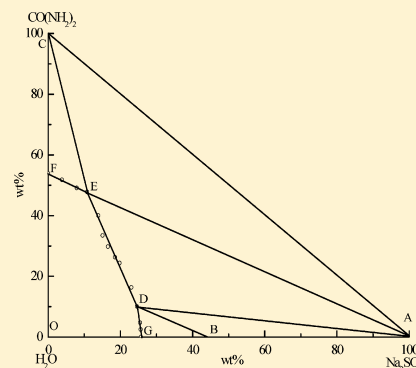


Phase Diagrams of $\text{Na}_2\text{SO}_4\text{--MgSO}_4\text{--CO}(\text{NH}_2)_2\text{--H}_2\text{O}$ System at 25 °C and Their Application

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ABSTRACT: Bloedite ($\text{Na}_2\text{SO}_4\cdot\text{MgSO}_4\cdot 4\text{H}_2\text{O}$) is an important natural chemical resource. So far, it has not been developed and utilized effectively because of its separation difficulties. To develop a new technology to produce Na_2SO_4 and Mg–N compound fertilizers by a $\text{CO}(\text{NH}_2)_2$ salting-out method to separate bloedite, the mutual solubilities of the ternary system $\text{Na}_2\text{SO}_4\text{--CO}(\text{NH}_2)_2\text{--H}_2\text{O}$ and the quaternary system $\text{Na}_2\text{SO}_4\text{--MgSO}_4\text{--CO}(\text{NH}_2)_2\text{--H}_2\text{O}$ at 25 °C were measured, and the phase diagrams of these two systems were investigated. According to the phase diagram analysis, it indicates that, by using the $\text{CO}(\text{NH}_2)_2$ salting-out method, Na_2SO_4 and MgSO_4 in bloedite can achieve better separation and anhydrous sodium sulfate can be directly obtained. The yield of Na_2SO_4 was 90.98 % in the case of the mother solution without cycling and utilizing. Adding a certain amount of $\text{CO}(\text{NH}_2)_2$ into the mother solution after Na_2SO_4 separation, $\text{MgSO}_4\cdot\text{CO}(\text{NH}_2)_2\cdot 2\text{H}_2\text{O}$ can be obtained. After separating $\text{MgSO}_4\cdot\text{CO}(\text{NH}_2)_2\cdot 2\text{H}_2\text{O}$ from the solution, the remain mother solution was recycled to dissolve bloedite. The new technology can get stable recycle production.



1. INTRODUCTION

The bloedite ($\text{Na}_2\text{SO}_4\cdot\text{MgSO}_4\cdot 4\text{H}_2\text{O}$) mineral is a kind of surface sediment which usually exists in salt lakes. The main chemical compositions of bloedite mineral are Na_2SO_4 and MgSO_4 . Bloedite is highly profitable and widely distributed in China. The reserves of bloedite only located in the A-La-Shan league region in Nei Mongol reach billions of tons.¹ In view of the development of bloedite mining, many studies have been done as early as 30 years ago. But bloedite has not been achieved industrialization production up until now.

The solid–liquid equilibrium data and phase diagram for the ternary system $\text{Na}_2\text{SO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ and its subsystems have been relatively completed.^{2–7} The results of phase diagram analysis indicated that the proper method to separate Na_2SO_4 and MgSO_4 was to produce sodium sulfate first by the cooling–crystallization process, and then magnesium sulfate was produced by evaporating and concentrating the solutions after sodium sulfate separation. Because the crystalline region of double salt of Na_2SO_4 and MgSO_4 was very large in the phase diagram of ternary system $\text{Na}_2\text{SO}_4\text{--MgSO}_4\text{--H}_2\text{O}$, pure sodium sulfate can be obtained under the conditions of low temperature and controlling system composition in a special small range. On other hand, after separating sodium sulfate from the solution of Na_2SO_4 and MgSO_4 , the magnesium sulfate can be obtained only by evaporating a good deal of water from the solution containing MgSO_4 . Therefore, the separation of Na_2SO_4 and MgSO_4 from bloedite was not only difficult but also high in energy costs according to the phase diagram of the $\text{Na}_2\text{SO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ system. Some new viewpoints on treatment of bloedite have been put forward. Huang et al. studied the synthesis of potassium sulfate from

bloedite and potassium chloride.⁸ Wang et al. studied turning magnesium sulfate in bloedite into sodium sulfate by a reaction of magnesium sulfate with alkaline.⁹ But there was no effective technology for developing bloedite resources so far.

One of the most important applications of MgSO_4 is fertilizers; Zhang et al. indicate that $\text{CO}(\text{NH}_2)_2$ and MgSO_4 in solution can form the double salt $\text{MgSO}_4\cdot\text{CO}(\text{NH}_2)_2\cdot 2\text{H}_2\text{O}$ which can be used as Mg–N compound fertilizers.¹⁰ Double salt $\text{MgSO}_4\cdot\text{CO}(\text{NH}_2)_2\cdot 2\text{H}_2\text{O}$ could be obtained by the reaction between $\text{CO}(\text{NH}_2)_2$ and magnesium-containing mother solution which comes from the separation of bloedite. The separation efficacy of bloedite may be improved, and the cost of magnesium fertilizer production may be reduced as well. Based on the above new idea, a study on the solid–liquid phase equilibrium of the quaternary system $\text{Na}_2\text{SO}_4\text{--MgSO}_4\text{--CO}(\text{NH}_2)_2\text{--H}_2\text{O}$ at 25 °C was carried out. There is no research on the phase equilibrium of the quaternary system $\text{Na}_2\text{SO}_4\text{--MgSO}_4\text{--CO}(\text{NH}_2)_2\text{--H}_2\text{O}$ and its subsystems $\text{Na}_2\text{SO}_4\text{--CO}(\text{NH}_2)_2\text{--H}_2\text{O}$ so far.

2. EXPERIMENTAL SECTION

2.1. Materials. The chemicals of Na_2SO_4 and $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ supplied by Tianjin Tanggu Chemical Plant were pure grade with a minimum purity of $w = 0.99$. $\text{CO}(\text{NH}_2)_2$ supplied by North Chemical reagent factory of Tianjin was pure grade with a minimum purity of $w = 0.99$. The water used to prepare

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solutions in this work was twice-distilled water (conductivity <math>< 5 \mu\text{S}\cdot\text{cm}^{-1}</math>).

2.2. Apparatus. The experimental apparatus of the phase equilibrium at (25 and 0) °C is illustrated in Figure 1. The

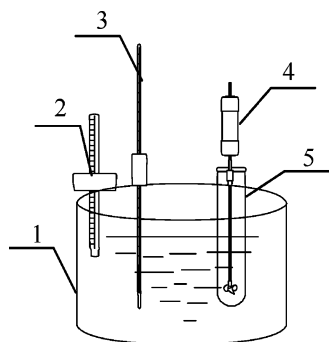


Figure 1. Experimental apparatus of the phase equilibria: 1, constant temperature bath; 2, spot contact thermometer; 3, thermometer; 4, electric stirrer; 5, equilibrium glass tube.

equilibrium glass tube (5) with a volume of 30 cm³ is immersed in a constant temperature water bath with an accuracy of ± 0.1 °C. The equilibrium glass tube was sealed with rubber, which was fixed in an agitator, to avoid water moisture that could volatilize during the experimental process. The temperature of constant temperature water bath was controlled in the set value during experiment. The mixture of magnesium sulfate, sodium sulfate, urea, and water with a certain ratio was added into the equilibrium glass tube and agitated by the stirrer. When the mixture reached the phase equilibrium, the stirrer was stopped. After the mixture standing and layering process, the solution was first pulled out from the equilibrium glass tube by 5 mL pipet and analyzed. Then the residual wet solids were pulled out from the equilibrium glass tube by a small glass ladle and analyzed. The experiment showed that the phase equilibrium time was 6 h.

The magnesium sulfate concentration was determined by the titration of ethylenediaminetetraacetic acid (EDTA) standard solution.⁴ The sulfate ion concentration was determined by the weight method of barium sulfate.⁴ The sodium sulfate concentration was determined by the subtraction method from sulfate ion concentration to magnesium ion concentration. The urea concentration was determined by the formaldehyde method.¹¹ The water content was determined by subtraction. The equilibrium phase solid was determined by the wet dregs method and the help of X-ray diffraction (XRD) analysis.

3. RESULTS AND DISCUSSION

3.1. Ternary System Na₂SO₄–CO(NH₂)₂–H₂O at 298.15 K. The solubilities of the ternary system Na₂SO₄–CO(NH₂)₂–H₂O at 298.15 K are given in Table 1. Based on the data in Table 1, the phase diagrams of the system Na₂SO₄–CO(NH₂)₂–H₂O at 298.15 K are plotted in Figures 2.

As shown in Figure 2, there are two isothermal invariant points D and E: D corresponds to the coexistence of solids Na₂SO₄·10H₂O and Na₂SO₄ with the saturated solution. E corresponds to the coexistence of solids CO(NH₂)₂ and Na₂SO₄ with the saturated solution. There are five crystallization fields and one unsaturated solution field: field DBG corresponding to the salt Na₂SO₄·10H₂O with saturated solution; field DAE corresponding to the coexistence of the

Table 1. Solubilities of the System Na₂SO₄–CO(NH₂)₂–H₂O at 298.15 K

point	composition of liquid phase/wt %			equilibrium solid phase ^a
	Na ₂ SO ₄	CO(NH ₂) ₂	H ₂ O	
D	25.64	2.510	71.85	S ₁₀
	25.44	4.700	69.86	S ₁₀
	24.59	10.08	65.33	S ₁₀ + S
	23.05	16.36	60.59	S
	19.80	24.37	55.83	S
	18.53	26.32	55.15	S
	16.52	29.81	53.67	S
E	15.08	33.47	51.45	S
	13.88	40.05	46.07	S
	10.79	47.77	41.44	S + U
F	3.830	51.81	44.36	U
	7.910	49.15	42.94	U
G	0	53.90	46.10	U
	25.70	0	74.30	S ₁₀

^aS₁₀: Na₂SO₄·10H₂O; S: Na₂SO₄; U: CO(NH₂)₂.

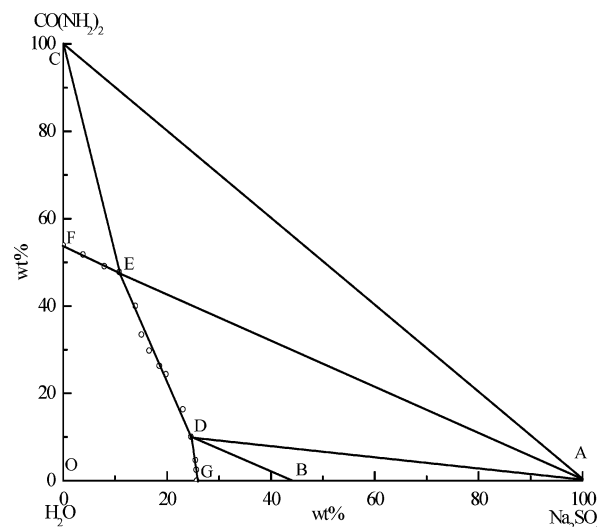


Figure 2. Phase diagram of the Na₂SO₄–CO(NH₂)₂–H₂O system at 25 °C.

salts Na₂SO₄·10H₂O and Na₂SO₄ with saturated solution; field ADB corresponding to the salt Na₂SO₄ with saturated solution; field AEC corresponding to the coexistence of the salts CO(NH₂)₂ and Na₂SO₄ with saturated solution; field FEC corresponding to the salt CO(NH₂)₂ with saturated solution. Field FEDGO corresponds to unsaturated solution. The results indicate that the compound Na₂SO₄ can be directly prepared in this system.

3.2. Quaternary System Na₂SO₄–MgSO₄–CO(NH₂)₂–H₂O at 298.15 K. The solubilities of the quaternary system Na₂SO₄–MgSO₄–CO(NH₂)₂–H₂O at 298.15 K are given in Table 2. Figure 3 is the corresponding dry salt phase diagram which is plotted according to the each composition mass fractions per 100 g of salt. There are also some broken lines which are applied in the following diagram analysis in Figure 3.

As shown in Figure 3, there are four isothermal invariant points, Q, P, R, and H. Q corresponds to the coexistence of solids MgSO₄·7H₂O, Na₂SO₄, and MgSO₄·CO(NH₂)₂·2H₂O with the saturated solution. P corresponds to the coexistence of solids MgSO₄·Na₂SO₄·4H₂O, Na₂SO₄·10H₂O, and Na₂SO₄

Table 2. Solubilities of the System $\text{Na}_2\text{SO}_4\text{--MgSO}_4\text{--CO}(\text{NH}_2)_2\text{--H}_2\text{O}$ at 25 °C

point	composition of liquid phase/wt %				composition of liquid phase (g/100 g dry salt)				equilibrium solid phase ^a
	Na_2SO_4	MgSO_4	$\text{CO}(\text{NH}_2)_2$	H_2O	Na_2SO_4	MgSO_4	$\text{CO}(\text{NH}_2)_2$	H_2O	
Q	3.420	26.51	32.05	38.02	5.520	42.77	51.71	61.34	$\text{M}_7 + \text{UM}$
	2.950	28.11	32.68	36.26	2.950	44.88	52.17	56.89	$\text{M}_7 + \text{UM}$
	2.970	28.00	33.43	35.60	4.610	43.48	51.91	55.28	$\text{M}_7 + \text{UM} + \text{S}$
	12.24	22.23	4.440	61.09	31.46	57.13	11.41	157.0	$\text{M}_7 + \text{Ast}$
	10.47	20.81	5.210	63.51	28.69	57.03	14.28	174.1	$\text{M}_7 + \text{Ast}$
H	4.610	21.03	8.300	66.06	24.00	54.50	21.50	194.6	$\text{M}_7 + \text{Ast}$
	8.190	22.25	13.84	55.72	18.49	50.25	31.26	125.8	$\text{M}_7 + \text{S} + \text{Ast}$
	24.36	4.810	11.22	59.61	60.32	11.91	27.77	147.6	$\text{S} + \text{S}_{10}$
	16.81	16.38	11.32	55.49	37.77	36.80	25.43	124.7	$\text{S} + \text{S}_{10}$
	19.57	11.12	11.34	57.97	46.56	26.46	26.98	137.9	$\text{S} + \text{S}_{10}$
P	22.16	8.170	11.25	58.42	53.29	19.65	27.06	140.5	$\text{S} + \text{S}_{10}$
	12.96	22.60	10.17	54.27	28.34	49.42	22.24	118.7	$\text{S} + \text{S}_{10} + \text{Ast}$
	6.150	11.08	47.00	35.77	9.570	17.25	73.17	55.69	$\text{U} + \text{S}$
	3.090	16.31	46.99	33.61	4.650	24.57	70.78	50.63	$\text{U} + \text{S}$
	6.980	4.910	46.44	41.67	11.97	8.42	79.62	71.44	$\text{U} + \text{S}$
R	2.993	18.65	48.62	29.74	4.260	26.54	69.20	42.33	$\text{U} + \text{S} + \text{UM}$
	15.77	18.77	4.43	61.03	40.47	48.16	11.37	156.6	$\text{S}_{10} + \text{Ast}$
	17.50	18.86	2.528	61.11	45.00	48.50	6.500	157.1	$\text{S}_{10} + \text{Ast}$
	3.240	28.41	37.16	31.19	4.710	41.29	54.00	45.33	$\text{S} + \text{UM}$
	2.620	22.89	34.51	39.98	4.360	38.14	57.50	66.61	$\text{S} + \text{UM}$
m_1	3.030	19.97	45.46	31.54	4.430	29.17	66.40	46.07	$\text{S} + \text{UM}$
	2.150	19.08	33.20	45.57	3.950	35.05	61.00	83.72	$\text{S} + \text{UM}$
	6.490	23.74	19.78	49.99	12.98	47.47	39.55	99.96	$\text{M}_7 + \text{S}$
	4.750	25.73	23.89	45.63	8.740	47.32	43.94	83.92	$\text{M}_7 + \text{S}$
	10.98	0	47.45	41.57	18.79	0	81.21	71.14	$\text{S} + \text{U}$
U	0	28.78	30.71	40.51	0	48.38	51.62	68.10	$\text{M}_7 + \text{UM}$
	0	22.62	50.80	26.58	0	30.81	69.19	36.20	$\text{U} + \text{UM}$
L	12.45	21.60	0	65.95	36.56	63.44	0	193.7	$\text{M}_7 + \text{Ast}$
N	18.63	15.63	0	65.74	54.38	45.62	0	191.9	$\text{S}_{10} + \text{Ast}$
V	24.38	0	9.240	66.38	72.52	0	27.48	197.4	$\text{S} + \text{S}_{10}$

^aNotice: S_{10} : $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; S: Na_2SO_4 ; M_7 : $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; Ast: $\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$; U: $\text{CO}(\text{NH}_2)_2$; UM : $\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$.

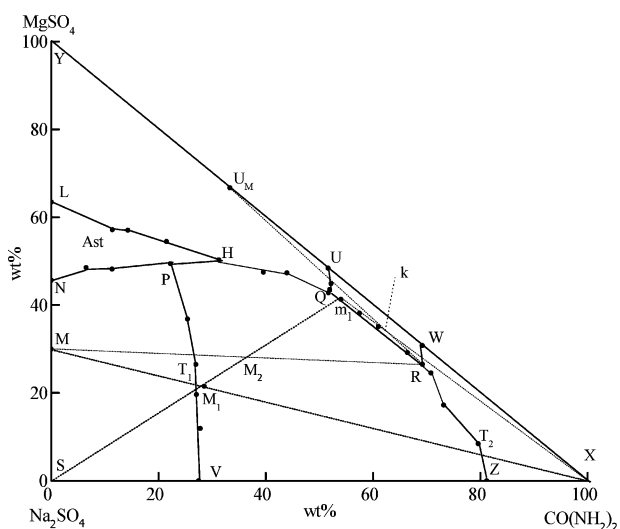


Figure 3. Dry salt phase diagram of the $\text{Na}_2\text{SO}_4\text{--MgSO}_4\text{--CO}(\text{NH}_2)_2\text{--H}_2\text{O}$ system at 25 °C.

with the saturated solution. H corresponds to the coexistence of solids $\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and Na_2SO_4 with the saturated solution. R corresponds to coexistence of solids Na_2SO_4 , $\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$, and $\text{CO}(\text{NH}_2)_2$ with the saturated solution. There are six crystallization fields: field SVPN corresponding to the equilibrium of crystal

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ with saturated solution; field VPHQRZ corresponding to solid Na_2SO_4 with saturated solution; field XWRZ corresponding to solid $\text{CO}(\text{NH}_2)_2$ with saturated solution; field UWRQ corresponding to solid $\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$ with saturated solution; field UQHLY corresponding to solid $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ with saturated solution; field HPNL corresponding to solid $\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ with saturated solution.

When $\text{CO}(\text{NH}_2)_2$ and water were added into this composition, spot M which represents the composition of bloedite, the mixture composition spot, will be on the line of MX in dry salt phase diagram. With the addition of $\text{CO}(\text{NH}_2)_2$ increasing, the mixture system spot in dry salt phase diagram will move along line MX from spot M to spot X. When mixture system is supersaturated solution and its composition spot located in the range of T_1 to T_2 in line MX, anhydrous Na_2SO_4 will be crystallized from the mixture system. T_1 and T_2 were the points of intersection of MX with PV and RZ separately. Comparing different spots in line T_1T_2 and applying the lever rule, it can be concluded that Na_2SO_4 production was at a maximum when the mixture composition spot is located in M_1 . The residual mother solution composition spot is m_1 after anhydrous Na_2SO_4 separation from the mixture system. When m_1 solution loses some water by evaporation and $\text{CO}(\text{NH}_2)_2$ is added into m_1 solution, the mixture system composition spot can be controlled in the intersection spot k of line m_1X and line U_MR . Then U_M ($\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$) will crystallize

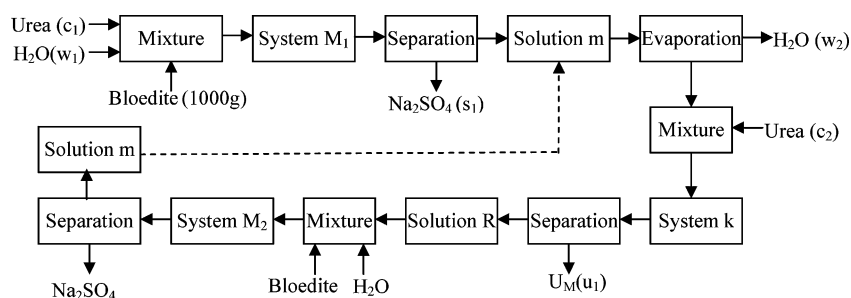


Figure 4. Technological flowchart of Na_2SO_4 and $\text{U}_M(\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O})$ production from bloedite.

Table 3. Phase Diagram Calculation Results of Producing Na_2SO_4 and $\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$ from Bloedite

composition and weight	Na_2SO_4	MgSO_4	$\text{CO}(\text{NH}_2)_2$	H_2O	amount
	wt %	wt %	wt %	wt %	kg (wt)
raw material of bloedite	42.47	35.99	0.00	21.54	1000
adding amount of H_2O (w_1)	0	0	0	100	182.5
adding amount of $\text{CO}(\text{NH}_2)_2$ (c_1)	0	0	100	0	470.7
solution (m_1) after Na_2SO_4 deposition	3.240	28.41	37.16	31.19	1267
amount (g) of Na_2SO_4 production	100	0	0	0	386.4
adding amount of H_2O (w_2)	0	0	0	100	43.26
adding amount of $\text{CO}(\text{NH}_2)_2$ (c_2)	0	0	100	0	248.5
solution (R) after U_M deposition	2.993	18.65	48.66	29.74	1371
amount of U_M ($\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$)	0.00	55.62	27.75	16.63	187.3
adding raw material of bloedite	42.47	35.99	0.00	21.54	705.7
adding amount of H_2O (w_1)	0	0	0	100	-0.180
amount (g) of Na_2SO_4 production	100	0	0	0	282.6
solution (m_1) after Na_2SO_4 deposition	3.240	28.41	37.16	31.19	1794

from the mixture k, and the residual mother solution spot will be located in R. After separating U_M from the mixture k, the R solution can be cycled to separate bloedite. The new mixture system spot can be controlled in the intersection spot M_2 of line Sm_1 and line MR. The mixture system M_2 is similar to M_1 and leads to the next cycling production of anhydrous Na_2SO_4 and U_M . Thereby a preparation process to produce Na_2SO_4 and urea-magnesium from the separation of bloedite can be achieved. Figure 4 is the technological flowchart of Na_2SO_4 and $\text{U}_M(\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O})$ production from bloedite by the urea salt-out method.

Based on the 1000 g of pretreated bloedite and the material balance principle, the phase diagram calculations were carried out. The key mother solution spot composition and calculated results are shown in Table 3.

The dry salt composition spot of bloedite is M in the phase diagram (Figure 2). When 470.7 g of $\text{CO}(\text{NH}_2)_2$ and 182.5 g of H_2O was added into M and the mixture system spot is M_1 , 386.4 g of Na_2SO_4 was crystallized, and the 1266.8 g of the mother liquor m_1 was produced. The weight percent of mother liquor m_1 is Na_2SO_4 $w = 0.0324$, $\text{CO}(\text{NH}_2)_2$ $w = 0.3716$, and MgSO_4 $w = 0.2841$.

Adding 86.73 g of H_2O and 323.0 g of $\text{CO}(\text{NH}_2)_2$ into the residues m_1 , the composition of the mixture will move to k in the field $\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$. Then 187.3 g of $\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$ products is crystallized, and 1371.3 g pf solution R are produced. The composition of solution R is Na_2SO_4 $w = 0.02993$, $\text{CO}(\text{NH}_2)_2$ $w = 0.4896$, and MgSO_4 $w = 0.1865$. Adding 705.7 g of bloedite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$) into R and evaporating 0.18 g of H_2O from R, the mixture composition spot moves to M_2 . After 282.6 g Na_2SO_4 are crystallized from the M_2 , the residual mother composition spot is

m_1 . So the next stable recycle production can get. The results of phase diagram calculation show that the yield of Na_2SO_4 can up to 90.98 % even though the mother liquor is not cycled.

4. CONCLUSIONS

- (1) The mutual solubilities of the ternary system Na_2SO_4 – $\text{CO}(\text{NH}_2)_2$ – H_2O and the quaternary system Na_2SO_4 – MgSO_4 – $\text{CO}(\text{NH}_2)_2$ – H_2O at 25 °C were measured. The phase diagrams of these two systems were constructed, and the invariant points and crystalline zones have been analyzed. There are big fields of anhydrous sodium sulfate in above phase diagrams of the two systems. It shows that compound Na_2SO_4 can be easily directly prepared from bloedite from the quaternary system at 25 °C.
- (2) A new technology to produce Na_2SO_4 and N–Mg compound fertilizers ($\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$) from bloedite was proposed based on the analysis of the phase diagram of Na_2SO_4 – MgSO_4 – $\text{CO}(\text{NH}_2)_2$ – H_2O at 298.15 K. It shows that the Na_2SO_4 and MgSO_4 in bloedite can achieve better separation by using the $\text{CO}(\text{NH}_2)_2$ salting-out method.

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