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Exploration on the Technology of Barium Extraction from Yellow Brine and Rock Brine Mixing

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1 Introduction

- Sichuan Jiuda Penglai Salt and Chemical Co., Ltd .is located in Daying County, Sichuan province, which is rich in barium-containing yellow brine resources.
- The newly-built 600,000 t/a salt making facility in Sichuan Jiuda Penglai Salt and Chemical Co., Ltd. has been put into operation. The composition and ratio of yellow brine used in the newly-built salt making is quite different from that in previous salt wells. To match the technical requirements in the project under construction, our institute conducted experimental studies on brine mixing of Penglai yellow brine and rock brine. The experiment has achieved good results, thus providing a reliable reference for design and a valuable reference for barium sulfate production.

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2 Precipitation dissolution equilibrium theories

Two contradictory processes, namely dissolution and precipitation, make the reversible reaction reach an equilibrium state at certain point (velocity of dissolution and precipitation is the same.). This is called precipitation dissolution equilibrium.

2.1 Solubility product constant K_{sp} of sparingly soluble electrolyte

The product of ion concentration coefficient power of each component in a saturated solution of a sparingly soluble electrolyte under a given temperature is a constant. It is called solubility product constant, with solubility product as an abbreviation. With its symbol as Ksp, its physical meanings are as follows.

(1) Ksp is only relevant to reaction temperature and is irrelevant to quality of the sparingly soluble electrolyte.
(2) Concentration in equation is ion concentration during equilibrium and the solution is saturated solution.
(3) With Ksp, the solubility of a sparingly soluble electrolyte of the same type can be compared.

for generally indissoluble electrolyte $\longrightarrow \mathrm{A}_{\mathrm{m}}B_n(s) \Leftrightarrow mA^{n+}(aq) + nB^{m-}(aq)$

Equilibrium constant $\longrightarrow \mathrm{K}_{sp} = \left[A^{n+}\right]^m \cdot \left[B^{m-}\right]^n$

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2 Precipitation dissolution equilibrium theories

2.2 Fractional precipitation

If there simultaneously exist in solution two or more ions which can react with a certain precipitating agent, there is the issue of successive precipitation, namely fractional precipitation, when the precipitating agent is added in. In fractional precipitation, the following may occur.

(1) When precipitation is the same and initial concentration of precipitated ions is basically the same, various precipitations are successively formed in accordance with the order of solubility product
(2) When different precipitations are formed or initial concentration precipitated ions is different, precipitation sequence cannot be judged merely based on solubility product. Minimum concentration of precipitant must be first obtained according to the solubility product rules. Various precipitations that are sequentially generated are then judged in accordance with the order of the required precipitant concentrations.

This is the case with barium and strontium in yellow brine.

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3 Brine mixing experiment

3.1 Pre-experiment preparation

(1) Scheme determination

In combination with field investigation conducted in Penglai Salt and Chemical Co., Ltd., it is determined that mixing of yellow brine and rock brine consists of two steps. Brine mixing process flow is shown in Figure 1.

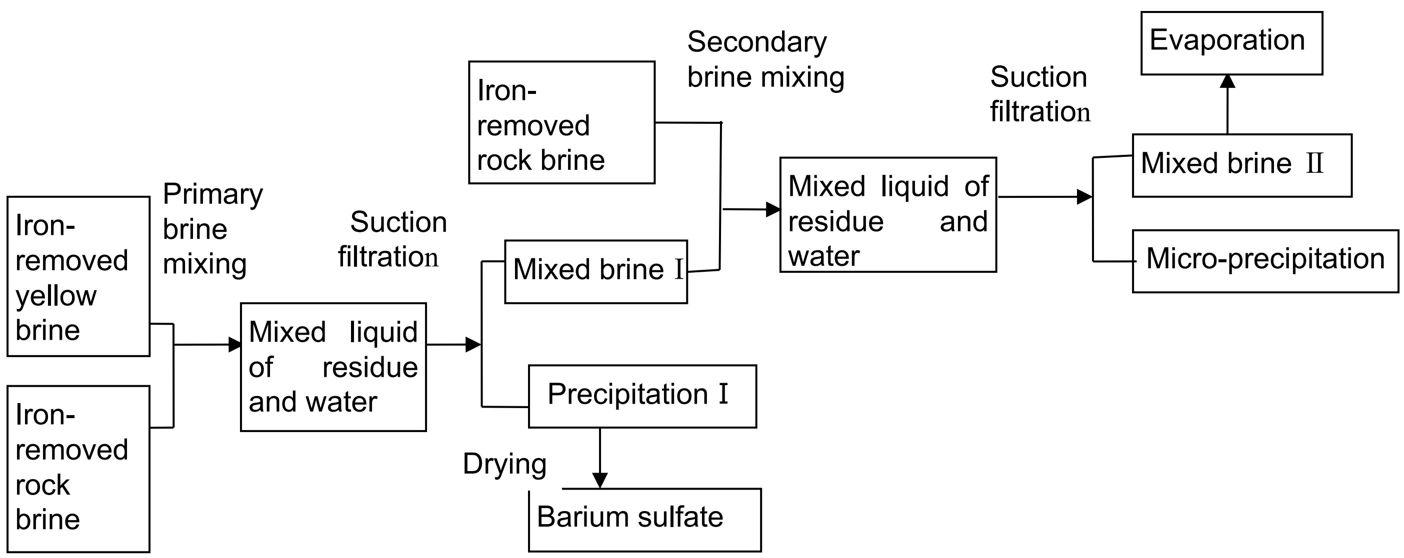

Figure 1 Brine mixing process flow

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3 Brine mixing experiment

3.1 Pre-experiment preparation

(2) Analysis on brine composition

First, brine composition in Penglai Salt and Chemical Co., Ltd. is taken for full analysis. Yellow brine from two brine wells is mixed in certain proportion. The analysis results are shown in Table 1.

Table 1 Analysis on brine composition in Penglai Salt and Chemical Co., Ltd.

Item	unit	content	
		Yellow brine	Rock brine
Ca^{2+}	g/L	15.53	1.52
Mg^{2+}	g/L	1.68	0.15
SO_4^{2-}	g/L	—	2.65
Cl^-	g/L	137.1	192.2
Ba^{2+}	g/L	1.42	—
Sr^{2+}	g/L	1.60	—
pH	—	5.48	6.92

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3 Brine mixing experiment

3.1 Pre-experiment preparation

(3) Preliminary analysis on precipitation

Ion molar concentration can be calculated based on Table 1. Concentration of Ba^{2+} and Sr^{2+} in yellow brine is 0.010mol/L and 0.018 mol/L respectively. Concentration of SO_4^{2-} in rock brine is 0.028 mol/L.
And we know the solubility product constant of barium sulfate, strontium sulfate and calcium sulfate are 1.1×10^{-10}, 3.2×10^{-7} and 9.1×10^{-6} respectively. Precipitation of the two-step brine mixing can be preliminarily estimated based on the data.

1) During the first step brine mixing, as the solubility product of barium sulfate is far lower than that of strontium sulfate, barium sulfate is first precipitated. However, because the molar concentration of strontium in brine is two times that of barium, a portion of strontium sulfate also precipitates. As a result, the barium sulfate and strontium sulfate co-precipitates during yellow brine and rock brine mixing. The content of barium sulfate is much higher than that of strontium sulfate.
2) In mixed brine from the first step, there are mainly calcium (higher than 10g/L) and strontium. Since there is little difference in solubility product of barium sulfate and strontium sulfate, the addition of sulfate radical will lead to significant co-precipitation during the second step brine mixing.

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3 Brine mixing experiment

3.2 The first step brine mixing experiment

(1) Mixing ratio selection

There is certain amount of iron in raw brine, so lime is first added in to remove it to eliminate its effect on brine mixing. When index requirement is met, the first step brine mixing experiment is carried out.

Brine mixing ratio is the most important factor in brine mixing, so different mixing ratio of rock brine and yellow brine are selected to conduct the experiment respectively. Optimum brine ratio is selected based on residual Ba^{2+} in brine after mixing.

In accordance with theoretic calculation and the operation situation in Penglai Salt and Chemical Co., Ltd., we selected three groups of ratios in experiment, in which the ratio for iron-removed rock brine SO_4^{2-}(mol): iron-removed yellow brine Ba^{2+}(mol) are 7:5, 6.5:5 and 6:5 respectively and the mixing time are 30 minutes. Suction filtration is carried out after clarification and clear liquid is sent for inspection and analysis. Analysis on experimental results of three groups of brine mixing in different ratio is shown in Table 2.

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3 Brine mixing experiment

3.2 The first step brine mixing experiment

(1) Mixing ratio selection

Table 2 Mixed brine (I)composition in different mixing ratio

Analysis item	Unit	Experiment condition		
		Molar ratio of brine mixing 7:5	Molar ratio of brine mixing 6.5:5	Molar ratio of brine mixing 6:5
Ca^{2+}	g/L	9.93	10.15	10.61
Mg^{2+}	g/L	0.87	0.86	0.87
SO_4^{2-}	g/L	0.26	0.21	0.15
Cl^-	g/L	159.0	159.1	157.3
Ba^{2+}	g/L	0.004	0.010	0.022
Sr^{2+}	g/L	0.97	1.01	1.03
pH	—	8.23	8.70	8.97

It can be seen that brine is mixed with molar ratio of iron-removed rock brine SO_4^{2-} (mol): iron-removed yellow brine Ba^{2+}(mol) being 7:5 and 6.5:5. Residual Ba^{2+} and SO_4^{2-} content in brine can meet the requirement for SO_4^{2-} 0.2～0.3g/L.
In order to both meet the requirement for brine quality and improve barium sulfate product quality, it is appropriate to select the brine mixing ratio of 6.5:5 (molar ratio of iron-removed rock brine SO_4^{2-} to iron-removed yellow brine Ba^{2+}). The mixed brine in this step is used as the raw material for the second step of brine mixing.

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3 Brine mixing experiment

3.2 The first step brine mixing experiment

(2) Precipitation analysis

Table 3 Precipitation components in the first step brine mixing

Analysis item	unit	content
$BaSO_4$	%	72.8
$SrSO_4$	%	7.3
$CaSO_4$	%	2.6
$CaCl_2$	%	1.3
NaCl	%	7.3
Burning weight loss	%(800℃)	7.0

It is concluded from calculation and experimental results that Barium salt has basically precipitated and about 12% strontium precipitates to form strontium sulfate precipitate.

As can be seen from Table 3, precipitate contains $BaSO_4$, higher content of $SrSO_4$ and minute quantity of $CaSO_4$, which conforms to composition in water.

Both mixed brine composition after first step brine mixing and precipitate composition indicate co-precipitation of Ba^{2+} and Sr^{2+} sulfate, which conforms to theory.

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3 Brine mixing experiment

3.3 The second step brine mixing

(1) Mixing ratio

After separation in the first step brine mixing, there has been minute quantity of barium ions in clear liquid. When the brine is mixed again, strontium and calcium should precipitate. Based on concentration of SO_4^{2-} and Sr^{2+} in mixed brine I and molar concentration of SO_4^{2-} in iron-removed rock brine, we calculate the quantity of iron-removed rock brine which should be added into the second step brine mixing. The data are shown in table 4.

Table 4 Brine mixing ratio in the second step mixing

	SO_4^{2-}(mol/L)	Sr^{2+}(mol/L)	Brine mixing ratio
Preliminary brine mixing	0.0023	0.011	3:1
Ion-removed rock brine	0.026	—	

Stirring speed of brine mixing is 300r/min and reaction time is 60 min. During brine mixing, brine is not turbid and no sediment precipitates. There is a trace amount of white substances after some period of placement.

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3 Brine mixing experiment

3.3 The second step brine mixing

(1) Mixing ratio

Table 5 Mixed brine II composition after the second step brine mixing

Analysis item	unit	content of the second brine mixing
Ca^{2+}	g/L	8.06
Mg^{2+}	g/L	0.63
SO_4^{2-}	g/L	0.82
Cl^-	g/L	164.3
Ba^{2+}	g/L	0.012
Sr^{2+}	g/L	0.77
pH	—	8.91

(2) Experiment summary

It is concluded from calculation that there is minute quantity of residual Ba^{2+}, little Sr^{2+} precipitate, slightly decrease in Ca^{2+} in mixed brine Ⅱ. About 1.5% is precipitated. It can be seen that small quantity of calcium sulfate precipitates during second step brine mixing, which conforms to experiment.

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4 Conclusion and discussion

- 4.1 Experiments show that barium sulfate basically precipitates and there is a minute quantity of residual barium during the first step brine mixing. A small amount of strontium sulfate precipitates. Therefore, the precipitation of the first step brine mixing is the mixed precipitation of barium sulfate and strontium sulfate, conforming to precipitation dissolution equilibrium theory.
- 4.2 During the second step brine mixing, a small amount of strontium sulfate and a minute amount of calcium sulfate precipitates. A large amount of strontium sulfate and calcium sulfate goes into the subsequent evaporation system.
- 4.3 Barium sulfate obtained from brine mixing is sold as a separate product. To increase the main content of barium sulfate product, relevant parameters during brine mixing should be controlled and subsequent treatment process after barium sulfate precipitation should be further optimized.
- 4.4 In yellow brine from Penglai Salt and Chemical Co., Ltd., the content of strontium, an extremely useful trace element, is relatively high. Strontium salt extraction can be further strengthened to achieve better economic results.

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Thanks !

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