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SERIAL No. 13

Navy Department - Office of Research and Inventions

NAVAL RESEARCH LABORATORY
Washington, D.C.

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CHEMISTRY DIVISION - PHYSICAL AND INORGANIC SECTION

November 1945

FR-2704

Production of Metallic Lithium and Lithium Salts - A Survey

By C. R. Witschonke

- Report P-2704 -

[redacted]

* * *

Approved by:

R. R. Miller, Head, Physical and Inorganic Section

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Chemistry Division

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Director, Naval Research Laboratory

Preliminary Pages... a-d
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NRL Problem No. P-50-1

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ABSTRACT

The present report outlines the factors to be considered in developing an economical process suitable for the commercial production of lithium materials. These factors include: (1) available lithium raw materials, (2) processing requirements, (3) removal of lithium values from the ore, and (4) purification and conversion to the desired lithium material. All available information pertaining to these factors has been analyzed with respect to its accuracy and possible application to the present problem.

The Kings Mountain, North Carolina spodumene ores appear to be the most attractive source of lithium raw materials due to the extent, uniformity, lithia concentration and availability of the deposits. A preliminary concentration by froth flotation should yield ore containing 5-6 percent lithia, with an 80-90 percent recovery of lithium. For methods of recovering the lithium values from the ore, it is recommended that a research program be carried out with emphasis on a CaO-$CaCl_2$ high temperature replacement reaction to free the lithium, followed by a vacuum distillation to remove it from the ore residue. A similar process, in which a cheap sodium salt, such as the chloride, sulfate or carbonate, is the replacing agent, should also be investigated.

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INTRODUCTION

A. Authorization

1. This summarizes part of the investigation authorized by the Bureau of Ships Project Order 253/45 for the production of chemicals to purify air for breathing purposes.

B. Statement of Problem

2. The success registered by lithium hydroxide as a carbon dioxide absorbent aboard submarines is evident from its continued use during the present war period. However, limited production capacity and high cost of materials make lithium hydroxide practical only for emergency tactical use. Should full scale operational utilization of this material be desired, marked expansion in the lithium industry, and reduction in production costs, would be necessary.

The purpose of the present investigation, therefore, is to develop an industrially attractive, economical process for the recovery of lithium salts from the ores.

C. Previous Work in the Field

3. The production of lithium materials has been studied, both on a laboratory and commercial scale, by numerous investigators. Unfortunately, much of the published work appears to be limited in scope, outmoded, and, due to the lack of any analysis for lithium in silicate ores which is both convenient and trustworthy, even unreliable. Also, operational details of the industrial processes in use today are usually closely-guarded secrets of the individual concerns manufacturing lithium compounds.

4. The present survey will concern itself with a critical analysis of the available information with respect to validity, scope, and possible application to the problem at hand.

OUTLINE OF PROBLEM

5. The production of metallic lithium and lithium compounds involves the following considerations:

A. Available Lithium Raw Materials

1. Ionic lithium (salt brines, mineral springs)
2. Spodumene
3. Lepidolite
4. Amblygonite
5. Others (zinnwaldite, montebrasite, triphylite, lithiophylite, petalite).

[redacted]

B. Processing

1. Securing lithium raw material (prospecting, test-drills, mining).
2. Preliminary concentrating (hand-sorting, decrepitation, flotation).
3. Preliminary processing (heat treatment, grinding, mixing).

C. Recovery of Lithium Values

1. As lithium compound
   a. Decomposition of ore (heat, acid, alkali)
   b. Alkali replacement of lithium values in ore
2. As metallic lithium
   a. Electrolysis
   b. Thermochemical reduction

D. Conversion to Desired Lithium Material and Purification

1. Chemical treatment in solution
2. Distillation

AVAILABLE LITHIUM RAW MATERIALS

A. General

6. Lithium is abundantly represented in nature, comprising approximately 0.004 percent of the lithosphere, according to Clarke and Washington (57), or more than lead and tin combined. It occurs as ionic lithium in mineral springs and salt brines, as complex aluminum silicates in lepidolite, spodumene, petalite, and zinnwaldite, and as alumino-phosphates in amblygonite and montebrasite. Although the above raw materials are widely distributed, few deposits are of sufficient magnitude and lithium concentration to warrant commercial exploitation.

7. Table I presents the theoretical composition of the important lithium raw materials and the approximate lithia content as mined and as sold. The last column is an estimate of the total lithia production accounted for by each type of raw material in 1941 (10).

[redacted]

TABLE I

Raw Material	Empirical Formula	Theo. Li_2O Content (%)	%Li_2O (As Mined)	%Li_2O (As Sold)	% of Total Li_2O Mined (1941)
Salt Brines	Li_2NaPO_4*	22.8	0.01	20	30
Spodumene	$LiAl(SiO_3)_2$	8.4	1-2	4-7	30
Lepidolite	$LiKAl_2F_2Si_3O_9$	4.1	1-3	3-4	30
Amblygonite	$LiAlFPO_4$	10.1	8-9	8-9	10

*Final Product

As most of the lepidolite ores are used "as is" in the glass industry, salt brines and spodumene together contribute over 80 percent of the lithia marketed as lithium salts. The total U.S. production for 1941 is equivalent to approximately 250 tons of lithia. Lithium ores sell for approximately $5 per unit of lithia, in which a unit is one ton of ore containing 1 percent lithia. For example, a ton of 6 percent spodumene ore would contain six units and sell for $30 per ton.

8. The total foreign production of lithium materials before 1941 was probably less than that produced in the U.S. alone, although Germany and Russia may have greatly expanded their facilities during the war. South West Africa and France were the greatest lithium ore producers outside the U.S. (20).

B. Ionic Lithium

9. Many mineral springs contain 0.03 percent lithium (calculated as the chloride) or more; in fact, a spring at Conneautville, Pennsylvania is reported to contain 0.08 percent lithium chloride (1). Although these small percentages represent a considerable total lithium tonnage, the cost of evaporating approximately 3000 pounds of water for each pound of lithium chloride recovered would make the cost of lithium compounds from this source prohibitive.

10. Salt brines also carry small but significant quantities of lithium. Here again the cost of evaporation and separation from other solids makes the production of lithium impractical except as a by-product. The American Potash and Chemical Company's plant at Trona, California (9), utilizing the Searles Lake brines, is the only industrial unit known to be producing lithium in quantity from this source. It was found that the

removal of the lithium from the brines reduced foaming during subsequent evaporations (3) and that the Li_2NaPO_4 so produced could be readily sold due to its high lithia content (approximately 20 percent Li_2O). Since 1938 roughly 300 tons Li_2NaPO_4 have been produced annually (10), contributing 40 percent of all the lithia sold as lithium salts. As the lithium removal from the brines is a necessary step, the selling price of Li_2NaPO_4 is not governed by the cost of its recovery or by current market prices for lithium ores. It, therefore, is a big factor in determining market prices for other lithium ores.

11. However, for each ton of Li_2NaPO_4, approximately 1200 tons of soda ash, potash, borax, and sodium sulfate are also produced from the Searles Lake brines (13). The production of Li_2NaPO_4 will therefore follow the production for the latter products and so remain fairly constant, becoming less and less of an economic factor as the lithium industry expands.

C. Lepidolite

12. This complex lithium mica is probably the most widely distributed lithium ore. It frequently occurs in large crystals, ideal for selective mining and hand-sorting, but the deposits are not extensive and the lithia concentration is only 3-4 percent in the sorted ore. On an ore-tonnage basis, lepidolite furnishes approximately 60 percent of the total sold in the United States, but, on the basis of the actual number of lithia units contributed, this ore accounts for only 30 percent of the total (10). Further, since the glass industry utilizes a large fraction of the ore production without recovery of the lithia, lepidolite actually furnishes considerably less than 30 percent of the lithia sold as lithium salts today.

13. Until 1930, the Harding Mine in Taos County, New Mexico (16), and the Stewart Mine at Pala, California (17) were the chief producers of lepidolite. Since then, the higher-grade, more abundant deposits in the Black Hills, South Dakota have been the major source of lepidolite in this country; the Ingersoll Mine of the Black Hills Keystone Corporation is the main producer. Other appreciable, but non-commercial, deposits occur in Colorado, Wyoming (10), Maine, Massachusetts, and Connecticut (15).

14. The Germans have been utilizing large deposits of low-grade lepidolite (less than 1 percent Li_2O) from the Harz Mountains, and also, a 3 percent ore from Czechoslovakia (21). Considerable lepidolite deposits are known to exist in Portugal, South West Africa, Northern Rhodesia, Russia, Manitoba (19), and Brazil (3).

15. The low lithia content of lepidolite, the difficulty of removal of the lithium values, and the scattered nature of the deposits make this ore unattractive for large-scale commercial exploitation. This picture could, of course, be changed by the not improbable discovery of extensive, high-grade deposits.

[redacted]

D. Spodumene

16. Although not as widely-occurring as lepidolite, spodumene, a lithium aluminum silicate, is probably the most important commercial source of lithium at present, and in the forseeable future, due to the extent of the known deposits. A medium grade ore has been found in the vicinity of Kings Mountain, North Carolina, which is conservatively estimated to contain 20,000 tons of metallic lithium (13). As the ore analyzes 1-2 percent Li_2O as mined (11, 12), occurs in one locality, and appears to have a uniform composition, it should be ideal for large-scale mining operations.

17. Most of the spodumene produced today comes from the Etta Mine, Keystone, South Dakota, and from the neighboring Tin Mountain Mine, where enormous crystals of relatively pure spodumene, ideal for hand-sorting, are found. The limited extent of these deposits, however, makes appreciable production increase impossible. The Tennessee Mineral Products Corporation is also producing significant quantities of spodumene at Spruce Pine, North Carolina. At Tinton, South Dakota there exist extensive deposits of a very fine grained spud-quartz (approximately 50-50 spodumene and quartz, intimately mixed), estimated to contain 3000 tons metallic lithium (3). While this deposit does not approach the one in North Carolina in magnitude, work is being carried out to try to recover the contained lithia (51). Spodumene deposits of some size are also found in Maine, Massachusetts (14), New Mexico (16), and California.

18. Useful deposits of spodumene are found in Northern Argentina (18), Brazil (3), Manitoba (19), and Sweden but none are of a size comparable with those found in this country. Careful prospecting should bring to light additional pegmatites containing possibly greater supplies of lithium than any known today.

E. Amblygonite

19. From the standpoint of the lithium industry, the most desirable raw material found in nature is the lithium aluminum fluo-phosphate, called amblygonite. This is due to the high contained-lithia and also to the ease of removal of the lithium values. Here again, the lack of extensive deposits restricts its recovery to small-scale mining and hand-sorting operations. Amblygonite is widely distributed but the largest single deposit known, on the Lawrence Judson property, Keystone, South Dakota, only contains approximately 1000 tons amblygonite (50 tons metallic lithium) (3). Almost all the amblygonite sold in the United States comes from the Black Hills, South Dakota, although small deposits are known to occur in California, Wyoming, and Colorado (10).

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20. Canada, Australia, Spain, France (3), and South West Africa (19) are producing some amblygonite but nothing to compare with the United States. Apparently amblygonite will never furnish more than a small fraction of the lithia demanded by industry.

F. Other Lithium Ores

21. Zinnwaldite, montebrasite, triphylite, petalite, and lithiophilite are the only other true lithium ores known to exist in any quantity, and of these, only zinnwaldite and montebrasite have commercial significance. Zinnwaldite is a lithium mica similar to lepidolite but containing approximately 10 percent ferrous oxide. Only Germany is known to be utilizing any of this low-grade ore (3). Montebrasite is a variety of amblygonite, found in small deposits in France and Brazil. Triphylite and lithiophilite are phosphates, high in lithia, but containing considerable iron and manganese, and iron, respectively. Significant quantities of petalite, a lithium aluminum silicate from which Arfvedson first identified lithia, are found only on the island Üto in Sweden.

None of the above ores are known to occur in any extensive deposits but the possibility of such a discovery is always present.

PROCESSING

A. Securing Lithium Raw Materials

22. Considerations incident to a choice of lithium deposits include, (1) extent of deposit, (2) lithia concentration in ore as mined, (3) uniformity of ore, (4) ease of removal of ore from ground, and (5) possible detrimental contaminants.

23. For large-scale production of lithium salts or metal at a reasonable cost, mining operations must be of a comparable size in order to insure an adequate raw material supply. An extensive prospecting program, including numerous test drills, must be carried out to determine what lithium deposits are available and how well they fulfill the five requirements mentioned above.

24. Mining, milling, and concentrating costs, as compared with the market value of the concentrated lithium ore, determine the lowest grade lithium raw material that can be utilized economically. Germany has processed lepidolite ores containing less than 1 percent lithia in the "as mined" state (4), and the 1-2

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percent lithia in the North Carolina spodumene deposits has been recovered commercially during the war. However, the lower concentrating efficiency of these ores and the increased cost of handling materials would indicate that a lithium ore containing less than 1-2 percent lithia, as mined, could not be economically processed at present market prices.

25. It is imperative that the lithium ore as mined be sufficiently extensive and uniform in composition so that power shovels, automatic conveyors, etc. can be used to mine the large quantity of material required to produce a ton of lithium salt. The ease of removal of the ore is also a vital consideration. Open-pit mining would be most desirable but is, of course, practical only if the lithium ore is near the surface.

26. Care must be exercised in a choice of lithium raw materials in order to recognize possible complications due to impurities. For example, lepidolite containing more than 1/2 percent iron is useless as a clear glass flux, and the removal of arsenic, antimony, sulfur, and bromine from Trona Li_2NaPO_4 (8) complicate its use by the lithium industry. Similarly, weathered lepidolite, spodumene, etc. may have part, or even all, of its lithium replaced by sodium, potassium, rubidium or cesium. These alkalies reduce the lithia content in the ore and are difficult to remove in subsequent purifications.

27. The only known deposits of lithium raw materials which would fulfill the above requirements of extent, contained lithia, uniformity and availability appear to be the Kings Mountain, North Carolina, spodumene deposits and, possibly, the smaller, spud-quartz mixture found around Tinton, South Dakota.

B. Preliminary Concentrating

28. Due to the low lithia content of lithium ores as mined, large masses must be handled per unit of metallic lithium. Thus, before recovering the lithium values in the ore by chemical means, a preliminary concentrating is desirable in order to reduce chemical and heat requirements, equipment size, etc. To date, three methods are known by which this can be accomplished - (1) hand-sorting, (2) decrepitation and (3) flotation. Of these, only the last appears to have any promise for industrial-scale operation.

29. Hand-sorting is, of course, suitable if large, pure crystals of lithium ore are present, and only small scale operation is required. Decrepitation methods are practical only with spodumene, which has the unique property of expanding to a

friable, chalky solid upon transition to its beta form at temperatures approaching 1000°C. In this process (20), the quartz, mica, and feldsopathic impurities remain unchanged so that the spodumene in the resultant mixture may be preferentially reduced in size by a gentle grinding and then separated by screening or by an air blast. Although 85-95 percent recovery has been obtained in concentrating 3 percent ore to 5-6 percent in the laboratory and small pilot plant scale (51), large-scale operation with the 1-2 percent ore that will probably be used, would reduce this recovery considerably. Other draw-backs are high heat requirements and difficult temperature control (14) - the materials in question are very poor heat conductors, requiring surface temperatures very near the sintering temperature of spodumene (1200-1300°C) in order to transfer heat to the inside of the necessarily large mass in a reasonable time.

30. Both gravity and froth flotation methods have been tried for concentrating spodumene ores. The usual gangue minerals occurring with spodumene have a density of 2.6 to 2.7 while the pure ore has a density of 3.1 (20) so that gravity separation should be possible. However, spodumene breaks into "woody" slivers which nullifies in part at least, the effect of its greater density. For example, in concentrating a 2.5 percent spodumene ore to 6-7 percent lithia only 50 percent recovery of lithium was attained (24).

31. Much better results have been obtained by froth flotation, especially if the ore is first cleaned by washing or attrition scrubbing to eliminate contamination at the mineral surfaces (22). This "cleaning" is important with weathered ore or ore stained with iron and manganese oxides. Thus a 20-60 minute blunge in an attrition mill, containing 50 percent solids and 2-5 pounds of NaOH per ton of ore, effectively cleaned six different spodumene ores, obtained from various localities, so that subsequent froth flotation, using 0.8-1.5 pounds of oleic acid and 0.10 pounds of pine oil per ton of ore, effectively concentrated all six ores (23). A 2 percent spodumene was concentrated to 5.5 percent lithia with an 80 percent recovery while a 3 percent ore was concentrated to 6 percent lithia with a 90 percent recovery of lithium. Froth flotation methods are now being used by the lithium industry to concentrate spodumene ores. Supposedly, lepidolite can also be concentrated by froth flotation after a preliminary cleaning using hydrofluoric acid, a long chain amine and small quantities of an iron or aluminum salt (21).

C. Preliminary Processing

32. Preliminary processing requirements, such as preheating,

grinding, screening, mixing with reactants, etc. will, of course, vary with the process used for removal of the lithium values in the ore. Particle size and intimacy of mixing are extremely important in determining the speed of reactions. Preheating may be important, as there are indications that the lithium in beta-spodumene is more readily removed than in the more dense alpha form. The optimum use of the above operations can only be determined by carefully controlled experiments.

RECOVERY OF LITHIUM VALUES

A. As Lithium Compound

33. General. The known methods of removing lithium values from ores fall readily into three general classes (1) direct decomposition, (2) chemical replacement, and (3) direct reduction. In each case it is necessary first to break the bond between lithium and the rest of the ore to free it for subsequent distillation or leaching. As each method for freeing lithium may be applicable to more than one type of mineral, the following discussion will be according to type of reaction rather than type of ore.

34. Direct Decomposition Methods. The most direct method of removing lithium from its ores would be by simply heating the ore until it decomposed, thus freeing Li_2O for further solution and purification. P. E. Billinghurst (35) proposed blowing a dust of finely powdered ore through a furnace chamber heated to 1500-1800°C, volatilizing the Li_2O, and leaving infusible silica residues behind. He doesn't, however, give any data as to actual results obtained, nor does he indicate what materials of construction would withstand the attack of strong alkalies at the temperatures given, nor how to prevent the ores from fusing before the lithia can be volatilized. These and other considerations throw considerable doubt on the practicability of the method.

35. Acids or acidic salts may also be used to decompose lithium ore matrices. In the laboratory hydrofluoric acid is used to volatilize silica from aluminum silicates such as lepidolite and spodumene. The large quantity of expensive hydrofluoric acid needed, cost of materials of construction, etc. indicate a lack of commercial application. What is essentially an HF method has been patented by C. Adamoli (36) in which silicates or aluminum silicates are mixed with alkaline earth fluorides, alkali chlorides, and hydrochloric acid until a paste is formed, heated at 65-85°C. for some hours and, after briquetting, heated above 600°C. for several hours. No data on quantities, reaction times, or yields are given for lithium ores however. Cost of materials and chemical recoveries would apparently be high even if the method should be efficient for freeing lithium from its ores.

36. Formerly, amblygonite and lepidolite were decomposed by digesting with a large excess of sulfuric acid to free the lithium values (5, 50, 37). In this treatment, however, all impurities except a gelatinous mess of silicic acid and aluminum hydroxide are also dissolved, which makes subsequent filtrations and purifications difficult.

37. According to a French Patent (46) the above difficulties may be eliminated by using only a small amount of sulfuric acid, in which case, only the alkalies and alkaline earths are rendered soluble in the subsequent leaching operations. The authors give an example in which 100 parts of a finely ground amblygonite ore, containing 8.5 percent lithia, are heated at 150-180°C with 55 parts of 73 percent sulfuric acid until a paste is formed. The time for this operation is not given. Then the temperature is slowly raised to 800-850°C to fume off excess sulfuric acid and other volatiles. The resulting mass, upon leaching, yields 95 percent of its lithium and most of the phosphorus to the solution, both of which are then recovered by fractional crystallization.

38. Laboratory experiments carried out by Löf and Lewis (48), in which hydrochloric acid vapor is passed over heated lepidolite, indicated greater than 90 percent lithium recovery after 13 hours at 935°C. The high temperature, slow reaction, and necessity for recirculating hydrogen chloride, due to the large excess required, would probably eliminate this process from commercial consideration.

39. In a patent by Roder and Siegens (53) it is claimed that the lithium in triphylite can be solubilized by treatment in water with elemental chlorine. The fact that no extensive triphylite deposits are known and that the ore must be ground to a 10,000-25,000 mesh size makes this method highly impractical.

40. Sodium bisulfate is also used as a decomposition agent for amblygonite. It has the advantage over H_2SO_4 in that the ore - $NaHSO_4$ mixture may be brought to red heat. It is reported that this method is at present used by at least one commercial lithium producer to recover approximately 90 percent of the lithium in amblygonite.

41. A preliminary alkali decomposition of amblygonite followed by acid treatment is described in a patent by Coleman and Jaffa (47) in which they claim 83 percent recovery of the lithium as crude Li_2CO_3. An example is cited in which 100 parts of amblygonite, containing 8.5 percent lithia, are digested at 100°C for 3 hours with 115 parts sodium hydroxide and 460 parts water. The mixture is then filtered, washed, and the residues, contain-

ing most of the lithium, digest with hot sulfuric acid. Everything dissolves except silica and gangue; 30 parts soda ash are added to precipitate most of the phosphorus, and another addition of 30 parts soda ash, precipitates the lithium. The difficulties and expensive procedures inherent in acid methods of decomposition are also present in this method.

42. It is apparent that acid or alkaline decomposition methods do not seem to lend themselves to large-scale, economical operation, especially for aluminum silicate type lithium ores.

43. Alkali Replacement of Lithium Values in Ores. The methods for recovering the lithium values in aluminum silicate type ores are mostly variations of a neutral-salt replacement at high temperatures, followed by leaching or distillation. The usual procedure is to mix the replacing agent with the finely ground ore and heat until the reaction takes place. Care must be taken not to fuse the mixture as this complicates the removal of the reacted ore and is said to considerably retard the reaction.

44. Girsewald (45) claims the use of a rotary furnace reduces the amount of replacing chemical needed by 50 percent due to better temperature control and more intimate mixing. His studies indicate that the optimum temperature for replacement of lithium by K_2SO_4 is 880-920°C and by KCl, 720-750°C. However, he was using lepidolite ore which apparently yields its lithium at slightly lower temperatures than spodumene.

45. Due to the high temperature necessary for the reactions to progress satisfactorily, high-melting salts are required to prevent the salt-ore mixture from slagging. Potassium sulfate is reported to be the best replacing agent but its high cost relative to sodium salts and, after leaching, the necessity for the use of additional potassium salts as precipitating agents (43), make this compound unattractive commercially. Also, it is stated that in spite of the high melting point of K_2SO_4 (melting point 1050°C), reaction temperatures above 850°C are impractical due to slagging. Sivander et al (40) claim this premature slagging is due to reduction in the furnace atmosphere of sulfate to sulfite and sulfide, which, if present in concentrations as low as several tenths of a percent, sinter the mixture. Thus, if oxidizing conditions are maintained, temperatures of 850-1200°C may be reached without slagging the ore even though the reacting salt is fused. However, none of the ores may be heated above their melting points without causing slagging, lepidolite melts at approximately 950°C; spodumene approximately 1350°C.

46. The above authors (40) state that 90 percent of the lithium

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in spodumene, crushed to 25 mesh, can be extracted by washing with liquid sodium sulfate at 1000°C for ten minutes. They also claim that only relatively small quantities of extractant are necessary but that the maximum percent lithium in the melt will not exceed the percent in the original ore. As this type of process could be made to operate continuously, is applicable to spodumene ores, and uses relatively cheap raw materials, further work in regard to lowering operating temperatures and separating the lithium from the resulting Na_2SO_4-Li_2SO_4 mixture should be carried out.

47. Siegens and Roder (43) reduce slagging in lepidolite ores by using K_2SO_4-Na_2SO_4 mixtures. This is difficult to see, yet they claim that a mixture of 100 parts lepidolite ore, containing 3.0 percent Li_2O and 9.0 percent K_2O, 5 parts K_2SO_4 and 33 parts Na_2SO_4 can be heated to 850°C without slagging and, after leaching and precipitating with Na_2CO_3, 85 percent of the original lithium is recovered as crude Li_2CO_3. No heating times are given. In a subsequent patent (42), the same authors substitute 39 parts $CaSO_4$ for the 5 parts K_2SO_4 used above, and, after 6-1/2 hours heating at 800-830°C and leaching, recover 99 percent of the original lithium and 50 percent of the potassium.

48. A novel method for carrying out the ion interchange in a water solution at 100-300°C is described in a patent by Linblad et al (38). Any finely divided lithium ore is heated with a saturated water solution of a sodium salt such as the nitrate, chloride or sulfate, and a small amount of CaO (1 part CaO per 100 parts ore). The CaO is supposed to prevent silicic acid from precipitating and stopping the reaction. No rates of reaction or yields are given, and the authors fail to mention that at 300°C the reaction vessel must withstand a steam pressure of the order of 1000 pounds per square inch. Unless further work should prove this ion exchange reaction to be quite rapid and complete, no possible commercial application is forseen.

49. The use of $CaCl_2$-CaO mixtures for replacing the lithia in aluminum silicate ores, has been patented by Rosett and Bichowsky (50). In this method approximately 30 parts CaO (or 50 parts $CaCO_3$), and possibly a small amount of $CaCl_2$ or $CaSO_4$ are intimately mixed with 100 parts lithium ore and roasted at 800-1000°C for an unspecified length of time. The sintered cake is then ground and leached. No yields are given in disclosing the patent. A variation on this method is described in a report by Fraas and Ralston (49) in which the lithia in spodumene is freed by heating to 950-1100°C with CaO and $CaCl_2$,

and the resulting lithium chloride volatilized. In these experiments no attempt was made to collect the lithium chloride. In a pilot plant erected on the Black Hills Tin Company property at Tinton, South Dakota (51), 100 pounds of spodumene, containing approximately 3 percent lithia, was treated with 100 pounds of $CaCO_3$ and 17 pounds of $CaCl_2$. Only 1/2 pound of 50 percent LiCl was collected per run, corresponding to a 3 percent yield. During the war, however, a plant capable of producing 50,000 pounds LiCl per month from spodumene by means of this reaction, was erected by one of the lithium companies. According to them, approximately 90 percent of the Li_2O contained in the ore is recovered as crude Li Cl (52).

50. The lithium industry appears to be sharply divided with respect to the feasibility of the CaO-$CaCl_2$ distillation method. Evidently the cheapness of raw materials and ease of purification are counterbalanced by high equipment costs and technical difficulties such as collection of volatilized LiCl. A thorough study of the variables affecting this reaction is indicated.

51. A patent application by R. A. Stauffer (27) states that heating 220 parts CaO per 100 parts spodumene, or 300 parts CaO per 100 parts amblygonite, to 1150°C under high vacuum, distills out 90 percent of the contained lithia in two hours. Further experiments directed towards a reduction in reaction temperature and chemical costs would be advisable.

B. As Metallic Lithium

52. Electrolysis. At present, all commercial producers of elemental lithium in this country use an electrolytic process, in which the bath contains approximately equal weights of fused lithium and potassium chlorides (32). The method has been improved in recent years so that 99-1/2 percent pure metallic lithium can be made with a conversion of lithium salt to metal of 95 percent and a 90 percent current efficiency (1). Although the method has been developed to such an extent that large-scale production is technically feasible, the use of 6-1/2 pounds of LiCl per pound of lithium produced, makes the cost of the metal necessarily high at present LiCl prices. Another drawback in electrolytic methods is the requirement that pure LiCl be used in order to produce high-grade lithium metal.

53. A patent by Huise (34), if applicable to the electrolytic production of lithium as well as sodium, might permit the use of technical grades lithium salts. In this patent, the author uses a column of pure sodium salt through which the metallic sodium,

contaminated with calcium, must pass before leaving the electrolytic cell. At temperatures above 400°C the calcium is supposed to react with the NaCl to yield $CaCl_2$ and sodium.

54. Thermochemical. No lithium has been produced commercially by chemical reduction of lithium salts although this method is finding increasing industrial application for the production of other metals. National Research Corporation, in a report to the U.S. Army Signal Corps (26), lists three processes which have been studied on a laboratory or small pilot plant scale and are considered feasible for commercial production of metallic lithium. The reducing agent in each case is ferrosilicon, although in the resulting patent application by R. A. Stauffer (27), aluminum is recommended. High temperature vacuum distillation, using retorts similar to those in which magnesium is produced by the Pidgeon process, removes the lithium from the reaction zone. Spodumene is the only lithium ore considered and the lithium is freed by high temperature reaction with CaO.

55. In the first process, the $FeSi_6$ is mixed with the ore and CaO in the ratio of 220 parts CaO and 18 parts $FeSi_6$ per 100 parts spodumene (6 percent Li_2O) and supposedly yields 90 percent of the theoretical lithium in 3 hours at 1100°C. Cost estimates on this process, presupposing 6 percent spodumene at $36 per ton and $FeSi_6$ at $150 per ton (75 percent Si), per ton lithium production per 24 hours, and 5 years amortization of plant and equipment, are given as $4.20 per pound of lithium.

56. In process two, the Li_2O is first freed from the spodumene by heating for one hour at 1050°C with CaO, in the ratio of 330 parts CaO per 100 parts spodumene. Subsequent leaching recovers approximately 12 parts LiOH (80 percent Li_2O recovery). The LiOH is then mixed with CaO and $FeSi_6$ in the ratio of 6 parts $FeSi_6$ and 25 parts CaO per 12 parts LiOH and heated under vacuum at 1100°C for 8 hours to recover 90 percent of the lithium present, or an overall recovery of 72 percent of the lithium in the ore. Cost estimates on the same basis as in process one indicate lithium production at $2.80 per pound.

57. Process three, although still in the beaker stage, is claimed as the cheapest method for producing metallic lithium. Here, the Li_2O is freed as in process two, but after leaching, the lithium in solution is recovered as lithium sulfite with SO_2, calcined with CaO and the resulting Li_2O-CaO clinker ground and reduced with $FeSi_6$ at an indicated cost of only $2.50 per pound of lithium.

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In Table II the steps, and quantities used in each step, are given for each process for the purpose of comparison.

TABLE II

Process	Reactants					Yield (%)	Time (hrs)	Temp. (°C)
1.(a)	CaO +	$FeSi_6$ +	Spodumene	→	Li	90	3	1100
(lbs)	220	18	100		2.5			
2.(a)	CaO +		Spodumene	→	Li_2O	80	1	1050
(lbs)	220		100		4.8			
(b)	Li_2O	(leach, evap.)		→	LiOH	99.4		100
(lbs)	4.8				7.7			
(c)	CaO +	$FeSi_6$ +	LiOH	→	Li	90	8	1100
(lbs)	25	5.8	7.7		2.0			
3.(a)	CaO +		Spodumene	→	Li_2O	80	1	1050
(lbs)	220		100		4.8			
(b)	Li_2O	(leach, SO_2, evap.)		→	Li_2SO_3	100*		
(lbs)	4.8				15			
(c)	Li_2SO_3 +	CaO	→	CaO +	Li_2O	100*		
(lbs)	15	25		25	4.8			
(d)	CaO +	Li_2O +	$FeSi_6$	→	Li	90*		
(lbs)	25	4.8	5.8		2.0			

*estimates.

58. It must be remembered that the above estimates are over-simplifications of results obtained in an exploratory type

investigation with small units. Further work is indicated in order to determine how material and equipment costs may possibly be reduced.

59. Aluminum, magnesium, iron and calcium carbide were eliminated as reducing agents due to higher costs, poorer yields, higher temperatures needed, etc. than for ferrosilicon. In the patent application by R. A. Stauffer (27), in which 140 parts CaO and 10 parts aluminum are mixed with 100 parts spodumene and heated to 1150°C under vacuum (0.01 mm) for 2 hours, 90 percent of the lithium is supposedly recovered in the condenser. The method is also claimed to be suitable for freeing lithium from amblygonite in which case the phosphorus is distilled and collected before the lithium.

60. A similar patent in which pure lithia is reduced at 750-900°C with finely divided magnesium or aluminum and then vacuum distilled, is assigned to M. G. Hanson (28). In this patent, however, the stress is placed on recovering fixed alloys of manganese and lithium rather than pure lithium — magnesium being only slightly less volatile than lithium.

61. An apparatus for distilling metallic lithium at atmospheric pressure is impractical due to the fact that the required temperatures are much too high for known materials of construction.

CONVERSION AND PURIFICATION

A. Chemical Treatment

62. Lithium is usually precipitated from water solution as one of the salts for which solubilities are given in Table III.

TABLE III

	T °C	Solubility (g. Lithium per liter)
Li_2CO_3	0°	2.1
Li_2CO_3	100°	1.4
LiF	18°	0.7
Li_3PO_4	10°	0.06

The phosphate appears to be most widely used industrially for precipitating dissolved lithium, with the fluoride a close second. Li_2CO_3 or LiOH would be the most desirable salts, due

to the ease of conversion to other lithium compounds, but they are not the least soluble in water.

Normally, for conversion, the acid of the desired anion, i.e., sulfuric, hydrochloric, acetic acids, is added to a solution of the pure carbonate or hydroxide and the resulting solution evaporated.

63. The purification procedure used to obtain the final lithium salt depends, of course, on the type of impurities present in the leach and, also, the desired final product.

Iron, aluminum, silicon and alkaline earths are readily removed from lithium solutions if not present in considerably greater concentrations than the lithium. The aluminum precipitates in neutral or slightly alkaline solution, the silicon in acid solution, and the alkaline earths by the addition of carbon dioxide to alkaline solutions or by the addition of sodium or potassium carbonate. The problem, therefore, is to recover the lithium free from other alkali metals.

Many methods have been proposed to remove the alkalies, but they are usually of doubtful value for an industrially successful process because no accounting is made of coprecipitation and adsorption problems, and of the fact that some of the more gelatinous precipitates are extremely difficult to filter.

64. As a guide to the methods which have been proposed for purifying lithium solutions the following table is offered:

TABLE IV

Ref.	Impure Solution	Precipitating Agent	Precipitate
(38)	Li, Na as SO_4	NaOH, cool 0°	Na_2SO_4
(54)	Li, K as SO_4	NH_3	K_2SO_4
(54)	Li, K as SO_4	K_2CO_3	Li_2CO_3 (impure)
(54)[1]	Li, K as SO_4	KCl	K_2SO_4
(54)[2]	Li, K as Cl	K_2CO_3	86% Li_2CO_3 (99.3% pure)
(55)[3]	Li, Na, K as Cl	Heat 147°, cool	96% Na and K as Cl
(49)[4]	Li, Na, K as Cl	$(NH_4)_2CO_3$	92% Li_2CO_3
(56)	Li, Na, K as Cl, SO_4	Na_2SiO_3	Li_2SiO_3
(42)5	Li, Na, K as SO_4	Na_2CO_3	50% Li_2CO_3

[1] 280 g. KCl added to solution containing 90 g. K_2SO_4 and 75 g. Li_2SO_4 per liter.
[2] 94 g. K_2CO_3 added per liter.
[3] Equal quantity Li, Na, and K present.
[4] 170 g. LiCl per liter present.
[5] 30 g. Na_2CO_3 added to solution containing 140 g. Na_2SO_4, 100 g. K_2SO_4 and 649 g. Li_2SO_4 per liter.

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65. Whichever purification method if finally used, recirculation of mother liquors and recovery of by-product chemicals will play an important part in determining the overall cost. Considerable laboratory research is needed before any of the above methods could be used on an industrial scale.

B. Distillation

66. The alkali metal chlorides boil at approximately 1360, 1420, and 1400°C for lithium, sodium, and potassium, respectively. This is higher than is practical industrially, but at reduced pressures it should be possible to separate these chlorides by fractional distillation. At 900° for example, the vapor pressure of LiCl (7.3 mm) is roughly one and one-half times that of KCl and four times that of NaCl (59).

67. Metallic lithium also boils considerably higher than sodium or potassium (60), so that here again reduced pressure distillation is needed to bring the temperature down to a practical range. Magnesium, however, has a vapor pressure intermediate between that for lithium and sodium so it would be much more difficult to remove than the alkali metals.

68. As molten lithium is only slightly soluble in molten sodium or potassium (58), and vice versa, it should be possible to effect a good separation merely by skimming off the lighter lithium layer. Thus, the use of sodium as a reducing agent for the production of metallic lithium should be seriously considered.

CONCLUSIONS AND RECOMMENDATIONS

69. For large-scale lithium production the North Carolina spodumene deposits appear to be the best source of raw materials. Concentration by froth flotation followed by a CaO-$CaCl_2$ heat to free the Li_2O, and a vacuum distillation, either to remove LiCl or, with a reducing agent, to remove metallic lithium, seems to show the most promise. The resulting product should be sufficiently concentrated to simplify conversion and purification problems considerably.

70. It is recommended that the above process be critically studied on a laboratory scale with respect to the effect of temperature, chemical concentrations, and type of spodumene ore, on the time and completeness of freeing of the lithia. Other chemical agents such as the cheaper sodium salts should also be investigated for ease of replacing lithia in spodumene.

71. As has been pointed out in this report, further investigations should be carried out on some of the processes which might be practical but for which the data is either too limited or of doubtful validity.

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