

Migration of Phosphorus in Sewage Sludge during Different Thermal Treatment Processes

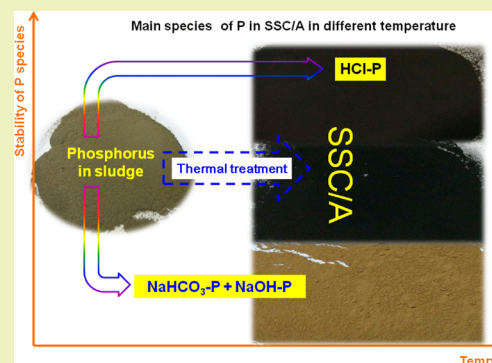
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S Supporting Information

ABSTRACT: The utilization of phosphorus (P) in activated sludge discharged from wastewater treatment plants is an important part of the global phosphorus circulation. Thermal treatment of excess sludge would become a promising method for their disposal throughout the world. Herein, we investigated the transformation and migration of P in sewage sludge during different thermal treatment conditions. The results indicate that the temperature can significantly influence the species and content of P in the sewage sludge char or ash (SSC/A), while the atmosphere of thermal treatment has a slight effect on the fate of P. ^{31}P NMR and XRD analysis indicated that P migrated mainly to the medium-term plant available P pool ($\text{pool}_{\text{NaOH}}$) on treating the sewage sludge at a low temperature (673–873 K), while it was prone to migration to the long-term plant available P pool (pool_{HCl}) when treated at a high temperature (873–1073 K).

KEYWORDS: Sewage sludge, Phosphorus, Thermal treatment, Char, Temperature and atmosphere



INTRODUCTION

An activated sludge method is used to efficiently treat sewage in wastewater treatment plants (WWTP) worldwide, but the disposal of the excess activated sludge discharged from WWTP is an arduous issue and a formidable task. Presently, over 70% of the sewage sludge is being disposed by agricultural reuse or in landfills.¹ However, considering the limited amount of sludge needed for agricultural reuse¹ and the rise in the landfill costs due to a decrease in the available landfill sites,² two traditional disposal methods of the sludge need to be held back. Thermal processing of the sewage sludge can substantially reduce the sludge volume and properly reuse the energy contained in the sludge, and it is a sustainable strategy for the disposal of sewage sludge.^{3,4} At present, the main methods involved in thermal processing of sewage sludge include incineration, pyrolysis, gasification, and wet oxidation.¹ The solid products (such as ash in the incineration process and char in the pyrolysis process) are usually used as soil conditioners, fertilizers, construction materials, and so on especially for those containing very low concentrations of heavy metals.^{3–6}

Activated sludge usually contains 1–10% phosphorus (P), which is an important part of the combined P circulation in the ecosystem.⁷ During the thermal treatment of sewage sludge, P gets enriched in the char/ash (SSC/A),^{4,8,9} of which the consequences are two-fold. On one hand, the use of SSC/A as fertilizer or soil conditioner requires the presence of the plant-available form of P that is easily released, while on the other hand, its use in construction materials necessitates its fixation as P is also responsible for eutrophication^{10,11} once excess P is released into water. Hence, the transformation and migration of P during thermal processing of excess sludge is of great concern for fully

understanding the behavior of P in SSC/A when SSC/A is applied to soil.

The release and retention of P is dependent on its existent chemical form (like orthophosphate, pyrophosphate, and minerals) and its combination with metal ions.^{12–17} McDowell et al.^{12,13} reported that the potentially mobile P forms are the soluble P species and the P that are weakly adsorbed on Fe, Al, and Ca. Sharpley et al.¹⁶ found that a decrease in water-extractable P in the soil was caused by the transformation of P in combination with Al, Fe–P, and Ca–P. The organic P in the environment also has different mobility; Hamdan et al.¹⁷ found that the organic P associated with organic matter containing plenty of O-alkyl groups is more labile than that associated with the organic matter containing ample refractory alkyl and aromatic carbon groups.

The temperature and atmosphere of the thermal treatment are two factors that influence the characterization of some elements in SSC/A, like the content and species of nonmetals (N, P, and S),^{4,18} alkali and alkaline earth metals,¹⁹ and some heavy metals in SSC/A.²⁰ However, the behavior of P species in sewage sludge during various thermal treatment conditions has been poorly reported. Thus, a systematic study on the migration and transformation of P during different thermal treatments of sewage sludge could shed light on the recycling and circulation of P in the ecosystem.

The objective of the present work was to elucidate the transformation and migration mechanism of P under different

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temperature and atmospheric conditions during its thermal treatment process: (1) The sewage sludge samples were thermally treated by different methods and at different temperatures (fast pyrolysis in N_2 and CO_2 and combustion in air). (2) The P species were determined by ^{31}P NMR and XRD, and the effects of variable thermal atmosphere and temperature were investigated. (3) The possible pathways for the formation of different P species during thermal treatment were proposed.

EXPERIMENTAL SECTION

Pretreatment of Sewage Sludge. The dewatered sewage sludge (moisture 79.6%) was obtained from Wangtang municipal wastewater treatment plant, Anhui, China. First, the dewatered sludge was air-dried outside for several days; then, the air-dried sludge (moisture, 46.6%) was kept drying at 343–353 K in an oven overnight. Finally, the dried sludge (moisture 5.4%) was pulverized and passed through a 60-mesh (250 μm) sieve, sealed in a plastic ziplock bag, and stored in a freezer until analysis.

Proximate and Ultimate Analysis of Sewage Sludge. The proximate and ultimate analyses of the sewage sludge are shown in Table S1 of the Supporting Information. The moisture, ash, and fixed carbon were measured by the method of the American Society for Testing and Materials (ASTM) D3172-89. Volatile matter was obtained through thermogravimetric analysis.^{21,22} Ultimate analysis was performed with an elemental analyzer (VARIO EL III, Elementar, Inc., Germany).

The sludge was digested in concentrated $H_2SO_4/HClO_4$ at 473 K for determination of the content of P in sewage sludge.²³ The concentration of P in the digestion solution was determined by the molybdate–ascorbic acid method. The content of Ca, Mg, Al, and Fe in the sewage sludge and some SSC/A samples was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Optima 7300 DV, PerkinElmer Co., U.S.A.) after digesting of the sample by $HNO_3/HClO_4$.²⁴

The thermal analysis was performed on a SDT Q600(V20.9 Build 20) instrument. The temperature went from ambient temperature to 1273 K with a heating rate of 10 K min^{-1} in a nitrogen atmosphere at a flow rate of 100 mL min^{-1} .

Thermal Treatment of Sewage Sludge. Three series of SSC/A, denoted as S- N_2 , S- CO_2 , and S-Air were prepared under three simulated thermal treatment conditions for the sewage sludge, i.e., fast pyrolysis in N_2 and CO_2 and combustion in the air. The first (S- N_2) and the second (S- CO_2) series of samples were produced by fast pyrolysis of the sludge in N_2 and CO_2 atmosphere (gas flow rate of 0.2 L min^{-1}) in a quartz tubular reactor with a length of 60 cm and internal diameter of 23 mm. Six grams of sludge was fed into the reactor each time and pyrolyzed at temperatures of 673, 773, 873, 973, and 1073 K. The third series of samples (S-Air) were obtained by combustion of 1.0 g of sludge in a muffle furnace at different temperatures (673, 773, 873, 973, and 1073 K) for 1 h. The temperature in the furnace was increased from ambient temperature to the final temperature with a heating rate of 10 K min^{-1} . As the amount of SSC/A that was prepared was not enough for the following analysis, several replicate thermal treatments were conducted to obtain enough sample. The replicate samples obtained in each treatment were homogeneously mixed, and then the mixed samples of each treatment were subjected to sequential extraction.

Water-Soluble Phosphorus (WSP). One gram of the solid sample was extracted by 60 mL deionized water.²⁵ Two replicate experiments were conducted on each sample. The mixed sample was shaken at 298 K for 16 h. After the extraction, the sample was centrifuged and filtered with 0.22 μm membrane. The filtrate was diluted and digested with potassium persulfate, and the P concentration in the digested filtrate was determined using molybdate–ascorbic acid methods. The proportion of WSP in SSC/A (R_{WSP}) can be written as

$$R_{WSP} = \frac{P_{WSP}}{P_{total}} \times 100\% \quad (1)$$

where P_{WSP} is the amount of P extracted by water ($mg g^{-1}$) in SSC/A, and P_{total} is the theoretical P content ($mg g^{-1}$) in the sample (in SSC/A). P_{total} can be described by eq 2.

$$P_{total} = \frac{P_{sludge}}{\eta} \quad (2)$$

where P_{sludge} is the P content in sludge ($mg g^{-1}$), and η is the yield of the sample (yields of different SSC/A are shown in Table S2, Supporting Information) during the thermal treatment.

Proportion of P in Different P Pools. The modified sequential extraction method based on the methods recorded in the *Handbook of Soil Analysis*²⁶ was adopted to extract the P in the sludge and SSC/A. In this experiment, 1.0 g of the solid sample was sequentially extracted (the ratio of solid to liquid is 1 to 60 (w/w)) by 0.5 M $NaHCO_3$ (pH adjusted to 8.5), 0.1 M NaOH, and 1 M HCl solutions. Two replicate experiments were conducted on each sample. The sample was shaken at 298 K for 16 h. After each extraction step, the sample was centrifuged and filtered. The filtrate was used to analyze the P concentration using the method described above.

The P fractions extracted by 0.5 M $NaHCO_3$, 0.1 M NaOH, and 1 M HCl solutions correspond to labile P ($NaHCO_3$ -P), the P adsorbed on iron and aluminum compounds (NaOH-P), and the P associated with or trapped in the minerals (HCl-P), respectively. $NaHCO_3$ -P can be available to the plant in the short term, NaOH-P is thought to be available to the plant in the medium term, and HCl-P can hardly be absorbed by plant directly.^{26–28} The three P fractions belong to different P pools, which are denoted as $pool_{NaHCO_3}$, $pool_{NaOH}$, and $pool_{HCl}$. In this extraction method, the WSP can be considered to be a portion of $NaHCO_3$ -P. The proportion of P (R) in different P pools in a sample can be written as eq 3.

$$R = \frac{P_x}{P_{total}} \times 100\% \quad (3)$$

where P_x is one of the P fractions in a certain P pool.

Phosphorus in Residue after Extraction. The proportion of P in the residue (Res.-P) after each extraction is the difference of the total P and the sum of the proportions of $NaHCO_3$ -P (WSP is assumed as a portion of $NaHCO_3$ -P), NaOH-P, and HCl-P.²⁵

^{31}P NMR Analysis. The P species of the sewage sludge and SSC/A that were treated at 673, 873, and 1073 K were characterized by ^{31}P NMR. One gram of sample was added to 40 mL of 0.25 M NaOH/0.05 M EDTA solution. After being shaken for 16 h at 298 ± 3 K, the mixture was centrifuged and filtered with 0.22 μm membrane. The supernatant was lyophilized, and about 0.2 g of solid sample was obtained. The solid sample was redissolved in the solution of 1 M NaOH/0.1 M EDTA at the solid to liquid ratio of 1:10 (w/w) and 0.5 mL D_2O . The recovery percent (RP) of P extracted by this method was calculated by eq 4.

$$RP (\%) = \frac{P_{NaOH-EDTA}}{P_{total}} \times 100\% \quad (4)$$

where $P_{NaOH-EDTA}$ is the amount of P extracted by 0.25 M NaOH/0.05 M EDTA ($mg g^{-1}$), and P_{total} is the theoretical P content ($mg g^{-1}$) in the sample.

The spectra of the liquid samples were obtained using a Bruker AVANCE AV III 400 MHz spectrometer operating at 162 MHz at 297 K. A 90° pulse width, acquisition time of 0.51 s, and relaxation delay of 50 s were applied. An 85% H_3PO_4 was used as the external standard. As the P content in sewage sludge is much lower than that of other samples, 128 scans were required for the sample of sewage sludge and 64 scans for other six samples. The spectra were analyzed by NMR software (MestReNova v 6.1.1–5475), and the peak areas was used to quantify the P of different species in the extraction.²⁹

X-ray Powder Diffraction (XRD). The samples were ground into fine powder (<200-mesh (74 μm)) prior to XRD analysis. The XRD tests were performed on a Panalytical X'pert PRO diffractometer (Philips X'pert PRO), and Cu $K\alpha$ radiation ($\lambda = 0.154$ nm) generated at 40 kV/200 mA and a scintillation counter were used. The data were collected in the range (2θ) from 10° to 70° with the scan step of 0.02°. The minerals

in the samples were identified using the XRD data analysis software (MDI JADE 5.0) and its corresponding powder diffraction file (PDF) database (a more detailed analysis method is shown in section S1, Supporting Information).

Statistical Analysis. One-way analysis of variance (ANOVA) was applied to analyze the experimental data ($p \leq 0.05$) using the software IBM SPSS 17.0 (SPSS, Inc., USA) for Windows.

RESULTS AND DISCUSSION

Characterization of Sewage Sludge. The contents of P, Ca, Mg, Al, and Fe in sewage sludge were determined to be 2.6, 2.9, 0.9, 3.1, and 0.9 wt %, respectively. The content of P in sewage sludge was much higher compared to many other kinds of biomass (such as crop residues and urban composted material),³⁰ which makes it possible to reuse the sewage sludge as an available P source. The presence of Ca, Mg, Al, and Fe in sewage sludge and SSC/A (Table S3, Supporting Information) is very important as they are closely related to the stabilization of P in the sludge and in SSC/A.³¹ From the analysis of the TG (thermogravimetry) and DTG (derivative thermogravimetry) of sewage sludge (Figure 1), its weight loss could be divided into

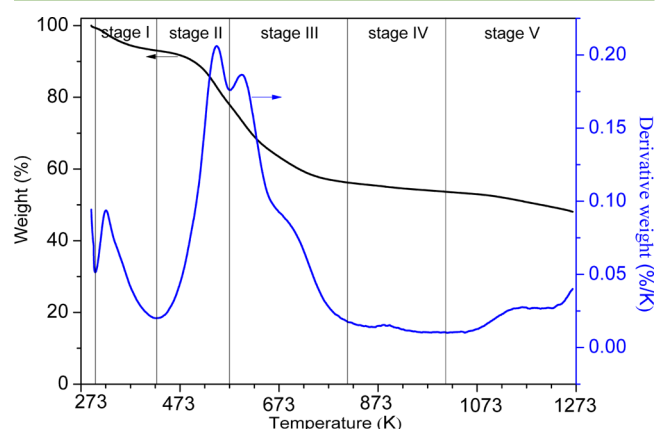


Figure 1. TG (black line) and DTG (blue line) curves of sewage sludge.

five stages. Thus initially (194–423 K), there is loss of free water and water in the microbial cells followed by the second (423–573 K) and third stage (573–811 K) weight losses resulting from release of some labile organic components (like biodegradable material) and polymers present in the microbial and original sludge, respectively,³² while the fourth stage (811–1006 K) corresponds to loss of some refractory organic matter.³³ Finally, the weight loss of the last stage may be related to the evaporation of some metal or metal minerals. From the temperature range set for combustion and pyrolysis, the evaporation of the metal may be neglected.

Changes of Water-Soluble P (WSP). The water-soluble P (WSP) is a good indicator to test the runoff P in the biosolid (such as manure, sewage sludge, etc.), which may lead to eutrophication.^{34–36} The WSP of the sewage sludge and SSC/A were tested, and the results are shown in Table 1 and Figure 2a. As the P contents in sewage sludge and different SSC/A are not the same, the amounts of WSP in sewage sludge and SSC/A (Table 1) are incomparable. Thus, the amount of WSP was normalized to the proportion of WSP in (R_{WSP}) different samples. From Figure 2a, we observe that most R_{WSP} values in SSC/A are no more than 2.5%, which is far less than R_{WSP} in sewage sludge (20.7%). Moreover, the R_{WSP} values in SSC/A can be even lower with an increase in temperature. The small

proportion of WSP in SSC/A indicates that thermal treatment can stabilize P in SSC/A.

Migration of P among Different P Pools. The amounts of P in sewage and SSC/A samples extracted by different solutions (Table 1) were also normalized to the proportion of the P (R (%)). $\text{NaHCO}_3\text{-P}$, NaOH-P , and HCl-P under different atmospheric conditions and temperatures (Figure 2b–d and Figure S1 (bar graph), Supporting Information) showed that on the whole, both $\text{NaHCO}_3\text{-P}$ (Figure 2b) and NaOH-P (Figure 2c) decreased with the elevation of thermal treatment temperature regardless of the atmospheric conditions, while HCl-P increased significantly. Compared to the proportion of P in the original sewage sludge (37.2% for $\text{NaHCO}_3\text{-P}$, 27.0% for NaOH-P , and 20.5% for HCl-P), the $\text{NaHCO}_3\text{-P}$ decreased significantly upon thermal treatment, while an appreciable increase was observed in NaOH-P and HCl-P at 673–873 and 973–1073 K, respectively. It indicated that the available P in the sewage sludge may be immobilized in more stable P pools ($\text{pool}_{\text{NaOH}}$ and pool_{HCl}) in the process of thermal treatment of sewage sludge at sufficiently high temperature.

Analysis of detailed migration trends of P from $\text{pool}_{\text{NaHCO}_3}$ to pool_{HCl} in SSA/C based on one-way ANOVA analysis revealed p values with different temperature groups (Figure 2b–d). At 673–873 K, irrespective of atmospheric conditions during the thermal treatment, neither NaOH-P nor HCl-P of SSA/C had changed significantly ($p > 0.05$), while at 873–1073 K, all the three P fractions changed significantly ($p < 0.05$) with temperature except for HCl-P of S-Air. The decrease in $\text{NaHCO}_3\text{-P}$ and NaOH-P and the increase in HCl-P indicated that the high temperature of fast pyrolysis (973–1073 K) may assist in migration of P from $\text{pool}_{\text{NaHCO}_3}$ and $\text{pool}_{\text{NaOH}}$ to pool_{HCl} . During combustion, the P migrated from $\text{pool}_{\text{NaHCO}_3}$ to more stable pools monotonously with an increase in temperature, which may be explained from combustion temperature acting as a direct driving force in converting P from $\text{pool}_{\text{NaHCO}_3}$ and $\text{pool}_{\text{NaOH}}$ to pool_{HCl} . Compared to combustion, there appeared to be an obvious threshold for P species between the low (673–873 K) and high temperatures (973–1073 K) during pyrolysis of the sludge under N_2 and CO_2 atmosphere, which may be due to the properties of organic matter presented on SSC. In pyrolysis, the feedstock went through the process of thermal decomposition in just 1–2 s.³⁷ At low temperatures, some labile organic matter was produced³⁸ and condensed rapidly on the SSC surface upon SSC leaving the heating zone. This labile organic matter contains certain carboxyl and hydroxy groups that may coordinate with Ca and Mg³⁸ and retard the contact between Ca, Mg, and P, thus preventing the formation of insoluble Ca,Mg-P compounds. However, raising the temperature led to the formation of some recalcitrant aromatic carbons,^{39,40} which could be confirmed by the low weight loss in the corresponding temperature range (873–1073 K) in TG analysis. This recalcitrant component of SSC is considered to be the carbon skeleton of SSC,⁴⁰ having few carboxyl and hydroxyl groups and consequently having little effect on the reaction between Ca, Mg, and P. Thus, the formation of insoluble Ca,Mg-P compounds increased significantly from 873–1073 K. In combustion, at sufficient retention time of 4 h and in the presence of O_2 , most of the labile organic matter would be mineralized and had little chance to inhibit the reaction between Ca, Mg, and P, eliminating the threshold between the low temperature range and the high temperature range. The change of residue P (Figure 2e) is discussed in Figure S1 of the Supporting Information.

Table 1. Amount of P in Sewage Sludge and SSC/A Extracted by Different Solutions and Stayed in Residues (mg g⁻¹)

S-WSP 5.3 ± 0.007 temperature (K)	S-NaHCO ₃ 9.5 ± 0.5 S-N ₂ -WSP	S-NaOH 6.9 ± 1.2 S-CO ₂ -WSP	S-HCl 5.3 ± 1.4 S-Air-WSP	S-Res. 3.9 ± 0.2
673	0.51 ± 0.01	0.76 ± 0.01	1.68 ± 0.05	
773	0.48 ± 0.01	1.0 ± 0.01	1.62 ± 0.03	
873	0.54 ± 0.01	0.86 ± 0.01	0.67 ± 0.01	
973	0.18 ± 0.01	0.39 ± 0.00	0.33 ± 0.00	
1073	0.07 ± 0.00	0.38 ± 0.00	0.25 ± 0.00	
	S-N ₂ -NaHCO ₃	S-CO ₂ -NaHCO ₃	S-Air-NaHCO ₃	
673	2.7 ± 0.1	4.0 ± 0.2	11.2 ± 0.2	
773	2.4 ± 0.0	4.4 ± 0.0	11.1 ± 0.3	
873	3.8 ± 0.0	5.0 ± 0.0	6.6 ± 0.0	
973	0.75 ± 0.02	4.8 ± 0.2	3.0 ± 0.1	
1073	0.45 ± 0.02	0.39 ± 0.01	2.1 ± 0.0	
	S-N ₂ -NaOH	S-CO ₂ -NaOH	S-Air-NaOH	
673	22.2 ± 0.2	20.1 ± 0.2	20.8 ± 0.1	
773	23.2 ± 0.3	23.2 ± 0.0	25.3 ± 0.2	
873	25.3 ± 1.9	26.6 ± 1.5	26.4 ± 1.1	
973	17.2 ± 0.2	19.7 ± 0.6	26.0 ± 0.6	
1073	7.0 ± 0.2	13.9 ± 1.0	20.4 ± 0.2	
	S-N ₂ -HCl	S-CO ₂ -HCl	S-Air-HCl	
673	11.6 ± 1.1	10.8 ± 1.1	10.8 ± 0.2	
773	10.8 ± 0.2	11.1 ± 0.2	17.1 ± 0.3	
873	14.3 ± 0.2	14.4 ± 0.5	24.6 ± 5.6	
973	21.6 ± 1.1	20.0 ± 1.0	24.8 ± 0.5	
1073	30.5 ± 1.0	29.3 ± 2.0	36.1 ± 3.3	
	S-N ₂ -Res.	S-CO ₂ -Res.	S-Air-Res.	
673	3.9 ± 0.9	2.4 ± 1.0	4.4 ± 0.4	
773	4.9 ± 0.1	4.2 ± 0.2	-0.4 ± 0.4	
873	4.3 ± 1.8	0.4 ± 1.0	2.0 ± 6.7	
973	4.0 ± 1.4	2.8 ± 1.4	4.7 ± 0.2	
1073	14.2 ± 0.8	3.9 ± 1.0	3.3 ± 3.6	

Transformation of Form of P. The existing form of P is an important factor related to the stability of P in SSA/C. Before the characterization of P species, samples were extracted in 0.25 M NaOH/0.05 M EDTA.^{41,42} The recovery percent of each sample is listed in Table S4 of the Supporting Information. The ³¹P NMR spectra of the sewage sludge and SSA/C subjected to three thermal treatments at different temperatures are recorded in Figure 3. Four P species, namely, orthophosphate (ortho-P), orthophosphate monoesters, orthophosphate diesters, and pyrophosphate (pyro-P) were identified in the sludge (Figure 3a) from their signals at 5.38, 4.16–3.79, -1.05, and -5.01 ppm, respectively. Among the four P species, the orthophosphate monoesters and diesters are typical organic P components of sludge.²⁹ Upon thermal treatment, the signals corresponding to organic P disappeared (Figure 3b–d), while those of inorganic P, ortho-P (5.38–5.44 ppm), and pyro-P (-5.03 to -5.11 ppm) remained, indicating that the organic P mainly transformed into ortho-P and pyro-P during the process of thermal treatment.

The proportion of each P species in the samples could be obtained from the corresponding peak area of each P species in the spectra along with the recovery percent (Table S4, Supporting Information). Treatment at 673 K resulted in the production of a considerable amount of pyro-P in each sample. As the proportion of both organic P and ortho-P decreased at this temperature, it could be ascertained that the pyro-P produced during the thermal treatment may be derived from two pathways, namely, the transformation of the organic P and the dehydration of the original ortho-P in sludge. On raising the temperature, the

proportion of pyro-P from each sample decreased significantly. Treating the sample at 1073 K led to the production of a little amount of pyro-P in S-N₂ and S-CO₂ but the absence of pyro-P in S-Air. The decrease in pyro-P with temperature can also be found in the sequential extraction process (see section S2 and Figure S2, Supporting Information). This indicated that in the process of thermal treatment, temperature is a crucial factor in the transformation of P species, while different atmospheric conditions had just a small effect on the content of each P species in the samples.

The ³¹P NMR spectra assisted in identifying the anions of P but not the metal ions in combination, which also play an important role in the migration and stability of P in SSA/C. The crystalline properties of the mineral of P were characterized using XRD, and the obtained XRD curves of the samples and the peaks of the compounds (minerals) presented in the samples have been marked with number symbols (Figure 4a–d, fitted peaks of each sample are also shown in Tables S5–S8, Supporting Information). The minerals, like quartz, silicon oxide, illite (K_{0.7}Al₂(Si,Al)₄O₁₀(OH)₂), and muscovite ((K,Na)-Al₂(Si,Al)₄O₁₀(OH)₂) were present in all samples. From the XRD curves of S-N₂, S-CO₂, and S-Air, (Figure 3b–d), it could be observed that irrespective of the atmospheric conditions (N₂, CO₂, or air) the samples that were processed under identical/similar thermal treatments displayed similar curves, implying that different atmospheric conditions had little effect on the transformation of the mineral structure, which is different from other metals and nonmetals. For example, Zhang et al.⁴³

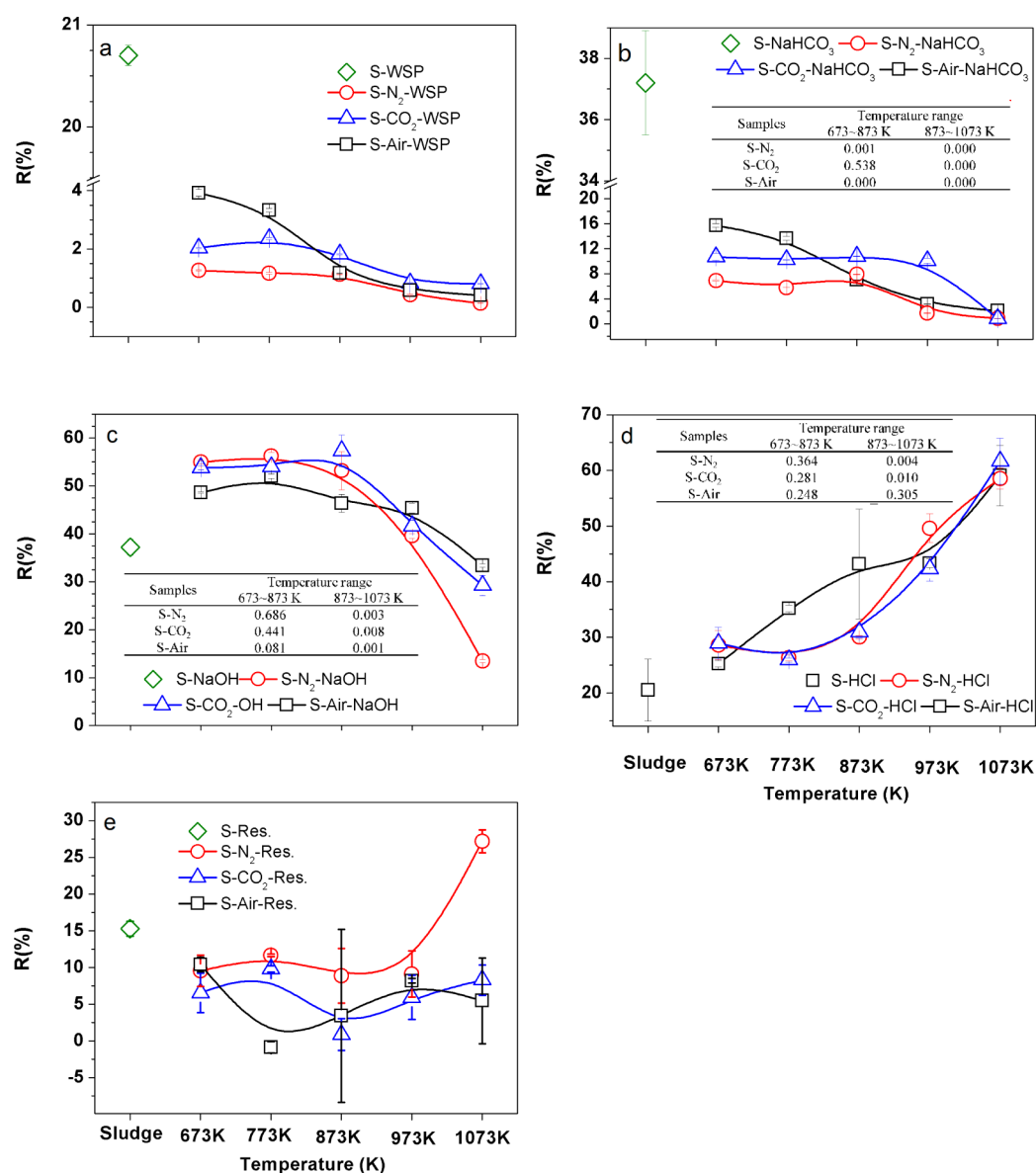


Figure 2. Change in the proportion of P in different pools with variable thermal treatment temperatures. (a) Change in WSP from SSC/A treated under differing atmospheric conditions (pyrolysis in N₂ and CO₂ and combustion). (b) Change in NaHCO₃-P from SSC/A treated under differing atmospheric conditions (pyrolysis in N₂ and CO₂ and combustion), (c) Change in NaOH-P at differing atmospheric conditions, (d) Change in HCl-P at differing atmospheric conditions, (e) Change in Res-P from SSC/A treated under differing atmospheric conditions (pyrolysis in N₂ and CO₂ and combustion). Error bars represent \pm SE ($n = 2$). The values presented in the tables of the three subfigures in b–d are the p values obtained from the ANOVA analysis conducted on the P proportion data (S-N₂, S-CO₂, and S-Air represent different atmospheric conditions during thermal treatment like N₂ and CO₂ and combustion).

investigated the release property of alkali and alkaline earth metals during the process of thermal treatment under variable atmospheric conditions (100% (v/v) N₂ and 1% (v/v) O₂ in N₂) and found that oxidizing atmosphere assists in the release of K and inhibits the release of Na, Ca, and Mg. In a similar work, Chen et al.¹⁸ studied the effect of varying atmospheric conditions (O₂, N₂, and CO₂) on the thermal treatment of Victorian brown coal and found that the S species in gaseous products were atmosphere dependent, while Pilon and co-workers⁴⁴ found that the volume/quantity of gaseous products (like CO, CO₂, and CH₄) vary considerably with different atmospheric conditions during pyrolysis (CO₂ and N₂).

The influence of temperature during the thermal treatment on the mineral structure of the samples was much more important than that of the atmospheric conditions. Although the XRD

curves of the samples treated at 673 K almost coincided with those treated at 873 K, several new peaks (marked by arrows in Figure 4b–d) appeared in the XRD curves produced from the samples treated at 1073 K. The new peaks presented in the samples belong to anorthite (Ca(Al₂Si₂O₈)) and the P-containing mineral stanfieldite (Ca₄(Mg,Fe)₅(PO₄)₆); the results are in agreement with some previous works.^{45,46} It is worth noting that the P, which is trapped in the lattice of the minerals, is more stable than that adsorbed on SSC/A. Those P-containing minerals are hard to use in a short term^{27,28} and thus hard to release. This may be the main reason for the stabilization of P into the pool_{HCl} at high temperatures (e.g., 1073 K). The XRD analysis indicated that except for the P-containing mineral stanfieldite, other compounds of ortho-P and pyro-P could not be detected, although these compounds made up a considerable

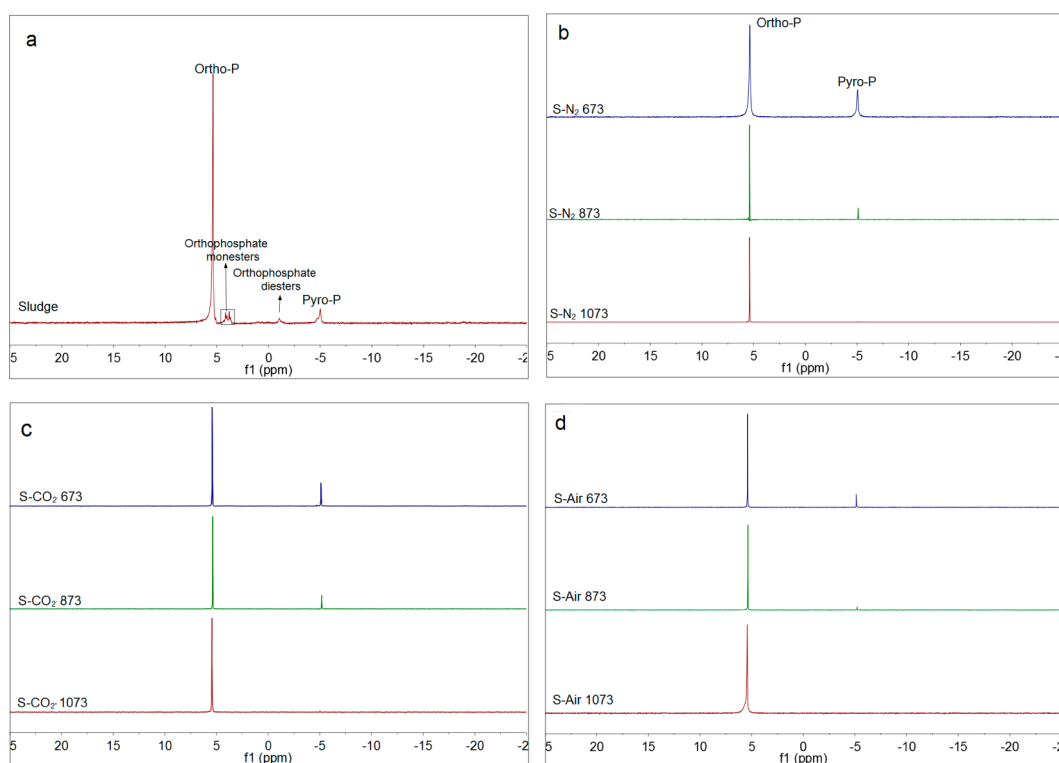


Figure 3. ^{31}P NMR spectra of (a) sewage sludge, (b) S- N_2 , (c) S- CO_2 , and (d) S-Air.

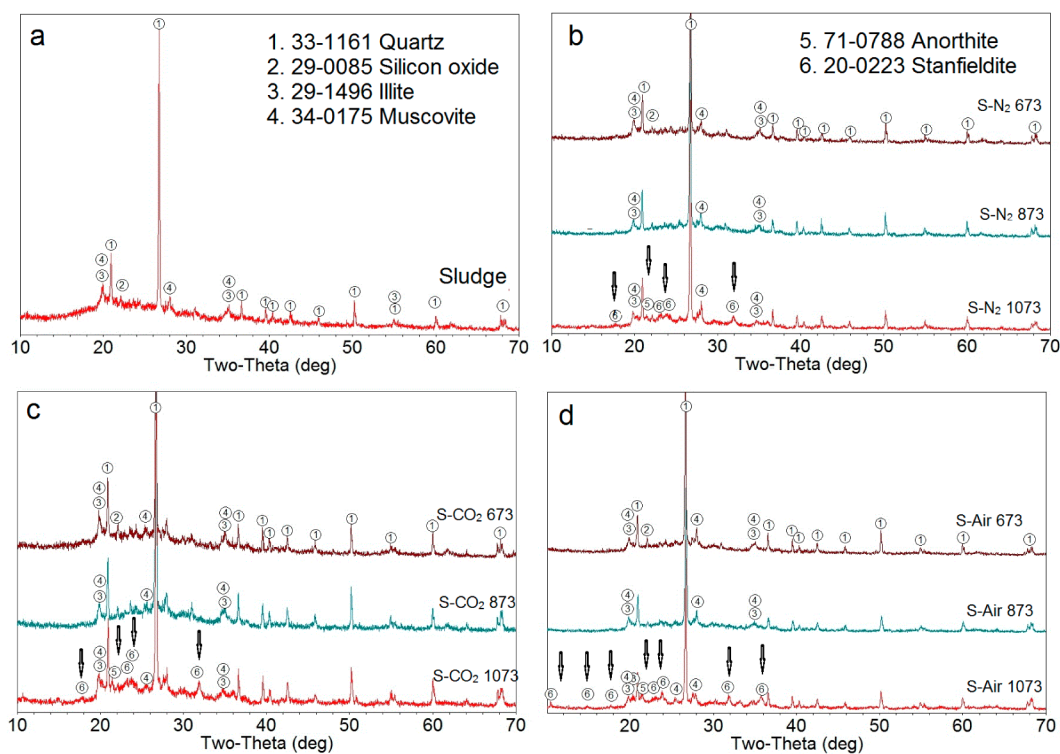


Figure 4. XRD curves of (a) sewage sludge, (b) S- N_2 , (c) S- CO_2 , and (d) S-Air.

portion of P in the total P of the samples, which may be due to the combinations between P and SSC/A in which P could be adsorbed on Al, Fe, or Ca, like in soil.^{12,16}

The inferences from the XRD curves of the samples are consistent with the results of the migration of P from $\text{pool}_{\text{NaOH}}$ to pool_{HCl} at the tested temperature ranges. Thus, samples treated

at low temperature (673–873 K) showed little difference in their XRD curves suggesting that the types of P compounds in the samples treated at low temperatures are similar thereby displaying comparable quantities of P in $\text{pool}_{\text{NaOH}}$ and pool_{HCl} in these samples. However, samples treated at high temperature (973–1073 K) produced/presented a new type of P-containing

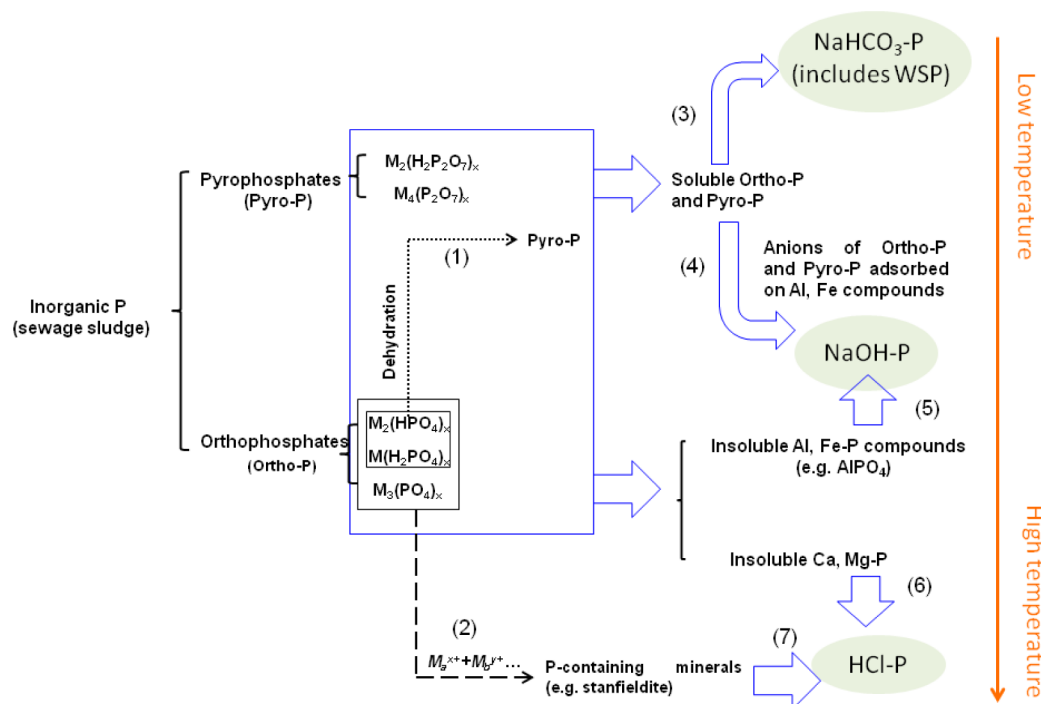


Figure 5. Pathway for the formation of different P species in SSA/C (dotted and dashed lines represent the pathways that may occur at low temperature and high temperature, respectively).

mineral, a considerable portion of which would be stabilized in the minerals, leading to a significant increase in the quantity of P in the $pool_{HCl}$ of these samples.

Formation Pathway of Different P Species. The migration patterns of sludge P during thermal treatment (migration from one P pool to other P pools) and its characterization from S-N₂, S-CO₂, and S-Air, a pathway for the formation of different P species in the SSA/C, was proposed. As the atmospheric conditions during thermal treatment had little effect on the formation of the P species, the formation pathways of the P species produced under different atmospheric conditions could be described using the same model (Figure 5).⁴⁷ However, the temperature of the thermal treatment is a crucial factor in influencing the formation of the P species making the P species produced at low temperatures (673–873 K) quite different from those produced at higher temperatures (973–1073 K); thus, there are some differences in the formation pathways of the P species produced at different temperature ranges, which are described by different lines.

The ³¹P NMR spectra indicated that the P in sewage sludge was composed of organic and inorganic P (including ortho-P and pyro-P). As the original organic P and pyro-P in the sludge only take up 10 and 0.8 wt % of the total P, respectively, the transformations of these P components may be ignored. Thus, we focused on the transformation of the ortho-P in the sludge, which takes up 75% of the total P. At low temperature, a considerable amount of pyrophosphates were produced. This is caused by the dehydration of $M_2(HPO_4)_x$ (or $M(H_2PO_4)_x$) in the sludge (path 1, dotted lines in Figure 5). However, at high temperature (973–1073 K), the formation of pyrophosphates was inhibited (Table S4 and Figure S2, Supporting Information). High temperature treatment of sludge may lead to the reaction between a large proportion of various phosphates with some metal ions ($M_a^{x+} + M_b^{y+} \dots$) in the sludge (path 2) that results in the formation of some P-containing minerals (like stanfieldite).

Some soluble ortho-P and pyro-P that are weakly associated with SSC/A can be easily released to the solution of NaHCO₃ and become NaHCO₃-P (path 3). The anions of ortho-P and pyro-P that are adsorbed by Al, Fe-compounds become NaOH-P (path 4). Some formed insoluble Al, Fe–P compounds that cannot be extracted by the solution of NaHCO₃ will dissolve in the solution of NaOH (path 5); this kind of P also belongs to NaOH-P. The more stable P species, such as insoluble Ca, Mg–P (and the P minerals formed at higher temperature (1073 K)) that can only be extracted by the solution of HCl become HCl-P (paths 6 and 7). With an increase of the temperature, formation of the P minerals (such as stanfieldite) occurred, which is accompanied by an increase in HCl-P.

As the composition of the sludge is complex, varied reactions may occur in the thermal treatment of the sludge, the details of which may be difficult to detect and describe. Moreover, the reasons for conversion of a large portion of P to minerals at higher temperatures rather than at lower temperatures are unclear. Further studies on the behavior of ashes of the sludge during the thermal treatment process are also required.

CONCLUSIONS

The form and stability of P in SSC/A is of vital importance to the application of SSC/A. Upon thermal treatment, irrespective of the atmospheric conditions, P in SSC/A gains more stability than P in sewage sludge. Temperature plays a decisive role in the characteristics of P in SSC/A. Thus, on treating the sewage sludge at a low temperature (673–873 K), a large portion of P is prone to migration to $pool_{NaOH}$, while a high temperature treatment (973–1073 K) would lead to the formation of P-containing minerals and be stabilized in $pool_{HCl}$.

■ ASSOCIATED CONTENT

Supporting Information

Tables S1–S8 and Figures S1 and S2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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