Supporting Information

Phase Equilibria and Phase Diagrams of Mn^{2+} , Mg^{2+} , $NH_4^+//SO_4^2$ — H_2O system at 298.15, 323.15 and 373.15 K

Min ZHANG¹, Peng WU², Yaoyao Li¹, Wenxuan Li², Huan ZHOU¹*

1. College of Chemical Engineering and Materials Science, 2. College of marine and environmental sciences

Tianjin Key Laboratory of Brine Resources and Eco-utilization, Tianjin University of Science and Technology, Tianjin TEDA, 300457, P.R. China

* Corresponding author: <u>zhouhuan@tust.edu.cn</u>

Supplementary Tables, Figures and Captions:

| 298 K | MgSO ₄ •7H ₂ O g 503.65 | | MnSO ₄ •H ₂ O g | | (NH ₄) ₂ SO ₄ g 39.84 | | Water g 297.52 |
|--------|---|----------------------------|---|------|---|-------------------------------------|----------------------|
| | | | | | | | |
| A(1-8) | | | 0.00 48.23 51.44 56.55 74.35 101.72 215.29 322.52 | | | | |
| C(1-6) | 0.00 225.47 423.61 | 122.81 329.31 522.92 | 447.46 | | 49.71 | | 505.03 |
| D(1-5) | 0.00 155.61 357.56 | 49.49 255.62 | 80.06 | | 375.82 | | 371.40 |
| E(1-9) | 207.29 | | 329 | 9.84 | 0.00 96.57 164.50 245.40 | 14.00 133.38 208.82 271.75 | 462.87 |

Table S1 Raw materials scheme for the phase equilibrium experiments at 298.15 K

Table S2 Raw materials scheme for the phase equilibrium experiments at 323.15 K

| 323 K | MgSO ₄ •7H ₂ O | MnSO ₄ •H ₂ O | $(NH_4)_2SO_4$ | Water |
|--------|--------------------------------------|-------------------------------------|----------------|--------|
| | g | g | g | g |
| | 715.24 | 0.00 35.00 | 41.00 | 242.02 |
| A(1-5) | /15.34 | 142.35 | 41.99 | 242.93 |
| | | | | |

| C(1-8) | 0.00 | 62.29 | | | | |
|---------|---------|---------|--------|--------|--------|--|
| | 122.29 | 192.29 | 401.96 | 41.00 | 201.24 | |
| | 282.29 | 392.29 | | 41.99 | 391.24 | |
| | 502.29 | 502.29 | | | | |
| | 0.00 | 40.00 | | | | |
| | 213.42 | 300.00 | 58.97 | 268.18 | | |
| | | | | | | |
| D(1-13) | 417.35 | 480.00 | | | | |
| | 627.69 | 820.00 | | | 263.99 | |
| | 833.07 | 1051.78 | | | | |
| | 1150.00 | 1600.00 | | | | |
| | 2600.00 | | | | | |
| | | | | | | |

Table S3 Raw materials scheme for the phase equilibrium experiments at 373.15 K $\,$

| 373 K | MgSO ₄ •7H ₂ O | | MnSO ₄ •H ₂ O | | $(NH_4)_2SO_4$ | Water |
|-------------------|--------------------------------------|---------|-------------------------------------|--------|----------------|--------|
| | g | | g | | g | g |
| | | | 0.00 | 35.28 | | |
| A(1-5) | 587.68 | | 97.67 | 153.23 | 67.18 | 364.64 |
| | | | 210.00 | | | |
| D | 137.12 | | 0.00 | 66.98 | 333.05 205.9 | 205.00 |
| В | | | 151.33 | 241.88 | | 205.90 |
| | 298.93 | | 0.00 | 80.27 | 42.2 32 | |
| C(1,0) | | | 163.25 | 241.45 | | 225.54 |
| C(1-8) | | | 321.95 | 421.22 | | 325.54 |
| | | | | 703.99 | | |
| | 0.00 | 72.81 | | | | |
| $\mathbf{D}(1,0)$ | 169.06 | 290.15 | 31.73 | | 277.5 | 225.07 |
| D(1-8) | 393.84 | 592.65 | | | 277.5 | |
| | 847.79 | 1057.11 | | | | |
| | | | | | | |



(c) $S_1+S_5+S_2$ at A_8



- S_1 : MgSO₄•7H₂O, S_2 : MnSO₄•H₂O, $S_5:MgSO_4{\scriptstyle\bullet}(NH_4)_2SO_4{\scriptstyle\bullet}6H_2O$
- Figure S2 XRD pattern of solid phase at typical points $C_2 C_3 C_5$ at 298.15 K

 S_2 : MnSO₄•H₂O, S₄: MnSO₄• $(NH_4)_2SO_4\bullet 6H_2O, S_5:MgSO_4\bullet (NH_4)_2SO_4\bullet 6H_2O$



(c) $S_2+S_4+S_5$ at E_4

Figure S3 XRD pattern of solid phase at typical points D_1 , D_2 and D_3 at 298.15 K

Figure S4 XRD pattern of solid phase at

typical points E_2 , E_3 and E_4 at 298.15 K

 $S_2: MnSO_4 \bullet H_2O, S_4: MnSO_4 \bullet$ (NH₄)₂SO₄•6H₂O, S₅:MgSO₄• (NH₄)₂SO₄•6H₂O typical points A₂, A₃ and A₅ at 323.15 K

 $S_1:MgSO_4\bullet7H_2O, S_2: MnSO_4\bulletH_2O,$

 $\begin{array}{c} S_{5}:\ gSO_{4}.(NH_{4})_{2}SO_{4}.6H_{2}O,\ S_{6}:\ 2MnSO_{4}\bullet\\ (NH_{4})_{2}SO_{4} \end{array}$



Figure S5 XRD pattern of solid phase at

(c) $S_1 + S_2 + S_6$ at C_7

- Figure S6 XRD pattern of C series solid phase sample at 323.15 K
 - S_1 : MgSO₄•7H₂O, S_2 : MnSO₄•H₂O,
 - S₆: $2MnSO_4 \cdot (NH_4)_2SO_4$



phase sample at 323.15 K

 $S_1: MgSO_4 \cdot 7H_2O; S_3 (NH_4)_2SO_4,$

S₅: MgSO₄• (NH₄)₂SO₄•6H₂O

- (c) $S_2+S_6+S_7$ at A_4
- Figure S8 XRD pattern of A series solid phase sample at 373.15 K

 S_2 : MnSO₄•H₂O, S₅: MgSO₄• $(NH_4)_2SO_4$ •6H₂O, S₆: 2MnSO₄• $(NH_4)_2SO_4$, S₇:





 S_2 : MnSO₄•H₂O, S₄: MnSO₄• $(NH_4)_2SO_4$ •6H₂O, S₆: 2MnSO₄• $(NH_4)_2SO_4$ phase sample at 373.15 K

 $S_3: (NH_4)_2SO_4, S_5: MgSO_4$ • (NH₄)₂SO₄•6H₂O,

S₆: $2MnSO_4$ • (NH₄)₂SO₄, S₇: MgSO₄•H₂O