

## Recovery of $\text{Na}_2\text{SO}_4$ , $\text{K}_2\text{SO}_4$ , Boric Acid and Lithium Salt from Da Chaidan Salt Lake Brine

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### ABSTRACT

A solar evaporation process has been designed for extracting sodium sulfate, potassium sulfate, boric acid and lithium salt from the brine of Da Chaidan Salt Lake, located in the north of the Chaidamu Basin, Qinghai Province, China. The brine is concentrated in a series of solar ponds. A sequence of three stages was defined for the crystallization of NaCl, hydrated magnesium sulfate and carnallite mixed salts. Mirabilite can be crystallized out from the surface brine of the lake by natural cooling in winter. Potassium sulfate is produced by decomposition and transformation of the harvested carnallite mixed salts with water. Boric acid is recovered by acidification from the  $\text{MgCl}_2$ -eutectic concentrated brine. Lithium salt can be extracted by TBP- $\text{FeCl}_3$ -kerosene extractant from the  $\text{MgCl}_2$ -concentrated brine after the boric acid is separated.

### INTRODUCTION

Da Chaidan Salt Lake in the north of Chaidamu Basin (Fig. 1), in the western part of Qinghai Province, China, has been the subject of geological, mineralogical, chemical and industrial chemical interest since its discovery in 1957 by the Scientific Investigation Group of Salt Lake, Academia Sinica (Liu, 1959). The area of salt deposit in the lake is more than  $130 \text{ km}^2$ , and its greatest depth is more than 20 m. The average efficient porosity of the deposit is about 15%. There is perennial surface brine in the lake; its area is more than  $30 \text{ km}^2$  and its annual average depth is less than 1 m. The altitude of the brine surface is 3140 m above sea level (Zhang, 1987). The brine contains lithium, sodium, potassium and magnesium as salts of chlorides, sulfates and borates. There are 22 types of minerals in the lake which contain 9 types of borate minerals, 10 types of sulfates and 3 types of chlorides (Gao and Li, 1982a).

In the region of the lake, the amount of evaporation is about fifty times more than the rainfall which is less than 80 mm per year. This high evaporation and low rainfall make it possible to use solar ponds to evaporate and concentrate the brine. The phase chemistry of the brine demonstrated that it is possible to crystallize mirabilite by natural cooling

in winter and to recover potassium sulfate from carnallite mixed salts which is crystallized out from the brine during solar evaporation in summer.

Early in 1963, it was suggested that boric acid could be recovered from the brine of the carnallite pond by acidification, and lithium salt might then be extracted from the mother liquor of boric acid.

### CHEMICAL CHANGE PATTERN OF THE SURFACE BRINE (Gao and Li, 1982b)

Because of the supplied water and the climatic conditions in the region of Da Chaidan Salt Lake, the composition of surface brine changes in accordance with the seasons (Fig. 2). The chemical change throughout the year can be divided into three periods. The first period is from April to October, during which time the amount of evaporation is much greater than that of rainfall and supplied water. The surface brine is evaporated and concentrated to crystallize NaCl. This is called the summer evaporation and crystallization process, shown by the solid line AB on Fig. 2.

The second is from October to January of the following year. Because the temperature in winter drops to below  $0^\circ\text{C}$ , it is, therefore, to be expected that the brine would separate the hydrated magnesium sulfate according to the phase diagram in Fig.

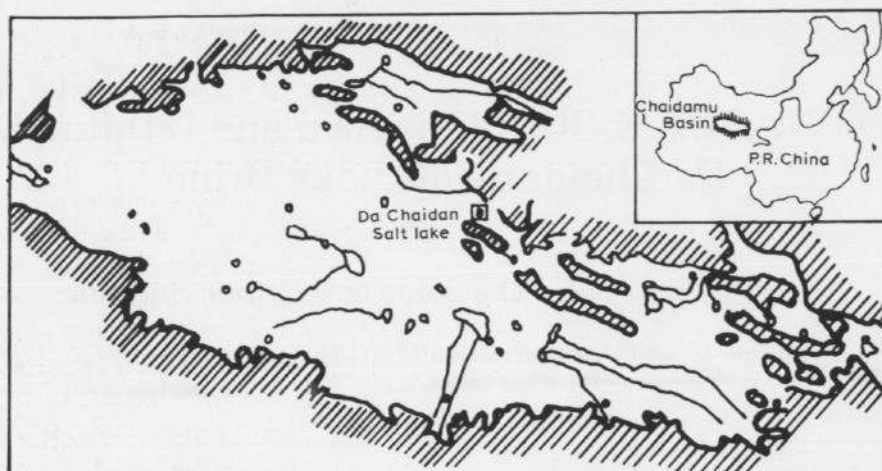


Fig. 1. Location of Da Chaidan Salt Lake in Chaidamu Basin.

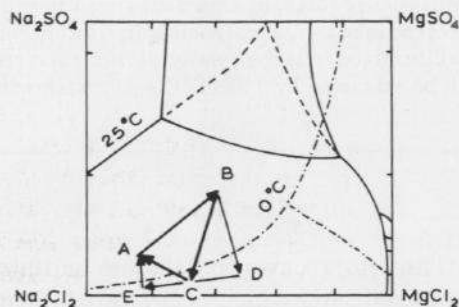


Fig. 2. Chemical change pattern of the surface brine.

2, but in practice, the salt separated from the surface brine in winter is mirabilite. This is consistent with results which show that the amount of magnesium sulfate in brine decreases and, at the same time, the amount of magnesium chloride increases. We may therefore divide the vector BC into two sub-vectors. One is BD expressing that the mirabilite is crystallized by cooling, and the other is DC denoting the process in which NaCl is dissolved by dilution.

The last period, represented by CA, is from January to April. It can clearly be seen that NaCl is continuously dissolved (represented by the sub-vector CE), and mirabilite has been crystallized just before occurrence of dissolution (represented by EA). This is because the temperature begins to rise, the frozen land starts to thaw and evaporation remains low during this period. The amount of supplied water increases so rapidly that large amounts of NaCl and mirabilite are again dissolved. Therefore, the vector CA can be divided into two sub-vectors CE and EA according to the vector rule of the phase diagram.

It can be seen from the above that the surface brine of Da Chaidan Salt Lake apparently displays

the alternate and periodic changes regarding crystallization and redissolution of sodium chloride as well as mirabilite.

#### PHASE CHEMISTRY OF THE BRINE (Gao and Li, 1982b)

The chemical composition of the surface brine can be altered by the weather conditions. It is found that the composition of the brine in winter differs greatly from that in summer, as do the crystallization paths of the brines during solar evaporation. The salt crystallization sequence of the summer brine is NaCl, hydrated magnesium sulfate and carnallite mixed salt, and that of the winter brine is NaCl, KCl, carnallite and bischofite (Fig. 3).

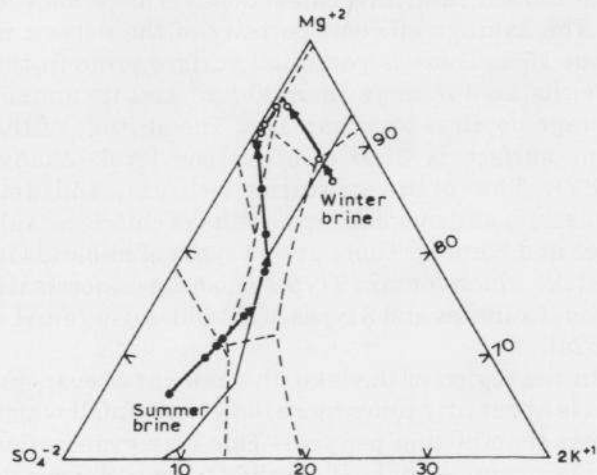


Fig. 3. Crystallization paths of surface brine (Gao and Li, 1982b). Solid line, unstable phase diagram; broken line, stable phase diagram.

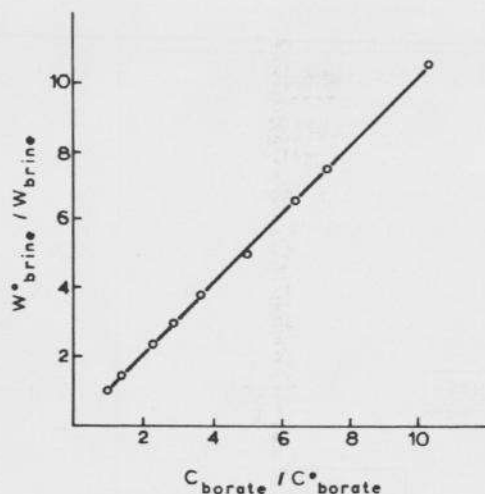


Fig. 4. Relation between  $W^{\circ}_{\text{brine}}/W_{\text{brine}}$  and  $C_{\text{borate}}/C^{\circ}_{\text{borate}}$ . (Gao and Li, 1982b).

The concentrated degree of brine ( $W^{\circ}_{\text{brine}}/W_{\text{brine}}$ ) is equal to that of the enrichment of borate ( $C_{\text{borate}}/C^{\circ}_{\text{borate}}$ ) in concentrated brine during solar evaporation (Fig. 4). It may be considered that borate does not generally crystallize until the bischofite stage and accumulates fully in the concentrated brine.

#### SEPARATION AND EXTRACTION OF SALTS FROM BRINE

The quantity and composition of the carnallite mixed salt crystallized out in the solar pond depends mainly on the chemical composition of the original brine. Therefore, the evaporation process must take two different operational arrangements into account. Two types of final concentrated brine should be obtained after solar evaporation: one from the summer brine and the other from the winter brine. It is emphasized that the final  $\text{MgCl}_2$ -eutectic concentrated brines containing boron and lithium are very similar.

Experimental research on producing  $\text{K}_2\text{SO}_4$  from the carnallite mixed salt with epsomite,  $\text{H}_3\text{BO}_3$  from the  $\text{MgCl}_2$ -eutectic concentrated brine, and lithium salt from the mother liquor of boric acid have been carried out. The results show that the comprehensive utilization of brine in the solar pond is both economically viable in terms of energy. The flow sheet for comprehensive utilization of Da Chaidan Salt Lake brine is shown in Fig. 5.

#### Separation of mirabilite by natural freezing

The best method for separating mirabilite from the surface brine of Da Chaidan Salt Lake was sug-

gested 25 years ago. The method is based on the fact that the surface brine is concentrated by natural solar evaporation near to saturation with sulfate before winter arrives. A large quantity of mirabilite can be crystallized out every year from the surface concentrated brine by natural freezing during winter. This new deposit of mirabilite can be harvested if there is a economic method to harvest it. It is well known that mirabilite can easily produce anhydrous sodium sulfate.

#### Separation of carnallite by solar evaporation

The potassium content in the starting brine is about 1% KCl. The enormous amount of water which must be evaporated would make the process uneconomic were it not for the possibility of using solar evaporation. However, the existence of good quality clay in the north part of the surface brine area enables the construction of large and inexpensive solar ponds.

Experimental study carried out in the field of the summer brine taken from the surface brine area has provided basic information on evaporation rates and the phase chemistry of Da Chaidan Salt Lake brine. This information was useful when defining the number of ponds and division sections needed in the design of the solar evaporation process. The arrangement of pilot plant solar ponds is shown in Fig. 6.

The summer brine pumped from the surface brine area is evaporated by solar energy and concentrated successively in three groups of solar ponds in order to separate NaCl, epsomite and carnallite and produce  $\text{MgCl}_2$ -eutectic concentrated brine containing high boron and lithium. In the first group of ponds, NaCl is crystallized during solar evaporation and some of the NaCl will be harvested if it is saleable. When the brine is concentrated to saturation with magnesium sulfate, it is transferred to the second group of ponds where the hydrated magnesium sulfate with halite will be continuously crystallized out by solar evaporation. In the third group of ponds, potassium in the form of carnallite with halite and epsomite will be separated during continuous evaporation. The carnallite mixed salts harvested from the carnallite ponds are transported to a chemical workshop and used as crude for refining potassium sulfate.

#### Production of boric acid

Boric acid is separated by acidifying the  $\text{MgCl}_2$ -eutectic concentrated brine containing high boron with hydrochloric acid. The amount of boric acid recovered by acidification is primarily dependent upon the initial concentration of borate in the concentrated brine. Laboratory studies have demon-

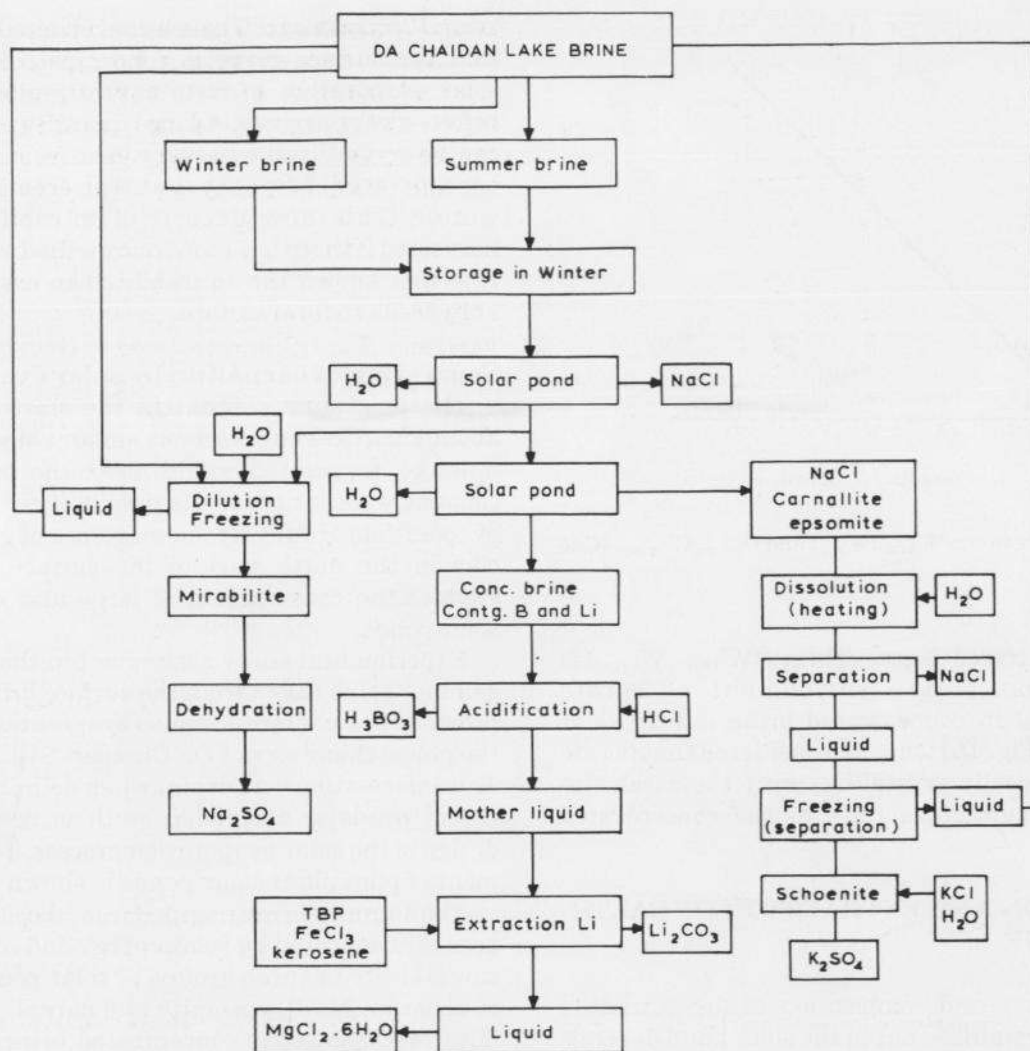
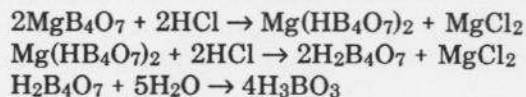


Fig. 5. Flow sheet of recovery of Na salts,  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{H}_3\text{BO}_3$  and Li salt from Da Chaidan Salt Lake brine.

stated that the boron existing in the concentrated brine can be expressed as tetraborate and the hydrochloric acid-pH titration curve during acidification of the concentrated brine containing boron is shown in Fig. 7 (Gao et al., 1989). The chemical reaction mechanism can be expressed as follows:



It is shown that one mole of hydrochloric acid should be consumed for production of two mole boric acid, and the consumption of hydrochloric acid will be increased for producing boric acid when the concentration of borate in the concentrated brine is low.

The production of boric acid in this design process is achieved by taking the end liquor from the last

pond of carnallite as raw material which contains an average concentration of more than 35 g  $\text{MgB}_4\text{O}_7$  per liter, so that an increase of the  $\text{MgB}_4\text{O}_7$  content in the concentrated brine increases the yield of boric acid. A flow sheet of the boric acid process is indicated in Fig. 8. Only a crystallizer and some other simple equipment are required. Care must be taken to disperse the hydrochloric acid gently and thoroughly into a large volume of recirculating slurry and maintain the required pH accurately. An excellent product should result directly without recrystallization.

#### EXTRACTION OF LITHIUM SALT (Tong et al., 1987)

Fifteen years ago Shanghai Institute of Organic Chemistry, Academia Sinica, studied the extraction

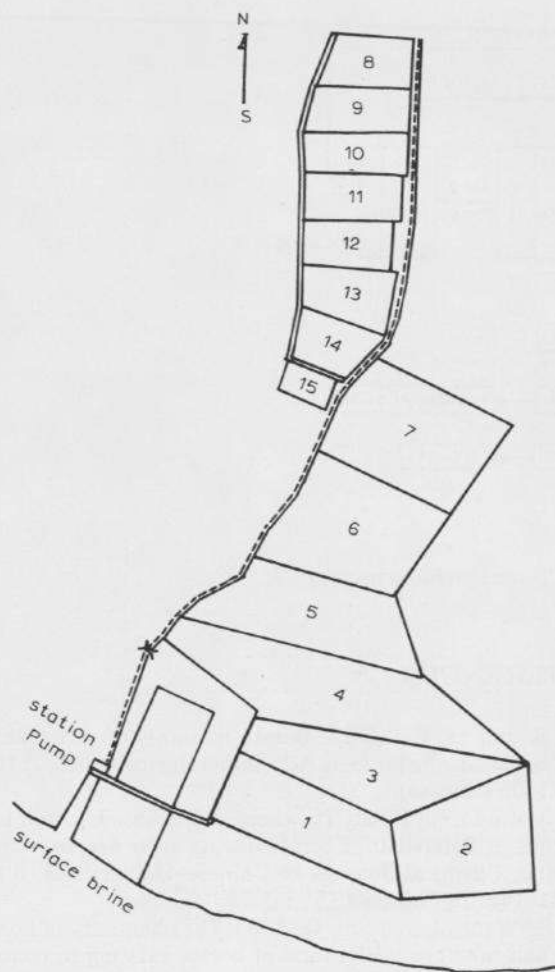


Fig. 6. Sketch of the solar ponds.

of alkali metal salt from brine by the TBP-N5O3-kerosene system. Subsequently, researchers at Qinghai Institute of Salt Lake, Academia Sinica, have studied the extraction of lithium from the  $\text{MgCl}_2$ -eutectic concentrated brine containing lithium by the TBP- $\text{FeCl}_3$ -kerosene system. This process is shown in Fig. 9.

The mother liquor of boric acid production is pumped using the extraction equipment and the lithium chloride is extracted by TBP- $\text{FeCl}_3$ -kerosene. The lithium chloride in the organic phase

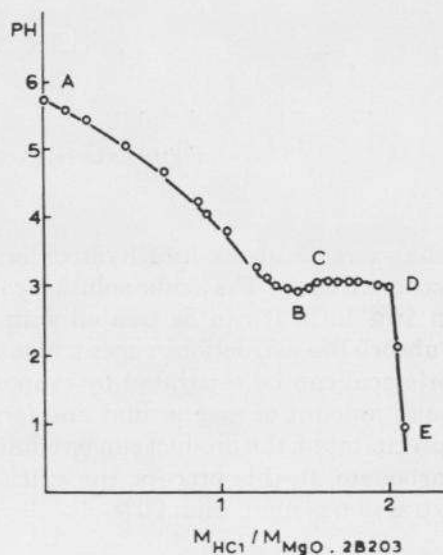


Fig. 7. Hydrochloric acid-pH titration curve.

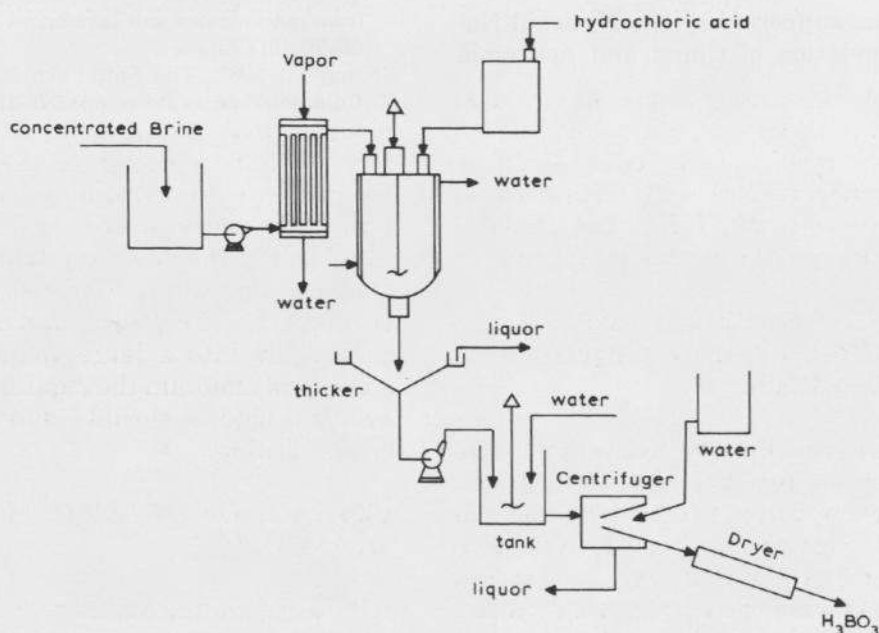


Fig. 8. Flow sheet of boric acid pilot plant.

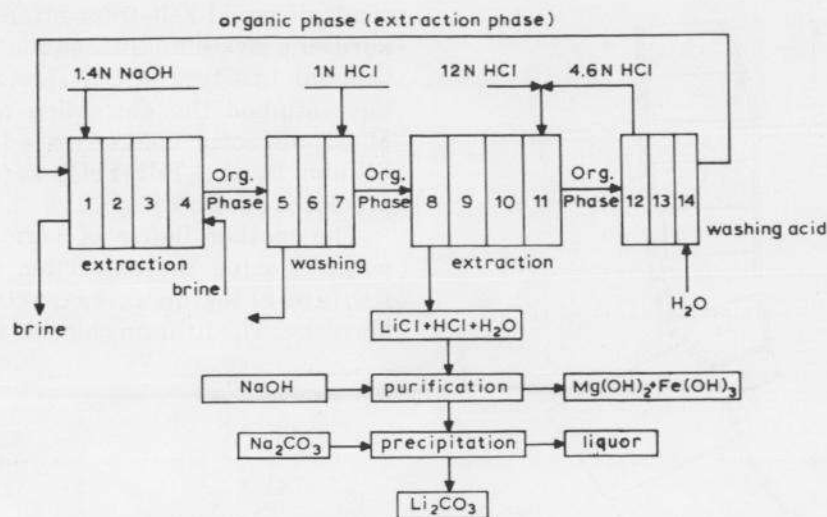


Fig. 9. Extraction of lithium from  $MgCl_2$ -concentrated brine.

can then be extracted back into hydrochloric acid with 6 M concentration. The acidic solution contains more than 10% LiCl. It can be treated with active carbon to absorb the extraction reagent. Most of the hydrochloric acid can be separated by evaporation. After a small amount of magnesium and ferric ion has been precipitated, the product can be obtained as lithium carbonate. In this process, the efficiency of lithium extraction is more than 90%.

#### ACKNOWLEDGMENT

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