

# STUDY ON THE PRODUCTION TECHNOLOGY OF SULPHATE-POTASSIUM MAGNESIUM FROM JINAIER SALT LAKE BRINE IN QINGHAI

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**Abstract:** Based on the phase diagram of  $\text{Na}^+, \text{K}^+, \text{Mg}^{2+} // \text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$  system at 25°C and 50°C, a technology was developed to produce sulphate-potassium magnesium from Jinaier salt lake brine in Qinghai. At the first-stage transformation, the recover rate of potassium was up to 77.17%. The optimal conditions were: the operational temperature was 50°C, the mixing time was 120 min. and the stirred speed was 600 rpm.. The purpose of the second-stage transformation was to eliminate chloride in the product, in which the solid phase of the first-stage transformation was used. The temperature used in experiment for the second-stage transformation was at 25°C, the mixing time was 60 min. and the stirred speed was 600 rpm.. Under these conditions the recover rate of potassium was more than 60.36% and the removal rate of chloride was 67.42%. The experimental results offered a sound foundation for a technology in producing sulphate-potassium magnesium product with higher potassium and lower chloride from Jinaier salt lake brine in Qinghai.

**Keywords:** sulphate-potassium magnesium fertilizer; phase diagram; Jinaier salt lake

## 1 Introduction

Sulphate-potassium magnesium is known as a good natural mineral fertilizer, especially for crops. It is a substitute for potassium sulfate and can provide full nutrients and necessary natural green fertilizers of potassium, magnesium and sulfur for the growth crops. Magnesium is the core component of chlorophyll, which determines the photosynthesis. Hence, it can promote photosynthesis process greatly, which plays a key role on the growth of crops. In short, magnesium plays a crucial role on crops growth. Besides, Magnesium can facilitate crops to greatly absorb phosphorus and help crops to form enzyme for their growth and to generate vitamins, carbohydrates, protein, fat etc., Magnesium can prevent defoliation and fruits abscission at the maturation period as well. Sulphate-potassium magnesium is suitable for all crops especially for vegetables, fruits, tobacco, tea and flowers. It can provide long-term and stable nutrients for the growth of crops and increase crop quality and enhance the ability of drought resistance, insect resistance, drug resistance and cold resistance of crops. As a result, the increased production of crops is very obvious.

Generally, potassium sulfate is produced by dechlorination of potassium chloride. In the long-term run fertilizing potassium sulfate will affect the pH of soil and make the soil acidification. On the contrary, sulphate-potassium magnesium fertilizer is a natural mineral and will not change the pH of soil, even if it is fertilized for a long time. It can combine utilization and nourishment of

land. In addition, compared with the traditional nutriment utilization rate of 40% to 50%, the nutriment utilization rate of sulphate-potassium magnesium is higher than 95%.

The basic theory used in this work is the phase diagram. The compositions of mixed potassium salts obtained by evaporating the brine of Jinaier salt lake were analyzed. The first-stage transformation experiments were arranged and carried out based on the analysis at the phase diagram of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ // $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  -  $\text{H}_2\text{O}$  at  $50^\circ\text{C}$  and on the optimum seeking method. The second-stage transformation experiments were arranged and carried out using the solid obtained from the first-stage transformation experiments based on the theory of the quintuple phase diagram of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ // $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  -  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$ . The results of the second-stage transformation experiments showed that the recover rate of potassium from sulphate-potassium magnesium was 60.36% and the removal rate of chloride was up to 67.42% at the conditions that the mixing time was 60min, the stirred speed was 600 rpm and the temperature was at  $25^\circ\text{C}$ .

## 1 Experiment

### 1.1 Materials

The analytical pure chemicals of potassium chloride, sodium chloride, magnesium sulfate heptahydrate and magnesium chloride hexahydrate were used in the experiments.

The chemicals were supplied by Tianjin Wendaxigui chemical Co.Ltd. China. All chemicals were without further purification before use.

## 1.2 Experimental Equipments

Experimental equipments were listed as follows: constant temperature heating magnetic stirrer(DF-101S), motor stirrer(JJ-1), constant temperature water bath(HK-2A), vacuum pump(SHB-III) and crucible etc.

## 1.3 Analytical Method

$K^+$ : Sodium Tetraphenylborate-Quaternary ammonium salt volumetry (GB/T7118-5.4);

$Mg^{2+}$ : EDTA compleximetry (GB/T13025.6);  $Cl^-$ : argentimetry (GB/T13025.5);  $SO_4^{2-}$ : Barium sulfate gravimetry (GB/T13025.8).

## 2 Results and Discussion

### 2.1 The First-Stage Transformation Experiment

#### 2.1.1 Theory of Phase Diagram

The components of mixed potassium salts obtained by evaporating the brine of Jinaier salt lake were shown in Table 1. The system point "M" in the phase diagram is located at the region of schoenite in the quintuple phase diagram of  $Na^+, K^+, Mg^{2+} // Cl^-, SO_4^{2-} - H_2O$ . The Janecke index J of the system point is  $K_2^{2+} = 13.97$ ,  $Mg^{2+} = 54.98$  and  $SO_4^{2-} = 31.24$ .

Table 1 Components of mixed potassium salts

Ions	$K^+$	$Mg^{2+}$	$Na^+$	$Cl^-$	$SO_4^{2-}$	$H_2O$
Weight percentage (wt%)	6.15	7.60	6.50	25.15	17.00	37.82

The salt forming laws were shown in Table 2 when evaporating the system point M based on the quintuple phase diagram of  $Na^+, K^+, Mg^{2+} // Cl^-, SO_4^{2-} - H_2O$  at  $50^\circ C$ . The

process of producing sulphate-potassium magnesium fertilizer from mixed potassium salts is the inverse process of evaporation, i.e. adding water process.



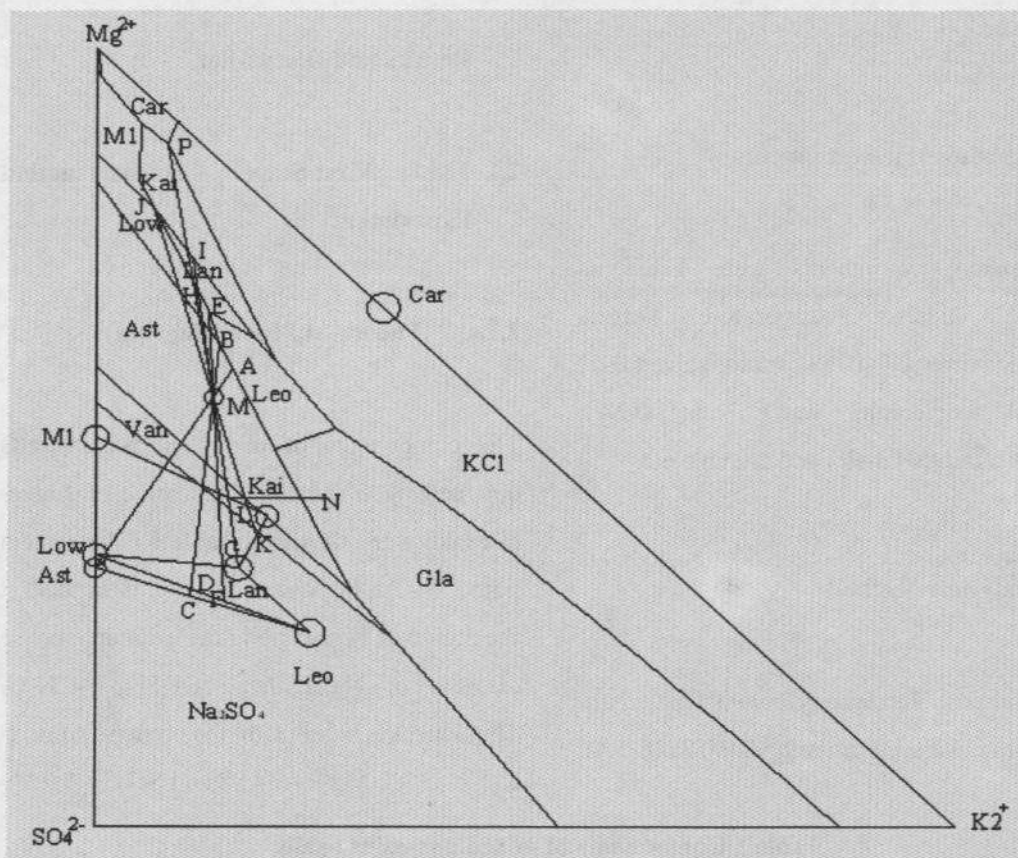


Fig.1  $\text{Na}^+, \text{K}^+, \text{Mg}^{2+} // \text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$  phase diagram at  $50^\circ\text{C}$

**Table 2** salt forming laws when evaporating the system point M in  $\text{Na}^+, \text{K}^+, \text{Mg}^{2+} // \text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$  phase diagram at  $50^\circ\text{C}$

Stage	1	2	3	4	5	6	7
Process	Evaporation of unsaturated solution	Crystallization of $\text{Na}_2\text{Cl}_2$	synchronous crystallization of Ast and $\text{Na}_2\text{Cl}_2$	Incomplete dissolution of Ast, synchronous crystallization of Leo, $\text{Na}_2\text{Cl}_2$	Complete dissolution of Ast, synchronous crystallization of Leo, Low, $\text{Na}_2\text{Cl}_2$	Incomplete dissolution of Low, synchronous crystallization of Leo, $\text{Na}_2\text{Cl}_2$	Dissolution of Leo, Low, complete dissolution of Leo, synchronous crystallization of Lan, $\text{Na}_2\text{Cl}_2$
Solution Track	M						
Liquid phase Track	M	M	M	$A \rightarrow B$	B	$B \rightarrow E$	E
Solid phase Track	-	-	Ast	$\text{Ast} \rightarrow \text{C}$	$\text{C} \rightarrow \text{D}$	$\text{D} \rightarrow \text{F}$	$\text{F} \rightarrow \text{G}$
Stage	8	9	10	11	12	13	
Process	Complete dissolution of Low, synchronous crystallization of Lan, $\text{Na}_2\text{Cl}_2$	synchronous crystallization of Lan, $\text{Na}_2\text{Cl}_2$	Incomplete dissolution of Lan, synchronous crystallization of Kai, $\text{Na}_2\text{Cl}_2$	Complete dissolution of Lan, synchronous crystallization of $\text{M}_1$ , Kai, $\text{Na}_2\text{Cl}_2$	synchronous crystallization of $\text{M}_1$ , Kai, $\text{Na}_2\text{Cl}_2$	Incomplete dissolution of Kai, synchronous crystallization of Car, $\text{M}_1$ , $\text{Na}_2\text{Cl}_2$	
Solution Track	M						
Liquid phase Track	$E \rightarrow \text{H}$	$\text{H} \rightarrow \text{I}$	$\text{I} \rightarrow \text{J}$	J	$\text{J} \rightarrow \text{P}$	dried in P	
Solid phase Track	$\text{G} \rightarrow \text{Lan}$	Lan	$\text{Lan} \rightarrow \text{K}$	$\text{K} \rightarrow \text{L}$	$\text{L} \rightarrow \text{N}$	$\text{N} \rightarrow \text{M}$	

Note: The salt forming laws was based on simplified chart of salt

### 2.1.2 Steps of the First-stage Transformation Experiment

- (1) Added fixed proportion chemicals (salts) and water into a beaker based on the components of mixed potassium salts and mixed them. Two samples were prepared for parallel experiments
- (2) Put the two beakers into a water bath pot in which the temperature was controlled at 50°C, the mixing was maintained with motor stirrer. The stirred speed was 400 rpm and the mixing time was 90 min.
- (3) Separated solid phase from liquid phase, and analyzed the components of solid phase and liquid phase.
- (4) Orthogonal experiments were carried out to find the optimal experimental conditions for the first-stage transformation.

### 2.1.3 Experimental Results and

### discussion

Based on the phase diagram analysis, the recover rate of potassium is 63.94% when adding water to form the solid phase Lan; the recover rate is 62.53% when adding water to form the solid phase G. The experimental results was proved that the recover rate of potassium is higher when adding water to form solid phase Lan, and liquid phase H than that when adding water to form solid phase G、liquid phase E. Thus, the amount of added water to obtain higher potassium recover rate was the key factor in this work.

The orthogonal test design is an effective mathematics method for multi-factor and level experiment design. Orthogonal test design table  $L_9(3^4)$  was used to arrange the experiments in order to find the optimal condition to get higher potassium recover rate. The orthogonal experimental results are shown in Fig. 2.

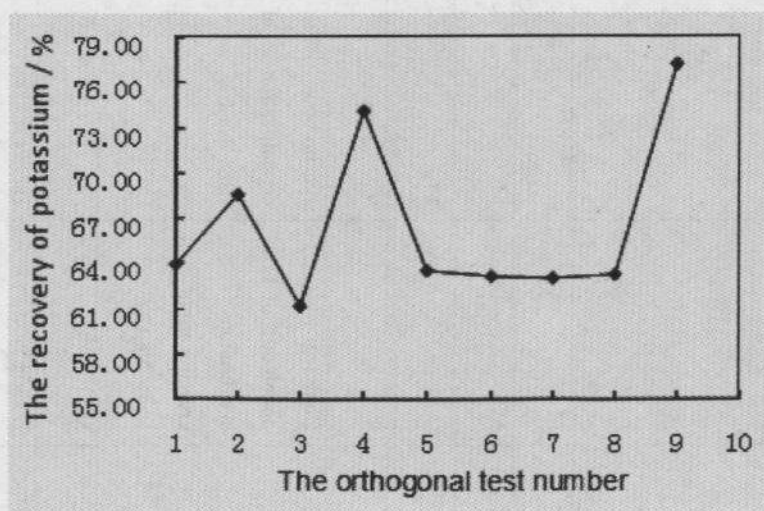


Fig. 2 Recovery ratio of potassium in the first-stage transformation



The optimal conditions of the first-stage transformation were: the mixing time was 120 min., the stirred speed was 600 rpm., the operational temperature was 50°C, the recover rate of potassium was up to 77.17%.

### 3.2 The Second-Stage Transformation Experiment

#### 3.2.1 Analysis of Phase Diagram Theory

Janecke index J of the wet solid phase

obtained from the first-stage transformation were:  $K_2^{2+} = 14.42$ ,  $Mg^{2+} = 52.93$ ,  $SO_4^{2-} = 32.61$ . The system point "M" was marked in the quintuple phase diagram of  $Na^+, K^+, Mg^{2+} // Cl^-, SO_4^{2-} - H_2O$  at 25°C as shown in Fig. 3. The analyzed salt forming laws was given in table 3 when evaporating the system point M at the isothermal condition. The experiment was carried out based on the phase diagram analysis by adding water to the solid phase obtained from the first-stage transformation in order to get the sulfate-potassium magnesium with higher potassium and lower chloride.

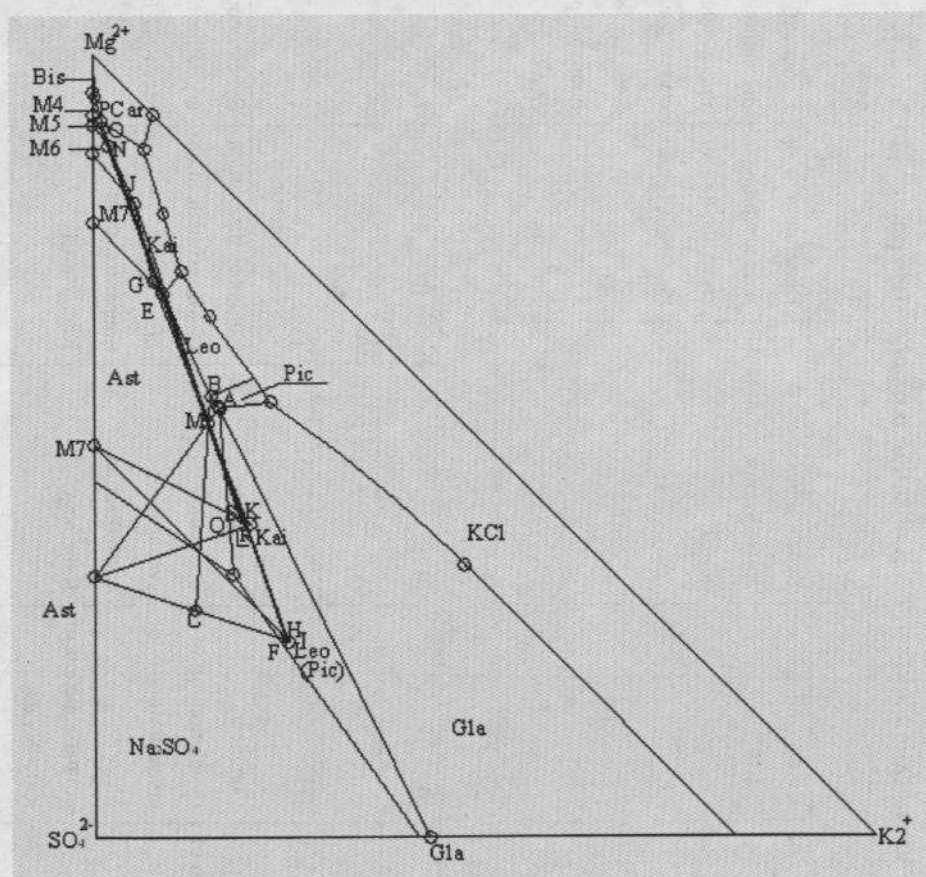


Fig. 3  $Na^+, K^+, Mg^{2+} // Cl^-, SO_4^{2-} - H_2O$  phase diagram at 25°C

**Table 3** Evaporation and salt crystallization laws of system point M in  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ // $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  -  $\text{H}_2\text{O}$  phase diagram at  $25^\circ\text{C}$

Stage	1	2	3	4	5	6	7	8	9
Process	Evaporation of unsaturated solution	Crystallization of $\text{Na}_2\text{Cl}_2$	Synchronous crystallization of Ast and $\text{Na}_2\text{Cl}_2$	Dissolution of Ast, synchronous crystallization of Pic, $\text{Na}_2\text{Cl}_2$	Complete dissolution of Pic, synchronous crystallization of Leo, $\text{Na}_2\text{Cl}_2$ , nonparticipation of Ast	Incomplete dissolution of Ast, synchronous crystallization of Leo, $\text{Na}_2\text{Cl}_2$	Complete dissolution of Ast, synchronous crystallization of Leo, $\text{Na}_2\text{Cl}_2$ , $\text{M}_7$	Incomplete dissolution of $\text{M}_7$ , synchronous crystallization of Lan, $\text{Na}_2\text{Cl}_2$	Complete dissolution of Leo, synchronous crystallization of $\text{M}_7$ , Kai, $\text{Na}_2\text{Cl}_2$
Solution Track	M								
Liquid phase Track	M	M	M	$A \rightarrow B$	B	$B \rightarrow E$	E	$E \rightarrow G$	G
Solid phase Track	-	-	Ast	$\text{Ast} \rightarrow \text{C}$	C	$\text{C} \rightarrow \text{F}$	$\text{F} \rightarrow \text{H}$	$\text{H} \rightarrow \text{I}$	$\text{I} \rightarrow \text{K}$
Stage	10	11	12	13	14	15	16	17	
Process	synchronous crystallization of $\text{M}_7$ , Kai, $\text{Na}_2\text{Cl}_2$	Complete dissolution of $\text{M}_7$ , crystallization of $\text{M}_6$ , nonparticipation of Kai, $\text{Na}_2\text{Cl}_2$	Incomplete dissolution of $\text{M}_6$ , synchronous crystallization of Kai, $\text{Na}_2\text{Cl}_2$	Complete dissolution of $\text{M}_6$ , crystallization of $\text{M}_5$ , nonparticipation of Kai, $\text{Na}_2\text{Cl}_2$	Synchronous crystallization of $\text{M}_5$ , Kai, $\text{Na}_2\text{Cl}_2$	Complete dissolution of $\text{M}_5$ , crystallization of $\text{M}_4$ , nonparticipation of Kai, $\text{Na}_2\text{Cl}_2$	Synchronous precipitation of $\text{M}_4$ , Kai, $\text{Na}_2\text{Cl}_2$	Incomplete dissolution of Kai, synchronous crystallization of $\text{M}_4$ , Car, $\text{Na}_2\text{Cl}_2$	
Solution Track	M								
Liquid phase Track	$G \rightarrow J$	J	$J \rightarrow N$	N	$N \rightarrow O$	O	$O \rightarrow P$	dried in P	
Solid phase Track	$K \rightarrow L$	L	$L \rightarrow Q$	Q	$Q \rightarrow R$	R	$R \rightarrow S$	$S \rightarrow M$	

Note: The salt forming laws was based on simplified chart of salt



### 3.2.2 Steps of the Second-Stage Transformation Experiment

The second-stage transformation experiments were carried out by adding water to the solid phase which was obtained from the first-stage transformation. The experimental steps were the same as the first-stage transformation. The stirred speed is constant. The temperature was controlled at 25°C. The mixing time was altered at 30, 40, 60, 70, 90 min. to find the optimal mixing time of the second-stage transformation.

The recover rate of potassium was the highest ones among the experimental points when the mixing time was 60 min. and 70 min, as shown in Fig.4. The mixing time 60 min. was appropriate for low energy consumption and low cost.

The optimal conditions for second-stage transformation on the basis of the high recover rate were: the stirred speed was 600 rpm, the temperature was 25°C and the mixing time was 60 min. The recover rate of potassium was up to 60.36% at the optimal conditions, the removal rate of chloride reached to 67.42%.

### 3.2.3 Experimental Results and Discussion

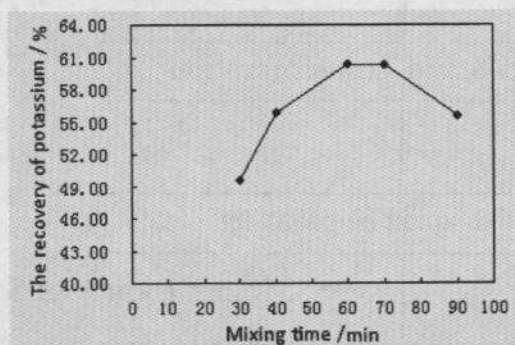
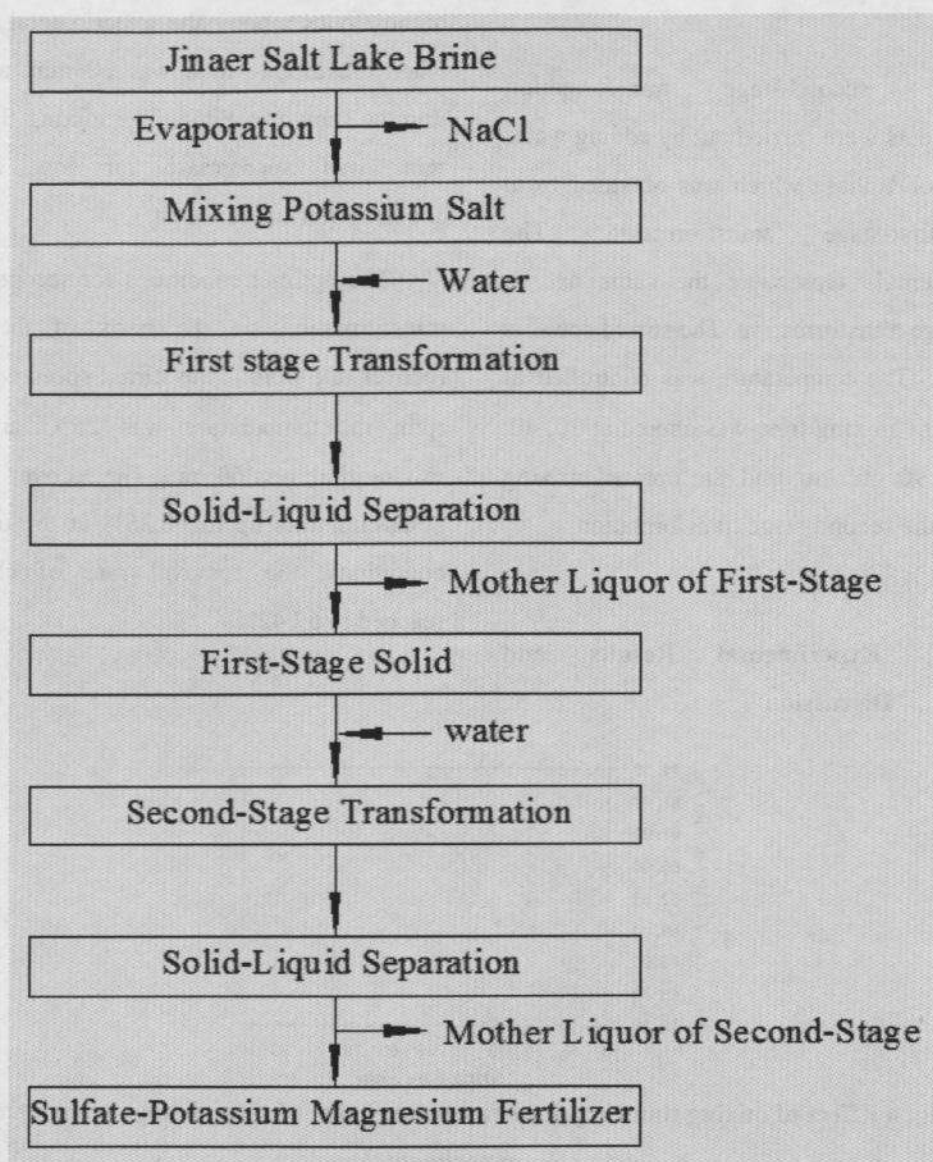


Fig. 4 Effect of mixing time on potassium recover rate of second-stage transformation experimental

### 3.3 Production technology of sulfate – potassium magnesium fertilizer from Jinaier salt lake brine

The schematic diagram of producing sulfate-potassium magnesium fertilizer with two stages transformation method from Jinaier salt lake brine in Qinghai was shown in Fig.5.



**Fig. 5 Production technology of sulfate – potassium magnesium fertilizer from Jinaier salt lake brine**

### 3 Conclusion

(1) Production technology of sulfate – potassium magnesium fertilizer with two stages transformation method from mixing potassium salts of Jinaier salt lake brine in Qinghai was developed, which was based on the quintuple phase diagram of  $\text{Na}^+, \text{K}^+, \text{Mg}^{2+} // \text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$  at 25°C and 50°C, respectively.

(2) The optimal conditions of the first-stage transformation were: the mixing time was 120 min., the stirred speed was 600 rpm., the reaction temperature was 50°C. The potassium recover rate was 77.17%.

(3) The optimal conditions of the second-stage transformation were: the mixing time was 60 min., the stirred speed was 600 rpm and the reaction temperature was 25°C. The recover rate of potassium in the production sulfate – potassium magnesium fertilizer was 60.36% in this stage, and the removal ratio of chloride was 67.42%.

(4) This study has great significance on developing potassium salt resource of Jinaier salt lake in Qinghai and producing sulfate -- potassium magnesium fertilizer of higher potassium and lower chloride.

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