

## Article

# Effect of Magnesium Additives on Phosphorous Recovery during Sewage Sludge Combustion and Further Improvement of Bioavailable Phosphorous

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**Abstract:** Sewage sludge (SS), a solid waste taking up a large amount of public resources, contains abundant phosphorous and urgently needs appropriate recovery, but incineration, the existing popular SS treatment method, fails to reuse phosphorous as a feasible product due to the poor phosphorous bioavailability of SS ash. Based on the mono-combustion of SS, magnesian minerals comprising of magnesium oxide were doped with SS to carry out the behavior of magnesium in phosphorous capture and its sensitivity to subsequent thermochemical modification. Five percent MgO improved phosphorous capture, and its effectiveness was disturbed by sulfur at 900 °C. The more H<sub>2</sub>O that was pumped into the atmosphere, the more phosphorous was captured by 5% MgO. The capacity of MgO in phosphorous capture was inferior to that of CaO. The utilization efficiency of MgO for phosphorous capture was inferior to that of CaO. A total of 7.2% MgO succeeded in recovering 97.46% phosphorous with 5% H<sub>2</sub>O at 900 °C. A total of 15.06% hydromagnesite merely promoted 1.85% and 5.13% of the phosphorous relative enrichment factor (RE) in SS ashes without or with 5% H<sub>2</sub>O, respectively, whereas it recovered 90.21% phosphorous with 10% H<sub>2</sub>O, supposing a potentiality in phosphorous capture for the direct combustion of wet SS. However, having been improved by magnesium, the bioavailability of phosphorous in SS ash remained extremely limited. Thus, thermal modification by K<sub>2</sub>CO<sub>3</sub> was applied, where the limited bioavailability of phosphorous in the SS ashes was remarkably alleviated; although, SiO<sub>2</sub> and sulfate were the main disturbers and led to the production of K<sub>2</sub>MgSiO<sub>4</sub> and K<sub>2</sub>Mg<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. The effective constituents were KMgPO<sub>4</sub> and K<sub>3</sub>CaH(PO<sub>4</sub>)<sub>2</sub> in the final mixed fertilizer. The obtained mixed fertilizer might be suitable for application on acidic soils.

**Keywords:** phosphorous; sewage sludge; combustion; magnesium; drop tube furnace; bioavailability



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## 1. Introduction

Since the Chinese economic reform and opening, the growth of GDP has exceeded 10% for almost 30 years [1]. Driven by the dramatic economic development, dwellings and various infrastructures have been rapidly constructed, especially in cities and towns. Thus, Chinese urban population has reached up to  $8.48 \times 10^8$ , accounting for 60.60% of total population [1]. However, the centralization of the population has imposed a huge amount of pressure on municipal drainage treatment [2], and consequently plenty of waste water treatment plants have been set up to purify and reuse the municipal drainage [3]. In these plants, chemical measures were taken to precipitate nutrients in drainage, such as nitrogen and phosphorous, and the precipitation has resulted in  $\sim 3 \times 10^7$  tons of sewage

sludge (SS) in China to prevent natural water from eutrophication [4]. Moreover, the proportion of toxic compounds such as proteins, enzymes, and heavy metals can also not be underestimated [5,6]. Unfortunately, there remains ~50% SS landfilled with only basic mechanical treatment or even without any further treatments, leaving continuous and uncontrollable damage to environment [7,8].

Technologies for SS reduction and recovery are needed, and several approaches had been put forward and conducted such as pyrolysis, incineration, gasification, etc. [9,10] According to the statistics provided by EU, in Germany, all SS has avoided being landfilled, and SS incineration technology has been adopted to reduce the majority of SS through the establishment of coal-fired plants from 2005 [11], where organisms and pathogens in SS as well as the volume of SS were eliminated effectively [12]. Meanwhile, it has been important to clarify the behavior of phosphorous during SS incineration to protect the combustion facilities and the environment [13–15]. Otherwise, it would cut the life span of electricity generation plants, i.e., heat-exchanging tubes and the SCR DeNO<sub>x</sub> catalysts, due to the extreme corrosivity of hydrophosphate [13–15]. Both bench-test and full-scale tests on the phosphorous combustion were conducted, where gaseous phosphorous at 400 °C was detected and 25% of sub-micron particles were found to consist of phosphorous compounds, which threaten the availability of SCR catalysts [16]. All these cases inspired researchers' curiosity on phosphorous problems derived from SS during incineration [17–20]. Phosphorous accumulated in the ashes of SS during incineration as a function of the decrement of the SS volume [17]. The heat-labile phosphorous compounds including pyro- and ortho-phosphate were decomposed and subsequently heat-resistant Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> was synthesized in the combustion zone with the extreme high temperature [18,19]. The addition of CaO improved total phosphorous (TP) in SS ash through fixing phosphorous as calcic phosphate [20].

Although the content of phosphorous in SS was promoted by SS incineration, the utilization of it, whether agriculture or any other sections, is extremely regulated because of the limited bioavailable phosphorous driven by high temperature [21–23]. For instance, only 5% of German SS ash was transported into ploughs to enhance soil fertilities, while the other ash was consumed by mine landfilling, soil landfilling, and road construction [24]. The high-temperature circumstance decomposed bioavailable phosphorous such as dihydrophosphate and hydrophosphate, and discharged gaseous phosphorous that was transformed into insoluble orthophosphate in ashes following its reaction with calcium [25–27]. The process of losing bioavailability was aggravated with temperature increase. Thus, Steckenmesser [28] and Stemann [29] put forward a method called alkaline metal modification to make SS ashes worthy of composting. They mixed SS ash with alkaline metal including K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>, and calcinated the mixtures at 850 °C and 950 °C, increasing the proportion of bioavailable phosphorous in TP up to 90%.

Besides alkaline metal, magnesian phosphate contributed to the production of bioavailable phosphorous [30]. It was confirmed by both chemical and pot experiments that the bioavailability of Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> much excelled that of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and AlPO<sub>4</sub>, and the phosphorous bioavailability in SS ashes was enhanced by calcination with MgCl<sub>2</sub> or MgO above 800 °C [22,31]. Moreover, magnesium phosphate has been found to be an important and effective phosphorous fertilizer, i.e., struvite [32–34]. Therefore, adding magnesium seemed to be a feasible approach to recover phosphorous as bioavailable phosphorous during the SS incineration. Then, modification by K<sub>2</sub>CO<sub>3</sub> calcination could be applied to produce a mixed fertilizer known as a mixed fertilizer containing calcium magnesium, phosphorous, and potassium [28,29]. However, the behavior of phosphorous in the case of magnesium during SS incineration has not been clarified, phosphorous bioavailability after K<sub>2</sub>CO<sub>3</sub> calcination and the sensitivity of magnesium to K<sub>2</sub>CO<sub>3</sub> modification all remained unclear. In this study, the incineration of SS doped with magnesium was conducted in a drop tube furnace (DTF) for the investigation of phosphorous migration and the phosphorous bioavailability in SS ashes, and the collected SS ash was selected and treated by K<sub>2</sub>CO<sub>3</sub> thermochemical modification to produce the mixed fertilizer.

## 2. Materials and Methods

### 2.1. Material

SS used in this study was dewatered SS coke from a wastewater treatment plant located in Jinan, China. SS coke was cracked easily and exposed to the sunlight for about 2 days until its moisture content was decreased down to ~40 to 50%, labelled with sun-dried SS. An 80 °C air oven was employed to further remove inner moisture in sun-dried SS, which was then grinded into 45–105 µm. Air-dried SS was obtained after 2 h drying process at 105 °C. The components of SS were displayed in Tables 1 and 2 including proximate, ultimate, and ash analyses. The phosphorous content was determined by spectrophotometer following acidic digestion. X-ray diffraction (XRD) was employed for the detection of samples' crystalline structure.

**Table 1.** Proximate and ultimate analysis of sewage sludge (mass%).

Sample	Proximate Analysis				Ultimate Analysis					Phosphorous
	M	V	A	FC	C	H	O *	N	S	
SS	3.97	37.50	55.18	3.35	17.78	1.91	17.58	2.05	1.53	3.01

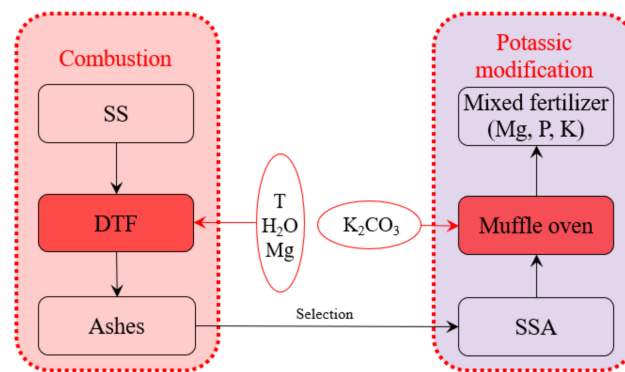
\* By difference.

**Table 2.** Ash composition of sewage sludge (mass%).

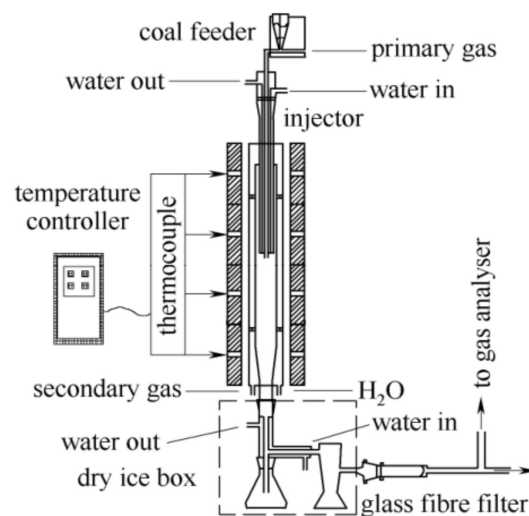
Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Others
SS	43.95	17.98	12.48	12.09	6.16	2.65	1.54	2.42	0.73

### 2.2. Combustion Experiments

As demonstrated in the left of Figure 1, combustion was at first used for accumulation of phosphorous in SS. A bench-scale DTF was established for the combustion experiments, of which a schematic graph is displayed in Figure 2 [35,36]. The temperatures of reaction zone in DTF were 800 °C, 900 °C, and 1000 °C and controlled by four thermocouples. The combustion atmosphere in reactor was 79% N<sub>2</sub> and 21% O<sub>2</sub> mixed in advance. The total volume flow of air was 10 L/min including 1 L/min primary gas and 9 L/min secondary gas. Primary gas went through feeder and carried ~3 g/min samples, while secondary gas was preheated in the annulus of the reaction tube and met with primary gas from the injector. According to the size of tube and the volume flow of gas, the nominal gas residence time in isothermal zone of reaction tube was calculated to be 4 s without considering reaction expansion. A steam generator was used to generate 5% and 10% volume fractions of water to simulate the combustion of wet SS. Deionized water was pumped into the annulus of the reaction tube and vaporized as secondary gas was preheated. The volume contents of moisture in reaction gas were 5% and 10%. All magnesian additives was also ground into 45–105 µm and mechanically mixed with SS evenly. First, 5% MgO was doped to confirm the optimum condition for phosphorous capture, and simultaneously, SS doped with 6.86% CaO was conducted as a control group. The proportion of CaO was determined in terms of the molar ratio of alkaline earth metal to phosphorous. The mass addition of MgO was gradually increased to 6%, 7.2%, and 10%. Furthermore, 15.06% hydromagnesite, 4MgCO<sub>3</sub>·Mg(OH)<sub>2</sub>·5H<sub>2</sub>O, was doped into SS prior to the combustion with and without moisture at 900 °C.



**Figure 1.** A method for thermal recovery of phosphorous in SS as fertilizer (DTF—drop tube furnace; SSA—SS ash with higher phosphorous recovery; P—phosphorous; K—potassium).



**Figure 2.** Schematic drawing of dope tube furnace.

Here, 800–1000 °C was investigated and the lower combustion temperatures were not investigated, as it was difficult to operate low-temperature combustion in reality. Sewage sludge combustion was usually coupled with electricity generation, and electricity generation plants had to meet the relevant regulations about pollutants. Low temperature usually caused the incomplete combustion and emitted more pollutants. For example, low-temperature combustion produced more PCDD/Fs, especially low-chlorinated PCDFs. It was reported that 250–650 °C was the optimum temperature for the precursor synthesis of PCDD/Fs [37]. There would be higher concentration of PCDD/Fs in flue gas of sewage sludge combustion. So, the current industrial production tried to avoid the circumstance that the combustion temperature was below 800 °C, unless pollutants such as PCDD/Fs could be controlled at a low cost. In terms of magnesium-based additives, chlorides were avoided considering the possible problems of corrosion brought about by chlorine in reality; although, chlorides exhibit advantages in removing several typical heavy metals [30].

To compare data intuitively, the relative enrichment factor (*RE*) of phosphorous [35,36] was defined as

$$RE = \frac{C_{ash}}{C_{ss}} \times \frac{Y_{ash}}{100} \times 100\% \quad (1)$$

where  $C_{ash}$  and  $C_{ss}$  referred to the concentrations of total phosphorous in ash/char sample and the SS, respectively. The symbol,  $Y_{ash}$  denotes the ash yield based on the mass of SS into the furnace.

### 2.3. Determination of Total Phosphorous and Bioavailable Phosphorous

Total phosphorous contents in SS and ashes were determined by photometric method, according to GB/T 223.59-2008 issued by standardization administration of the P.R.C. [38]. Neutral ammonia citrate (NAC) solution was prepared following EN 15957-2011 published by Association Francaise de Normalization (FR-AFNOR) to extract bioavailable phosphorous from solid samples [39]. Then, 1 L NAC solution containing 185 g citric acid was neutralized by ammonium hydroxide solution until pH = 7 at 20 °C. Samples were cracked and sieved in a 160 µm mesh. A 3 g sample was transferred into a flask and mixed with 100 mL NAC solution. The mixture was stirred for 1 h in a 65 °C water-bath kettle. Extracted bioavailable phosphorous in supernatant was also determined by the photometric method.

Analogously, the relative enrichment of bioavailable phosphorous extracted by NAC solution ( $P_{nac}$ ) of phosphorous was defined by Equation (2).

$$P_{nac} = \frac{P_{ash,nac}}{P_{ss}} \times \frac{Y_{ash}}{100} \times 100\% \quad (2)$$

where  $P_{ash,nac}$  referred to the concentrations of total phosphorous in supernatant derived from the NAC extraction of SS ash, and  $P_{ss}$  referred to the concentrations of total phosphorous in raw SS.

### 2.4. Thermochemical Modification by $K_2CO_3$

Thermochemical modification by  $K_2CO_3$  was the second step in phosphorous recovery following combustion, which corresponded with the right part of Figure 1. The ash of SS collected from the combustion with 7.2% MgO and 5% moisture at 900 °C was selected as the crude material based on the higher RE of phosphorous, labelled as SSA, for further thermochemical modification by  $K_2CO_3$ . Before calcination, 10–40%  $K_2CO_3$  were doped into SSA and stirred mechanically for 30 min, and subsequently these mixtures were calcinated with air for 1 h at 950 °C.  $P_{nac}$  in modified SSA was extracted by NAC solution and examined by spectrophotometer. Moreover, an ammonia citrate solution with a pH of 5 was also prepared to extract phosphorous in modified ash, where the same extraction procedure of NAC extraction was repeated.

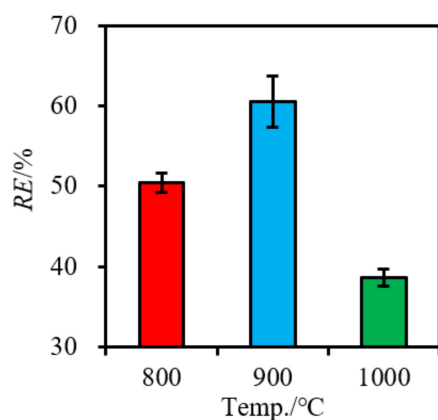
Furthermore, it should be emphasized why  $K_2CO_3$  rather than  $Na_2CO_3$  was selected. Here, if the potassium-based additive was replaced by sodium-based additive, there would be a high content of sodium in the final product, fertilizer. Unfortunately, sodium is not involved in the three main elements (N, P, K) for plant growth. It would hardly be possible for agriculture or the environment to remove the huge amount of sodium. If used, as a result, sodium would damage the value of soil for agriculture and bring various problems, i.e., soil salinization, based on the study of sodium damaging soil conducted by Balks [40]. Therefore, potassium rather than sodium was selected as the modifier, when the initial plan was made.

## 3. Results and Discussions

### 3.1. Phosphorous Migration during Mono-Combustion of SS

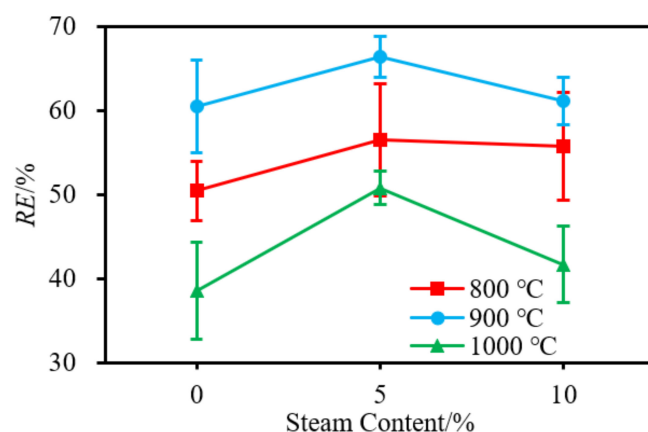
The phosphorous migration during the mono-combustion of SS at 800–1000 °C was firstly carried out as depicted in Figure 3. The results showed that more phosphorous was fixed in the ash of SS with temperature increasing from 800 °C to 900 °C. It was accounted for by the faster decomposition of  $CaCO_3$  and the velocity of the calcium capturing phosphorous, which were stimulated by higher temperature. Afterwards, a dramatic drop of 21.88% was created by increasing temperature from 900 °C to 1000 °C. According to Table 2, the molar ratio of calcium plus magnesium to phosphorous was roughly calculated to be 1.04, far below the 1.5 of tricalcium phosphate, which was recognized as one of the most stable compounds under extreme-high temperature. Thus, the instability of non-apatite phosphate such as  $AlPO_4$  emitted more phosphorous, and the relatively deficient calcium failed to fix the phosphorous derived from the decomposition of non-apatite

phosphate again, which corresponds with many other studies about phosphorous in SS incineration [17–20].



**Figure 3.** Phosphorous fixed in the ash of SS during combustion at 800–1000 °C.

The RE of phosphorous in the ash of SS during combustion with 0–10% moisture was displayed in Figure 4. More phosphorous was fixed in the ash of SS with moisture at 900 °C and all the RE of phosphorous in the ash of SS were promoted by 5% or 10% moisture. It had been verified that moisture accelerated the decomposition of calcite, which facilitated to more efficient phosphorous capture by calcite [41]. On the other hand, due to the inherent hygroscopicity of  $P_4O_{10}$ , a  $P_4O_{10}$  molecule derived from solid matrix absorbed  $H_2O$  to form three hydrophosphate molecules, strengthening its diffusion ability and consequently improved phosphorous capture [42]. Whereas, adding  $H_2O$  to 10% hindered phosphorous capture. The hydrogenation of  $H_2O$  increased the molar ratio of calcium to phosphorous of resultants from 1.5 to 1.67 by changing tricalcium phosphate into hydroxyapatite, and therefore decreased the utilization efficiency of calcium on phosphorous capture.



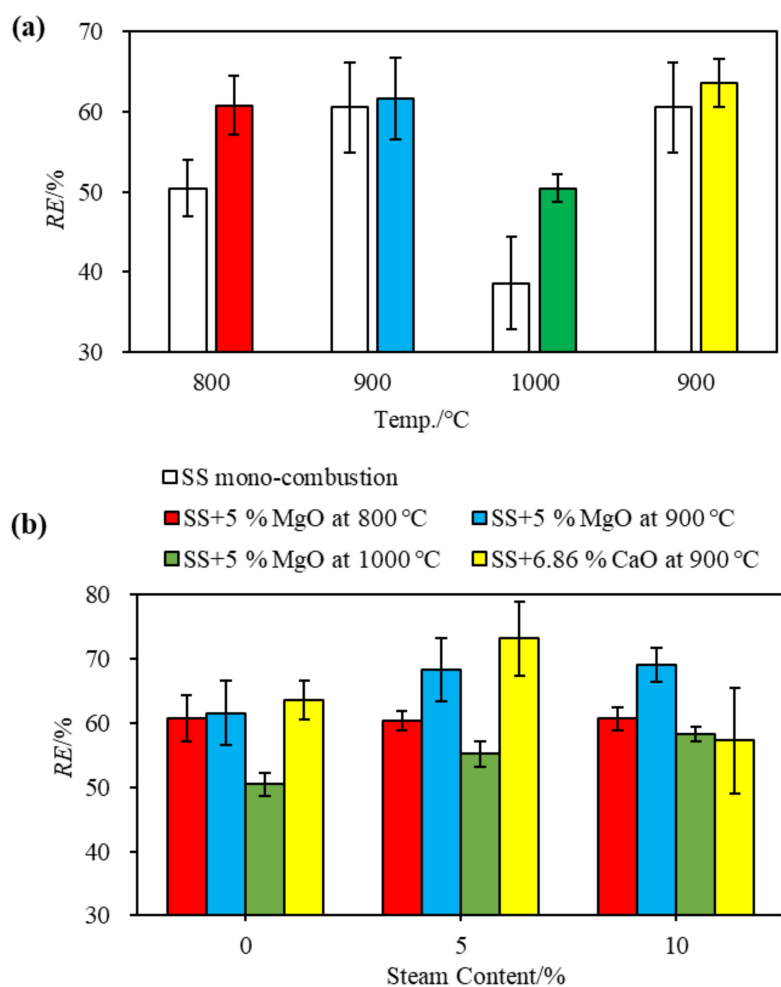
**Figure 4.** Fixation of phosphorous in the ash of SS during combustion with extra 5–10% steam.

Furthermore, for the mono-combustion of SS, only 66.35% RE of phosphorous in ash of SS was achieved with 5% moisture at 900 °C. Thus, it was necessary to take some necessary measures to promote phosphorous recovery and weaken avoidable damage caused by emitted phosphorous.

### 3.2. Phosphorous Capture Improved by MgO during Combustion with Various Moisture Content at 800–1000 °C

SS doped with 5% MgO was combusted by DTF and the REs of phosphorous in ash are summarized in Figure 5. Various increments of phosphorous fixed in the ashes of SS were created by MgO at 800–1000 °C. In Figure 5a, 10.33% and 11.83% phosphorous are further adsorbed by 5% MgO at 800 °C and 1000 °C, respectively. Whereas at 900 °C only

1.11% RE of phosphorous was increased, which was less than the 3.08% promoted by the identity molar CaO. Adsorbing phosphorous was more inefficient for MgO than that for CaO at 900 °C. It resulted from the difference in the density between magnesian and calcic crystals. For magnesium, the density of  $\text{Mg}_3(\text{PO}_4)_2$  was 2.2 g/cm<sup>3</sup>, smaller than 2.66 g/cm<sup>3</sup> of  $\text{MgSO}_4$  and 3.58 g/cm<sup>3</sup> of MgO. For calcium, the density of  $\text{CaSO}_4$  was 2.32 g/cm<sup>3</sup>, smaller than 3.14 g/cm<sup>3</sup> of  $\text{Ca}_3(\text{PO}_4)_2$  and 3.35 g/cm<sup>3</sup> of CaO. The phosphorylation of MgO was bound to be accompanied by a blocking problem similar to the case of calcic desulfurization and consequently inhibited itself.

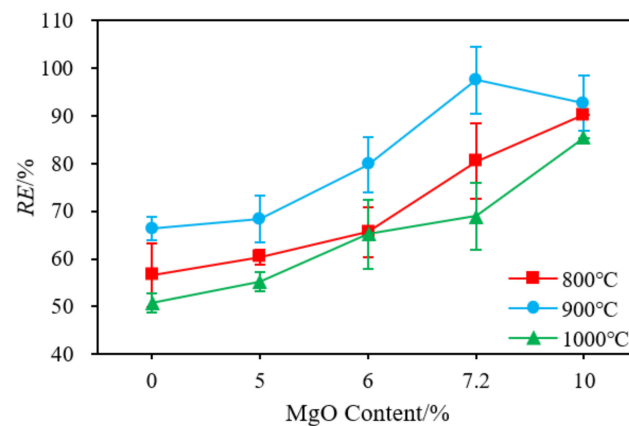


**Figure 5.** The RE of phosphorous in SS ash achieved by magnesian or calcic additive during SS combustion at 800–1000 °C: (a) without extra steam; (b) with extra 5% or 10% steam.

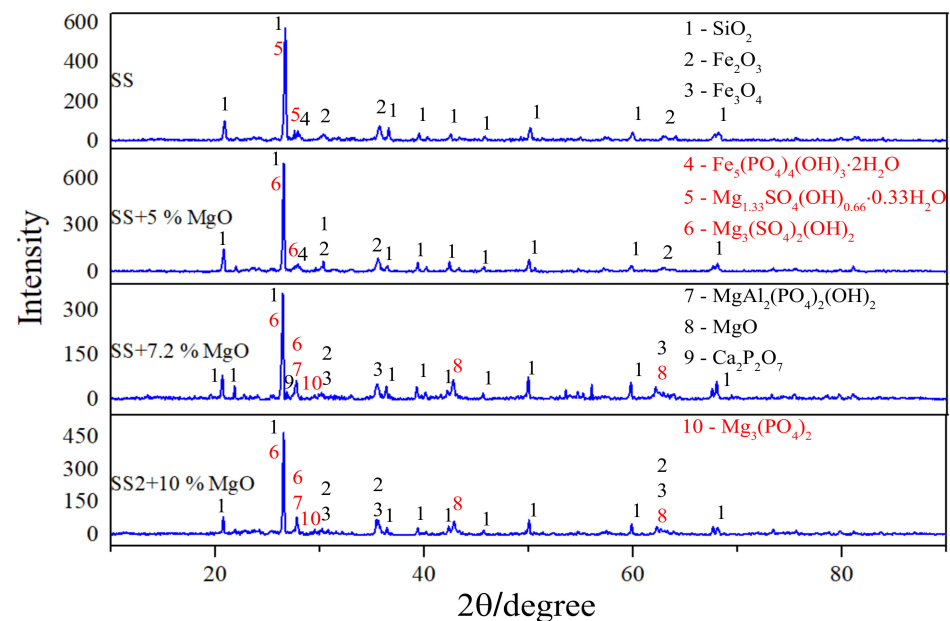
When the dry air in the reaction tube was transformed into humid air, the capacity of MgO for phosphorous capture was greatly stimulated at 900 °C and 1000 °C, as illustrated in Figure 5b. However, no significant increments were detected at 800 °C after H<sub>2</sub>O addition. The existence of competition between sulfur and phosphorous has been verified by previous researches [43,44]. Besides faster adsorption of phosphorous brought by H<sub>2</sub>O, the reaction between MgO or CaO and SO<sub>2</sub> was simultaneously facilitated [45]. The competition of SO<sub>2</sub> on both MgO and CaO generally led to the stable REs of phosphorous, which stayed ~60% in ashes of SS at 800 °C with 5–10% moisture content. Moreover, different from the variation in the RE in cases of raw SS or with CaO in Figure 4, the more H<sub>2</sub>O that was pumped, the more phosphorous was captured with MgO above 900 °C. The positive effect of H<sub>2</sub>O on phosphorous capture overwhelmed the negative impact brought by the production of magnesian phosphate with hydroxyl, due to the weaker inherent capacity of MgO in capturing phosphorous than CaO.

### 3.3. Further Phosphorous Capture by Adding More MgO or Other Magnesian Minerals at 900 °C

Since the highest RE of phosphorous was achieved by 5% MgO with an extra 5% steam, 6–10% MgO was utilized at the same atmosphere and the results are shown in Figure 6. In general, REs of phosphorous in ash gradually increased as a function of the content of MgO, and 97.46% phosphorous was recovered with 7.2% MgO at 900 °C. It seemed to be adequate for the subsequent investigation of phosphorous recovery. Nevertheless, there was inconspicuous influence on RE of phosphorous in ashes when the content of MgO was less than 5%. XRD was employed to distinguish the crystalline compounds in ashes and the XRD curves are collected in Figure 7. Magnesium sulfate involving  $\text{Mg}_{1.33}\text{SO}_4(\text{OH})_{0.66}\cdot 0.33\text{H}_2\text{O}$  and  $\text{Mg}_3(\text{SO}_4)_2(\text{OH})_2$  peaked in all the four curves, while magnesian phosphate was only found in the conditions with 7.2% and 10% MgO. The XRD suggested that the majority of the initial 5% MgO was taken up by  $\text{SO}_2$  and exhibited an unobvious ability of phosphorous capture. Furthermore, MgO peaked when the addition of MgO achieved 7.2%, and thus the optimum content of MgO for phosphorous capture might be a bit lower than 7.2%.

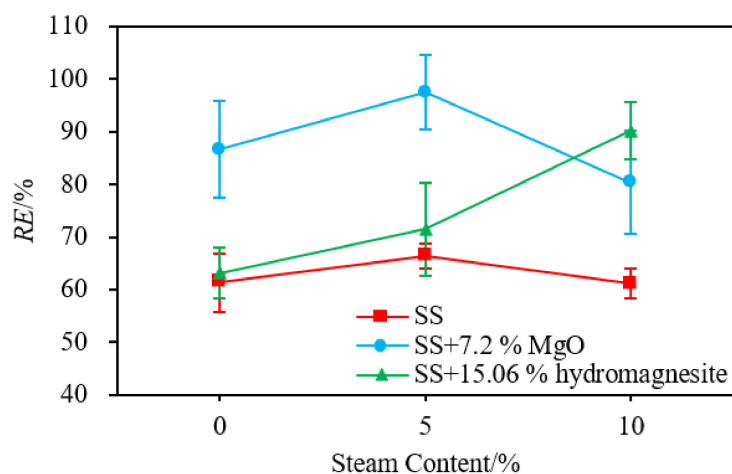
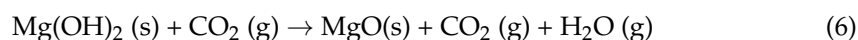
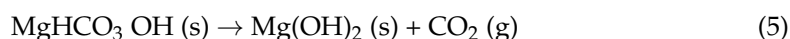
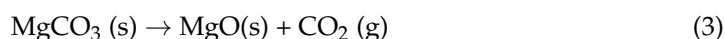


**Figure 6.** Improvement of MgO on phosphorous RE in ash of SS during SS combustion with 5% extra  $\text{H}_2\text{O}$ .



**Figure 7.** XRD curves of ashes collected from the combustion of SS and 0–10% MgO with 5% extra  $\text{H}_2\text{O}$  at 900 °C.

In terms of the 7.2% content of MgO, alternative magnesium additives were selected to search for a better method for phosphorous capture. Considering the blocking problem of  $Mg_3(PO_4)_3$ , MgO was replaced by hydromagnesite, and the content was calculated to be 15.06% to ensure the same molar ratio of magnesium to phosphorous, as demonstrated in Figure 8. Phosphorous capture was not greatly promoted by hydromagnesite, and the REs of phosphorous in ashes were elevated only by 1.85% and 5.13% with 0% or 5%  $H_2O$ , respectively. The relatively slow decomposition of hydromagnesite played an important role. During the decomposition,  $CO_2$  was released and adsorption sites in sorbent particles with stronger reaction activity were able to be exposed. Therefore, the slow decomposition of hydromagnesite delayed phosphorous capture. When 10%  $H_2O$  was fed into the DTF, the RE of phosphorous soared up to 90.21% with the addition of hydromagnesite. Based on the influence of  $H_2O$  on  $CaCO_3$  decomposition [41], it was supposed that  $H_2O$  reduced the activity energy of hydromagnesite decomposition by transforming the reaction from Equation (3) to Equations (4)–(6). Moreover, during the formation of the  $Mg_3(PO_4)_2$  shell with high specific volume, the decomposition process continuously discharged  $CO_2$  from the interior of additive particles and subsequently broke the shell, which created a porous morphology for additive particles to effectively capture phosphorous. Considering the excellent effect of hydromagnesite on phosphorous capture with high  $H_2O$  atmosphere, porous magnesium adsorbents seemed to have more potential in terms of phosphorous purification.



**Figure 8.** Further improvement of phosphorous RE by hydromagnesite in SS ash during combustion with moisture at 900 °C.

### 3.4. Evaluation and Improvement of Bioavailable Phosphorous in Ashes of SS

Having recovered 97.46% phosphorous by 7.2% MgO during SS combustion with 5% moisture at 900 °C, the contents of bioavailable phosphorous in raw SS and its various ashes were extracted by NAC and determined, as listed in Table 3. Combustion deteriorated the bioavailability of phosphorous in SS, and the  $P_{nac}$  in almost all ashes were declined down to below 20%, which was consistent with other previous studies [25–27]. It was caused by the effect of the high temperature on the phosphorous-bearing compounds. Elevated temperature typically led to a more severe fall of  $P_{nac}$ , as bioavailable phosphorous such as  $CaHPO_4$  was quickly decomposed into emitted gaseous phosphorous or transformed into

phosphate with poor bioavailability, i.e.,  $\text{Ca}_3(\text{PO}_4)_2$  [19]. Moreover, the effect of moisture on phosphorous bioavailability was consistent with the variation in TP in ashes during the sole combustion of SS or with magnesium. However, unmatched increments of  $RE$  and  $P_{nac}$  in ashes brought by magnesian additives suggested that the main products of magnesium and phosphorous exhibited unattractive bioavailability, particularly those most thermostable compounds, i.e.,  $\text{Mg}_3(\text{PO}_4)_2$ . As a result, although hydromagnesite seemed to be a potential sorbent for both phosphorous recovery and bioavailability, the value of these ashes as phosphorous fertilizers remained limited.

**Table 3.** Determination of bioavailable phosphorous content in SS and its ashes during combustion.

Additives	Combustion Temp./°C	Content of $\text{H}_2\text{O}/\%$	$P_{nac}/\%$
/	/	/	39.23 *
None	800	0	$13.39 \pm 0.82$
		5	$15.64 \pm 1.85$
		10	$15.37 \pm 1.77$
None	900	0	$13.30 \pm 1.20$
		5	$14.37 \pm 0.52$
		10	$13.26 \pm 0.61$
None	1000	0	$9.99 \pm 1.32$
		5	$13.06 \pm 0.51$
		10	$11.90 \pm 1.30$
5% MgO	800	0	$20.06 \pm 1.20$
		5	$19.44 \pm 0.49$
		10	$9.67 \pm 0.29$
5% MgO	900	0	$15.94 \pm 1.90$
		5	$16.16 \pm 2.20$
		10	$17.33 \pm 2.00$
5% MgO	1000	0	$11.82 \pm 0.41$
		5	$13.69 \pm 0.50$
		10	$13.64 \pm 0.27$
6% MgO	800		$18.98 \pm 1.54$
	900	5	$15.67 \pm 1.13$
	1000		$13.93 \pm 1.55$
7.2% MgO	800		$12.24 \pm 1.22$
	900	5	$11.78 \pm 0.85$
	1000		$7.04 \pm 0.72$
15.06% hydromagnesite	900	0	$14.66 \pm 1.14$
		5	$19.99 \pm 3.75$
		10	$20.78 \pm 1.25$

\* Ratio of phosphorous solubilized by NAC to total phosphorous in raw SS.

$\text{K}_2\text{CO}_3$  modification at 950 °C was applied on SS ash with higher phosphorous recovery (SSA) to produce a mixed fertilizer containing phosphorous, magnesium, and potassium. Data concerning  $P_{nac}$  of modified SSA are illustrated in Figure 9.  $\text{K}_2\text{CO}_3$  modification was proven to make a difference to the bioavailability of phosphorous in ash.  $P_{nac}$  in NAC solution was gradually increased as a function of the  $\text{K}_2\text{CO}_3$  content and 52.35%  $P_{nac}$  was obtained with 35%  $\text{K}_2\text{CO}_3$ .  $P_{nac}$  in ammonia citrate solution with a pH of 5 reached up to 74.72% following a calcination with 40%  $\text{K}_2\text{CO}_3$ . After the 40%  $\text{K}_2\text{CO}_3$  modification, the modified ash was scanned by XRD, as depicted in Figure 10. Compared with the XRD results in Figure 7, it was concluded that during the calcination process,  $\text{K}_2\text{CO}_3$  preferentially combined with MgO and  $\text{SiO}_2$  to form  $\text{K}_2\text{MgSiO}_4$ , which was the major compound in the final product. Furthermore, the peak representing  $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$  was also recognized. The peaks of  $\text{K}_2\text{MgSiO}_4$  and  $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$  accounted for the unattractive improvement of  $\text{K}_2\text{CO}_3$ . Except for silicon and sulfur, phosphorous was transformed

into bioavailable  $\text{KMgPO}_4$  and  $\text{K}_3\text{CaH}(\text{PO}_4)_2$  by  $\text{K}_2\text{CO}_3$ .  $\text{KMgPO}_4$  and  $\text{K}_3\text{CaH}(\text{PO}_4)_2$  are valuable constituents for agriculture and they are usually the effective compounds in a kind of mixed fertilizer called calcium magnesium potassium phosphate [33]. Moreover, the  $P_{nac}$  in ammonia citrate solution with  $\text{pH} = 5$  suggested an approach to apply the modified ash in some acidic soils such as those red soils in the Chinese southeast hilly region. Moreover, what should be mentioned is that the results of the NAC method could only qualitatively reflect the improvement of phosphorous bioavailability, and that a more precise evaluation should be further practiced, i.e., a pot experiment.

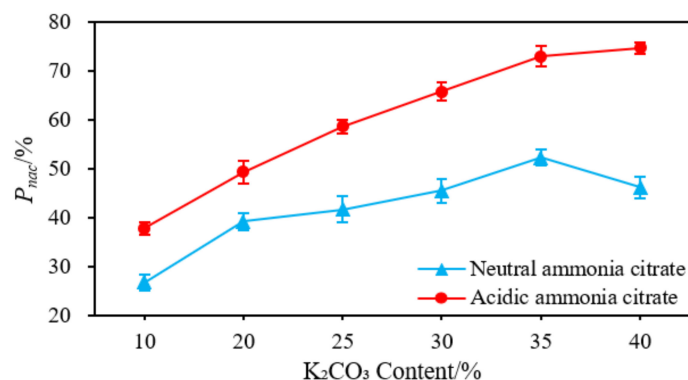


Figure 9. Bioavailable phosphorous in SSA improved by  $\text{K}_2\text{CO}_3$  calcination in air at  $950\text{ }^\circ\text{C}$ .

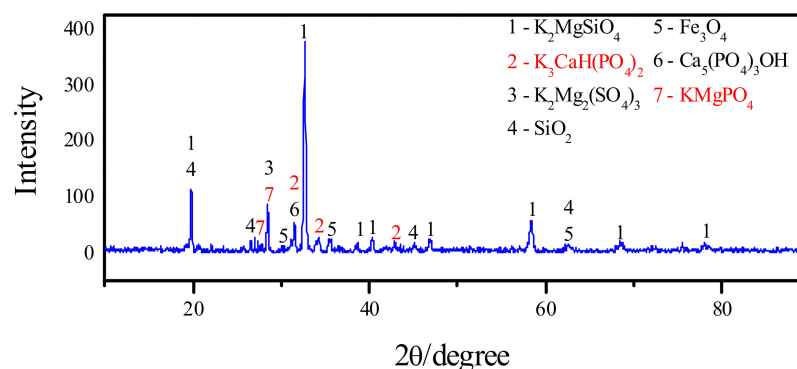


Figure 10. The XRD curve of SSA modified by 40%  $\text{K}_2\text{CO}_3$  calcination in air at  $950\text{ }^\circ\text{C}$ .

#### 4. Conclusions

The existing popular SS incineration technology failed to recover SS as feasible product, as its high temperature broke the phosphorous bioavailability of SS. Thermochemical modification by alkaline carbonate has attracted great attention as it has provided an alternative and valuable method to fix and recover phosphorous in SS ash. Magnesian minerals were doped with SS to carry out the behavior of magnesium in phosphorous capture. During air-dried SS incineration, more phosphorous was fixed in ash of SS at  $900\text{ }^\circ\text{C}$ . It was elucidated that 5% moisture facilitated phosphorous capture, whereas 10% moisture hindered the process. Five percent  $\text{MgO}$  improved phosphorous capture, but it did not work as well at  $900\text{ }^\circ\text{C}$  due to the disturbance of sulfur. Adding moisture from 0 to 10% gradually increased the  $RE$  of phosphorous in ashes of SS doped with  $\text{MgO}$ . The promotion of phosphorous capture with  $\text{MgO}$  was inferior to that with  $\text{CaO}$  at  $900\text{ }^\circ\text{C}$ . There was a considerable blocking problem on the surface of  $\text{MgO}$  caused by  $\text{Mg}_3(\text{PO}_4)_2$ , which was not the principal problem in case where the additive was switched into  $\text{CaO}$ . A total of 7.2%  $\text{MgO}$  succeeded in recovering 97.46% phosphorous with 5%  $\text{H}_2\text{O}$  at  $900\text{ }^\circ\text{C}$ . A total of 15.06% hydromagnesite promoted 1.85% and 5.13% of  $RE$  in SS ashes without or with 5%  $\text{H}_2\text{O}$ , respectively. However, when 10%  $\text{H}_2\text{O}$  was fed into DTF, hydromagnesite made a real difference on phosphorous recovery and 90.21% phosphorous was recovered in this condition. Although magnesium improved bioavailability of phosphorous,  $P_{nac}$  of

SS ashes in NAC solution remained limited. The  $K_2CO_3$  thermochemical modification and the sensitivity of magnesium to  $K_2CO_3$  calcination were conducted. During  $K_2CO_3$  calcination,  $SiO_2$  and sulfate were the main disturbers that were not conducive to phosphorous bioavailability, and this led to the production of  $K_2MgSiO_4$  and  $K_2Mg_2(SO_4)_3$ . However, the limited bioavailability of phosphorous in SS ashes was remarkably alleviated. The effective constituents involving  $KMgPO_4$  and  $K_3CaH(PO_4)_2$  were detected in the final products. Furthermore, the results of acidic ammonia citrate seemed to provide the possibility that the obtained mixed fertilizer might be suitable for application on acidic soils.

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