LITHIUM RECOVERY FROM GEOTHERMAL WATERS OF CESANO (ITALY) AND CRONEMBOURG (ALSACE, FRANCE)

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ABSTRACT

As a part of ongoing studies into the economic use of geothermal fluids, we carried out experiments on the recovery of lithium from reconstituted French and Italian geothermal fluid samples. The method consisted of adding different concentrations of $AlCl_3.6$ H20 and KOH to the starting solutions, at different temperatures and pH, leading to the precipitation of aluminium phases. Encouraging results were obtained: without any prior treatment, high lithium recovery was obtained at 80°C, at a pH similar to that of the starting solution, and with the addition of relatively low amounts of aluminium. Investigation of the chemistry of solid and fluid phases showed that the encouraging results were strongly influenced by the chemical composition of the initial fluids.

INTRODUCTION

Because of the existence of highly saline geothermal fluids, the extraction of minerals from these waters has often been considered. The production of fluids being financed by geothermal exploitation, reasonable costs are expected for extracting the contained minerals.

Lithium is one of the minerals in geothermal fluids that have a potential value and many extraction techniques have been proposed in the literature (Dang and Steinberg, 1978; Schultze and Bauer, 1984; Abe and Chitrakar, 1987; Sakamoto et al.. 1987). One of the best known methods for lithium extraction is its precipitation with an Al hydrous oxide (Yaganase et al., 1983; Yoshinaga et al., 1982, 1986; Schultze, 1984; Rothbaum and Middendorf, 1987), which was applied to non-geothermal fluids (Epstein et al., 1981; Pelly, 1978; Takeuchi, 1980).

Aluminium hydroxides are used in water treatment to remove colloids and organic pollutants. For this reason, their properties are quite well known (Fripiat and Pennequin, 1965; Bottero et al., 1980, 1987; Axelos et al., 1987; Rakotonarivo et al., 1985. 1988).

The objective of this paper is to present a basic Investigation of lithium extraction of two high-salinity fluids from Cesano (Italy) and from Alsace (France), using aluminium hydroxides. In fact because of technical reasons, it was not possible to use fresh samples of the fluids and we had to reconstitute them from literature data.

AREAS OF INTEREST

The respective compositions of the two geothermal fluids are given in Table 1. The first one is a fluid from the geothermal area of Cesano, near Rome. The second one (Cronembourg) is a fluid of the Buntsandstein level in North Alsace (France), which presents a good geothermal potential, the geothermal gradient being over 6" per km. Studies are carried out to evaluate the geothermal potential of the different sedimentary reservoirs and since 1986, field tests have been conducted to study the suitability for H.D.R.-energy production.

	Cesano	Cronembourg
Na	63570	32200
K	21370	3978
Ca	43	4600
Mg	12	145
Li	350	220
NH_4	12	
Fe	0.7	5.2
HCO_3	1900	305
SO_4	91010	508
B	13800	
Cl	37010	61415
F	100	4,6
SiO_2	130	235

Table 1: Chemical composition (mg/l) of the geothermal fluids of Cesano (Calameii et al., 1975) and Cronembourg.

EXPERIMENTAL WORK

The reconstituted samples of the waters with the composition given in Table 1 and used in the present study, were prepared just before the experiment started from the analytical reagents NaCl, KCl, LiCl, $CaCl_2$, Na_2SO_4, $Na_2B_4O_7.10H_2O$, $NaHCO_3$, $MgSO_4.7H_2O$, $MgCl_2.6H_2O$, RbCl, NH_4Cl, HF, $FeCl_3.6H_2O$. The silica was obtained by removal of Na^+ by H^+ of an $Na_2SiO_3.nNaOH$ solution (Baker, "dilut-it") on Dowex ion-exchange resin.

To a 150 cm^3 sample of the geothermal water, aluminium was added as solid $AlCl_3.6H_2O$, the required pH was adjusted with potassium hydroxide and the solution was maintained at the working temperature and stirred throughout the experiment.

Periodically, the pH was measured and 10 cm^3 of solution were filtered through a 0.45 μm Millipore filter, and analysed for Li and, in most cases, for Al.

Reaction times varied from 5 minutes to 6.5 hours. Time zero was the time at which the adjustment of pH was begun.

After the completion of some experiments, the remaining sample was filtered, the solid material was conserved, analysed and studied by X-ray powder diffraction.

The influence of three variables was investigated: experiments were performed at three different temperatures (20, 50 and 80°C), at different pH values, and for different aluminium contents.

RESULTS AND DISCUSSION

The chemical composition of solutions and precipitated phases are given in figures 1 to 12 and in tables 1 and 2. On the upper half of the figures 1 to 8 are given the residual Li concentrations in the solution versus time, and in the lower part of the figures the pH evolution is shown as a function of time. Generally, lithium concentration in the solution decreases rapidly after aluminium and KOH addition, and reaches a steady-state value.

The discussion will first consider the influence of several parameters on lithium recovery, then the aluminium behaviour and finally the solid phase properties.

Influence of temperature, aluminium content and pH on Li recovery

Extensive investigations of lithium recovery have been made by many authors. The conditions of lithium extraction are influenced by several factors, such as nature and concentration of precipitating reagents, the occurrence of dissolved salts, the pH, or the temperature. The observed results can be contradictory from one study to another, which was one of the main reasons for investigating the effects of these parameters on Li recovery from the Cesano and Cronembourg fluids.

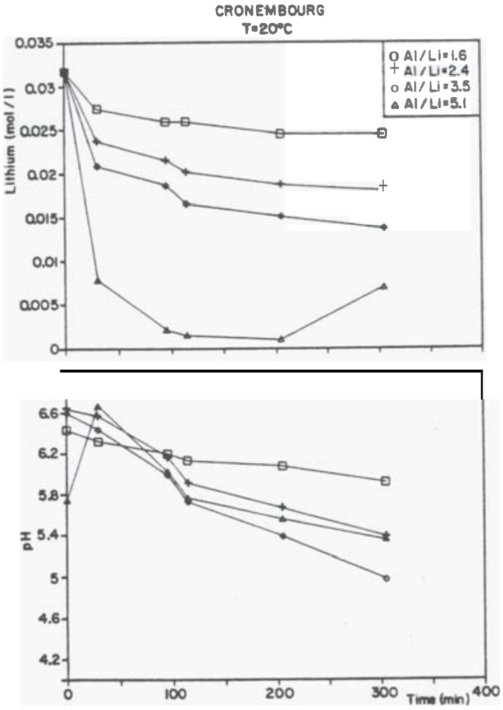

Figure 1: Residual Li concentration and pH versus time for Cronembourg fluid.

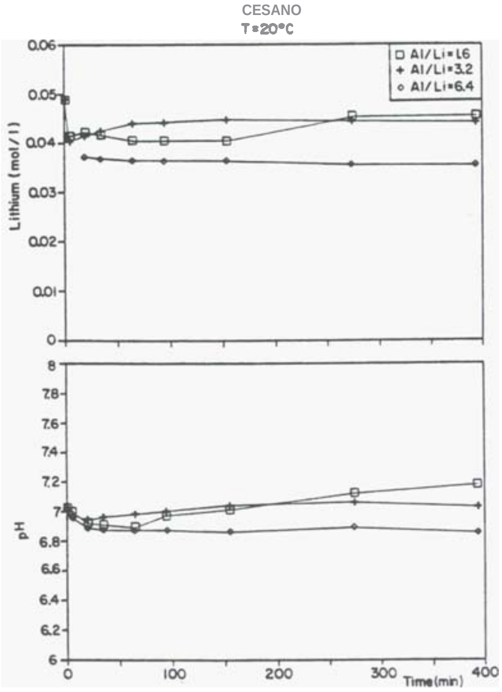

Figure 2: Residual Li concentration and pH versus time for Cesano fluid,

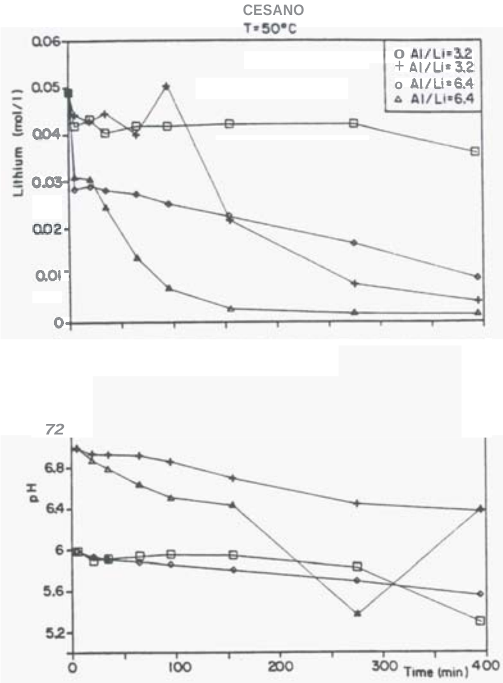

Figure 3: Residual Li concentration and pH versus time for Cesano fluid.

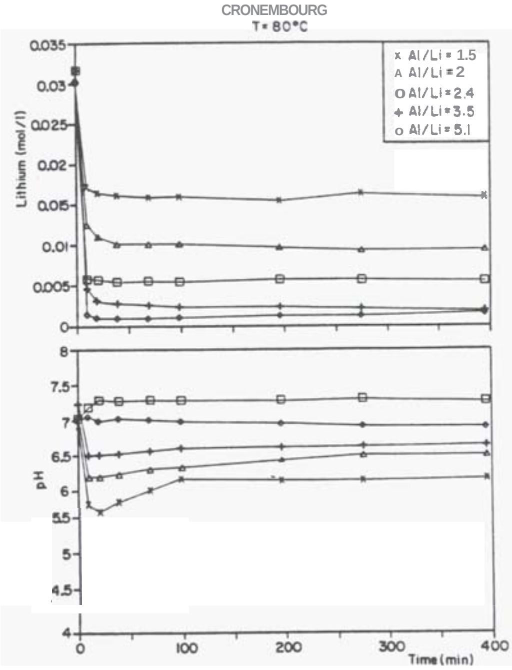

Figure 4: Residual Li concentration and pH versus time for Cronembourg fluid. Effect of Al content.

In view of the fact that any recovery will always be as secondary production from geothermal water, operations at high temperature will be required. Previous studies have investigated the influence of temperature, which showed that it can inhibit lithium recovery (Pelly, 1978; Yaganase et al., 1983).

Temperature dependence on Li yield was investigated for both the Cesano and Cronembourg fluids. In both cases, the higher the temperature, the higher the Li recovery will be. In the same way, the extraction kinetics increase with increasing temperature.

The influence of the Al content (e.g.: initial Al/Li ratio) on lithium yield was investigated. Whatever the temperature and the fluid, Li recovery increases with the initial Al/Li ratio (figures 1, 3, 4 and 5). It is interesting to point out that high recovery rates (about 50%) may be attained with an initial Al/Li ratio of around 1 (figure 5). This result shows that it is not necessary to use a large amount of aluminium for lithium extraction. Recovery higher than 95% is achieved when the initial Al/Li ratio is equal to 2.76. In other situations, lithium extraction requires higher Al/Li ratios, going as high as 66.5 (Rothbaum and Middendorf, 1986).

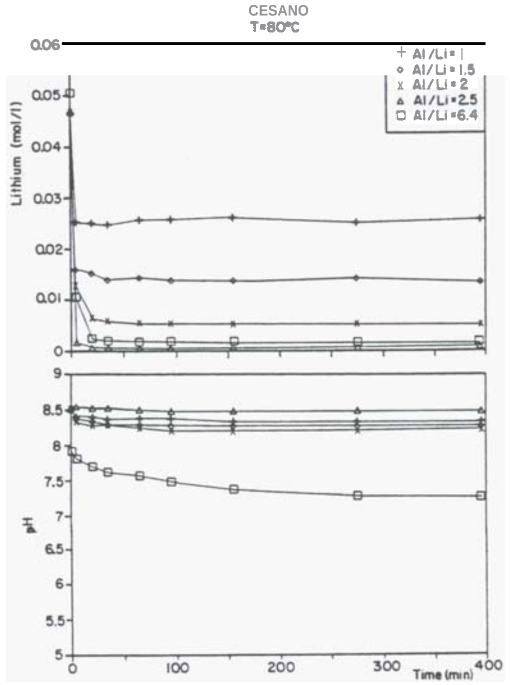

Figure 5: Residual Li concentration and pH versus time for Cesano fluid. Effect of Al content.

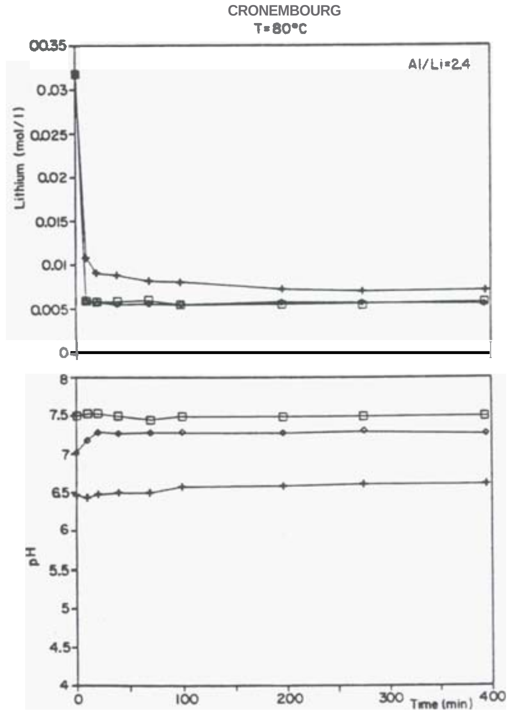

Figure 6: Residual Li concentration and pH versus time for Cronembourg fluid. Effect of the pH on Li recovery.

The pH influence on Li recovery at various Al contents was examined at 80°C, between about pH=5 and pH=9. Its effect is presented on figures 6 to 8. For both fluids, the extraction rate rises with the pH and we could not observe an optimum pH for extraction as shown in previous tests (Pelly, 1978: Yochinaga,1986). Moreover, it seems that the Li recovery increases with the pH until a plateau value is reached. For example, in the fluid from Cronembourg, if extraction proceeds with an Al/Li ratio of 2, the pH has no longer any effect above a value of 7 (figure 6). However, the effect of the Al/Li ratio seems to be more important than that of the pH.

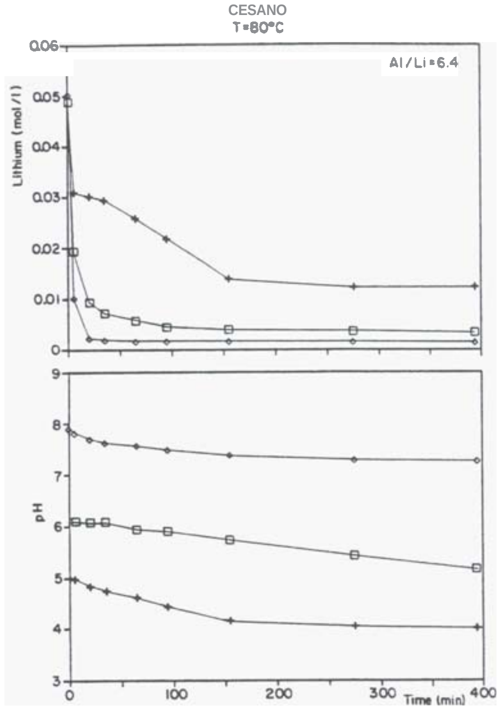

Figure 7: Residual Li concentration and pH versus time for Cesano fluid. Effect of the pH on Li recovery.

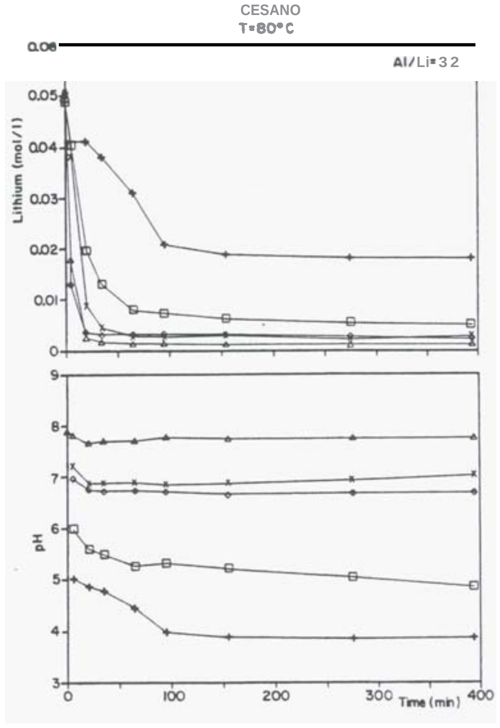

Figure 8: Residual Li concentration and pH versus time for Cesano fluid. Effect of the pH on Li recovery.

There are some differences between the two studied fluids: the effect of the pH seems more important on the recovery rates and kinetics from the Cesano fluid (figures 7 and 8). However, in both cases a high recovery could be obtained at a pH equivalent to the initial pH of the fluid. This is a very important result which indicates that there is not much point in the acidity of the fluid, which means that the process will not changing the reinjection procedure.

All three initial parameters of the two fluids (temperature, initial Al/Li ratios and pH) are encouraging for achieving good lithium extraction. It is possible to recover lithium from geothermal water in very few minutes without cooling of the fluids, at the pH of the fluids, and with relatively little addition of aluminium. These results can be explained by both the chemical composition of the fluids and the nature of the Li-precipitating solid phase.

Formation of the Li-precipitating phase

(1) Solid phase

Chemical analysis of the solid phase checked the presence of Al, Li, Ca, K and Na (table 2), but the amount of anions has not been determined.
These solid phases are very rich in water. The molar ratios Na/Ca are the same for both geothermal fluids and precipitates, indicating that these elements are in the remaining aqueous phase and not in the solid material.

X-ray diffraction of the precipitate indicates the occurrence of an amorphous phase and of halite (NaCl), Sylvite (KCl) and aphritalite ($K_3Na(SO_4)_2$). Because these phases are under-saturated in the geothermal water, their occurrence in the solid material results from the evolution of the precipitate before its study (evaporation and then crystallization). No aluminous phase was detected by X-ray diffraction.

Some leaching experiments of the precipitate with distilled water indicate an increase of the Li/Al ratio in solution with respect to the solid. From this we deduce that lithium is adsorbed on the aluminous phase.

Sample		Al %	Li %	Ca %	K %	Na %
Cesano 20°C	r-6.4	4.5	0.042	0		-
Cesano 50°C	r-6.4	2.82	0.18	0.008	-	-
Cesano 80°C	r-3.2	1.1	0.16	0.009	-	
	r-6.4	2.7	0.	0		
Cronemb 50°C	r-3.5	2.5	0.18	0.28	1.1	2.02
	r-2.4	2.18	0.2	0.57	1.67	4.18
Cronemb 80°C	r-3.5	3.9	0.16	1.0	1.43	-
	r-5.1	4.2	0.11	0	1.67	-

Table 2: Analyses of Li-A1 precipitates; concentrations are expressed in percentages;
r: refers for the Al/Li initial ratio (before KOH addition)
-: not analysed

(2) Aluminium precipitation

In all cases the precipitation of aluminium is very rapid and after 10 minutes the concentration had reached a steady-state value. During KOH addition, the turbidity of the solution increased because of the formation of a non-settling gel.

The formation of such a gel at 25°C during aluminium-chloride hydrolysis is quite well known. Under these conditions, the aluminium ion $Al3+$ above pH-3 is hydrolysed to produce more-or-less soluble polynuclear forms: $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$ or $Al_{13}O_4(OH)_{24}^{7+}$ the polycation called Al_{13} (Brosset et al., 1954; Johanson. 1960; Baes and Mesmer, 1976; Bottero et al., 1977). Black (1967) demonstrated that "Al_{13}" is predominant at equilibrium with amorphous, relatively soluble, aluminium hydroxyde. During the neutralization of an $AlCl_3$ solution with NaOH at 25°C, Bottero et al., (1988) observed only Al_{13} between DH 6.5 and 8.5. Conversely, the polynuclear species are always negligible at equilibrium with well-crystallized gibbsite (Baes and Mesmer, 1976).

During our experiments the precipitate was a gel regardless of the temperature, and no crystallized phase was detected. Because of the pH of the solution, two aqueous Al species are expected: the ion aluminate $Al(OH)_4^-$ and the polycation Al_{13}. We analysed for both in our samples as total dissolved aluminium.

The precipitation of an aluminium trihydroxyde from these two species is described by the two relationships:

$$Al_{13}O_4(OH)_{24}^{7+} + 11\ H_2O \rightleftharpoons 13\ Al(OH)_3 + 7H^+ \qquad (1)$$

With the equilibrium constant:

$$K = (Al_{13}O_4(OH)_{24}^{7+})/(H^+)^7 \qquad (2)$$

$$Al(OH)_4^- + H^+ \rightleftharpoons Al(OH)_3 + H_2O \qquad (3)$$

With the equilibrium constant:

$$K = (Al(OH)_4^-)(H^+) \qquad (4)$$

where the brackets () represent the activities of the species.

In the first case and at equilibrium with the Al trihydroxide gel, the Al_{13} concentration has to decrease when the pH rises. Inversely, in the second case, the concentration of $Al(OH)_4^-$ has to increase with the pH when equilibrium is reached.
In figure 9 we present the log distribution of total aluminium concentration after 395 minutes for the experiments at 80°C on the Cronembourg fluid. Above pH-7.3 the total concentration increases with pH, indicating that under these conditions the ion $Al(OH)_4^-$ at 80°C is the predominant species instead of the Al_{13} polycation. Below pH=7.3 the behaviour of aluminium is not clear. The difference may result from a larger proportion of the Al_{13} polycation. Nevertheless, some changes of the aluminium-gel structure were observed with a changing pH of the solution and with the [Alt]/[OHt] ratio at 25°C. resulting from the various proportions of the Al_{13} polycations in the gel (Axelos et al.,1985; Bottero et al., 1988).

This hypothesis agrees with the results of Sanjuan and Michard (1987), who observed a shift at the same pH on the solubility curve of the aluminium at equilibrium with well-crystallized aluminium hydroxyde. At low pH gibbsite precipitates, whereas at high pH bayerite or norstrandite precipitate.

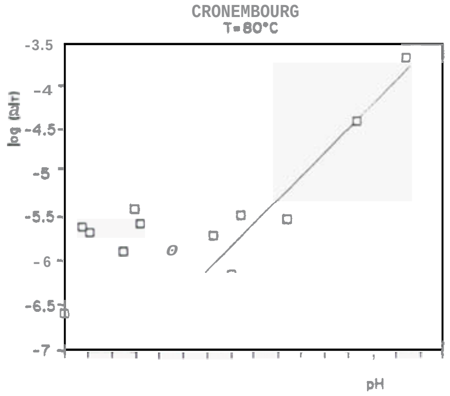

Figure 9: Total aluminium concentration versus pH at 80°C.

(3) Evidence for high recovery rates

The chemical composition of the fluids and the nature of the solid phase must both be factors favouring high Li recoveries.

- In this case of chemical composition, it may well be the low silica concentration in the solutions. These concentrations prevent the precipitation of an aluminous silicate phase. which would adsorb Li with more difficulty than amorphous aluminium hydroxyde. For Cesano, this concentration may result from precipitation of silica during the ascent of the fluid. For the Alsacian fluids, the low concentration can be explained by the particular geological context. In Alsace, it is known that high-salinity fluids of the Buntsandstein reservoir circulate very deep in the Rhine Graben, where they reach high temperatures and obtain high concentrations in lithium, sodium, potassium, silica, etc. During their ascent, they gradually cool and the silica concentration is first to achieve equilibrium (Kappelmeyer and Gerard, 1989). For this reason, the fluids contain a relatively high lithium concentration and a low silica concentration.

- In this study no crystallized aluminium phase has been detected, which may explain the difference with the results obtained by Yaganase et al, (1983), who observed the occurrence of a crystallized lithium aluminate. The non-settling gel prepared during our experiments must move to a crystallized phase as gibbsite or bayerite, which do not adsorb lithium. Nevertheless, it would seem that the transformation occurs when the chloride content has reached a low-enough level (Fripiat et Pennequin, 1965). Because the solutions of interest are very rich in Cl^- anions, the solid phase must be charged with them, thus favouring lithium extraction.

Adsorption on the aluminium phase

(1) Differences in Li recovery between the Cesano and Cronembourg fluids.

Several differences have just been described between both fluids, but the main one concerns the extraction rate at 20°C (figure 10). For experiments performed at the same pH, whatever the Al/Li ratio, the Li-extraction rate from the Cesano fluid is always lower than the one for the Cronembourg fluid. The occurrence of some species (Ca, SiO_2, Mg, Na) in fluids is known to affect the Li recovery and, in fact, the Cesano fluid contains more Na than the Cronembourg one. However, sodium seems to act more on the recovery kinetics than on the recovery rate, and the Cronembourg fluid is richer in Ca and Mg than the Cesano one. Because Li should be adsorbed on the aluminious phase, we will now examine the possible mechanisms of adsorption.

The surface of the aluminium phase is constituted by the amphoteric site $-Al-OH$ which can ionize as follows:

$$-Al-OH_2^+ \rightleftharpoons -Al-OH + H^+ \qquad pKa=6.37 \qquad (5)$$

$$-Al-OH \rightleftharpoons -Al-O^- + H^+ \qquad pKa=10.3 \qquad (6)$$

whose pKa at 25°C are given by Rakotonarivo et al., (1988).

The charged sites $-Al-OH_2^+$ and $-Al-O^-$ can react with an anion (A^-) or a cation (C^+):

$$-AlOH_2A \rightleftharpoons -Al-OH_2^+ + A' \qquad (7)$$

$$-Al-OC \rightleftharpoons -Al-O^- + C^+ \qquad (8)$$

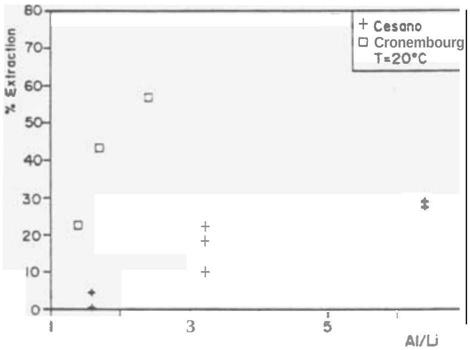

Figure 10: Li recovery percent at 20°C as a function of the Al/Li ratio.

However, the experiments were performed at a pH between the pKa of both reactions (5) and (6), and thus the amphoteric sites $-Al-OH$ can react with either a cation or an anion:

$$-Al-OHC^+ \rightleftharpoons -Al-OH + C^+ \qquad (9)$$

$$-Al-OHA^- \rightleftharpoons -Al-OH + A^- \qquad (10)$$

The occurrence of anions in the Cesano fluid may explain the difference of lithium behaviour: sulphates or fluorides, which occur at high concentrations when compared with the concentrations in the Cronembourg fluid, may be adsorbed on the surface of the aluminium phase.

At 80°C, lithium recovery is the same for both fluids (figure 11), suggesting a better adsorption of the considered anion at room temperature than at high temperatures. This difference may result from the thermodynamic constants of the reactions (6) or (10).

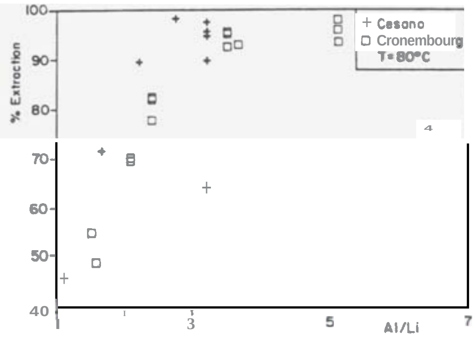

Figure 11: Li recovery percent at 80°C as a function of the Al/Li ratio.

(2) Adsorption of lithium at 80°C

During the experiments performed, different extraction rates were obtained. However, as conditions varied from one case to another, it appeared easier to calculate the Li-adsorbed quantities in order to compare the results in a meaningful way.

The adsorbed Li quantities Q_{ads}, expressed in mole per gramme (mol/g) of precipitated aluminium, are determined by the expression:

$$Q_{ads} = \underline{(Ci - Cs)} \qquad (11)$$

where m is the mass of precipitated aluminium, and Ci and Cs are the initial and steady-state Li concentrations.

The Q_{ads} for the 80°C experiments were calculated and are presented in figure 12 as a function of the initial Al/Li ratio. For low Al/Li the data are dispersed, but the adsorbed quantity seems to be stable. After this, the Q_{ad} decreases as the Al/li ratio increases. Because of the scattering of the data, it seems that the influence of pH is more important for the low Al/Li ratios.

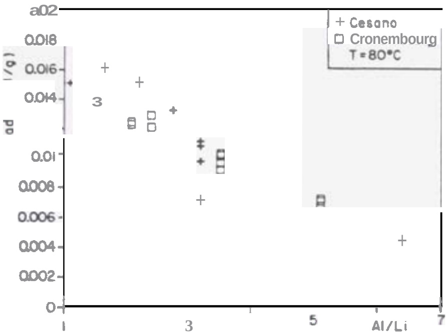

Figure 12: Adsorbed Li quantities on aluminium hvdroxide as a function of the Al/Li ratio.

At low Al/Li ratios, Qads is close to 0.0125 mol/g for the Cronembourg fluid and close to 0.015 mol/g for that of Cesano. These values certainly represent the saturation of the adsorption sites of the solid. This slight difference between both fluids can be assigned to the pH of the experiments. The experiments at low Al/Li ratio on the Cesano fluid were investigated at higher pH than those on the Cronembourg fluid, and thus the the formation of an $\equiv$Al-O$^-$ site that adsorbs lithium is favoured.

A change in the structure of the aluminium hydroxyde around pH-7 appeared, but it cannot explain the observed difference since Rakotonarivo et al. (1985) show that, at 25°C, the change resulting from an increase of the base content, induces a decrease of the specific surface area and of the Q_{ads} value.

CONCLUSIONS

Li extraction from geothermal fluids of Cesano and of the Alsatian Trias was investigated during the precipitation of an aluminium phsse.

Regardless of the temperature of the fluid (20°C-80°C), an amorphous aluminium hydroxyde precipitates and lithium is adsorbed on it. The results are very encouraging for Li recovery from these fluids without any prior treatment. Very high Li recovery rates are obtained in few minutes at a pH equivalent to the initial pH of the solution, using only small quantities of precipitating agents and at elevated temperatures. These conditions are relevant to a secondary economic use of such fluids.

The positive results are obtained because of the composition of the fluids: the silica concentration is low enough to prevent precipitation of an aluminous silicate phase, and the chloride concentration is high enough to delay crystallization of the aluminium hydroxyde.

It appears that the recovery rate can be disturbed not only by the occurrence in solution of cations (Ca^{2+}, Mg^{2+} etc), but also by that of anions, which can be adsorbed on the surface of the aluminium hydroxyde.

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