RESEARCH ARTICLE



# Transformation of phosphorus by MgCl<sub>2</sub> and CaCl<sub>2</sub> during sewage sludge incineration

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### Abstract

Phosphorus (P) recovery from sewage sludge (SS) have been regarded as an effective method of P recycling. The effects of incineration temperature, incineration time, and chlorine additives on the distribution of P speciation during sludge incineration were studied. Moreover, the reactions between model compounds AlPO<sub>4</sub> and additives (MgCl<sub>2</sub> and CaCl<sub>2</sub>) were investigated by thermogravimetric differential thermal analysis and X-ray diffraction measurements. The results demonstrated that the increase in temperature and time stimulated the volatilization of non-apatite inorganic phosphorus (NAIP) instead of apatite phosphorus (AP). MgCl<sub>2</sub> and CaCl<sub>2</sub> can greatly promote the conversion of NAIP to AP. Additionally, AlPO<sub>4</sub> reacted with MgCl<sub>2</sub> are incinerated at 500–600 °C to form  $Mg_3(PO_4)_2$ , which is mainly due to the reaction of the intermediate product MgO and AlPO<sub>4</sub>. Reactions between AlPO<sub>4</sub> and CaCl<sub>2</sub> occurred at 700–750 °C and produced Ca<sub>2</sub>PO<sub>4</sub>Cl, which can be directly used with high bioavailability. These findings suggested that chlorine additives in the SS incineration process can obtain phosphoruscontaining minerals with higher bioavailability to realize the resource utilization of P in sludge.

Keywords Phosphorus · Sewage sludge · Sewage sludge incineration · Apatite phosphorus · Non-apatite inorganic phosphorus · Chlorine additives

# Introduction

Phosphorus (P) is a kind of non-renewable and irreplaceable natural resource, which is widely used in chemical industry and agricultural production and plays a vital role in modern society (Cieślik and Konieczka [2016](#page-6-0)). In order to feed the growing population, the demand for phosphate rock will continue to increase. It is predicted that global production of economically exploitable phosphate rock will peak in 2033 or earlier (Cordell et al. [2009](#page-6-0); Sorensen et al. [2015\)](#page-7-0), and then global P demand will exceed P supply. At present, the most promising way of sustainable utilization of P resources is to replace phosphate ore with phosphorus-rich materials. Sewage sludge (SS) is a by-product produced in the wastewater treatment process rich in P, and nearly 98% of P is discharged into wastewater and eventually enriched in SS,

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indicating that the sludge is an important source for P recycling (Franz [2007;](#page-6-0) Liang et al. [2019](#page-7-0)). However, the presence of contaminants prevents the SS from being directly used in agriculture (Chen and Yan [2012](#page-6-0); Nowak et al. [2012b\)](#page-7-0). Sewage sludge ash (SSA) is the product of SS incineration which is rich in high concentration of P; the  $P_2O_5$ -content of SSA typically ranges from 10 to 25.7% (Adam et al. [2009,](#page-6-0) Fang et al. [2018,](#page-6-0) Lee and Kim [2017\)](#page-7-0). Therefore, SSA has significant potential as a source of P fertilizer production.

SS contains various forms of P due to the different P removal processes in the wastewater treatment plant (Donatello and Cheeseman [2013\)](#page-6-0). P in SS can usually be divided into organic P (OP) and inorganic P (IP). Most of the P in the sewage is finally present in the sludge in the form of IP after chemical treatment. Studies have shown that it accounts for 70–90% of total phosphorus (TP) (Desmidt et al. [2014;](#page-6-0) Zhang et al. [2016\)](#page-7-0). In addition, some P exists in the form of OP after biological action (Huang and Yuan [2015](#page-7-0), Zhang et al. [2017\)](#page-7-0). However, the above P forms are not ideal in terms of bioavailability, and in order to realize the resource utilization of phosphorus in the sludge, it is necessary to convert its morphology to achieve better bioavailability. There are several different additives that can be used in the thermochemical treatment

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method, including chloride additives  $(MgCl<sub>2</sub>, CaCl<sub>2</sub>, Fe Cl<sub>2</sub>)$ , KCl, HCl), sodium-based additives (Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>), Mgbased additives ( $MgCO<sub>3</sub>$ ,  $MgO$ ), and Ca-based additives (CaO) to react with sludge (Cai et al. [2012,](#page-6-0) Havukainen et al. [2016](#page-7-0), Nowak et al. [2012a,](#page-7-0) Steckenmesser et al. [2017,](#page-7-0) Vogel and Adam [2011,](#page-7-0) Vogel et al. [2014](#page-7-0)). It mainly reacts with heavy metals (HMs) and then removes them at a temperature of about 1000 °C (Gorazda et al. [2017](#page-7-0)). At the same time, it can change the forms of P in ash and generally can improve its bioavailability. The temperature during the incineration of sludge will significantly affect the species of P and the removal of HMs (Qian and Jiang [2014\)](#page-7-0). High temperature promoted the formation of IP, and the P forms will be converted from non-apatite inorganic phosphorus (NAIP) to apatite phosphorus (AP) (Wang et al. [2013](#page-7-0)). Additionally, the addition of chlorinating agents (PVC, NaCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>) during the heat treatment of sludge can largely remove HMs to a large extent, and the formation of  $Mg_3(PO_4)_2$  leads to a significant increase in the bioavailability of P (Xia et al. [2020\)](#page-7-0). The additives of MgO and CaO in the process of sludge incineration also had a positive effect on the conversion of NAIP to AP, and the main phosphorus minerals in the SSA were  $Ca_5(PO_4)_3OH$ ,  $Ca_4P_2O_5$ ,  $Mg_3(PO_4)_2$ ,  $Mg_3Ca_3(PO_4)_4$ , and CaHPO<sub>4</sub> (Li et al.  $2017$ ; Li et al. [2019\)](#page-7-0).

The mechanism of different P species chemical conversion by adding chlorinating agents during the sludge incineration is still unclear. Therefore, this study focused on the regulation of the P content and morphology of sludge in the process of incineration and the related mechanism. The chlorinating agents  $MgCl<sub>2</sub>$  and  $CaCl<sub>2</sub>$  were used to enhance the formation of Mg-P and Ca-P, which has higher bioavailability than Fe/ Al-P. The simulation experiment was used to qualitatively analyze the transformation process of P forms during incineration.

## Materials and methods

### **Materials**

The SS used in the experiments was dewatered waste activated sludge obtained from a municipal wastewater treatment plant located in Shanghai, China. After 3 days of outdoor ventilation, the SS was dried in an oven at 105 °C. Then the dried SS was ground with a grinder and passed through a 100 mesh sieve to obtain a fine particle sludge powder sample with a particle size of less than 150 μm. The samples were stored in closed plastic containers in a freezer at 4 °C until the experiments were carried out. The characteristics of raw sewage sludge have been described in previous studies (Yang et al. [2019\)](#page-7-0).

#### Incineration experiments

In the incineration experiments, 10 g of pretreated sludge was incinerated in a muffle furnace, and the SSA samples were prepared by setting the parameters of the muffle furnace to control the sludge incineration conditions. The dried raw SS was incinerated at different incineration temperatures (800, 850, 900, 950, and 1000 °C) for 2 h or at 800 °C for different incineration time (0.5, 1, 2, 3, and 4 h). After being naturally cooled to room temperature in the furnace, the incineration products were ground and passed through a 100 mesh sieve and then placed in a vacuum dryer for storage. The P speciation and content in incineration products were explored.

The dried 10 g SS sample was mixed uniformly with the required amounts of chlorinating agents  $MgCl<sub>2</sub>$  (1, 1.6, 2.5, and 3.0 wt% Mg) and CaCl<sub>2</sub> (1, 3, 5, and 10 wt% Ca) and then burned in a muffle furnace at 800 °C for 2 h. In order to further explore the mechanism of adding  $MgCl<sub>2</sub>$  and  $CaCl<sub>2</sub>$  to the transformation of P species in sludge, model compound incineration experiments were carried out. AlPO<sub>4</sub> was selected as model material of sludge and then mixed with  $MgCl<sub>2</sub>$  or CaCl<sub>2</sub> for incineration experiments. The molar ratio of Al to Mg (n(Al):n(Mg)) in the mixed sample was set to 1:1, and the molar ratio of Al to  $Ca (n(A)) : n(Ca)$  was set to 1:3. Then the homogenized sample was incinerated at 800 °C for 2 h. The P speciation and content in the pure substance incineration products were analyzed.

#### Analysis methods

### X-ray diffraction

The crystalline compounds in the samples obtained from the incineration of  $AIPO<sub>4</sub>$  and chlorine additives at different temperatures were identified by an X-ray diffractometer (XRD) (DX2700, Haoyuan, China). The XRD test was performed by using Cu K $\alpha$  radiation at 40 kV and 40 mA, scanning in the range of 15° to 75° with a scan rate of 4°/min. In addition, the samples obtained after incineration were milled and sieved before XRD analysis.

### Phosphorus speciation analysis

The determination of the P speciation in the samples before and after the sludge incineration was analyzed using the standards, measurements, and testing (SMT) program extraction protocol (Medeiros and Cid [2005](#page-7-0); Xu et al. [2015](#page-7-0)). According to the SMT protocol, the TP was defined as the sum of OP and IP content, and the IP was divided into AP (calcium-bound P) and NAIP (P bound to aluminum, iron, and manganese oxides and hydroxides). Since OP was almost converted to IP during hightemperature incineration, its content can be ignored. The molybdenum blue method was used to determine the various P speciations by spectrophotometer at the wavelength of 700 nm.

#### Thermal characteristics

To determine the temperature range of transformation from NAIP to AP, a simultaneous thermal analyzer (STA-449F5, Germany) equipped with thermogravimetry (TG) and differential thermal analysis (DTA) was used to analyze the weight changes and physical and chemical processes of pure chemical substances and model compounds. The sample was dried and mixed thoroughly before testing, and approximately 10 mg of sample was used for each test. The test was carried out in an atmosphere where the gas environment was air, the test temperature range was 30–800 °C, and the ramping rate was 10 °C/min.

# Results and discussion

# Effect of incineration time on the distribution of phosphorus speciation

The changes in the content of various P forms, NAIP/IP and AP/IP, in the products obtained by sludge at 800 °C for different incineration time are shown in Fig. 1.

As can be seen from Fig. 1, the IP content in the SSA after incineration at 800 °C was significantly increased compared with the untreated raw sludge, which was 1.7–2.1 times than that of the raw sludge. As the incineration time increases, the IP content increased slowly, but the whole trend was not obvious, which indicated that the time had little effect on the IP content. In order to ensure that most of the organic matter in the sludge is destroyed (Chen and Yan [2012](#page-6-0)), the incineration time of 2 h is more suitable.

In addition, with the increase of incineration time, the NAIP content in sludge incineration ash decreased first and then stabilized. When the time was 0.5–3 h, the NAIP content decreased from 23.41 to 7.78 mg/g. The AP content increased



Fig. 1 Distribution of phosphorus speciation in raw sludge and sludge products incinerated at different time

at first and then remained stable, increasing from 17.02 to 44.93 mg/g. Meanwhile, with the increase of time, NAIP/IP decreased continuously, from 51.4 to 14.6%, while AP/IP gradually increased from 37.4 to 84.5%. The above phenomenon indicated that the increase of incineration time promoted the morphological transformation of NAIP into AP in the SS.

# Effect of incineration temperature on the distribution of phosphorus speciation

Figure 2 shows the changes in phosphorus content, NAIP/IP and AP/IP, in the product obtained by incineration of sludge at different temperatures for 2 h.

According to Fig. 2, the IP content of the sludge product after incineration is significantly increased compared with the untreated raw sludge, which was 2.1–2.9 times than that of the raw sludge. As the incineration temperature increases, the IP content increased first and then decreased.

When the temperature was 800–950 °C, the IP content increased from 57.27 to 77.73 mg/g, which is mainly due to the decomposition of organic matter at 800–950 °C. The degree gradually increased with increasing temperature. Most of the P remains in the solid phase due to its low volatility, which increased the relative content of IP in the sludge. However, at a temperature of 1000 °C, the IP content begins to decrease, possibly because some of the P begins to volatilize at temperatures above 950 °C (Li et al. [2015\)](#page-7-0), causing a drop in IP content in the SSA.

Additionally, compared with the original sludge, the P in the sludge product after incineration mainly exists in the form of AP, and NAIP accounts for a small amount. As the temperature increases, both IP and NAIP content increased at first and then decreased, while AP content increased slowly. At the same time, NAIP/IP increased slightly and then decreased, while AP/IP is exactly the opposite. Combined with the study by Li et al. (Li et al. [2015](#page-7-0)), it is speculated that during the



Fig. 2 Distribution of phosphorus speciation in raw sludge and sludge products incinerated at different temperatures

<span id="page-3-0"></span>incineration process, due to the gradual conversion of NAIP to AP, partially unstable NAIP began to volatilize at temperatures above 950 °C, resulting in a decrease in IP and NAIP content and an increase in AP.

### Effect of  $MgCl<sub>2</sub>$  on the distribution of phosphorus speciation

The content of various P forms, NAIP/IP and AP/IP, in the product obtained by incineration of sludge with different proportions of MgCl<sub>2</sub> at 800 °C for 2 h are displayed in Fig. 3.

From Fig. 3, with the amount of  $MgCl<sub>2</sub>$  increased, the content of IP first increased and then decreased slightly in the sludge. A  $3\%$  addition of MgCl<sub>2</sub> resulted in a slight decrease in IP, which is related to the increase of product quantity after  $MgCl<sub>2</sub>$  addition. With the increase of  $MgCl<sub>2</sub>$ , the NAIP content decreased at first and then increased. The NAIP decreased from 11.75 mg/g without addition of  $MgCl<sub>2</sub>$  to 9.06 mg/g when the Mg added was 1.6%. When the MgCl<sub>2</sub> added was continuously increased, the NAIP content began to increase and reached the maximum of 19.17 mg/ g when the addition of Mg in the mixture was 3.0%. However, the AP content increased first and then decreased. Meanwhile, the trend of NAIP/IP and AP/IP is consistent with NAIP and AP, respectively. This result indicated that the addition of  $MgCl<sub>2</sub>$  could change the distribution of P speciation during sludge incineration. Studies has pointed out that Mg-P be-longs to the NAIP (He et al. [2016](#page-7-0)). In addition, the bioavailability of Mg-P is slightly higher than that of Ca-P and significantly higher than that of Fe-P and Al-P (Vogel and Adam [2011\)](#page-7-0). Based on the SMT protocol, it is speculated that the following P transformation process may occur: When a small amount of  $MgCl<sub>2</sub>$  is present, some Fe/Al-P (NAIP) in the sludge is converted into Ca-Mg-P, which leads to a decrease in NAIP/IP and an increase in AP/IP. When the content of



Fig. 3 Distribution of phosphorus speciation in sludge products with different MgCl<sub>2</sub> additions **Fig. 4** TG-DTA of MgCl<sub>2</sub>·6H<sub>2</sub>O (a) and MgCl<sub>2</sub>·6H<sub>2</sub>O+AlPO<sub>4</sub> (b)

 $MgCl<sub>2</sub>$  is high, AP may react with  $MgCl<sub>2</sub>$  to form  $Mg-P$ (NAIP), which causes an increase in NAIP/IP and a decrease in AP/IP.

Since the sludge product without any additives contains more AlPO<sub>4</sub>, the pure material  $MgCl<sub>2</sub>·6H<sub>2</sub>O$  and the mixture of AlPO<sub>4</sub> and MgCl<sub>2</sub>·6H<sub>2</sub>O are subjected to TG analysis to further analyze the reaction process of  $MgCl<sub>2</sub>$  with phosphorus-containing substances in the sludge and determine the temperature range in which  $MgCl<sub>2</sub>$  and  $AlPO<sub>4</sub>$  react.

Figure 4 shows the TG analysis results of pure  $MgCl<sub>2</sub>$ .  $6H<sub>2</sub>O$  (a) and the mixture of AlPO<sub>4</sub> and MgCl<sub>2</sub>·6H<sub>2</sub>O  $(n(A)):n(Mg) = 1:1$  (b).

According to Fig. 4, the trends of the TG and DTA curves of the pure  $MgCl<sub>2</sub>·6H<sub>2</sub>O$  and  $AlPO<sub>4</sub>+MgCl<sub>2</sub>·6H<sub>2</sub>O$  mixtures are almost identical at temperatures between 29 and 600 °C, and there is a significant quality degradation. Similar peaks were observed on the DTA curve at 150–350 and 500 °C. It can be inferred that  $AIPO_4$  will not react with  $MgCl_2$  in this temperature range. According to previous studies, the pure material  $MgCl<sub>2</sub>·6H<sub>2</sub>O$  undergoes dehydration and hydrolysis reactions between 29 and 500 °C, wherein the hydrolysis



reaction produces intermediates products Mg(OH)Cl and HCl, which coincide with the trend of the TG and DTA curves in Fig. [4.](#page-3-0) When the temperature was 500 °C, Fig. [4a, b](#page-3-0) both show mass reduction, and there is an obvious endothermic peak on the DTA curve. According to the relevant literatures, this is mainly caused by the decomposition of Mg(OH)Cl to produce MgO and HCl (Xiang et al. [2016\)](#page-7-0).

When the temperature was between 600 and 650 °C, there is no significant change in the TG and DTA curves of  $MgCl<sub>2</sub>$ .  $6H_2O$ , while the TG curve of MgCl<sub>2</sub>· $6H_2O$  +AlPO<sub>4</sub> shows almost no mass loss, and a small endothermic peak appears on the DTA curve. It can be inferred that  $MgO$  and  $AlPO<sub>4</sub>$ have undergone a solid-phase endothermic reaction within this temperature range. Studies have also shown that the addition of MgO was beneficial for the transformation of NAIP to AP (Li et al. [2019\)](#page-7-0).

In order to further verify the above speculation, the pure  $MgCl<sub>2</sub>·6H<sub>2</sub>O$  and  $AlPO<sub>4</sub>$  were incinerated at 500, 600, and 700 °C, respectively. The XRD detection results are shown in Fig. 5. By comparing the P forms in the incineration products at different temperatures, the exact temperature at which  $MgCl<sub>2</sub>·6H<sub>2</sub>O$  reacts with  $AIPO<sub>4</sub>$ , and the P form before and after the reaction can be determined.

As shown in Fig.  $5a$ , no peak of MgCl<sub>2</sub> was detected in the incineration products of pure MgCl<sub>2</sub> and AlPO<sub>4</sub> at 500 °C, and signals of MgO and  $Al(PO<sub>3</sub>)<sub>3</sub>$  appeared. This indicated that when  $MgCl<sub>2</sub>$  is added, it will react with  $AIPO<sub>4</sub>$  to generate some intermediate products and eventually lead to the formation of Mg-P, resulting in the formation of Mg-P, thus improving the bioavailability of P. When the temperature was raised to 600 °C, the new phosphate mineral phases of  $Mg_3(PO_4)_2$ were observed; this implied that  $A_1PO_4$  reacted with  $MgCl_2$  to produced Mg-P at 500–600 °C. At 700 °C, no new phosphate mineral phase were formed, and  $Mg_3(PO_4)_2$  was still the main phosphate mineral produced by the reaction of  $AIPO<sub>4</sub>$  and MgCl<sub>2</sub>. The XRD analysis of the reaction between  $AIPO<sub>4</sub>$ and MgCl<sub>2</sub>·6H<sub>2</sub>O in the temperature range of 500–700 °C indicated that  $MgCl<sub>2</sub>$  could effectively promote  $AlPO<sub>4</sub>$  transformation to Mg-P, which can be considered as the conversion of NAIP to AP, and the AP can be produced in the range of 500–600 °C with higher bioavailability.

To further examine the mechanism of the reaction between  $MgCl<sub>2</sub>$  and AlPO<sub>4</sub>, MgO and AlPO<sub>4</sub> were incinerated at 500, 600, and 700 °C, respectively. XRD analysis was performed to explore the changes in the form of P before and after the reaction at different incineration temperatures, and the results are shown in Fig. 5b.

Figure 5b shows that there were no new peaks in the incineration of MgO and AlPO<sub>4</sub> at 500  $^{\circ}$ C, indicating that the two substances have not react. When incinerated at 600 °C, a new peak of phosphorus-containing mineral phase  $Mg_3(PO_4)_2$  appeared, and the main mineral phase was also  $Mg_3(PO_4)_2$  at 700 °C. This result proves that the reaction between  $MgCl<sub>2</sub>$ 





Fig. 5 XRD patterns of AlPO<sub>4</sub> + MgCl<sub>2</sub>·6H<sub>2</sub>O (a) and AlPO<sub>4</sub> + MgO (b) heated at different temperature

and  $AIPO<sub>4</sub>$  was mainly through the formation of the intermediate product MgO, which reacts with  $AIPO<sub>4</sub>$  to form Mg-P.

### Effect of CaCl<sub>2</sub> on the distribution of phosphorus speciation

Figure [6](#page-5-0) shows the changes of the content of various P, NAIP/ IP and AP/IP, in the product obtained by adding different CaCl<sub>2</sub> incineration for 2 h at 800  $^{\circ}$ C.

It can be seen from Fig. [6](#page-5-0) that with the increase of  $CaCl<sub>2</sub>$ , the IP content increased and then decreased slightly in the sludge. The dilution effect of excessive  $CaCl<sub>2</sub>$  addition leads to a decrease in IP content when the CaCl<sub>2</sub> was  $10\%$ . When the addition of CaCl<sub>2</sub> increased from 0% Ca to 10.0% Ca, the NAIP content decreased from 11.75 to 0.09 mg/g, and the AP

<span id="page-5-0"></span>

Fig. 6 Distribution of phosphorus speciation in sludge products with different CaCl<sub>2</sub> additions

content increased first and then decreased. However, AP/IP continues to increase with the addition of  $CaCl<sub>2</sub>$ , while NAIP/ IP was the opposite. When the Ca content reaches 5%, the IP is almost entire in the form of AP. The results showed that the addition of CaCl<sub>2</sub> changed the distribution of P forms during sludge incineration. The possible reason was that  $CaCl<sub>2</sub>$ reacted with Fe/Al-P in the sludge to form Ca-P during sludge incineration, which resulted in the continuous decrease of NAIP and the increase of AP.

In order to further analyze and determine the reaction process of  $CaCl<sub>2</sub>$  and  $AlPO<sub>4</sub>$ , thermal analysis of the mixture of AlPO<sub>4</sub> and CaCl<sub>2</sub> was carried out.

Figure 7 shows the TG analysis results of pure  $CaCl<sub>2</sub>(a)$ and the mixture of AlPO<sub>4</sub> and CaCl<sub>2</sub> (n(Al):n(Ca) = 1:3) (b).

According to Fig. 7 and the previous researches, when the temperature was between 29 and 300 °C, the TG curves of pure  $CaCl<sub>2</sub>$  and the mixture of  $CaCl<sub>2</sub>$  and  $AlPO<sub>4</sub>$  showed significant mass loss, and two endothermic peaks appeared in the DTA curve, which was speculated to be caused by the removal of crystal water.

When the temperature was between 740 and 750 °C, there is no mass loss in the TG analysis of the pure  $CaCl<sub>2</sub>$  and no endothermic or exothermic peak appears in the DTA curve, which indicated that no reaction occurred within this temperature range. However, the thermogravimetric analysis of  $CaCl<sub>2</sub>+AlPO<sub>4</sub>$  showed that the mass began to decrease between 740 and 750 °C, and a small endothermic peak appeared in the DTA curve. This may be due to the endothermic reaction of CaCl<sub>2</sub> and AlPO<sub>4</sub> that occurs within this temperature range, which produces gas and leads to mass loss (Fraissler et al. [2009\)](#page-6-0).

The TG analysis of pure CaCl<sub>2</sub> showed no mass loss, and a strong endothermic peak appeared in the DTA curve between the temperatures of 770 and 800 °C. Since the melting point of CaCl<sub>2</sub> is about 782 °C, it is presumed that this phenomenon is caused by the melting of CaCl<sub>2</sub>. However, the TG analysis of



Fig. 7 TG-DTA of CaCl<sub>2</sub> (a) and CaCl<sub>2</sub>+AlPO<sub>4</sub> (b)

 $CaCl<sub>2</sub>+AlPO<sub>4</sub>$  showed that the quality still showed a downward trend, and a strong endothermic peak also appeared in the DTA curve. It is speculated that this is mainly caused by the melting of  $CaCl<sub>2</sub>$ , and the loss of mass may be caused by an endothermic reaction at 740–750 °C.

In order to further verify the above speculation, the pure CaCl<sub>2</sub> and AlPO<sub>4</sub> were incinerated at 700, 750, and 800 °C, respectively, and subjected to XRD test. By comparing the P forms in the incineration product at different temperatures, the temperature range of the reaction between CaCl<sub>2</sub> and AlPO<sub>4</sub> and the form of P before and after the reaction can be determined.

Figure [8](#page-6-0) shows the results of XRD detection of  $CaCl<sub>2</sub>$  and AlPO<sub>4</sub> compounds incinerated at 700, 750, and 800  $^{\circ}$ C.

As shown in Fig. [8,](#page-6-0) peaks of AlPO<sub>4</sub>,  $Al_2O_3$ , and  $Al(PO_3)_3$ appeared at 700 °C, but no peaks of CaCl<sub>2</sub> appeared. It is speculated that CaCl<sub>2</sub> may react with  $AIPO<sub>4</sub>$  to form phosphorus-containing minerals. As the temperature increased to 750 °C, the peak of AlPO<sub>4</sub> and  $Al_2O_3$  disappeared, and the new mineral phases of Ca<sub>2</sub>PO<sub>4</sub>Cl were observed,

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Fig. 8 XRD patterns of AlPO<sub>4</sub> +CaCl<sub>2</sub> heated at different temperature

indicating that the reaction between  $AIPO<sub>4</sub>$  and  $CaCl<sub>2</sub>$  produced Ca-P in the temperature range of 700–750 °C. The peak of Al(PO<sub>3</sub>)<sub>3</sub> disappeared, and only the peak of Ca<sub>2</sub>PO<sub>4</sub>Cl exists at 800 °C, indicating that no new phosphorus-containing mineral phase were formed as the temperature rises. The main phosphorus-containing mineral formed by the reaction of AlPO<sub>4</sub> and CaCl<sub>2</sub> was Ca<sub>2</sub>PO<sub>4</sub>Cl, which has higher bioavailability and can be directly used as fertilizer.

## **Conclusions**

This study focused on the conversion mechanism between various P speciations when chlorine additives were added during SS incineration. The SS was incinerated at various temperatures and time, and the results showed that as the incineration temperature and time increased, the content of IP in the SSA increased, and the conversion of NAIP to AP in SS was promoted. Additionally, SS was incinerated at 800  $\rm{^{\circ}C}$  with the addition of MgCl<sub>2</sub> and CaCl<sub>2</sub>, and the reaction between  $AIPO_4$  and  $MgCl<sub>2</sub>$  or CaCl<sub>2</sub> promoted the formation of AP with higher P bioavailability. The temperature and the minerals produced of the reaction between the model compound of NAIP in the sludge and the chloride additives were analyzed by TG-DTA and XRD detection. AlPO<sub>4</sub> reacted with MgCl<sub>2</sub> at 500–600 °C to produced Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> were determined. And the reaction between  $AlPO<sub>4</sub>$  and  $MgCl<sub>2</sub>$  is mainly due to the reaction of the intermediate product MgO and  $AIPO<sub>4</sub>$  to produce phosphorus-containing minerals. When AlPO<sub>4</sub> and CaCl<sub>2</sub> compounds were incinerated,  $Ca<sub>2</sub>PO<sub>4</sub>Cl$ was formed at 700–750 °C, which has higher P bioavailability and can be used in agriculture to alleviate the shortage of phosphorus resources. As proposed by this paper, it was

expected to provide a basis for obtaining products with more agricultural use value in the process of sludge incineration.

Author contribution All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Jingyan Chen, Fei Yang, and Yangfan Fang. The first draft of the manuscript was written by Yunfeng Xu, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

### **Declarations**

Ethics approval and consent to participate Not applicable

Consent for publication Not applicable

Competing interests The authors declare no competing interests.

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