

Review

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

Jie Li ^{1,2}, Li Li ^{1,2}, Changzhou Weng ³, Jiemin Qin ^{1,2}, Zhulin Xue ^{1,2}, Lijuan Jia ⁴, Changyong Yu ⁵, Xiaoqin Li ^{1,2}, Weizhen Liu ^{1,2,*} and Zhang Lin ³

¹ School of Environment and Energy, Guangdong Provincial Key Laboratory of Solid Wastes Pollution Control and Recycling, South China University of Technology, 382 Zhonghuan Road East, Guangzhou Higher Education Mega Centre, Guangzhou 510006, China

² The Key Laboratory of Pollution Control and Ecosystem Restoration in Industry Clusters (Ministry of Education), Guangzhou 510006, China

³ Chinese National Engineering Research Center for Control & Treatment of Heavy Metal Pollution, School of Metallurgy and Environment, Central South University, Changsha 410083, China

⁴ School of Chemistry and Environment, Yunnan Minzu University, Kunming 650500, China

⁵ Hunan Research Center for Green and Low-Carbon Utilization of Industrial By-Product Gypsum, Pingjiang 414501, China

* Correspondence: weizhliu@scut.edu.cn

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Abstract: Calcium sulfate is a widely occurring inorganic salt in natural environments and industrial systems. It mainly occurs as dihydrate gypsum, hemihydrate gypsum, and anhydrite. During the nucleation and growth of calcium sulfate, impurity elements can bind to the calcium sulfate matrix through surface adsorption, coprecipitation, physical encapsulation, or lattice incorporation. Industrial processes generate large amounts of impurity-bearing calcium sulfate wastes, in which impurities are associated with the calcium sulfate matrix. The growing annual production and stockpiling of this waste pose challenges for environmental management and resource recovery. On the other hand, phase transformation in the calcium sulfate system provides possibilities for controlling impurity behavior. During dissolution-recrystallization, thermal dehydration and physical enhancement, the reconstruction of the calcium sulfate matrix can promote the release of impurities. Conversely, under specific crystallization conditions, foreign ions can also be immobilized in the calcium sulfate phase. This review summarizes the nucleation and phase transformation behavior of calcium sulfate and discusses the distribution of impurity ions in calcium sulfate. It then discusses different treatment methods based on calcium sulfate phase transformation. For calcium sulfate wastes, phase transformation can be used to promote impurity release and calcium sulfate purification through wet recrystallization, thermal dehydration–rehydration, or physical enhancement. the dissolution-recrystallization process of calcium sulfate is promoted to achieve deep extraction of impurities. Typical examples include gypsum containing heavy metals, as well as industrial by-product gypsum such as phosphogypsum and red gypsum. Then, immobilization applications based on calcium sulfate crystallization are discussed. Finally, the practical limitations and remaining challenges of these approaches are discussed. This review aims to guide the treatment of calcium sulfate waste from a microstructural perspective and promote the sustainable recycling of resources.

Keywords: gypsum waste; phase transformation; heavy metal; resource recovery



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1. Introduction

Calcium sulfate is a widely occurring inorganic salt in natural environments and industrial systems. In nature, calcium sulfate is one of the typical evaporite minerals, participating in salt lake sedimentation, diagenetic processes, and aqueous chemical cycling [1–4]. In industrial systems, calcium sulfate is the main phase of gypsum waste [5–7]. Calcium sulfate can undergo phase transformation under different temperatures, water activities, and solution chemistries [8–12]. The phase transformation process of the calcium sulfate system is not merely a mineralogical change; it also serves as an important basis for regulating the migration, release, and immobilization of impurities.

The regulation of impurity behavior through calcium sulfate phase transformation mainly involves two application directions. The first is impurity removal and resource recovery from calcium sulfate wastes. Numerous industrial processes generate by-product gypsum or neutralization gypsum, such as non-ferrous smelting, electroplating, phosphate fertilizer production, titanium dioxide manufacturing, and other chemical processes [6,13–15]. These wastes often contain hazardous metals or metalloids such as As, Cr, Cd, Pb, Cu, and Zn, as well as process impurities such as P, F, Fe, rare earth elements (REEs), silicates, organic matter, or radioactive components [5,15–22]. These impurities degrade the quality of calcium sulfate products and limit their utilization in building materials, agriculture, and other fields [15]. Conventional water washing and mechanical separation are generally only effective for water-soluble or weakly surface-bound impurities, and have limited efficacy for impurities that are encapsulated, co-precipitated, or incorporated into the crystal lattice [23–30]. By reconstructing the calcium sulfate matrix through phase transformation, the release, migration, or enrichment of impurities can be promoted, offering possibilities for the detoxification of hazardous gypsum waste and the recovery of metals [31–34]. The second direction is the immobilization of hazardous elements. In the second direction, hazardous elements such as Cr, Cd, Cu, Zn, and Se can be captured through calcium sulfate crystallization or recrystallization.

To date, numerous studies have been reported on calcium sulfate phase transformation or the treatment of calcium sulfate waste, but the discussions on these topics have often been rather scattered. In this context, the present review focuses on impurity regulation during calcium sulfate crystallization and phase transformation. First, the nucleation, growth, phase transformation behavior, and the occurrence of foreign ions in calcium sulfate are summarized. Then, the sources, impurity characteristics, and treatment challenges of typical calcium sulfate wastes are introduced, and studies on phase transformation-driven impurity removal, calcium sulfate purification, and resource utilization are reviewed according to waste type. Subsequently, the application of calcium sulfate crystallization in the immobilization of hazardous elements is discussed. Finally, the advantages, limitations, and industrial application potential of these methods are analyzed.

The literature search was primarily based on the Web of Science and Scopus databases, using keywords including “calcium sulfate”, “gypsum”, “phase transformation”, “crystallization”, “heavy metal”, “impurity removal”, “impurity extraction”, “resource recovery”, and “immobilization”. This review does not strictly limit the publication year or region. It mainly includes studies in which the crystallization or phase transformation of calcium sulfate directly influences the release, migration, recovery, or immobilization of impurities. Studies focusing solely on cement-based solidification/stabilization, general building material applications, or pure calcium sulfate systems without direct relevance to impurity regulation are not considered as the focus of this review.

2. Impurity Characteristics in Calcium Sulfate

2.1. Structure and Transformation of Calcium Sulfate

Calcium sulfate can be divided into three types of minerals according to the degree of hydration: gypsum (DH, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), bassanite (HH, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), and anhydrite (AH, CaSO_4). Details of crystal structures are provided in Text S1. Generally, the solid phase with the lowest solubility at a given temperature represents the stable phase. DH is stable at low temperatures, whereas AH is stable at high temperatures; HH remains metastable at all temperatures [35–39].

The nucleation of calcium sulfate from aqueous solution proceeds through at least two steps: (1) the formation of sufficiently large amorphous clusters and (2) the reorganization of the clusters into an ordered structure [1,40–43]. Numerous researchers have identified various disordered intermediate states during the nucleation process including amorphous matter [42,44], nanoclusters [45], oligomers [46,47], and dense liquid-like states [48]. Jia et al. [41] found that amorphous calcium sulfate gradually crystallizes and forms domains with single-crystal DH lattice fringes. The amorphous or disordered aggregate state is less kinetically constrained than the crystalline state and can be slowly arranged into more stable crystals [49,50]. The primary crystalline phase formed during precursor transformation depends on external conditions such as solution concentration, temperature, water activity, and pressure (Figure 1a) [51].

The conversion between different types of calcium sulfate in a liquid environment is mainly achieved by the dissolution–recrystallization process, where calcium sulfate is dissolved in water and the dissolved ions are recrystallized to form solid calcium sulfate again [50,52–63]. The dissolution of the solid phase provides a slightly supersaturated environment. However, the crystallization of HH or AH requires external factors such as temperature or pressure to drive the process [64–66]. Therefore, the dehydration of DH typically occurs at temperatures above 100 °C (Figure 1b). The dehydration reaction proceeds more efficiently when the water activity is below the equilibrium value at a constant temperature. This has been verified by a series of studies, for example, the transition temperature required for DH dehydration decreases with increasing concentration of substances in systems containing acids or organic matter [64–70]. In addition, the hydration processes of HH and AH also follow a dissolution–recrystallization mechanism [71–73].

The thermal dehydration of DH involves up to three steps. The DH phase transforms into HH, which has a smaller molar volume (74.53 cm³/mol for DH and 53.17 cm³/mol for HH) at temperature above 100 °C. In the next step, typically at 200–400 °C, HH can be completely dehydrated to γ -AH when residual water is removed from the porous structure through the vapor phase [53,54,56,59,60,62]. At temperatures above 400 °C, soluble γ -AH gradually transforms into stable insoluble β -AH, which in turn transforms into α -AH at temperatures above 1180 °C (Equations (1)–(3)) [74]. Some studies have shown that the thermal dehydration pathway is related to pressure [62,75–79]. Under low-pressure conditions, DH can directly dehydrate to γ -AH, while at pressures above 900 Pa, HH tends to appear as an intermediate phase.

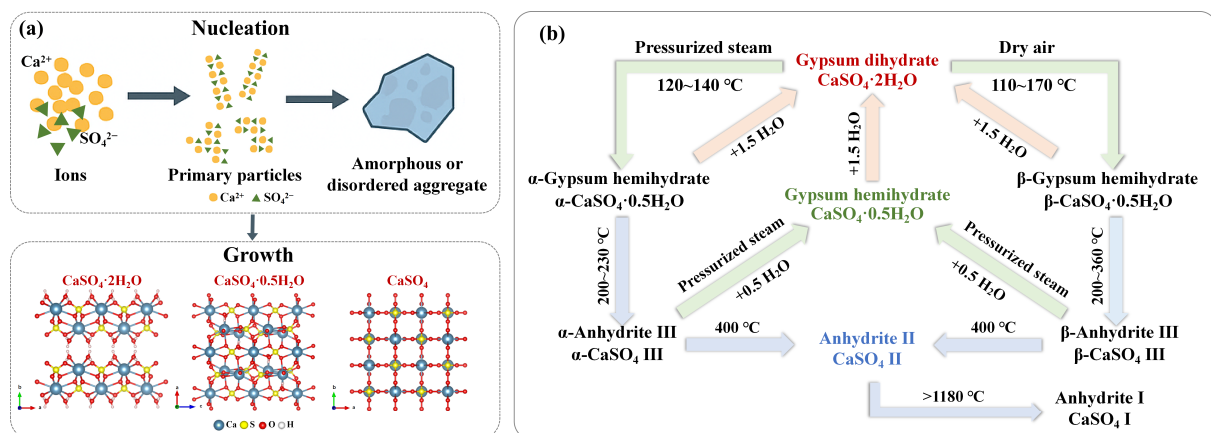
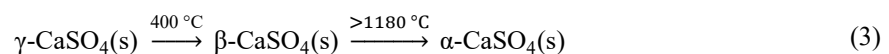
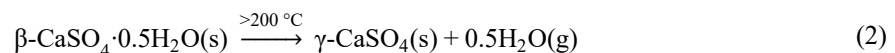
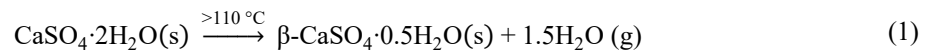


Figure 1. (a) Nucleation and growth of calcium sulfate; (b) transformation path of calcium sulfate system.

2.2. Impurity Occurrence and Incorporation in Calcium Sulfate

Based on crystal chemistry and mineralogy, impurity occurrence can be classified into three categories: surface adsorption, coprecipitation, and structural incorporation [23–30]. Among these, impurities adsorbed on the surface can be easily removed by washing with water, whereas physically encapsulated and coprecipitated impurities require the host phase to be disrupted for their release. However, once impurities replace the host ions and become part of the crystal structure, conventional methods (such as washing, leaching, or mechanical grinding) are often ineffective [23–25,28,29]. Therefore, determining the speciation of impurities in waste is beneficial for selecting appropriate treatment methods [20,80].

Impurities may enter the calcium sulfate lattice, and cations such as Cd^{2+} , Zn^{2+} , Sr^{2+} , K^+ , and Mg^{2+} may substitute for Ca^{2+} during the coprecipitation process because of their similar ionic radii (Table 1, Figure 2). In addition, the availability of Ca vacancies, local coordination constraints, and the lattice distortion induced by foreign ions may all influence incorporation into the calcium sulfate structure. Ke et al. [81] used dispersion-corrected density functional theory to investigate the adsorption and incorporation of Cd^{2+} in DH under aqueous conditions. They found that an increase in Ca vacancy defects promotes the incorporation of Cd^{2+} into the DH lattice. Ma et al. [82] reported that Zn^{2+} and Cd^{2+} mainly replace Ca^{2+}

in DH through isomorphous substitution at low pH, while Cu^{2+} may be incorporated into the water channels of the DH structure. The incorporation of trace Cu, Zn, and Cd was further confirmed by analysis of both natural gypsum and hydrometallurgical gypsum samples.

Anion substitution has also been widely reported. SO_4^{2-} can be replaced by other anions with similar coordination structures, such as CrO_4^{2-} , AsO_4^{3-} , HPO_4^{2-} and SeO_4^{2-} (Table 1, Figure 2). In HH, AsO_4^{3-} has been reported to adsorb on the surface and to substitute for SO_4^{2-} in the crystal lattice [83]. Using density functional theory calculations, Wang et al. [23] showed that HAsO_4^{2-} is preferentially incorporated into the DH lattice because this process is energetically more favorable than incorporation of AsO_4^{3-} . CrO_4^{2-} can theoretically replace SO_4^{2-} during DH crystallization because it has a similar tetrahedral geometry and ionic radius [28]. Zhang et al. examined As incorporation into DH over a range of pH values and initial arsenic concentrations and found that the DH structure can accommodate up to 23.7 mg/g of arsenic. Another study by Zhang et al. [84] proposed that strong coordination between Cr and DH surfaces induces local lattice distortion and promotes the formation of SO_4^{2-} vacancy defects. Jia et al. [85] found that HPO_4^{2-} readily adsorbs on gypsum surfaces during the formation of phosphogypsum, which leads to the gradual substitution of SO_4^{2-} by HPO_4^{2-} owing to their similarity.

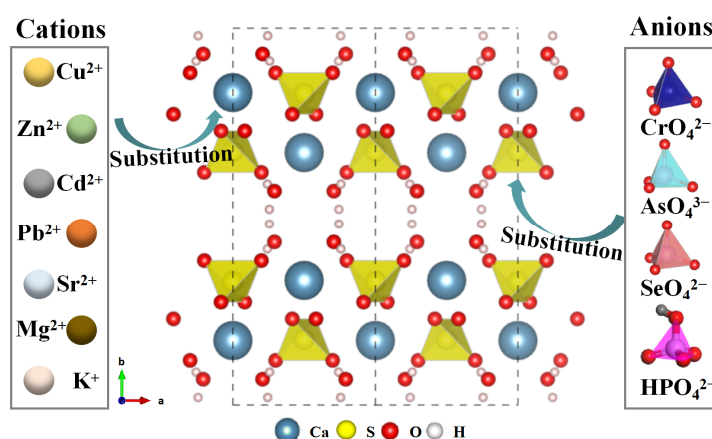


Figure 2. Lattice substitution of cations and anions in gypsum.

Table 1. Cations and anions that can substitute for Ca^{2+} and SO_4^{2-} in the gypsum lattice.

Cations		Anions		
Species	Ionic Radius (Å)	Species	Ionic Radius (Å)	Steric Configuration
Ca^{2+}	0.99	SO_4^{2-}	2.90	tetrahedral
K^{+}	1.38	CrO_4^{2-}	2.40	tetrahedral
Mg^{2+}	0.72	AsO_4^{3-}	2.48	tetrahedral
Cd^{2+}	0.96	HAsO_4^{2-}	2.70	tetrahedral-related
Zn^{2+}	0.72	PO_4^{3-}	2.30	tetrahedral
Sr^{2+}	1.12	HPO_4^{2-}	2.50	tetrahedral-related
Pb^{2+}	1.19	SeO_4^{2-}	2.43	tetrahedral

2.3. Typical Industrial Calcium Sulfate Wastes

Based on sources and impurity characteristics, the wastes discussed in this review are classified into two categories: heavy metal-bearing gypsum (HMBG) and industrial by-product gypsum (IBG). It should be noted that HMBG refers to calcium sulfate waste in which hazardous heavy metals (HMs) or metalloids pose the primary environmental risk, while IBG refers to chemical by-product gypsum for which the primary treatment objectives are calcium sulfate recovery and the removal of process-related impurities.

(1) Heavy metal-bearing gypsum (HMBG)

HMBG is mainly generated during the treatment of acidic wastewater or sulfur-containing flue gas from non-ferrous smelting, coal-fired power generation, electroplating, and related chemical industries [15,82,86,87]. HMBG typically contains high concentrations of toxic HMs and may be classified as hazardous waste depending on local regulations and leaching characteristics.

A major source of HMBG is flue gas desulfurization. Sulfur in the raw material converts to SO_x during high-temperature processing in non-ferrous metal smelting and coal combustion processes [15,31,88–93]. The lime-gypsum wet flue gas desulfurization process is widely used to remove SO_x , and the resulting desulfurization

gypsum may contain substances such as zinc (5–14%) and arsenic (0.01–0.2%). In China, the total volume of desulfurization gypsum residue containing Zn and other HMs has reached approximately 10 Mt [33]. Another important source is the neutralization of acidic wastewater. Depending on the composition of the pollutants and the neutralization process used, different types of HMBG may be formed. For example, when the As content is high, lime-iron salt, lime-aluminum salt, or sulfide-lime combined methods are typically used, generating arsenic-bearing gypsum (ABG) with As contents of about 0.3 to 20% [31,32,82,86,87,94]. China alone produces about 5.47 Mt of ABG per year [94]. Chromium-bearing gypsum (CBG) is generated during the neutralization of chromium-containing wastewater in electroplating and chromium salt production processes. The Cr content in CBG ranges from approximately 0.5% to 2.5% [22,28,95], and annual production exceeds 10 Mt [26,96]. The main types and basic characteristics of HMBG are summarized in Table 2, and detailed elemental compositions are provided in Table S1.

(2) Industrial by-product gypsum (IBG)

IBG is mainly generated as a by-product of chemical manufacturing processes. This review mainly discusses phosphogypsum (PG) and red gypsum (RG). Phosphogypsum (PG) is generated during the production of phosphoric acid in the phosphate fertilizer industry. Approximately 5 tons of PG are produced for every ton of phosphoric acid. Its chemical properties are similar to natural gypsum, though it is typically acidic and contains impurities such as phosphorus, fluorine, organic matter, HMs, and rare earth elements (REEs) [5,16–22]. RG is a calcium sulfate residue generated during titanium dioxide production by neutralizing acidic wastewater with lime or calcium carbide slag [5,17]. Its main impurities are iron, aluminum, and silicon. In China, the annual production of PG and RG has reached 70 and 28 million tons respectively [97]. Due to low utilization rates, PG and RG are typically stored in uncovered piles, which can contaminate surrounding soil and water bodies during rainy conditions [98]. The main types and basic characteristics of IBG are summarized in Table 2, and detailed elemental compositions are provided in Table S2.

Table 2. Summary of major impurity-bearing calcium sulfate wastes, including their sources, annual production, phase composition, and representative impurities.

Waste Type		Industry/Process	Annual Production Volume	Source	Typical Treatment Processes	Main Mineral Phase	Representative Impurities
Heavy metal-bearing gypsum	Arsenic-bearing gypsum	Nonferrous metal smelting	5.5 Mt	Neutralization of acidic wastewater and smelting wastewater, flue gas desulfurization	Lime-ferrous sulfate, Lime	Gypsum, Calcium arsenate, Arsenic-iron co-precipitate	As (0.3–20%)
	Zinc-bearing gypsum	Smelting	10 Mt	Neutralization of acidic wastewater, flue gas desulfurization	Lime	Gypsum, Zinc hydroxide, Silicate	Zn (5–14%)
	Chromium-bearing gypsum	Chromium salt production	10 Mt	Electrolyte treatment	Calcium chloride	Gypsum, Sodium chromate	Cr (0.6–2.5%)
Industrial by-product gypsum	Red gypsum	Titanium dioxide production	28 Mt	Neutralization of acidic wastewater	Lime	Gypsum, Ferric hydroxide, Ferrous sulfate	Fe (1–15%)
	Phosphogypsum	Phosphoric acid production	70 Mt	Wet-process phosphoric acid production	Sulfuric acid method	Gypsum	P (0.5–3%), REEs (0.01–0.5%), F (0.3–4%)

Note: “Representative impurities” refers to impurity components that are commonly reported.

3. Impurity Removal and Resource Recovery from Calcium Sulfate Solid Wastes

The suitable treatment pathway depends mainly on the impurity composition, impurity occurrence, and phase characteristics of the calcium sulfate matrix. This section discusses treatment methods for calcium sulfate wastes according to waste type. For each waste type, processes such as wet treatment, thermal treatment, and physically enhanced treatment are further described (Table 3).

- (1) Wet treatment: In wet treatment, calcium sulfate phase transformation is mainly driven by differences in the solubility of DH, HH, and AH under different temperatures and solution chemistry conditions [50,55,57,58,61]. During dissolution of the parent phase, impurities may be released into the solution (Figure 3). Subsequently, during the recrystallization, structural changes may prevent impurity elements originally incorporated into DH from being reincorporated into the newly formed HH or AH, thereby facilitating deep extraction.

- (2) Thermal treatment: Thermal dehydration can convert DH into HH or AH and produces internal defects and surface cracks in the calcium sulfate matrix, making it more porous and structurally fragile (Figure 4a) [8,64,99–102]. First, the increased porosity and specific surface area increase the contact area between impurities and the leaching solution, which can improve extraction efficiency in subsequent leaching steps. Second, during high-temperature treatment, some volatile impurity species (such as compounds containing arsenic, selenium, and mercury) may be partially released [53,54,56,59,60,62].
- (3) Physically enhanced treatment: Physical methods can improve impurity removal by reducing particle size, increasing surface defects, and accelerating phase transformation, thereby making impurity elements more accessible to the leaching solution (Figure 4b). This approach is particularly relevant for calcium sulfate wastes with densely packed structures. Physical enhancement is usually used together with wet and thermal treatment rather than as an independent process.

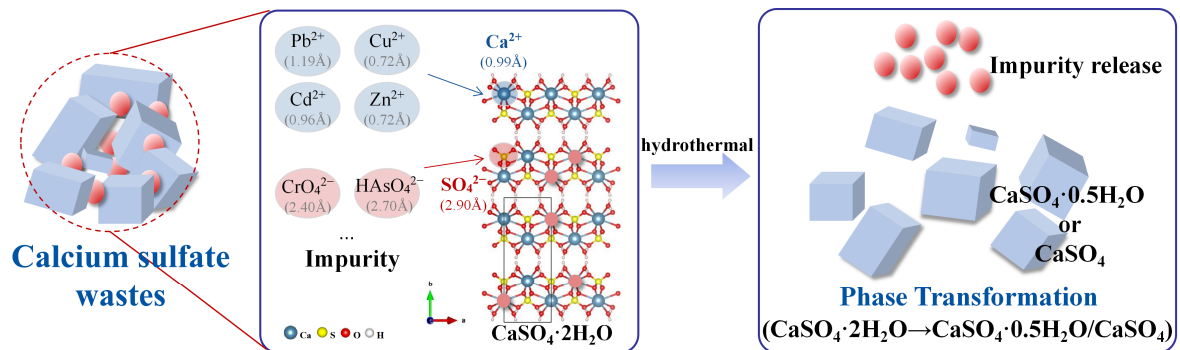


Figure 3. The mechanism of impurity extraction from calcium sulfate wastes via dissolution-recrystallization.

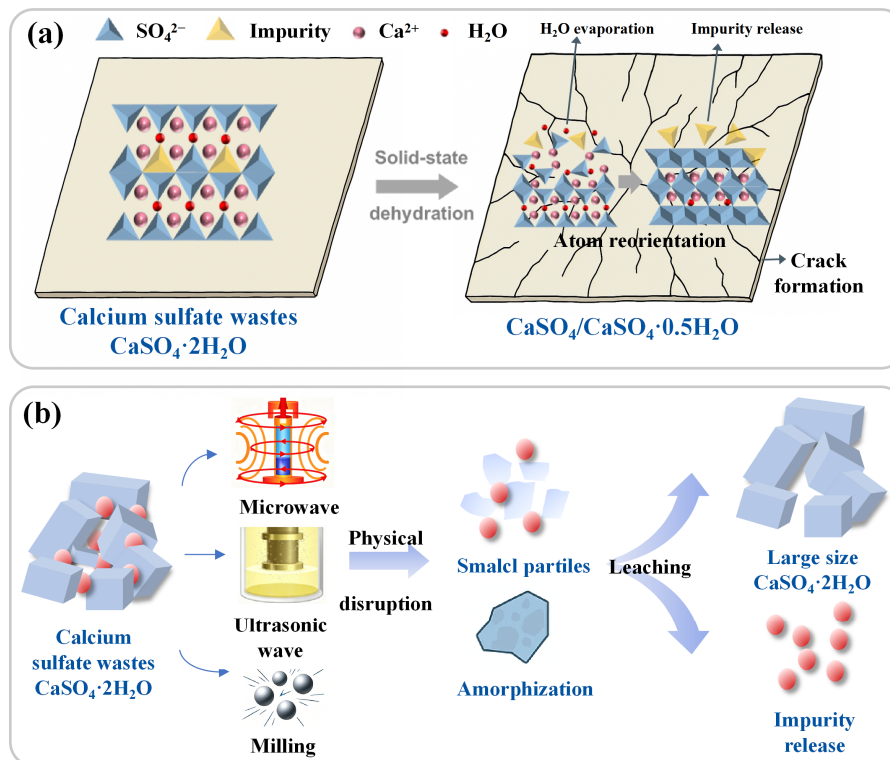


Figure 4. (a) Impurity extraction from calcium sulfate wastes using thermal dehydration; (b) The physical structural disruption promotes the regrowth of calcium sulfate crystals.

3.1. Heavy Metal-Bearing Gypsum

3.1.1. Chromium-Bearing Gypsum

The difficulty of extracting Cr from CBG is related to its chemical form. Extended X-ray absorption fine structure (EXAFS) analysis at the Cr K-edge revealed that chromate (CrO_4^{2-}) can tightly bind to the calcium sulfate lattice by substituting for SO_4^{2-} [28], indicating that chromium in CBG primarily exists as a structurally

incorporated impurity. In contrast, dichromate ($\text{Cr}_2\text{O}_7^{2-}$) interacts more weakly with the calcium sulfate structure, making it more prone to release during phase transformation and less prone to reincorporation [22,28,96]. For this reason, effective Cr extraction requires not only phase transformation of the calcium sulfate matrix but also conversion of lattice-compatible chromate species into less compatible dichromate species.

Liu et al. [28] used $\text{K}_2\text{S}_2\text{O}_8$ under hydrothermal conditions to promote the dehydration of DH to form AH, thereby achieving deep extraction of incorporated CrO_4^{2-} . The free radicals generated during the decomposition of $\text{K}_2\text{S}_2\text{O}_8$ further promoted the conversion of CrO_4^{2-} to $\text{Cr}_2\text{O}_7^{2-}$, reducing its affinity for the calcium sulfate surface. Subsequently, the rehydration of AH back to DH further promoted the release of chromium, leading to an extraction efficiency exceeding 99.5%. Additionally, Zheng et al. [103] found that the H^+ ions generated during the decomposition of $\text{K}_2\text{S}_2\text{O}_8$ lower the pH of the solution and cause the valence state of Cr to change from CrO_4^{2-} to $\text{Cr}_2\text{O}_7^{2-}$. Acidic conditions also accelerate the dissolution of DH and promote the growth of AH crystals. Both of the above effects facilitate the release of Cr from CBG.

Zhong et al. [22] also observed the selective exclusion of Cr during the transformation from DH to AH. They investigated the doping behavior of various HM ions during the DH-to-AH transformation. The results showed that CrO_4^{2-} inhibits the growth of normal AH crystals, causing crystal growth along the c-axis. More importantly, the CrO_4^{2-} content in AH is significantly lower than that in DH. This property was later applied to a high-pressure CO_2 treatment system, in which a Cr removal efficiency of up to 99.6% was achieved through multiple dehydration and rehydration cycles between DH and AH. Although most studies have focused on the DH $\rightarrow$ AH route, other transformation pathways may also promote Cr extraction. Liao et al. [96] indicated that the DH $\rightarrow$ HH transformation appears to be more favorable for the release of Cr from CBG. Microwave-assisted processing can selectively dehydrate DH to HH within 10 min, achieving a Cr extraction efficiency of over 99%. Compared to AH, HH has a more open channel structure, which may facilitate faster release of impurities.

Zheng et al. [104] found that the leaching efficiency of impurities from HMBG increased when DH was dehydrated to form HH and then rehydrated back to DH. In particular, the extraction efficiencies of Cr and Cd reached 99.9% and 98.8%, respectively, and the extraction rates of trace metals such as Pb, Zn, Hg, and As were all greater than 98.5%. During dehydration, the loss of water molecules triggered the first rearrangement of localized atoms and excluded the partially bound metals from the HH lattice. The subsequent rehydration completely releases the trapped HMs.

3.1.2. Arsenic-Bearing Gypsum

Under acidic conditions, the reduced ability of arsenate to replace sulfate makes it more likely to remain in the liquid phase. However, some of the dissolved As may also remain on the newly formed crystals as surface-adsorbed impurities. To address this issue, Chen et al. [86] introduced a seed-induced strategy for crystal control during the DH-to- α -HH phase transformation. The added seed promoted the growth of large, short, columnar α -HH crystals, which had reduced specific surface area, minimizing surface adsorption of dissolved As species by α -HH. Ma et al. [82] achieved a 99.9% As extraction efficiency by hydrothermally treating ABG in concentrated hydrochloric acid. The acidic hydrothermal environment promotes the conversion of DH to AH, while the high acid concentration converts the released arsenate to H_2AsO_4^- or H_3AsO_4 . The alteration of the arsenate anion species causes distortion of the tetrahedral geometry, reducing its ability to bind to the calcium sulfate lattice [23]. Several studies have investigated the efficient extraction of arsenic by utilizing the transformation of arsenate species [23,82,86].

Jia et al. [105] studied the distribution of arsenate during the DH-to- α -HH phase transformation and confirmed that both increasing temperature and decreasing pH inhibit the incorporation of arsenate into the α -HH lattice. Most of the methods described above rely on elevated temperatures or large volumes of aqueous solution. More recently, lower-energy approaches have been explored by adjusting local thermodynamic conditions. For example, Li et al. [83] developed a nanoscale sulfuric acid film strategy for arsenic extraction under near-ambient conditions at 30 °C. Evaporation of free water concentrated the acid film on the solid surface, creating a local microenvironment with low water activity that drove the DH-to-AH transformation without external heating. At the same time, the high proton concentration in the film converted released arsenate into H_3AsO_4 , preventing its reincorporation into newly formed AH crystals. This approach achieved an arsenic removal efficiency of 99.6% with substantially lower chemical and energy inputs.

3.1.3. Other Heavy Metal-Bearing Gypsum

In addition to CBG and ABG, calcium sulfate phase transformation can also regulate impurity release from other types of HMBG. Li et al. [106] treated beryllium-containing gypsum using a sulfate-assisted hydrothermal

method, in which beryllium compounds were encapsulated in DH and amorphous silica. Under such conditions, DH dissolved and recrystallized into large columnar AH crystals, releasing the encapsulated beryllium into the solution. Acidic conditions prevent the released beryllium from reincorporating into the newly formed calcium sulfate phase. Weng et al. [107] used mechanical grinding to reduce the particle size of DH in HMBG from approximately 10 μm to less than 50 nm. This process induced a solid-state transformation of DH into HH and promoted the dissolution and recrystallization rates. Chemical additives were then added to form complexes or precipitates with the released metal ions, thereby preventing them from re-incorporating into the newly formed calcium sulfate. The extraction efficiencies for P, Cr, As, Sr, Cd, and Hg all exceeded 94.0%, with As and Hg achieving extraction efficiencies of 99.8% and 99.2%, respectively.

The phase transformation of calcium sulfate can also promote the physical separation of encapsulated impurities. For example, Chai et al. [108] found that ZnS particles encapsulated in neutralized sludge tend to aggregate on the surface of calcium sulfate, hindering the efficiency of subsequent flotation. By inducing the hydration of HH to DH, the crystal length increased from 10 μm to over 100 μm , causing the encapsulated ZnS particles to be released and more easily separated by physical screening. Guan et al. [109] treated lithium-bearing gypsum containing fine aluminosilicate impurities with sodium chloride under hydrothermal conditions, increasing its whiteness to 86.3%. During the conversion of DH to α -HH, the aluminosilicate impurities were released. Meanwhile, the introduction of sodium succinate as a crystal modifier promoted the formation of larger, short-prismatic α -HH crystals with a smaller specific surface area. These crystals settled faster than the fine aluminosilicate particles and could be separated by gravitational sedimentation.

3.2. Industrial By-Product Gypsum

3.2.1. Phosphogypsum

(1) Extraction of REEs

REEs in PG substitute for Ca^{2+} in the DH lattice [110]. During the transformation from DH to HH, REEs and [110] P be released simultaneously [30,111]. However, α -HH typically forms fine needle-like crystals during the transformation, which have a large specific surface area. This promotes the readsorption of REEs and consequently reduces extraction efficiency [19,20,80,111]. Therefore, controlling the crystal morphology of HH during the phase transformation process is crucial for improving the recovery rate of REEs.

Guan et al. [111] used EDTA-2Na as a crystal modifier for the conversion of PG to α -HH in sulfuric acid solution. The modifier selectively adsorbed on the end planes of α -HH crystals, promoting the formation of coarse short columnar crystals with a smaller specific surface area. This morphological control prevented the readsorption of dissolved REEs and improved leaching efficiency. Lu et al. [19] recovered REEs from PG under subcritical water conditions in dilute hydrochloric acid. Under these conditions, PG rapidly transformed from the DH phase to the AH phase. The low viscosity and low dielectric constant of subcritical water enhanced mass transfer during the dissolution-recrystallization process and prevented the recombination of REEs and AH crystal, achieving extraction efficiencies close to 100% for elements such as yttrium and cerium.

Physical enhancement methods have also been used to treat PG [112,113]. Lambert et al. [113] used microwave heating to extract REEs from PG, achieving a 20% improvement in extraction efficiency. Under microwave irradiation, as DH was converted to HH or AH, the lattice water was rapidly removed, creating microcracks and pores on the particle surface, thereby increasing the reaction surface area. Similarly, Rychkov et al. [20] used mechanical grinding and ultrasonic impact to reduce the particle size of PG from 500 μm to 0.1–5 μm , achieving an extraction rate of over 70% for REEs.

(2) Extraction of Phosphorus Impurities

Phosphorus in PG typically exists in three forms: soluble P (H_3PO_4 , H_2PO_4^- , HPO_4^{2-}), co-crystal P ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), and insoluble P [114–116]. Among these, soluble P can be easily removed by water washing, while insoluble P is relatively stable. Co-crystal phosphorus, on the other hand, is more difficult to remove and is gradually released during the weathering of PG.

Guan et al. [18] used hydrothermal treatment combined with seed-assisted crystallization to extract co-crystal P, achieving an extraction efficiency of 82.31%. The acidic environment not only promoted the conversion of DH to HH but also converted the released HPO_4^{2-} into H_3PO_4 , thereby inhibiting its reincorporation into the HH lattice. The crystal seeds promoted the growth of large, short-columnar α -HH crystals with a small specific surface area, reducing the probability of phosphorus species readsorption. He et al. [116] used a two-step phase transformation ($\text{DH} \rightarrow \alpha\text{-HH} \rightarrow \text{DH}$) in concentrated sulfuric acid to purify PG for use as a cement retarder. This transformation released co-crystal P into the liquid phase in the first step, and the subsequent rehydration process further purified

the DH crystals. Guan et al. [117] used a NaCl-HCl solution to convert PG into large α -HH crystals with a small specific surface area. During the phase transformation, 89.1% of co-crystallized P was released (89.1%). Ma et al. [118] used a CaCl_2 solution at 97 °C to convert PG into α -HH. This process reduced the P impurity content to $0.18 \pm 0.03\%$ and achieved a whiteness of 93.5 ± 0.4 . During the transformation, the introduction of inorganic or organic components led to their preferential adsorption or doping on the side facets of calcium sulfate, forcing the crystals to grow along the c-axis and resulting in a high aspect ratio [119–121]. The increased aspect ratio enhanced the elastic modulus, heat resistance, and tensile strength of the α -HH material.

(3) Extraction of fluorine impurities

The speciation of fluorine in PG determines its removal difficulty. Previous studies have shown that fluorine is mainly distributed in the DH phase, with a small amount present in associated minerals (such as potassium silicate and calcium aluminate minerals), and some in soluble form. When the pH is higher than 2, soluble F tends to react with Ca^{2+} to form insoluble CaF_2 , which increases the difficulty of removal [122,123]. Therefore, in the wet-process phosphoric acid production system and the PG purification process, a lower pH helps keep F in a soluble state, which improves the efficiency of subsequent washing [122,124].

It should be noted that simple water washing or acid washing is usually insufficient for the deep removal of F that is coprecipitated in or adsorbed on the inside of crystals. In contrast, the phase transformation of calcium sulfate, such as $\text{DH} \rightarrow \alpha\text{-HH}$ or $\text{HH} \rightarrow \text{DH}$, is accompanied by a dissolution-recrystallization process, which can promote the transfer of coprecipitated or incorporated impurities into the liquid phase and thus achieve deeper defluorination [124,125]. For example, Chen et al. [125] found that during hydration under acidic conditions, the HH phase in PG can transform into larger rhombic particles, with water-soluble P, co-crystallized P, and soluble fluorine were transferred into the liquid phase, with removal rates exceeding 85% for all three. Li et al. [126] and Yi et al. [127] used the $\text{DH} \rightarrow \alpha\text{-HH}$ pathway to achieve the synergistic removal of P and F impurities (both greater than 90%). Dong et al. [124] further confirmed through XRD, XPS, and FT-IR that the “dissolution-crystallization” reaction during the $\text{HH} \rightarrow \text{DH}$ transformation enhances fluoride leaching.

In addition, thermal treatment can also achieve partial removal of F. However, impurities compatible with the AH or HH structure may remain in the solid phase, reducing the treatment efficiency of thermal methods. Li et al. [128] found that β -HH obtained by calcining PG could remove structural water effectively, but impurities such as P and F remained. Some studies have also shown that during high-temperature calcination at 500–800 °C, harmful impurities in PG can be converted into inert compounds [129]. These inert products tend to adhere to the crystal faces of AH, leading to crystal defects [130]. Although such deposits may enhance hydration activity, the compressive strength of AH may decrease when the content of inert impurities exceeds a certain threshold, thereby affecting the performance of the calcium sulfate product [16].

3.2.2. Red Gypsum

Iron in RG exists in two forms: a coprecipitated form, where iron is adsorbed onto the calcium sulfate surface as amorphous oxides or hydroxides; and a structurally incorporated form, where iron substitutes for Ca^{2+} within the crystal lattice. Therefore, it is necessary to both transform the coprecipitated form into a soluble species and control the morphology of the recrystallized crystals to make them less prone to adsorption. Peng et al. [5] treated RG using a hydrochloric acid hydrothermal method, achieving an iron extraction efficiency of over 99.0%. The acidic environment provided by hydrochloric acid facilitates the dissolution of iron oxides and hydroxides into soluble Fe^{3+} , while the newly formed AH crystals have a smooth and dense surface that effectively limits iron readsorption. Chen et al. [17] treated RG with concentrated sulfuric acid under hydrothermal conditions to promote the conversion of DH to AH, and subsequently recovered iron (96.44%) via a stepwise precipitation method. Du et al. [131] used density functional theory calculations to demonstrate that Fe^{3+} can substitute for Ca^{2+} in α -HH, and that the extraction efficiency through this pathway is lower than that achieved through conversion to AH. Furthermore, the substituted Fe^{3+} increases the adsorption energy of the crystal modifier on the (111) plane of α -HH, inhibiting crystal growth along the c-axis and ultimately resulting in short, columnar crystals.

Table 3. Impurity removal and resource recovery from calcium sulfate wastes assisted by phase transformation.

Waste Type	Impurity	Speciation	Content (%)	Treatment Condition	Removal Efficiency/Product Index	Phase Transformation	References	
Heavy metal-bearing gypsum waste	Cr-bearing gypsum	Cr	Incorporation	0.57%	K ₂ S ₂ O ₈ (0.5 mol/L), 120 °C, S/L = 1:1, 12 h	99.5%	DH → AH → DH	[28]
		Cr	Incorporation	0.63%	HCl (0.2 mol/L), H ₂ SO ₄ (0.2 mol/L), 110 °C, S/L = 1:1, 12 h	≥99.8%	DH → AH	[103]
		Cr	Incorporation	0.66%	5 MPa CO ₂ , 120 °C, S/L = 2:1, 24 h	≥99.6%	HH/DH → AH → DH	[22]
		Cr	Incorporation	2.30%	H ₂ SO ₄ (0.1 mol/L), 110 °C, S/L = 1:5, 10 min	≥99.0%	DH → HH	[96]
	As-bearing gypsum	As, Cu, Zn, Pb	Incorporation	0.067–1.81%	H ₂ SO ₄ and HCl (0.5 mol/L), 120 °C, S/L = 1:1, 12 h	As 99–100%, Cu, Zn, Pb > 90%	DH → AH	[82]
		As	Incorporation	2.26%	H ₂ SO ₄ (30%), S/L = 5:1, 30 °C, 24 h	99.6%	DH → AH	[83]
		As	Incorporation	0.27–0.41%	Na ₂ SO ₄ -H ₂ SO ₄ (pH = 2), S/L = 1/5, 95 °C, 75 min	92.45%	DH → HH	[86]
	Zn-bearing gypsum	ZnS	Coprecipitation	14.30%	60 °C, 4 h	90.66%	AH → DH	[108]
	Li-bearing gypsum	Si, Al	Coprecipitation	3.44–6.87%	NaCl, 94 °C	whiteness of 86.3%	DH → HH	[109]
	Be-bearing gypsum	Be	Coprecipitation and incorporation	0.14%	H ₂ SO ₄ (0.5 mol/L), S/L = 1:5, 120 °C, 24 h	95.82%	DH → AH	[106]
Heavy metal-bearing gypsum	Cr, Cd, Pb, Zn, Hg, As	Incorporation	0.54%, 0.06%, 0.19%, 0.30%, 0.75%, 1.61%	Calcination + H ₂ SO ₄ leaching	>98.5 %	DH → HH → DH	[104]	
Heavy metal-bearing gypsum	As, Hg	Incorporation	1.61%, 0.74%	ball mill + water leaching	90.85% As and 97.30% Hg	DH → HH → DH	[107]	
Industrial by-product gypsum	Phosphogypsum	REEs	Incorporation	0.021%	EDTA-2Na (0.5%), S/L = 1:10, 95 °C, 2 h	59.3%	DH → HH	[111]
		REEs	Incorporation	0.028%	HCl (0.1 mol/L), S/L = 10:1, 125–150 °C, 10 kg/cm ² , 5 min	96.58–100%	DH → AH	[19]
		REEs	Incorporation	/	250 g ion exchange resin/kg	40%	HH → DH	[132]
		REEs	Incorporation	/	H ₂ SO ₄ film	~100%	DH → AH	[133]
		P	Incorporation	0.34%	CaCl ₂ (0.2 mol/L), S/L = 1:5, 95 °C, 2 h	82.31%	DH → HH	[18]

Table 3. Cont.

Waste Type	Impurity	Speciation	Content (%)	Treatment Condition	Removal Efficiency/Product Index	Phase Transformation	References
Industrial by-product gypsum	P	Incorporation	0.02%	H ₂ SO ₄ (30%), S/L = 1:7, 90 °C, 90 min	98.00%	DH → HH → DH	[116]
	P	Incorporation	0.45%	K ₂ S ₂ O ₈ (0.3 mol/L), S/L = 1:5, 120 °C, 12 h	>80%	DH → AH	[6]
	P	Incorporation	0.86%	15% NaCl (15%) and HCl (0.4 mol/L), S/L = 1:5, 95 °C, 120 min	89.1%	DH → HH	[117]
	P, F	Coprecipitation	0.12% and 0.043%	Water washing, S/L = 1:3, 60 °C, 25 min	86.4% and 95.71%	HH → DH	[134]
	P, F	Coprecipitation	1.48% and 0.35%	H ₂ SO ₄ (5%), S/L = 1:3, 89 °C, 100 min	74.95% and 90.91%	DH → HH/AH	[127]
	P, F	Coprecipitation	0.61% and 0.85%	H ₂ SO ₄ (2%) and H ₃ PO ₄ (1.5%), S/L = 1:3, 95 °C, 4 h	~100%	DH → HH	[126]
	REEs	Incorporation	0.03–0.4%	Microwave Treatment + HCl leaching	80% Nd, 99% Y, and 99% Dy	DH → AH/HH → DH	[113]
	P, REEs	Incorporation	0.14%, 0.026%	Microwave Treatment + H ₂ SO ₄ leaching	87.0% P and ~100% REEs	DH → AH/HH	[112]
	REEs	Incorporation	0.43–0.52%	Ultrasonic impact + H ₂ SO ₄ leaching	>70%	DH → DH	[20]
	Fe	Coprecipitation and incorporation	4.44%	HCl (1.5 mol/L), 140 °C, S/L = 1:10, 6 h	≥99.0%	DH → AH	[5]
	Fe	Incorporation	8.20%	CaCl ₂ (23%), S/L = 1:4, 95 °C, 150 min	77.40%	DH → HH	[131]
	Fe	Incorporation	3.18%	Na ₂ SO ₄ (8%) + maleic acid (0.12%), S/L = 1/5, 95 °C, 2 h	81.5%	DH → HH	[135]
	Fe	Coprecipitation and incorporation	16.04%	H ₂ SO ₄ (35%), 85 °C, 2 h	96.44%	DH → AH	[17]

4. Immobilization Applications of Calcium Sulfate Crystallization

The slow nucleation and crystallization of calcium sulfate allow foreign ions to enter the growing crystal lattice through isomorphous substitution. Therefore, controlled recrystallization can be used not only for impurity extraction but also for impurity immobilization. This mechanism has been studied in two main contexts: the immobilization of HMs during thermal treatment of hazardous sludge and the removal of toxic ions from industrial wastewater.

Zhang et al. [84] added AH to dyeing sludge ash to capture Cr. During the incineration of dyeing sludge, HMs can volatilize and become mobile in the produced ash. The calcium sulfate formed during sulfur fixation can capture HMs through structural incorporation. During the leaching process, the added AH initially transformed into HH and subsequently into DH. Cr was first adsorbed onto the surface of the newly formed DH crystals and then replaced the sulfate ions in the lattice. Du et al. [136] investigated the capture of Cu^{2+} and Zn^{2+} by externally added AH in dyeing sludge ash. Cu^{2+} and Zn^{2+} enter the interlayer regions of AH crystals, causing expansion of specific crystal planes. This substitution may lead to lattice contraction because Cu^{2+} and Zn^{2+} have smaller ionic radii than Ca^{2+} . During this process, some of the crystalline AH also transforms into an amorphous sulfate phase. Dai et al. [137] incinerated dyeing sludge with rice husks, directly generating crystalline AH in the bottom ash to capture HMs. The formed AH, together with silicoaluminate minerals, immobilized Cu^{2+} and Zn^{2+} . However, dissolution of the AH phase under strongly acidic conditions can release the immobilized HMs back into solution. This suggests that immobilization via structural incorporation may be reversed when the host calcium sulfate phase dissolves. The selectivity of structural incorporation during calcium sulfate phase transformation has also been reported for Cd^{2+} . Li et al. [138] found that, at the mineral-solution interface, the phase transformation from DH to AH selectively enriches Cd^{2+} while repelling coexisting Cu^{2+} and Zn^{2+} ions. The partition coefficient of Cd^{2+} is significantly higher. This selectivity is attributed to changes in the free energy of ion desolvation during the phase transformation, which reduces the energy barrier for Cd^{2+} to incorporate into the AH lattice.

The same mechanism has been applied to the removal of Se from industrial wastewater, such as acid mine drainage and metallurgical wastewater. Wang et al. [139] further confirmed the effectiveness of structural incorporation in an Fe- and Ca-mediated coprecipitation system. Se(IV) replaces sulfate ions in the DH lattice, causing the unit cell to expand slightly due to the larger ionic radius of SeO_3^{2-} compared to SO_4^{2-} . This structural incorporation enables Se-containing gypsum to resist secondary leaching. The preference of Se(IV) over Se(VI) for incorporation into the DH lattice has also been studied. Lin et al. [11] found that SeO_3^{2-} substitutes for sulfate more readily than SeO_4^{2-} . This was attributed to a closer structural match between SeO_3^{2-} and SO_4^{2-} , and to the higher stability of calcium selenite complexes. This selectivity is important, as Se(IV) is about five to ten times more toxic than Se(VI). In contrast, Das et al. [140] showed that the coprecipitation of SeO_4^{2-} with DH does not provide a permanent immobilization mechanism under sulfate-rich conditions. The DH precipitate dissolved rapidly within 24 h, releasing the coprecipitated SeO_4^{2-} back into solution, consistent with the higher solubility of $\text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$ ($\log K_{\text{sp}} = -3.09$) compared with DH ($\log K_{\text{sp}} = -4.58$). These results show that the stability of Se immobilization by DH depends strongly on Se speciation.

5. Practical Considerations

The previous sections discussed two types of application directions based on calcium sulfate crystallization or phase transformation. For calcium sulfate waste, the key question is whether impurities can be effectively released and separated. For immobilization systems, the key question is whether the immobilized elements can remain stable under long-term environmental exposure.

5.1. Selection of Treatment Methods for Calcium Sulfate Waste

Overall, thermal treatment does not require large amounts of acid or salt solutions, and it is easier to integrate with existing calcination equipment (such as rotary kilns or fluidized-bed calciners). However, it may release non-target elements and cause a decrease in selectivity. Physical enhancement methods are generally more suitable as supplementary measures to increase the probability of contact between impurities and the leachate by reducing particle size and increasing defects.

Wet treatment is more suitable for impurities incorporated into the crystal lattice and for systems that require simultaneous production of high-value calcium sulfate products. Its main limitations are the requirement for large amounts of acid and salt solutions, and the generation of wastewater that still requires secondary treatment. In addition, hydrothermal or pressurized conditions increase equipment and operation costs. The nanoscale sulfuric acid film approach developed by Li et al. [83] and Gou et al. [133] can effectively remove impurities from HMBG at room temperature, but it has so far been validated only on a gram scale. Furthermore, this method appears to

require relatively dry feed solids. For many calcium sulfate wastes precipitated from wastewater, moisture typically remains after dewatering (usually around 5–20%, depending on the source and processing conditions). Therefore, the applicability of this strategy to wet calcium sulfate wastes remains unclear.

5.2. The Limitations and Potential Risks of Immobilization

In the case of multi-metal systems, co-existing ions may compete for lattice sites and affect the stability. It cannot be assumed that all HMs can simultaneously enter and become immobilized within the calcium sulfate lattice. Short-term laboratory leaching tests may not fully reflect the behavior of the stabilized material during weathering, matrix dissolution, or microbially mediated transformation. Consequently, the risk of secondary release over the long term remains uncertain.

6. Conclusion and Outlook

6.1. Conclusions

This review focuses on impurity removal and immobilization strategies based on the phase transformation of calcium sulfate. The phase transformation pathways discussed in this review can be applied to different impurity management scenarios. In calcium sulfate waste, the phase transformation pathway is primarily used to release impurities from the parent phase, recover valuable elements, and purify the calcium sulfate product. Alternatively, the crystallization process of calcium sulfate can also be used to incorporate harmful ions into the calcium sulfate structure for the capture and immobilization of impurities.

6.2. Outlook

Although calcium sulfate phase transformation has shown clear promise for impurity removal and immobilization, several issues still need to be resolved before these approaches can be translated into reliable industrial technologies. Future work should pay particular attention to the following directions.

- (1) Establish a clearer relationship between impurity forms and process selection.

Existing research indicates that surface-adsorbed, coprecipitated, and structurally incorporated impurities exhibit distinctly different behaviors during phase transformation. However, in actual calcium sulfate waste, these forms often coexist, and their relative abundances are rarely quantified. In the future, advanced characterization techniques will be needed to identify impurity forms more quickly and to establish a mapping relationship between the forms and the selection of treatment methods.

- (2) Multicomponent impurity coupling during calcium sulfate recrystallization.

Most current research focuses on a single target impurity. Strong coupling between impurities is highly likely to occur during the processing. A reasonable hypothesis is that, during the recrystallization of calcium sulfate, coexisting impurities may compete for similar lattice incorporation sites, thereby affecting the degree of incorporation. Multicomponent impurities may also alter the local solution chemistry and hydration environment at crystal boundaries, affecting crystal nucleation and phase transformation kinetics, and ultimately influencing the distribution of impurities between the solid and liquid phases.

- (3) Develop more universal processing methods

Currently, many methods rely on high liquid-to-solid ratios or hydrothermal treatment. Although these methods are highly effective on a laboratory scale, such process conditions may be difficult to adopt in industrial production due to issues such as reagent consumption, wastewater generation, and energy requirements. More mild treatment methods should be developed.

Overall, the field still has substantial room for development. Calcium sulfate phase transformation based treatment is likely to become a more practical option for the detoxification, purification, and resource utilization of calcium sulfate wastes.

Supplementary Materials

The additional data and information can be downloaded at: <https://media.scilit.com/articles/others/2607311508220886/ESG-26050060-SI.pdf>. Refs. [142–167] are cited in the supplementary materials.

Author Contributions

J.L.: investigation, conceptualization, writing—original draft preparation; L.L.: supervision, writing—reviewing and editing; C.W.: investigation, writing—reviewing and editing; J.Q.: investigation, data curation; Z.X.: investigation; L.J.: writing—reviewing and editing; C.Y.: validation; X.L.: validation, writing—reviewing and editing; W.L.: supervision, writing—reviewing and editing; Z.L.: conceptualization, supervision. All authors have read and agreed to the published version of the manuscript.

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