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Sedimentation-Based Separation and Purification of Solid Industrial Waste: A Case Study of Phosphogpusym

Shuomin Hou, Hua Deng,* Zhongjun Li, Shanzhu Jiang, Buxiao Kuang, Ruan Chi, Benjun Xi, and Shaoping Li

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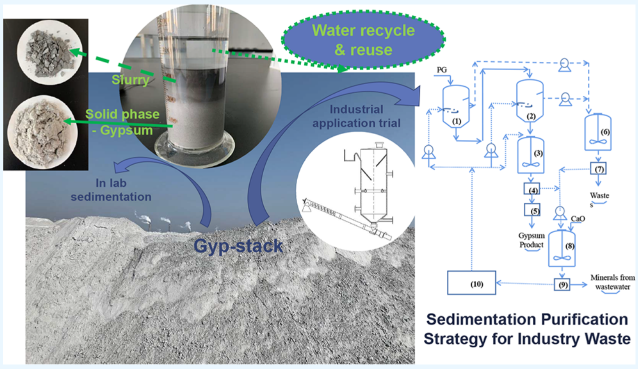
ABSTRACT: The continuous accumulation of solid industry waste, such as phosphogypsum, has emerged as a global environmental hazard and a significant obstacle to achieving a green and sustainable industry. To convert this industry waste to reusable resources, the development and implementation of simple and cost-efficient purification techniques is crucial. A sedimentation-based separation approach was developed to achieve this objective. Through a sedimentation process, a suspension of phosphogypsum particles is transformed into three distinct phases: a supernatant liquid, a concentrated slurry, and a solid precipitate. These phases primarily consist of soluble salts, a mixture of oxides and organic matter, and calcium phosphate dihydrates mixed with calcium phosphate, respectively. Through a sedimentation process, calcium sulfate dihydrate concentration can be significantly enhanced from 87.45 to 91.60% and further improved to 95.72% by repeating the sedimentation process three times. The various components obtained from this process can be effectively reused as mineral resources, soil amendment, and industry gypsum. The sedimentation process is expounded upon using both the classical mechanics model and Stokes' law. To foster a seamless industrial application, we have also designed a continuous settling skittle and a trail setup for industrial treatment of phosphogpysum. This innovative technique holds immense promise for its broader application, especially within but not limited to the phosphoric acid industry.



1. INTRODUCTION

Proper disposal and reuse of massive industrial waste have always been a challenging topic worldwide. For instance, phosphogypsum (PG) is a byproduct of the phosphates industry, primarily composed of calcium sulfate dihydrate ($CaSO_4{\cdot}2H_2O$). It is generated from the wet process of phosphoric acid production, where phosphate rock reacts with sulfuric acid to produce phosphoric acid and phospgypsum. Approximately five tons of phosphogypsum are produced per ton of phosphoric acid. The global annual production of phosphogypsum is estimated to be between 100 and 280 million metric tons.[1] Over 70% of phosphogypsum has been stored indefinitely as man-made hills, known as "gyp-stacks", resulting in a current global stockpile of up to 6 billion tons. Some are directly dumped in the sea. These practices have caused significant harm to the land, sea, and air.[2−4] Consequently, the issue of phosphogypsum has garnered widespread attention.

Phosphogypsum can be potentially used as gypsum, which finds extensive use in the construction industry. However, the presence of impurities in phosphate rocks results in the transfer of these impurities to phosphogypsum, hindering its widespread large-scale utilization as gypsum.[5,6] The impurities vary from different phosphate rock resources. Phosphogypsum produced in Florida is known for its weak radioactivity caused by naturally occurring uranium (U) and thorium (Th), and their daughter isotopes radium (Ra), radon (Rn) and polonium (Po).[7−10] Although phosphogypsum has been used in construction materials,[11−14] fillers,[15] soil conditioners,[16−18] and other applications, the amount and its widespread adoption are very limited due to the impurities, including between 0.1 and 1.5% of F^- and from 0.1 to 1.8% of P_2O_5 in addition to small amounts of organic matters and heavy-metal ions.[19]

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Therefore, the removal of impurities from phosphogypsum is crucial to promote its broader application. Much work has been done in terms of washing, flotation, neutralization, and more. Singh et al.[20] attempted to purify phosphogypsum and enhance its quality by treating it with an aqueous solution of citric acid. This treatment converted phosphatic and fluoride impurities into water-removable citrates, aluminates, and ferrates. The purified phosphogypsum exhibited lower levels of phosphate, fluoride, and organic matter impurities compared with the impure form. Kaziliunas et al.[21] employed lime suspension to neutralize phosphogypsum, converting acidic impurities into insoluble compounds such as $Ca_5(PO_4)_3OH \cdot mH_2O$; $Ca_3(PO_4)_2 \cdot nH_2O$; CaF_2 and $CaSiF_6$. The alkali treatment did not adversely affect the product properties. The flotation method can effectively remove organic matter, SiO_2, soluble phosphorus, and other impurities from phosphogypsum and improve the purity of gypsum.[22,23]

These conventional methods have been extensively studied at both laboratory and industrial scales, enabling the purification of phosphogypsum to yield gypsum products of comparable or superior quality to those derived from power plant desulfurization.[24−26] Despite their proven efficacy, these techniques have not been widely implemented on an industrial scale due to their typically higher cost compared with the value of the resulting gypsum products. Consequently, such practices are deemed economically unviable and unprofitable for the industry. Therefore, there is a pressing need within the phosphogypsum industry for a simple and cost-efficient technique that can render phosphogypsum usable. Such a technique would ultimately address the environmental threat posed by phosphogypsum, ensuring its sustainable utilization.

This study presents a straightforward sedimentation-based method for the purification of phosphogypsum. During the settling process, phosphogypsum was effectively partitioned into distinct 3−4 layers. The substances present in these layers were found to facilitate the separation of different components within phosphogypsum, thereby contributing to its purification. The underlying principles of this technique can be explained using Stoker's theory. The technique is simple to operate, energy saving, and absence of the need for additional chemical reagents, rendering it environmentally friendly and suitable for widespread implementation.

2. EXPERIMENTAL SECTION

2.1. Materials. The phosphogypsum was obtained from a phosphoric acid production line located in Yichang (Hubei, China). It was used fresh without further pretreatment. Nitric acid (65%) and chloric acid (37%) were purchased from Sinopharm Reagent, China. Distilled water was used throughout the entire experiment.

2.2. Sedimentation-Based Technique. An optimized sedimentation-based technique consists of three fundamental steps. First, phosphogypsum is mixed with water at a solid/liquid mass ratio ranging from 1:1.0 to 1:2.0. The mixture is stirred for 30 min at a stirring speed of 80−400 rpm. Alternatively, water can be substituted with other solvents or modified by incorporating acids, bases, or organic compounds to enhance the separation process.

Second, the mixture is allowed to settle undisturbed for a minimum of 24 h in a container with a diameter-to-height ratio below 3:4. Opting for a lower diameter-to-height ratio facilitates more effective separation of distinct layers within the mixture.

Finally, the different layers obtained from the settling process are collected separately for subsequent characterization and utilization.

By following this optimized sedimentation-based technique, improved separation and purification of phosphogypsum can be achieved, enabling further analysis and application of the separated components.

2.3. Characterization Methods. The composition of each layer was characterized by analyzing various parameters, including cations, anions, organic content, pH, whiteness, morphology, and particle sizes. The supernatant was filtered through quantitative filter paper before analysis. Solid samples were dissolved using freshly prepared aqua regia (a mixture of nitric acid and hydrochloric acid, with a molar ratio of 1:3) and diluted with DI water, followed by filtration.

Cations were determined by inductively coupled plasma-optical emission spectroscopy (Agilent, 5800 ICP-OES) and major anions via ion chromatography (Thermo Fisher Scientific, ICS6000). Total carbon content is obtained by a total organic carbon analyzer (analytikjena, multi N/C 3100). Fluoride concentration was determined by titration (Thermo, PHS-3E) in solid samples. The chlorine content in solids was obtained by using the volumetric method with ammonium thiocyanate. All phosphorus elements in solids were assessed by the quinoline phosphomolybdate weight method. A scanning electron microscope (Zeiss, Sigma 500 Model) was used to observe the morphology. Whiteness was tested by an automatic whiteness meter (Beijing Kangguang Instruments Co., Ltd., WSD-3C Model). The particle size is obtained by a laser particle sizer (Better, 2600 Model). Water content was evaluated by weight loss at different temperatures of 40 and 230 °C, and $CaSO_4 \cdot 2H_2O$ percentage was obtained by calculating the content of water of crystallization.

2.4. Statistical Analysis. To confirm statistical significance of each component among different layers, one-way ANOVA in SPSS software was used. A $p < 0.05$ is used for significant responses.

3. RESULTS AND DISCUSSION

A phosphogypsum sedimentation process forms distinct layers, as illustrated in Figure 1a. The mixture exhibits clear stratification, with the uppermost layer characterized by black foam, termed the foam layer. This foam layer gradually disappeared and merged into a mud layer when the stir speed increased to more than 200 rpm. Mass of this layer counts for less than 1.5% of the total mass of phosphogypsum. Below the foam layer lies the transparent and clarified liquid phase containing water-soluble substances from phosphogypsum. Subsequently, the slurry layer is called the mud phase. Mass of dried mud phase counts 18.6−23.2% of added phosphogypsum. Finally, the bottom layer consists of mainly solid particles, referred to as the solid phase, that count over 81.0% mass percentage of phosphogypsum. Each layer is subjected to individual characterization, which is further discussed below. The solid phase can undergo the sedimentation process repeatedly for further purification. The dried solids from each layer are compared in Figure 1b.

3.1. Component Analysis. Analysis of total organic matter in the foam layer showed that the content of total organic matter in foam was 44.69 mg/kg, indicating that more organic matter components were gathered in foam.

Concentrations of major elements in each layer are compared in Table 1. The main component of this

(a) (b)

Figure 1. Typical sedimentation of phosphogypsum was achieved by mixing hosphogypsum with water with a solid−liquid ratio of 1:1.2 and stirred under 350 rpm for 1 h, followed by still set for 48 h. Resulted mixture showed three distinct layers (a), from top to bottom: clear supernatant, mud/slurry phase and solid phase. The boundary is indicated by the dashed yellow line. The slurry phase and solid phase were collected, filtered, and dried. The resulting solids are compared in (b).

phosphogypsum was calcium sulfate dihydrate (around, 87.45%), followed by the attached water. There were many impurity elements, mainly P, F, K, Na, Fe, Al, Mg, Sr, etc., but also a small amount of B, Ba, Co, Cr, Cu, Mn, Ni, Pb, Zn, Si, and other elements. The elements such as Al, Mg, Si, and P were mainly dissolved in aqueous solution, and the content in the solid phase decreases significantly after three natural settling times. Light elements such as B, K, Mn, and Na are more present in the mud phase layer after one settling time, and elements such as Fe, Ni, and Zn were mainly present in the solid phase layer. Elements such as Pb and Sr were more uniformly distributed in the mud and solid phases without significant differences. This was related to the solubilities of their oxides and salts and the size of their atomic masses. After three times of sedimentation, some soluble elements in the solid phase did not exist in the solid phase because they were dissolved in water such as B and Co, and there were still trace amounts of insoluble apatite, insoluble P_2O_5, eutectic P_2O_5, fluoride and phosphate, sulfate, iron oxide, aluminum oxide and silica in the solid phase. Notably, radionuclides are not detected in the phosphogypsum samples we used. In the case that they are present in a very trace amount, below the detection limit of the instrument, they are suspected to settle down along with $CaSO_4·2H_2O$ and unreacted phosphate rock particles to the bottom of the device.

The average concentration of $CaSO_4·2H_2O$ in fresh phosphogypsum was 87.45%, which increased to 91.60% in the solid phase after one sedimentation process and further reached 95.72% after three sedimentation repeats. This is convincing evidence that the sedimentation-based separation technique is capable of purifying and concentrating $CaSO_4·2H_2O$ in phosphogypsum effectively and efficiently. This is also in accordance with the whiteness test data that increased from 5.23 to 41.65% after three times of sedimentation.

3.2. Mechanism and Theory of the Sedimentation Process.

Before we dive into the theory underlying the

Table 1. Content of Each Component Element before and after the Sedimentation Process of Phosphogypsum with Fresh Phosphogypsum Used as the Control and the Solid Phases after Three Repeated Sedimentations Also Listed for Comparison

	phosphogypsum	liquid phase	mud phase	solid phase	solid phase of three repeats
Al, ppm	913.38 ± 48.51	315.04 ± 15.41	306.66 ± 9.29	397.62 ± 5.64	202.41 ± 12.99
B, ppm	5.79 ± 2.77	0.22 ± 0.07[a]	4.20 ± 2.76[a]	0	0
Ba, ppm	80.54 ± 5.29	0.16 ± 0.02[a]	86.60 ± 11.45	73.87 ± 16.26	43.29 ± 1.57
Co, ppm	0.70 ± 0.04	0.02 ± 0.01	0.11 ± 0.05	0.40 ± 0.05	0
Cr, ppm	6.83 ± 2.03	0.92 ± 0.20	2.82 ± 0.24	2.82 ± 0.07	1.38 ± 0.08
Cu, ppm	7.22 ± 0.35	0.27 ± 0.02[a]	4.24 ± 0.49	5.44 ± 0.23[a]	3.88 ± 0.49
Fe, ppm	2614.65 ± 47.36	36.87 ± 1.68[a]	1544.66 ± 111.80	2221.37 ± 69.03	1993.68 ± 170.21
K, ppm	4878.90 ± 191.00	426.65 ± 13.01[a]	3759.69 ± 190.95	3261.02 ± 40.38	1991.82 ± 159.64
Mg, ppm	222.53 ± 7.38	106.26 ± 8.75[a]	54.00 ± 3.37	58.04 ± 1.88	16.08 ± 4.34
Mn, ppm	23.17 ± 1.76	6.76 ± 0.38	23.63 ± 7.88[a]	9.70 ± 0.17	9.09 ± 0.71
Na, ppm	2257.29 ± 49.18	843.40 ± 42.72	1505.87 ± 501.96	494.5 ± 10.68[a]	224.75 ± 78.45
Ni, ppm	4.70 ± 0.18	0.22 ± 0.02[a]	2.43 ± 0.35	3.33 ± 0.10	2.79 ± 0.30
Pb, ppm	9.11 ± 0.21	0	7.59 ± 0.48	7.20 ± 0.43	7.03 ± 0.55
Sr, ppm	406.6 ± 10.81	3.47 ± 0.15[a]	378.91 ± 3.46	367.28 ± 6.51	321.55 ± 8.04
Zn, ppm	8.72 ± 2.51	0.38 ± 0.02	7.27 ± 1.01	8.02 ± 1.51	4.31 ± 0.86
Si, ppm	63.98 ± 3.23	56.02 ± 3.58[a]	33.43 ± 2.43	40.71 ± 2.03	23.84 ± 1.15
Cl, ppm	115.9 ± 11.33	37.57 ± 1.87[a]	51.60 ± 9.75	44.43 ± 3.15	35.93 ± 4.30
P_2O_5, %	1.04 ± 0.03	0.39 ± 0.03	0.27 ± 1.01	0.31 ± 0.02	0.16 ± 0.02
F, %	0.90 ± 0.01	0.21 ± 0.01	0.5 ± 0.02	0.51 ± 0.08	0.22 ± 0.03
attached water, %	13.27 ± 0.23	/	23.19 ± 1.53	19.52 ± 2.68	19.96 ± 0.84
crystallized water, %	18.30 ± 0.46	/	18.02 ± 0.90	19.17 ± 3.19	20.03 ± 0.26
$CaSO_4·2H_2O$, %	87.45 ± 2.20	/	86.10 ± 4.30	91.60 ± 15.24[a]	95.72 ± 1.24
whiteness, %	5.23	/	19.76	31.36	41.65
pH	2.51 ± 0.02	1.78 ± 0.01	3.07 ± 0.03	3.12 ± 0.02	3.37 ± 0.04

[a] Elements that are significantly lower or higher than other phases from one sedimentation process.

sedimentation process, we confirmed the shape and size of phosphogypsum particles, which are essential factors to illustrate the behavior of the particles. The scanning electron microscope image of phosphogypsum is shown in Figure 2 where the phosphogypsum particles had an irregular particle shape with a nonuniform particle size.

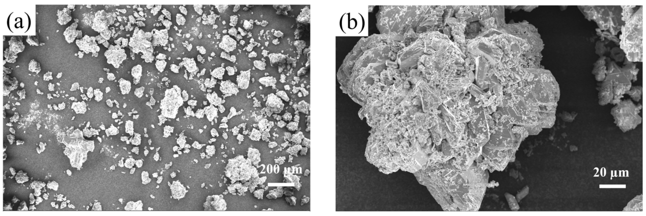

Figure 2. Images obtained from scanning electron microscopy (SEM) of phosphogypsum particles at different magnifications. The scale bar is 200 μm for (a) and 20 μm for (b).

Two techniques were employed to obtain size distribution of dry phosphogypsum particles and in solution, namely, dry method and wet method, respectively. Results are compared in Table 2 and Figure 3. The particle size of dry phosphogypsum was mainly distributed in the range 10−150 μm. Adding water dissolves soluble components attached on the particle surface, causing the particle size slightly smaller in water, indicated by the shift to small size of the wet method in Figure 3. The aggregated particles in the dry state are also separated and dispensed, showing a wider size distribution of phosphogypsum particles in water. The percentage of particles in the range of 10−200 μm decreased from 91.23% (dry) to 77.17% (wet) when water was added. These observations lay a foundation for an effective and clear separation by sedimentation processes.

The behavior and dynamics of phosphogypsum particles were analyzed by using two distinct models to gain a comprehensive understanding of the sedimentation mechanisms at play. The first model draws upon classical mechanics, rooted in Newton's laws of motion, and is most applicable when there's a high water-to-phosphogypsum ratio, allowing for free and unobstructed particle movement. Conversely, when this ratio is minimal, indicating a limited amount of water (or other viscous solvents) in the system, Stokes' law offers a more fitting model. In such a scenario, the Reynolds number drops significantly, and the mixture becomes more viscous, causing particles to be somewhat "trapped".

In both models of the sedimentation process, several assumptions were made: (1) For simplicity and based on SEM images (as shown in Figure 2), phosphogypsum particles are treated as spheres. (2) Chemical constituents within phosphogypsum are formed independently and are randomly distributed. During the sedimentation process, these components act as distinct entities. Their sizes are approximated using empirical data. (3) We have ignored the acceleration phase leading to terminal velocity, positing that all particles achieve linear Newtonian motion instantaneously during sedimentation. As such, the speed at which particles settle is taken as the terminal velocity, and every particle's movement is deemed independent of others.

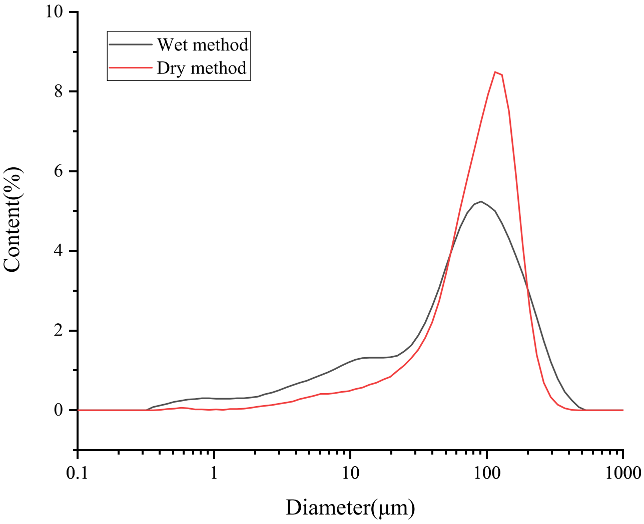

Figure 3. Particle size distribution of phosphogypsum.

In an ideal classical mechanic model, a phosphogypsum particle starts to fall with acceleration caused by the difference between gravity and buoyancy. Both forces are constant since the buoyant force is tersely defined as the weight of displaced fluid and the particle size of phosphogypsum is fixed. However, as the particle starts to fall, drag force appears which is expressed as the drag eq 1.

$$F_D = \frac{1}{2} \times \rho_l \times v^2 \times \mathrm{Cd} \times A \tag{1}$$

where F_D is the drag force, ρ_l is the density of the fluid, v is the speed of the object relative to the fluid, A is the cross-sectional area that is a half sphere of a phosphogypsum particle in our case, and Cd is the drag coefficient, 0.47 for a rough sphere.

The drag force increases as speed increases, causing a decreasing acceleration during the sedimentation process. Ultimately, acceleration becomes 0 and the particle reaches a constant precipitating speed, namely, the terminal velocity. Combine eq 1 with gravity and buoyant force equation, the terminal velocity can be estimated by

$$\nu^2 = 1.24 \times g \times d\left(\frac{\rho_s - \rho_l}{\rho_l}\right) \tag{2}$$

where ν is the terminal velocity of the settling particle, g is the acceleration of gravity, d represents the diameter of the particle, ρ_s and ρ_l are the densities of particle and solvent (water) respectively.

This agrees with illustration in 1956 by McGauhey,[27] the settling velocity will be essentially constant and will depend upon the size, shape, and density of the particle, and the density and viscosity of the water. The general equation for the settling velocity of particles under any flow conditions is as follows:

Table 2. Particle Size Distribution in Phosphogypsum

diameter, μm		0.000−1.000	1.000−5.000	5.000−10.000	10.00−50.00	50.00−100.00	100.0−150.0	150.0−200.0	200.0−250.0	250.0−350.0
content, %	wet	2.03	5.95	5.80	23.93	27.81	16.45	8.98	4.77	3.47
	dry	0.25	1.65	2.47	17.30	33.40	28.04	12.49	3.32	1.01

Table 3. Terminal Velocity of Particles of Each Component in Phosphogypsum in an Ideal Classical Mechanic Model and Stokes' Law Model during a Sedimentation Process with the Terminal Velocity Used as Precipitating Velocity, Which Mainly Depends on Density and Particle Size of the Particles

name	formula	density, g/cm^3	empirical diameter, μm	velocity, $\times 10^{-3}$ m/s, classical mechanics	velocity, m/s, Stokes' law
silicon dioxide	SiO_2	2.4	0.125	1.56	1.33×10^{-8}
calcium sulfate dihydrates	$CaSO_4 \cdot 2H_2O$	2.3	100[a]	42.53	7.91×10^{-3}
calcium sulfate dihydrates	$CaSO_4 \cdot 2H_2O$	2.3	12[b]	14.73	1.14×10^{-4}
calcium phosphate	Ca_3PO_4	3.1	7	14.30	6.26×10^{-5}
iron oxide	Fe_2O_3	5.2	0.8	6.84	1.64×10^{-6}
aluminum oxide	Al_2O_3	4.0	0.02	0.91	7.30×10^{-10}
magnesium oxide	MgO	3.6	1	6.02	1.58×10^{-6}

[a] The size of calcium sulfate dihydrate particles is determined to be around 100 μm in the phosphogypsum when water is added. [b] The empirical particle size of calcium sulfate dihydrate particles is generally around 12 μm.

$$\nu^n = \frac{4}{3}\frac{g}{\kappa}\left(\frac{\rho_s - \rho_l}{\rho^{n-1}}\right)\mu^{n-2}d^{3-n} \tag{3}$$

For a spherical particle, d as diameter and ρ_s as density, ρ_l as liquid density, μ as viscosity, ν as velocity. In which n represents the state of flow, that is, $n = 1$ for streamline flow, n is more than 1 but less than 2 for transitional flow, and n is 2 for turbulent flow. In our model, the fluid is in laminar flow, so $n = 1$ and this equation can be expressed as Stokes' law,[27]

$$\nu = \frac{4}{3}\frac{g}{\kappa}\left(\frac{\rho_s - \rho}{\mu}\right)d^2 \tag{4}$$

In our case, the liquid density ρ and viscosity μ are constant. Thus, velocity ν mainly depends on the diameter d and particle density ρ_s.

Based on the two models, values of terminal velocities of possible particles of each component in phosphogypsum are listed and compared in Table 2. Equations 2 and 4 are used for classical mechanics and Stokes' law respectively. As constants, $k = 24$ in eq 2, g is the acceleration of gravity, 9.80 m/s^2, ρ is the density of water, 1.0 g/cm^3, μ is the viscosity of water in poises, 0.8949×10^{-3} Pa s at 25 °C.

As we assume that phosphogypsum particles reach the terminal velocity in a timely manner and follow a linear Newtonian motion, the precipitating speed, that is, the terminal velocity, is the key to efficiently separate various components. As compared in Table 3, calcium sulfate dihydrate particles, as the main composition of phosphogypsum, have the highest precipitating velocity when the determined particle diameter is used. As it is impossible to fully separate the particles of each chemical component and measure their sizes, we use empirical diameters to compare the terminal velocity of the particles. Calcium sulfate dihydrate and calcium phosphate that is unreacted rock particles from phosphoric acid line have indistinguishable precipitating velocity in the classical mechanics model, indicating that they cannot be separated by the sedimentation process in water. The velocities of other components, mainly oxides, are significantly lower. For instance, the terminal velocity of silicon oxide is roughly 10 times slower, and aluminum oxide is 16 times slower in the classical mechanic model. This demonstrates the possibility of separating the oxide impurities through a sedimentation process in water.

Time and device height are key factors in separating the particles. Taking calcium sulfate dehydrate, silicon oxide, and aluminum oxide as examples, their precipitating speeds are 1.47×10^{-2}, 1.56×10^{-3}, and 9.1×10^{-4} m/s, respectively. Their traveling distances in 10 min yield 8.82, 0.94, and 0.55 m, respectively, indicating that any device higher than 8.82 m could separate these three particles after 10 min' still setting. The efficiency of sedimentation-based separation depends on both the terminal velocity difference and the time for calcium sulfate dihydrate particles to completely precipitate. The minimal separation time is the threshold time when the calcium phosphate and calcium sulfate dehydrate particles completely settle to the bottom of the device. Also, the higher the sedimentation device, the more efficient the sedimentation process is.

The difference of terminal velocities between calcium sulfate dihydrates and other impurities is enlarged in Stokes' model. For example, the precipitating speed of silicon oxide and aluminum oxide particles are approximately 8.57×10^3 and 1.56×10^5 times slower than calcium sulfate dihydrates, respectively. For the same particle, the terminal velocity in Stokes' model is much lower than that in classical mechanics model due to the low Reynolds number caused by the high viscosity. This means that substituting water with other solvent of higher viscosity could slow down the precipitating, increase the difference of terminal velocities among various components, ultimately lead a more efficient and effective separation, and ideally, even make the separation of calcium phosphate from calcium sulfate dehydrate particles possible.

3.3. Sedimentation Device Design.

Theoretically, any device with a specific height could serve as a device for natural sedimentation. But the natural sedimentation process has a pot-by-pot operation. For industrialization, a continuous operable device is favored. Therefore, a device is designed to achieve a continuous load of phosphogypsum and discharge of separated components, as shown in Figure 4. This design applies to all the solid mixtures that can be purified via the sedimentation process.

The continuous sedimentation is achieved by the equipment with an internal liquid spray ring along with a plurality of liquid spray nozzles setting in the upward direction. The pressured solvent flow upward, creating a "drag force" to all the particles, and in an optimum situation, allowing only calcium phosphate and calcium sulfate dehydrate particles to precipitate while other impurities remain "floated" (very low precipitating/terminal velocity compared with calcium sulfate dihydrate) in the solvent that can be collected along with solvent. The collected solvent is designed for recycling and reuse after going through a filtration process.

The solid phase, mainly composed of calcium phosphate and calcium sulfate dehydrate particles, is discharged from the

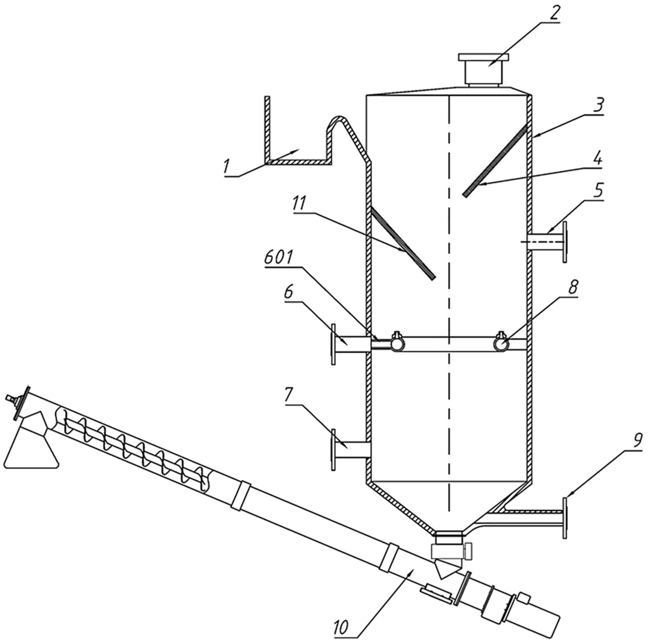

Figure 4. Sketch drawing of a continuous loading and discharge device for phosphogypsum sedimentation. Annotation: 1, foam recovery tank; 2, loading inlet; 3, sedimentation tank; 4, first baffle; 5, drain port; 6, pressured solvent inlet; 601, connecting piping; 7, mud phase outlet (optional); 8, solvent spray ring; 9, manual discharge port (optional); 10, screw conveyor discharge port; 11, second baffle.

bottom of the settling tank through the screw conveyor discharge port.

3.4. Industrial Feasibility. The practicality of the sedimentation technique for phosphogypsum purification is crucial for its industrial application. Thus, we proposed a trial setup for phosphogpysum treatment, as shown in Figure 5.

The above continuous loading and discharge device is the core in this setup, marked as settling kettles (1) and (2). One or more settling kettles can be aligned for the desired purification purpose. In our demo, two kettles are shown. As the first stage of the process, the phosphogypsum is initially added into primary settling kettle (1), and sedimentation begins. The heavier particles start to settle at the bottom of the kettle, which is transferred to the secondary settling kettle (2) for further sedimentation. This stage allows for the separation of finer particles that did not settle in the primary kettle. The settled solids from the secondary settling kettle are transferred to solid phase treatment tank (3) for further treatment and processing. This tank is also optional depending on practical needs, for example, pH amendment. Then the solid residue from the vacuum filtration is dried in the blast oven to remove any remaining moisture, and final product gypsum is generated.

The mud phase or slurry, which contains the fine particles and impurities, is collected and treated in a slurry treatment tank upon practical needs, i.e., to separate the usable components or directly treated as wastes. It is also potential to be used as or added into soil amendments.

The aqueous phase collected during vacuum filtrations is collected into an aqueous solution treatment tank (8), where CaO or other chemicals like $Ca(OH)_2$ is added to precipitate anions, mainly soluble phosphorus and fluorine.[28] These ions are recovered and can be used as phosphate rocks and fluorite.

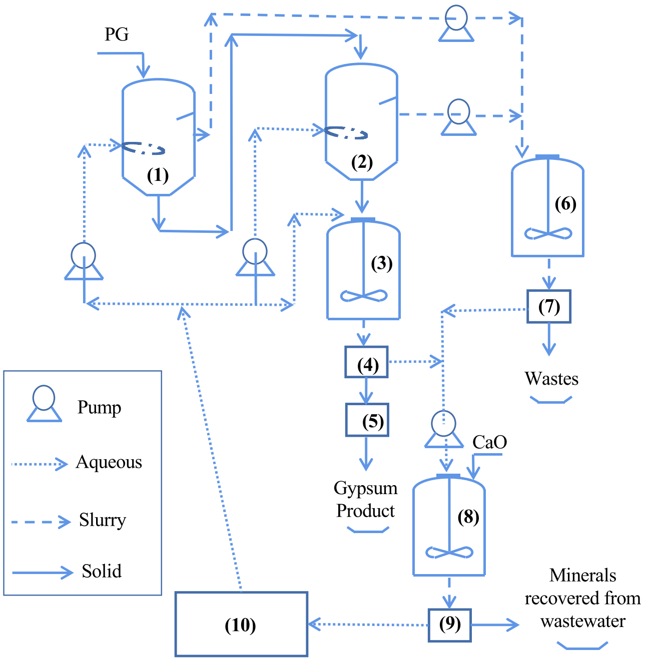

Figure 5. Schematic diagram of a trial setup for the treatment of phosphogypsum based on sedimentation, separation, and purification technology. Key components are (1) primary settling kettle, (2) secondary settling kettle, (3) solid phase treatment tank, (4), (7), and (9) vacuum filtration, (5) blast oven, (6) mud/slurry phase treatment tank, (8) aqueous solution treatment tank, and (10) water reservoir.

This process also recovers water that is stored in a water reservoir and reused for sedimentation cycles.

While the research shows innovation and promising application, our proposed trial setup further solidates the industrial feasibility by addressing several practical considerations, including but not limited to:

(1) Efficiency. Natural sedimentation often requires hours of complete separation. In our lab, we let phosphogypsum precipitate for 48 h to guarantee a complete settle and optimum separation, which may be considered inefficient for industrial application. However, the efficiency is significantly improved using the continuous loading and discharge device. This device facilitates continuous operation, eliminating the need for the batchwise process of natural sedimentation, which takes hours and therefore enhances the overall efficiency of the process.

(2) Flexibility. The flexibility of the trial setup is one of the key advantages. It is designed to accommodate various adjustments to achieve different purposes. Solid, slurry, and aqueous phases are collected separately, subject to further treatment upon various needs. For instance, the settling tank can be added or removed from the system. The pH of the precipitated phospogypsum can be easily modified in a solid treatment tank.

A common issue with industrial pipelines is clogging. It occurs due to the accumulation of solids, formation of scale on the inner walls of the pipes, or precipitation of materials, especially at the joints. The flexibility of the proposed trial setup allows the adjustment of the concentration of phosphogypsum in the system that can be easily tailored by adjusting the solid−liquid ratio. The sealed system is designed to bear high pressures. Therefore, clogging is easily prevented by lowering the phosphogypsum concentration and increasing pressure and flow rates, which theoretically will not affect the separation and purification efficiency.

(3) Water recycles and reuse. The management of wastewater is a critical component of the phosphogypsum sedimentation process and for all the industries. All the "wastewater" is gathered as aqueous phase into an aqueous solution treatment tank, where chemicals such as CaO or $Ca(OH)_2$ are added to precipitate phosphate and fluoride. Then a filtration process can be used to separate precipitates and water. This step is crucial for the recovery of valuable materials and for reducing the environmental impact of the wastewater, while the water can then be reused for subsequent sedimentation cycles, reducing the overall water consumption of the process and achieving water balance for a sustainable industry.

(4) Economic. Cost and profit cannot be ignored in any industry. We compared the proposed sedimentation technique with existing methods to assess its economic viability. Existing methods, as reported by Chen et al.[29] and Chanouri et al.,[30] involve several steps including drying, grinding, high-speed centrifugation, and the addition of chemical reagents, surfactants, and EDTA. These steps can be cumbersome, energy-intensive when come to widespread usage in industries.[31] In contrast, the proposed method requires only the addition of distilled water, stirring, and standing, without any pretreatment of phosphogypsum, chemical reagents, grinding, drying, or centrifugal separation. This simplicity translates to energy savings, higher efficiency, and environmental friendliness.

The main costs associated with the proposed method are the common costs of energy, labor, and wastewater filtration if a membrane is desired to achieve higher purification outcomes. There is no need for expensive chemical reagents or high-energy-consuming processes, which significantly reduce the overall cost of the process. The chemical used in our proposal to neutralize phosphogypsum or precipitate phosphate and fluoride ions is CaO or $Ca(OH)_2$, much cheaper than other chemical reagents like surfactants used in flotation,[32] or chelating agents like EDTA.[30] They can be substituted by other alkaline industrial waste, such as carbide slag, leading to an even higher cost efficiency.

4. CONCLUSIONS

This study presents sedimentation as a novel sedimentation-based strategy for purifying phosphogypsum. The sedimentation process can be repeated for a better purification outcome. A three times sedimentation can increase the percentage of calcium sulfate dehydrate from 87.45 to 95.72% in phosphogypsum. This process can be illustrated by classical mechanics and Stokes' law. The terminal speed of calcium sulfate dihydrate particles is estimated to be 1.47×10^{-2} m/s. It is challenging to separate calcium phosphate from calcium sulfate dihydrate, whereas other oxide impurity particles can be efficiently separated in water. Substituting water with other solvents of higher viscosity could theoretically increase the efficiency of the sedimentation-based separation.

To facilitate industrialization, a sedimentation device with continuous loading and discharge was designed, which achieved efficient purification of phosphogypsum with low energy consumption, high efficiency, and easy operation. It can be further incorporated into a trial setup for industry implication. This setup leverages the advantages of simple operation, energy savings, high efficiency, and green environmental protection, making it a more sustainable and economically viable option compared to existing methods. It is expected that batch purification of phosphogypsum will have high economic and environmental benefits.

■ AUTHOR INFORMATION

Corresponding Author

Hua Deng − *Hubei Three Gorges Laboratory, Yichang 443007, China;* orcid.org/0000-0002-5908-8372; Email: dh.antoniotan@yahoo.com

Authors

Shuomin Hou − *Hubei Three Gorges Laboratory, Yichang 443007, China*
Zhongjun Li − *Hubei Three Gorges Laboratory, Yichang 443007, China*
Shanzhu Jiang − *Hubei Three Gorges Laboratory, Yichang 443007, China*
Buxiao Kuang − *Hubei Three Gorges Laboratory, Yichang 443007, China*
Ruan Chi − *Hubei Three Gorges Laboratory, Yichang 443007, China; Xingfa School of Mining Engineering, Wuhan Institute of Technology, Wuhan 430074, China*
Benjun Xi − *Hubei Three Gorges Laboratory, Yichang 443007, China*
Shaoping Li − *Hubei Three Gorges Laboratory, Yichang 443007, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.3c05351

Author Contributions

S.H.: phosphogypsum characterization, sedimentation experiment, data collection and analysis, and writing original draft; H.D.: conceptualization, supervision, sedimentation experiment design and data analysis, sedimentation device design, manuscript review, and editing; Z.L.: resources, data processing, and analysis; S.J.: phosphogypsum sample preparation and component determination; B.K.: assistance with device design; R.C.: resources and manuscript revision; B.X.: assistance with data collection and analysis; S.L.: supervision and characterization. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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