Effect of Surfactant on Water Content of Phosphogypsum

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Abstract: Phosphogypsum is a kind of solid waste produced in wet process of producing phosphoric acid, which affects the filtration rate and water content of phosphogypsum. The effects of single surfactant sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (SDBS), stearic acid (SR) and polydimethylsiloxane (PDMS) and coupled surfactants on the water content of phosphogypsum were investigated. The results show that, during the leaching process, surfactant strengthened the interfacial interactions between molecules through hydrophobic and hydrophilic orientation on solid–liquid interface, reduced the surface tension and contact angle to improve the filtration rate and reduced the soluble phosphorus loss, thereby improving the leaching rate of phosphate rock and reducing the water content of phosphogypsum. Among them, the water content of phosphogypsum was better controlled by stearic acid and sodium dodecylbenzene sulfonate than the other surface surfactants. Compared with the blank group, the stearic acid and sodium dodecylbenzene sulfonate increased the filtration rate of phosphogypsum by 24.34%, the moisture content decreased by 3%, and the phosphate leaching rate increased by 4.36%.

Keywords: crystallization; filtration rate; phosphogypsum; surfactant; water content

1. Introduction

Key processes during the wet process of producing phosphoric acid are the leaching behavior and crystallization process of phosphogypsum. CaSO₄·2H₂O is the main content of phosphogypsum; its crystal structure and particle size can directly affect the filtration rate and the loss rate of phosphate. Many materials can improve the crystal structure during the production process of CaSO₄·2H₂O, e.g., activated carbon, activated silicone, aluminum sulfate, and some inorganic compounds [1–4] as well as some polymers and surfactants, phosphoric acid, and carboxylate.

Rashad [5–11] simulated the production process of phosphate acid with sulfate and calcium hydrophosphate and showed that the existence of hex-adeyl trim-ethyl ammonium bromide, 1,2-benzodiazepines, Al³⁺ and Mg²⁺ can improve the crystallization of phosphogypsum, while citric acid has the opposite effect. Zhang [12] found that increased crystallization temperature can enlarge particle size and improve the crystal structure in optimal crystallization time. Zhang [13] simulated the production process with calcium chloride and sulfate, finding that the crystal structure of phosphogypsum can change from acicular crystal to prismatic crystal, bowknot shape crystal, and spherical crystal, thusenlarging the particle size. Most research is focused on improving crystal structure of CaSO₄·2H₂O with pure chemicals, while ignoring the effect of impurities such as Mg²⁺, Al³⁺, Fe³⁺, and SiO₂ during the process [14–16]. During the wet process of producing phosphoric acid, the effect of the impurities in the phosphate rock cannot be ignored. However, few studies focused
analyze the effect of surfactants on the growth behavior of phosphogypsum crystal and water content of phosphogypsum.

This study investigated the effects of single surfactant SDS, SDBS, SR and PDMS on the water content of phosphogypsum. At the same time, the effect of SDBS+SDS, SDBS+SR and SDBS+PDMS on the water content of phosphogypsum was also investigated. The regulation mechanism of single surfactants and two-element compound surfactants on water content of phosphogypsum was analyzed from the following aspects: the interfacial tension of solution, the contact angle of system solid–liquid interface, the morphology of CaSO₄·xH₂O, and the fractal growth behavior of phosphogypsum.

2. Materials and Methods

2.1. Materials

The SDS, SDBS, SR and PDMS used were of analytical grade, purchased from Kelong Co., Ltd, Chengdu, China, and used as received without purification. The phosphate rock was collected from Sinochem Fuling Chongqing Chemical Industry Co., Ltd, Chongqing, China. The chemical composition of the phosphate rock is listed in Table 1; the phase composition measured by X-ray diffraction (XRD-6000, Shimadzu, Japan) is detailed in Figure 1a. The phosphate was mainly composted of Ca₅(PO₄)₃F, SiO₂, CaMg(CO₃)₂. The phosphogypsum was produced by acid leaching of phosphate rock; the composition and phase are detailed in Table 2 and Figure 1b. The results shown in Figure 1b indicate that the phosphogypsum existed as CaSO₄·2H₂O, SiO₂, and FeS₂.

| Compounds | P₂O₅ | Al₂O₃ | Fe₂O₃ | CaO | MgO | K₂O | Na₂O | SiO₂ |
|-----------|------|-------|-------|-----|-----|-----|------|------|
| Amount (wt.%) | 29.20 | 1.98  | 1.31  | 40.60 | 0.55 | 0.47 | 0.20 | 16.83 |

Table 1. Composition of phosphate rock.

![XRD diffraction pattern of phosphate ore and phosphogypsum: (a) XRD diffraction pattern of phosphate rock; and (b) XRD diffraction pattern of phosphogypsum.](image)

**Figure 1.** XRD diffraction pattern of phosphate ore and phosphogypsum: (a) XRD diffraction pattern of phosphate rock; and (b) XRD diffraction pattern of phosphogypsum.

| Compounds | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | P₂O₅ | CaO | SO₃ |
|-----------|------|-------|-------|-----|------|-----|-----|
| Amount (wt.%) | 12.51 | 1.58  | 0.96  | 0.37 | 2.56 | 31.24 | 39.83 |

Table 2. Composition of phosphogypsum.
2.2. Experimental Procedure

All experiments were performed in an agitation reactor (self-made) with liquid-to-solid of 2.5:1 g/mL. A predetermined amount of phosphate rock and water was added to the reactor to produce homogeneous slurry under constant stirring. The slurry was heated to a predetermined temperature. Next, the H₂SO₄ was added to the reactor, and then the surfactant. After the required reaction time, the leachate was separated from the residue by vacuum filtration. The residue was dried in an oven and grounded to fine particles and analyzed by Scanning Electron Microscopy (SEM; S4800; HITACHI, Japan). The concentration of phosphate was determined by quinoline phosphomolybdate gravimetric method.

3. Results and Discussion

The surfactant was an amphiphilic structure containing hydrophobic group and water-based group; it was energized at surface or interface of the solution and changed the physicochemical property (surface tension and contact angle) to display effect of wetting or solubility (Figure 2).

![Figure 2. Process of surface-active agent in the leaching system of phosphate rock.](image)

3.1. Effect of Surfactant

The results shown in Table 3 display the effects of the species of surfactant on the surface tension of the leaching solution of phosphate rock. The concentration of surfactant was kept as 10 mg/L⁻¹. The surface tension was measured as 75.70 mN/m (without surfactant), 60.99 mN/m (with SDBS), 64.75 mN/m (with SDS), 62.54 mN/m (with SR), 64.36 mN/m (with PDMS), 53.21 mN/m (with SDBS+SDS), 40.26 mN/m (with SDBS+SR) and 59.77 mN/m (with SDBS+PDMS), respectively. The contact angle of the leaching solution of phosphate rock was also affected by the species of surfactant and, as shown in Table 4. The addition of SDBS could decrease the surface tension, which was more effective than SDS, SR and PDMS. However, adding more species was more effective than single species, and the performance of SDBS+SR was better than SDBS+SDS or SDBS+PDMS.
Table 3. Of the species of surfactant on the surface tension of the leaching solution of phosphate rock.

| System          | Surface Tension | Mean Deviation |
|-----------------|-----------------|----------------|
| No Surfactant   | 75.70 mN/m      | 1.2 mN/m       |
| SDBS            | 60.99 mN/m      | 1.4 mN/m       |
| SDS             | 64.75 mN/m      | 1.3 mN/m       |
| SR              | 62.54 mN/m      | 1.5 mN/m       |
| PDMS            | 64.36 mN/m      | 1.3 mN/m       |
| SDBS+SDS       | 53.21 mN/m      | 1.4 mN/m       |
| SDBS+SR        | 40.26 mN/m      | 1.2 mN/m       |
| SDBS+PDMS      | 59.77 mN/m      | 1.1 mN/m       |

Table 4. Of the species of surfactant on the contact angle of the leaching solution of phosphate rock.

| System          | Contact Angle | Mean Deviation |
|-----------------|---------------|----------------|
| No Surfactant   | 80.12°        | 1.2°           |
| SDBS            | 72.54°        | 1.4°           |
| SDS             | 78.69°        | 0.9°           |
| SR              | 79.53°        | 0.8°           |
| PDMS            | 73.25°        | 1.0°           |
| SDBS+SDS       | 71.89°        | 1.1°           |
| SDBS+SR        | 70.65°        | 0.9°           |
| SDBS+PDMS      | 72.68°        | 1.0°           |

The addition of surfactant could decrease the interface energy and block the hydrogen bond to rearrange the water molecule, and then increased the bond-angle of water [17] (Figure 3), thus decreasing the surface tension and enlarged the contact area of leaching solvent and phosphate rock, which favored the mass transfer rate and improved the leaching efficiency.

3.2. Effect of Surfactant on Morphology of Phosphogypsum

The SEM of phosphogypsum is shown in Figure 4. The results indicate that morphology of the phosphogypsum was displayed as tabular and the particle size was about 20–25 µm without surfactant. The phosphogypsum grew to 25–30 µm with the addition of SDBS, while the phosphogypsum changed to virgate with the addition of SR and PDMS, and the particle size grew to 30–35 µm. The particle size changed little with the addition of two species of surfactant, remaining 20–30 µm.
Figure 4. Effect of surfactants on phosphogypsum crystal. (a) SEM of gypsum crystals without surface active agent. (b) SEM of gypsum crystals with SDBS. (c) SEM of gypsum crystals with SDS (d) SEM of gypsum crystals with SR. (e) SEM of gypsum crystals with PDMS. (f) SEM of gypsum crystals with SDBS+SDS. (g) SEM of gypsum crystals with SDBS+SR. (h) SEM of gypsum crystals with SDBS+PDMS.

The addition of SDBS, SDS, or PDMS could increase the interfacial energy and hinder the formation of crystal nucleus, which avoided the formation of fine grain [18]. In addition, the addition of SDBS,
SDS, or PDMS decreased the supersaturating of the phosphate rock, and avoided the deposition of fine
grain on the surface of rock. The diffusion velocity of Ca\(^{2+}\) and SO\(_4^{2-}\) was increased due to the change
of surface tension, which was beneficial for the growth of phosphogypsum.

The fractal dimension of the phosphogypsum was calculated according to Equation (1) and the
results are displayed in Table 5. The correlation of contact angle with fractal dimension was calculated
(see Equation (2)) and the \(R^2\) was 0.9986 shown in Figure 5. Low fractal dimension indicated low
contact area, which was not beneficial for adsorption of water at low fractal dimension. However,
it was good for separation of the leachate and phosphogypsum, as well as increasing the filtrate rate
and decreasing water content in the phosphogypsum.

\[
D = \frac{\ln P - \ln \delta}{\ln A^2 - \ln \delta + \ln a}
\]

\[
D = -5 \times 10^{-6} \theta^5 + 0.0014 \theta^4 - 0.166 \theta^3 + 8.4517 \theta^2 - 161.2 \theta \quad R^2 = 0.9986
\]

**Table 5.** Effects of surfactant on the fractal dimension of phosphogypsum.

| System       | Fractal Dimension | Mean Deviation |
|--------------|-------------------|----------------|
| No Surfactant| 1.2753            | 0.0128         |
| SDBS         | 1.2240            | 0.0132         |
| SDS          | 1.2750            | 0.0127         |
| SR           | 1.2754            | 0.0137         |
| PDMS         | 1.2447            | 0.0131         |
| SDBS+SDS     | 1.1931            | 0.0121         |
| SDBS+SR      | 1.0249            | 0.0112         |
| SDBS+PDMS    | 1.2354            | 0.0128         |

![Figure 5. Effect of contact angle on fractal dimension.](image)

3.3. **Effect of Surfactant on Filtrate Rate of Phosphogypsum**

The addition of surfactant not only decreased the surface tension and contact angle, and changed
the wetting characteristics of the phosphate rock, but also obtained large size of phosphogypsum.
The results shown in Table 6 display the effect of surfactant on the filtrate rate of phosphogypsum.
The filtrate rate was 905.80 kg·m\(^{-2}\)·h\(^{-1}\) without surfactant. The addition of surfactant could affect
the filtrate rate significantly. The rate increased 13\% (with SDS), 20\% (with SDBS), 16.7\% (with PDMS),
20.86\% (with SDS+SDBS), 24.34\% (with SR+SDBS) and 17.41\% (PDMS+SDBS), respectively.
Table 6. Of the species of surfactants on the filtration rate of phosphogypsum.

| System          | Filtration Rate | Mean Deviation |
|-----------------|-----------------|----------------|
| No Surfactant   | 905.80 kg/m²·h  | 2.12 kg/m²·h  |
| SDBS            | 1089.56 kg/m²·h | 2.11 kg/m²·h  |
| SDS             | 1031.46 kg/m²·h | 2.43 kg/m²·h  |
| SR              | 870.86 kg/m²·h  | 2.31 kg/m²·h  |
| PDMS            | 1056.89 kg/m²·h | 2.14 kg/m²·h  |
| SDBS+SDS        | 1094.76 kg/m²·h | 2.21 kg/m²·h  |
| SDBS+SR         | 1126.34 kg/m²·h | 2.23 kg/m²·h  |
| SDBS+PDMS       | 1063.49 kg/m²·h | 2.24 kg/m²·h  |

The addition of SDBS, SDS, PDMS, SDBS+SDS, SDBS+SR, or SDBS+PDMS could increase the interfacial energy and hinder the formation of crystal nucleus, avoiding the formation of fine grain [19]. The addition of surfactant also increased the growth rate of crystal and the filtrate rate.

3.4. Effect of Single Surfactant

3.4.1. Effect of Surfactant on the Water Content

The phosphogypsum was dried in an oven at 45 °C for desorption of free-water; the loss of phosphogypsum mass is shown in Figure 6. The water content was calculated according to Equation (3) by weighing method. The mass of phosphogypsum in the oven was not changed, which indicated that the free-water was extripated.

\[ \omega = \frac{m_1 - m_2}{m_1} \times 100\% \]  

Figure 6. Of phosphogypsum changes with time.

The results shown in Figure 6 indicate that the water-loss rate was faster than blank group with addition of SDS, SDBS, PDMS and SR. Table 7 displays the effect of single surfactant on water content of phosphogypsum. The water content of phosphogypsum was 20.3%, and decreased to 18.0%, 19.4% and 18.9%, respectively, with addition of SDBS, SDS and PDMS, while increased to 23.1% with addition of SR. SDS and SDBS are anionic surfactants containing hydrophilic group and oil-based, while the silicon methyl group in PDMS is strongly hydrophobic. Tables 3 and 4 show that the addition of SDS, SDBS or PDMS could decrease the surface tension of phosphogypsum and contact angle and was beneficial for separation. In addition, the size of phosphogypsum grew up with the addition of surfactant, which could increase the filtrate rate and decrease the water content.
Table 7. Rate of water content of phosphogypsum after the modification of the compound surfactants.

| System        | Water Content | Mean Deviation |
|---------------|---------------|----------------|
| No Surfactant | 20.30%        | 2.12%          |
| PDMS          | 18.90%        | 2.21%          |
| SR            | 23.10%        | 2.07%          |
| SDBS          | 18.00%        | 2.01%          |
| SDS           | 19.40%        | 2.07%          |

3.4.2. Effect of Couple Surfactant

The effect of coupled surfactant on the water content of phosphogypsum was investigated with SDBS+SDS (1:1), SDBS+SR (1:1), and SDBS+PDMS (1:1). The loss of phosphogypsum mass is shown in Figure 7.

The results shown in Figure 8 indicate that the water-loss rate was faster than blank group with addition of SDBS+SDS (1:1), SDBS+SR (1:1), and SDBS+PDMS (1:1). Table 8 displayed the effect surfactant on water content of phosphogypsum. The water content was decreased to 18.0%, 17.3%, and 18.6%, respectively, with addition of SDBS+SDS (1:1), SDBS+SR (1:1), and SDBS+PDMS (1:1). The synergistic effect was not obvious, as SDS and SDBS had the same hydrophobic group. SR reacted with SDBS to form complex compound (Figure 8), which was easy to overcome the low hard water of SDBS. The coupling of SDMS and SR showed good synergistic effect.

![Graph](image-url)
The addition of surfactant decreased the surface tension and contact angle, favoring the mass transfer during the leaching process, surfactant strengthened the interfacial interactions between molecules through hydrophobic and hydrophilic orientation on solid–liquid interface, reduced the surface tension and contact angle to improve the filtration rate and reduce the loss, thereby improving the leaching rate of phosphate rock and reducing the moisture content by 3%, and increased the interfacial energy and hindered the formation of crystal nucleus, which avoided the formation of fine grain and improved the decomposition rate of phosphate ore.

| System                  | Water Content | Mean Deviation |
|-------------------------|---------------|----------------|
| No Surfactant           | 20.30%        | 1.03%          |
| SDBS                    | 18.00%        | 1.21%          |
| SDBS+SDS(1:1)           | 18%           | 1.24%          |
| SDBS+SR(1:1)            | 17.30%        | 1.09%          |
| SDBS+PDMS(1:1)          | 18.60%        | 1.28%          |

Table 8. Rate of water content of phosphogypsum after the modification of the compound surfactants.

3.5. Effect of Surfactant on Leaching Efficiency

The effect of addition of surfactant on the leaching efficiency of phosphate was investigated and the results are shown in Table 9. The leaching efficiency was increased by about 3.32% (SDBS and SDS), 1.35% (PDMS), 3.49% (SDBS+SDS), 4.36% (SDBS+SR) and 2.49% (SDBS+PDMS), respectively. The addition of surfactant decreased the surface tension and contact angle, favoring the mass transfer during the leaching process, which improved the leaching efficiency. The addition of surfactant could increase the interfacial energy and hinder the formation of crystal nucleus, which avoided the formation of fine grain and improved the decomposition rate of phosphate ore.

| System          | Leaching Rate | Mean Deviation |
|-----------------|---------------|----------------|
| No Surfactant   | 90.31%        | 1.21%          |
| SDBS            | 93.15%        | 1.48%          |
| SDS             | 93.07%        | 1.32%          |
| SR              | 90.37%        | 1.25%          |
| PDMS            | 91.53%        | 1.35%          |
| SDBS+SDS        | 93.46%        | 1.21%          |
| SDBS+SR         | 94.25%        | 1.15%          |
| SDBS+PDMS       | 92.56%        | 1.24%          |

Table 9. Of the species of surfactant on the leaching rate of phosphate rock.

4. Conclusions

The effects of single surfactants SDS, SDBS, SR and PDMS and coupled surfactants SDBS+SDS, SDBS+SR and SDBS+PDMS on the water content of phosphogypsum were investigated. The results show that, during the leaching process, surfactant strengthened the interfacial interactions between molecules through hydrophobic and hydrophilic orientation on solid–liquid interface, reduced the
surface tension and contact angle to improve the filtration rate and reduced the soluble phosphorus loss, thereby improving the leaching rate of phosphate rock and reducing the water content of phosphogypsum. Among them, the water content of phosphogypsum was better controlled by SR + SDBS than by other surface surfactants. Compared with the blank group, SR + SDBS increased the filtration rate of phosphogypsum by 24.34%, decreased the moisture content by 3%, and increased the phosphate leaching rate by 4.36%. In addition, the fractal dimension of phosphogypsum crystal increased with the increase of contact angle of solid–liquid interface, and the mathematical relationship between fractal dimension and contact angle was well fitted.

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References

1. Nizevičienė, D.; Vaičiukynienė, D.; Vaitkevičius, V.; Rudžionis, Ž. Effects of waste fluid catalytic cracking on the properties of semi-hydrate phosphogypsum. J. Clean. Prod. 2016, 137, 150–156. [CrossRef]
2. Wang, W.; Zeng, D.; Chen, Q.; Yin, X. Experimental determination and modeling of gypsum and insoluble anhydrite solubility in the system CaSO₄–H₂SO₄–H₂O. Chem. Eng. Sci. 2013, 101, 120–129. [CrossRef]
3. Zhu, Z.; Peng, Y.; Hatton, T.A.; Samrane, K.; Myerson, A.S.; Braatz, R.D. Crystallization of Calcium Sulphate During Phosphoric Acid Production: Modeling Particle Shape and Size Distribution. Procedia Eng. 2016, 138, 390–402. [CrossRef]
4. Singh, N.B.; Middendorf, B. Calcium sulphate hemihydrate hydration leading to gypsum crystallization. Prog. Cryst. Growth Charact. Mater. 2007, 53, 57–77. [CrossRef]
5. Rashad, M.M.; Baioumy, H.M.; Adbel-Aal, E.A. Structural and spectral studies on gypsum crystals under simulated conditions of phosphoric acid production with and without organic and inorganic additives. Cryst. Res. Technol. 2003, 38, 433–439. [CrossRef]
6. Rashad, M.M.; Mahmoud, M.H.H.; Ibrahim, I.A.; Abdel-Aal, E.A. Effect of citric acid and 1,2-dihydroxybenzene 3,5-disulfonic acid on crystallization of calcium sulfate dihydrate under simulated conditions of phosphoric acid production. Cryst. Res. Technol. 2005, 40, 741–747. [CrossRef]
7. Rashad, A.M. Phosphogypsum as a construction material. J. Clean. Prod. 2017, 166, 732–743. [CrossRef]
8. Mahmoud, M.H.H.; Rashad, M.M.; Ibrahim, I.A.; Abdel-Aal, E.A. Crystal modification of calcium sulfate dihydrate in the presence of some surface-active agents. J. Colloid Interface Sci. 2004, 270, 99–105. [CrossRef] [PubMed]
9. Rashad, M.M.; Mahmoud, M.H.H.; Ibrahim, I.A. Crystallization of calcium sulfate dihydrate under simulated conditions of phosphoric acid production in the presence of aluminum and magnesium ions. J. Cryst. Growth 2004, 267, 372–379. [CrossRef]
10. El-Shall, H.; Rashad, M.M.; Abdel-Aal, E.A. Effect of cetyl pyridinium chloride additive on crystallization of gypsumin phosphoric and sulfuric acids medium. Cryst. Res. Technol. 2005, 40, 860–866. [CrossRef]
11. Abdel-Aal, E.A.; Mahmoud, M.M.H.; El-Shall, H.; Ismail, A.K. Increasing the filtration rate of phospho-gypsum using surfactant. Hydrometallurgy 2007, 85, 53–61. [CrossRef]
12. Zhang, Y.L.; Zhang, B.L.; Li, D.G. Study on the crystallization process of calcium sulfate two water and the effect of activator loosening agent on it. Chem. Miner. Process. 2004, 33, 11–13.
13. Zhang, B.L.; Hou, Q.H. Study on the effect of two water calcium sulfate crystal change agent on crystallization. Chem. Miner. Process. 2005, 34, 19–21.
14. Hamdona, S.K.; Al Hadad, U.A. Crystallization of calcium sulfate dihydrate in the presence of some metal ions. J. Cryst. Growth 2007, 299, 146–151. [CrossRef]
15. Tolonen, E.T.; Ramo, J.; Lassi, U. The effect of magnesium on partial sulphate removal from mine water as gypsum. J. Environ. Manag. 2015, 159, 143–149. [CrossRef] [PubMed]
16. Manar, S. Increasing the Filtration Rate of Phosphor-gypsum by Using Mineral Additives. *Procedia Eng.* **2016**, *138*, 151–163. [CrossRef]

17. Paruchuri, V.K.; Nalaskowski, J.; Shah, D.O.; Miller, J.D. The effect of cosurfactants on sodium dodecyl sulfate micellar structures at a graphite surface. *Colloids Surf. A* **2006**, *272*, 157–163. [CrossRef]

18. Licong, D.E.N.G.; ZHANG, Y.; Fangfang, C.H.E.N.; Shaotao, C.A.O.; Shaowei, Y.O.U.; Yan, L.I.U.; ZHANG, Y. Reactive Crystallization of Calcium Sulfate Dihydrate from Acidic Wastewater and Lime. *Chin. J. Chem. Eng.* **2013**, *21*, 1303–1315.

19. Wu, P.Z. *Phosphoric Acid by Wet Process*; Chemical Industry Press: Beijing, China, 1987.