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Influence of disodium hydrogen phosphate dodecahydrate on hydrothermal formation of hemihydrate calcium sulfate whiskers

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ABSTRACT

The influence of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ on the hydrothermal formation of hemihydrate calcium sulfate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) whiskers from dihydrate calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) at 135°C was investigated. Experimental results indicate that the addition of phosphorus accelerates the hydrothermal conversion of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ via the formation of $\text{Ca}_3(\text{PO}_4)_2$ and produces $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers with thinner diameters and shorter lengths. Compared with the blank experiment without $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, the existence of minor amounts (8.65×10^{-4} – 4.36×10^{-3} mol/L) of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ led to a decrease in the diameter of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers from 1.0–10.0 to 0.5–2.0 μm and lengths from 70–300 to 50–200 μm .

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1. Introduction

Non-toxic, low cost, and environmentally friendly (Freyer & Voigt, 2003; Imahashi & Miyoshi, 1994; Xu, 2005) calcium sulfate whiskers are used widely as the filler or reinforcing material in plastics, rubber, paper-making, cement, and so on (Wang, Han, Yuan, & Qiao, 2005; Wang & Li, 2006; Zhu, Xu, Chen, & Li, 2010). Much research has reported on the hydrothermal formation of calcium sulfate whiskers over the last ten years. For example, using $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ formed by co-precipitation from CaCl_2 and Na_2SO_4 solutions as the precursor, Luo, Li, Xiang, Li, and Ning (2010) studied the influence of temperature on the formation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers and found that at 130 – 160°C , whiskers were produced via the dissolution-precipitation route. Yuan, Wang, Han, and Yin (2008) reported on the hydrothermal formation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers with a diameter of 0.19 – $2.3 \mu\text{m}$ and length of 70 – $100 \mu\text{m}$ at 120 – 140°C , using natural gypsum with high purity and fine particles (diameter smaller than $18 \mu\text{m}$) as the raw material. However, the process is costly because a long grinding time is required for the gypsum ore. Xu, Li, Luo, and Xiang (2011) reported on the formation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers from CaCO_3 -bearing desulfurization gypsum via the acidification-hydrothermal route. They

found that acidification rather than sintering of the desulfurization gypsum favored the removal of CaCO_3 and the formation of active $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, which promoted the subsequent hydrothermal formation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers with high aspect ratio.

Some researchers studied the influence of organic surfactants amino trimethylene phosphonic acid (ATMP), cetyltrimethyl ammonium bromide (CTAB), 1,2-dihydroxybenzene 3,5-disulfonic acid (DHBDSA), a mixture of C_6 – C_{22} sorbitan esters (CMR-100), citric acid (TCA), sodium dodecyl sulfate, cetyl pyridinium chloride (CPC) and so on or inorganic ions such as Al^{3+} , Mg^{2+} , and SO_4^{2-} on the formation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ by mixing $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ and H_2SO_4 at 80°C . The presence of CTAB, DHBDSA, CMR-100, CPC, Al^{3+} , and SO_4^{2-} favored the formation of plate- or column-like $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals with large size, while the addition of ATMP and TCA decreased the crystal size (Abdel-Aal, Rashad, & El-Shall, 2004; El-Shall, Abdel-Aal, & Moudgil, 2000; Mahmoud, Rashad, Ibrahim, & Abdel-Aal, 2004; Rashad, Baioumy, & Abdel-Aal, 2003; Rashad, Mahmoud, Ibrahim, & Abdel-Aal, 2004, 2005; Singh & Middendorf, 2007). Former studies reveal that the growth environment, structure and surface properties of the crystals varied with the addition of organic or inorganic additives, which led to a change in nucleation and growth speeds and produced crystals with different shapes.

This paper reports on an alternative way to produce $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers with high aspect ratio by co-precipitation of CaCl_2 and Na_2SO_4 solutions at room temperature followed by hydrothermal treatment of the slurry in the presence of minor

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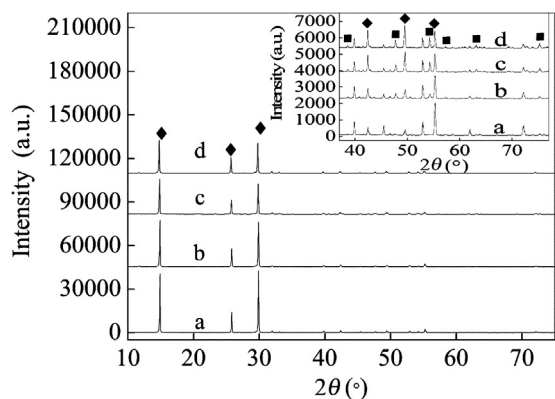


Fig. 1. Influence of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ on XRD spectra of hydrothermal products. $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (mol/L): a, b, c, and d denote 0 , 8.65×10^{-4} , 4.36×10^{-3} , 8.72×10^{-3} , respectively; time (h): 3.0; temperature ($^\circ\text{C}$): 135; ■— $\text{Ca}_3(\text{PO}_4)_2$, ◆— $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$.

amounts of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$. The influence of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ on the conversion of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ was discussed and a possible mechanism proposed.

2. Experimental

2.1. Experimental procedure

Commercial analytical grade Na_2SO_4 and CaCl_2 reagents were provided by Beijing Chemical Reagent Factory (Beijing, China). In a typical experiment, 80 mL of 0.2–1.2 mol/L Na_2SO_4 was added (3.0–6.0 mL/min) to 160 mL of 0.2–1.2 mol/L CaCl_2 at room temperature, keeping the stirring speed at 200–350 min^{-1} . The slurry was stirred for 0.5 h and then the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ precipitate was filtered, washed and dried at 45°C for 4.0 h.

The $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co., Ltd., with a purity more than 99.0%, Beijing, China) precipitate and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (Beijing chemical works, with a purity more than 99.0%, Beijing, China) were mixed with deionized water to form a slurry containing 3.0–10.0 wt% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and 0 – 8.72×10^{-3} mol/L $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$. Then the slurry was transferred to an 80 cm^3 Teflon-lined stainless steel autoclave and treated at 110–150 $^\circ\text{C}$ for 0–3.0 h. After hydrothermal treatment, the autoclave was cooled to room temperature naturally and the suspension was filtered. The solution was sampled for chemical analysis and the precipitate was washed and dried at 60°C for 4.0 h.

2.2. Analysis

The sample morphology was examined with a field emission scanning electron microscope (FESEM, JSM-7401F, JEOL, Japan). The sample elements were measured with an energy dispersive spectrometer (EDS, GENESIS, EDAX, Utah, USA). The sample structure was determined using an X-ray powder diffractometer (XRD, D/max 2500, Rigaku, Japan) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The concentrations of Ca^{2+} , SO_4^{2-} and soluble P were analyzed by ethylene diamine tetraacetic acid titration, barium sulfate precipitation and the chinoline molybdc acid method, respectively.

3. Results and discussions

3.1. Influence of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ on hydrothermal formation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers

Figs. 1 and 2 show the influence of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ on the XRD spectra and hydrothermal product morphology,

Table 1
Composition of whiskers and particles.

Element	Mass in whisker (%)		Mass in particle (%)	
	1	2	1	2
O	48.94	48.69	55.43	53.30
Ca	28.17	28.83	24.24	24.12
S	22.89	23.47	8.15	7.08
P	–	–	12.17	15.50

respectively. The presence of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ led to the formation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ with poor crystallinity and a $\text{Ca}_3(\text{PO}_4)_2$ impurity phase. In the absence of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (Fig. 2(a1)–(a3)), irregular $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ plates were produced within 2.0 h and $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers with a length of 70–300 μm , diameter of 1.0–10.0 μm and aspect ratio of 40–200 were produced at 3.0 h. In the presence of 8.65×10^{-4} – 4.36×10^{-3} mol/L $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers with lengths of 50–200 μm , diameters of 0.5–2.0 μm and aspect ratios of 50–200 were produced after 2.0 h of reaction (Fig. 2(b1)–(b3) and (c1)–(c3)). This indicates that the presence of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ accelerated the hydrothermal conversion of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. The whisker length and diameter decreased with increase in $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ concentration. The whiskers formed in the presence of 8.72×10^{-3} mol/L $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ were unstable and redissolved partially with increase in reaction time from 2.0 to 3.0 h, accompanied by a decrease in whisker length from 70–150 to 30–70 μm (Fig. 2(d2)–(d3)).

The hydrothermal products formed in the presence of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ were composed mainly of whiskers and a minor amount of irregular particles with typical morphology shown in Fig. 3. An energy spectrum analysis of the selected areas showed that no P was detected in the whiskers and the mass ratio of Ca:S:O was 0.97:1.00:4.22. Ca, S, O, and P were detected in the particles with a Ca:S:O:P mass ratio of 1.65:0.49:6.97:0.90 (Table 1). The occurrence of P in the particle is attributed mainly to the formation of $\text{Ca}_3(\text{PO}_4)_2$.

3.2. Influence of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ on solution composition

Fig. 4 shows the variation of soluble P and the formation of $\text{Ca}_3(\text{PO}_4)_2$ with hydrothermal reaction time. The gradual decrease in concentration of soluble P with reaction time should be connected with the formation of $\text{Ca}_3(\text{PO}_4)_2$. The increase in initial $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ concentration favored the formation of $\text{Ca}_3(\text{PO}_4)_2$.

Fig. 5 shows the variation of soluble Ca^{2+} ($[\text{Ca}^{2+}]$) and SO_4^{2-} ($[\text{SO}_4^{2-}]$) with hydrothermal reaction time. In the blank experiment without $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, $[\text{Ca}^{2+}]$ (0.016–0.017 mol/L) and $[\text{SO}_4^{2-}]$ (0.013–0.015 mol/L) were quite similar and stable and their low concentration is attributed to the low solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ under the experimental conditions (Luo et al., 2010).

In the presence of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, $[\text{Ca}^{2+}]$ and $[\text{SO}_4^{2-}]$ increased gradually with increase in reaction time, indicating a faster dissolution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ than precipitation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. Moreover, $[\text{SO}_4^{2-}]$ was higher than $[\text{Ca}^{2+}]$ and the difference between the $[\text{SO}_4^{2-}]$ and $[\text{Ca}^{2+}]$ became more obvious at higher initial $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ concentration. This should be linked to the formation of $\text{Ca}_3(\text{PO}_4)_2$ precipitate. Compared with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, $\text{Ca}_3(\text{PO}_4)_2$ was more stable under the experimental conditions owing to the different K_{sp} at 135°C (5.16×10^{-6} for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 4.53×10^{-6} for $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, and 9.41×10^{-40} for $\text{Ca}_3(\text{PO}_4)_2$). As shown in Eqs. (1)–(4), Ca^{2+} and SO_4^{2-} were produced mainly by the dissolution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

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