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Recovery of Lithium Compounds from Natural Salt Brines

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ABSTRACT

Subterranean waters can be regarded as a potential source for the recovery of different elements. A new process was developed to use not only the Li content of the subterranean waters in the Altmark but also the contents of bromine and strontium. The essential processing steps are preliminary purification, evaporation, hot debromination, LiCl extraction, $SrCl_2$ crystallization.

INTRODUCTION

In many cases, subterranean waters from the recovery of natural gas and oil contain components which are a potential source for the production of several salts. In the natural gas field of the Altmark in Germany, such waters can be regarded as relatively concentrated NaCl-$CaCl_2$ solutions with a high content of LiCl and $SrCl_2$ (Table 1). In addition, suspended solids and dissolved heavy metal salts are present.

TABLE 1

Typical analyses of the mineralized subterranean waters of the Altmark

Li^+	0.315 g/l
Na^+	49.9 g/l
K^+	4.43 g/l
Mg^{2+}	0.682 g/l
Ca^{2+}	38.8 g/l
Sr^{2+}	1.53 g/l
Cl^-	152.5 g/l
SO_4^{2-}	0.12 g/l
Boron	110 mg/l
Iodine	12 mg/l

Our institute has investigated the possibility of a complex use of these solutions with the main aim being the recovery of LiCl and $SrCl_2$.

A comparison of the composition of the subterranean waters from the Altmark with other Li-containing mineralized waters is shown in Table 2. The following conclusions can be derived:

– The mineralized waters of the Altmark contain a Li concentration which is equal to or higher than that of other solutions,

– The Mg concentrations are very low but the Ca content is extremely high,

– The total salinity is equal to that of other solutions.

It must be stated, however, that all other solutions are surface waters. The main difference between depth and surface waters is the high content of suspended solids and the reducing environment of these solutions. This reducing environment is the cause of the high content of dissolved heavy metal salts.

An overview of methods of producing Li compounds from natural salt brines shows that in all cases the first processing step is an enriching process, usually by solar evaporation. There are two methods to recover a lithium compound from such solutions:

– Precipitation of the lithium content by addition of an $AlCl_3$ solution. The resulting lithium–aluminium hydroxide is dissolved in HCl and the Li content can be won by an extraction process.

– Separation of the lithium content from the enriched solutions by a direct liquid–liquid extraction.

The high content of $CaCl_2$ in the subterranean waters of the Altmark does not allow the use of such a process without some changes or new developments.

TABLE 2

Typical analyses of different natural brines (wt.%) (according to Bauer, 1980)

Brine	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	SO_4^{2-}	Cl^-
Clayton Valley (Nevada)	0.03	7.5	1.0	0.06	0.05	0.75	11.7
Salar de Atacama (Chile)	0.15	7.65	1.93	0.86	0.02	1.48	16.3
Salar de Uyuni (Bolivia)	0.024	9.42	0.51	0.44	0.05	0.72	15.91
Dead Sea (Israel/Jordan)	0.002	3.0	0.6	4.0	0.3	0.05	16.0
Great Salt Lake (USA)	0.006	7.0	0.4	0.8	0.03	1.5	14.0
Bonneville (USA)	0.007	9.4	0.6	0.4	0.12	0.5	16.0
Searles lake (USA)	0.005	11.1	2.49	?	?	4.71	9.92
Subterranean waters in Germany	0.029	4.5	0.4	0.09	3.6	0.011	14.2
Sea water	0.000017	1.8	0.038	0.13	0.04	0.027	1.94

RESULTS

To use not only the Li content of the subterranean waters in the Altmark but also the contents of bromine and strontium, the following process was developed in cooperation between our institute and the Erdgas Salzwedel GmbH (Holldorf et al., 1988). The main processing steps are (Fig. 1):

– preliminary purification of the mineralized subterranean waters,

– evaporation of the mineralized subterranean waters accompanied by the crystallization of NaCl,

– hot debromination of the residual solution of NaCl crystallization,

– LiCl extraction from the final solution after the hot debromination,

– further evaporation of the residual solution of LiCl extraction,

– $SrCl_2 \cdot 2H_2O$ cooling crystallization from the solution of the last evaporation step.

Figure 2 shows the precipitation process of the heavy metal salts. The addition of $Ca(OH)_2$ leads to a pH value between 8 and 8.5 and, in connection with an addition of air to the solution, gives the possibility of a quantitative precipitation of the heavy metal salts. After neutralization of the suspension a separation process of the suspended solids by filtration and sedimentation is carried out. The solids, mainly $Fe(OH)_3$ and $Mn(OH)_2$, go to a waste storage and the clear solution is used for the recovery of bromine. This process is a conventional oxidation process with chlorine.

For the recovery of lithium by liquid–liquid extraction the process of the evaporation of the subterranean waters is very important, because only highly concentrated $CaCl_2$ solutions yield good distribution equilibria. The crystallization path of the subterranean waters in the process of vacuum crystallization can be

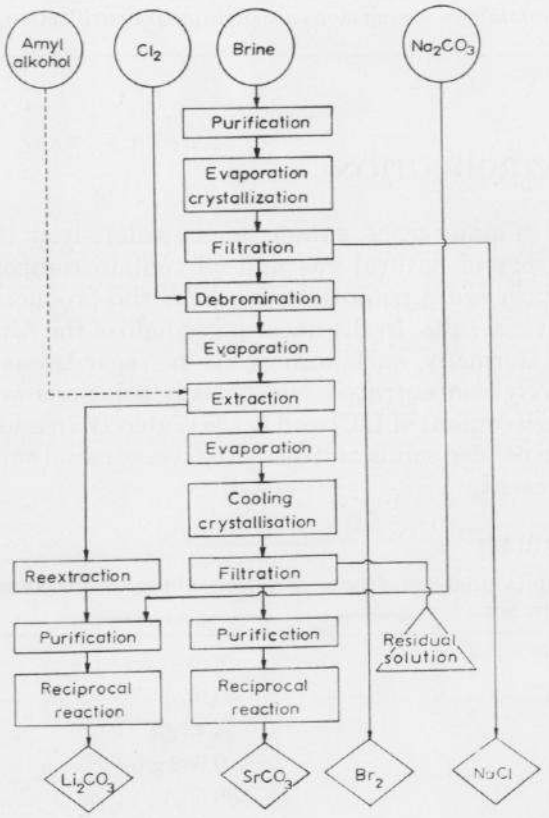

Fig. 1. Scheme of the complex utilization of the subterranean waters.

shown on the basis of the solid–liquid phase equilibria of the system NaCl–KCl–$CaCl_2$–H_2O (Fig. 3). The marked crystallization path of the vacuum evaporation at 100°C shows that the crystallization field of the double salt $KCl \cdot CaCl_2$ at a final concentration of 1200 g/l will not be reached and therefore only the crystallization of NaCl takes place. A balance of the evaporation process shows that the NaCl output lies over 95%. The initial solution for the liquid–liquid

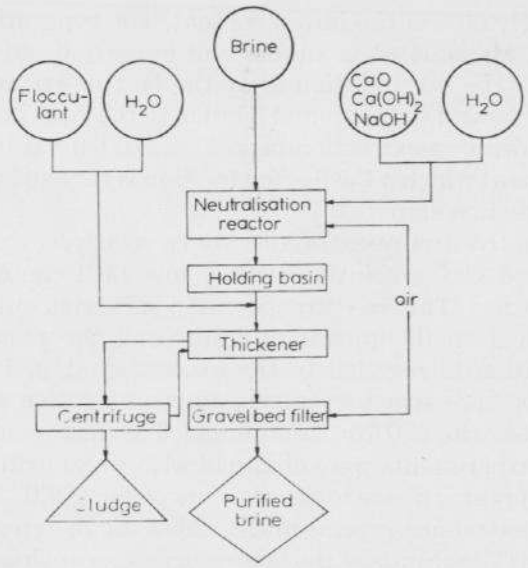

Fig. 2. The process of purification of the subterranean waters.

extraction has the composition shown in Table 3. The extraction of LiCl from concentrated $CaCl_2$ solutions can be carried out with lower alcohols, alkyl phosphate and phosphonates as well as crown ethers. Our investigations showed that fermentation amyl alcohol, a mixture of 52.1% 2-methylbutanol-1 and 47.9% 3-methylbutanol-1, is especially suitable for the extraction of LiCl. Figure 4 shows the distribution equilibria in the system LiCl-$CaCl_2$-H_2O-fermentation alcohol at 50°C and different $CaCl_2$ concentrations in the aqueous solution (Schmidt et al., 1988). The densities of the solutions are equivalent to the $CaCl_2$ concentrations. It can be seen that favourable distribution equilibria can be obtained only at high $CaCl_2$ concentrations.

TABLE 3

Typical analyses of the initial solutions for LiCl-extraction

0.98 g Li^+ / 1000 g solution
3.70 g Na^+ / 1000 g solution
1.50 g K^+ / 1000 g solution
2.95 g Mg^{2+} / 1000 g solution
4.95 g Sr^{2+} / 1000 g solution
121.15 g Ca^{2+} / 1000 g solution

Because of the high $CaCl_2$ content the miscibility of the phases can be neglected. By the use of a chromatographic method it was found that the solubility of the alcohol in the aqueous phase is less than 0.1%. $CaCl_2$ but also $MgCl_2$ act as a salting-out agent in the extraction system. At constant $CaCl_2$/LiCl concentrations the LiCl content in the organic phase decreases in the course of an increase of the temperature. On the other hand, at temperatures below 30°C the separation of organic and aqueous phases becomes more difficult and very long time periods are necessary. The temperature for LiCl extraction with fermentation amyl alcohol should lie between 35 and 50°C. Because in all cases a part of the $CaCl_2$ of the aqueous solution is also extracted a process consisting of two extraction and re-extractions was developed (Fig. 5). The process contains an additional evaporation step which is necessary to obtain optimum $CaCl_2$/LiCl concentration ratios for the second extraction. After the first extraction the organic phase is re-extracted with water, the solvent is recycled and the aqueous phase is evaporated. The initial solution of the first extraction step contains a Ca:Li ratio of 125:1. In the result of the extraction, a Ca:Li ratio of 25:1 is obtained.

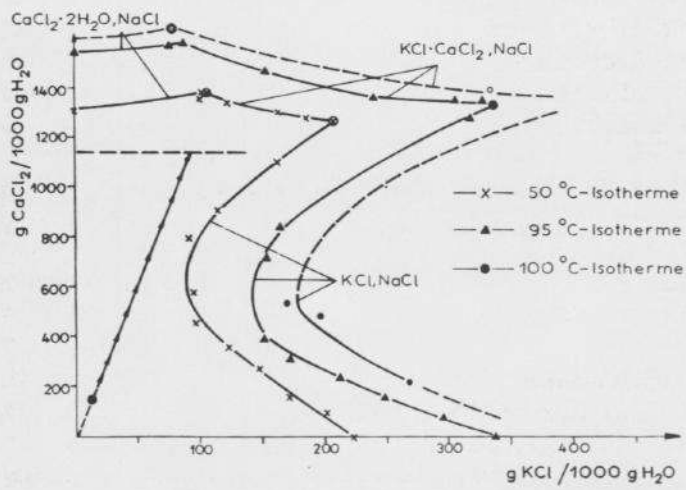

Fig. 3. The system NaCl–KCl–$CaCl_2$–H_2O. →→, crystallization path in the course of evaporation.

Apart from LiCl and $CaCl_2$, NaCl, KCl, $MgCl_2$ and $SrCl_2$ are dissolved in the initial solution. Of these compounds only $MgCl_2$ is extracted at a ratio of nearly 60% of the initial content. The separation of this Mg content is simple and is carried out as a $Mg(OH)_2$ precipitation after the last re-extraction. The second extraction is similar to the first but the following re-extraction process is carried out in two steps at which a $CaCl_2$-rich fraction is recycled to the extraction step.

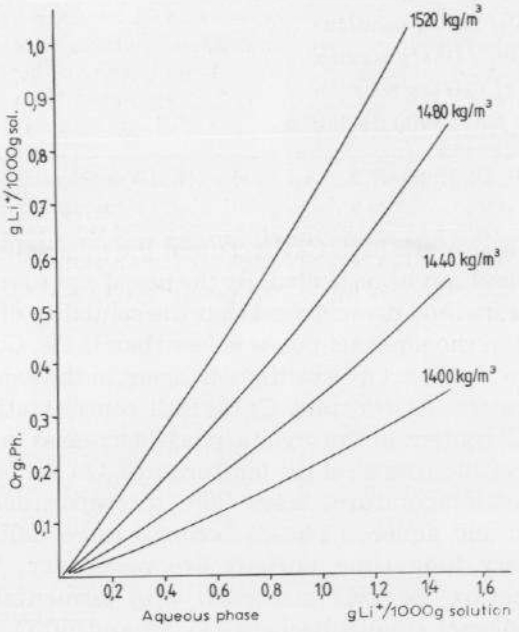

Fig. 4. Distribution equilibria in the system LiCl–$CaCl_2$–H_2O–fermentation amyl alcohol at 50°C and different contents of $CaCl_2$.

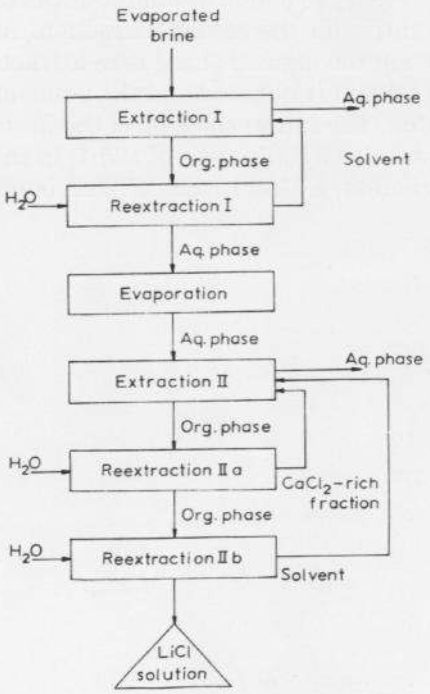

Fig. 5. Scheme of the extraction process.

In the first re-extraction step a relatively concentrated $CaCl_2$ solution with a low LiCl content is obtained. This re-extraction step is carried out only with a small amount of water and the resulting solution is recycled to the extraction step. In the second re-extraction step an aqueous solution with a Ca:Li ratio of 0.75:1 is obtained. The best results in all experiments were obtained with weight ratios of the organic phase to the aqueous phase of 2.0...2.5 in the extraction process and 8...20 in the re-extraction step. The results of the laboratory experiments were confirmed by technical tests in a mixer-settler apparatus with 6 stages. After 20 passages, in the stationary state, there is a Li yield of 95%. Combined with the Li extraction is a transition of about 52% of the primary Mg content. Equal results were obtained by investigations in a rotary disk evaporator. The resulting rich Li solution is easily processed into pure Li_2CO_3 by a reciprocal reaction.

The process of $SrCl_2$ recovery from the residual solution of the Li extraction is based on the fact that the solubility of $SrCl_2$ in highly concentrated $CaCl_2$ solutions strongly depends on temperature. Therefore a cooling crystallization of the solution of the last evaporation step creates the possibility to crystallize $SrCl_2 \cdot 2H_2O$ (Fig. 6). Nearly 60% of the $SrCl_2$ content of the subterranean waters can be obtained in this a way.

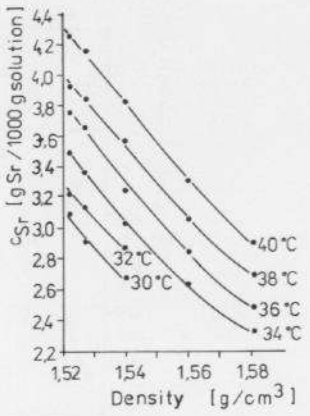

Fig. 6. The system $CaCl_2$–$SrCl_2$–H_2O between 30 and 40°C.

CONCLUSIONS

All investigations showed that a complex use of subterranean waters of complex composition is possible. The newly developed process allows the production of LiCl, Br_2, $SrCl_2$ and NaCl. Essential processing steps are preliminary purification, evaporation hot debromination, LiCl extraction, $SrCl_2$ crystallization.

The application of the process to recover LiCl depends mainly on the costs of energy and the possibility of utilizing the by-products.

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