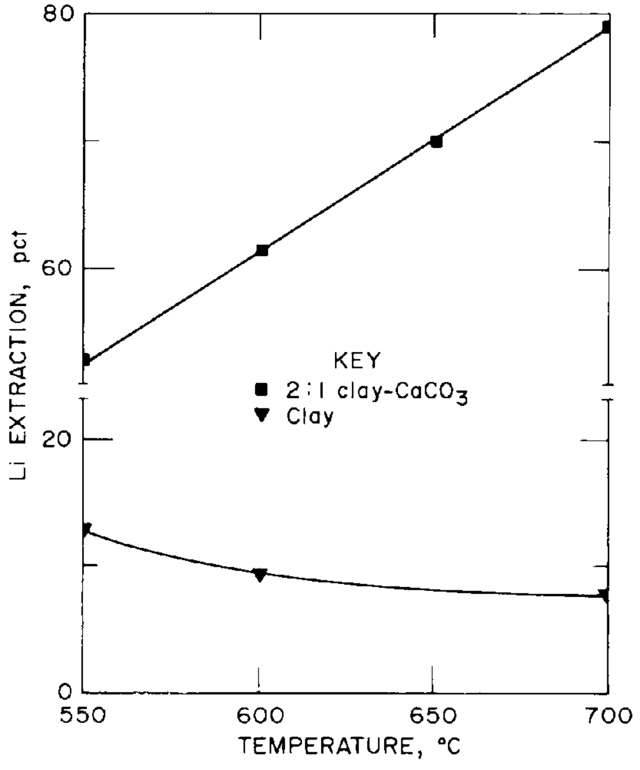

Figure 7.—Lithium extraction from clay and clay-$CaCO_3$ mixtures after chlorinating for 60 min with 20 pct HCl.

Chemical analysis of the leached calcine showed large amounts of insoluble chloride. The insoluble chloride was assumed to be a chlorosilicate that was formed by the reaction of chloride with free silica (SiO_2) present in the clay. The chlorosilicate compound would have a structure similar to that of sodalite [$Na_8(AlSiO_4)_6Cl_2$]. Chlorosilicate formation would tie up the alkali metal chlorides and reduce their solubility in water. Thus, lithium extraction was much lower than anticipated.

Selective Chlorination of Clay-$CaCO_3$ Mixtures With HCl-H_2O

The formation of chlorosilicate might be avoided if the SiO_2 in the clay was combined into a nonreactive compound. Thermodynamic calculations show that SiO_2 should react with lime (CaO) at 700° C to form $CaSiO_3$. Therefore, the addition of CaO as $CaCO_3$ should improve the lithium recovery by decreasing the amount of free silica.

This theory was supported by tests which showed that lithium extraction was much improved by adding $CaCO_3$ to the charge. Mixtures of McDermitt clay and $CaCO_3$ in a 2:1 ratio were chlorinated with 20 wt pct HCl for 1 h at 550° to 700° C. The upper curve in figure 7 shows that lithium extractions were as high as 80 pct. These recoveries, which represent a dramatic improvement over extractions obtained with chlorination of clay alone, indicate that SiO_2 reacted with CaO to form a calcium silicate.

Several types of calcium silicates can be formed by the reaction of CaO and SiO_2. The ratio of CaO to SiO_2 determines which calcium silicates form. A clay-carbonate ratio of 4:1 corresponds to a 1:1 ratio of CaO to SiO_2, which yields the silicate, $CaSiO_3$. As the CaO-SiO_2 ratio is increased, the more basic silicates will be formed. Ratios of 3:2, 2:1, and 3:1 of CaO-SiO_2 produce the silicates $Ca_3Si_2O_7$, Ca_2SiO_4, and Ca_3SiO_5, respectively. Ratios of CaO-SiO_2 higher than 3:1 form Ca_3SiO_5 plus CaO.

Free-energy values for chlorination of the various calcium silicates and CaO are compared with the free energy of chlorination for $Li_2Si_2O_5$ (the lithium silicate found in McDermitt clay) in figure 8. Selective chlorination between compounds with large differences in free energy is theoretically possible. Therefore, $Li_2Si_2O_5$ can be selectively chlorinated in mixtures containing $CaSiO_3$, $Ca_3Si_2O_7$, and Ca_2SiO_4. Clay-carbonate mixtures greater than 2:1 will form Ca_3SiO_5, which has a free energy of chlorination about equal to that of $Li_2Si_2O_5$. Thus, selective chlorination between $Li_2Si_2O_5$ and Ca_3SiO_5 is thermodynamically impossible. The free energy of chlorination of CaO is less than the free energy of chlorination of $Li_2Si_2O_5$; therefore, CaO will chlorinate in preference to $Li_2Si_2O_5$. Based on these observations, selective chlorination between lithium and calcium is possible using clay-carbonate mixtures greater than 2:1.

Thermodynamic calculations, together with preliminary test data, indicated that selective extraction of lithium would depend on the HCl-H_2O ratio, reaction time, and $CaCO_3$ addition. Therefore, an extensive test series was conducted to study the effects of the following chlorination conditions on lithium extraction: (1) HCl concentrations of 8 to 20 wt pct, (2) reaction temperatures of 600° to 750° C, and (3) clay-$CaCO_3$ ratios of 4:1 (the minimum amount needed to tie up the free silica), 3:1, and 2:1 (the maximum amount that will yield a calcium silicate that can be selectively chlorinated). Test results, presented in figure 9, show that the order in which chlorination conditions improved lithium extraction was first, the clay-$CaCO_3$ ratio; second, reaction temperature; and third, HCl concentration. Also, the data indicate that HCl concentration and reaction temperature may be interacting variables. Increasing either HCl concentration or temperature improves the effect of the other variable on lithium extraction.

Figure 9 indicates that the optimum selective chlorination conditions for lithium recovery from McDermitt clay were 2:1 clay-$CaCO_3$ (at ratios lower than 2:1 calcium begins to chlorinate), 20 wt pct HCl (higher HCl concentrations are expensive to obtain), and 750° C (higher temperatures cause fusion of the charge, which decreases lithium extraction).

LARGE-SCALE TESTING

Large-scale chlorination testing was conducted to (1) determine if the operating conditions established in bench-scale studies would be applicable to larger scale operations, and (2) provide information for a material balance and subsequent cost evaluation of the process.

Roasting Equipment and Procedure

Roast tests were conducted in a 3.5-in vertical tube furnace. The reaction vessel was a 3-in-diam, 316 stainless steel pipe. The 450-g samples of pelletized

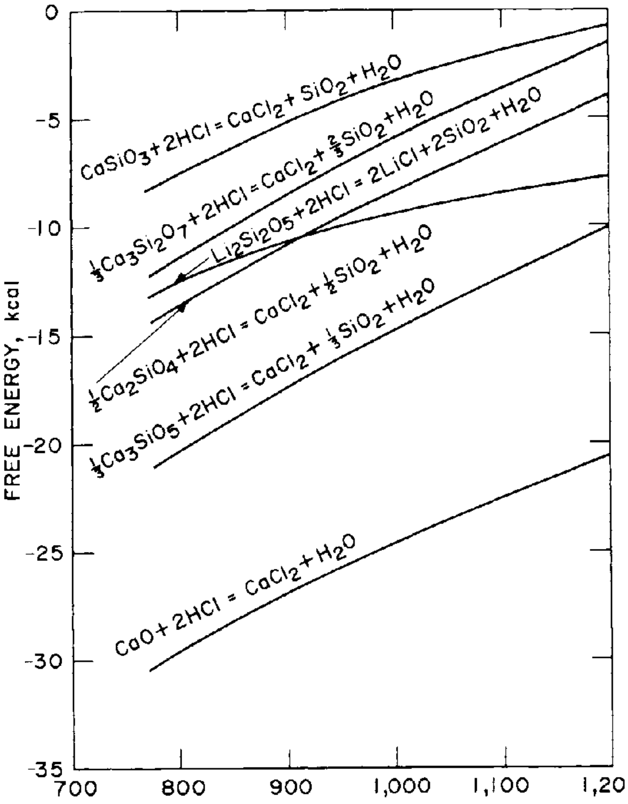

Figure 8.—Free energies of reaction for chlorination of $Li_2Si_2O_5$, CaO, and the different calcium silicates with gaseous HCl.

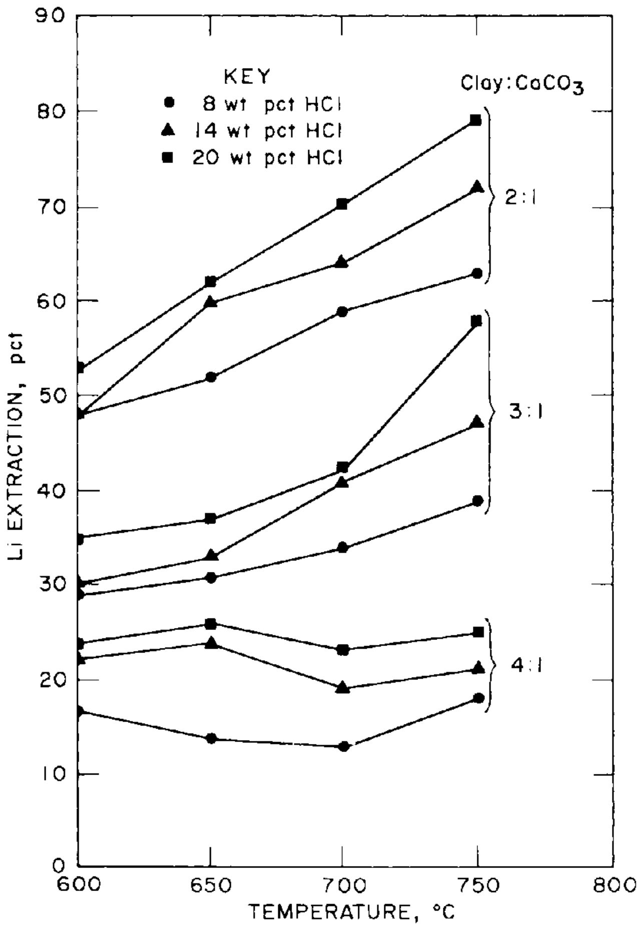

Figure 9.—Effect of $CaCO_3$ additions, HCl concentration, and reaction temperature on extraction of lithium from McDermitt clay.

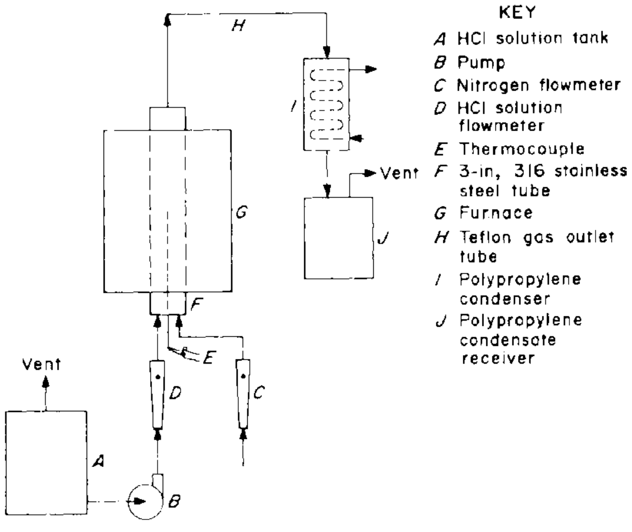

Figure 10.—Larger scale selective chlorination apparatus.

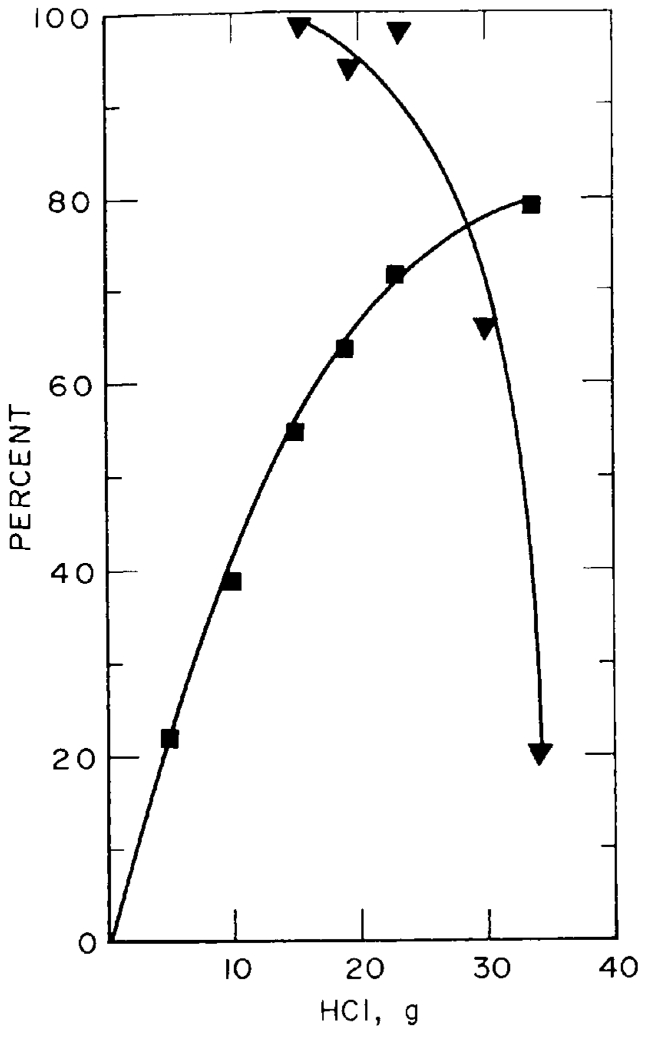

Figure 11.—HCl efficiency and lithium extraction when chlorinating 2:1 clay-$CaCO_3$ charge with 20 pct HCl at 750° C.

clay-$CaCO_3$ mixtures were charged directly to the furnace tube. Figure 10 shows a schematic of the experimental apparatus. The HCl-H_2O mixture was pumped into the bottom of the furnace tube through a Pyrex-lined stainless steel tube that served as a vaporizer. Nitrogen gas was fed through the charge during heat up and cool down. The reactor outlet tube was Teflon polymer because of the extremely corrosive nature of the hot offgases. The water-cooled condenser and the condensate receiver were also constructed of corrosion-resistant plastic. The HCl solution was generally fed at a rate of 1 to 2 mL/min, and the roasting time was varied from 30 min to 3 h.

Roast Tests

Chlorination roasts were conducted at 750° C using 20 wt pct HCl and a clay-carbonate ratio of 2:1 to determine the efficiency of HCl consumption. The efficiency was defined as the amount of HCl consumed by the chlorination reaction divided by the amount of HCl introduced to the test. Test results, presented in figure 11, show that 70 pct of the lithium in the clay was extracted with an overall HCl efficiency of over 90 pct. The HCl efficiency decreased rapidly for lithium extractions above 70 pct. Nearly twice as much HCl was required to obtain 80-pct Li extraction as for 70-pct extraction. Also, test data showed that the quantity of HCl used determined the percent lithium extraction regardless of HCl flow rate or HCl consumption.

Overall, the test results indicate that the realistic level of lithium extraction using selective chlorination was about 70 pct; HCl consumption at this point was 140 lb HCl per short ton clay. Extractions above 70 pct would be costly, in terms of both HCl used and processing time.

Lithium Recovery From Calcine

Recovering lithium from the calcine required a series of unit operations. The calcine was ground to minus 100 mesh and leached for 1 h with either fresh water or recycle solution from the product precipitation step. Filtration and washing of the residue produced a dilute solution containing lithium, sodium, potassium, and a small amount of calcium, all as chlorides. The calcium was removed by adding a stoichiometric amount of soda ash to the dilute solution. The calcium-free solution was concentrated by evaporation, causing KCl and NaCl to crystallize. These salts were separated from the solution. Soda ash was then added to the concentrated brine to precipitate Li_2CO_3, which was washed and dried. The product filtrate and product wash were recycled to the leach step.

PROCESS EVALUATION AND DISCUSSION[2]

The Bureau's headquarters Process Evaluation Office prepared a cost evaluation based on the larger scale testing. The capital cost estimate was of the general type called a study estimate by Weaver and Bauman (*35*). This type of estimate, prepared from a flowsheet and a minimum of equipment data, should be within 30 pct of the actual plant cost.

The estimated capital cost on a third quarter 1983 basis (Marshall and Swift index of 781.7) for a plant processing 1,000 st/d McDermitt clay was $121 million. The plant would operate 330 d/yr with an annual estimated operating cost of $68 million. Assuming that 69 pct of the lithium in the clay was recovered (recovery based on large-scale test data), the plant would produce 27 st/d Li_2CO_3 at a cost of $3.85/lb. In contrast, the selling price of Li_2CO_3 is $1.50/lb (as of July 1987).

The unfavorable economics are primarily due to the relatively low rate of lithium recovery and to the high energy costs associated with evaporation; over 50 pct of the operating costs involved leach solution concentration. To improve the economics, kinetic studies should be conducted on the chlorination step to determine if higher chlorination rates and efficiencies can be attained using a continuous countercurrent flow furnace. Water consumption in the leaching and washing of the calcine should be minimized to reduce the evaporation load.

---

[2] For this subsection, the authors acknowledge D. A. Kramer, chemist, Avondale Research Center, Bureau of Mines, Avondale, MD (now commodity specialist, Bureau of Mines, Washington, DC).

CHAPTER 5.—LIMESTONE-GYPSUM ROAST-WATER LEACH PROCESS

By L. Crocker, R. H. Lien, and V. E. Edlund[1]

The limestone-gypsum roast-water leach extraction technique evolved from exploratory roast tests designed to develop basic lithium extraction data and to establish the reaction mechanism (*10*). The success of these preliminary tests led to extensive batch-roast studies to establish optimum roast conditions and to investigate roasting atmosphere (*10*). Subsequently, larger scale roasting in a rotary furnace was conducted to study the dynamic variables affecting the calcine (*10-11*). These tests generated a sufficient quantity of calcine for process research unit (PRU) studies in which leach solution purification and product (Li_2CO_3) precipitation were investigated (*11*).

BATCH ROAST TESTS (*10*)

Raw Materials, Test Procedures, and Equipment

The limestone-gypsum roast tests were conducted with McDermitt B clay. Chemical analysis of a typical clay sample is given in table 5. The roast feed was a mixture of clay, limestone, and gypsum. Both reagent-grade and naturally occurring limestone and gypsum were used; the CaO and SO_4 analyses of the natural materials are presented in table 13.

The general test procedure involved (1) thoroughly mixing selected portions of the dry ingredients, (2) pelletizing the mixture, (3) roasting the pelletized mix, and (4) water leaching the calcines to extract the lithium. The calcine was ground to minus 100 mesh before leaching.

The preroast charge was mixed in a "V" blender. A revolving pan mixer (fig. 12) was used to pelletize the mix. Roasts were conducted in a muffle furnace (fig. 13) and in a tube furnace (fig. 14).

Exploratory Studies To Develop Basic Data

Exploratory roasting studies were conducted to determine the approximate ingredient mix required to effectively extract lithium from McDermitt clay. Subsequently, a test series was conducted to determine the effect of preparation and physical character of the preroast charge on lithium extraction. In addition, tests were conducted to determine the reaction mechanism.

Determination of Preroast Mixture

Preliminary roasting studies were conducted to determine the approximate ingredient mix that would result in the best lithium extraction. Pelletized charges of 40 g were roasted in a muffle furnace for 1 h at 1,000° C under oxidizing conditions. The weight ratios of the clay-$CaCO_3$-$CaSO_4 \cdot 2H_2O$ mixes ranged from 5:0:6 to 5:6:0. The calcines were allowed to cool and were then water-leached to determine lithium extraction. A 5:3:3 mix was found to be optimum (table 14); lithium extraction from this mix was 90 pct. Extraction of potassium, sodium, and fluorine from the same mix was 95, 85, and 2 pct, respectively. Lithium extraction from clay roasted alone was only 0.1 pct.

TABLE 13.—Analysis of additives used in limestone-gypsum roast tests, percent

Additive	CaO	SO_4
Limestone:		
Natural (Nevada)	53.6	0.03
Reagent grade	56.1	0
Gypsum:		
Blue Diamond (Nevada)	29.6	53.1
Georgia Pacific (Utah)	33.3	51.7
Reagent grade	33.6	55.8

Figure 12.—Drum pelletizer.

---

[1] Metallurgist, Salt Lake City Research Center, Bureau of Mines, Salt Lake City, UT (retired)

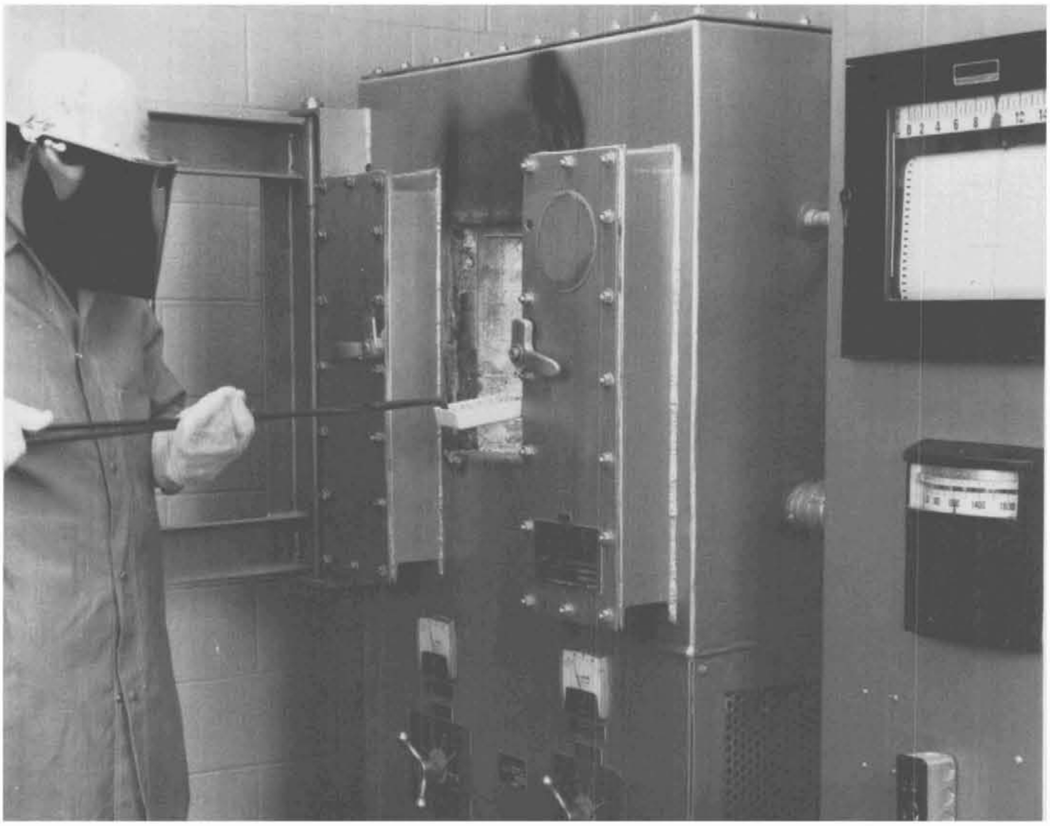

Figure 13.—Muffle furnace for limestone-gypsum roast tests.

Figure 14.—Electrically heated tube furnace.

TABLE 14.—Leaching results for clay mixtures with different ingredient weight ratios[1]

Weight ratio			Weight loss, pct	Extraction, pct			
Clay	$CaCO_3$	$CaSO_4 \cdot 2H_2O$		Li	K	Na	F
5	0	6	11.0	61.6	26.3	38.4	7.9
5	1	5	12	70	46.8	49.2	3.3
5	2	4	14.3	84.7	93	79.5	2.2
5	3	3	16	89.6	94.7	84.7	2.1
5	4	2	19.5	80.8	93.1	72.2	1.4
5	5	1	23.8	73.3	78.2	77.9	1.1
5	6	0	28.3	12.5	18.8	13.6	1.2
5	0	0	8.5	.1	.5	.9	1

[1] Each mixture was roasted 1 h at 1,000° C.

TABLE 15.—Lithium extraction using different methods for preroast charge preparation,[1] percent

Method[2]	1,000° C roast	1,100° C roast
Dry mixed:		
Without agglomeration	87.7	80.3
Pelletized with H_2O	89.2	79.1
Wet mixed and filtered:		
Filter cake dried and ground to 100 mesh	86.4	73.1
Filter cake dried and broken (but not ground)	90.5	86.3

[1] 2-h roast.

[2] Pebble mill used for mixing samples (all 4 methods).

TABLE 16.—Reaction mechanism test results[1]

Weight ratio of charge mix		Li extraction, pct
Clay-$CaCO_3$	$CaSO_4 \cdot 2H_2O$-SiO_2	
2:1	None	7.0
2:1	[2]2.87:1	31.5
4:1	None	3.1
4:1	[2]2.87:1	13.4

[1] 1-h roast at 1,000° C. [2] 1:1 mol ratio.

Charge Preparation Methods

A test series was conducted to determine the effect of preparation and the physical character of the preroast charge on lithium extraction. In each test, a 5:3:3 mix was roasted for 2 h in a muffle furnace, and the resultant calcine was leached. Using a pebble mill, the mix samples were prepared by (1) dry mixing only, for roasting without agglomeration, (2) dry mixing followed by pelletizing with water and drying of the pellets, (3) wet mixing followed by filtering, drying of the filter cake, and grinding of the dried filter cake to minus 100 mesh, and (4) wet mixing followed by filtering, then drying and breaking of the filter cake (but without grinding). The pebble mill ensured good mixing while minimizing grinding of the mix ingredients. Test results, shown in table 15, indicate that the best lithium extraction, 91 pct, resulted from wet mixing followed by filtering and roasting of the dried (and broken) filter cake. Using the dry-mix, pelletized-feed method, 89-pct extraction was obtained. The advantage of the slightly higher lithium extraction made possible by wet mixing was more than offset by the disadvantage of slow filtering. Thus, pelletized mixtures were used in subsequent roasting studies. However, in a large-scale operation, feeding the slurry directly to a drying or roasting kiln might be feasible.

Determination of Reaction Mechanism

Exploratory roasting tests were conducted to determine if Li_2SO_4 from the roasting operation forms as a solid-to-solid or gas-to-solid reaction. Pelletized samples of different clay-$CaCO_3$ and $CaSO_4 \cdot 2H_2O$-SiO_2 mixtures were placed in separate boats and then heated together in a tube furnace for 1 h at 1,000° C. The furnace tube was sealed at both ends with rubber stoppers to maintain a static atmosphere of air. At the conclusion of the run, the boats were allowed to cool in the furnace to ambient temperature. A sample of the clay-$CaCO_3$ calcine was leached, and the products were analyzed.

Test results, presented in table 16, show that more lithium was extracted from the calcines roasted in the presence of the $CaSO_4 \cdot 2H_2O$-SiO_2 mix than from the clay-$CaCO_3$ calcines roasted alone. These results indicate that SO_2 from the $CaSO_4 \cdot 2H_2O$-SiO_2 reacted with the $Li_2Si_2O_5$ in the clay to form Li_2SO_4. The lithium extracted from the clay-$CaCO_3$ mix calcined alone was attributed to the small amount of sulfur contained in the clay. In addition, leach solution analyses showed that the lithium was extracted as Li_2SO_4. Therefore, the test data indicate that Li_2SO_4 was formed by the following reactions:

$$CaSO_4 \cdot 2H_2O + SiO_2 \rightarrow CaSiO_3 + SO_2 + \tfrac{1}{2} O_2 + 2H_2O \qquad \text{(A)}$$

and

$$Li_2Si_2O_5 + SO_2 + \tfrac{1}{2} O_2 \rightarrow Li_2SO_4 + 2SiO_2. \qquad \text{(B)}$$

Although the reaction of limestone is not shown, limestone is a necessary additive for attaining high lithium extraction. Limestone in the charge limits the back reaction of Li_2SO_4 with free silica by reacting with the silica to form a calcium silicate.

Muffle Furnace Tests To Determine Optimum Roast Conditions

The exploratory roast-leach studies indicated that lithium extractions approaching 90 pct can be realized in the limestone-gypsum processing of McDermitt clay. A pelletized 5:3:3 clay mix was found to be about optimum when batch-roasted under oxidizing conditions for 1 h at 1,000° C. An expanded laboratory study was undertaken to verify these results and better determine the best conditions for calcine production.

Effect of Charge Composition and Roast Temperature on Lithium Extraction

Tests were conducted to determine the leaching responses of various clay mixtures roasted at 900° to 1,050° C. Pelletized mix samples were placed in open refractory boats and roasted for 1 h at different temperatures in a muffle furnace. The calcines were then leached to determine lithium extraction. Table 17 shows that the best overall results were achieved with a 5:3:3 mix at 1,000° C. These data, together with test results presented in table 14, show that excellent lithium extraction was obtained over a fairly wide range of charge ratios and roast temperatures; the optimum charge ratio appears to be 5:3:3.

TABLE 17.—Effect of charge composition and roasting temperature on lithium extraction[1]

Weight ratio			Lithium extraction, pct, at —			
Clay	$CaCO_3$	$CaSO_4 \cdot 2H_2O$	900° C	950° C	1,000° C	1,050° C
5	2	3	ND	83.2	83.7	75.4
5	2	4	82.4	83.7	85.8	87.9
5	3	2	86.7	87.7	87.6	89.1
5	3	3	83.1	87.3	90.7	89.3
5	3	4	85.3	86.7	87.8	87.8
5	4	3	79.6	81.7	80.9	77.6
5	4	4	80.9	81.6	78.9	78.5
5	5	3	74.2	78.7	81.2	81.3

ND Not determined. [1] 1-h roast.

Effect of Roast Time and Temperature on Lithium Extraction

Several series of tests were conducted in a muffle furnace to define the influence of time and temperature on lithium extraction. The test conditions and results for a 5:3:3 mix are presented in table 18.

Test data show that increasing the roast temperature from 750° to 1,000° C increased lithium extraction; however, above 1,000° C, lithium extraction decreased. A 1-h roasting period was sufficient to convert the lithium in the clay to a water-soluble sulfate. Generally, prolonged roasting for 4 h reduced lithium recovery. Extraction of potassium, sodium, and fluorine followed the same general trends as lithium extraction.

Effect of Additive Type on Lithium Extraction

A test series was conducted in a muffle furnace to determine if additive type (naturally occurring versus reagent-grade chemicals) would affect lithium extraction. Test results, presented in table 19, show that slightly higher extractions were obtained with reagent-grade chemicals than with naturally occurring materials. The difference in extraction may have been due to impurities in the natural materials. Also, the natural materials were not as finely ground as the reagent-grade chemicals. Table 19 shows that finer grinding of the natural material increased the lithium extraction.

Reagent-grade additives were used for subsequet batch tests; natural materials were used in the larger scale continuous tests in the rotary roaster.

Tube Furnace Tests To Investigate Roasting Atmosphere

Muffle furnace roasts were conducted in an oxidizing atmosphere employing indirect heating. Scaleup of the limestone-gypsum roast would probably involve using a direct-fired roaster in which the roasting atmosphere would be neutral. Thus, testing was conducted to determine if clay mixtures roasted in neutral combustion atmospheres would leach as effectively as those roasted under oxidizing conditions. In this test series, samples of standard 5:3:3 mix were roasted in a simulated gas combustion atmosphere analyzing, in volume percent, 10 CO_2, 18 H_2O, and 72 N_2; this mixture approximated the composition of natural gas combustion products.

Pelletized samples were roasted at various temperatures for different time periods in a tube furnace assembly (fig. 14). Metered amounts of CO_2 and N_2 were introduced through a glass dispersion tube into a flask partially filled with hot water. Here the gaseous components intermixed and were preheated to the temperature required to establish the desired concentration of water vapor in the gas flow. At the conclusion of each run, the furnace was cooled to 600° C, the gas flow was discontinued, and the calcine was cooled to ambient temperature inside the furnace. The roasted product was then leached and the filtrate residue analyzed. Comparison of the results presented in tables 18 and 20 revealed that roasting in neutral combustion atmospheres did not adversely affect the conversion of lithium in the clay to the water-soluble sulfate.

In addition, tests were conducted to study the effect of low carbon monoxide (CO) concentrations on lithium extraction. The roasting atmosphere in a direct-fired roaster may contain CO since all commercial fuels contain hydrocarbons that may give off CO in the initial or early stages of combustion.

Several tests were conducted to define the influence of variations in the concentration of CO, temperature, and time on the production of a leachable calcine. Samples of pelletized 5:3:3 mix were placed in Alundum combustion boats and then into a tube furnace (fig. 14). An inert N_2 atmosphere was maintained during heating and cooling. Metered flows from compressed cylinders of CO and N_2

TABLE 18.—Effect of roasting time and temperature on lithium extraction using a 5:3:3 clay-limestone-gypsum mix

Roast temp and time, h	Extraction, pct				Roast temp and time, h	Extraction, pct			
	Li	K	Na	F		Li	K	Na	F
750° C:					950° C:				
1	59.4	43.6	ND	0.8	1	85.6	92.0	75.7	ND
2	66.6	56	59.7	.9	2	85.5	90.3	75.6	ND
3	66.5	53.1	57.3	.8	3	85.1	91.2	76.8	ND
4	71.5	62.7	59.7	.9	4	82.2	94.7	72.1	ND
800° C:					1,000° C:				
1	73.3	62.7	62.9	1.0	1	88.4	94.9	81.6	1.3
2	75.7	73.1	65.1	.8	2	88.4	94.9	78.1	1.7
3	76.3	73.5	68.6	1	3	86.9	96.5	79.1	1.9
4	77.7	76.6	65.2	1	4	86.5	95.7	79.1	1.9
850° C:					1,050° C:				
1	79.5	79.0	74.0	.8	1	83.0	97.4	77.0	2.8
2	81.3	84.2	75.5	1.2	2	80.7	96.7	73.6	4.1
3	81.3	83.3	75.5	.9	3	77.3	96.3	72.1	5.5
4	80	85.1	73.7	1	4	63.6	95.2	60	2.7
900° C:					1,100° C:				
1	83.8	87.6	75.5	ND	1	65.7	92.8	62.4	3.8
2	84.3	89.4	75.6	ND	2	68.9	95.5	67.2	2
3	83.9	89.5	72.6	ND	3	67.1	94.4	64.8	1.5
4	83.1	90.4	75.6	ND	4	68.8	95.5	68.9	2.4

ND Not determined.

TABLE 19.—Leaching results for clay calcined[1] with natural and reagent-grade $CaCO_3$ and $CaSO_4 \cdot 2H_2O$

Weight ratio of mix, clay-$CaCO_3$-$CaSO_4 \cdot 2H_2O$	Roast temp, °C	Li extraction, pct
Reagent grade: 5:3:3	950	87.3
	1,000	89.2
	1,050	89.3
Natural,[2] 5:3.14:3.41:[3] Standard (minus 200-mesh) size	900	83.5
	1,000	85.3
Minus 100-mesh size	900	82.7
	1,000	84.1

[1] 1-h roast.
[2] Nevada limestone and Blue Diamond gypsum.
[3] Equivalent to 5:3:3 mix.

TABLE 20.—Lithium extraction for calcines roasted in a neutral combustion gas atmosphere[1]

Roast conditions		Li extraction, pct
Temp, °C	Time, h	
800	2	73.1
900	1	84.1
	2	85.6
	4	83.4
1,000	1	88.4
	2	87
	4	80.4

[1] 10 pct CO_2, 18 pct H_2O, 72 pct N_2.

were combined in the proper ratio to give the desired gas mixture; mixtures containing less than 1 pct CO were obtained by blending a calibrated 1-pct CO-in-N_2 premix with N_2. Samples of the roasted products were leached, and the leach products were analyzed.

Test results, presented in table 21, show that lithium extraction decreased with prolonged roasting when the CO concentration was increased to 1 pct or greater. Comparison of the data with those presented in table 20 indicates that the decrease in lithium recovery was minimal for roasting temperatures lower than 1,000° C in furnace atmospheres containing less than about 0.5 pct CO. (This CO concentration represents a natural gas combustion efficiency of approximately 98 pct.)

TABLE 21.—Effect of CO in roasting atmosphere on lithium extraction

Roast temp and CO concentration, pct	Li extraction, pct		
	1-h roast	2-h roast	3-h roast
800° C:			
0.1	ND	73.2	76.6
0.5	69.5	74.9	74.9
1	71.2	71.2	66.1
5	63.7	57.3	32.3
900° C:			
0.1	ND	ND	83.7
0.5	ND	ND	83.7
1	ND	80.2	66.1
5	64.6	43.6	12.5
1,000° C:			
0.1	ND	ND	85.8
0.5	ND	ND	73.2
1	86.6	ND	69.8
5	66.1	37.7	8.9

ND Not determined.

PROCESS RESEARCH UNIT STUDIES (*11*)

A PRU was constructed to investigate lithium recovery from McDermitt clay on a larger scale. Roasting was conducted in a gas-fired rotary roaster (fig. 15) to study the dynamic variables affecting the calcine and to confirm batch test results. Also, the larger-scale roast operation generated calcine for leaching, solution purification, and product recovery tests.

A process for recovering lithium from McDermitt clay evolved from this research; the process flowsheet is shown in figure 16. The process involves several unit operations including feed preparation, roasting, leaching, evaporation, precipitation, and crystallization.

Appendix A presents a material balance for a typical PRU test; appendix B presents a cost evaluation based on this material balance.

Process Description

This process is designed to recover lithium, as Li_2CO_3, from McDermitt clay. A mixture of clay, limestone, and gypsum is pelletized, dried, and fed to the roasting furnace. Roasting the pellets at 900° C converts the lithium in the clay to water-soluble Li_2SO_4. Water leaching the calcine produces a solution containing lithium, potassium, sodium, and a small amount of calcium, all as sulfates. The leach solution, together with recycled product wash and mother liquor, is concentrated by evaporation. During this concentration operation, carbonate ion, present in the recycle solutions, causes calcium to precipitate as $CaCO_3$, which is removed by filtration. The concentrated solution is then heated to boiling, and Na_2CO_3 is added to precipitate Li_2CO_3 product.

The product filtrate contains about 3 g/L Li. To recover this lithium, the solution is cooled to crystallize glaserite ($3K_2SO_4 \cdot Na_2SO_4$) and glauber salt ($Na_2SO_4 \cdot 10H_2O$) and then recycled to the evaporation step.

Removing calcium from the leach solution as $CaCO_3$ prevents calcium contamination of the product. The solution recycled to the evaporation step contains sufficient carbonate ion, as either Li_2CO_3 or excess Na_2CO_3, to precipitate over 99 pct of the calcium contained in the leach solution.

Materials

Analysis of the clay used for the PRU tests is shown in table 22. Agricultural-grade gypsum and natural limestone from Nevada were used in making up the charge. Analysis of these materials is shown in table 13. Simulated solutions used in laboratory evaporation and product purification tests were made up with reagent-grade chemicals.

PRU Equipment

Feed for the roast was ground and mixed in a ball mill (16-in diam by 24-in length). The minus 100-mesh mixture was pelletized with water in a 20-in-diam drum pelletizer (fig. 12).

The pellets were roasted in a direct-fired rotary roaster (fig. 15) that was fired with natural gas and had a working capacity of 0.5 ft^3. The roast product (calcine) was leached with water in a 55-gal, baffled, polyethylene vessel. A propeller mixer agitated the slurry.

Figure 17 shows the evaporation, filtration, and product precipitation equipment. To recover the leach solution, the slurry from the leach tank was transferred

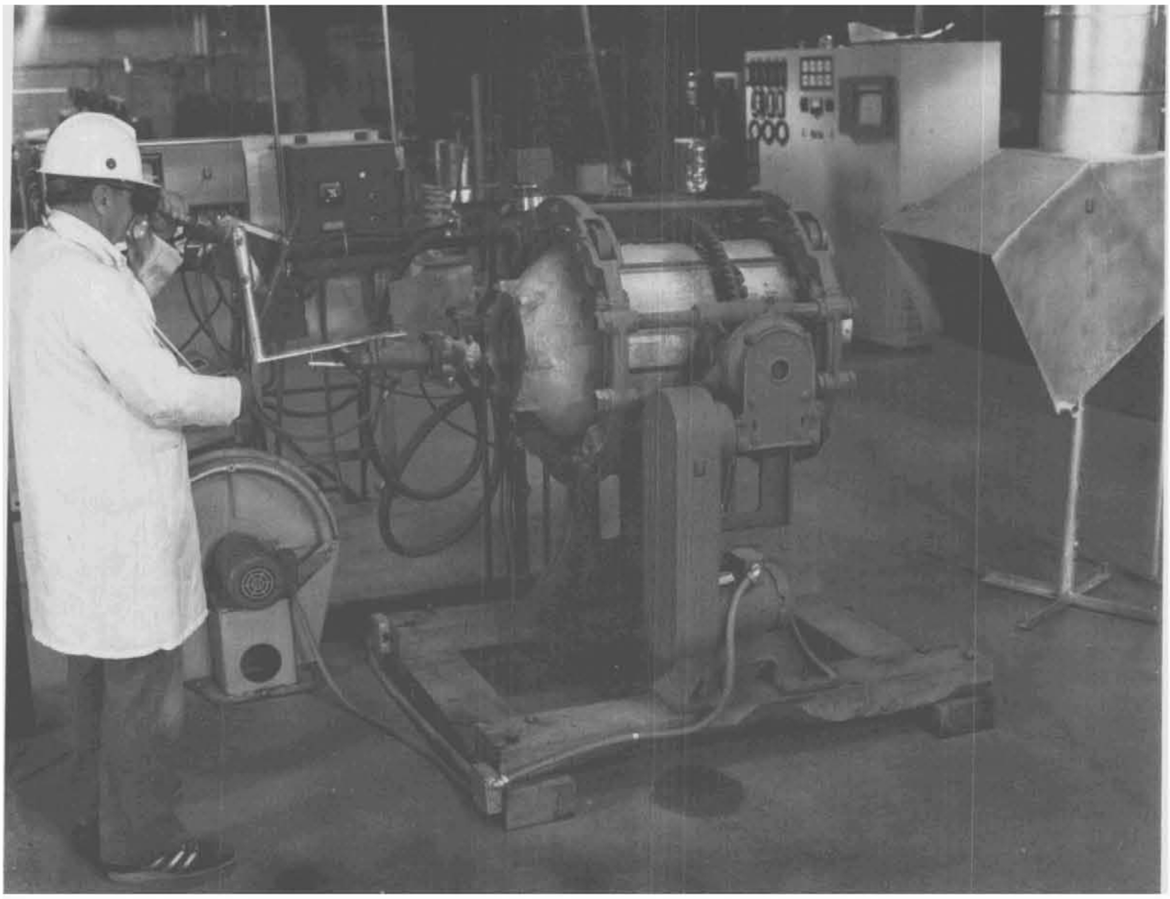

Figure 15.—Gas-fired rotary roaster.

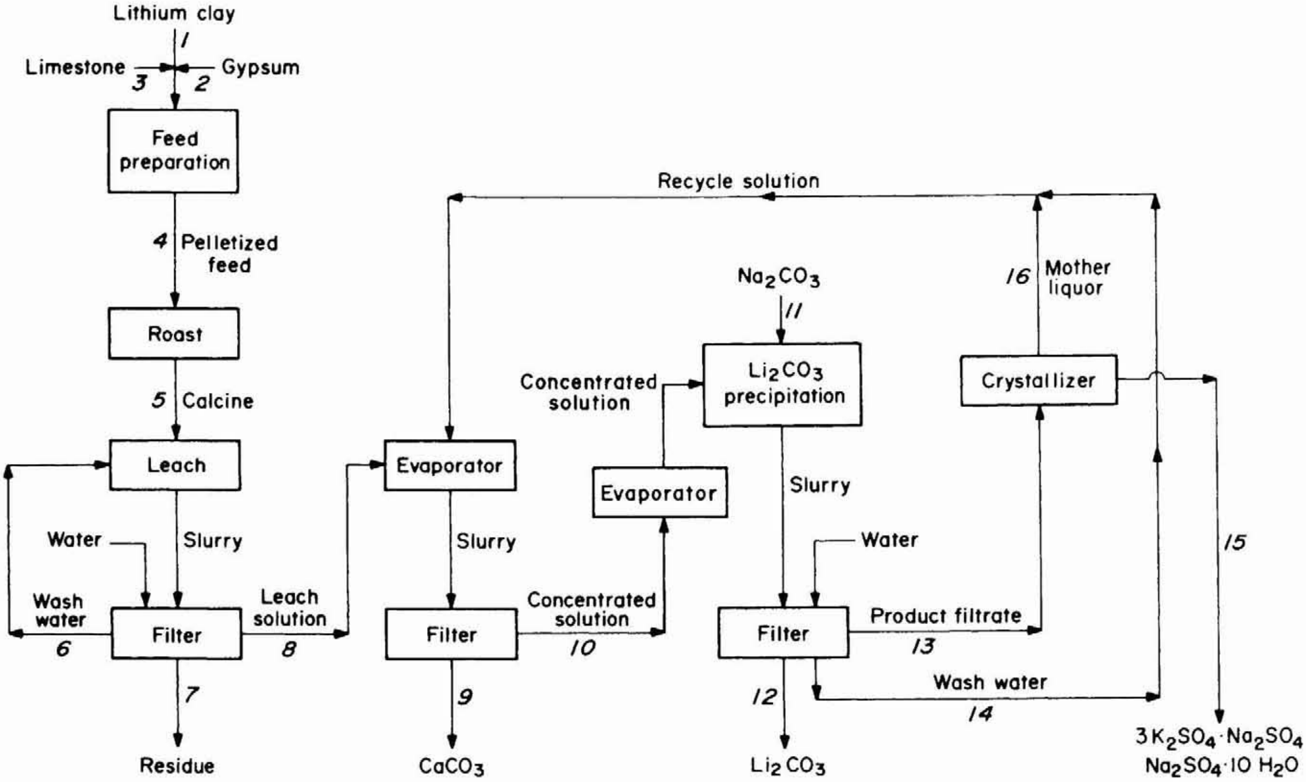

Figure 16.—Generalized process flowsheet for limestone-gypsum process.

TABLE 22.—Composition of McDermitt B clay, dry basis, percent

Al	3.1	Li	0.6
Ca	1.8	Mg	9
F	2	Na	.58
Fe	2.5	Total SiO_2	53
K	3.7	Free SiO_2	15

by gravity flow to a pan filter with a surface area of 9 ft^2. A tubing pump transferred the leach solution to a 55-gal stainless steel tank for concentration. The tank was equipped with a 9,000-W over-the-side immersion heater. The concentrated solution was filtered on a tabletop Buchner funnel to remove $CaCO_3$. A tubing pump transferred the concentrated solution to the product precipitation unit, which consisted of a 6.5-gal stainless steel vessel equipped with a 1,000-W over-the-side immersion heater. An impeller mixer agitated the solution. The Li_2CO_3 product was recovered and washed on a Buchner funnel.

The product filtrate was cooled by refrigeration to crystallize glauber salt and glaserite.

Operating Conditions and Test Results

Each process unit operation including feed preparation, roasting, leaching, evaporation, product precipitation, and crystallization was studied in detail both in the PRU and in the laboratory. The objective of the work was to determine operating conditions that would (1) maximize lithium recovery, (2) minimize process operating costs, and (3) produce a high-purity product.

Feed Preparation

The McDermitt clay contains lithium principally as hectorite. To convert the lithium to Li_2SO_4, the clay was mixed with limestone and gypsum and roasted. As received, the clay was soft and friable and required no heavy crushing. However, it was air-dried and passed through a jaw crusher to produce a minus 10-mesh material before blending. The other raw materials, limestone and gypsum , were treated similarly. Further feed preparation entailed grinding and mixing the ingredients for 1 h in a ball mill. The resultant mixture (80 pct finer than 200 mesh) was pelletized with water to

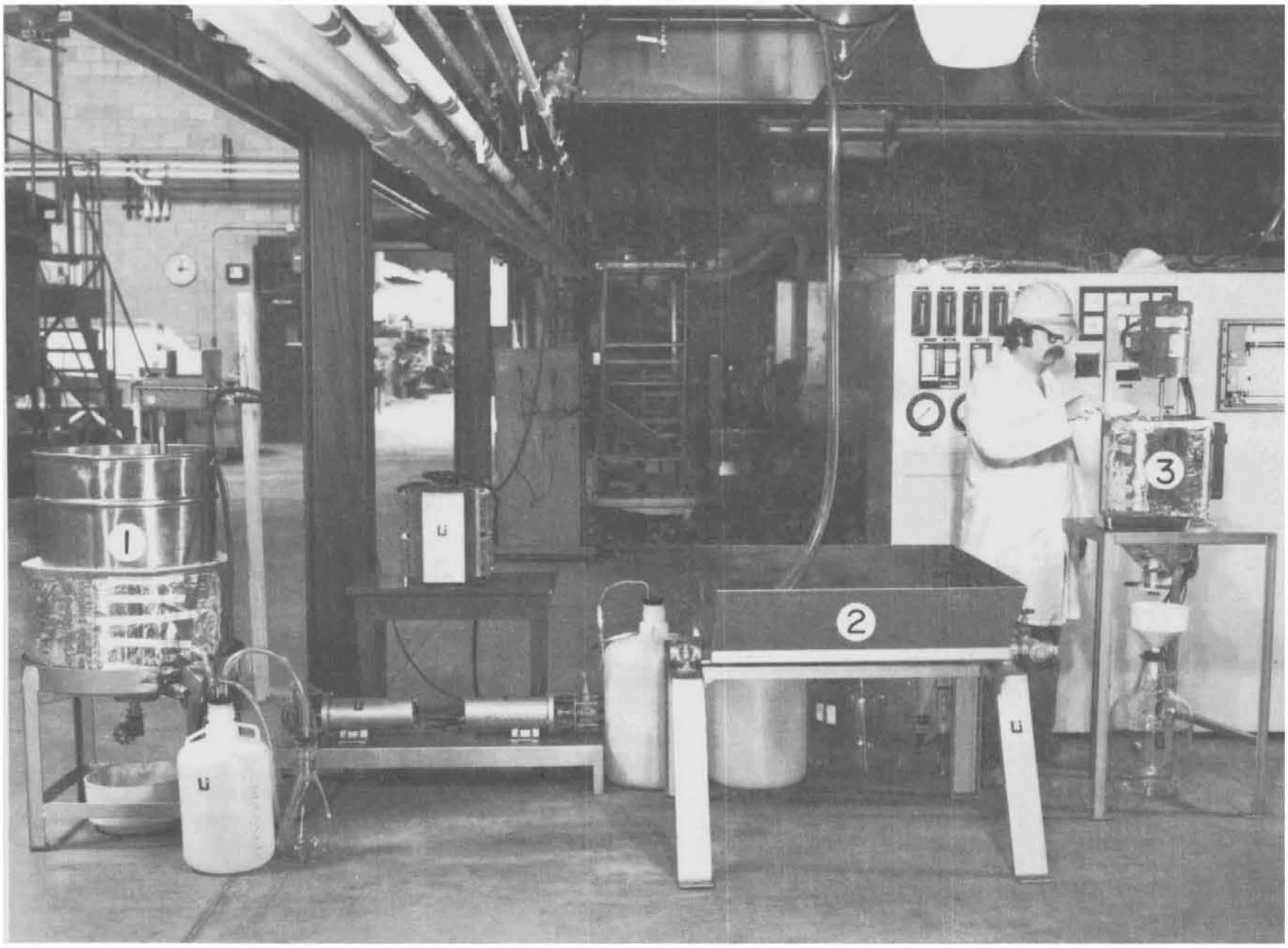

Figure 17.—PRU equipment.

produce nominal 6.5-mm-diam pellets. These pellets contained up to 20 pct moisture and were dried at 70° C before roasting.

Roasting

The objectives of the roasting tests were to (1) generate calcine for leaching, purification, and product recovery studies, (2) determine optimum roasting conditions, and (3) determine typical gas emissions.

Initially, a series of batch tests was conducted in the rotary roaster to determine optimum retention time and roast temperature (*10*). In these tests, small charges (500 g) of pelletized 5:3:3 mix were roasted. The test results showed a 2-h retention time and 900° C to be optimum. This retention time was used throughout the rotary roaster studies; the temperature was varied in a few tests in which the effect of temperature on lithium extraction was investigated.

To generate calcine for use in PRU solution studies, an equivalent 5:3:3 mixture of clay, limestone, and gypsum was used; batch testing had established the 5:3:3 mix as optimum. The pelletized feed was charged to the roaster in 600-g increments every 5 min to simulate continuous operation. Generally, each test produced 80 lb of calcine in 6.5 h operating time.

The final phase of the PRU roast studies involved investigating the effects of charge composition and roast temperature on lithium extraction. A test series was conducted in which various mixes were roasted; lithium extraction was determined by water-leaching composite samples of the calcines.

Test results, presented in table 23, show that lithium extractions of at least 80 pct were attained with a wide range of clay-limestone-gypsum ratios. Also, the data indicate that good lithium extraction was achieved over a temperature range of 850° to 975° C. The 5:2:2 mix was chosen for cost evaluation because this mix provided high extraction with a relatively low reagent addition.

Emissions of SO_2 and fluorine were calculated from material balances for two-thirds of the tests listed in table 23. The calculated emissions from representative roasts are presented in table 24. In a commercial operation, these offgases would require scrubbing before being vented to the atmosphere.

Leaching

The objective of the PRU leach tests was to determine the relationship between leach-system variables and optimal lithium extraction. The following variables were studied: (1) leach pulp percent solids, (2) wash water recycle, (3) calcine particle size, and (4) leach time.

The calcines leached in these tests were produced by roasting 5:3:3 mixtures of clay, limestone, and gypsum. Generally, 70 lb of calcine was water-leached in each test. A slurry filter recovered the leach solution. The filter cake was washed and discarded.

Solids Content and Wash Water Recycle

A series of 30-min leach tests was conducted at ambient temperature to study the effect of percent solids and wash water recycle on lithium extraction. The test results, presented in table 25, show that the calcine was leached effectively at 40 pct solids with recycled wash water. At 50 pct solids, the lithium extraction decreased. Since the wash water was recycled to the leach step, the volume of wash water used was equal to the volume of makeup water required for the next leach. In the material balance calculations, 40 pct solids was used as the optimum.

Calcine Particle Size and Leach Time

The calcine pellets do not break apart during the leach. If a coarse particle could be leached effectively, grinding requirements would be minimized. Therefore, a test series was conducted to study the effect of calcine particle size on lithium extraction.

The calcine was leached for 30 min at 40 pct solids using recycled wash water. Test results, given in table 26, show that the 30-min leach extracted the lithium equally well from all particle sizes tested. To determine the effect of leach time on lithium extraction, a test series was conducted with coarse-crushed and whole pellets. The pellets were leached at 40 pct solids in recycled wash water. Test results, presented in table 27, show that lithium was extracted from coarse-crushed pellets with a 5-min leach; whole pellets were not effectively leached in 5 min.

TABLE 23.—Effect of charge composition and roasting temperature on lithium extraction under dynamic conditions[1]

Roast temp, °C	Weight ratio			Number of roasts	Li extraction,[2] pct
	Clay	$CaCO_3$	$CaSO_4 \cdot 2H_2O$		
850	5	2	2	1	84.6
900	5	1	1	1	59
	5	1.5	1.5	1	80.5
	5	2	1	1	81.6
	5	2	2	3	84.3-86.9
	5	2	3	1	84.4
	5	3	2	2	86.8-88.5
	5	3	3	17	83.3-86.6
	5	3	4	1	85.1
950	5	2	2	1	89.3
975	5	1.5	1.5	1	81

[1] 2-h roast.

[2] For analysis, calcine samples were leached with water at 25 pct solids; the residues were then washed. Lithium extraction was based on calcine and residue analyses.

TABLE 24.—Gas emissions from PRU continuous tests

Feed ratio, clay-$CaCO_3$-$CaSO_4 \cdot 2H_2O$	Temp, °C	Calculated gas analysis,[1] vol pct	
		F	SO_2
5:1.5:1.5	900	0.1535	0.0640
	975	.1928	.1162
5:2:2	850	.1870	.0796
	900	.1193	.0607
	950	.1705	.1110
[2]5:3:3	900	.1189	.0457

[1] Based on material balance of furnace charge and calcine, assuming each 1,000 ft^3 natural gas produced 10,550 ft^3 of combustion gas.

[2] Gas analysis averaged for 15 roasts at 900° C.

TABLE 25.—Effect of solids content and wash water recycle on lithium extraction[1] (30-min leach)

Solids content, pct	Li extraction, pct	
	Using fresh water	Using recycled wash water
[2]25	83.4	82.7
[2]40	81.4	83.6
[3]50	80.9	69.4

[1] Extractions based on lithium concentrations in calcine and leached residue.

[2] 96-L leach and wash water volume.

[3] 48-L leach and wash water volume.

TABLE 26.—Effect of calcine particle size on lithium extraction (30-min leach)

Particle size	*Li extraction, pct*[2]
Minus 100 mesh	82.6
Coarse-crushed pellets[1]	83.6
Whole pellets	83.9

---

[1] Screen analysis of calcine particles was 70 pct plus 10 mesh.

[2] Based on Li concentrations in calcine and leached residue.

TABLE 27.—Effect of leach time on lithium extraction

Particle size	Leach time, min	Li extraction, pct
Coarse-crushed pellets	5	84.2
	15	84.2
	30	83.6
	60	83.1
Whole pellets	5	70.7
	30	83.9
	60	84.2

Although the pellets did not break apart during the leach, prolonged agitation generated fines which affected filtration rates. The data presented in table 28 show that filtrate rates decreased with increased leach time and increased particle size. For 30-min leaches, the whole pellet slurry filtered slowly because the filter cloth was blinded with fines. As the calcine particle size decreased, the fines tended to remain on top of the filter cake, allowing faster filtration. Overall, the test results indicate that coarse-grinding the calcine and leaching it for 5 min at 40 pct solids provided good extraction and high filtration rates. Under these conditions, lithium extractions of 82 to 84 pct could be expected; the leach solution generally contained 2.5 to 3.0 g/L Li.

Evaporation

As figure 16 shows, the evaporator was fed with leach solution and solution recycled from the previous test. The recycled solution (mother liquor plus product wash) accounted for about 20 pct of the total volume in the evaporator.

In addition to concentrating the solution, calcium as $CaCO_3$ was removed from the leach solution in this step of the process. The leach solution was saturated with $CaSO_4$ (about 0.6 g/L Ca^{2+}). Extensive laboratory testing showed that reducing the calcium ion concentration to about 0.015 g/L prevented calcium contamination of the product.

The evaporation procedure involved the following steps:

1. The solution (leach plus recycle) was evaporated to about 50 pct of its original volume and then filtered to remove $CaCO_3$. Carbonate ion (approximately 15 g/L) present in the recycled solution precipitated over 99 pct of the calcium contained in the leach solution.
2. The filtrate was returned to the evaporator. Evaporation continued until the solution was reduced to 20 pct of its original volume.
3. The hot concentrated solution, containing 12 to 13 g/L Li, was transferred to the product precipitation step. Generally, this concentrated solution was cloudy because a small amount of Li_2CO_3 precipitated during evaporation.

TABLE 28.—Effect of calcine particle size and leach time on filtrate rates

Calcine particle size	Leach time, min	Filtrate rate,[1] L/(m²·h)
Minus 100 mesh	30	86
Coarse-crushed pellets	5	155
	15	111
	30	68
	60	67
Whole pellets	5	150
	30	42

---

[1] Rates calculated from data obtained by filtering leach slurry on process pan filter.

Product Precipitation

Lithium recovery involved heating the concentrated solution to boiling and adding a stoichiometric amount of Na_2CO_3 to precipitate a Li_2CO_3 product. The objective of this step was to recover a product of at least 99-pct purity.

Initially, the product was recovered from the hot solution by vacuum filtration and then dried. This procedure yielded a product of about 80-pct purity with the principal contaminants being Na_2SO_4 and K_2SO_4. Numerous tests were conducted in the PRU and laboratory (using PRU leach solution) to investigate product purification techniques. Test results were erratic because precise control of solution concentration was difficult; therefore, synthetic solutions were used to study operating variables.

A series of laboratory tests was conducted using 1-L batches of synthetic concentrated solution (made up with reagent chemicals) containing 97 g/L Li_2SO_4, 158 g/L K_2SO_4, and 87 g/L Na_2SO_4. Adding a stoichiometric amount of Na_2CO_3 to the hot solution precipitated Li_2CO_3. Product filtration and washing procedures were then studied. From the test results presented in table 29, the following observations were made:

1. Pressure filtration yielded a product of higher purity than vacuum filtration by reducing the moisture content of the filter cake.
2. With pressure filtration, 4 to 6 L of wash water per kilogram of dry product was required to produce a 99-pct-pure product. A much higher volume of water was needed to produce a comparable product by vacuum filtration.
3. For pressure filtration, wash water volumes above 6 L/kg of dry product did not further improve product purity. Also, single-stage washing was as effective as either multistage washing or product reslurry.
4. Adding Na_2CO_3 as a saturated solution, rather than as a dry powder, had little effect on product purity. However, this procedure generated a coarse grainy product, in contrast to the fine powdery product obtained by adding dry Na_2CO_3.

The wash water and product filtrate recovered in these tests contained 14 to 16 g/L Li_2CO_3. The wash was recycled to the evaporator. After a crystallization step, the mother liquor was also recycled.

TABLE 29.—Results of product purification tests using synthetic solutions

Wash water volume, mL	Water per dry product, L/kg	Product analysis, wt pct[1]		Comments[2]
		K	Na	
Vacuum filtration:[3]				
0	0.0	4.1	3.9	No wash.
300	5.7	.86	.6	Single wash.
600	12.8	.4	.3	Do.
700	15.3	.12	.14	Do.
800	17.5	.16	.16	Do.
Pressure filtration:[4]				
0	0	2.3	2	No wash.
	0	1.9	1.8	Na_2CO_3 added as saturated solution; no wash.
100	0	1.6	1.5	Do.
200	2	.3	.3	Single wash.
300	4.1	.17	.17	Do.
	6.1	.16	.15	Do.
	6.3	.16	.1	Product reslurried with 200 mL, filtered, then washed with 100 mL.
	6.6	.26	.18	Na_2CO_3 added as saturated solution; single wash.
	6.2	.16	.16	3 separate 100-mL washes.
600	12.9	.18	.16	Single wash.
	13.2	.14	.14	6 separate 100-mL washes.
800	17.7	.18	.2	Single wash.

[1] K and Na present as sulfates; product also contained traces of Ca (0.02 wt pct) and Mg (0.01 wt pct), probably present as carbonates.

[2] Except as indicated, Na_2CO_3 added to the concentrated solution as dry powder.

[3] Carried out on a laboratory-size Buchner funnel.

[4] Conducted with a tabletop filter connected to a 45-psi air supply.

Crystallization

In addition to residual Li_2CO_3, the product filtrate contained high concentrations of K_2SO_4 and Na_2SO_4 (over 150 g/L of each). If the solution is to be recycled, the buildup of these salts must be prevented.

Laboratory and PRU tests showed that the most effective method for reducing the sulfate concentration involved crystallizing the salts by chilling the product filtrate to between 0° and -4° C; below -4° C, the filtrate freezes. The mother liquor, which contained 70 g/L Na_2SO_4 and 100 g/L K_2SO_4, was recovered by either vacuum or pressure filtration. Pressure filtration tended to reduce lithium loss by decreasing the amount of mother liquor present in the filter cake. The filter cake was a mixture of glauber salt and glaserite.

Laboratory tests showed that, if desired, glaserite and glauber salt could be recovered separately by a two-step crystallization procedure. At product filtrate temperatures down to about 17° C, glaserite crystallized. The salt was recovered by vacuum filtration and analyzed as 33 wt pct K, 8 wt pct Na, and <0.1 wt pct Li. Further cooling of the product filtrate (to as low as -4° C) crystallized glauber salt. These salts were recovered by pressure filtration and dried. The dried salts contained 28 wt pct Na, 6 wt pct K (a small amount of glaserite crystallized with the glauber salt), and 0.15 wt pct Li.

Overall Lithium Recovery

PRU roast-leach test results (tables 25-27) indicate 82- to 84-pct Li extraction as optimum. Treating the leach solution by the methods specified resulted in 95- to 98-pct recovery of the contained lithium. Losses occurred in $CaCO_3$ filtration (0.5-pct loss) and in the crystallization step (2- to 5-pct loss, depending on the filtration method used to separate the mother liquor from the salts). Overall, 78 to 82 pct of the lithium contained in the clay was recovered as 99-pct-pure Li_2CO_3.

MATERIAL BALANCE AND ECONOMIC EVALUATION

A material balance and a cost evaluation for a 5:3:3 ratio of clay-limestone-gypsum was prepared and reported by Lien (*11*). The operating cost for this feed ratio was \$2.12/lb Li_2CO_3; this figure was revised to \$2.27/lb Li_2CO_3 as of May 1985. The cost evaluation showed raw materials (primarily limestone and gypsum) used in the process to be the most costly component. To lessen this expense, the evaluation recommended a reduction in the quantity of reagents used in the roast feed.

As table 23 shows, the feed ratio can be reduced from 5:3:3 to 5:2:2 without affecting lithium extraction. Appendix A shows a material balance for a typical PRU test using a 5:2:2 mixture of clay, limestone, and gypsum. In May 1985, the Bureau's headquarters Process Evaluation Office prepared a cost evaluation based on the material balance and other process data supplied by the Salt Lake City Research Center. The evaluation estimated the operating cost of the process at \$1.86/lb Li_2CO_3 produced. The evaluation was revised as of July 1987 and is presented in appendix B; the updated operating cost is \$2.02/lb Li_2CO_3. The selling price of Li_2CO_3 as of July 1987 was \$1.50/lb.

Figure B-1 presents sectional operating costs. As in the initial cost evaluation, a principal cost is the purchase of limestone and gypsum raw materials, which amounts to \$0.39/lb Li_2CO_3. Another high-cost section is evaporation, which, because of high fuel costs, adds about \$0.35/lb Li_2CO_3 produced. Operating costs are further broken down in table B-3 to show the cost of individual materials, utilities, and other charges.

The capital cost, summarized in table B-2, was estimated to be about \$105 million. As pointed out in the cost evaluation, no cost was allowed for land acquisition, mine development, and royalties on the ore. These costs would have to be considered before development of the resource could occur.

DISCUSSION AND RECOMMENDATIONS

For the limestone-gypsum roast process to be economical in today's market, the operating costs must be reduced. The process unit operations that show promise for cost reduction are roasting, leaching, and evaporation.

Limited rotary roaster testing was conducted to determine if the reagent requirement for the roast could be further reduced. The testing involved recycling Li_2CO_3 product filtrate and product wash water, without salt removal, to the roast step. Test results indicated that the salts in the recycled solution improved lithium recovery for the 5:1.5:1.5 feed ratio by about 1 pct; recovery for a 5:2:2 mix was improved by 3 to 5 pct. In this proposed modification, the recycled solution would be used in pelletizing the roast feed; thus, the water requirements for feed preparation, as well as evaporation load, would be decreased.

To reduce the capital costs associated with agitation leaching, percolation leaching was investigated. Tests were conducted using calcine from a 5:2:2 roast. The calcine was leached in a series of four acrylic columns measuring 4 in in diam by 4 ft high. Preliminary test results indicated that lithium extraction was comparable to that achieved using agitation leaching. The percolation leach solution contained about 7 g/L Li; leach solution obtained by agitation leaching generally contained 2.5 to 3 g/L Li. This increase in solution loading could significantly reduce the evaporation load.

A cost-saving alternative for the evaporation step would involve the use of solar evaporation. Although solar evaporation tests were not conducted, this modification could be a viable alternative because of the hot, dry Nevada climate.

These potential process modifications would all require expanded investigation to determine if they are viable alternatives to established procedures.

REFERENCES

1. Ferrell, J. E. Lithium. Ch. in Minerals Facts and Problems. BuMines B 675, 1985, pp. 461-470.

2. Chilenskas, A. A., G. J. Bernstein, and R. O. Ivins. Lithium Requirements for High-Energy Lithium-Aluminum Iron-Sulfide Batteries for Load-Leveling and Electric-Vehicle Applications. Ch. in Lithium Resources and Requirements by the Year 2000, ed. by J. D. Vine. U.S. Geol. Surv. Prof. Paper 1005, 1976, pp. 5-9.

3. Cooper, J. F., I. Y. Borg, L. G. O'Connell, E. Behrin, B. Rubin, and H. J. Wiesner. Lithium Requirements for Electric Vehicles Using Lithium-Water-Air Batteries. Ch. in Lithium Resources and Requirements by the Year 2000, ed. by J. D. Vine. U.S. Geol. Surv. Prof. Paper 1005, 1976, pp. 9-12.

4. Vine, J. D. The Lithium-Resource Enigma. Ch. in Lithium Resources and Requirements by the Year 2000, ed. by J. D. Vine. U.S. Geol. Surv. Prof. Paper 1005, 1976, pp. 35-37.

5. Glantzman, R. K., J. H. McCarthy, Jr., and J. J. Rytuba. Lithium in the McDermitt Caldera, Nevada and Oregon. Ch. in Lithium Needs and Resources, ed. by S. S. Penner. Pergamon, 1978, pp. 347-353.

6. Vine, J. D. Where on Earth Is All the Lithium? U.S. Geol. Surv. OFR 80-1234, 1980, 114 pp.

7. Davidson, C. F. Recovery of Lithium From Clay by Selective Chlorination. BuMines RI 8523, 1981, 19 pp.

8. ———. (assigned to U.S. Dep. Interior). Recovery of Lithium From Low-Grade Ores. U.S. Pat. 4,285,914, Aug. 25, 1981.

9. May, J. T., C. F. Davidson, and V. E. Edlund. Extracting Lithium From McDermitt Clay. Ch. in Light Metals 1982. TMS-AIME, Warrendale, PA, pp. 1159-1168.

10. Edlund, V. E. Lime-Gypsum Processing of McDermitt Clay for Lithium Recovery. BuMines RI 8832, 1983, 15 pp.

11. Lien, R. H. Recovery of Lithium From a Montmorillonite-Type Clay. BuMines RI 8967, 1985, 26 pp.

12. May, J. T., D. S. Witkowsky, and D. C. Seidel. Extracting Lithium From Clays by Roast-Leach Treatment. BuMines RI 8432, 1980, 16 pp.

13. Margolis, M. P. (ed.). Lithium. Eng. and Min. J., Metal and Mineral Markets, Aug. 1, 1966, pp. 8-17.

14. Singleton, R. H., and H. B. Wood. Lithium. Ch. in Mineral Facts and Problems. BuMines B 667, 1975, pp. 619-635.

15. Hess, F. L. Lithium in North Carolina. Eng. and Min. J., v. 137, July 1936, pp. 339-342.

16. Nicholson, P. Past and Future Development of the Market for Lithium in the World Aluminum Industry. Ch. in Lithium Needs and Resources, ed. by S. S. Penner. Pergamon, 1978, pp. 243-246.

17. Chemical Week. From Base Metals to Precious Alloys. V. 131, No. 24, 1982, pp. 27-28.

18. Gyongyossy, Z. D., and E. T. C. Spooner. Lithium: An Energy Element. Min. Sci. Eng., v. 11, No. 3, 1979, pp. 155-176.

19. Alexander, J. H. Lithium. Min. Eng., v. 35, May 1983, p. 498.

20. Ferrell, J. E. Lithium. Ch. in BuMines Minerals Yearbook 1984, v. 1, pp. 607-613.

21. Bach, R. O., and J. R. Wasson. Lithium and Lithium Compounds. Ch. in Kirk-Othmer: Encyclopedia of Chemical Technology. Wiley, v. 14, 3d ed., 1981, pp. 448-476.

22. Evans, K. R. Lithium Reserves and Resources. Ch. in Lithium Needs and Resources, ed. by S. S. Penner. Pergamon, 1978, pp. 379-385.

23. U.S. Bureau of Mines and U.S. Geological Survey. Principles of a Resource/Reserve Classification for Minerals. BuMines Mineral Commodity Summaries 1986, pp. 182-185.

24. Schultze, L. E., and D. J. Bauer. Recovering Lithium Chloride From a Geothermal Brine. BuMines RI 8883, 1984, 13 pp.

25. Peterson, J. A., and G. H. Gloss (assigned to International Minerals and Chemicals Corp., NY). Lithium Values Recovery Process. U.S. Pat. 2,893,828, July 7, 1959.

26. Colton, J. W. (assigned to Scientific Design Co., Inc.). Continuous Recovery of Chlorides of Rubidium, Cesium, and Especially Lithium From Ores. U.S. Pat. 3,024,082, Mar. 6, 1962.

27. Kepter, R. J., and R. Pfanstiel (assigned to Grasseli Chemical Co.). Treating Lithium-Bearing Ore. U.S. Pat. 2,022,003, Nov. 26, 1935.

28. Whaley, T. H. (assigned to Texaco Development Corp.). Recovery of Metal Values From Lithium Ores. U.S. Pat. 3,087,782, Apr. 30, 1963.

29. MacDougall, A. J. Lithium Chloride. Can. Pat. 265,499, Nov. 2, 1926.

30. Lof, G. O. G., and W. Lewis. Lithium Chloride From Lepidolite. Ind. and Eng. Chem., v. 34, No. 2, 1942, pp. 209-216.

31. Sternberg, W. M., E. T. Hayes, and F. P. Williams. Production of Lithium Chloride From Spodumene by a Lime-Gypsum Roast Process. BuMines RI 3848, 1946, 10 pp.

32. Hayes, E. T., F. P. Williams, and W. M. Sternberg (assigned to U.S. Dep. Interior). Production of Lithium Chloride From Spodumene. U.S. Pat. 2,533,246, Dec. 12, 1950.

33. Stull, D. R., and H. Prophet. JANAF Thermodynamic Tables. NSRDS-NBS 37, 2d ed., 1971, 1141 pp.

34. Pankratz, L. B. Thermodynamic Properties of Halides. BuMines B 674, 1984, 826 pp.

35. Weaver, J. B., and H. C. Bauman. Cost and Profitability Estimation. Sec. in Chemical Engineer's Handbook, ed. by R. H. Perry and C. H. Chilton. McGraw-Hill, 5th ed., 1973, pp. 25-46.

36. Alexander, J. H. Lithium. Eng. and Min. J., v. 186, No. 3, March 1985, pp. 123-124.

APPENDIX A.—MATERIAL BALANCE FOR 5:2:2 RATIO

(Streams referred to in tables A-1 through A-6 are identified in figure 16.)

TABLE A-1.—Feed preparation

Material	Stream 1	Stream 2	Stream 3	Stream 4
Lithium:				
Weight g	21.79	0	0	21.79
Analysis wt pct	0.59	0	0	0.33
Potassium:				
Weight g	131.6	1.19	1.48	134.27
Analysis wt pct	3.55	.08	0.1	2.01
Sodium:				
Weight g	23.72	.59	.89	25.2
Analysis wt pct	.64	0.04	0.06	.38
Calcium:				
Weight g	66.72	352.89	567.9	987.51
Analysis wt pct	1.8	23.8	38.3	14.8
Magnesium:				
Weight g	333.62	1.48	19.73	354.83
Analysis wt pct	9	0.1	1.33	5.32
Sulfate:				
Weight g	2.59	87.34	0.44	790.37
Analysis wt pct	0.07	53.1	0.03	11.84
Carbonate:				
Weight g	51.9	0	892.56	944.46
Analysis wt pct	1.4	0	60.2	14.15
Water:				
Weight g	170.52	295.25	0	465.77
Analysis wt pct	4.6	19.91	0	6.98
Other:				
Weight g	2,904.54	44.26	0	2,948.8
Analysis wt pct	78.35	2.98	0	44.19
Total weight g	3,707	1,483	1,483	6,673

[1] The clay-limestone-gypsum mixture was pelletized with 1.086 L of water; the pellets were dried at 70° C to drive off this water.

TABLE A-3.—Leach

Material	Stream 5	Stream 6	Stream 7	Stream 8
Lithium:				
Weight g	21.79	4.65	3.49	18.3
Analysis wt pct	0.4	NAp	0.05	NAp
Conc g/L	NAp	0.58	NAp	2.9
Potassium:				
Weight g	134.27	41.3	52.24	82.03
Analysis wt pct	2.48	NAp	0.77	NAp
Conc g/L	NAp	5.15	NAp	13
Sodium:				
Weight g	25.2	5.85	5.64	19.56
Analysis wt pct	0.47	NAp	0.08	NAp
Conc g/L	NAp	.73	NAp	3.1
Calcium:				
Weight g	987.51	4.25	984.1	3.41
Analysis wt pct	18.26	NAp	14.57	NAp
Conc g/L	NAp	0.53	NAp	0.54
Magnesium:				
Weight g	354.83	0.24	354.4	0.19
Analysis wt pct	6.56	NAp	5.25	NAp
Conc g/L	NAp	0.03	NAp	0.03
Sulfate:				
Weight g	728.16	105.14	452.72	275.44
Analysis wt pct	13.46	NAp	6.70	NAp
Conc g/L	NAp	13.11	NAp	43.65
Fluorine:				
Weight g	31.89	0	31.89	0
Analysis wt pct	0.59	NAp	0.47	NAp
Conc g/L	NAp	0	NAp	0
Water:[1]				
Weight g	0	7,973	1,746.43	6,226.57
Analysis wt pct	0	NAp	25.85	NAp
Other:				
Weight g	3,124.35	0	3,124.35	0
Analysis wt pct	57.77	0	46.25	0
Specific gravity	NAp	1.0143	NAp	1.05
Total:				
Weight g	5,408	8,134	6,755.26	6,625.5
Volume L	NAp	8.0195	NAp	6.31

NAp Not applicable. [1] Filter cake was washed with 7.973 L water.

TABLE A-2.—Roast[1]

Material	Stream 4	Stream 5
Lithium:		
Weight g	21.79	21.79
Analysis wt pct	0.33	0.40
Potassium:		
Weight g	134.27	134.27
Analysis wt pct	2.01	2.48
Sodium:		
Weight g	25.2	25.2
Analysis wt pct	0.38	0.47
Calcium:		
Weight g	987.51	987.51
Analysis wt pct	14.8	18.26
Magnesium:		
Weight g	354.83	354.83
Analysis wt pct	5.32	6.56
Sulfate:		
Weight g	790.37	728.16
Analysis wt pct	11.84	13.46
Carbonate:		
Weight g	944.46	0
Analysis wt pct	14.15	0
Fluorine:		
Weight g	86.75	31.89
Analysis wt pct	1.3	0.59
Water:		
Weight g	465.77	0
Analysis wt pct	6.98	0
Other:		
Weight g	2,862.05	3,124.35
Analysis wt pct	42.89	57.77
Total weight[2] g	6,673	5,408

[1] Furnace was fed with 583.8 L natural gas per kilogram of charge.

[2] The difference in total weight between the streams was accounted for in the roaster offgas. Excluding combustion gases, the offgas contained 41.47 g SO_2, 10.37 g O_2, 692.6 g CO_2, 465.77 g H_2O, and 54.86 g F.

TABLE A-4.—Evaporation

Material	Stream 8	Stream 9	Stream 10	Stream 14	Stream 16
Lithium:					
Weight g	18.3	0.07	24.29	1.44	4.62
Analysis wt pct	NAp	0.47	NAp	NAp	NAp
Conc g/L	2.9	NAp	13.50	2.48	4.45
Potassium:					
Weight g	82.03	0.17	130.54	2.15	46.53
Analysis wt pct	NAp	1.14	NAp	NAp	NAp
Conc g/L	13	NAp	72.56	3.70	44.83
Sodium:					
Weight g	19.56	0.09	46.44	2.15	24.82
Analysis wt pct	NAp	0.6	NAp	NAp	NAp
Conc g/L	3.1	NAp	25.81	3.70	23.91
Calcium:					
Weight g	3.41	3.41	0.013	0.003	0.01
Analysis wt pct	NAp	22.89	NAp	NAp	NAp
Conc g/L	0.54	NAp	0.01	0.005	0.01
Magnesium:					
Weight g	0.19	0.17	0.02	0	Trace
Analysis wt pct	NAp	1.14	NAp	NAp	NAp
Conc g/L	0.03	NAp	0.01	0	NAp
Sulfate:					
Weight g	275.44	0.84	390.84	7.14	109.1
Analysis wt pct	NAp	5.64	NAp	NAp	NAp
Conc g/L	43.65	NAp	217.25	12.29	105.1
Carbonate:					
Weight g	0	5.83	20.17	6.18	19.82
Analysis wt pct	NAp	39.13	NAp	NAp	NAp
Conc g/L	0	NAp	11.41	10.64	19.1
Water:[1]					
Weight g	6,226.57	4.32	1,564	574	999.19
Analysis wt pct	NAp	28.99	NAp	NAp	NAp
Specific gravity	1.05	NAp	1.21	1.020	1.16
Total:					
Weight g	6,625.5	14.9	2,176	593.06	1,204.09
Volume L	6.31	NAp	1.799	0.581	1.038

NAp Not applicable. [1] Solution was concentrated by evaporating approximately 6.23 L water.

TABLE A-5.—Product precipitation

Material	Stream 10	Stream 11	Stream 12	Stream 13	Stream 14
Lithium:					
Weight g	24.29	0	17.93	4.92	1.44
Analysis wt pct	NAp	0	15.35	NAp	NAp
Conc g/L	13.50	NAp	NAp	2.88	2.48
Potassium:					
Weight g	130.54	0	0.16	128.23	2.15
Analysis wt pct	NAp	0	0.14	NAp	NAp
Conc g/L	72.56	NAp	NAp	74.99	3.70
Sodium:					
Weight g	46.44	64.08	0.16	108.21	2.15
Analyis wt pct	NAp	43.3	0.14	NAp	NAp
Conc g/L	25.81	NAp	NAp	63.28	3.70
Calcium:					
Weight g	0.013	0.03	0.02	0.03	0.003
Analysis wt pct	NAp	.02	0.017	NAp	NAp
Conc g/L	0.01	NAp	NAp	0.02	0.005
Sulfate:					
Weight g	390.84	0	0.53	383.17	7.14
Analysis wt pct	NAp	0	0.45	NAp	NAp
Conc g/L	217.25	NAp	NAp	224.1	12.29
Carbonate:					
Weight g	20.17	84.02	76.87	21.14	6.18
Analysis wt pct	NAp	56.7	65.8	NAp	NAp
Conc g/L	11.41	NAp	NAp	12.30	10.64
Water:[1]					
Weight g	1,564	0	21.16	1,543	574
Analysis wt pct	NAp	0	18.1	NAp	NAp
Specific gravity	1.21	NAp	NAp	1.28	1.020
Total:					
Weight g	2,176	148.13	116.83	2,189	593.06
Volume L	1.799	NAp	NAp	1.710	.581

NAp Not applicable. [1] Product washed with approximately 0.574 L hot water.

TABLE A-6.—Crystallization

Material	Stream 13	Stream 15	Stream 16
Lithium:			
Weight g	4.92	0.30	4.62
Analysis wt pct	NAp	0.03	NAp
Conc g/L	2.88	NAp	4.45
Potassium:			
Weight g	128.23	81.7	46.53
Analysis wt pct	NAp	8.3	NAp
Conc g/L	74.99	NAp	44.83
Sodium:			
Weight g	108.21	83.39	24.82
Analysis wt pct	NAp	8.47	NAp
Conc g/L	63.28	NAp	23.91
Calcium:			
Weight g	0.03	0.02	0.01
Analysis wt pct	NAp	0.002	NAp
Conc g/L	0.02	NAp	0.01
Sulfate:			
Weight g	383.17	274.07	109.1
Analysis wt pct	NAp	27.84	NAp
Conc g/L	224.1	NAp	105.1
Carbonate:			
Weight g	21.09	1.32	19.82
Analysis wt pct	NAp	0.13	NAp
Conc g/L	12.33	NAp	19.09
Water:			
Weight g	1,543	543.81	999.19
Analysis wt pct	NAp	55.23	NAp
Specific gravity	1.21	NAp	1.16
Total:			
Weight g	2,177	984.61	1,204.09
Volume L	1.799	NAp	1.038

NAP Not applicable.

APPENDIX B.—ECONOMIC EVALUATION OF A PROCESS TO RECOVER LITHIUM FROM McDERMITT CLAY BY LIME-GYPSUM ROASTING WITH REDUCED LIME AND GYPSUM REQUIREMENTS

By P.C. Cologer[1] and J. H. Schwier[2]

The Bureau of Mines Salt Lake City Research Center is developing a process to recover lithium from clay found in the McDermitt caldera, which spans the Nevada-Oregon border. The lithium occurs as $Li_2Si_2O_5$ and is converted to Li_2SO_4 by roasting the clay with limestone and gypsum. The Li_2SO_4 is water-leached and concentrated by evaporation. Reaction with soda ash results in the precipitated Li_2CO_3 product.

The process was evaluated in 1985 for roasting clay with limestone and gypsum using a mass ratio of 5:3:3, respectively. Acting on recommendations from that evaluation, the researchers investigated the use of less limestone and gypsum. The costs of extracting lithium at a clay-limestone-gypsum ratio of 5:2:2 were examined in 1985 and updated as of July 1987.

PROCESS DESCRIPTION

The proposed plant is designed to process 1,000 st/d of McDermitt clay and is based on the material balance and research data provided by the researchers at the Salt Lake City Research Center. Table B-1 presents the composition of dry McDermitt clay, which contains 0.6 wt pct Li, found as $Li_2Si_2O_5$. This process recovers 82 pct of the lithium, producing 27 st/d Li_2CO_3.

Table B-1.—Composition of McDermitt clay (dry basis)

Component	*Composition, wt pct*
Li	0.6
K	3.7
Na	.6
Mg	9
Fe	2.5
Ca	1.8
Al	3.1
F	2
SiO_2	53
Other	23.7
Total	100.0

In the process, the clay, limestone, and gypsum are ground, mixed, and pelletized. Lithium in the pellets is converted by roasting from $Li_2Si_2O_5$ to Li_2SO_4. Soluble Li_2SO_4 is extracted by leaching the roasted pellets with water. Concentration of the leach solution by evaporation precipitates some carbonate impurities. Soda ash is added to the concentrated solution, precipitating a Li_2CO_3 product from the now barren solution. Undesired sulfates are crystallized by cooling the barren solution before recycling it to the evaporator to recover any remaining lithium. For description purposes, the plant is arbitrarily divided into six sections: feed preparation, roasting, leaching, evaporation, lithium recovery, and crystallization.

Feed Preparation Section

The plant can store a 60-day supply of as-mined clay and a 30-day supply of both limestone and gypsum. Each raw material is screened at 3/16 in, and the oversize fractions are crushed in hammer mills.

Wet clay (1,050 st/d) is mixed with 420 st/d of both gypsum and limestone. The three components are fed directly to dry ball mills, where they are mixed and ground to minus 100 mesh. The ball mill fines are pelletized with water on pelletizing disks and dried in a rotary dryer.

Roasting Section

The dry pellets are roasted at 900° C in a rotary kiln where the gypsum reacts with the $Li_2Si_2O_5$ to produce Li_2SO_4. The overall reactions are

$$2CaSO_4 \cdot 2H_2O + 2SiO_2 \rightarrow 2CaSiO_3 + 2SO_2 + O_2 + 4H_2O$$

and $2Li_2Si_2O_5 + 2SO_2 + O_2 \rightarrow 2Li_2SO_4 + 4SiO_2$.

To ensure complete reaction, the kiln is designed to provide a 2-h residence time. Limestone is converted to lime, and many of the minor salts are converted into sulfates. After roasting, the pellets are cooled to 60° C in a rotary cooler and conveyed to the leaching section.

The kiln flue gases pass through cyclones, which remove entrained solids. Heat is removed from the gas with a waste-heat boiler. The cooled gases are further cleaned in baghouses, and finally scrubbed to remove SO_2 and hydrogen fluoride (HF).

Leaching Section

Pellets from the roasting section are leached for 5 min in an agitated tank. During this time, 84 pct of the Li_2SO_4 and 30 pct of the other sulfates are solubilized. The pregnant solution is then separated from the leach slurry with belt filters and pumped to the evaporation section for concentration. The remaining 1,900 st/d of wet solids are washed with water and conveyed to a tailings pond. After washing the solids, the water is used as leach solution.

Evaporation Section

Pregnant solution from the leaching section is collected in a surge tank and mixed with washings from the lithium recovery section and recycled mother liquor

---

[1] Chemical engineering technician, Avondale Research Center, Bureau of Mines, Avondale, MD (now with private industry; address unknown).

[2] Engineering data assistant, Process Evaluation Group, Bureau of Mines, Washington, DC.

from the crystallization section. This mixed solution is then concentrated in a five-effect evaporator from 1.7 pct by weight Li_2SO_4 to 6.5 pct. At the same time, $CaSO_4$ converts to $CaCO_3$ by reaction with other aqueous salts and precipitates from solution. The $CaCO_3$ solids represent less than 0.2 pct of the concentrated effluent and are removed with pressure-leaf filters. The filtrate is collected in a sump and pumped to the lithium recovery section.

Lithium Recovery Section

Concentrated solution (615 st/d) from the evaporation section is heated to 95° C in agitated tanks and mixed with 42 st/d of soda ash. Soda ash reacts with the aqueous Li_2SO_4 and generates 27 st/d of Li_2CO_3 precipitate. The overall reaction is

$$Li_2SO_4 + Na_2CO_3 \rightarrow Li_2CO_3 + Na_2SO_4.$$

The product slurry is separated with two pressure-leaf filters into Li_2CO_3 solids and barren filtrate. The solids are dried at 300° C, cooled, and conveyed to storage silos.

Crystallization Section

Potassium and sodium sulfates are removed from the hot barren solution in the crystallization section. The hot solution is first pumped through a water-cooled heat exchanger and reduced to 40° C. Warm solution is then pumped through a two-stage crystallizer and cooled to 0° C. Stage 1 of the crystallizer cools the solution to 25° C by recycling the mother liquor from stage 2 as coolant. Stage 2 is cooled by refrigeration. Seventy-six percent of the sodium and 64 pct of the potassium in solution are removed by the crystallizer. Potassium crystallizes as glaserite, and the remaining sodium as glauber salt.

The crystal slurry is pumped to pressure-leaf filters, where the crystals are separated from the mother liquor and sent to the tailings pond. Mother liquor is pumped to the evaporation section for recovery of its lithium content.

ECONOMICS

The economics in this study are based on a plant processing 1,000 st/d of McDermitt clay and designed from a material balance and research data supplied by the Salt Lake City Research Center. The proposed plant produced 27 st/d of Li_2CO_3, which on an annual basis equals 70 pct of the estimated North American consumption of lithium during 1984 (*36*).[3]

The expense of developing and operating the McDermitt clay surface mining operation is excluded from this evaluation. Charges for this operation cannot be assigned with confidence but are expected to have a small effect on the overall economics. Nevertheless, these costs will have to be included in the sale price of the Li_2CO_3.

Capital Costs

Equipment designs in this evaluation are based on data extrapolated from bench-scale research. The capital costs in this study estimate are expected to fall within 30 pct of the actual costs.

The estimated fixed capital costs, based on first quarter 1987 prices (Marshall and Swift [M and S] index of 803.7), total $95.1 million and are presented in table B-2. This index is used to update manufacturers' informal cost quotations and capacity-cost data used in this study. Construction materials are selected to optimize a unit's service life. The tailings pond is designed with a 2-yr capacity. It is assumed that after 2 yr, process residues may be disposed of as backfill at the mine site.

Factors for piping, etc., except for the foundation and electrical factors, are assigned to each section, using as a basis the effect fluids, solids, or a combination of fluids and solids may have on the process equipment. The foundation factor is estimated for each piece of equipment individually, and a factor for the entire section is calculated from the totals. The electrical factor is based on the motor horsepower requirements for each section. A factor of 10 pct, referred to as miscellaneous, is added to each section to cover minor equipment and construction costs that are not shown with the equipment listed.

For each section, the field indirect cost, which covers field supervision, inspection, temporary construction, equipment rental, and payroll overhead, is estimated at 10 pct of the direct cost. Engineering cost is estimated at 5 pct, and administration and overhead cost is estimated at 5 pct of the construction cost. A contingency allowance of 10 pct and a contractor's fee of 5 pct are included in the section costs.

The costs of plant facilities and plant utilities are estimated as 10 and 12 pct, respectively, of the total process section costs and include the same field indirect costs, engineering, administration and overhead, contingency allowance, and contractor's fee as are included in the section costs. Included under plant facilities are the cost of material and labor for auxiliary buildings such as offices, shops, laboratories, and cafeterias, and the cost of nonprocess equipment such as office furniture, and safety, shop, and laboratory equipment. Also included are labor and material costs for site preparation such as clearing, grading, drainage, roads, and fences. The costs of water,

Table B-2.—Estimated capital cost[1]

Fixed capital:	
Feed preparation section	$14,050,800
Roasting section	12,443,200
Leaching section	19,278,500
Evaporation section	8,649,500
Lithium recovery section	1,706,800
Crystallization section	3,366,100
Tailings pond section	1,749,200
Steamplant	297,400
Subtotal	61,541,500
Plant facilities, 10 pct of above subtotal	6,154,200
Plant utilities, 12 pct of above subtotal	7,385,000
Basic plant cost	75,080,700
Escalation costs during construction	6,057,500
Total plant cost	81,138,200
Land cost	0
Subtotal	81,138,200
Interest during construction period	13,972,300
Fixed capital cost	95,110,500
Working capital:	
Raw material and supplies	814,400
Product and in-process inventory	2,845,800
Accounts receivable	2,845,800
Available cash	2,144,200
Working capital cost	8,650,200
Capitalized startup costs	951,100
Subtotal	9,601,300
Total capital cost	104,711,800

[1] Basis: M and S equipment cost index of 803.7.

---

[3] Italicized numbers in parentheses refer to items in the list of references preceding the appendixes.

power, and steam distribution systems are included under plant utilities.

Working capital is defined as the funds in addition to fixed capital, land investment, and startup costs that must be provided to operate the plant. Working capital, shown in table B-2, is estimated from the following items: (1) raw material and supplies inventory (cost of raw material and operating supplies for 30 days), (2) product and in-process inventory (total operating cost for 30 days), (3) accounts receivable (total operating cost for 30 days), and (4) available cash (direct expenses for 30 days).

Capitalized startup costs are estimated as 1 pct of the fixed capital costs. Land investment is not included in this estimate.

Operating Costs

Estimated operating costs are based on a schedule of 3 shifts per day, 7 days per week, and 330 days of operation per year. The remaining time is allotted for scheduled or unscheduled downtime. Operating costs are divided into direct, indirect, and fixed costs and are presented in table B-3. The total estimated operating cost is about \$2.02/lb Li_2CO_3; the current selling price (July 1987) of Li_2CO_3 is \$1.50/lb.

Direct costs include raw materials, utilities, direct labor, plant maintenance, payroll overhead, and operating supplies. Raw materials and utility requirements per pound of Li_2CO_3 are shown in table B-3. The direct labor cost is estimated on the basis of assigning 4.2 employees for each position that operates 24 h/d, 7 days per week, and 1.4 employees for each position that operates 8 h/d, 7 days per week. The cost of labor supervision is estimated as 15 pct of the labor cost.

Plant maintenance is separately estimated for each piece of equipment and for the buildings, electrical system, piping, plant utility distribution systems, and plant facilities.

Table B-3.—Estimated annual operating cost

	Annual cost	Cost, \$/lb Li_2CO_3
Direct costs:		
Raw materials:		
McDermitt clay at \$0/st	\$0	\$0.000
Limestone at \$24.50/st	3,395,700	.198
Gypsum at \$24/st	3,326,400	.194
Soda ash at \$163/st	2,313,000	.135
Replacement balls for grinding at \$0.27/lb	122,300	.007
Chemicals for steamplant water treatment	3,600	.001
Total	9,161,000	.535
Utilities:		
Electric power at \$0.047/kW·h	1,190,600	.069
Process water at \$0.25/Mgal	63,000	.004
Heavy oil at 0.85/gal	8,240,100	.480
Total	9,493,700	.553
Direct labor:		
Labor at \$11.75/h	1,437,100	.084
Supervision, 15 pct of labor	215,600	.013
Total	1,652,700	.097
Plant maintenance:		
Labor	1,700,000	.099
Supervision, 20 pct of maintenance labor	340,000	.020
Materials	1,700,100	.099
Total	3,740,100	.218
Payroll overhead, 35 pct of above payroll	1,292,400	.075
Operating supplies, 20 pct of plant maintenance	748,000	.044
Total direct cost	26,087,900	1.522
Indirect cost, 40 pct of direct labor and maintenance	2,157,100	.126
Fixed costs:		
Taxes, 1 pct of total plant cost	811,400	.047
Insurance, 1 pct of total plant cost	811,400	.047
Depreciation, 20-yr life	4,755,500	.277
Total operating cost	34,623,300	2.019

Payroll overhead, estimated as 35 pct of direct labor and maintenance labor, includes vacation, sick leave, social security, and fringe benefits. The cost of operating supplies is estimated as 20 pct of the cost of plant maintenance.

Indirect costs are estimated as 40 pct of the direct labor and maintenance costs. The indirect costs include the expenses of control laboratories, accounting, plant protection and safety, plant administration, marketing, and company overhead. Research and overall company administrative costs outside the plant are not included.

Fixed costs include the cost of taxes (excluding income taxes), insurance, and depreciation. The annual costs of both taxes and insurance are each estimated as 1 pct of the plant construction cost. Depreciation is based on a straight-line, 20-yr period.

Evaluation

By reducing the McDermitt clay-limestone-gypsum ratio from 5:3:3 to 5:2:2, 19 pct less material is handled by the process. This translates to 441 st/d less gypsum and limestone going through the plant which results in a substantial cost savings.

Figure B-1 shows the breakdown of operating costs by section. The raw material costs are presented separately by the light regions in the graph. Gypsum and limestone costs are added to the feed preparation section even though they are essential to the entire process. The cost of soda ash is added to the fifth section, where it is used to precipitate the product.

Ninety percent of the operating costs, excluding raw materials, are shared almost equally by the first four sections. The last three sections handle much less material and have correspondingly smaller costs. Limestone, gypsum, and soda ash purchase costs contribute \$0.53/lb Li_2CO_3, which represents 26 pct of the total operating budget.

Figures B-2 through B-7 and tables B-4 through B-11 give additional details on the economic evaluation of recovering lithium from McDermitt clay.

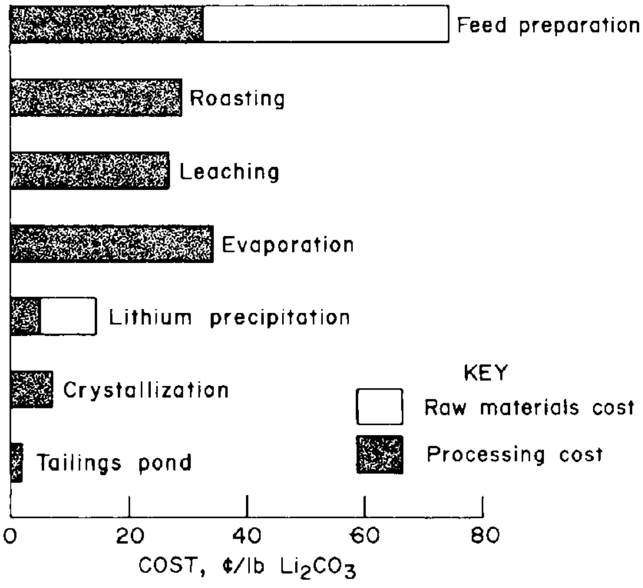

Figure B-1.—Sectional operating costs.

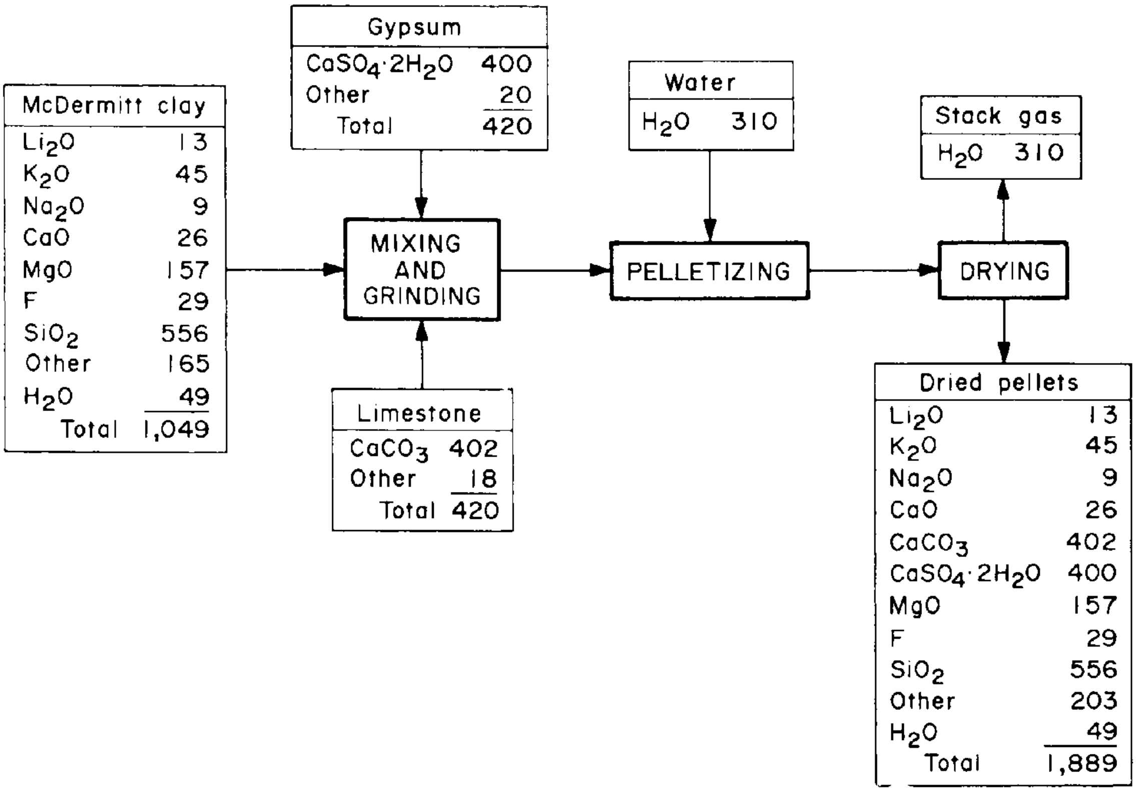

Figure B-2.—Feed preparation section material balance, st/d.

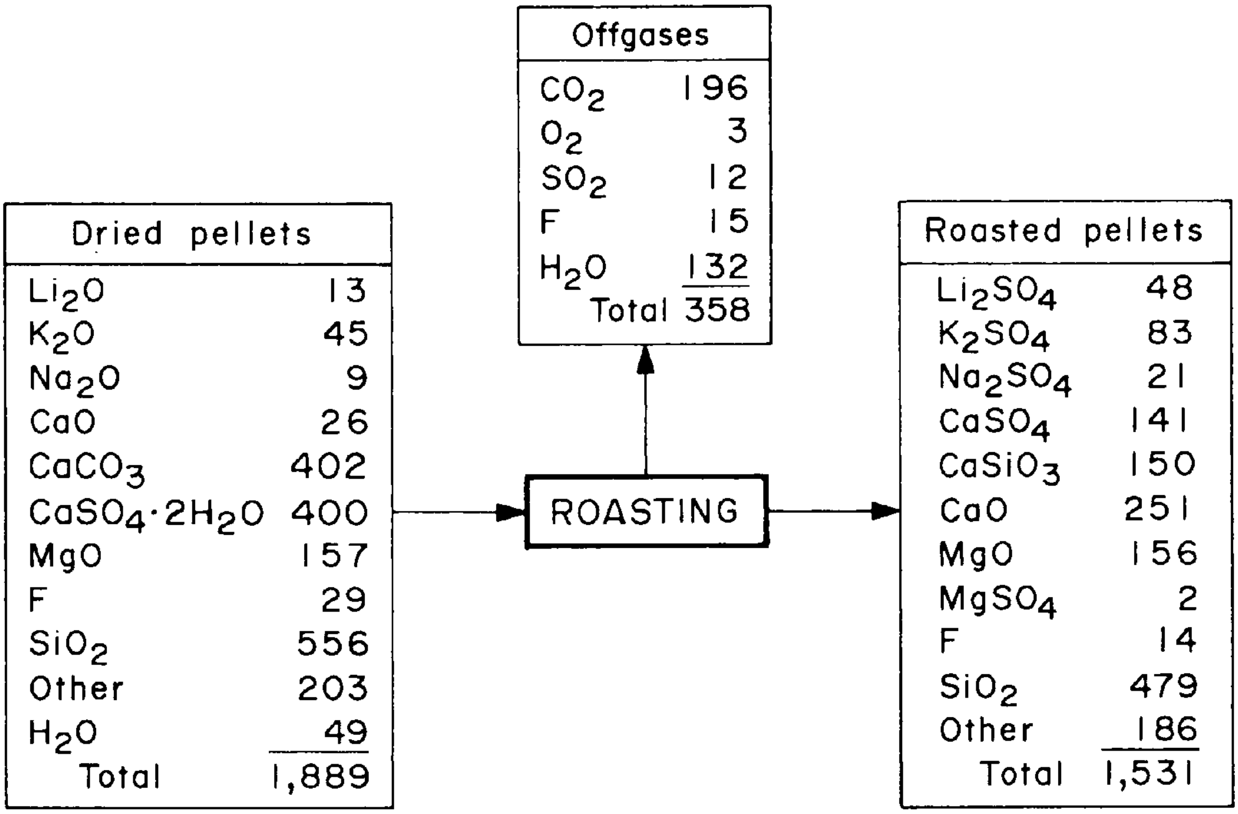

Figure B-3.—Roasting section material balance, st/d.

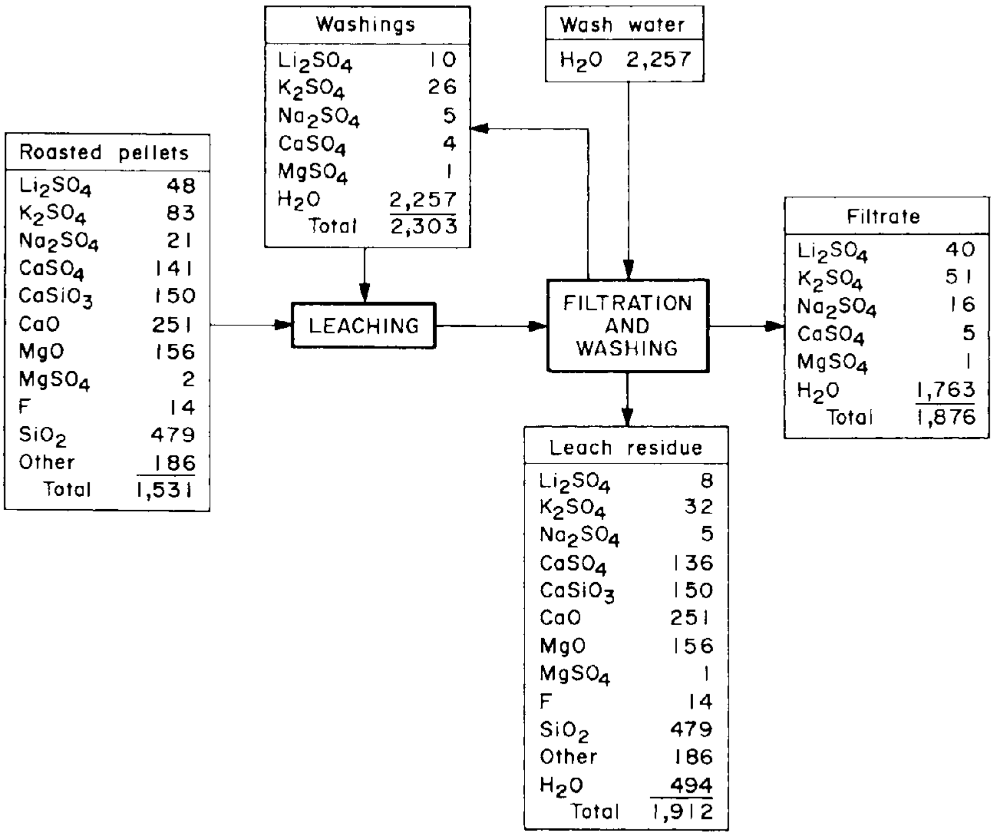

Figure B-4.—Leaching section material balance, st/d.

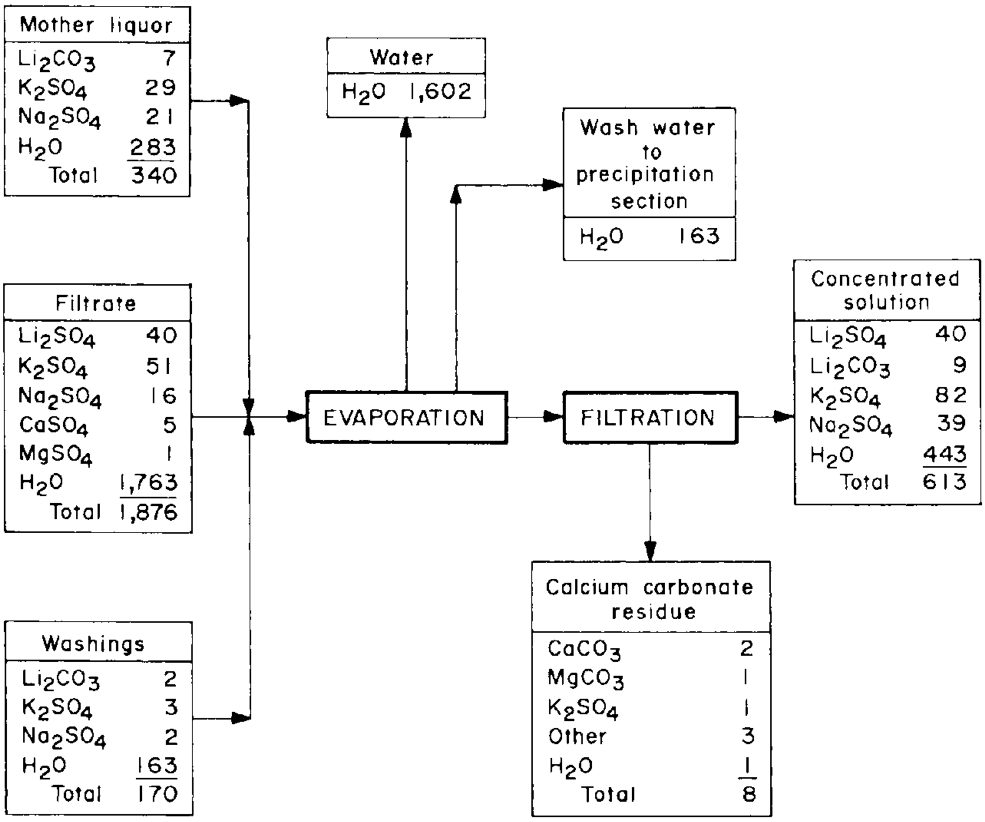

Figure B-5.—Evaporation section material balance, st/d.

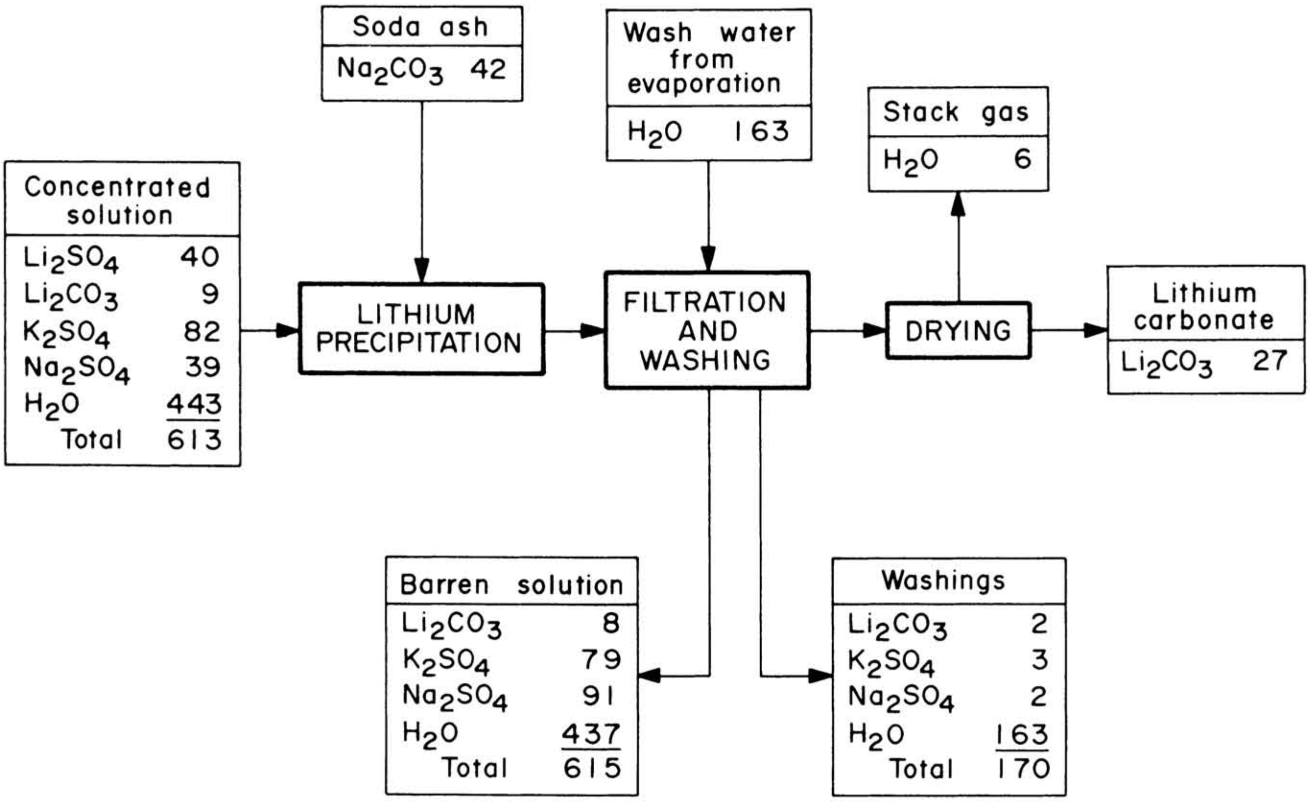

Figure B-6.—Lithium recovery section material balance, st/d.

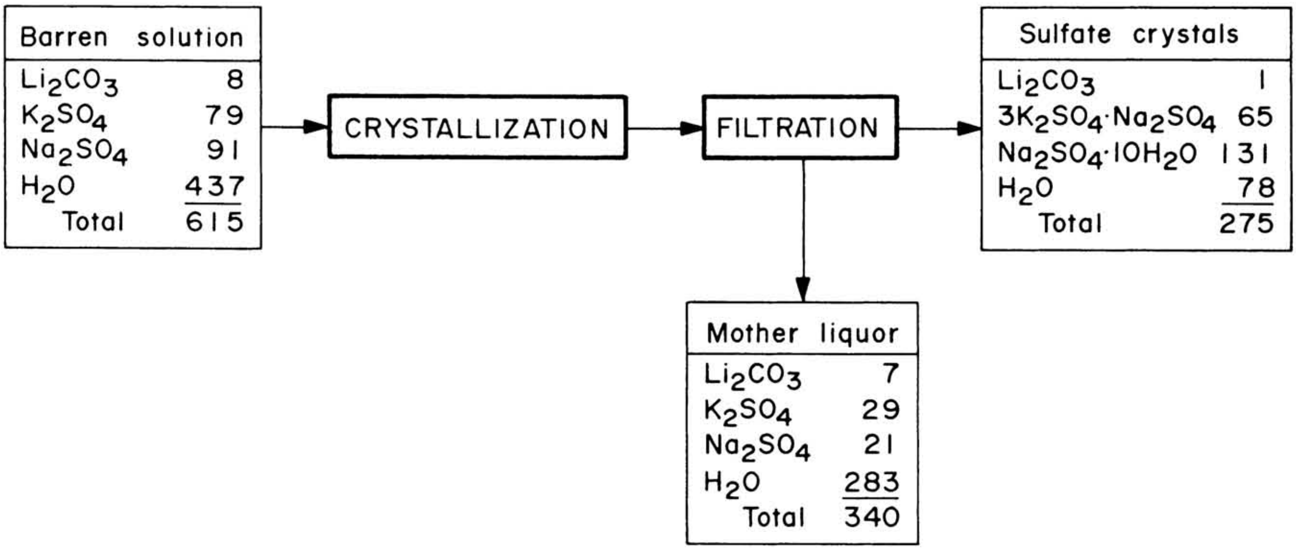

Figure B-7.—Crystallization section material balance, st/d.

Table B-4.—Raw material and utility requirements

		Quantity per pound Li_2CO_3
Raw materials:		
McDermitt clay	st	0.020
Limestone	st	0.008
Gypsum	st	0.008
Soda ash	st	0.001
Replacement balls for grinding	lb	0.026
Utilities:		
Electric power	kW·h	1.476
Process water	Mgal	.015
Heavy oil	gal	.565

Table B-5.—Daily thermal requirements

Section and item	Steam, MM Btu	Heavy oil,[1] MMBtu
Feed preparation: Rotary dryers	0.00	925.00
Roasting:		
Rotary kilns	.00	3.016.00
Waste-heat boiler	−709.40	.00
Subtotal	−709.40	3,016.00
Evaporation: Evaporator	977.50	.00
Lithium recovery:		
Mixing tank	12.90	.00
Rotary dryer	.00	17.00
Subtotal	12.90	17.00
General plant	.00	47.00
Total process requirements	281.00	4,005.00
Steamplant	−281.00	489.59
Total	.00	4,494.59

[1] Quantity of heavy oil (153,000 Btu gal)–29,376.6 gal d.

TABLE B-6.—Equipment cost summary, feed preparation section

Item	Equipment[1]	Labor	Total
Apron feeder	$10,200	$1,700	$11,900
Belt conveyor	103,800	21,000	124,800
Do	49,800	8,200	58,000
Reclaimer feeders	35,300	5,900	41,200
Belt conveyor	28,100	6,000	34,100
Vibrating screen	18,200	2,500	20,700
Hopper	4,100	200	4,300
Hammer mill	134,420	21,100	155,500
Belt conveyor	70,900	12,100	83,000
Surge bins	35,900	13,900	49,800
Belt feeders	13,300	2,200	15,500
Belt feeder	7,200	1,200	8,400
Belt conveyor	125,760	26,000	151,700
Screw feeders	8,700	1,500	10,200
Belt conveyor	38,500	9,300	47,800
Vibrating screen	9,900	1,300	11,200
Hopper	2,300	100	2,400
Hammer mill	70,100	11,000	81,100
Belt conveyor	69,500	13,100	82,600
Surge bins	15,300	5,000	20,300
Belt feeders	11,000	1,800	12,800
Belt feeder	7,200	1,200	8,400
Belt conveyor	118,000	24,200	142,200
Screw feeders	8,200	1,400	9,600
Belt conveyor	61,300	11,200	72,500
Surge bins	15,700	5,200	20,900
Belt feeder	11,000	1,800	12,800
Do	13,300	2,200	15,500
Ball mills	990,700	66,700	1,057,400
Belt conveyors	68,300	10,000	78,300
Hoppers	6,100	300	6,400
Belt feeders	26,500	4,500	31,000
Pelletizing disks	378,400	2,000	380,400
Belt conveyors	73,700	17,700	91,400
Surge bins	10,500	3,200	13,700
Belt feeders	13,300	2,200	15,500
Rotary dryers	1,281,700	230,300	1,512,000
Bag dust collectors	199,200	1,800	201,000
Belt conveyor	12,600	2,800	15,400
Bucket elevators	28,300	8,500	36,800
Bag dust collector	18,300	300	18,600
Do	7,400	200	7,600
Do	32,000	400	32,400
Total	4,243,900	563,200	4,807,100
Clay unloading hopper[2]			19,200
Limestone unloading hopper[2]			19,200
Limestone storage silos[2]			677,800
Gypsum storage silos[2]			700,200
Front-end loader			73,100
Total equipment cost × factor indicated:			
Foundations, × 0.254			1,079,500
Buildings, × 0.156			663,000
Structures, × 0.100			424,400
Instrumentation, × 0.080			339,500
Electrical, × 0.075			317,100
Piping, × 0.100			424,400
Painting, × 0.020			84,900
Miscellaneous, × 0.100			424,400
Total			3,757,200
Total direct cost			10,053,800
Field indirect, 10 pct of total direct cost			1,005,400
Total construction cost			11,059,200
Engineering, 5 pct of total construction cost			553,000
Administration and overhead, 5 pct of total construction cost			553,000
Subtotal			12,165,200
Contingency, 10 pct of above subtotal			1,216,500
Subtotal			13,381,700
Contractor's fee, 5 pct of above subtotal			669,100
Section cost			14,050,800

---

[1] Basis: M and S equipment cost index of 803.7.

[2] Installed cost.

TABLE B-7.—Equipment cost summary, roasting section

Item	Equipment[1]	Labor	Total
Hoppers	$4,400	$200	$4,600
Belt feeders	13,300	2,200	15,500
Rotary kilns	2,844,300	958,100	3,802,400
Bag dust collectors	378,200	3,000	381,200
Belt conveyor	15,800	3,700	19,500
Scrubber	15,100	400	15,500
Rotary coolers	821,700	147,600	969,300
Belt conveyor	18,600	3,800	22,400
Total	4,111,400	1,119,000	5,230,400
Waste-heat boiler[2]			193,700
Cooling tower[2]			179,200
Total equipment cost × factor indicated:			
Foundations, × 0.393			1,614,400
Buildings, × 0.001			4,500
Structures, × 0.100			411,100
Instrumentation, × 0.080			328,900
Electrical, × 0.019			78,100
Piping, × 0.100			411,100
Painting, × 0.010			41,100
Miscellaneous, × 0.100			411,100
Total			3,300,300
Total direct cost			8,903,600
Field indirect, 10 pct of total direct cost			890,400
Total construction cost			9,794,000
Engineering, 5 pct of total construction cost			489,700
Administration and overhead, 5 pct of total construction cost			489,700
Subtotal			10,773,400
Contingency, 10 pct of above subtotal			1,077,300
Subtotal			11,850,700
Contractor's fee, 5 pct of above subtotal			592,500
Section cost			12,443,200

---

[1] Basis: M and S equipment cost index of 803.7.

[2] Installed cost.

TABLE B-8.—Equipment cost summary, leaching section

	Equipment[1]	Labor	Total
Leach tank	$7,800	$3,400	$11,200
Pumps	16,300	3,300	19,600
Horizontal belt filters	6,367,800	286,000	6,653,800
Sumps	7,100	5,400	12,500
Pumps	20,100	4,400	24,500
Sumps	8,300	6,000	14,300
Pumps	22,100	4,800	26,900
Surge tanks	182,500	36,300	218,800
Pumps	11,000	3,000	14,000
Belt conveyor	172,600	41,700	214,300
Total	6,815,600	394,300	7,209,900
Total equipment cost × factor indicated:			
Foundations, × 0.048			327,700
Buildings, × 0.017			116,200
Structures, × 0.150			1,022,300
Instrumentation, × 0.080			545,200
Electrical, × 0.011			74,900
Piping, × 0.500			3,407,800
Painting, × 0.060			408,900
Miscellaneous, × 0.100			681,600
Total			6,584,600
Total direct cost			13,794,500
Field indirect, 10 pct of total direct cost			1,379,500
Total construction cost			15,174,000
Engineering, 5 pct of total construction cost			758,700
Administration and overhead, 5 pct of total construction cost			758,700
Subtotal			16,691,400
Contingency, 10 pct of above subtotal			1,669,100
Subtotal			18,360,500
Contractor's fee, 5 pct of above subtotal			918,000
Section cost			19,278,500

---

[1] Basis: M and S equipment cost index of 803.7.

TABLE B-9.—Equipment cost summary, evaporation section

Item	Equipment[1]	Labor	Total
Surge tank	$11,300	$4,400	$15,700
Pump	5,600	1,400	7,000
Evaporator	2,393,300	204,100	2,597,400
Pump	2,000	1,300	3,300
Pump	5,000	900	5,900
Pressure leaf filters	20,100	1,400	21,500
Belt conveyor	136,300	35,200	171,500
Sumps	2,100	1,700	3,800
Pumps	6,300	1,400	7,700
Total	2,582,000	251,800	2,833,800
Cooling tower[2]			238,700
Total equipment cost × factor indicated:			
Foundations, × 0.164			423,500
Building, × 0.012			31,000
Structures, × 0.200			516,400
Insulation, × 0.022			57,600
Instrumentation, × 0.150			387,300
Electrical, × 0.009			22,400
Piping, × 0.500			1,291,000
Painting, × 0.050			129,100
Miscellaneous, × 0.100			258,200
Total			3,116,500
Total direct cost			6,189,000
Field indirect, 10 pct of total direct cost			618,900
Total construction cost			6,807,900

TABLE B-9.—Equipment cost summary, evaporation section —Continued

Item	Equipment[1]	Labor	Total
Engineering, 5 pct of total construction cost			340,400
Administration and overhead, 5 pct of total construction cost			340,400
Subtotal			7,488,700
Contingency, 10 pct of above subtotal			748,900
Subtotal			8,237,600
Contractor's fee, 5 pct of above subtotal			411,900
Section cost			8,649,500

---

[1] Basis: M and S equipment cost index of 803.7.
[2] Installed cost.

TABLE B-10.—Equipment cost summary, lithium recovery section

Item	Equipment[1]	Labor	Total
Mixing tank	$8,000	$3,200	$11,200
Pumps	12,100	1,800	13,900
Pressure leaf filters	27,200	1,800	29,000
Sumps	900	1,000	1,900
Pumps	6,300	1,000	7,300
Sumps	2,100	1,700	3,800
Pumps	6,700	1,400	8,100
Belt conveyor	15,800	3,800	19,600
Hopper	300	100	400
Belt feeder	5,500	900	6,400
Rotary dryer	32,300	5,800	38,100
Bag dust collector	6,200	200	6,400
Belt conveyors	23,400	5,300	28,700
Rotary cooler	17,200	3,100	20,300
Belt conveyor	60,200	11,600	71,800
Screw feeder	2,700	500	3,200
Belt conveyor	37,600	9,500	47,100
Screw feeder	2,400	400	2,800
Belt conveyor	20,800	5,000	25,800
Hopper	300	100	400
Belt feeder	5,500	900	6,400
Standby water heater	2,200	300	2,500
Total	295,700	59,400	355,100
Product storage silo[2]			188,800
Soda ash unloading hopper[2]			19,200
Silo[2]			106,500
Total equipment cost × factor indicated:			
Foundations, × 0.716			211,600
Buildings, × 0.126			37,300
Structures, × 0.100			29,600
Insulation, × 0.036			10,700
Instrumentation, × 0.080			23,700
Electrical, × 0.147			43,500
Piping, × 0.500			147,900
Painting, × 0.060			17,700
Miscellaneous, × 0.100			29,600
Total			551,600
Total direct cost			1,221,200
Field indirect, 10 pct of total direct cost			122,100
Total construction cost			1,343,300
Engineering, 5 pct of total construction cost			67,200
Administration and overhead, 5 pct of total construction cost			67,200
Subtotal			1,477,700
Contingency, 10 pct of above subtotal			147,800
Subtotal			1,625,500
Contractor's fee, 5 pct of above subtotal			81,300
Section cost			1,706,800

---

[1] Basis: M and S equipment cost index of 803.7.
[2] Installed cost.

TABLE B-11.—Equipment cost summary, crystallization section

Item	Equipment[1]	Labor	Total
Condenser	$35,600	$1,000	$36,600
Pump	4,400	900	5,300
Crystallizer	709,400	80,000	789,400
Pumps	10,100	1,700	11,800
Pressure leaf filters	54,800	6,200	61,000
Belt conveyor	136,300	35,200	171,500
Sumps	1,500	1,400	2,900
Pumps	6,300	1,200	7,500
Total	958,400	127,600	1,086,000
Cooling tower[2]			190,600
Total equipment cost × factor indicated:			
Foundations, × 0.334			320,000
Buildings, × 0.024			22,700
Structures, × 0.150			143,800
Instrumentation, × 0.120			115,000
Electrical, × 0.023			22,400
Piping, × 0.400			383,400
Painting, × 0.030			28,800
Miscellaneous, × 0.100			95,800
Total			1,131,900
Total direct cost			2,408,500
Field indirect, 10 pct of total direct cost			240,900
Total construction cost			2,649,400
Engineering, 5 pct of total construction cost			132,500
Administration and overhead, 5 pct of total construction cost			132,500
Subtotal			2,914,400
Contingency, 10 pct of above subtotal			291,400
Subtotal			3,205,800
Contractor's fee, 5 pct of above subtotal			160,300
Section cost			3,366,100

---

[1] Basis: M and S equipment cost index of 803.7.

[2] Installed cost.

CONCLUSIONS

The estimated operating cost for the modified process is $2.02/lb Li_2CO_3, which is $0.52 more than its present market price. Reducing the limestone and gypsum input reduces the operating cost. Decreased raw material input also permits the use of smaller equipment, which reduces the estimated capital cost.

NTIS DISCLAIMER

- This document has been reproduced from the best copy furnished by the sponsoring agency.