RECOVERY OF LITHIUM FROM GEOTHERMAL WATER IN THE HATCHOBARU AND OHTAKE AREA IN KYUSHU

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ABSTRACT

The recovery of lithium from geothermal water at the Hatchobaru area in Kyushu, Japan was investigated. A coprecipitation method using aluminium salts was employed, The lithium concentration in geothermal water used in the present study was about 10 ppm. To make our experimental results more applicable for geothermal water, the reference lithium solution($[Li^+]=10$ ppm) was also studied as a control solution. A perfect recovery of lithium was obtained for the reference lithium solution by choosing appropriate conditions. For geothermal water, the yield of Li recovery was not so good comparing with a control solution. However, an almost complete recovery of lithium was attained from geothermal water by the removal of calcium ion and polymeric silicic acid. The mechanism of lithium recovery was also discussed.

INTRODUCTION

In Japan, lithium resources from mineral are practically naught. Although the concentration is very dilute(0.18 ppm), there is a vast supply of lithium in seawater(estimated to be 2.5x1014Kg), probably the most reliable energy resources in the near future. At the present stage, however, the recovery of lithium from seawater in a commercially practical way is very difficult. These recent years possible substitutes for petroleum are being investigated in Japan. One of them is a geothermal energy. Geothermal water from the Hatchobaru power plant(5MW), for example, gives the Li values of about 140(Kg/day),(5.3x104Kg/year), provided that the Li content is 10 ppm and the fluid velocity of geothermal water 600(ton/hour). Though the Li content to be obtained is small, if the lithium is transformed into nuclear fusion energy, it will be equal to about one hundred million people's electric demand(as 1 KW·year/man·year). The Li content in seawater is about 0.2 ppm, while the concentration in geothermal water from the Hatchobaru bore is about 10 ppm. Thus, the recovery from the geothermal water seems relatively easy and practicable comparing with that from seawater.

In the present work, the recovery of lithium from geothermal water is aimed at, As techniques to recover lithium from the Li-containing solution, there have been the adsorption method using many kind of adsorbents, the solvent extraction method, the coprecipitation method, the inorganic ion exchange method, and so on. The coprecipitation method seemed to be the simplest among these and was employed in the present study. Although the lithium recovery from the low concentration solution has been extensively investigated, the detailed mechanism for the Li recovery seems not to have been clarified yet. Since the many factors concerning the Li recovery are complicated, the reported results are sometimes in conflict among them. Thus, in the present work, the basic investigation using the reference Li solution as a control, was made first, and then the results were applied to geothermal water.

WATER SAMPLING AND PROCEDURE

Geothermal water used in the present study was sampled out from the bores at the Hatchobaru power station in Kyushu, Japan. The typical constituents of the discharge water are shown in Table 1.

The procedure for the measurement of the residual lithium concentration is shown in Fig.1.

REFERENCE LI SOLUTION

To examine the basic character of the Li-containing solution, the "reference lithium solution"(ref. Li solution) which has the same lithium concentration as in geothermal water was prepared as a control solution. That is, the ref. Li solution was prepared by LiCl and distilled water. Extensive investigations on the Li recovery from the Li-containing solution have been made by many researchers.(Goodenough, 1960; Kaplan, 1963; Goodenough et al, 1967; Kitamura et al, 1978; Pelly, 1978; Frenkel et al, 1980; Takeuchi, 1980). But the effectiveness of the Li extraction from the Li containing solution is influenced by many factors such as the Li concentration, many other kinds of salt constituent, concentrations of precipitating agents, pH, temperature, stirring time, and so on. Thus, the optimum conditions reported are of a wide range owing to the characteristics of the solutions. First, the results from the ref. Li solution is shown in Fig.2. The figure shows the plots of the residual Li concentration vs. time and the (apparent) pH vs. time at room temperature. The influence of the initial (apparent) pH is very large. In this case, the experiment at

Table 1, **Typical compositions** (and pH) of geothermal waters from, borer at Ohtake and Hatchobaru areas (in ppm)

Constituents	Ohtake well Nos.		Hatchobrru well Nor.	
	No.9	No.10	No.4	No.7
Na	1050	1030	2250	2140
K	132	124	277	266
Li	4.79	4.73	10.9	10.2
Ca	28.4	29.7	60.2	76.3
Mg	0.01	0.21	1.21	1.21
F	2.95	2.35	4.05	3.80
Cl	1774	1738	3954	3651
HCO_3	57	77	12	11
SO_4	145	193	138	95
HBO_2	84	78	191	170
SiO_2	531	433	679	746
As	2.0	2.1	3.2	3.6
pH	8.57	8.44	6.99	7.04

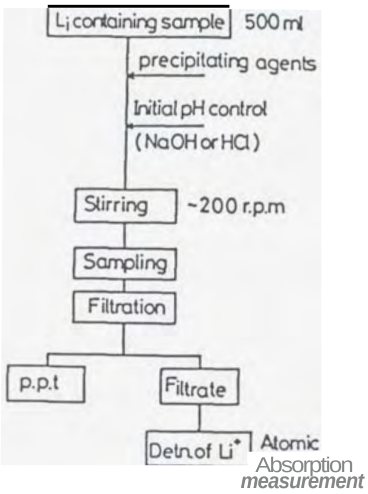

Fig.1 Experimental procedure for Li recovery.

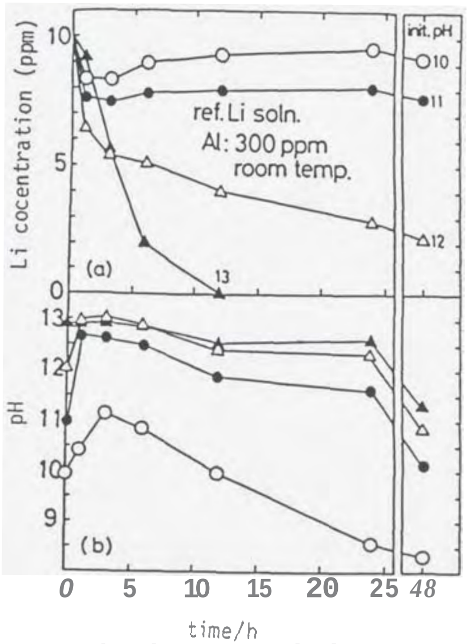

Fig. 2 The plots of residual Li concentration vs. time and pH vs. time for ref. Li solution at room temperature.

the initial pH of 12 gives the maximum effect within about an hour. However, from Fig.2, it seems that after 24 hours, the higher the pH is, the better the yield of Li recovery in the range of pH used in the present study. As the example shows, the pH control is a very important factor in the recovering of the lithium. Although alkaline earth metal ions are absent in this case, the optimum pH obtained was quite different from that(pH 6-8) obtained by Goodenough(1960). The effect of the Al concentration on the Li recovery was also studied, For the Li recovery, a general tendency was found that the higher the Al concentration is, the better the percent recovery of lithium, However, when extremely high Al concentrations were used(ex. 1000 pprn), the extent of the Li recovery decreased. The reason is not clear, but it might be interpreted as follows: In the present work, from the practical point of view, the aluminium concentrations in the Li-containing solutions were adjusted by direct addition of aluminium salts powder of an amount previously calculated, then stirred with magnetic stirrer, So, in case of too high Al concentrations, the conditions of coprecipitation might differ from those of lower Al concentrations. And the partial crystallization of aluminium hydroxide might have occurred. (The X ray diffraction analysis confirmed the evidence qualitatively,) Kitamura et al(1978) reported that amorphous aluminium hydroxide adsorbs much lithium, and crystallized aluminium hydroxides(bayerite, pseudo böhmite etc.) do not adsorb.

As easily expected, although the complete recovery of lithium for the Al concentration of 100-500 ppm was achieved, the Li yield to one-gram of aluminium depends on the stirring time. (For example, within 24 hours, the Al concentration of 200 ppm gives the best result, and within 48 hours, that of 100 ppm gives the best result). The effects of Al concentration vary according to the pHs adjusted. The present study shows that the relatively higher pH leads to the higher recovery of lithium, This suggest that the use of sodium aluminate is better than any other kind of aluminium salt,

MECHANISM OF LI RECOVERY

On the Li recovery by the coprecipitation method, two explanations are possible: One is the recovery by adsorption, and the other by precipitation, by the formation of water insoluble lithium aluminate complex. However, no satisfactory explanations have been given yet. So, in the present study, both mechanisms were examined, It was found that the Li recovery from Li-containing solution could not be explained by the adsorption only, And the following mechanism will be introduced: First, stoichiometrically excess amount of aluminium salt causes the reaction of Li^+ and AlO_2^-(or $Al(OH)_4^-$) to form the lithium aluminate complex, $LiAlO_2 \cdot yH_2O$.[Ex. a residual Li concentration of about 0.5 ppm will exist, after adding Al salt(200 ppm as Al).] Then, the residual Li will be adsorbed by the aluminium hydroxide which is formed by extra amount of aluminium salt. The existence of lithium aluminate complex was confirmed by measuring the X ray diffraction patterns, This two-step mechanism will explain the major part of the Li recovery by the coprecipitation method in case of the ref. Li solution, The solubility of $LiAlO_2$ will depend upon the pH, the temperature, various kinds of polynuclear aluminium complexes,and other kinds of salts in solution, At a very high pH solution(pH 13), the freshly precipitated lithium aluminate complex dissolves relatively easily when it is dispersed in a dilute state. The reason is not clear at the present stage. However, the solubility product obtained in the present study[$K_{sp}= 5.3 \times 10^{-9}$(at 20°C)] may be useful in estimating roughly the yield of Li recovery in advance.

INFLUENCE OF TEMPERATURE ON LI RECOVERY

It is clear that when the Li concentration of 10 ppm is used, the formation of the lithium aluminate complex is essential and the solubility may largely depend upon the solution temperature, Geothermal water at the Hatchobaru bore has a relatively high temperature(80-90°C) at the outlet, In view of the effective utilization of the geothermal water, operations at a high temperature will be required, The experimental results on the Li recovery at 80°C are shown in Fig.3. The figure depicts a fairly different behavior comparing with one at room temperature, That is, for all the ref, Li solutions with variously set pHs, the minima were found. Within one to six hours, the plot of the residual Li concentration vs. time shows the minima, then the Li concentration shows a linear rise to 9-10 ppm with passage of time. This phenomenon might be interpreted as follows: At the first stage, the lithium aluminate complex precipitates rapidly, then the complex dissolves linearly according to the solubility equilibrium and in this case, a high temperature seems to accelerate the precipitating speed and to shift the optimum pH to the lower region as shown in the figure. When the Li recovery is made at a high temperature, the pH control ought to be made accurately and a short time recovery is desirable,

LI RECOVERY USING GEOTHERMAL WATER

The basic study on the Li recovery showed us several important factors, and now the Li recovery from geothermal water should be in order. For geothermal water, even in the best condition, only a recovery of 80-85% was attained as shown in Fig.4, and the optimum pH was in the range of pH 10-10.5. While for the ref. Li solution, at the optimum pH, the percent recovery of lithium was 100%. As stated above, there seems to be a relatively great difference between geothermal water and the ref. Li solution concerning the Li recovery. Geothermal water seems to have a kind of

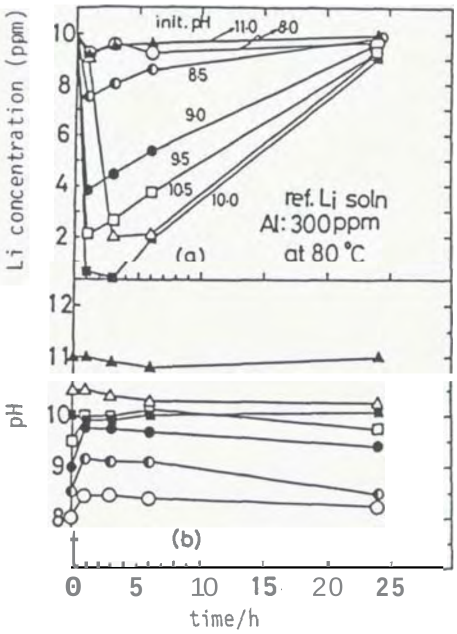

Fig. 3 The plots of residual Li concentration vs. time and pH vs. time for ref. Li solution at 80°C.

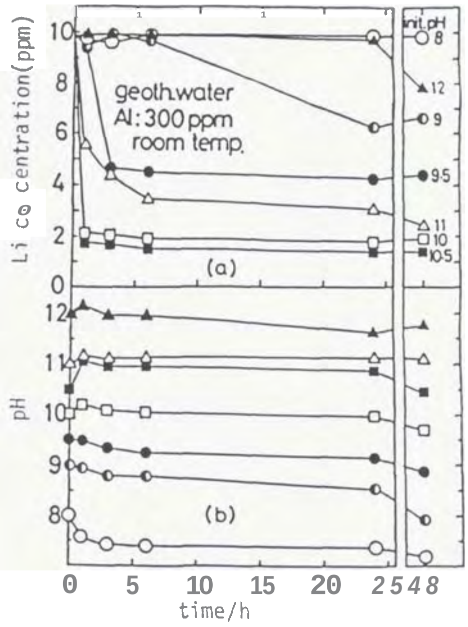

Fig. 4 The plots of residual Li concentration vs. time and pH vs. time for geothermal water at room temperature.

* Al concentrations were adjusted using $AlCl_3$ salt.

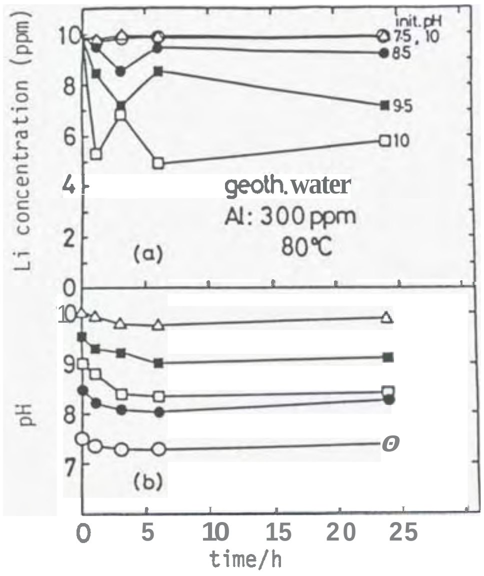

Fig. **5** The plots of residual Li concentration vs. time, and pH vs. time for geothermal water at 80°C.

buffering action. The use of the Al concentration of 500 ppm increased the yield of Li recovery and the optimum pH region became wider (pH 10-11). Figure 5 shows the experimental results for geothermal water at 80°C using the Al concentration of 300 ppm. The extent of Li recovery is very low as is expected and the optimum pH is around 9, which is lower than that of geothermal water at room temperature. Comparison of the ref. Li solution and the geothermal water at 80°C shows that for the ref. Li solution, a relatively higher yield of Li recovery is possible within a few hours, but that for geothermal water there is no possibility of such a rapid recovery of lithium.

The relatively large difference between the ref. Li solution and the geothermal water may be due to the various kinds of salts in the geothermal water. The most probable constituents which negatively function will be the high-concentration sodium chloride, polymeric silicic acid and the salts, and calcium ions. The addition of a large amount of NaCl(1×10^4-3×10^4 ppm) to the ref. Li solution did not change the effect on the Li recovery. It was found that calcium ion was the cause of the poor yield of the Li recovery, and the effects of silicic acid and the salts were relatively small comparing with those of calcium ion. Fig.6 shows the results from the calcium-free geothermal water. Calcium ion was removed by the formation of calcium oxalate at a low temperature. As shown in the figure, the yield of Li recovery from geothermal water becomes very satisfactory by the removal of calcium ions.

CONCLUDING REMARK

We may conclude that the lithium recovery from geothermal water in the Hatchobaru area will be successfully carried out by controling the pH, the treatment temperature, and the stirring time, as well as by the removal of calcium ions.

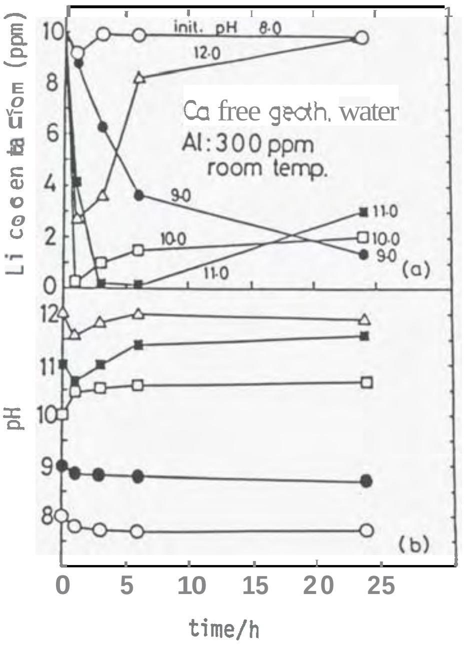

Fig. 6 The plots of residual Li concentration vs. time and pH vs. time for Ca free geothermal water at room temperature.

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