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# Utilizing $CaCl_2$ to promote the enrichment and bioavailability of phosphorus in incinerated sludge ash

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## ABSTRACT

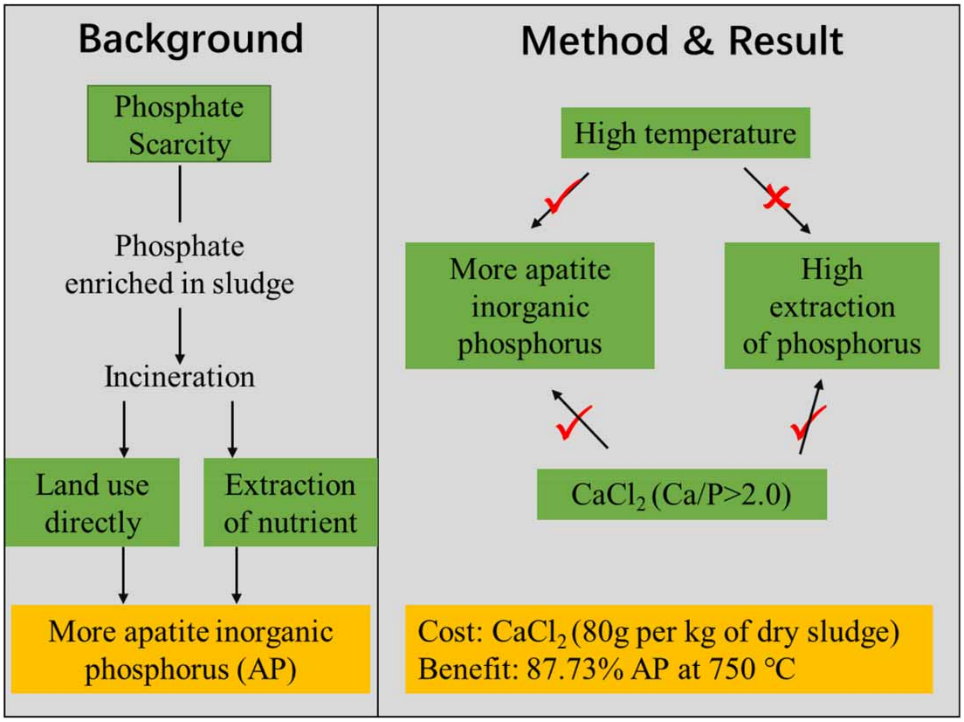
Recovering phosphorus from incineration sludge sewage ash (ISSA) is a well-established technology, with a greater recovery potential than that of supernatant or sludge. ISSA can be utilized as a secondary raw material in the fertilizer industry, or as a fertilizer if heavy metal concentrations do not exceed permissible limits, thus reducing the cost of phosphorus recovery. Increasing the temperature to produce ISSA with higher solubility and plant availability of phosphorus is advantageous for both pathways. But a decrease in the extraction of phosphorus is also observed at high temperatures, thereby diminishing the overall economic benefits. In this study, $CaCl_2$ was utilized to mitigate the decrease in the extraction rate and also to promote the bioavailability of phosphorus. The addition of $CaCl_2$ (80 g/kg of dry sludge) effectively promoted the conversion of non-apatite inorganic phosphorus to apatite inorganic phosphorus at a rate of 87.73% at 750 °C. Furthermore, the decrease in the extraction rate of phosphorus at 1,050 °C was comparatively smaller in the presence of $CaCl_2$. If iron flocculants are used to capture P in wastewater management, it may be necessary to pay special attention to the amount of addition and incineration temperature to maximize the economic potential of recycling.

**Key words:** phosphorus form, recovery, sintering, sludge ash, waste treatment

## HIGHLIGHTS

- The decrease in the extraction of phosphorus at high temperatures is due to the enwrapping of some phosphorus-containing minerals by molten phases.
- The decrease in the extraction of phosphorus in sludge ash at high temperatures is mitigated by $CaCl_2$.
- The acceptable conversion rate of apatite inorganic phosphorus (87%) can be achieved at 750 °C with a Ca/P ratio of 2.0.

## GRAPHICAL ABSTRACT




## INTRODUCTION

Phosphorus is a crucial nutrient for the growth of animals and plants (Sun *et al.* 2018), but the world's phosphate rock reserves (about 69 billion tons) are estimated to last only 50–100 years (Nakakubo *et al.* 2012). The distribution of phosphate rock is uneven among different countries and regions, with over 70% of the world's phosphate rock reserves located in Morocco and Western Sahara (Kroiss *et al.* 2011). The local insufficient phosphate rock reserves and the huge demand for phosphate fertilizers will eventually lead most countries in the world to import phosphate rock or phosphate fertilizers from Morocco and Western Sahara in the future (Desmidt *et al.* 2015). Approximately 80–90% of phosphorus extracted from phosphate rocks is used in agricultural production, and the phosphorus absorbed by crops during growth accumulates in the food chain, eventually accumulating in sewage sludge through wastewater treatment processes (Egle *et al.* 2016). Europe added phosphorus rock to its list of 20 critical raw materials, encouraging several countries (The Netherlands, Switzerland and Germany) to invest in technologies to recycle phosphorus from wastewater and sewage sludge in May 2014. As the most populous country in the European Union, Germany produces 300,000 Mg of ISSA per year (Ma & Rosen 2021). China had the largest influx of P into wastewater treatment plants, but the low level of P recovery efficiency among the countries studied (Rahman *et al.* 2019), with a large amount of phosphorus lost in sludge.

Numerous new technological approaches have been developed to recover wastewater P at different access points in wastewater treatment plants during wastewater and sewage sludge treatment or before/after incineration. Financial gains from P recovery digester supernatant are possible if enhanced biological phosphorus removal is applied at the wastewater plant (Egle *et al.* 2016). A recent study proposed a biochar sorbent from fermentation residues to capture P in wastewater (Marousek & Gavurova 2022). The phosphorus captured by the biochar presents a better plant availability than struvite. However, P in the supernatant cannot be removed completely, and the insoluble P is eventually enriched in sludge. Recovering P from sewage sludge is more expensive than from supernatant or incinerated sludge ash (Montag *et al.* 2009). Therefore, recovering P from sewage sludge ash seems the most efficient and economic form for P recovery. The phosphorus content ($P_2O_5$) in the dry base of sewage sludge is about 13.5–25.7 wt%, comparable to the phosphorus content (5–40 wt%) in phosphate rock (Liu *et al.* 2021). Europe and Japan began industrial practices of recovering phosphorus from sewage sludge incineration ash in 2010, and the fertilizer efficiency of recovered phosphorus has been verified in field experiments (Hao *et al.* 2020). The economic potential of recovering P from incineration sludge sewage ash (ISSA) strongly depends on the cost–benefit balance between the additional cost of the chemical agent and the revenue benefit from products, as the product is either a depolluted ash without plant availability or a fertilizer with improved plant availability and consequently higher revenues (Liu *et al.* 2021). Soil experiments on phosphorus-containing minerals in ISSA show that apatite inorganic phosphorus (AP, mainly Ca/Mg-bound P) has a long-lasting sustained release and strong bioavailability. But, poorly soluble non-apatite inorganic phosphorus (NAIP, in which P is bound to Al or Fe) is usually dominant in ISSA, which restricts the bioavailability of ISSA (Li *et al.* 2017). The mineralogy of ash influences the related phosphorus and heavy metal extraction. The conversion of Al–P and Fe–P to Ca–P is enhanced by a higher incineration temperature, resulting in more soluble Ca–P and higher extraction (Luyckx & Caneghem 2022). Overall, there is currently no ideal technology for phosphorus removal and recovery. For areas where separate sludge incineration devices exist, recovering phosphorus from sludge ash may reduce costs through economies of scale, optimizing leaching conditions, improving recovery rates, or integrating with the fertilizer industry (Hao *et al.* 2020). Therefore, the direction of optimization is to increase the AP content of sludge ash, which is beneficial for both direct land use and wet chemical extraction.

In order to enhance the conversion of NAIP to AP in ISSA, various methods have been investigated. One approach is to increase the Ca/P ratio, with a ratio between 1.50 and 1.67 being favorable for the formation of AP according to Equation (1) (Joris & Amberg 1971). However, the Ca/P ratio in sludge typically does not reach this level, and the introduction of an external calcium source, such as CaO, CaOH, $CaCl_2$, $MgCl_2$, or $CaCO_3$, can improve the AP content in ISSA (Li *et al.* 2019; Han *et al.* 2021). Particularly, Cl-based compounds such as $MgCl_2$ and $CaCl_2$ help to fix P under bioavailable forms in solid residues while promoting heavy metal vaporization through the gas phase (chlorination mechanisms) (Jeon & Kim 2018). Another method to enhance AP content in ISSA is to increase the incineration temperature. However, it should be noted that the total phosphorus (TP) content in ISSA, as measured by the Standards, Measurements, and Testing (SMT) method (Standards, Measurements, and Testing protocol, extracted by HCl), decreases significantly when the temperature exceeds 900 °C (Li *et al.* 2015), but the decrease in the extraction rate is sometimes not the central topic of discussion. This phenomenon also exists in some studies on extracting the phosphorus of sludge incinerated at 1,000 °C with sulfuric acid and oxalic acid. It is speculated that alkali metals that cause sintering in sludge are the reason (Liang *et al.* 2019). Studies by Luyckx show that phosphorus does not volatilize during incineration (Luyckx & Caneghem 2021). Despite the exact mechanism not being fully understood, the decrease in the extraction rate by HCl or $H_2SO_4$ means a lower yield of phosphorus recovery from ISSA, which greatly reduces the overall economic benefits.

In this study, $CaCl_2$ was utilized to mitigate the decrease in the extraction rate of phosphorus at high incineration temperatures and also to promote bioavailability. The effects of temperature and $CaCl_2$ on the extraction rate and mineral transformation were investigated in the range of a Ca/P ratio of 0.92–3.50. To clarify the reason for the decrease in the extraction rate of TP at high temperatures, the extraction of phosphorus by the SMT method was compared with elemental analysis after complete digestion and the X-ray fluorescence result of the sludge. The study combined mineral evolution and the degree of melting and sintering to gain a better understanding of the underlying mechanisms:

$$Ca_{10-x}(PO_4)_{6-x}(HPO_4)_x(OH)_{2-x} \longrightarrow (1-x)Ca_{10}(PO_4)_6(OH)_2 + 3xCa_3(PO_4)_2 \tag{1}$$

## MATERIALS AND METHODS

### Material preparation

The sludge used in the experiment was from a wastewater treatment plant in Kunming, Yunnan Province. The sludge was dried at 105 °C for 48 h to constant weight and ground to below 0.178 mm. Proximate and elemental analyses of sludge were tested according to ASTM D5142 (ASTM, American Society for Testing and Materials) 'Industrial Analysis Method of Coal' and ASTM D3286-96 'Elemental Analysis Method of Coal'. The results are listed in Table 1.

**Table 1** | The proximate and ultimate analysis of sludge

| Sample | Proximate analysis (wt. %) | | | | Ultimate analysis (wt. %) | | | |
|---|---|---|---|---|---|---|---|---|
| Sludge | Moisture | Ash | Volatile | Fixed carbon | C | H | N | S |
| | 5.72 | 51.17 | 39.64 | 3.47 | 20.91 | 4.1 | 3.41 | 0.84 |

The ISSA was prepared in a high-temperature atmosphere tube furnace (SGL-1700, SIOMM, China). The tube furnace was purged with 300 mL/min of air for 10 min before and during heating. About 5.0 g of the sample was heated to the target temperature at 10 °C/min and kept at a constant temperature for 1 h. The target temperatures were set to 600, 750, 900, and 1,050 °C. The chemical composition of sludge ash was tested by X-ray fluorescence (XRF, ARLPERFORM'X, Thermo Fisher, USA). The result is shown in Table 2. The molar ratio of calcium to phosphorus (Ca/P) of the original ISSA is about 0.92. $CaCl_2$ (96.00%, Aladdin, China) was used as an additive to increase the Ca/P ratio as the positive effect of $CaCl_2$ in promoting bioavailability. The mixed sample was prepared by adding $CaCl_2$ into dry sludge according to the Ca/P ratio ,from 1.5 to 3.5, and grounding for 10 min to make it evenly mixed. The mixed sample was incinerated with the same method as the original sludge.

## Extraction protocol of phosphorus fractions

Phosphorus fractions of phosphorus in the samples were determined using the SMT method. The detailed analysis and extraction process are shown in Figure 1 (Ruban *et al.* 1999). The SMT method divides phosphorus into different forms by continuously extracting phosphorus from ISSA, including TP, organic phosphorus (OP), inorganic phosphorus (IP), NAIP (combined with Fe, Mn, Al), and AP (phosphorus combined with Ca, Mg), where IP = AP + NAIP, TP = IP + OP.

The solution obtained in the SMT method was centrifuged in a centrifuge (TG16-WS, CENCE, China) at 7,500 rpm for 15 min. The suspension was filtered with 0.45 mm film. Appropriate dilution with ultrapure water was applied to determine the proper range of phosphate concentration (1.5–15 mg/L) for spectrophotometric determination (752, Jinghua, China). The phosphate concentration–absorbance standard curve established in the experiment is shown in Figure 2, and the phosphate concentration under the corresponding absorbance can be calculated according to the equation of the fitted line. The content of phosphorus fractions in sludge ash was calculated by Equation (2):

$$P_i = \frac{cv\beta}{m} \tag{2}$$

where $P_i$ is the content of different phosphorus fractions in the sample, the subscript $i$ stands for TP, IP, OP, NAIP, and AP, mg/g; $v$ is the diluent volume in a colorimetric tube with a plug, mL; $c$ is the phosphate concentration in a diluent, μg/mL; $\beta$ is the dilution factor; and $m$ is the sample mass, g.

## X-ray diffraction analysis

An X-ray diffractometer (Panalytical X'Pert PRO, Netherlands) was used to analyze the types of crystalline minerals in the samples. The samples were ground into powder less than 0.074 mm to facilitate the preparation of the tableting method. They were scanned at the range of 5–80° with X-ray (wavelength: 1.5406 nm, Cu K$\alpha$ radiation) by a step size of 5°/min under the conditions of 40 kV and 40 mA.

## Inductively coupled plasma optical emission spectroscopy

The TP content in residual ash prepared at 900 and 1,050 °C was determined using an inductively coupled plasma optical emission spectrometer (ICP-OES, ICP7000, Thermo Fisher, USA). About 0.1 g of ISSA and digest reagent (4 mL of HCl (37.00%, Aladdin, China), 6 mL of $HNO_3$ (65–68%, Aladdin, China), and 3 mL of HF (40%, Aladdin, China)) were added into a polytetrafluoroethylene tank. The reaction lasted 12 h at 210 °C in a high-pressure reaction kettle. The mixture after the reaction was transferred and diluted to 50 mL for testing.

**Table 2** | The chemical composition of sludge ash

| Sample | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $P_2O_5$ | CaO | $K_2O$ | MgO | $TiO_2$ | $Na_2O$ | $SO_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| ISSA | 35.51 | 19.44 | 16.88 | 9.44 | 6.85 | 2.90 | 2.80 | 1.64 | 0.298 | 3.33 |

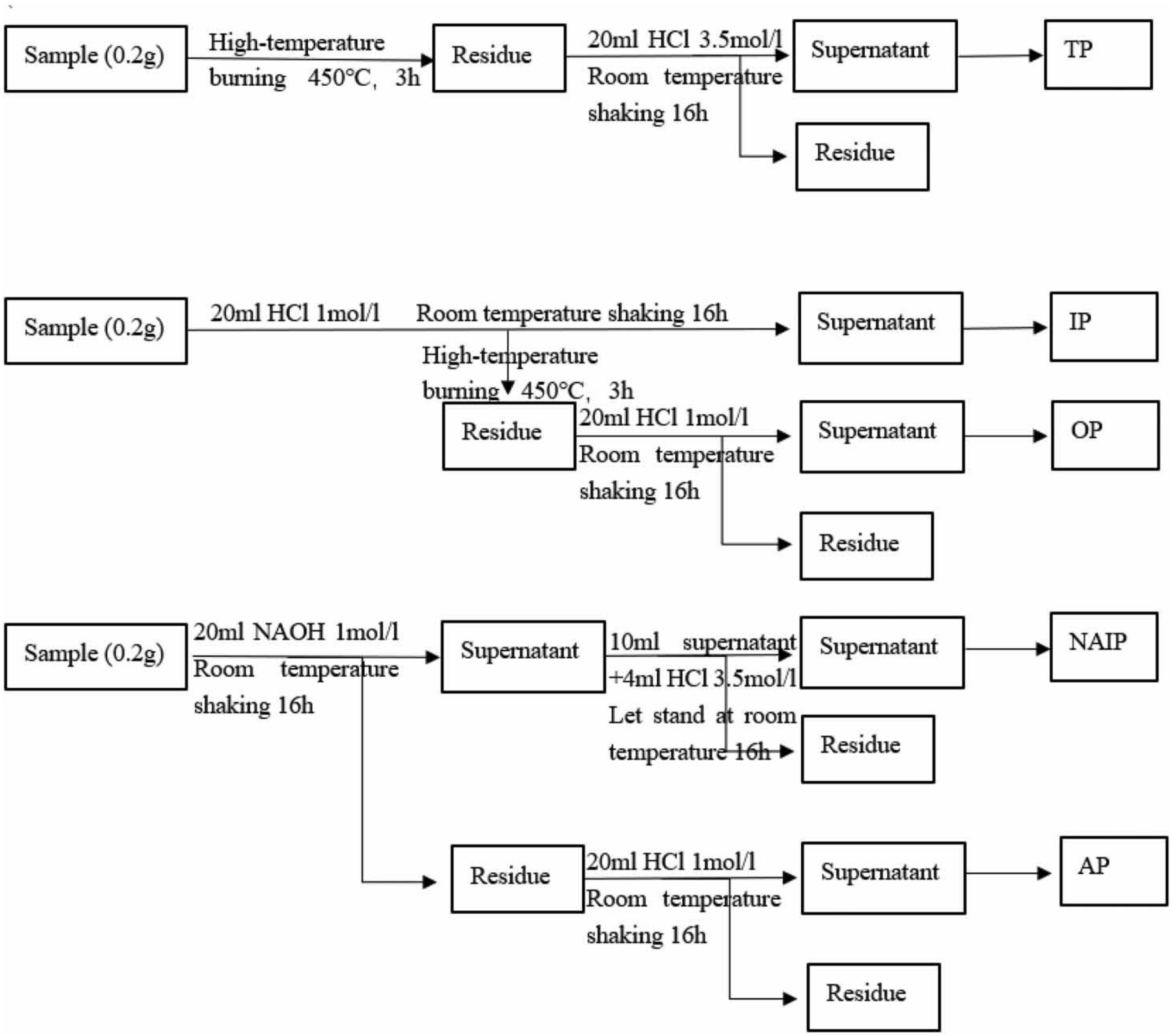



**Figure 1** | SMT extraction protocol of phosphorus fractions.

## RESULTS AND DISCUSSION

### Effect of temperature on phosphorus enrichment in sludge

Tables 1 and 2 present the physicochemical properties of sludge. The high volatile content is conducive to the ignition of sludge, and the high level of ash content (51%) shows that the weight of ISSA is about a half of the dry sludge. The chemical composition shows that the $P_2O_5$ content in sludge ash is 9.44%, which reaches the level of $P_2O_5$ content (5–12%) in traditional compound fertilizers (Adam *et al.* 2009). However, the concentration of phosphorous fractions in dry sludge (Table 3) shows that NAIP is dominant in dry sludge, accounting for 60.27% of IP and 45.54% of TP, respectively.

Higher incineration temperatures stimulate the ash transformation of NAIP to AP, which improves the P extraction efficiency and P bioavailability. The incineration temperature from 600 to 1,050 °C was applied to improve the bioavailability of P, but what we first observed was the decrease in the extraction rate of TP determined by SMT. The extraction rate determined by SMT in the ash of the original sludge and the sludge samples with $CaCl_2$ prepared at different temperatures is shown in Figure 3. The sample with a Ca/P ratio of 0.92 is the ash of the original sludge. The incomplete incineration of organic matter in sludge ash prepared at 600 °C resulted in the lower TP content of samples (Liang *et al.* 2019). The TP of ash

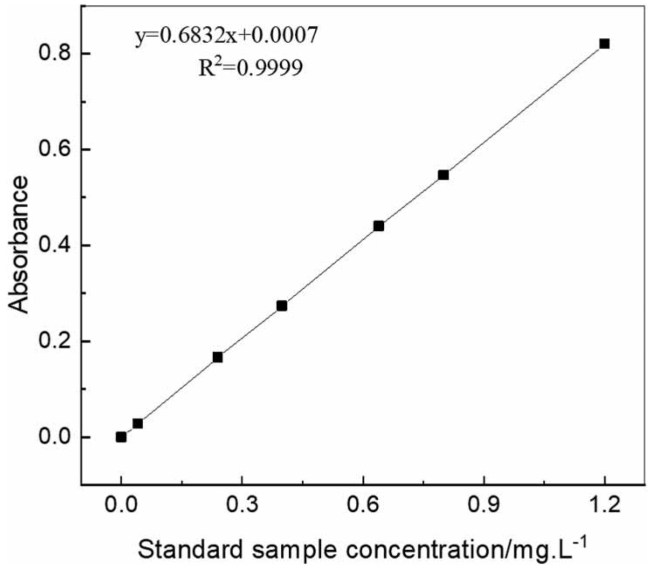



**Figure 2** | Molybdenum blue spectrophotometry – a standard curve of phosphate concentration.

**Table 3** | Content of different phosphorus fractions in raw sludge

| | TP | OP | IP | AP | NAIP |
|---|---|---|---|---|---|
| Content (mg/g) | 23.16 ± 0.09 | 3.88 ± 0.13 | 17.05 ± 0.16 | 5.91 ± 0.08 | 10.55 ± 0.03 |

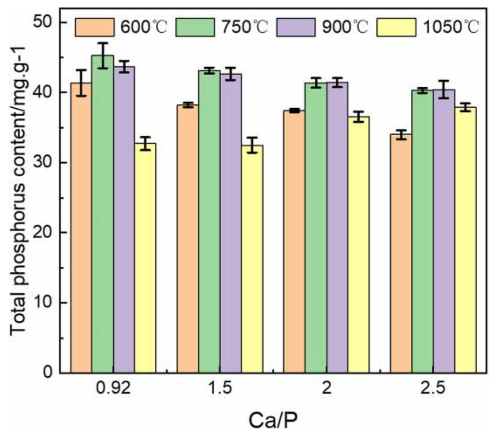



**Figure 3** | The extraction rate of total phosphorus determined by the SMT of sludge with different Ca/P shows a significant decrease in the extraction rate of sludge at 1,050 °C.

incinerated at 750 °C rose to 45.26 mg/g, which is about double of TP of dry sludge. It is a reasonable value after complete incineration for the sludge with an ash content of 51%. The TP content decreased significantly at 1,050 °C. The extraction rate of the original sludge at 1,050 °C decreased to 75% of that at 900 °C, meaning that the extraction rate of phosphorus decreased from 43.71 to 32.71 kg P/t ISSA. The decreased extraction rate of phosphorus by $H_2SO_4$ and $H_2C_2O_4$ at 850 °C was also reported by Liang *et al.* (2019). The reason was attributed to alkali-induced sintering as the content of Na and K in sludge is high. It can be seen from the morphology of residual ash incinerated at different temperatures (Figure 4) that the sintering degree of residual ash increases with temperature. Partial melting in the sample at high temperatures led to a local sintered

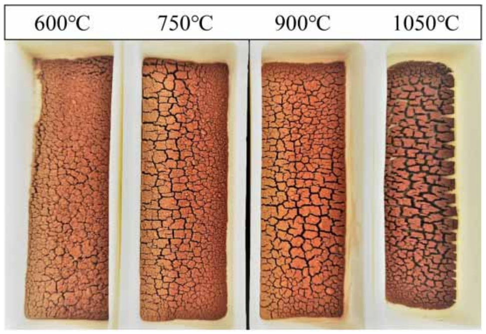



**Figure 4** | The image of the original sludge ash at different temperatures shows the sintering degree of residual ash increasing with temperature.

block, in which phosphorus-containing minerals were encapsulated by the molten liquid phase (Saleh Bairq *et al.* 2018). The TP content of ISSA was observed to decrease at 1,050 °C even after the addition of $CaCl_2$. However, the decrease was comparatively smaller in the presence of $CaCl_2$.

To determine the reason for the decrease in the extraction rate of TP measured by the SMT method, X-ray fluorescence analysis was carried out to analyze the chemical composition of ISSA at different temperatures, and Fe, Ca, and P elements were also analyzed by the ICP test after digesting the ISSA. Table 4 shows the XRF results of sludge ash at different temperatures. The chemical composition of sludge ash at different temperatures changed little, indicating that phosphorus in sludge ash was not lost at high temperatures. ICP results in Table 5 also support this conclusion. It is worth noting that the content of Fe is high in sludge ash. In the literature, sludge with a decrease in TP is also characterized by a higher iron content (Li *et al.* 2015). Low-temperature eutectic melting of Fe-containing minerals with silicate was reported in research focusing on the sintering phenomenon of sludge ash during the combustion of plants (Hannl *et al.* 2021). The amorphous glass-like structure of the melted phase cannot be observed in crystal diffraction, but the framework structure is extremely stable. If phosphorus-containing minerals were encapsulated by the melted phase, the value of TP determined by SMT decreased, as this part of phosphorus-containing minerals was more difficult to extract. The findings reveal that optimizing incineration temperatures is crucial for enhancing P bioavailability, and caution should be exercised when increasing the temperature to avoid a decrease in TP recovery.

**Table 4** | The main chemical composition of sludge ash at different temperatures as measured by XRF indicated that the chemical composition of sludge ash changed little with temperature (%)

| Incinerate temperature (°C) | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $P_2O_5$ | CaO | $K_2O$ | MgO | $TiO_2$ | $Na_2O$ | $SO_3$ | ZnO |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 815 | 35.51 | 19.44 | 16.88 | 9.44 | 6.85 | 2.90 | 2.80 | 1.64 | 0.298 | 3.33 | 0.279 |
| 900 | 35.09 | 18.21 | 18.75 | 10.09 | 7.15 | 2.88 | 2.73 | 1.58 | 0.245 | 2.36 | 0.275 |
| 1,050 | 36.97 | 16.49 | 19.74 | 9.43 | 7.57 | 2.92 | 3.09 | 1.71 | 0.256 | 0.8 | 0.301 |

**Table 5** | The comparison of phosphorus extraction by the SMT method and the ICP method showed that the phosphorus extraction amount of the two methods did not change much at 900 °C, but there was a difference in phosphorus extraction at 1,050 °C

| | SMT extraction (spectrophotometric method)/(mg/g) | Acid digestion (ICP measurement)/(mg/g) | | |
|---|---|---|---|---|
| Incinerate temperature (°C) | P | Fe | Ca | P |
| 900 | 43.71 | 112.4 | 53.01 | 45.28 |
| 1,050 | 32.71 | 112.7 | 52.28 | 47.53 |

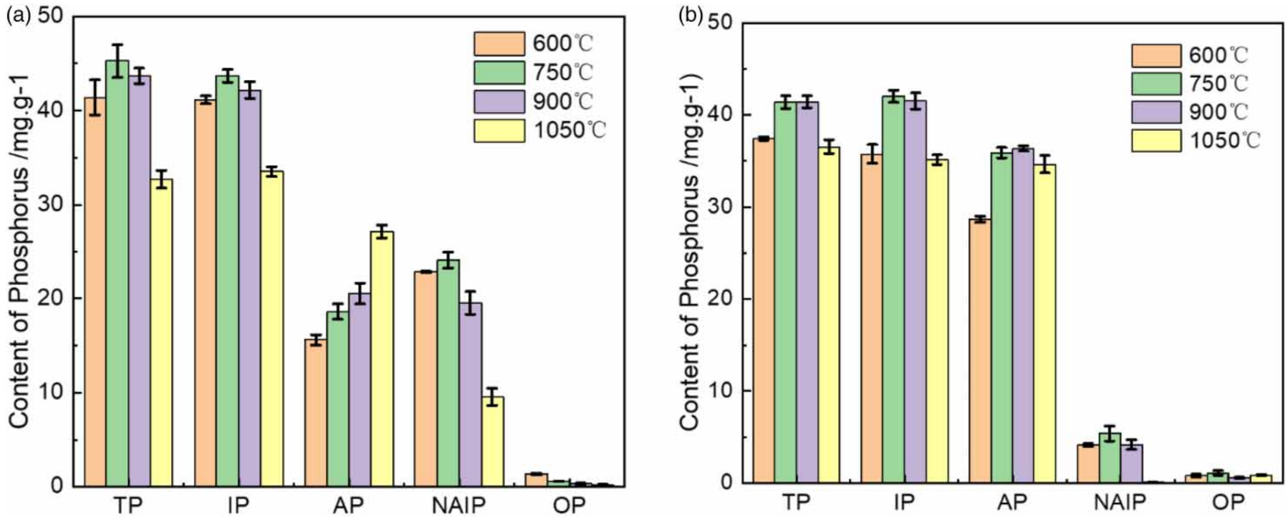



**Figure 5** | The content of different phosphorus fractions by the SMT method in sludge ash with Ca/P ratios of 0.92 and 2.00 at different temperatures indicate that NAIP is converted to AP with the increase in temperature. (a) Ca/P ratio is 0.92 and (b) Ca/P ratio is 2.00.

### Effect of temperature on the fractions of phosphorus

The effect of temperature on phosphorus speciation of ISSA with Ca/P ratios of 0.92 and 2.00 is shown in Figure 5. Higher temperature is beneficial to the conversion of NAIP to AP, but the NAIP content of the original sludge at 1,050 °C is still high, indicating that the calcium content of the original sludge itself is insufficient. The AP content in sludge ash with a Ca/P ratio of 2.00 reached 28.65 mg/g at 600 °C, which exceeded the AP content of the original sludge at 1,050 °C. It is worth noting that the significant decrease of TP at 1,050 °C in the original sludge or the mixed sample with a Ca/P ratio of 2.00 (Figure 5) was accompanied by a decrease in IP and NAIP, but the content of AP did not decrease, indicating that the decrease was mainly due to the more difficult extraction of NAIP.

Figure 6 shows the X-ray diffraction (XRD) results of ISSA with Ca/P ratios of 0.92 and 2.00 at different temperatures. For the original sludge (Figure 6(a)), the diffraction peak intensity of $AlPO_4$ and $FePO_4$ decreased, and that of $Ca_3(PO_4)_2$ and $Ca(PO_3)_2$ increased, which is consistent with the increasing trend of the AP content in ISSA with temperature. The diffraction peaks of $Ca_2P_2O_7$, $Ca_3(PO_4)_2$, and $Ca(PO_3)_2$ appeared at 600 °C for ISSA with a Ca/P ratio of 2.00 (Figure 6(b)), which is consistent with the fact that the AP content of this sample at 600 °C is already more than the AP content of the original sludge at 1,050 °C. $CaCl_2$ effectively promotes the conversion of NAIP to AP at a low temperature. $FePO_4$ completely disappeared in both the original sludge and mixed samples at 1,050 °C, and the intensity of diffraction peak for $SiO_2$ decreased, indicating the formation of a low-temperature eutectic between the silicate and Fe–P minerals. The resulting difficulty in the extraction of NAIP is the reason for the decrease in TP and IP of ISSA at 1,050 °C.

### Effect of adding $CaCl_2$ on phosphorus enrichment and phosphorus form in sludge

$CaCl_2$ was used to complement the calcium source in the original sludge. The content of different phosphorus fractions in ISSA with different Ca/P ratios at 1,050 °C is shown in Figure 7. The increase of AP at 1,050 °C illustrated that the addition of $CaCl_2$ is useful even in the case of strong thermodynamic driving force (Xu *et al.* 2021). The benefit of the addition of $CaCl_2$ at lower temperatures can be seen in Figure 8, which shows the change of AP percent in IP with Ca/P of sludge ash at different temperatures. The AP percent in IP varies little with the temperature at 600–900 °C if Ca/P is the same, which illustrates that an adequate calcium content is more important than the temperature. The gap of AP percent between 1,050 and 900 °C is because of the higher relative content of AP that resulted from the decrease of NAIP and IP at 1,050 °C. Higher temperature is beneficial to the conversion of NAIP to AP, but the same effect is achieved at a lower temperature if the calcium source is sufficient. In practice, the incineration temperature range of 750–900 °C is suitable with a comprehensive consideration of the complete incineration of sludge and the transformation of apatite phosphorus.

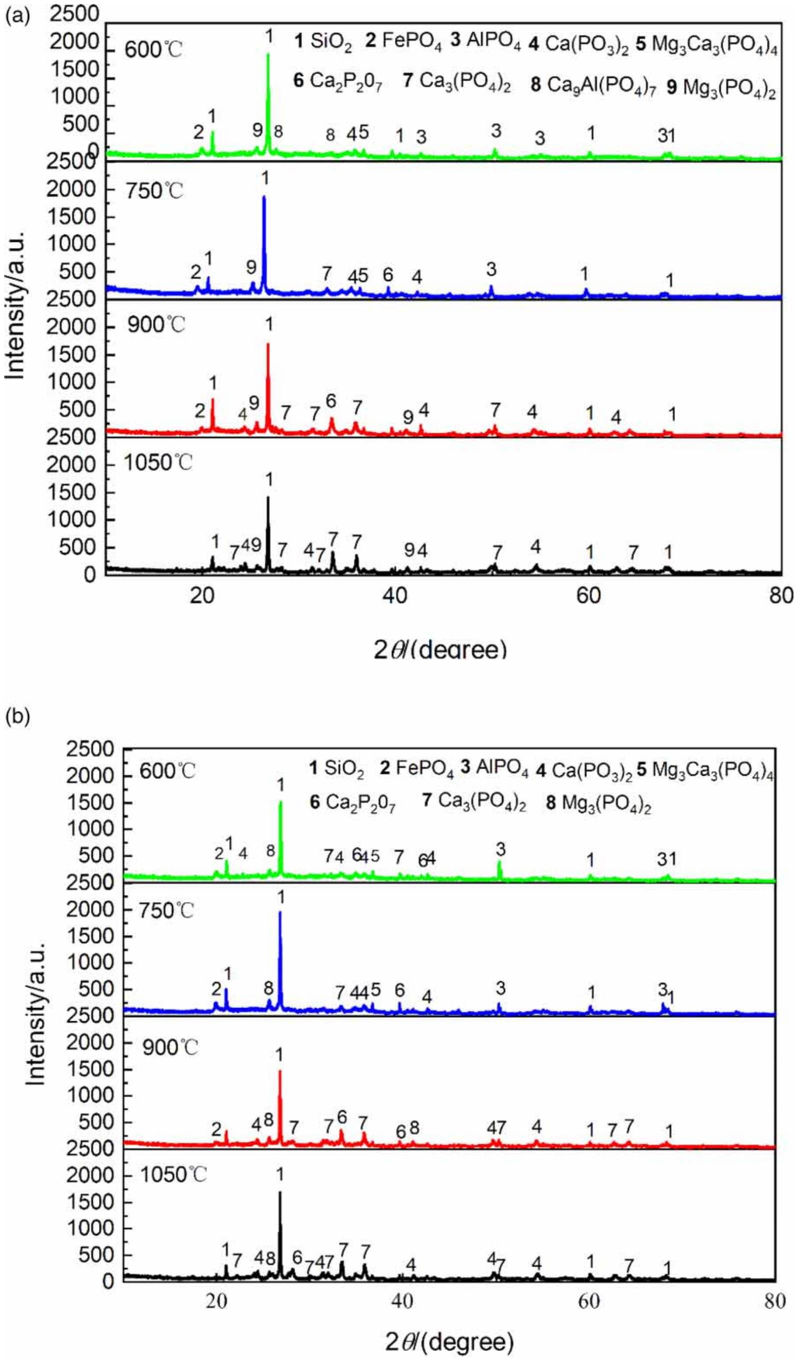



**Figure 6** | XRD patterns of sludge ash with Ca/P of 0.92 and 2.00 at different temperatures show that Fe–P and Al–P are converted into Ca–P during the heating process. (a) XRD patterns of sludge ash with a Ca/P ratio of 0.92 at different temperatures. (b) XRD patterns of sludge ash with a Ca/P ratio of 2.00 at different temperatures.

The extraction rate of phosphorus at 1,050 °C also benefits from the addition of $CaCl_2$. Figure 9 shows the extraction rate of TP determined by the SMT of sludge with different Ca/P from 600 to 1,050 °C. The temperature ranges from 600 to 900 °C, and the extraction rate gradually decreased with Ca/P, because the addition of $CaCl_2$ increased the residual ash content of the mixed sample at the same temperature, resulting in less enrichment of phosphorus in the ash. At 1,050 °C, the extraction rate

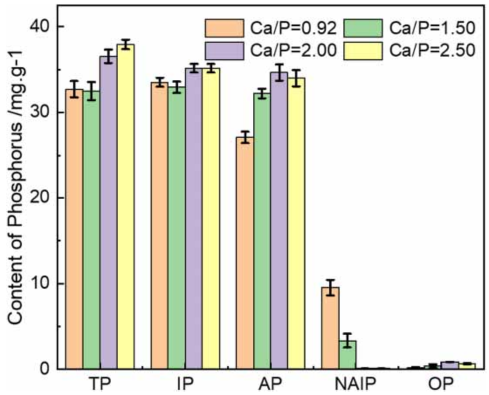



**Figure 7** | The content of different phosphorus fractions in sludge ash with different Ca/P at 1,050 °C shows that the increase of Ca/P could promote the conversion of NAIP to AP.

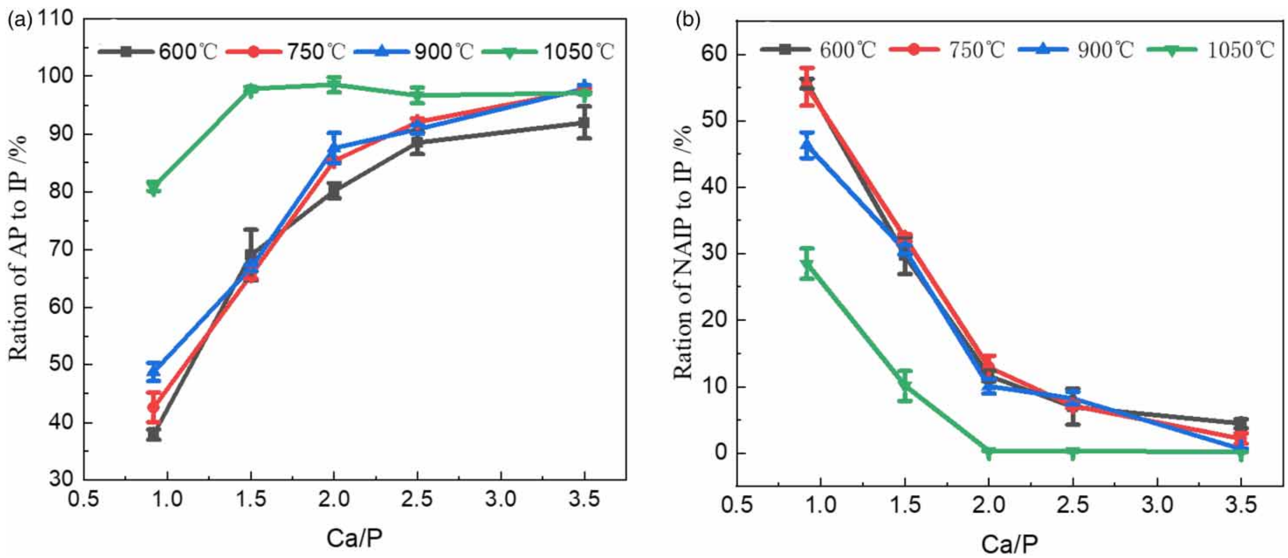



**Figure 8** | The percentage of different forms of phosphorus in sludge ash prepared at different temperatures changing with Ca/P shows that NAIP is basically converted to AP at 750 °C when Ca/P = 2.0. (a) AP/IP and (b) NAIP/IP.

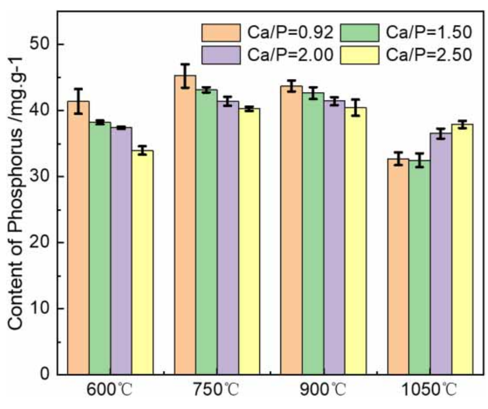



**Figure 9** | The extraction rate of total phosphorus determined by the SMT of sludge with different Ca/P shows an increase in the extraction rate of sludge at 1,050 °C in the presence of $CaCl_2$.

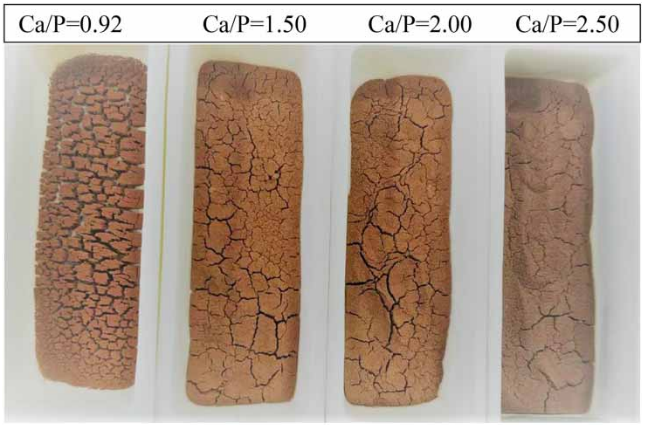



**Figure 10** | The image of sludge ash at 1,050 °C shows that the sintering degree of the samples decreases and becomes loose with the increase of the Ca/P ratio.

increased from 32.71 to 37.93 mg/g with Ca/P, illustrating that the addition of $CaCl_2$ alleviates the phenomenon of the significant decrease in the extraction rate for the original sludge ash at 1,050 °C. Figure 10 shows the morphology of ISSA with different Ca/P at 1,050 °C. The original sludge had obvious agglomeration at 1,050 °C, and the samples gradually became loose as Ca/P increased. The sintering degree of ISSA decreased with Ca/P, thereby alleviating the phenomenon that the extraction rate decreases due to melting at high temperatures. The reason may be related to the change of Fe–P minerals under high-temperature conditions. $FePO_4$ in the sludge forms eutectic melting with the silicate component easily. After adding $CaCl_2$, $FePO_4$ reacts with $CaCl_2$ and transforms into $Fe_2O_3$, of which the melting temperature is higher (Han *et al.* 2021). The degree of melting and sintering of the samples at 1,050 °C decreased, thus mitigating that the decrease in the extraction rate is due to melting at 1,050 °C.

Adding $CaCl_2$ at the level of 80 g/kg of dry sludge increases the Ca/P ratio from 0.92 to 2.0. The cost of the addictive is $2.56 per ton of sludge (the price of $CaCl_2$ is $160/t), which is roughly equivalent to the increase in wastewater treatment costs by $0.0018/t (in terms of 10,000 tons of wastewater producing 7 tons of sludge with a moisture content of 80%). The increase in costs is small. Furthermore, the incineration temperature is reduced by 200 °C, which means a saving in the cost of energy.

Figure 11 shows the XRD patterns of ISSA with different Ca/P ratios at 600 and 1,050 °C. At 600 °C, the diffraction peaks of $AlPO_4$ and $FePO_4$ observed in all the samples show the incomplete conversion of NAIP to AP. The change with Ca/P is the type of the produced Ca–P mineral. Compared with the original sludge, more Ca–P minerals with higher Ca/P ratios, such as $Ca_3(PO_4)_2$ (Ca/P = 1.50) and $Ca_5(PO_4)_3Cl$ (Ca/P = 1.67), exist in samples that add $CaCl_2$. The crystal diffraction results of incineration sludge ash prepared at 1,050 °C changed little with the Ca/P ratio, which was consistent with the small change of the AP content with Ca/P. Unfortunately, $FePO_4$ and $Fe_2O_3$ were not detected in samples with different Ca/P ratios at this temperature. $FePO_4$ may have undergone low-temperature eutectic or transformed into amorphous $Fe_2O_3$ that cannot be detected in XRD. The transformation of related minerals influences the decrease of the total extraction rate that needs further work. A better method to detect and extract the different species Fe–P may help to clarify the mineral evolution of phosphorus.

## CONCLUSIONS

For a sludge with a low level of Ca/P ratio (<1.5), improving temperature is not efficient in improving the bioavailability since the AP percent only changes from 18 to 28 mg/g with a temperature increase from 600 to 1,050 °C. Even worse, the TP and IP contents of the samples determined by SMT decreased significantly at 1,050 °C. The addition of $CaCl_2$ (80 g/kg of dry sludge) effectively promotes the conversion of NAIP to AP at the rate of 87.73% (35.9 mg/g) at 750 °C. As to the extraction rate of phosphorus at 1,050 °C, the decrease was comparatively smaller in the presence of $CaCl_2$. The reason is attributed to the reaction between $CaCl_2$ and $FePO_4$, converting $FePO_4$ into $Fe_2O_3$ and Ca–P with high melting points.

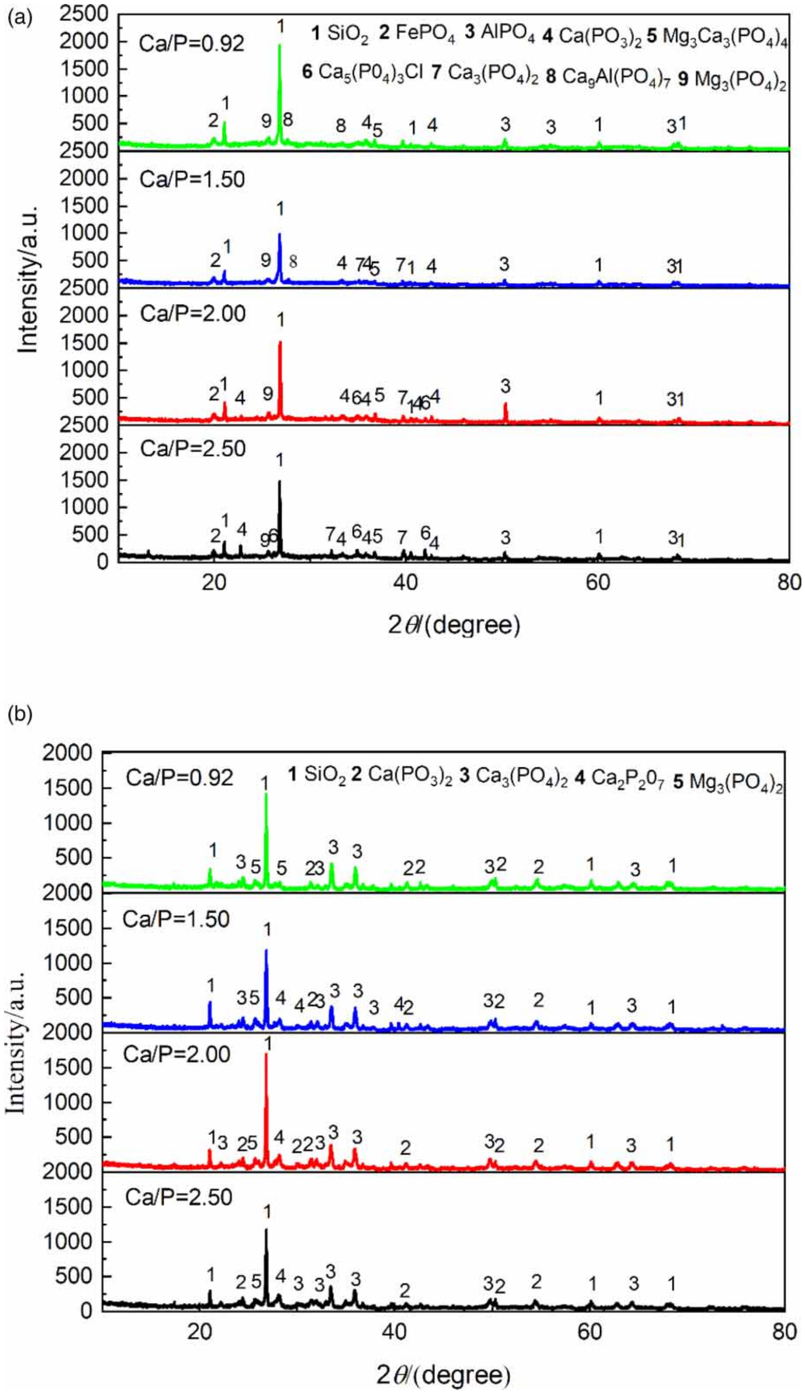



**Figure 11** | The XRD patterns of sludge ash with different Ca/P ratios at 600 and 1,050 °C show that the peaks of Ca/P diffraction increase with the increase of Ca/P. (a) XRD patterns of sludge ash with different Ca/P at 600 °C. (b) XRD patterns of sludge ash with different Ca/P at 1,050 °C.

In addition to the known disadvantage of low bioavailability, we found that iron phosphates (Fe–P) were responsible for the decrease in the extraction rate of phosphorus in sintered sludge ash. If iron flocculants are used to capture P in wastewater management, it may be necessary to pay special attention to the addition amount and incineration temperature for the whole economic potential of recycling.

## AUTHOR CONTRIBUTION

All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Y.X. and X.Z. The first draft of the manuscript was written by R.Y., and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

## CONFLICT OF INTEREST

The authors declare there is no conflict.

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