METHODS
for the
PRODUCTION OF LITHIUM CARBONATE
from
LIPIDOLITE.

Thesis

by

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INTRODUCTION.

The object of this investigation has been to determine a method to extract lithium from its ores in order to produce Li_2CO_3 which is used in medicine. Lithium salts command very good prices (averaging about $1.50 per pound) and a simple method of production would form a successful commercial enterprise. Lithium occurs in lepidolite (a lithium mica) and in amblygonite and other moderately rare minerals. In Southern California there are deposits of lepidolite with which this work has been conducted.

The metal belongs to the alkali group but shows many properties characteristic of the alkaline-earths. It acts vigorously with water, hydrogen, nitrogen and oxygen, thus resembling the alkalies. The relative insolubility of the hydroxide, carbonate and phosphate, makes it resemble the alkaline-earths. Lithium gives a very characteristic spectrum which makes it easy to test for traces with a hand spectroscope.

PREVIOUS WORK.

There is only a limited amount of information in chemical literature concerning the extraction of lithium from its ores. In lepidolite it occurs as lithium aluminum silicate, which is practically insoluble, necessitating a chemical change in order to get the lithium in a soluble form. In general two methods of decomposition have been proposed. They are (1) the use of an acid to break down the ore and (2) the fusion of the ore with various salts.

Schieffeln and Cappon[1] propose a method making use of an acid decomposition. Concentrated H_2SO_4 is thoroughly mixed with the finely ground ore in the weight proportions of 1.1 of acid to 1 of ore. This mixture is run into a brick furnace. The temperature is slowly raised to 340°C during a period of eight hours and kept at that temperature for one hour. It was found that a very poor decomposition resulted if the mass was rapidly heated. When properly heated the recovery runs around 94%. The mixture after heating is run into tanks and lixiviated for some time with hot water. At this point the silica separates out. The liquor is decanted off for the next step of the process.

It is necessary to separate the large amount of aluminum present. It can not be separated by the precipitation of the hydroxide as it will carry down all the lithium, which is then impossible to wash out. To take the aluminum out, K_2SO_4 is added in calculated quantities, and alum precipitates upon cooling and stirring. This is allowed to stand for six days, after which it is filtered. There is still an appreciable amount of aluminum left in the solution which must be separated. This is accomplished by adding freshly precipitated $Al(OH)_3$ and boiling for an hour. The aluminum and potash separate as

[1] Journal of the Society of Chemical Industry.1908.549.

a basic alum or alunite. Complete separation is obtained this way.

Calcium is precipitated as it's oxalate, in an alkaline solution. Iron and magnesium are precipitated by adding sodium hypochlorite. These are not present in great amounts and do not require large amounts of materials.

The lithium is precipitated by adding $Na_2 CO_3$, after the solution has been concentrated. The yield as shown by results given was very good.

The disadvantages of the process are numerous. The careful heat treatment, the great number of soluble compounds formed by the decomposition of the ore and the complexity of their removal make the process unsuitable for commercial application. Only ores of 3-5% of $Li_2 O$ can be used. The price of extraction of one pound of Li2 CO_3 is around $1.00. This process is reputed to have worked for six months near San Diego, California, but it failed due to a drop of the price of lithium salts.

Another type of extraction is that found in a French Patent. The powdered ore is fused with $NaHSO_4$ (nitre cake) in a cast iron retort until any fluoride present in the ore is driven off as HF and SiF_4 and then it is further heated in a refractory furnace for an hour. The product is lixiviated for some time. The liquor contains only a trace of calcium, aluminum, iron and other impurities. Calcium is precipitated by oxalic acid and the others, by a small portion of $Na_2 CO_3$. The clear liquor is drawn off and concentrated. It is then treated with Na_2CO_3, giving a precipitate of Li_2CO_3. This affords a simple means of extracting lithium but there were no data given regarding the commercial success of the process.

ANALYTICAL METHODS.

The method used to determine the lithium content in the ore was that given by Treadwell-Hall and recommended by other authorities as the best procedure. It depends on the solubility of LiCl in amyl alcohol and the slight solubility of KCl and NaCl in this reagent. The determination requires about three days to complete.

The finely ground ore was kept at a bright red heat with $CaCO_3$ and NH_4Cl for an hour. The mass partly fused. After heating it was leached with 50 cc. of water for one-half hour, and filtered. The filtrate contained the alkalies and a moderate amount of calcium. The calcium was precipitated twice with $(NH_4)_2CO_3$ in an ammoniacal solution, uniting the filtrates. These were evaporated to dryness and the ammonium salts driven off by gentle ignition. The residue was dissolved in a few cc. of water and the few remaining milligrams of calcium precipitated by $(NH_4)_2C_2O_4$ in an alkaline solution. The filtrate was again evaporated to dryness and the ammonium salts driven off as before. The residue was dissolved in water and evaporated until salts began to crystallize out. Amyl alcohol (Boiling Point 130°C) was added and the solution heated until all the water had been driven off. A drop of concentrated HCl was added to decompose any $Li(OH)_2$ formed by hydrolysis and the solution was again evaporated. When the HCl had been driven off, the alcoholic solution was filtered and evaporated to dryness. The LiCl was converted to the sulphate and weighed after ignition. Lithium chloride cannot be weighed as it is very hygroscopic. A correction was made for the very small amount of sodium and potassium salts that dissolved in the alcohol.

When Li_2O was determined in a residue or in soluble salts, the procedure was partly modified. Calcium and iron were separated and the filtrate containing the lithium salts was treated according to the amyl alcohol procedure after evaporating to dryness twice with HCl.

Sulphate was determined by the usual precipitation of $BaSO_4$. This was ignited and weighed.

Iron was estimated by the precipitation of the hydroxide. The solution containing 0.5 grams of the substance was diluted to 100 cc. This was heated to boiling and a slight excess of NH_4OH added. A brown precipitate appeared when iron was present. After digesting slowly for ten minutes, the solution was filtered and the precipitate was ignited and weighed.

The filtrate from the above procedure was usually analyzed by the permanganate method for calcium. It was diluted to 300 cc. and a drop of methyl orange added. Dilute HCl was carefully poured in until the end point was reached. Then the solution was heated to boiling and an excess of oxalic acid solution added. After standing about one and one half hours, the solution was filtered. The precipitate was washed and transferred to a beeker, where it was dissolved in 5 cc. of concentrated H_2SO_4 and 200 cc. of water. After heating to 80°C it was titrated with standard $KMnO_4$ solution.

EXPERIMENTAL WORK.

The work was started by an analysis of the ore for Li_2O. The first three runs of the determination were not successful as it was found later that the amyl alcohol was impure and would not dissolve the LiCl. With a new supply of alcohol values of 14.7% and 20.1% of Li_2O were obtained but these values were greater than could be expected from pure lepidolite. The alcohol, when tested, dissolved appreciable amounts of NaCl, which caused the inaccuracy. When it's Boiling Point was determined, it was found to be constant at 115°C. The Boiling Point of the pure alcohol should be near 136°C. This showed that it was not the compound desired. The impure alcohol used in the first determinations was found to have a wide range of Boiling Points. By fractionation, about 50% of this alcohol was found to have the desired Boiling Point. With this, three runs gave an average of 0.43% Li_2O. The value checked within 0.007%. The reason for the low percentage of lithia is that there is a large amount of quartz in the ore. By hand picking it was roughly determined that the lepidolite constituted only about one third of the total. Ordinarily the percentage of lithia should run from 2-4%.

In order to extract the lithium, a plan roughly resembling that used by the analysis was proposed. The ore was heated as before with $CaCO_3$ but NaCl was substituted for the NH_4Cl. The ignited mass was extracated with water. The clear liquor, after the insoluble substances have settled, was decanted off and analyzed for CaO. The theoretical amount of Na_2CO_3 to precipitate the CaO was added. By calculation it was found that a good separation should take place, with about 2% of the lithium going out with the $CaCO_3$. However, this did not take into account the affect the large amount of NaCl would have on the solubilities. The lithium was precipitated by Na_2CO_3, after the $CaCO_3$ separation.

Run 1.

Ten grams each of ore, NaCl, and $CaCO_3$ were intimately mixed with a mortar and pestle. The mixture was kept at a bright red heat for one-half hour. The mass did not fuse at this or even higher temperatures. The resulting substance was granular and gray, resembling cement in color.

To it was added 500 cc. of water and the mass lixiviated for one hour. After filtering, the insoluble material was washed with 100 cc. of water. If complete decomposition had taken place, the residue would dissolve in HCl. Upon trial, it was found that there was a large amount of insoluble material. This closely resembled the quartz and did not look as if any of the ore were undecomposed.

The filtrate was diluted to 1000 cc. and 100 cc. takes out for a CaO determination. Analysis by the permanganate method gave 0.00426 grams of CaO in the 1000 cc. per gram of ore taken.

The solution was evaporated to 500 cc. and 1.1 times the amount of Na_2CO_3 necessary to precipitate the CaO present, was added. The solution was slowly evaporated. There was a constant precipitation of the $CaCO_3$. At times a small portion of the precipitate was taken out and washed thoroughly and tested spectroscopically. It always gave the characteristic line of lithium. More washing did not change this result. The calcium evidently carried some of the lithium down with it and held it very tenaciously.

The precipitate was filtered out when the volume reached 100 cc. There was about 0.3 grams of precipitate. This was before a concentration was reached at which any of the lithium should have been precipitated. The product was analyzed and gave 2.74% Al_2O_3 and Fe_2O_3; 2.2% Li_2O and

and 7.14% CaO. The rest was not determined but contained sodium salts. The filtrate showed only a trace of CaO. It was concentrated after the addition of an excess of Na_2CO_3. There was no crystallization of any salts until at the last a large amount of NaCl and Na_2CO_3 crystallized out. This residue gave only a faint lithium line.

The results of the run were (1) that incomplete decomposition of the ore was obtained, (2) the Li_2CO_3 and $CaCO_3$ precipitate out together, under these conditions. With a low grade ore, such as this, it is doubtful if it would be possible to keep the lithium from going down with the calcium. In the analysis of the ore, two precipitations of the $CaCO_3$ were made for this reason.

Run 2.

For this run, 20 grams of $CaCO_3$ were mixed with 10 grams of NaCl and 10 grams of ore. It was thought that a better decomposition of the ore would result as this mixture was used in the analysis. After washing the ignited mass as before, it was treated with HCl to see if it was all decomposed. Again there was a large amount of undecomposed ore which gave a strong test for lithium with a spectroscope. The filtrate was diluted to 1000 cc. and analyzed for CaO. The amount of soluble calcium salts was greatly increased. The analysis gave 0.5450 grams of CaO per gram of ore as compared with 0.00426 grams of the previous run. Evidently a large amount of the excess

$CaCO_3$ had been converted to $CaCl_2$.

The solution was evaporated as before to 500 cc. allowing the small amount of $Ca(OH)_2$ which was continually separating to remain in the solution. The equivalent amount of Na_2CO_3 was added and the evaporation slowly continued. On the addition of the carbonate, no immediate precipitation resulted. As the solution was evaporated, however, there was a continual deposition. This precipitate was tested, after washing thoroughly, with a spectroscope and always contained lithium. When a small portion of the liquor gave only a trace of CaO, with an oxalic acid solution, the evaporation was stopped and the liquid filtered. The calcium precipitate was a mixture of the carbonate and hydroxide. The percentages on analysis gave 46.7% CaO; 1.67% Fe_2O_3; 0.62% Li_2O. No further precipitate was obtained with Na_2CO_3.

This run showed that increasing the $CaCO_3$ content in the mix did not materially increase the decomposition of the ore. The ability of the $CaCO_3$ to carry down the lithium was further substantiated. The action is probably largely due to occlusion, the solubilities being well apart. Calcium carbonate is soluble to the extent of 0.0013 parts per 100 parts of water at room temperatures, while Li_2CO_3 is soluble to the extent of 1.539 parts at the same temperature. The solutions were cooled each time before filtering off the $CaCO_3$ precipitate because the

Li_2CO_3 is more soluble at low temperatures and $CaCO_3$ is less soluble. The Li_2CO_3 should not precipitate under these conditions.

After this run it was decided to do no further work with this method. A large amount of calcium was always present in the liquor after lixiviation. As the above runs showed, lithium came down readily with the calcium and could not be washed out. The decomposition of the ore was very imperfect, only about 50% of the lithium appearing in the liquor after lixiviation. In general, the ore with which the work was done, was of too small a percentage of Li_2O for this treatment. With greater lithium content some could be recovered, though it is doubtful if yields could be obtained which would make the production by this method economical.

Heat Treatment of Ore:

This method used to decompose the ore was dependent upon the volatility of lithium salts. Lithium oxide sublimes at 1000°C and lithium chloride is volatile at slightly higher temperatures. It was thought that this might prove an economical method for obtaining the lithium in a low grade ore.

The heating of the ore was carried out in an electric furnace at about 1000°C. The first heatings showed that in condensing, the volatile substances formed very small particles that could not be absorbed by bubbling through water. Finally an apparatus was designed that brought the particles in an atmosphere of condensing steam. The small, solid particles acted as nuclei around which droplets of water formed from the steam. These were readily absorbed by the water.

The apparatus was as follows. Air was passed at a rapid, uniform rate through a tube in the furnace of Figure 1. It was then jetted onto the surface of boiling water in flask A. The steam and air passed up through the reflux condenser. The air issuing from the top of the condenser was bubbled through the tower B containing glass beads and water. Most of the particles were removed in the reflux condenser and were returned in solution to the flask A. A few went through and were absorbed in the tower B. In order to provide for a rapid flow of air through the system, a long path through slowly condensing steam was necessary. This was accomplished by raising the temperature of the cooling water sufficiently to cause condensation to take place over the entire inner surface of the reflux condenser.

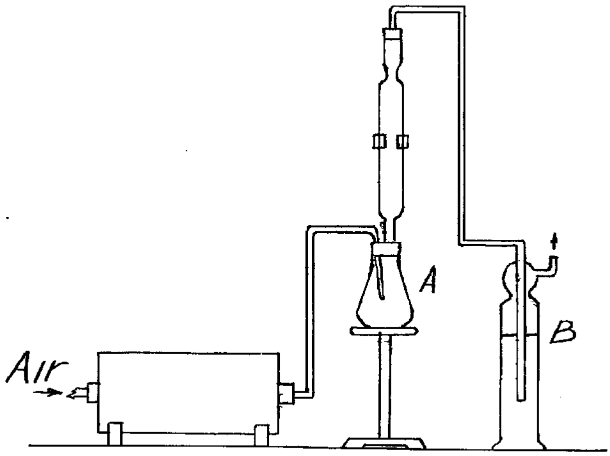

Fig. 1

The furnace was provided with a silica tube containing a nickel shield that extended the entire length of the furnace. This was to prevent possible combination of the charge with the heated silica. A charge of 1 gram was the maximum amount of ore that could be used in this furnace for a run. This necessitated considerable care in the lithium analysis as only 0.0043 grams of Li_2O were present in 1 gram of ore. This gave approximately 0.014 grams of Li_2SO_4 to be weighed for each analysis.

Run 3.

The first experiment was a trial run to perfect the use of the apparatus and to ascertain qualitatively the results to be later expected. The ore was mixed with CaO and heated for two hours. The air leaving the furnace showed spectroscopically the presence of sodium and a small amount of lithium. The charge after heating showed no signs of fusion. The water from the flask and tower was evaporated to dryness. There was estimated to be about 0.1 grams of salts present. Qualitative tests of this residue were made and gave: calcium, small; iron, small; sodium, large; lithium, trace; and chloride, large. It was thought that possibly the Li_2O formed had entered into combination with some of the materials in the furnace to some extent. The calcium was carried over mechanically by the air.

Run 4.

A weighed amount of the ore was mixed with an equal weight of Na_2CO_3. The heating was carried on until the air from the furnace gave no lithium spectrum. Nearly two hours were required for this heating. Upon removing the boat from the furnace, a glassy black substance was found. The ore and carbonate had entirely fused. The water containing the volatile salts was evaporated to dryness and weighed. An analysis was made for CaO, Fe_2O_3 and Li_2O. Calcium oxide was determined by the permanganate method, ferric oxide by precipitation of the hydroxide and Li_2O was separated from the remaining sodium and potassium salts by the amyl alcohol method. The results are given below. The first column gives the percentage of the substance in the salts obtained by volatization. The second column gives the grams of substance per gram of ore used and forms a basis for comparing the different results.

Weight of Ore 3.4592 grams   Volatile 0.1145 grams

	Percentage	Weight/gram ore
Fe_2O_3	16.20%	0.0053
CaO	1.98	0.00065
Li_2O	1.64	0.00054

The yield of Li_2O was small and corresponded to 12.7% of the total amount in ore taken. It was thought advisable to investigate the possibility of loss due to a corrosive action on the furnace. The nickel shield quickly became covered with a scaly crust varying in color from gray to black. The boats containing the mixture could only be used for one run.

Run 5.

It was thought that if HCl were passed through the system with the air, it would combine with the Li_2O formed and prevent loss by combination with the silica. The run was of two hours duration as before. The results were:

Weight of Ore 0.6683 grams Volatile 0.3344 grams

	Percentage	Weight/gram ore
Fe_2O_3	2.09%	0.0104
CaO	0.50	0.00025
Li_2O	0.75	0.00037

The yield in this case was 87% as compared to 12.7% in the previous run. This gave evidence that the Li_2O was reacting with the materials of the furnace. Lithium chloride apparently did not have the tendency as much. Upon removal of the nickel shield it was found quite encrusted with a thick grayish black layer. It was easily broken and when broken showed an inner portion of nickel that consisted of large crystals.

A large increase in the amount of iron volatized was noted in this run. The ore contained a medium amount of iron. The volatility of the iron was probably due to the formation of $FeCl_3$ by combination with the HCl. This is volatile at 285°C.

Run 6.

For this run, NaCl was substituted for the Na_2Co_3. Equal amounts of NaCl and the ore were used. The results of the run were:

Weight of Ore 1.4098 grams Volatile 1.0095 grams

	Percentage	Weight/gram ore
Fe_2O_3	2.78%	0.0199
CaO	0.95	0.0068
Li_2O	0.61	0.0060

This percentage of Li_2O corresponds to a yield of 102%. The excess was due to experimental errors. This run gave evidence that NaCl could be used to better advantage than Na_2CO_3 and HCl.

As in the previous run the chloride present volatized medium amounts of iron.

The nickel lining of the silica tube was found to be completely corroded and broke into several pieces upon its removal from the furnace. A new one was used for the following runs.

Run 7.

With this run, the proportions of 1 of ore to ½ of NaCl was used. A small amount of $CaCO_3$ was added as it was thought to reduce the volatility of the iron. When the final analysis of the volatile salts was made, an appreciable amount of nickel was found present. This was probably due to the action of some of the alkaline chlorides on the nickel. Nickelic chloride is more volatile than either LiCl or NaCl, as it sublimes at low temperatures.

The results of the analysis were:

Weight of Ore 1.0173 grams   Volatile 0.0996 grams

	Percentage	Weight/gram ore
Fe_2O_3	8.84%	0.0088
CaO	0.91	0.0008
Li_2O	3.16	0.0032

The yield in this case was 73.5%. This was less than that of Run 4. Upon removing the nickel tube, it was very much corroded. This probably accounted for some loss of lithium. The lowering of NaCl content could possibly have decreased the volatization of the lithium, although there was an excess of chloride above that theore[illegible]quired.

The volatization of the iron was lowered to approximately 2/3 of that of Run 6. This indicated that possibly the $CaCO_3$ affected its volatility.

No more runs were made as it was not thought to be of sufficient value to carry the work further with this apparatus. The results obtained apparently were dependent upon the amount of corrosion of the nickel and silica. In the first quantative run (Run 4) a very low percentage yield was obtained. By converting the Li_2O formed to the chloride much better yields resulted. At the ends of Run 5 the nickel was well corroded and chance of combination with it was lessened. Thus with Run 6, 100% yield was obtained. With substitution of a new shield the recovery immediately dropped off to 75%. It was impossible to maintain uniform conditions in the various runs, so that attempts to ascertain the effect of varying the different conditions in the mix were too greatly affected by the state of the furnace to be of comparative value.

The next work to be done on the problem could best be undertaken on a much larger scale. It is suggested that an apparatus be constructed that could handle charges of 25 pounds or more. The materials of construction would probably be firebrick[1] as it seems to stand the corrosive vapors well. A rotary kiln has been used to advantage in

[1] Chloride Volatization Process. Bulletin Bureau of Standards.

the volatization of both the base and noble metals. With these processes, a Cottrell Separator has been used, but an apparatus could be designed similar in principle to that of Figure 1. Steam could be passed into a long pipe with the suspended volatile salts, and allowed to cool through a small temperature range. It is thought, that this would form an efficient means of removing the salts from the air current.

The investigation would consist of the determination of the yields, the effect of the corrosive gases on the furnace and the heat requirement for the material. Only a limited amount of heat could be used in order to have an economical process. It is very probable that the heat consumption would prove too great to make the process successful. Interesting results could be obtained, as this method of chloride volatization has proven successful in the recovery of many metals. No references are to be found regarding the volatization of this particular metal.

Recovery of Li_2CO_3 from the Volatile Salts.

The work was carried on by making samples conforming approximately to the composition of the volatile salts. About 12 grams of salts were treated for each run. The capacity of the furnace was too low to permit the volatization of a sufficient amount of the salts without the loss of time. Iron was added to the mix as $FeCl_3$, calcium as $CaCl_2$, sodium as NaCl and lithium as Li_2SO_4. Lithium chloride cannot be weighed accurately except under special conditions so Li_2SO_4 was used. This departed slightly from the true conditions by the introduction of SO_4.

No references were found giving the details of the precipitation of Li_2CO_3. Previous works state that the liquor containing only the alkalies was sufficiently concentrated and Na_2CO_3 added, precipitating Li_2CO_3. References were also found indicating that the solubility of Li_2CO_3 increased with the presence of large amounts of the alkalies. The solubility decreases with a rise in temperature.

The procedure studied in this investigation closely followed that given by the French Patent (Page 3), which began with the liquor obtained after lixiviation of the decomposed ore. Calcium was first separated by the addition of oxalic acid. It was found that small amounts of calcium were present and as oxalic acid is only worth 13 cents a pound, this would not prove to be a great expense.

Iron was precipitated by the addition of small amounts of Na_2CO_3, while the solution was dilute. Lithium carbonate was precipitated by Na_2CO_3 after concentration of the liquor. A large amount of NaCl was present in solution during the precipitation.

Run 8.

The amounts of salts used in the mix were 2.1256 grams of Li_2SO_4, 0.7 grams of $FeCl_3$, 0.3 grams of $CaCl_2$ and 12 grams of NaCl. This was dissolved in 300 cc. of water and heated to boiling. Small amounts of Na_2CO_3 were added until, after the iron precipitate settled, the solution was clear. It was found that with careful additions of Na_2CO_3, the iron all came down when the solution did not affect red litmus appreciably; that is, with only a slight excess of Na_2CO_3. This was filtered and the precipitate well washed. Oxalic acid solution was added in slight excess and allowed to stand for some time. The small amount of CaC_2O_4 was filtered off and carefully washed. The iron precipitate and CaC_2O_4 were tested spectroscopically and found to give only a very faint lithium line, indicative of very small amounts of lithium.

To the clear liquor, Na_2CO_3 was added and evaporation continued. No precipitate appeared until a volume of approximately 50 cc. was reached. Continued evaporation gave a slimy, white precipitate. This was filtered off at intervals but there was no apparent point at which one particular salt precipitated. The first portions were principally carbonates. All portions gave tests for lithium and sodium. No satisfactory method could be seen at this time to take out the salts and be certain which one was present.

Run 9.

The proportions of the mix were taken approximately as before. The weight of Li_2SO_4 used was 1.1852 grams. The calcium and iron separations were perfectly satisfactory for this run as in the previous one. The precipitation of the lithium was conducted on a different basis. The solution containing the sodium and lithium salts was evaporated until salts began to crystallize out. Then enough water was added to dissolve the crystals, when cold, and the solution heated to boiling. A cold saturated solution of Na_2CO_3 was made and enough of this was added to have twice the theoretical amount of Na_2CO_3 present. A white precipitate separated which, upon further boiling, formed what appeared to be crystals. This was filtered and converted to sulphate and weighed. The amount found was 1.858 grams. This proved to be sodium and lithium salts.

Before continuing with the next run a method of analysis for sodium and lithium in the precipitate was necessary. Use of a sodium determination or the lithium determination was too tedious. An approximate method was devised. The weight of the precipitate was determined after converting to sulphate by evaporating twice to dryness with H_2SO_4. Then the SO_4 content was determined by the $BaSO_4$ method and from these two the percentage of sodium and lithium could be calculated.

Run 10.

The proportions of the mix were taken the same as in Runs 8 and 9. The weight of Li_2SO_4 used was 0.9827 grams. Iron and calcium precipitated well, and offered no trouble. The solution was concentrated until salts crystallized and these redissolved by the addition of a small amount of water. The solution was heated to boiling and a saturated solution of Na_2CO_3 added in sufficient quantities to give 1.5 times the theoretical amount. A precipitate resembling the previous one came down. This was filtered and converted to the sulphate giving 0.5408 grams. Upon analysis, it was found to be 91% Na_2SO_4 and 9% Li_2SO_4 showing that the greater part of the lithium remained in solution. This corresponds to a yield of 4.9% of Li_2SO_4. The large amount of NaCl present, apparently had a salting out effect on the Na_2CO_3 and increased the solubility of Li_2CO_3.

Run 11.

The separation of iron and calcium was perfect enough to be dropped with this run. Only NaCl and Li_2SO_4 were mixed. The mix contained 1.1183 grams of Li_2SO_4.

Before starting the run the specific gravity of a salt solution, that just precipitated a small portion of Na_2CO_3 at a boiling temperature, was determined. This was found to be 1.065 at 20°C.

The salts previously weighed out were dissolved in water and the solution evaporated. When the solution reached a specific gravity of 1.065 at 20°C, the evaporation was stopped and the precipitation with Na_2CO_3 solution carried out. Only 0.2799 grams of salts were obtained. These upon analysis gave 5.6% Li_2SO_4 and 94.4% Na_2SO_4. This was a yield of 1.4% lithium.

With the weaker concentration much less lithium came down. Apparently the NaCl markedly increased the solubility of Li_2CO_3.

Run 12.

For this run 1.3920 grams of Li_2SO_4 were taken. The evaporation was stopped when a specific gravity of 1.090 was reached. A larger weight of precipitate resulted, being 0.4557 grams. This gave by analysis, 6.2% Li_2SO_4 and 93.8% Na_2SO_4. The yield was 2.04% of the lithium.

Run 13.

The purpose of this run was to find whether the small amount of SO_4 introduced with the lithium had a marked effect on the solubility of Li_2CO_3. References[1] were found at time stating that the alkaline sulphates affected its solubility very decidedly. The weight of Li_2SO_4 taken was 1.1976 grams. This was dissolved and the SO_4 precipitated by $BaCl_2$. After filtering, the excess barium was precipitated by CO_2 after making al-

[1] Journal of the American Chemical Society. A247, 1905.

kaline. The precipitate was filtered off. Twelve grams of NaCl were added and the solution was treated as in Runs 8 and 9. The amount of salts obtained was 0.3887 grams. This was analyzed and found to be 25.8% Li_2SO_4, giving a yield of 6.67% lithium. This was a larger yield than occurred in any previous run.

The solution was evaporated further. A large amount of NaCl came down with the carbonates. This was not analyzed as it was thought that no distinct separation could be found at any point.

The methods outlined above are impossible to use as a means of separating the Li_2CO_3 due to the large amount of NaCl present and its affect on the solubility of Li_2CO_3. The presence of SO_4 introduced with the lithium has an appreciable affect on the solubility of the Li_2CO_3. However, the absence of SO_4 does not make the yields sufficient for commercial use.

For further work it is suggested that attempts be made to separate the NaCl and LiCl by crystallization. The solubilities are well apart. The difficulty found in this work is that it is impossible to make accurate qualitative tests to determine which salt is crystallizing out. Probably spectroscopic means could be used to test the crystals at intervals in order to see if more than a trace of LiCl were separating out with the NaCl.

For the proposal of the problem, and numerous helpful suggestions in the methods of solution, acknowledgement is here made to Dr. William N. Lacy.

SUMMARY.

Methods of decomposing lepidolite to give soluble lithium salts and of recovering lithium as the carbonate from the soluble residues have been investigated. The results are:

(1). Decomposition of the ore by means of $CaCO_3$ and NaCl is imperfect. It takes a very high temperature to fuse this mixture which probably accounts for the poor decomposition.

(2). LiCl and Li_2O are readily volatized around 1000°C.

(3). The quantitative yields of the volatization were unsatisfactory due to corrosion of the furnace materials used. If the furnace were lined with firebrick, these difficulties probably would be obviated.

(4). The presence of SO_4 markedly increases the solubility of Li_2CO_3.

(5). The presence of large amounts of NaCl increases the solubility of Li_2CO_3 to such an extent that it cannot be separated from Na_2CO_3 or NaCl.

(6). Iron is precipitated readily with Na_2CO_3 without loss of lithium.

(7). Calcium cannot be separated as $CaCO_3$ without the loss of large amounts of lithium but it can be separated as the oxolate.

(8). The recovery of lithium from the volatile salts is very imperfect and additional work must be done before the volatization process can be tried on a larger scale.