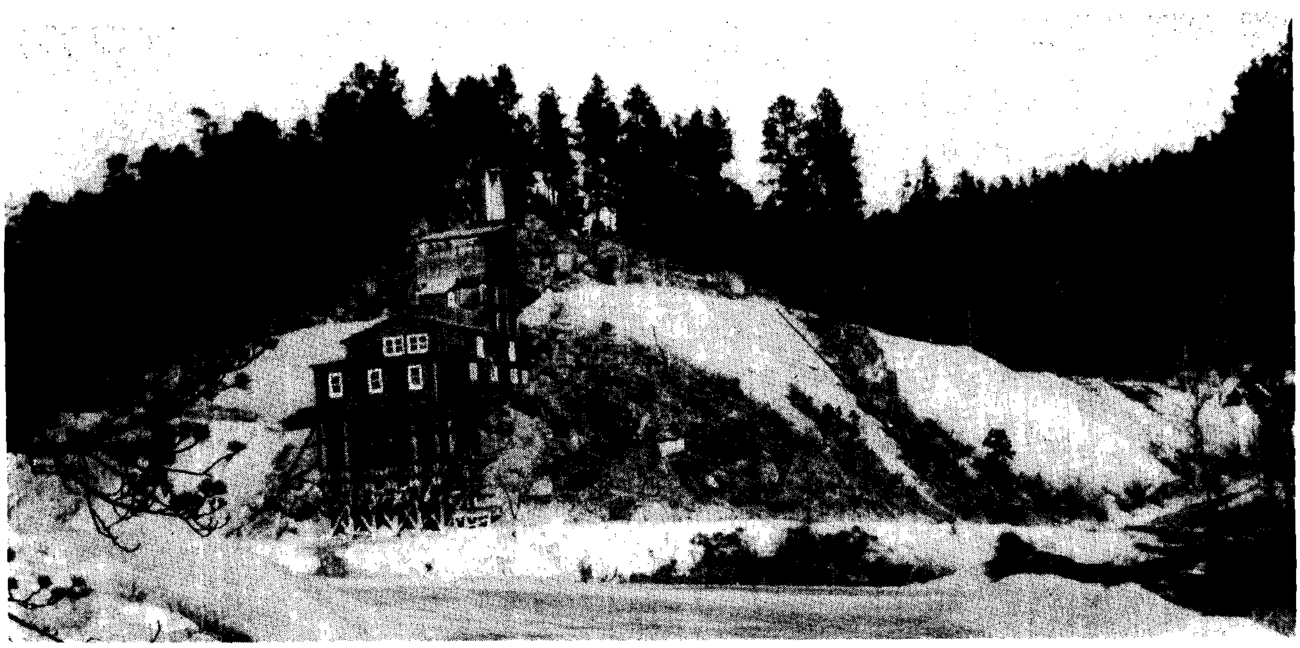

Heavy-Media separation plant and mine area, Keystone, S. D.

Mining and Concentrating Spodumene In the Black Hills, South Dakota

by Gerald A. Munson and Fremont F. Clarke

DURING recent years the use of lithium has expanded greatly in industrial, chemical, and metallurgical fields, while at the same time modernized methods of mining and refining lithium have increased production. Technical literature includes many papers describing the geology and mineralogy of lithium deposits. Mining and beneficiating problems, however, have not been thoroughly described. Published reports have failed to emphasize that one of the chief reasons lithium minerals were not extensively mined until recently is the difficulty of beneficiation.

Four lithium minerals of pegmatites and the lithium-sodium-phosphate byproduct from the brines at Searles Lake, Calif., have been sources of lithium. Among the pegmatite minerals, only spodumene and petaline are known to occur in deposits large enough to support large tonnage operations. Spodumene, a lithium-aluminum-silicate, is the principal lithium mineral mined in the U. S.

Lithium Corp. of America, during its rapid development and growth, has successfully employed three different methods of concentration: 1) hand sorting, 2) Heavy Media separation, and 3) froth flotation. Each method, though economic in its sphere, is becoming outdated as extractive techniques improve. The most recent development has taken place at Lithium Corp.'s new operation in North Carolina, where the extractive process yields lithium compounds directly from mined rock without an intervening concentrating step.

G. A. MUNSON and F. F. CLARKE, Members AIME, are, respectively, General Manager of North Carolina Operations and Vice President and Production Manager, Lithium Corp. of America Inc., Minneapolis.

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Until 1954 Lithium Corp. mined only in the southern part of the Black Hills of South Dakota, where the various types of lithium-bearing pegmatite could be used to develop untried processes of beneficiation. Concentrates from these operations are shipped to the corporation's chemical plant in St. Louis Park, Minn., where actual extraction of lithium and production of commercial compounds takes place.

Nature of Deposits

The geology of the southern Black Hills pegmatite deposits is admirably presented by a U. S. Geological Survey publication.[1] Only the factors pertinent to exploitation need be mentioned here. Lithium Corp. has been interested primarily in three deposits, the Edison, the Mateen, and the Longview-Beecher No. 2. The history of these deposits dates back to the mining boom of 1880 to 1900 in the Black Hills, when most of the deposits were prospected for tin by the ill-fated Harney Peak Tin Mining Co. The three deposits described here, however, lay idle and unwanted until Lithium Corp. opened the Edison mine in 1943 and the Mateen and Longview-Beecher No. 2 in 1951.

Edison Deposit: The Edison deposit is about a mile southeast of Keystone, S. D., on the northeastern flank of the Harney Peak uplift. The deposit consists of no less than four and probably at least six separate pegmatites that coalesce in a central mass from which the individual pegmatites finger outward and downward in complexly folded schist and gneiss beds of the country rock.

The Transactions papers appearing in Mining Engineering during 1955 will subsequently appear in AIME Transactions Volume 202 and may be permanently referenced to that volume.

Each of the pegmatites has a wall zone consisting of quartz, albite feldspar, and muscovite, and a core consisting of spodumene, albite, and quartz. The internal structure is not readily recognized in the area where the pegmatites coalesce, but even here spodumene-bearing pegmatite can be readily distinguished from barren pegmatite for mining purposes. The central mass of this deposit measures 300 ft long by 150 ft wide and has been explored to a depth of 250 ft below the original outcrop.

Structure is further complicated by four major faults and a host of minor faults and fractures. Three of the major faults follow the trend of the long axis of the deposit and the fourth intersects the others at an angle.

The deposit averages 25 pct spodumene. Length of the spodumene crystals ranges from a fraction of an inch to 10 ft; the average is probably 1 ft. The mineral is free at 6 mesh or coarser size.

Mateen Deposit: The Mateen deposit on the southern edge of Hill City, S. D., is on the northwestern flank of Harney Peak and some 14 miles west of the Edison deposit. It consists of three and possibly four pegmatite dikes, which lie in close echelon, forming a ridge at the outcrop. Two of the dikes coalesce approximately 100 ft below the surface and outcrop as a single dike. The third has a narrow outcrop along the crest of the ridge and the fourth (or possibly the downward extension of the third) is seen only in development workings 200 ft below surface. All the dikes, plunging steeply to the north, are discordant to the foliation of the enclosing schists.

The main mass of the deposit is exposed along the surface for 700 ft in length and over 35 to 50 ft in width. It is known to extend an additional 250 ft in length on the 200-ft level.

The third dike outcrops over a length of 200 ft. The fourth shows a width of 30 ft in a crosscut on the 200 level, but its linear extent has not been determined.

The more southerly of the coalescing dikes stands nearly vertical, but its companion dips flatly eastward across the schist from the horizon of coalescence. The vertical dike appears to bottom shortly below the 200-ft level, but the other dike maintains its thickness at the greatest depth of exploration to date. The coalescing dikes form a single body in the surface workings, but a small parting has been observed some 35 ft above the 100-ft level. Fingers of pegmatite meander from the southerly end of the main mass. The dikes are laced with fracture partings, which admit percolating waters and contribute to minor weatherings and deposition of secondary minerals. This condition becomes pronounced in areas near the keel of the dikes.

All the dikes are zoned. The fine grained pegmatite 1 to 3 ft thick that encases the central mass is generally barren of spodumene and is composed of quartz, albite, microline, mica, and accessory cassiterite. The spodumene-rich core of this deposit contains about 20 pct spodumene; range in grade is from 15 to 35 pct. Spodumene crystals are uniformly oriented in a nearly horizontal position normal to the walls. The crystals are closely packed in a matrix of quartz-albite-microline pegmatite.

Contrary to earlier exploratory data, mining has shown that this deposit can yield a uniform product. Only near the keel of the vertical dike is the lithium content low, and no barren areas of any size have been encountered. Otherwise the spodumene content at the 200-ft level is the same as in the surface pits.

Fig. 1—Mateen open pit and underground development structures, Hill City, S. D.

The spodumene crystals range downward from about 10-in. length, averaging perhaps 6 in. The mineral is free when crushed to 50 mesh.

Longview-Beecher Deposit: The Longview-Beecher No. 2 deposit is located far out on the southwestern flank of Harney Peak range, some four miles south of Custer, S. D., and 18 miles south of the Mateen deposit. This deposit is one of a series of three major pegmatites, including the widely publicized Beecher lode and the Beecher No. 3 beryl mine. All strike northward and dip steeply to the west concordantly with the enclosing schists. The Longview-Beecher dike is separated from the other two dikes by more than 50 ft of country rock.

Roof pendants and rolls of country rock indicate that only the uppermost reaches of the dike have surfaced. The deposit outcrops solidly over a length of 1200 ft and has a fairly constant width of 200 ft. Spodumene-rich pegmatite is exposed in major areas aggregating some 78,000 sq ft. Three areas have been exploited to some extent. The main mass to the south covers an area 170x100 ft while another mass in a southwesterly extension of the pegmatite is exposed over a length of 180 ft and average width of 80 ft. These units have been explored only 150 ft below the outcrop. For the most part the spodumene is contained in a quartz-albite matrix, but microcline is common. The spodumene crystals show no orientation. They range in size from a fraction of an inch long to rare crystals 6 ft long, averaging less than 1 ft. The spodumene is free at 50 mesh.

Other Deposits: The Black Hills have many other lithium pegmatites including the famous Etta mine, which contains spodumene crystals up to 47 ft long.

Many crystals in the deposit are 10 ft long. In contrast, the Tinton deposit, in the northern Black Hills, contains few spodumene crystals visible to the naked eye, and the largest are no more than ¼ in. long. At Tinton the spodumene is free at 100 mesh or finer.

The theoretical maximum lithia content of spodumene, $LiAl\ (SiO_3)_2$, is 8.0 pct, but the highest grade specimens contain no more than 7.5 pct Li_2O. The difference is accounted for partly by substitution of other elements for Li in the spodumene lattice; partly by the presence of quartz, feldspar, and mica that enter even the cleanest concentrates; and partly by alteration of spodumene to micaceous and clayey minerals.

Weathering is most pronounced along and near fault planes and to a lesser degree along the more remote fracture patterns. It is most often accompanied by deposition of ferrous or manganous clay fractions or stains upon the mineral affected. Sometimes the color cast may extend throughout the attacked minerals; otherwise it is confined to the surface, fracture, or cleavage planes.

Spodumene crystals tend toward euhedral form, but most crystals are in part embayed by adjacent minerals. The thickness-width-length ratio approximates 1:2:12, but the long axis may be far greater than the others. In many deposits the crystals show no orientation and in rich deposits are intergrown in jackstraw patterns. In some deposits, however, spodumene crystals are oriented perpendicular to the contact.

The color is usually white or gray but may be light to dark brown, blackish, reddish, greenish, or bluish depending on impurities or alteration. Pink spodumene (kunzite) and green spodumene (hiddenite) are rarely found. A common alteration product is a dull, soapy, green material very low in lithia.

The spodumene readily breaks free of the matrix on crushing and grinding, the fine crystal fragments tending to break into long needlelike splinters or flat rectangular particles. Under 100X magnification many of these particles show parallel, longitudinal traces of altered material. In hand specimens, a claylike coating may be scraped from cleavage surfaces in all but the freshest and hardest specimens.

Mining

Spodumene pegmatite had never been mined by modern mechanized techniques prior to the time Lithium Corp. began operations in the area. Many deposits worked for feldspar, mica, beryl, and lithium minerals were too small for mechanized mining, but the Edison deposit presented a good opportunity for developing mass mining operations. During the formative years of Lithium Corp. spodumene was concentrated by hand sorting, and initial exploitation of the Edison was geared to this productive rate. An open cut was started near the bottom of a draw bordering the base of the pegmatite exposure, about 115 ft below the highest outcrop. This pit cut into the most westerly dike and for a time supported the operation. Then an adit was started from the pit eastward 125 ft to transect the other dikes, a room was cut along the footwall over a length of 100 ft, and stope raises were driven and expanded to form a glory hole some 110x80 ft at surface.

By 1947, when increased demand for lithium required more rapid and efficient exploitation, the corporation transferred a ¾-yd P&H shovel to the property and began the first mechanized lithium operation in the southern Black Hills. All of the deposit above the adit level was then mined as one open pit.

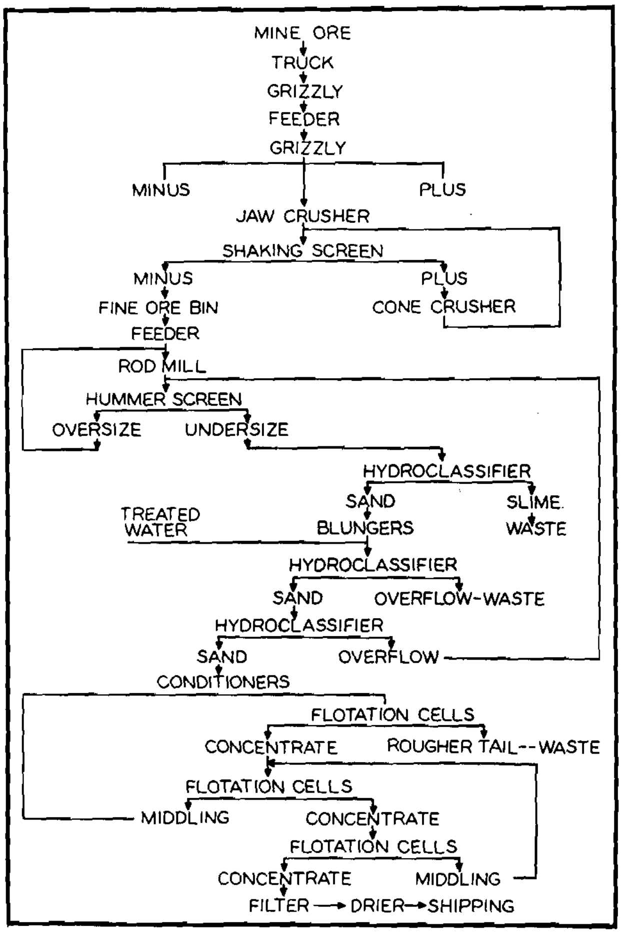

Fig. 2—Flowsheet of operations at Hill City, S. D.

Subsequent operations lowered the floor of the pit 60 ft below the adit level. Reserves below this level are in divided remnants of the pegmatite, and mining returned to underground methods.

Equipment was moved to the Mateen mine at Hill City, where the pegmatite outcrop forms a 170-ft high ridge. A series of horizontal benches were driven along the strike of the deposit, and access is easily maintained by slabbing short entry cuts in the exposed sheath of country rock. The Beecher mine is also an open pit, but there the topographic relief is very low, a disadvantage offset by the great area of spodumene-bearing pegmatite. As mining progressed from operation at the Edison to later operations at the Mateen, Fig. 1, and Beecher, techniques for breaking and moving ore and waste improved. After the ¾-yd shovel was put in operation, 1½-ton trucks displaced the hand mining system of the Edison open pit and have continued in use at later operations at the Mateen and Longview-Beecher mines. Experience soon taught that best results were obtained by carrying a 12-ft face drilled horizontally on a basic 3x4-ft pattern to a depth of 16 ft. Blasting is successful with an average 1 lb of 45 pct Gelex dynamite per ton of rock, and no more than 5 pct of the broken material requires secondary blasting. Originally the oversize was laid aside in the pit, blockholed, and blasted, but more recently plastering with 60 pct gelatin dynamite for secondary breakage has given good results.

Table I. Mill Run Results

Product	Weight, Pct	Lithia, Pct	Distribution
No. 1. Partly Altered Spodumene Pegmatite			
Concentrate	15.9	4.92	63.5
Slime	31.8	0.68	17.2
Tail sand	52.3	0.46	19.3
Composite	100.0	1.26	100.0
Flotation efficiency,* 75.8 pct			
No. 2. Altered Spodumene Pegmatite			
Concentrate	13.1	5.13	57.1
Slime	38.3	0.75	24.1
Tail sand	48.6	0.46	18.8
Composite	100.0	1.21	100.0
Flotation efficiency, 76.0 pct			
No. 3. Hard Rock with Altered Spodumene			
Concentrate	14.2	3.94	66.4
Slime	20.4	0.53	12.6
Tail sand	65.5	0.27	21.0
Composite	100.0	0.82	100.0
Flotation efficiency, 76.0 pct			

* Lithia recovery from deslimed flotation feed.

Successful mining depends largely on the judgment of the miners and pit bosses. The variable nature of the composition and the structural character of the rock is such that it is unwise to depend on a predetermined pattern of drilling and loading the holes. In mining, indiscriminate blasting of waste and ore together is avoided by alert attention to the variation in rock hardness and by noting the composition of the cuttings during drilling. Where hard, tough rock is encountered the drilling pattern is closed accordingly, and with soft or highly fractured rock the pattern is extended or the loading spaced. Where waste rock is recognized in the holes, the hole is stopped near the contact and blasted to that point. The waste is probed during drilling of the next round and the waste is blasted and disposed of separately. Remnants are carefully probed and slabbed to maintain clean faces and adequate working space for the equipment. Usually three working faces are maintained for each mine crew.

The power shovel operator becomes adept at rough sorting of ore and waste from the blasted material. Tractor front-end loaders have also been used recently.

Concentration of Spodumene Ore

Hand Sorting: During the earliest operation at the Edison mine spodumene was hand sorted at the mine face, but subsequently a picking belt was installed. The arrangement consisted of a 12-in. rail grizzly, ore bin, 18x30-in. jaw crusher, shaking screen with 1½-in. square mesh cloth, transfer conveyor, surge bin, and 30-in. flat picking belt 30 ft long. The −1½-in. material was removed by a small lateral conveyor.

The picking belt was housed over the final ore bin, which was divided to receive both reject material and spodumene concentrate. The concentrate was hauled to the railroad at Keystone for shipment and the reject to waste dumps near the mine.

Production data shows that the sorting operation yielded 10.5 pct by weight of mine run rock as a concentrate which averaged 4.8 pct lithia. Quartz, feldspar, muscovite, and alteration products of spodumene contaminated the concentrate.

The −1½-in. material, representing 43.5 pct by weight of the crude feed, was stockpiled for future concentration. The crude feed contained 1.1 pct lithia, and the undersize rejects contained 1.76 pct lithia.[2] About 0.4 ton of barren pegmatite and country rock per ton of crude feed was rejected at the mine face before delivery to the sorting circuit.

Heavy Media Separation: Early in 1949 a Heavy Media separation plant was put into operation to increase production at the Edison mine. This was the first plant ever to employ this process to separate minerals having such similar properties as the pegmatite minerals.

The plant consisted of a 12-in. grizzly, crude ore bin, 18x30-in. jaw crusher, shaking screen (1½ in. square mesh), 9x16-in. jaw crusher set at 1½ in. for the oversize, conveyor, truck haulage to 250-ton mill bin, 20-in. belt feeder, a 3x8-ft split deck Niagra screen, 35-in. bucket elevator, and a Wemco Mobilmill with 5-ft separatory cone.

Mill feed was −1½-in. crushed pegmatite. Undersize was wet screened at 6 mesh on the Niagra screen, and the coarse material elevated and fed to the cone. Minus 200 mesh ferrosilicon and water was the medium for the separatory cone. Occasionally, as much as 10 pct magnetite was added to the slurry to balance magnetic characteristics of the solid media.

The difference in specific gravities of the pegmatite minerals is very small for this type of separation. Typical figures are listed as follows:

Spodumene	3.1
Quartz	2.65
Microline	2.56
Albite	2.60
Muscovite	2.76 to 3.1
Apatite	3.2
Tourmaline	3.0 to 3.2
Triphylite	3.4 to 3.56

Because altered spodumene containing micaceous and clay minerals has a lower specific gravity than pure spodumene, the difference in specific gravity between spodumene and gangue may be virtually nil.

Perhaps the most important difficulty in gravity separation of spodumene is its characteristic breakage to acicular particles which even in a minor current become buoyant and tend to float off with the gangue minerals. This characteristic prevented the success of attempts to treat the −6 mesh fraction in a Dutch State Cyclone circuit, although laboratory test work showed efficient separation to 35 mesh.

The plant successfully treated Edison ore at 12 tph of crude feed, yielding the following results:

Product	Weight, Pct	Lithia, Pct	Distribution, Pct
Sink	7.1	5.36	47.4
Float	66.5	0.16	13.4
Fines	26.4	1.19	39.2
Composite	100.0	0.80	100.0

These results, obtained at 2.70 sp gr, were the best obtainable from low grade feed.

Flotation Concentration: Early in 1951 a research project was undertaken to determine the best methods of concentrating the fine grained pegmatite of the Beecher and Mateen lodes. It was soon learned that the spodumene could be beneficiated satisfactorily by the relatively simple procedure of desliming, caustic blunging, and collecting and floating with an anionic fatty acid. In general the process follows Falconer[3] and other writers of the 1940's. Clean mica and feldspar concentrates were also obtainable. Unfortunately, however, neither feldspar nor mica could be readily marketed. The soda and potash content of the feldspar concentrate could not be controlled well enough to meet marketing conditions while the flake size of the mica concentrate grain size was too large for use as wet ground mica and too small for use as dry ground mica. The silica sand tailings could not be transported profitably to market under prevailing freight rates. The mill as finally operated, therefore, is used solely to concentrate spodumene.

The plant constructed at Hill City, S. D., was put into operation early in 1952. It has operated successfully without major change except that the classifier in the grinding circuit has been replaced by Hummer screens. The plant is comprised of standard metallurgical equipment, but some of the equipment has had to be modified to correct for the rapid pulp settling rate and the extreme abrasiveness of the pegmatite material. The generalized flowsheet is shown in Fig. 2.

Location of the plant in the heart of a National Forest and in a widely publicized recreational area makes it necessary that waste water returning to the drainage area be entirely free of contamination. Mill waste is pumped some 200 ft vertically and 2000 ft horizontally to dry draws where the solids are settled in normal tailing ponds equipped with underdrains to bleed the clarified water from the back of the lagoons. The dams are constructed of the tailing sands after dewatering in sand cones that are located at the discharge end of the tailing pump lines and at the heads of the distributing launders. The overflow liquid from the cones is directed to the pool of the lagoon. Crude burnt lime fed at the overflow of the cones effectively coagulates the dispersed slimes. The double diking method[4] of dam construction provides adequate pool area in the relatively narrow and steep draws to permit winter operation.

Insofar as possible, therefore, mill control has been made fully automatic so that operators may devote their full attention to pulp trends. Milling of pegmatite is subject to even more intuitive control than the mining operations, for added to the continual variations in the mineral character and associations, attention must be given to the dissolved mineral content of the pulp, pulp temperature, and pH as well as to changing mechanical and hydraulic conditions related to nature of the feed.

Metallurgical control is based chiefly on analysis by flame photometer, but grain estimates under the microscope are also used. Microscope determination applied to critical products in the circuit gives adequate information for proper adjustment of the machines. Typical mill results on three ores are given in Table I.

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[3] S. A. Falconer and B. D. Crawford: Froth Flotation of Some Non-sulphide Minerals of Strategic Importance. *AIME Trans.*, 1946, vol. 169.

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Extraction of Lithium from Its Ores

Lithium chemical plant extraction methods are discussed with reference to 1) base exchange with alkali sulphates; 2) processing based on roasting with lime; 3) miscellaneous methods; and 4) application of the Lithium Corp. process to extraction of lithium from run-of-mine, low grade spodumene ore, or concentrates.

by Reuben B. Ellestad and Fremont F. Clarke

IN the early days of the lithium industry most of the production was from lepidolite, zinnwaldite, and amblygonite. Nearly all the early extraction processes described in the literature involve heating the finely ground mineral with sulphuric or hydrochloric acid. On subsequent water leaching most of the bases present in the mineral (especially aluminum) are dissolved as sulphates. As a result, the leach solution required extensive chemical purification before the lithium could be precipitated as carbonate. Following the remarkable growth of the lithium industry to its present size, zinnwaldite and amblygonite ores must be considered of minor importance only. Attention is now focused on spodumene, abundant enough in North America to be a major source of supply, and there are important supplies of lepidolite and petalite in Africa. The extraction processes described below all apply to spodumene, although several will also operate on other lithium minerals, such as petalite.

Base Exchange with Alkali Sulphates: A distinct advance was made with the disclosures of Wadman and von Girsewalt. In these methods the finely ground silicate ore (spodumene or lepidolite) is intimately mixed with an excess of alkali sulphate (usually K_2SO_4) in at least a 1 to 1 proportion, and the mixture was heated to a relatively high temperature. Base exchange results, with the formation of lithium sulphate. A water leach dissolves the lithium sulphate, together with the excess potassium sulphate. Successful operation of this type of process requires very thorough grinding and mixing, as well as careful temperature control. The use of K_2SO_4 is objectionable from cost considerations since purification of lithium carbonate requires the use of potassium carbonate, if the K_2SO_4 is to be recovered and recycled. The lower solubility of K_2SO_4 as compared with Na_2SO_4 is also objectionable, since it limits the concentration of the Li_2SO_4 solution to be precipitated by K_2CO_3. Early laboratory-scale investigation of this process by Lithium Corp. was not encouraging.

Other related base exchange processes are those of Lindblad, Wallden, and Sivander[3] and Sivander, Gard, Villestad, and Wallen[4]. The former covers the reaction of lithium silicate minerals with a sodium sulphate solution, at 100° to 300°C (under pressure), while the latter involves the extraction of silicate minerals with molten sodium sulphate. Both these processes would seem to be difficult and expensive to operate.

R. B. ELLESTAD is Director of Research and F. F. CLARKE, Member AIME, is Vice President and Production Manager, Lithium Corp. of America Inc., Minneapolis.

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