Supplementary Materials

Impurity Regulation During Calcium Sulfate Crystallization and Phase Transformation: Purification, Resource Recovery, and Immobilization

Text S1 Structure and mineralogy of Calcium Sulfate

Calcium sulfate minerals in nature can be divided into three types according to the degree of hydration: gypsum ($CaSO_4 \cdot 2H_2O$), bassanite ($CaSO_4 \cdot 0.5H_2O$) and anhydrite ($CaSO_4$).

(1) $CaSO_4 \cdot 2H_2O$

Calcium sulfate dihydrate (DH), commonly known as gypsum, crystallizes in the monoclinic form (I2/*a*) [1]. It is composed of a layered structure of Ca^{2+}/SO_4^{2-}, which are parallel to the (010) plane and bounded to each other by ionic bonds [2].

(2) $CaSO_4 \cdot 0.5H_2O$

Calcium sulfate hemihydrate (HH), also called bassanite, can be divided into two forms according to the different crystal forms: α-HH and β-HH. The molecular structures of α-HH and β-HH are identical, consisting of chains of SO4 tetrahedral arrayed around channels containing water molecules. However, the arrangement of the crystals and formation process are different. α-HH crystallizes in a monoclinic form (I2) [3] while β-HH crystallizes in a tripartite or hexagonal form (P3(1)) [3, 4]. The subtle distinction in the crystal structure has a great influence on its mechanical strength, water absorption and dehydrated products [5]. Moreover, α-HH is usually obtained under hydrothermal condition, while β-HH is usually obtained under heating condition. α-HH features high strength (compressive strength 60-70 MPa, flexural strength 10-15 MPa), low standard consistency (25%-30%) and high density (hardened density 2.6-2.7 g/cm³), making it suitable for applications requiring high strength and water resistance. Conversely, β-HH is lower than α-HH in all aspects and is only suitable as a general building material.

(3) $CaSO_4$

Anhydrous gypsum (AH), known as anhydrite, is widely used as a building material, industrial filler, soil conditioner, cement production or desiccant.

AIII phase, or "γ-AH", with hexagonal symmetry structure (P6(2)22) [4]. The crystal structures of HH and γ-AH are structurally similar only depending on the presence of water molecules. γ-AH is considered as a "water-free HH" and also has two forms (α-AIII and β-AIII), which can be converted to α-HH or β-HH in moist air [6]. AII phase (insoluble anhydrite), or "β-AH", belongs to orthorhombic (*Cmcm*(63)) [7]. This structure is relatively inert and insoluble. AI phase, or "α-AH", belongs to trigonal [4] or cubic system [7].

Table S1. The main element types and contents in heavy metal-bearing gypsum.

Type		Industry/Process	Ca	S	As	Zn	Cd	Pb	Cu	Ni	Cr	Tl	Ref
Heavy metal-bearing gypsum	Arsenic-bearing gypsum sludge	Copper smelting	33.45	11.63	11.96	1.23	0.22	0.21	0.55	/	ND	/	[8]
	Neutralization gypsum sludge		35.65	22.21	0.02	0.02	ND	0.005	ND	/	0.003	/	
	Arsenic-bearing gypsum sludge	Copper smelting	22.59	8.15	6.60	0.68	0.10	0.57	/	/	/	/	[9]
	Arsenic-bearing gypsum sludge	Lead-zinc smelting	40.62	8.51	0.47	0.05	0.84	0.04	/	/	/	/	[10]
	Neutralization gypsum sludge		30.69	15.43	6.81	11.56	0.48	ND	/	/	/	/	
	Arsenic-bearing gypsum sludge	Copper smelting	37.50	9.60	11.50	1.27	/	/	0.37	/	/	/	[11]
	Arsenic-bearing gypsum sludge	Copper smelting	28.35	7.31	8.56	0.97	0.04	0.09	0.24	/	/	/	[12]
	Arsenic-bearing gypsum sludge	Lead-zinc smelting	28.20	9.70	2.50	/	1.30	0.47	/	/	/	/	[13]
	Arsenic-bearing gypsum sludge	Lead-zinc smelting	34.97	18.08	0.27	0.01	/	0.04	/	/	/	/	[14]
	Arsenic-bearing gypsum sludge	Copper smelting	27.82	13.52	4.94	0.34	0.35	/	/	/	/	/	[15]
	Arsenic-bearing gypsum sludge	Lead-zinc smelting	39.70	19.50	12.00	3.51	2.68	/	/	/	/	/	[16]
	Arsenic-bearing gypsum sludge	Lead-zinc smelting	10.2	10.3	19.5	0.46	/	5.20	/	/	/	/	[17]
	Zinc-bearing gypsum	Steel plant	35.40	42.10	/	5.26	/	/	/	/	/	/	[18]
	Zinc-bearing gypsum	Zinc smelting	17.89	14.13	/	12.78	/	/	/	/	/	/	[19]

Zinc-bearing gypsum	Zinc smelting	17.40	8.70	0.12	13.80	0.19	0.99	0.09	/	/	/	[20]
Zinc-bearing gypsum	Zinc smelting	17.89	14.31	0.09	12.78	0.29	0.39	0.13	/	/	/	[21]
Cr-containing gypsum	Sodium chlorate industry	30.90	6.60	/	/	/	/	/	/	0.63	/	[22]
Cr-containing gypsum	Sodium chlorate industry	16.03	13.24	/	/	/	/	/	/	0.57	/	[23]
Cr-containing gypsum	Sodium chlorate industry	44.77	26.02	/	0.008	/	/	/	/	2.30	/	[24]
Cr-containing gypsum	Sodium chlorate industry	/	/	/	/	/	/	/	/	0.67	/	[25]
Neutralization gypsum sludge	Electroplate	13.61	6.63	/	0.08	/	/	11.09	/	29.26	/	[26]
Neutralization gypsum sludge	Electroplate	30.90	7.20	/	3.30	/	/	7.60	/	7.50	/	[26]
Neutralization gypsum sludge	Electroplate	7.99	7.07	/	1.17	/	/	11.10	/	38.60	/	[26]
Neutralization gypsum sludge	Electroplate	7.32	2.05	/	0.77	/	0.25	5.97	10.91	8.23	/	[27]

Table S2 The main element types and contents in industrial by-product gypsum

Type		CaO	SO_3	Al_2O_3	SiO_2	P_2O_5	Fe_2O_3	F	MgO	TiO_2	Na_2O	Ref
Industrial by-product gypsum	Phosphogypsum	41.73	54.59	0.29	1.60	0.89	0.44	/	/	/	/	[28]
	Phosphogypsum	37.65	52.34	0.29	8.20	1.12	0.05	/	0.02	/	/	[29]
	Phosphogypsum	27.80	41.70	0.62	6.40	0.70	0.30	0.80	0.50	/	/	[30]
	Phosphogypsum	40.40	54.0	0.75	2.85	1.03	0.54	/	/	/	/	[31]
	Phosphogypsum	32.12	46.02	0.50	5.94	1.39	1.54	0.06	0.30	/	/	[32]
	Phosphogypsum	27.16	40.68	0.42	5.78	2.46	0.23	0.99	0.23	/	/	[33]
	Phosphogypsum	37.73	50.73	0.75	4.97	0.91	0.59	3.96	/	/	/	[34]
	Phosphogypsum	36.11	51.40	0.57	8.98	0.59	0.68	/	/	/	/	[35]
	Phosphogypsum	37.93	47.59	0.62	11.88	0.67	0.14	0.29	0.12	/	/	[36]
	Phosphogypsum	44.13	50.80	0.37	2.33	0.90	0.48	0.24	/	/	/	[37]
	Phosphogypsum	24.01	33.93	1.37	7.84	2.47	1.21	5.03	0.33	/	/	[38]
	Red gypsum	26.36	32.39	0.98	1.50	0.14	16.04	/	0.82	0.76	0.07	[39]
	Red gypsum	25.53	31.03	1.61	4.75	0.72	11.75	/	1.17	2.45	0.80	[40]
	Red gypsum	31.39	39.51	2.73	4.39	/	[41] 15.37	/	1.51	2.24	/	[42]
	Red gypsum	26.15	30.63	1.64	4.63	/	11.85	/	1.22	2.34	/	[43]
	Red gypsum	37.68	39.13	1.16	3.21	0.02	11.18	/	0.33	4.14	0.62	[44]
	Red gypsum	36.67	38.19	1.35	4.21	0.13	15.84	/	1.65	2.90	0.57	[41]

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