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Glauber' Salt Precipitation Rules of Yabulai Salt Lake Brine

Salt Production

Abstract:

In this work, the rules of glauber's salt precipitation was studied with the help of the equilibrium phase diagram of the quaternary system (Na^+, Mg^{2+}//Cl^-, SO_4^{2-}-H_2O) in the simulation of Yabulai Salt Lake climate conditions. A fixed temperature precipitation experiment varied temperature precipitation experiment were done. The results showed that temperature had a great influence on the precipitation rate of glauber's salt brine. Relative low temperature is beneficial to the precipitation of glauber's salt under the condition of constant temperature. At -10 ºC fixed temperature, the adding water rate was controlled at 7.82%, which was the water content was at ice salt eutectoid boundary point. In the above-mentioned condition, the SO_4^{2-} concentration fell below 0.15mol/L in the liquid phase, following by the common precipitation of mirabilite and ice. The glauber's salt precipitation ratio was up to 82.61%, and the residual brine could meet the requirement of high quality salt production. Between -20 ºC to 5 ºC varied temperature, the adding water rate was controlled at 7.82%, the SO_4^{2-} concentration in mother liquid was increased with temperature. When the temperature rises to -10 C, the mirabilite and ice precipitated simultaneously, then the SO_4^{2-} concentration in mother liquid felt to 0.12mol/L, and the glauber's salt precipitation ratio was up to 85.66%. It was a better result than in fixed temperature.

Key words: Yabulai salt lake, Precipitation rules, Glauber, Recycled salt, Phase diagram

Introduction

Alxa Youqi is located in the west of the Inner Mongolia Autonomous Region, the northern foot of fold belt between Longshou Mountain and Heli Mountain. It possesses the temperate arid desert climate with cold in winter, less rain and snow and the large temperature difference between day and night.

Yabulai salt lake is located in the southwest edge of Alashan Town, whose coldest month is from December to February, with the larger temperature difference between day and night. According to the field monitoring of salt lake, the average temperature at night is -20 ºC and temperature in the afternoon can rise to 5 ºC. From December to February, -30 ºC is the lowest temperature and 10 ºC is the highest in accordance with the data monitored in the past two years.

Simulate the normal climate and extreme climate for salt lake and research the freezing and thawing rules of brine in frozen pool under these two conditions to provide reference data for production in salt lake.

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Experimental section

The raw brine of freeze-thaw craft derived from the first liquor after salt separation. The composition of raw brine is shown in Table 1. Since the temperature changes into -20 °C to 5 °C, 15% water is determined to add, then, the brine configured is placed in a freezer, which will be froze in constant temperature from 21pm to 7am under -20 °C. From 7am, the constant temperature of brine will arise(the heating rate is controlled, 6 °C /2h; from 15pm, the temperature will decrease, whose cooling rate is 8 °C /2h. So the cycle is. Take samples after 72 hours and monitor the changes of ion concentration of the first liquor with temperature.

Table 1 The raw brine composition in low freezing process

Concentration (g/L)						Physical property	
Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na+	H_2O	tempertu re(°C)	Density (g/cm^3)
172.11	77.32	0.01	27.82	95.24	883.51	25	1.2560

Result and discussion

Table 2 Liqud phase composition of purified salt mother liquor under the condition of variable temperature from -20 °C to 5 °C

Temperature (°C)	concentration (w%)				Glauber salt yield(%)
	Cl^-	Mg^{2+}	SO_4^{2-}	Na^+	
-20.0	13.87	2.27	0.40	4.81	1.1952
-16.5	13.77	2.25	0.40	4.85	1.1962
-10.0	13.58	2.23	0.96	5.00	1.1971
-6.5	13.46	2.20	1.20	5.09	1.1975
0.0	13.18	2.18	1.92	5.28	1.1982
5.0	13.03	2.14	2.16	5.33	1.1988
1.0	13.27	2.18	1.60	5.20	1.1985
9.0	13.62	2.23	0.88	4.96	1.1968
15.0	13.71	2.23	0.48	4.85	1.1959
-20	13.82	2.25	0.40	4.83	1.1948

The changes of ion concentration in the first liquor are shown in Table 1 and 2. The former is heating process and the latter is cooling procedure.

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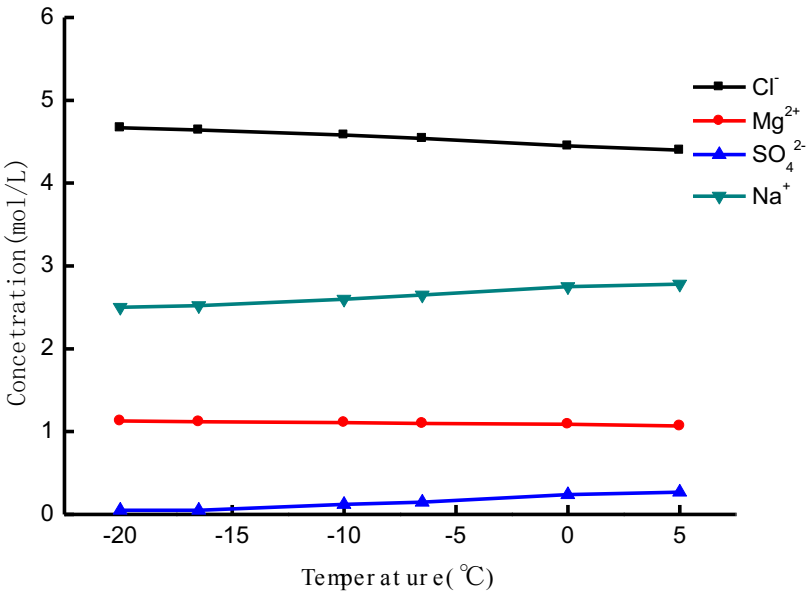

Figure 1: Trends of ion concentration of purified salt mother liquor in liquid phase in heating process

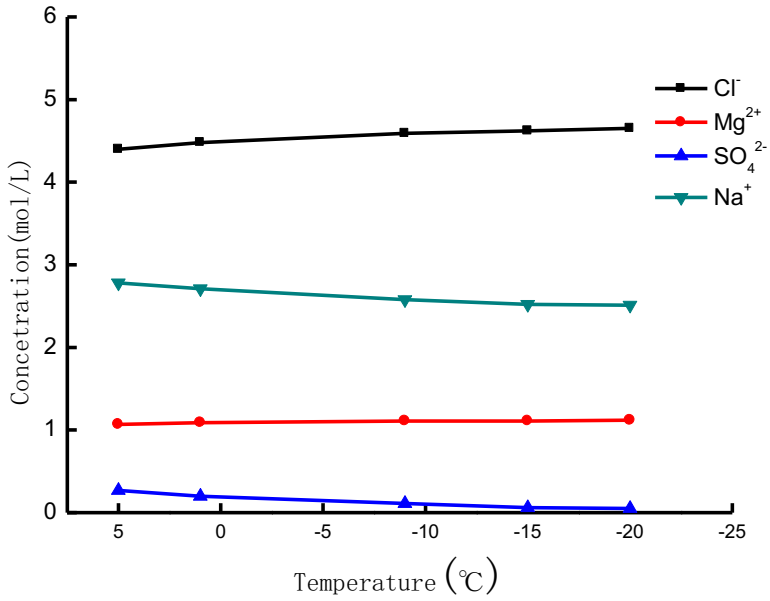

Figure 2: Trends of ion concentration of purified salt mother liquor in liquid phase in cooling process

From the Figure 1 and 2, it can be seen when the temperature of brine is -20 ºC at

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7am, the concentration of ion SO_4^{2-} is 0.05mol/L in the first liquor of frozing mirabilite which can reach the requirement of salt lake, but with the heating temperature, the concentration of ion SO_4^{2-} begins to arise slowly. When the temperature reaches -10 ºC, the concentration of SO_4^{2-} ion reaches 0.12mol/L, and with the increase of temperature, the rising rate of concentration of SO_4^{2-} also becomes big. When the temperature rises above 0 ºC, the SO_4^{2-} ion concentration has risen to above 0.2mol/L, which can not meet the requirements to producing high quality salt in the next step. With the temperature rising, the concentration of Cl and the concentration of Mg^{2+} in the frozen mother liquor decreased slightly, which may be due to the rising temperature, the dissolution of mirabilite in the brine releases a certain amount of free water and the dissolution of ice.

From 3pm, the temperature begins to decrease and so is the concentration of ion SO_4^{2-} . When the temperature decreases to -10 ºC, the concentration of SO_4^{2-} reaches 0.11mol/L to meet the new requirements of salt lake. The Cl^- concentration and Mg^{2+} concentration in the liquid rise slowly with temperature decreasing.

Mirabilite is eliminated in frozen brine to reproduce the super salt, the concentration of Na_2SO_4 in the freeze-thaw mother liquor needs to be controlled below 15 g / L. Therefore, it is suggested that the time of brine transfer should be controlled as much as possible within -10ºC for a brine temperature.

The fraction in solid phase of brine is analyzed in Table 3. Due to 15% addition of water, $NaCl{\cdot}2H_2O$, the second solid phase, is separated above the limited point. There is no NaCl precipitation in solid phase. With the increase of temperature, the precipitation rate of Glauber's salt decreased obviously.

Table 3 Solid phase composition of purified salt mother liquor under the condition of variable temperature from -20 ºC to 5 ºC

Temperature (°C)	Mass fraction in solid phase(g/100g)				Glauber salt yield(%)
	Cl^-	Mg^{2+}	SO_4^{2-}	Na^+	
-20.0	0.12	0	12.33	5.99	94.08
-16.5	0.32	0	12.65	6.27	91.65
-10.0	0.22	0	12.11	5.95	85.66
-6.5	0.25	0	11.96	5.89	62.07
0.0	0.55	0	13.21	6.69	52.33
5.0	0.11	0	12.9	6.25	38.65
1.0	0.29	0	13.33	6.58	40.98
9.0	0.32	0	12.99	6.43	77.99
15.0	0.22	0	11.58	5.69	89.65
-20	0.11	0	12.55	6.08	93.20

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The composition of raw brine is shown in Table 1. The water addition rate is 15%. The brine configured will be placed in the freezer and frozen at -25 ºC constant temperature from 21:00pm to 7:00am the next day, from 7 pm, the temperature of brine is increased in constant temperature (control the heating rate of about 5 ºC / h), from 15:00, it begins to cool with cooling rate of about 5 ºC /h, so the cycle is. After 72 hours, take sample, the concentration of various ions in the freeze-nickel mother liquor will change with temperature. The changes are seen in Table 4.

Table 4 Liqud phase composition of purified salt mother liquor under the condition of variable temperature from -25 ºC to 10 ºC

Temperature (ºC)	Concentration (%)				Glauber salt yield(%)
	Cl^-	Mg^{2+}	SO_4^{2-}	Na^+	
-25.0	13.79	2.29	0.24	4.66	1.1948
-20.0	13.77	2.27	0.40	4.79	1.1959
-15.5	13.64	2.25	0.64	4.84	1.1969
-5.0	13.23	2.17	1.76	5.24	1.1972
0.0	13.04	2.14	2.24	5.40	1.1979
10.0	12.84	2.09	2.63	5.57	1.2056
5.0	13.03	2.16	2.16	5.33	1.1991
-3.5	13.31	2.18	1.60	5.20	1.1980
-9.0	13.50	2.23	1.04	5.00	1.1965
-15.0	13.74	2.25	0.72	4.94	1.1966
-18.0	13.69	2.25	0.56	4.85	1.1957
-25.0	13.81	2.27	0.40	4.79	1.1950

Figure 5 shows the changes of ions in mother liquor of frozen mirabilite with temperature. Figure 3 shows the heating process and Figure 4 for the cooling process. It can be seen that the concentration of Cl- and Mg^{2+} in the brine liquid phase is relatively high when the temperature is low, and the concentration of SO_4^{2-} increases with the temperature rising. When the temperature rises to -10 ºC, the SO_4^{2-} concentration reaches 0.14mol / L. If the temperature continues to rise, it will exceed the salt requirements (liquid Na_2SO_4 content will be less than 15g / L). When the temperature drops to -9 ºC, the liquid phase SO_4^{2-}concentration meets the requirements again. It is suggested that the temperature of brine in the salt lake be below -10 ºC, in which transfer frozen mother liquor and store it for the production of salt with high quality, whose liquid density is 1.1970g/cm^3 at this time.

The fraction in solid phase of brine is analyzed in Table 5. When there is a 15% addition of

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water, the second solid phase is not separated obviously. When the temperature decreases below -10 ℃, the precipitation rate of mirabilite reaches above to 70% to meet the new requirements of salt lake.

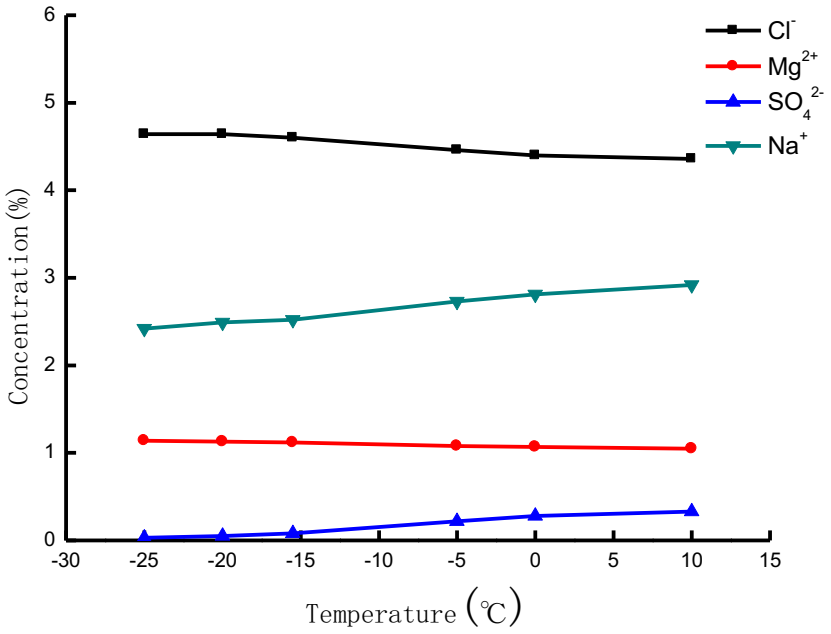

Figure 3 Trends of ion concentration of purified salt mother liquor in liquid phase in heating process

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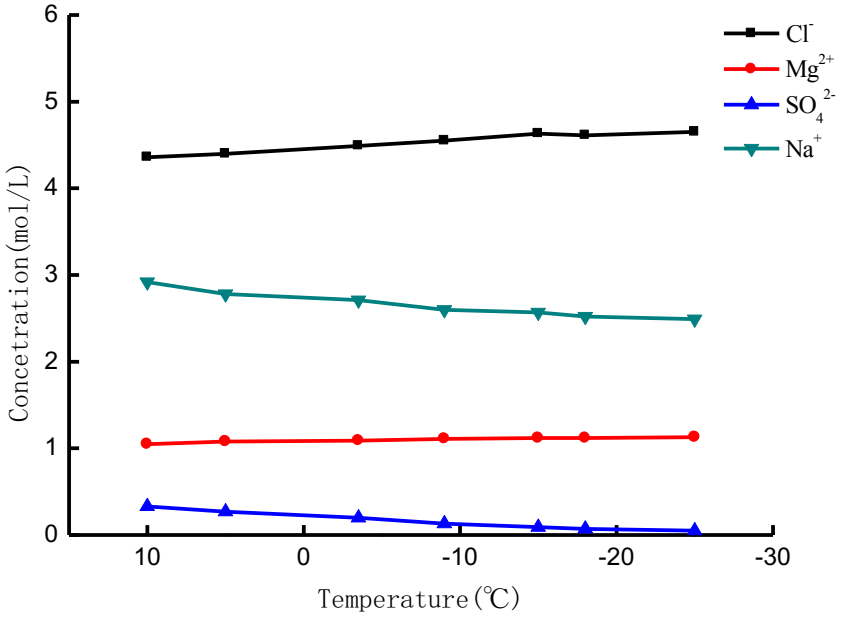

Figure 4 Trends of ion concentration of purified salt mother liquor in liquid phase in cooling process

Table 5 Solid phase composition of purified salt mother liquor under the condition of variable temperature from -25℃ to 10℃

Temperature (°C)	Mass fraction in solid phase(g/100g)				Glauber salt yield(%)
	Cl^-	Mg^{2+}	SO_4^{2-}	Na^+	
-25.0	0.11	0.00	11.11	5.39	94.02
-20.0	0.20	0.00	12.47	6.11	94.11
-15.5	0.10	0.00	12.43	6.02	88.32
-5.0	0.37	0.00	12.70	6.32	67.58
0.0	0.53	0.00	14.51	7.30	51.09
10.0	0.47	0.00	15.92	7.93	36.06
5.0	0.34	0.00	14.37	7.11	38.21
-3.5	0.42	0.00	12.47	6.25	52.99
-9.0	0.37	0.00	10.99	5.50	74.49
-15.0	0.21	0.00	15.57	7.60	88.33
-18.0	0.19	0.00	9.17	4.52	85.21
-25.0	0.27	0.00	10.01	4.97	92.01

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Conclusions

The temperature disparity between day and night is very large in Yabulai Salt Lake in winter. From the analysis of precipitation of frozen mirabilite from -20 ºC to 5 ºC or 10 ºC, it can be seen that the solubility of mirabilite is very sensitive to the temperature. When the temperature rises from -20 ºC to 5 ºC (5% water addition rate), the concentration of sulfate ion in the liquid phase is slowly increased. When the temperature rises to -10 ºC, the concentration of sulfate ion in the liquid phase reaches 0.12mol / L with 85.66% precipitation of mirabilite. Compared with the constant temperature conditions, the concentration of sulfate ions in the liquid phase is relatively low, which is caused by the dissolution rate of mirabilite. In the process of the temperature decreasing from 5 ºC to -20 ºC, when the temperature decreases to -10 ºC, the concentration of sulfate ion in brine liquid phase reaches 0.11mol / L again, which could meet the demand of salt lake. In the extreme climatic conditions, that is -25 ºC to 10 ºC for the brine, when the temperature is below -10 ºC, the sulfate ion concentration in liquid phase can also be reduced to 0.15mol / L or less, which can meet the brine demand of salt lake to reproduce salt with high quality.

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