Recovery behaviors of acid-modified cement hydration material on phosphorous

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Abstract. Silicate cement hydration product is a promising phosphorus adsorption material. In view of the strong alkali characteristics of early hardening cement paste, this study adopted acid leaching method to modify and then investigated its phosphorus recovery performance. The results showed that acid modification could weaken the strong alkali property, nevertheless, it also lowered phosphorus removal efficiency. The decline of phosphorus recovery was closely related to the depletion of calcium source. By the fit calculation, it can be determined that the adsorption kinetics of modified material on phosphorus met the pseudo-second-order model. This was consistent with the behavior of unmodified material. Additionally, XRD analysis demonstrated that the phosphorus species enriched on the surface of modified material mainly consisted of hydroxyapatite and variscite, which was different from the brushite of unmodified material. Acid modification would provide much more aluminum sites on the adsorption of phosphorous.

1. Introduction
It is well known, when calcium ions encounters phosphates in solution, especially under alkaline conditions, it is easy to form precipitates, such as CaHPO$_4$, Ca$_3$(OH)(PO$_4$)$_2$ and Ca$_3$(PO$_4$)$_2$. Several studies have described that the dissolved Ca$^{2+}$ from the dissolution of calcium hydroxide (Ca(OH)$_2$), gel hydrate (C-S-H) and calcium carbonate (CaCO$_3$) are preferably precipitated by phosphates in high pH solution[1-3]. In addition to calcium, dissolved aluminum ions can also combine with phosphates to form precipitates (such as AlPO$_4$). Compared with Ca$_3$(PO$_4$)$_2$, the solubility of AlPO$_4$ is smaller and the precipitation becomes much easier[4]. Due to contains rich soluble calcium and aluminum sources, silicate cement hydration materials have behaved obvious advantages in the removal of phosphate in water. The commonly used materials include cement mortar[5], cement paste[6] and waste concrete products[7,8].

Despite silicate cement hydration materials show strong ability to recover phosphorus, there are still some problems in their selection and usage. For example, as to the usage of early hardening cement materials. Affecting by the short hardening time, intense hydration reaction will continue to occur in their adsorption process. This will accompany by the release of a large amount of alkalinity and leads to the high pH value of effluent. In addition, the activities of aluminate minerals in such materials are often limited. As the hydration reaction begins, tricalcium aluminate (C$_3$A) of cement clinker reacts with gypsum first to form ettringite. If the gypsum is excessive, ettringite will further react with gypsum to form monosulfide calcium aluminate hydrate (Afm). However, these aluminate minerals may be encapsulated by C-S-H gel hydrates and CaCO$_3$, resulting in less active sites of Al exposed to the surface of the material.
In view of above-mentioned problems, this research attempts to use acid treatment to modify the early hardening cement materials. On the one hand, with the help of acid-base neutralization reaction, it urges the internal hydration reaction of the materials, so as to reduce the release of residual alkalinity in the subsequent phosphorus adsorption reaction. On the other hand, by using acid dissolution effect to eliminate part of exteiors coverage CaCO₃ and C-S-H to increase much more active sites of Al. On this basis, to investigate the phosphorus recovery behavior of the modified materials, and to compare it with the unmodified material.

2. Materials and methods

2.1. Portland cement board
The cement board used in the experiment was made of ordinary portland cement clinker (P·O 42.5, Hailuo brand, produced in Xinyu City, Jiangxi Province). The elements constitution of clinker was as follows, CaO 47.36%; SiO₂ 31.01%; Al₂O₃ 9.83%; SO₃ 3.31%; MgO 1.48%; Fe₂O₃ 4.09%; K₂O 1.15%; TiO₂ 0.51%; Na₂O 0.42%; P₂O₅ 0.16%. The mixing ratio of clinker and water was 3:1 (mass ratio). The cement paste was demoulded after hardening 5 days. The size of the board (length×width×thickness) was 111mm×58mm×6mm. Its total surface area was about 149.04cm². In order to delay carbonation reaction, the surface of cement board was wrapped with plastic film.

2.2. Modification of cement board
Prepared 0.05mol/L hydrochloric acid solution, immersed the cement board entirely in hydrochloric acid solution according to the proportion of 300mL solution for each board. soaked the board in room temperature for 8 hours and then took out, washed it with deionized water for 2-3 times. After natural drying, wrap the board with plastic film for standby.

2.3. Investigation of adsorption characteristics
The phosphorus adsorption experiments were conducted in a special device (Figure 1). The main reactor is a cylindrical (diameter=65mm) plexiglass vessel. Its effective volume is about 530ml. The main accessories consist of sampler, siphon sampling tube, siphon holder, plastic hose, hanger, etc. The distance between the hanger and the bottom of the reactor is about 16cm. In experiment, the cement board is suspended on the hanger and its height is adjustable.

![Figure 1. Experimental device for adsorption](image)

Prepared 50mg/L potassium dihydrogen phosphate solution and injected 300mL solution into the reactor. Adjusted the height of the cement board to ensure its immersion depth is about 60mm (± 1mm). The effective contact area between cement board and solution was calculated to be 80.3cm² approximately. Placed the experimental device in the water bath of magnetic stirrer. The water
temperature was controlled at 20°C, and the stirring time was set 12 hours at medium speed. During the reaction, the pH value and the phosphorus concentration in the solution were measured regularly. The water sample was collected by siphon sampling pipe. Sucked about 30 ml of solution, and first detected its pH value with a portable pH meter, then extracted 10 ml of solution with a needle syringe. After filtration with 0.45μm filter membrane, the dissolved phosphorus in the filtrate was determined. Except for the solution needed for phosphorus determination, the rest of the solution was all recycled into the reactor to continue the reaction. In this study, molybdenum antimony antispectrophotometry method[9] was used for the determination of dissolved phosphorus. The absorbance of the solution was checked by visible spectrophotometer (TCL-6, General analysis, Beijing China), and its maximum absorption wavelength was 700nm. The calculation formula of phosphorus removal rate was as follows:

\[ R = \frac{C_0 - C_t}{C_0} \times 100\% \]  

Where, \( C_0 \) and \( C_t \) represent the concentration of phosphorus at initial and time \( t \), respectively (mg/L). \( R \) is the removal rate of phosphorous, (%).

The adsorption kinetic model mainly referred to pseudo first order and pseudo second order model[10]. The expression of pseudo first order kinetic model was as follows,

\[ \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \]  

The expression of pseudo second order kinetic model was as follows,

\[ \frac{t}{q_t} = \frac{1}{k_2} \cdot \frac{1}{q_e^2} + \frac{t}{q_e} \]  

Where, \( q_e \) and \( q_t \) represent the adsorption capacity of phosphorus at initial and time \( t \), respectively (μg/cm²). \( k_1 \) is the reaction rate constant of pseudo first order, (h⁻¹). \( t \) is the reaction time, (h). \( k_2 \) is the reaction rate constant of pseudo second order, (cm²/μg·h⁻¹).

2.4. Physical and chemical characterization

The crystal phase composition of the material surface was determined by XRD polycrystalline powder diffractometer (Ultima IV, Science of Physics, Japan). Angle range, 5°-90°, scanning speed: 5°/min, working voltage, 40kV, working current, 40mA. The surface morphology was observed by SEM (Gemini, Zeiss, Germany). The element composition was analyzed by energy dispersive spectrometer (Xflash, Brooke, Germany).

3. Results and discussion

3.1. Effect of modification on physical and chemical properties of materials

The crystal mineral compositions on the surface of the cement before and after modification is shown in Figure 2(a). It can be seen that, before the modification, the crystal minerals mainly include calcite (CaCO₃, PDF# 47-1743), quartz (SiO₂, PDF# 46-1045) and gypsum (CaSO₄·2H₂O, PDF# 33-0311). But after the modification, its composition changed and the characteristic peak of gypsum (2θ=11.59, d=0.7637nm) disappeared. In addition, the characteristic peak intensity of quartz (2θ=26.64, d=0.3345nm) surpassed that of calcite (2θ=29.40, d=0.3036nm) obviously. This indicated that gypsum, calcium carbonate and some calcium oxides of calcium silicate hydrates were dissolved under the action of acid erosion. It worth to note that there have no characteristic peaks of mineral compositions related to aluminum in Figure 2(a), which means that aluminum oxides mainly existed in amorphous form. Figure 2(b) and (c) showed the surface morphologies and element compositions before and after modification. Obviously, after the modification, the particle size of minerals on the surface of cement became smaller. EDS analysis demonstrated that, before the modification, the mass fraction of aluminum and silicon on the surface of the cement was 1.55% and 3.80%, respectively, while after the modification, the mass fraction of aluminum and silicon increased to 6.04% and 13.62%. This also revealed that the dissolution action of acid could make much more aluminum sites exposed.
3.2. Phosphorus recovery behavior

The removal efficiencies of cement board on phosphorus before and after modification were investigated comparatively (Figure 3). As shown in Figure 3(a), before the modification, the efficiency of the board was very high. Its removal rate on phosphorus could reach 90% as contact of 1h, and almost close to the equilibrium state at the fourth hour. The final removal rate kept stable at 99.8%. After the modification, the phosphorus removal efficiency decreased significantly (Figure 3(c)). Its’ final removal rate was only 70.5%.
Figure 2. The results of XRD, SEM and EDS on modified and unmodified cement board (a, XRD; b, SEM and EDS of unmodified board; c, SEM and EDS of modified board).

Through continuous monitoring of the pH value of the solution, it was found that both modified and unmodified cement board on the phosphorus absorption were carried out in alkaline conditions. In contrast, the alkalinity before the modification was stronger. For 50 mg/L potassium dihydrogenphosphate solution, its initial pH value was 6.05. When the solution contacted with unmodified cement board for 1 h, its pH value rapidly increased to 10.98, and then kept a continuous growth trend. At the 12 h, the pH value reached 12.03 (Figure 3(a)). Here, we think the changes of pH value of solution are in the charge by the release of residual alkalinity of the materials. In light of the new prepared cement board is stored by wrapping with plastic film, its carbonation process in the air will slow down obviously. A large amount of Ca(OH)\(_2\) components would remain on the surface and internal pores of the material. Unfortunately, there were no representative signals about the mineral composition of Ca(OH)\(_2\) in the above-mentioned XRD results, for example, portlandite. So, we speculated that this part of Ca(OH)\(_2\) mainly existed in the form of amorphous. Additionally, affected the relative short hardening period of cement, some clinker components within the hydrated materials maybe not participate in the hydration reaction in time, including tricalcium silicate (C\(_3\)S) and dicalcium silicate (C\(_2\)S). In the subsequent contacting process with phosphate solution, these components will continue to hydrate and produce Ca(OH)\(_2\). These should be the main reasons for the different alkalinity of the solution during the reaction period. The hydration reaction process of tricalcium silicate and dicalcium silicate can be described as follows[11]:

\[
2(3\text{CaO} \cdot \text{SiO}_2) + 6\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{SiO}_2 \cdot 3\text{H}_2\text{O} \quad (\text{C-S-H}) + 3\text{Ca(OH)}_2 \quad (4)
\]

\[
2(2\text{CaO} \cdot \text{SiO}_2) + 4\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{SiO}_2 \cdot 3\text{H}_2\text{O} \quad (\text{C-S-H}) + \text{Ca(OH)}_2 \quad (5)
\]
After the modification, although the pH value of the solution behaved the increase trend, the real alkalinity of the cement board decreased significantly. In Figure 3(c), when the contact time was 1 h, the corresponding pH value of the solution was 9.49. It took about 4h to reach 10.96. However, this was only equivalent to the level of unmodified board of 1h. The final pH value at 12 h was 11.30. By the data contrast, it’s clear that the higher pH value would gain the higher phosphorous recover efficiency. The decline of phosphorous recovery should be related to the depletion of calcium source.

The fit calculation results of adsorption kinetics are shown in Table 1. By comparing the correlation coefficient, it can be judged that the adsorption of phosphorous before and after modification were in more line with the pseudo second-order kinetic model. This results also roughly reflect that, in this study, the chemical adsorption would be the predominant adsorption mechanism on phosphorous.

### Table 1. Kinetic parameters of phosphorous adsorption(20°C).

| Type                  | Pseudo-first-order | Pseudo-second-order |
|-----------------------|--------------------|---------------------|
|                       | Qe (µg/cm²) | k (h⁻¹) | R²       | Qe (µg/cm²) | k₂ (cm²·µg·h⁻¹) | R²     |
| Before modification   | 17.81             | 0.276     | 0.9419  | 219.78      | 0.0347          | 0.9998 |
| After modification    | 128.09            | 0.297     | 0.9659  | 183.49      | 0.0023          | 0.9659 |

With regards to the phosphorous species enriching on the board, it can be determined by XRD (Figure 4(a)) that, for the unmodified board, phosphorous mainly existed in the form of CaHPO₄·2H₂O (PDF# 09-0077) (2θ=11.60°, d=0.7620nm), while that for modified board was hydroxyapatite (Ca₅(PO₄)₃(OH), PDF# 09-0432) (2θ=31.54°, d=0.2834nm). In theory, hydroxyapatite has three strong peaks in the angle range of 30°-33° (2θ=31.54°,32.12°,32.80°), the broad peak occurred in the Figure should be the result of superposition. As shown in Figure 4(b) and (c), there exists enormous morphology variation of the two species. This result is basically consistent with the viewpoint supported by Wang [5]. According to his report, when the concentration of phosphorous solution is relatively high, the calcium rich hydration products would precipitate brushite (CaHPO₄·2H₂O). In this study, the change of calcium phosphate precipitation species before and after modification might be related to the amount of calcium source and its dissolution efficiency. Of course, this speculation still need further verification. In addition to hydroxyapatite, it’s worth to note that variscite (AlPO₄·2H₂O, PDF# 33-0033) (2θ=29.34°,d=0.3041nm) was also detected on the the modified board. This fully demonstrated that after the acid treatment, much more aluminate active sites play the role of phosphorus absorption. With respect to the formation of variscite, it probably carried out according to the following steps[4]:

\[
Ca(OH)_{2(S)} \rightleftharpoons Ca^{2+} + 2OH^{-} \\
3H_{2}O(l) + Al_{2}O_{3(S)} + 2OH^{-} \rightarrow 2Al(OH)_{4}^{2-} \\
Al(OH)_{4}^{2-} + PO_{4}^{3-} \rightarrow AlPO_{4} + 4OH^{-}
\]
Figure 4. The results of XRD, SEM and EDS on modified and unmodified cement board (a, XRD; b, SEM and EDS of unmodified board; c, SEM and EDS of modified board)
4. Conclusions
In this study, we adopted the acid leaching method to modify the early hardening cement paste and then investigated its phosphorus recovery performance. If just seen from the recover rate of phosphorous, the acid modification did not achieve the goal of further improving the phosphorus removal performance of materials. The main reason should be related to the deplete of calcium source. In spite of it, acid modification still has a certain reference value for increasing the active sites of aluminum and the selective precipitation of phosphorus species, for example, hydroxyapatite.

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