

Study on the Recycling of P in Phosphogypsum Leachate

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Abstract

After washing and curing, P is transported from the phosphogypsum to the leachate during the phosphogypsum detoxification process, providing two ideas for phosphorus recovery from phosphogypsum leachate: 1) preparation of calcium hydrogen phosphate for feed; 2) preparation of calcium phosphate. A ready-to-use calcium oxide slurry was used to recover P from phosphogypsum leachate at a slurry concentration of 20% and a quantitative link between calcium to phosphorus ratio and fixation rate was fitted by mixed use batch experiments, reaction kinetics and thermodynamics, and theoretical calculations were used to demonstrate that phosphorus cannot be completely reused in the preparation of calcium hydrogen phosphate. The findings demonstrated that: a) the residual phosphorus concentration was in the range of 1300 - 1500 mg/L for the preparation of type I feed grade calcium hydrogen phosphate from phosphogypsum leachate; b) the P removal effect could reach 99.99% for the preparation of calcium phosphate from phosphogypsum using the theoretical equation: fixation rate = $87.91 - 10.96(\text{Ca/P}) + 3.22(\text{Ca/P})^2$ ($R^2 = 0.9954$); c) The procedure follows the suggested secondary kinetics, and according to the Freundlich isothermal model, the reaction process is under the control of the chemical reaction, with a reaction index of 0.7605. This study can be used as a theoretical guide for the recovery of P from phosphogypsum leachate, the preparation of products to bring about economic by-products, and the purification of wastewater for reuse.

Keywords

Phosphorus Recovery, Industrial Wastewater, Precipitation, Phosphogypsum Leachate

1. Introduction

Phosphorus is considered to be one of the most essential elements for the growth

and development of living organisms and is a component of living organisms as well as being able to maintain their metabolism. Additionally, P also shows great potential for application in the field of new energy, as lithium iron phosphate is considered to be the most promising anode material for lithium-ion batteries due to its environmental friendliness, good cycling performance and excellent thermal stability. With the increased annual consumption of P fertilizer worldwide, however, phosphate ore is estimated to be exhausted by the end of this century as a non-renewable resource, which may severely affect social development and human life (Shu et al., 2006). Therefore, much attention has been attracted to the secondary extraction of P resources from phosphate smelting slag. As the demand for P in industry is small and demanding compared to agricultural uses, most of the P should be recycled as fertiliser or used for livestock, which is important in forming the phosphorus cycle. When converted to feed grade calcium hydrogen phosphate, monocalcium phosphate monohydrate (MCPM, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) provides water soluble phosphorus, calcium hydrogen phosphate dihydrate (DCPD, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) provides berry soluble phosphorus, and tricalcium phosphate (TCP, $\text{Ca}_3(\text{PO}_4)_2$) is part of the total phosphorus, providing an additional benefit to phosphogypsum companies that need 200 mL/h of water washing to process 100 g.

Phosphogypsum (PG) is an inevitable solid waste produced from the wet process of phosphoric acid (Chen et al., 2021), which may cause secondary pollution to the environment due to the presence of water-soluble phosphorus and fluorine (Zhong et al., 2010). Currently, water washing is often used to solidify the removal of P and F from phosphogypsum to achieve harmless phosphogypsum, while in the water washing stage, phosphogypsum leachate is enriched with a large amount of P (Wu et al., 2022). The washing process is depicted in Figure 1, with a recirculating water tank under the washing process aqueous washing solution is phosphogypsum leaching solution (Fu et al., 2014).

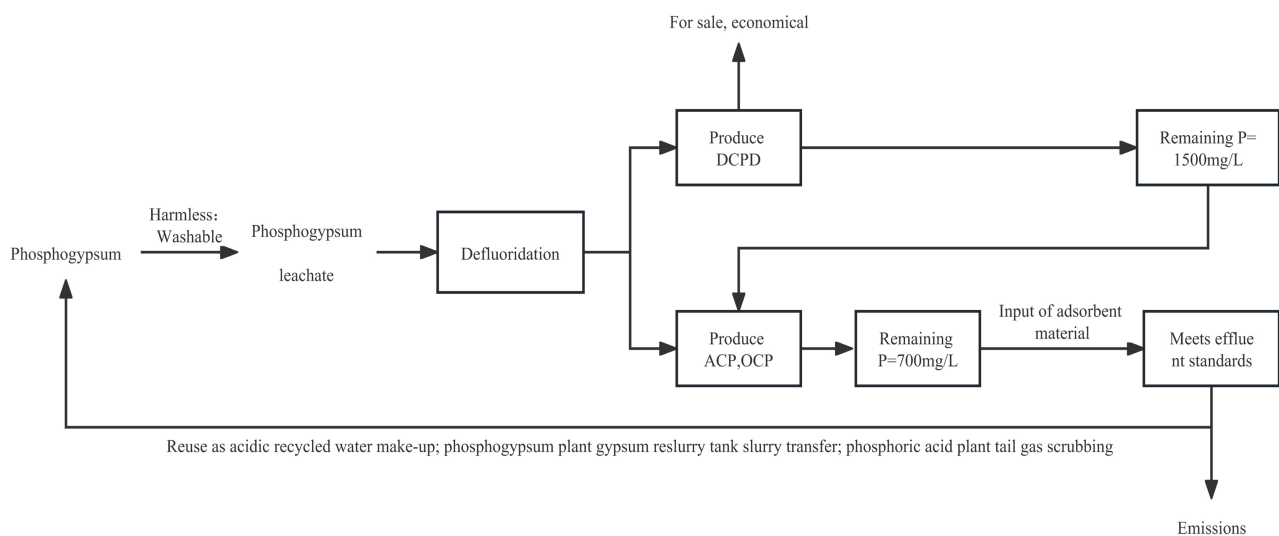


Figure 1. CaO recovery P two pathways.

Prior to now, wastewater discharged into surface waters was the primary target for phosphorus removal (Bal Krishna et al., 2016). Instead, the researcher chose to recover P from phosphogypsum leachate and prepare a more economical product to achieve P recycling and create by-products.

Biological methods can use phosphorus accumulating bacteria (PAO) to absorb excess phosphorus (Ye & Li, 2013), for example, in 2021 an MBBR process was introduced in a wastewater treatment plant in North China, and phosphorus-containing sludge cannot be reused, which is contrary to the concept of phosphorus recovery (Wan et al., 2017). The ion exchange and electro dialysis methods are unable to recover phosphorus and prepare products, resulting in phosphorus loss. When chemical precipitation method is used to recover phosphogypsum leachate, the recovery efficiency is high and by-products can be produced (Li et al., 2022). A phosphogypsum slag site in Fuling, Chongqing, uses chemical precipitation to recover phosphorus, adding magnesium oxide and controlling conditions to produce ammonium magnesium phosphate as a compound fertiliser, but chemical recovery of phosphorus is almost ineffective for phosphogypsum leachate with low P concentrations. The simulated wastewater feedstock in this study does not contain ammonium ions, and the addition of magnesium oxide does not produce magnesium ammonium phosphate, but rather calcium hydrogen phosphate and calcium phosphate by adding calcium oxide.

Numerous studies have been done to develop methods of recovering phosphorus from phosphogypsum leaching solution for the production of fertilizers, with a wide recovery rate of 10% to 90%. Han attempted to prepare calcium hydrogen phosphate from low concentration phosphorus-containing wastewater using CaO (Han & Zhang, 2021), which can be used as a feedstock for the production of animal feed. Wang also used diatomaceous earth, sodium chloride and lime to produce calcium hydrogen phosphate feed from phosphorus-containing wastewater (Wang et al., 2008). However, there are still challenges even though recycling phosphogypsum leachate is the best option. The first is the recovery of phosphorus from the liquid phase, which is only 50% - 60%. No one has given an explanation for the reasons behind the low efficiency of recovering P from phosphogypsum or the fact that in actuality, regardless of the original phosphorus content, the residual phosphorus concentration always stays within a specific set range (Jensen et al., 2021). This study will mathematically calculate this range to obtain a specific set range as well as to explain the presence of residual phosphorus.

In this work, 20% CaO emulsion was used to separate and recover P from phosphogypsum leachate. The objectives of this study were to 1) Two recovery P paths are available: Preparation of DCPD, preparation of HAP (As shown in Figure 1), 2) investigate the numerical relationship between the calcium-to-phosphorus ratio and the rate of phosphorus fixation, 3) analyze the phosphorus cycle losses caused by the two recovery methods.

2. Materials and Methods

2.1. Experimental Samples and Reagents

The raw material for this paper was prepared in the laboratory by taking 1 mL of DALONG analytically pure phosphoric acid with a Beijing Dalong pipette gun, and the exact phosphoric acid concentration was measured by the ammonium molybdate precipitation method, and then the original solution was made. 100 mL of the original solution was placed in a 250 mL beaker and placed on a HJ-6A multi-head magnetic stirrer. Another 50 mL small beaker was taken, 12 mL distilled water, State Pharmaceutical Chemically Pure CaO 3 g, mixed well with stirring of a disposable homemade spoon to prepare slurry of calcium oxide with a mineral slurry concentration of 20%. The 20% CaO slurry was added in small amounts several times towards the original solution, pH was monitored with Remagnet PHS-3E, pH was adjusted and stirred continuously for 24 h, aged for 12 h, and the supernatant was set aside after centrifugation at 5000 r/min and precipitated as the prepared sample.

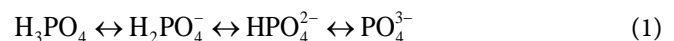
2.2. Analysis Methods and Principles

The contents of PO_4^{3-} -P were determined according to the standard methods.

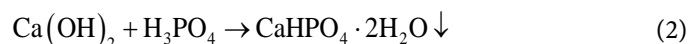
The prepared feed grade calcium hydrogen phosphate (DCPD) was evaluated for quality using the ammonium molybdate precipitation titration method in accordance with the national standard "Feed Additive Calcium Hydrogen Phosphate (GB 22549-2017)" for total phosphorus, LBP, and water soluble phosphorus content in the samples.

2.3. Principle of Analysis

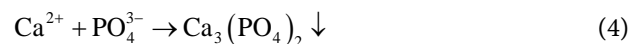
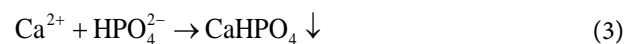
Depending on the pH, there are various forms of phosphate in the phosphogypsum leachate, with the phosphate form shifting from the left to the right as the pH rises.



When pH = 5.5 - 6.



When pH \geq 7,



Theoretical calculations are as follows.

$$\text{Generate DCPD}(\text{mg}) = \frac{P_{\text{初}} \times (\text{Ca} : \text{P}) \times V}{18\%} \quad (5)$$

Of which:

$P_{\text{初}}$ —initial phosphorus concentration, mg/L.

Ca: P—molar ratio of calcium to phosphorus, molar;

V —volume of leachate, in 1 L.

V —volume of leachate, in 1 L.

Actual TCP mass produced Same TCP content and DCPD conversion as for calcium hydrogen phosphate in feed.

Therefore generates

$$\text{TCP}(\text{mg}) = \frac{\text{DCPD} \times (1 - 77.8\%)}{77.8\%} \quad (6)$$

$$P_{\text{Remaining}} (\text{mg/L}) = P_{\text{Initial}} \times (1 - (\text{Ca} : \text{P})) \times 1 - \text{TCP} \times 16.22 \quad (7)$$

In order to ensure the irreversible and stable fixation of phosphate from the leachate, when the goal is to form a specific calcium phosphate, the insoluble precipitated hydroxyapatite, the higher the pH, the higher the fixation rate (Christensen et al., 2022). Orthophosphate ions can react with calcium ions to form a variety of different calcium phosphates, enabling the primary synthesis of calcium hydrogen phosphate when ensuring utilisation as a competent feed. The fixation rate increases with pH, therefore when the starting pH is low, more OH^- is needed to accomplish the task.

In order to provide guidelines for phosphogypsum plants and to evaluate affordability, the amount of CaO emulsion added for fixation rates must be estimated in various phosphorus-containing waters. This method can be used to predict the effect of interacting system parameters on CaO emulsion and pH requirements without the need for extensive batch trials, but it is important to note that the calcium to phosphorus ratio and CaO emulsion concentration all affect the two rates.

Through two main focuses, this research advances the investigation of P fixing in phosphogypsum leachate by CaO.

1) To discover out why P is converted by CaO to feed-grade calcium hydrogen phosphate in phosphogypsum leachate at pH 5.5 - 6, and why the conversion rate increased with P content. The remaining P is only 1500 mg/L. Examine the causes of the incomplete conversion of the phosphogypsum leachate to feed-grade calcium hydrogen phosphate.

2) Examine the connections between the calcium-phosphorus ratio and the fixation rate, residual phosphorus concentration, and the reasons why the leachate phosphorus concentration does not meet the discharge standard even when the treated pH is at the required level—even when the pH is increased to 12 and use the chemical equilibrium model to predict the right calcium-phosphorus ratio to direct the phosphogypsum plant to meet the standard.

3. Results and Discussion

3.1. Utilization of P in DCPD Feed Grade Phosphogypsum Leachate

In part 2.1, the created 20% CaO emulsion was slowly added to 1 L \pm 5 mL of phosphogypsum leachate. The pH was adjusted to 5.5 - 6 while the reaction was

being carried out, and it was aged for 30 minutes before being filtered and dried at 100°C. The procedure outlined in Section 2.2 was used to determine the total phosphorus content of 5 mL of the filtrate.

The results are displayed in **Table 1**; only the phosphogypsum leachate was tested for recovery as Type I feed grade calcium hydrogen phosphate in the subsequent analysis. The mass fractions of total phosphorus, LBP, and water-soluble phosphorus had just reached Type I feed grade calcium hydrogen phosphate.

Table 2 displays information on termination pH, utilization rate, and residual phosphorus concentration. The pH was maintained at 5.5 - 6 when the initial phosphorus concentration rose. Because of the increased acidity of the reaction system, the reaction between the CaO emulsion and phosphoric acid became more rapid, and the majority of the calcium ions combined with the hydrogen phosphate ions to produce calcium hydrogen phosphate, the utilisation rate increased with initial phosphorus concentration under the same reaction conditions. initial concentration of phosphorus at around 12,000 mg/L, utilization rate of 88% - 89%, and remaining concentration of phosphorus at 1300 - 1500 mg/L; Initial phosphorus concentration of 3500 - 4500 mg/L, utilization rate of 60.89% - 64.15%, and remaining phosphorus concentration at this time, compared to the range of 1400 - 1500 mg/L, show that the utilization rate and the initial phosphorus concentration have decreased. The initial phosphorus concentration and the remaining phosphorus concentration did not correlate.

Table 1. Neutralization for preparation of feed grade DCPD.

Termination pH	Total phosphorus mass fraction (%)	LBP mass fraction (%)	Mass fraction of water-soluble phosphorus (%)
5.68	16.65	16.38	4.40
5.57	15.52	15.41	4.03
5.21	17.23	16.75	2.39
5.70	16.51	15.60	2.33
5.70	16.42	15.47	2.89
5.70	16.52	15.87	2.26

Table 2. Relationship between conversion rate and initial and residual phosphorus concentrations.

Initial pH	Termination pH	Initial phosphorus concentration (mg/L)	Utilisation rate (%)	Residual phosphorus concentration (mg/L)
3.06	5.68	12763.57	89.63	1323.58
3.08	5.57	12171.61	88.02	1458.17
3.03	5.21	12076.01	88.24	1420.14
3.35	5.92	4407.70	64.15	1580.16
3.35	5.70	3932.21	62.31	1482.05
3.35	5.65	3826.00	60.89	1496.35

The major question is how the utilisation rate and residual phosphorus content are related based on the basic information below.

Total phosphorus (P) (w/%) in Type I feed-grade calcium hydrogen phosphate was 16.5; citrate soluble phosphorus (P) (w/%) was 14.0; and water-soluble phosphorus (P) (w/%) was 0.0. MCPM provided the water-soluble phosphorus, with a content of 0.0; DCPD provided the citrate soluble phosphorus, which is defined as phosphorus that can be soluble in neutral ammonium citrate TCP is included in the total phosphorus, and the total phosphorus, excluding the water-soluble and citrate soluble phosphorus fractions, is calculated to be 15.4. The DCPD content is equal to the citrate soluble phosphorus content, *i.e.* the DCPD content is 77.8.

If used as Type I feed grade calcium hydrogen phosphate, and according to the base data given in **Table 3**, theoretical calculations for the addition of CaO at a slurry concentration of 20% to 1L of phosphogypsum leachate are provided in **Table 4**. **Table 4** solely uses the calcium to phosphorus ratio as an indicator due to its simplicity; however the synthesis of feed grade calcium hydrogen phosphate should first be indexed by pH before doing so.

The solubility product theory states that when calcium hydrogen phosphate precipitation occurs, $\text{Ca}^{2+} + \text{HPO}_4^{2-} \rightarrow \text{CaHPO}_4$ and $K_{sp}[\text{CaHPO}_4] = 1 \times 10^{-7}$, *i.e.* $[\text{Ca}^{2+}] \times [\text{HPO}_4^{2-}] > 1 \times 10^{-7}$, exist. The homoion effect is known to cause the response to move to the right in the presence of a significant excess of Ca^{2+} . Throughout the process, HPO_4^{2-} is formed as $\text{H}_3\text{PO}_4 + \text{OH}^- \rightarrow \text{H}_2\text{PO}_4^- + \text{H}_2\text{O}$ and $\text{H}_2\text{PO}_4^- + \text{OH}^- \rightarrow \text{HPO}_4^{2-} + \text{H}_2\text{O}$. Calcium hydrogen phosphate causes the reaction to move to the left when the solution is dynamically equilibrated, leaving P unused. The use of phosphogypsum leachate in the P cannot be fully utilized as feed grade calcium hydrogen phosphate, regardless of how high the utilization rate and the initial phosphorus concentration. As can be seen from **Table 4**, the initial phosphorus concentration of 9000 - 13,100 mg/L, the removal rate of up to 88%, and the theoretical residual phosphorus concentration is still 1310 - 1550 mg/L. Residual phosphorus can be treated by precipitation-nanofiltration (Al-harashseh et al., 2017), or by using triple neutralisation, or by immobilising the residual phosphorus as shown in Section 3.2.

3.2. P Fixation to Calcium Phosphate in Phosphogypsum Leachate

The prepared 20% CaO emulsion was slowly dripped into 10,000 mL \pm 5 mL of

Table 3. Theoretical calculation base data.

Compound	Molecular formula	Molecular weight	Ca/P (molar)	Percentage of P (w %)
MCPM	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	252.04	0.5	24.58
DCPD	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	172.07	1	18.00
TCP	$\text{Ca}_3(\text{PO}_4)_2$	381.96	1.5	16.22

Table 4. Utilisation as a function of initial and residual phosphorus concentrations concentrations.

Initial phosphorus concentration (mg/L)	Input Ca/P (molar)	DCPD theoretical mass (mg)	TCP theoretical mass (mg)	Residual phosphorus concentration (mg/L)	Actual Ca/P (molar)	Utilisation rate (%)
13,080	0.5	36365.14	10376.69	4858.38	0.54	62.86
	0.6	43638.17	12452.02	3214.05	0.65	75.43
	0.7	50911.19	14527.36	1569.73	0.76	88.00
12763.57		49636.11	14163.52	1530.41	0.76	88.00
12171.61	0.7	47334.04	13506.63	1459.43	0.75	88.00
12076.01		46962.26	13400.54	1447.97	0.75	88.00
10,900	0.5	30304.28	8647.24	4048.65	0.53	62.86
	0.6	36365.13	10376.68	2678.37	0.64	75.43
	0.7	42425.99	12106.13	1308.1	0.75	88.00
4360	0.5	12121.72	3458.90	1619.46	0.51	62.86
	0.6	14546.07	4150.68	1071.35	0.62	75.43
	0.7	16970.41	4842.46	523.24	0.72	88.00
4407.7		10922.81	3116.79	1635.75	0.51	62.86
3932.21	0.5	11905.86	3397.30	1459.28	0.51	62.86
3826		11921.56	3401.78	1419.87	0.51	62.86

phosphogypsum leachate in Section 2.1. pH was adjusted at 6.5 - 9.5/9.5 - 12 at 25°C ± 5°C and 400 r/min, the reaction was carried out for 24 hours, aged for 12 hours, filtered and the precipitate was dried in an oven at 100°C. 5 mL of the filtrate was taken and dried using the method described in Section 2.2 Test the concentration of phosphorus pentoxide.

The effect of calcium to phosphorus ratio on fixation rate was investigated. pH = 6.5 - 9.5 was controlled in experiments 1 - 5 to comply with the Comprehensive Sewage Discharge Standard GB8978-1996 and the Water Quality Standard for Sewage Discharge into Urban Sewers CJ343-2010 pH; pH = 9 - 12 was controlled in experiments 6 - 10 to investigate the change in removal rate with increasing calcium to phosphorus ratio.

P₂O₅ was initially controlled in experiments 1 - 3, 5, and 8 using potassium dihydrogen phosphate, while experiments 4, 6, and 9 - 10 were controlled by analytically pure phosphoric acid. The outcomes are displayed in **Table 5**.

According to Christensen assume that a 1.5 lime: P ratio removes around 99% of the dissolved P from effluent from greenhouses that contains 30 - 60 mg/L of phosphorus (Dunets et al., 2014). By raising the pH to 9.5, which results in P < 2 mg/L in the wastewater, phosphate can be removed by precipitation without the use of calcium ions. Phosphate can also be removed at pH 9 (P < 1 mg/L) with the addition of calcium salts (Ca: P = 2), but this approach is not used for high

Table 5. Relationship between fixation rate and calcium to phosphorus ratio.

Initial pH	Termination pH	Calcium to phosphorus ratio	Initial phosphorus concentration (mg/L)	Fixation rate (%)	Residual phosphorus concentration mg/L
1.9	6.29	1.9	3825.97	78.38	827.17
1.9	7.10	2.2	3825.97	79.42	787.39
2.1	7.34	2.3	3825.97	80.45	747.98
1.97	8.56	2.5	4407.7	80.23	871.4
1.9	9.09	2.8	3825.97	82.23	739.17
1.9	9.56	2.9	4407.7	83.95	707.44
1.97	9.98	3.0	4407.7	85.94	619.72
2.1	11.3	3.4	4407.7	87.39	555.81
1.9	11.62	3.9	3825.97	88.85	426.6
1.9	11.58	4.0	4407.7	95.07	217.3
1.9	12.16	4.1	4407.7	99.35	28.65
2.1	12.54	4.2	4407.7	99.68	14.1
2.1	12.6	4.3	4407.7	99.99	0.44

concentrations of phosphorus-containing wastewater in the paper. Cichy used CaO in addition to 0.6% P₂O₅, with a ratio of 1.4 between calcium and phosphorus (Cichy et al., 2019). When utilizing CaO, the removal rate is 80%, although it is unclear how the ratio of calcium to phosphorus and removal rate relate to one another.

In **Table 5**, the regression connection was regressed on the association between removal rate and calcium to phosphorus ratio following treatment. The removal rate increased with increasing molar ratio of calcium to phosphorus (molar ratio Ca: P) at a similar rate for all initial P values. The test resulted in the following equation ($R^2 = 0.9954$) after the offset points were eliminated.

$$\text{Fixation rate} = 87.91 - 10.96(\text{Ca/P}) + 3.22(\text{Ca/P})^2 \quad (8)$$

This implies that Equation (8), independent of the initial phosphorus concentration, can be used to determine the calcium to phosphorus ratio necessary for a particular fixing rate. While this estimate is meant to serve as a general guideline for the calcium to phosphorus ratio requirement based on the desired fixation rate, in practice the effluent pH will also be taken into consideration. For instance, a calcium to phosphorus ratio of 4.36 achieves 99.99% fixation.

The fit is shown in **Figure 2**, with three points of error caused by different experimental manipulations, which were excluded from the fit, but a separate study could lead to more conclusions. In experiment 7, a small amount of saturated sodium hydroxide supplied OH⁻ to help some phosphoric acid be converted to H₂PO₄⁻, lowering the amount of CaO. By secondary neutralization, Experiments 9 and 11 were produced. Experiment 9 was produced by first raising pH = 1.9 to pH = 6.13 and then secondarily raising pH = 6.13 to pH = 11.62

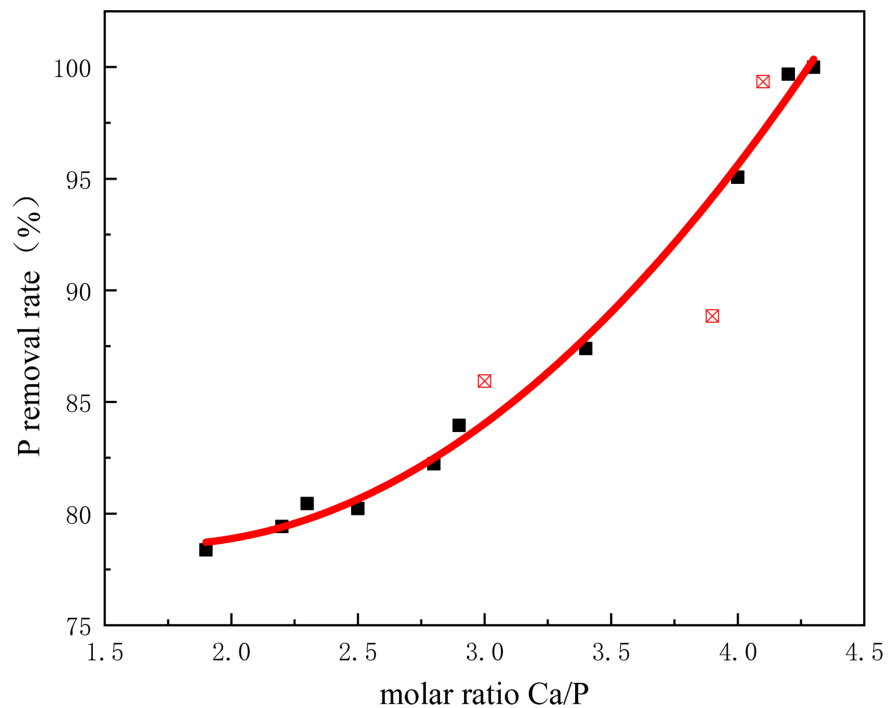


Figure 2. Relationship between calcium-phosphorus ratio and fixation rate.

with CaO, whereas experiment 11 was produced by first raising pH = 1.9 to pH = 9.67 and then secondarily raising pH = 9.67 to pH = 12.16 with CaO. The initial solution employed in Experiment 9 was potassium dihydrogen phosphate, which was able to buffer the CaO-induced pH increase. The two buffers, however, required more lime to reach a particular pH, which increased the amount of CaO. The principle of Experiment 11 was similar to Experiment 7, except that Experiment 7 used a small amount of saturated sodium hydroxide to provide OH^- and Experiment 11 was neutralized twice, allowing for increased digestion. During one neutralization, the lime milk particles were encapsulated by an impermeable precipitation film in which the phosphate reacts or precipitates onto the surface of the unreacted core.

The mineral-based ceramic material was mixed with 50 mL of the filtrate from Experiments 5 and 6, and the reaction was then carried out as follows.

As shown in **Table 6**, the P concentration can be lowered from 700 mg/L to less than 20 mg/L when the pH is adjusted to 9 - 9.5 and mineral-based ceramic materials are added. It can be used as acidic recycled water make-up water, slurry adjustment in the gypsum reslurry tank of the phosphogypsum plant, and tail gas scrubber water of the phosphoric acid plant because the pH and residual P concentration are in compliance with the "Water Quality Standard for Discharge of Wastewater into Urban Sewers (CJ343-2010)".

3.3. Analysis of the CaO-Induced Precipitation of P

3.3.1. Kinetics of Reactions

The pH was adjusted to 7, the temperature was 25°C, the speed was 400 rpm,

Table 6. Mineral-based ceramic materials for the treatment of residual P.

Serial number	pH	Mass of ceramic material (g)	Initial P concentration (mg/L)	Residual P concentration (mg/L)
5	9.09	19.53	739.17	99.35
6	9.56	46.41	707.44	16.73

and the sampling times were 0.5 hours, 1.5 hours, 2.5 hours, 5 hours, 9 hours, 12 hours, 18 hours, 24 hours, 30 hours, and 48 hours. The prepared 20% CaO emulsion was slowly dropped into the 10,000 mL \pm 5 mL 1.1 section of phosphogypsum leachate. Each time, 10mL of filtrate was put into 10mL centrifuge tubes, and the supernatant was spun at 2000 rpm for 10 minutes. **Figure 3** depicts the CaO reaction rate curve, and **Figure 4** displays the results of the kinetic fitting.

According to **Figure 4**, the CaO reaction amount increased gradually over the first 0.5 to 2.5 hours of the reaction, dramatically from 2.5 to 24 hours, and then gradually leveled off after 24 hours until the reaction equilibrium. The reaction time chosen was 24 hours. The suggested secondary kinetic equation has the following linearized form.

The reaction time chosen was 24 hours. The suggested secondary kinetic equation has the following linearized form.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (9)$$

Of which:

q_e —reaction capacity at equilibrium, mg/g.

q_t —reaction capacity at time t , mg/g.

k_1 —reaction constants for the proposed primary kinetic model, /min.

The linearized form of the proposed secondary kinetic equation is as follows

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

Of which:

q_e —reaction capacity at equilibrium, mg/g.

q_t —reaction capacity at time t , mg/g.

The linearised form of the Elovich kinetic equation is as follows

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (11)$$

Of which:

α —initial reaction rate constant, mg/(g*min).

β —the constant associated with the activation energy of the reaction, g/min.

The results of the fit are shown in Table by **Table 7**.

The proposed primary kinetic equation with a correlation coefficient R^2 of 0.9372 does not fully describe the entire reaction process and the mechanism of

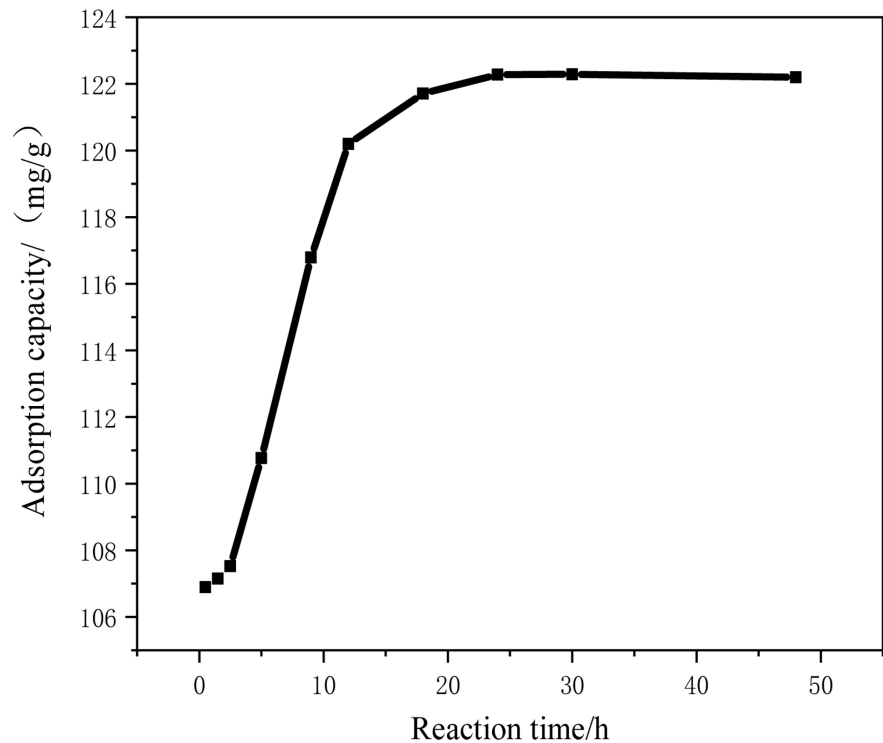


Figure 3. CaO adsorption P rate curve.

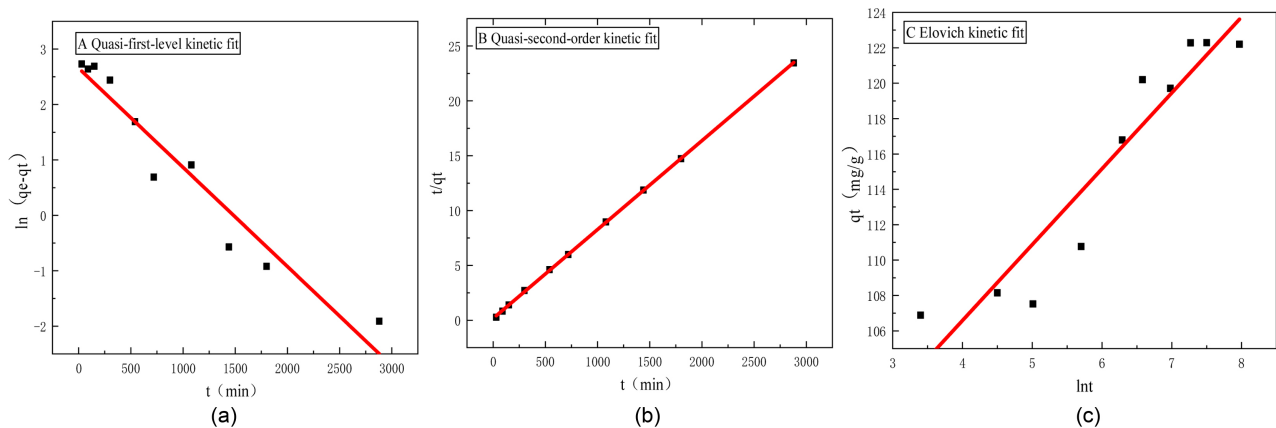


Figure 4. Fitting of the quasi primary (a), quasi secondary (b) and Elovich (c) kinetic equations.

CaO reaction to phosphate is not only a physical reaction process controlled by diffusion. The proposed secondary kinetic equation has the largest correlation coefficient R^2 of the three, above 0.98, with an excellent linear correlation, indicating that the proposed secondary is more suitable to describe this reaction process, suggesting that the reaction of CaO to phosphate is controlled by a chemical reaction through electron sharing or electron transfer between CaO and phosphorus.

The CaO to phosphate conversion is governed by a chemical reaction, through electron sharing or electron transfer between CaO and phosphate, according to the Elovich kinetic equation's weak fit, which has a lower correlation

Table 7. Results of fitting the reaction kinetic equations for the precipitation of phosphorus by CaO emulsions.

Models	Fitting equation	R ²	Fitting constants	
Proposed Level 1	$y = -0.00179x + 2.655$	0.9372	$K_1 = 0.00179$	$q_e = 14.224$
Proposed Level 2	$y = 0.0081x + 0.17035$	0.9999	$K_2 = 0.00039$	$q_e = 0.7605$
Elovich	$y = 4.288x + 89.4368$	0.8933	$\alpha = 4.4986$	$\beta = 0.2332$

coefficient R² of 0.8933. This supports the conclusions of the previous proposed secondary kinetic model by showing that the activation energy change of CaO in the reaction of phosphate ions is minor and that a portion of the reaction process involves chemical reaction.

3.3.2. Reaction Thermodynamics

The experiments were carried out in accordance with 2.3.1 as shown in **Figure 4**, using the Langmuir and Freundlich reaction model for data fitting under isothermal conditions. The theoretical reaction volume of the CaO emulsion to phosphate ions is an important indicator of its ability to fix the reaction (Balsamo et al., 2010).

The following version is used to linearize the Langmuir isothermal reaction equation.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (12)$$

Of which:

q_e —reaction capacity at equilibrium, mg/g.

q_m —maximum reaction capacity, mg/g.

C_e —equilibrium concentration of the reaction, mg/L.

K_L —Langmuir reaction constant, L/mg.

The Freundlich isothermal reaction equation is linearised in the following form

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f \quad (13)$$

Of which:

q_e —reaction capacity at equilibrium, mg/g.

$1/n$ —response index.

C_e —equilibrium concentration of the reaction, mg/L.

K_f —Freundlich reaction constant.

Figure 5 shows the results of the fit. **Table 8** displays the outcomes of the linear data fit utilizing the Langmuir and Freundlich isotherm models. The highest reaction predicted by Langmuir, 669.32, was far more than the maximum reaction that actually occurred, and the Langmuir equation was unable to account for this reaction.

The R² for the Freundlich equation was 0.9990, exceeding 0.98 and reaching a highly significant level. The reaction index at this moment was 0.7605, showing that the 20% CaO reaction P is more likely and effective. The smaller the 1/n, the

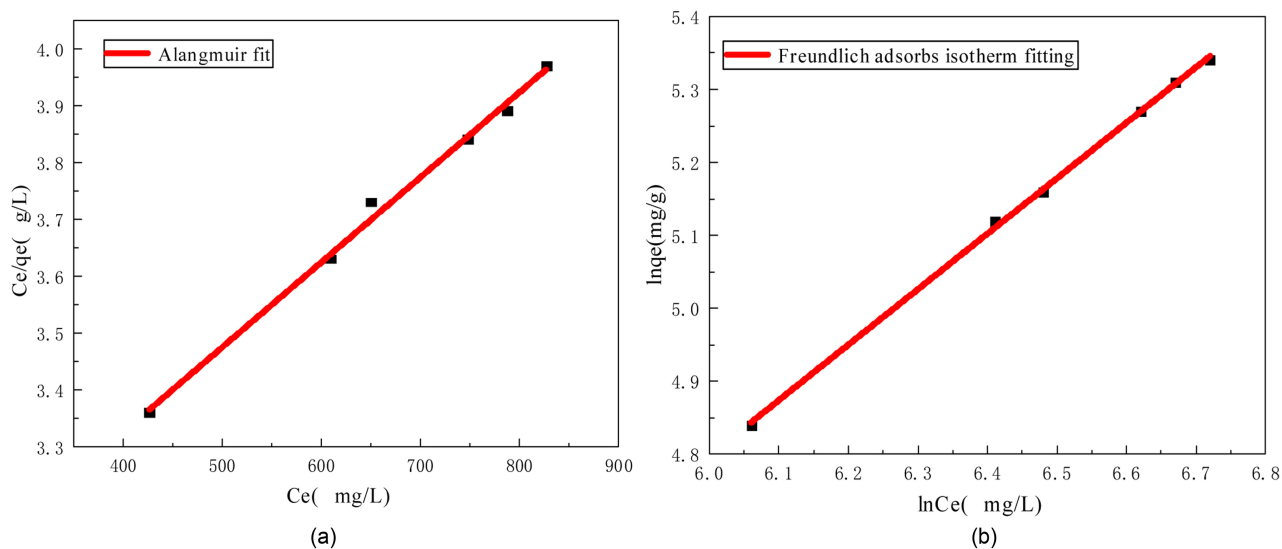


Figure 5. Isothermal adsorption lines of calcium oxide adsorbed phosphate in water.

Table 8. Results of fitting the kinetic equations for phosphorus fixation in CaO emulsions.

Models	Fitting equation	R^2	Fitting constants	
Langmuir	$y = 0.0015x + 2.7286$	0.9947	$k_L = 0.0005$	$q_m = 669.32$
Freundlich	$y = 0.7605x + 0.2351$	0.9990	$k_f = 1.2651$	$1/n = 0.7605$

better the reaction performance, and when $1/n$ is more than 2, the reaction does not progress easily (Juang et al., 2002).

3.3.3. Characterization Analysis

Figure 6(a) displays the XRD pattern of the precipitate formed with the addition of CaO, which brought the pH value to 11. The spectrum shows that after the CaO reaction of phosphorus, diffraction peaks form, but the baseline is not smooth and the peak pattern broadens. The analysis results in its surface crystalline products, such as amorphous calcium phosphate (ACP) and octacalcium phosphate (OCP). The impurities introduced during the drying process can muddy the background, but have no effect on the main peak shapes (Sujinpram et al., 2011).

The CaO reaction after P results in a characteristic PO_4^{3-} spectrum in the FTIR spectrum (Figure 6(b)), which corresponds to the P-O-H plane bending: the stretching vibration peak of O-H prior to the reaction of CaO (Zyman et al., 2009); PO_4^{3-} band at 567.53 cm^{-1} , 604.14 cm^{-1} , and 1032.94 cm^{-1} (Mhla et al., 2017). A faint characteristic peak at 873.89 cm^{-1} , which is the characteristic absorption peak of CO_3^{2-} , indicates the entry of air during the crystallization of calcium phosphate, which is followed by the crystallization of CaCO_3 (Xiao et al., 2022). The stretching vibration peak before the reaction of CaO is 3644.04 cm^{-1} , and after the reaction of P, the stretching vibration peak is shifted to 3444.03 cm^{-1} .

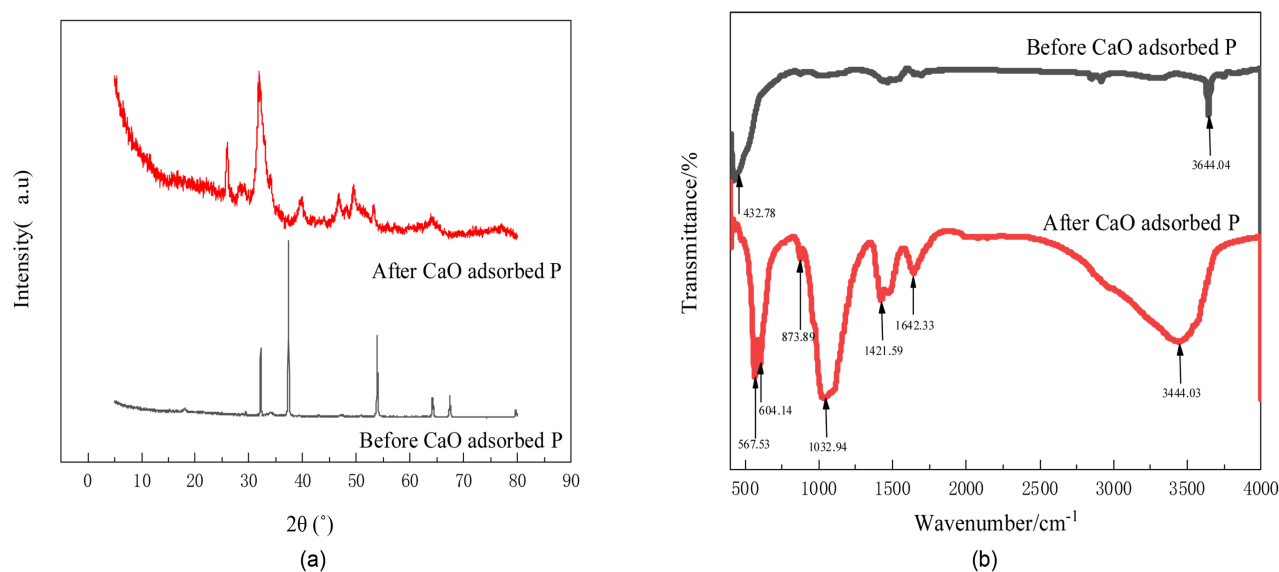


Figure 6. XRD and FTIR spectra of CaO before and after the reaction. (a) XRD pattern; (b) FTIR pattern.

4. Conclusion

The following conclusions were reached using batch experiments and chemical equilibrium models to reveal two paths for the recovery of P from phosphogypsum leachate using CaO, to meet the resourcefulness of phosphogypsum leachate.

1) This study offers two options for businesses. When pursuing quality, they can prepare DCPD from P in phosphogypsum leachate, which can recover P in high quality, but the recovery rate is low and the theoretical residual phosphorus concentration still exists 1300 - 1500 mg/L. On the other hand, when pursuing fixation rate, P is recycled as ACP and OCP, with the fixation rate being calculated as follows: fixation rate = $87.91 - 10.96(\text{Ca}/\text{P}) + 3.22(\text{Ca}/\text{P})^2$ ($R^2 = 0.9953$).

2) With a quick and high spontaneous potential, the reaction of CaO precipitating P approaches equilibrium in 24 hours.

3) The proposed secondary kinetic equation can well describe the process of phosphorus adsorption by calcium oxide for chemisorption, as can be demonstrated laterally by the Elovich kinetic equation. The adsorption of phosphorus by calcium oxide is consistent with the Freundlich isothermal adsorption model and the adsorption is between monolayer and multilayer adsorption, at which point the adsorption index is 0.7605.

The findings of this study can serve as a reference for phosphogypsum treatment plant operators and regulators in order to help recover P from phosphogypsum leachate, discharge water that complies with the standard, or reuse it as acidic recycled water make-up water, gypsum reslurry tanks for phosphogypsum plants, and tail gas scrubber water for phosphoric acid plants.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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