Phosphorous Transformation during Coal and Sewage Sludge Co-Combustion

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Abstract. Sewage sludge (SS) contained considerable phosphorous resource and SS incineration technology had become an important method to reuse SS. To alleviate the difficulty of SS mono-combustion caused by its low heating value, high-rank fuels should be introduced. Effects of SS and coal co-combustion on phosphorus fixation rate in ash were studied through drop tube furnace. It was concluded that rising temperature increased the fixation rate of phosphorus in SS ash. Due to the obvious high calcium content in Xiaolongtan coal (XLT), the co-combustion of SS and XLT effectively increased the fixation rate of phosphorus in ash and phosphorous capture by solid minerals was improved by temperature increase. In the meanwhile, more XLT introduced more calcium into the combustion system, which captured more phosphorous in ash. Whereas, there were just a small quantity of calcic and magnesian minerals in Xiheishan coal (XHS) and as a result, higher temperature accelerated phosphorous emission. The fixation rate of phosphorus during co-combustion of SS and XHS was not significantly affected by the different proportions of XHS. Finally, the co-combustion of 70% XLT and 30% SS effectively fixed phosphorus at 1000 ℃, where the fixation rate in ash was risen dramatically to as high as 93.29 %.

1 Introduction

Sewage sludge (SS) produced by the disposal of waste water in cities contained 5 % P₂O₅ averagely and in some SS the P₂O₅ content reached up to about 8.5 % [1]. Phosphorous, one of the three fundamental elements (nitrogen, phosphorous and potassium), served as an essential element in ADP and ATP, which participated in most organisms’ energy transformation processes around the world [2]. Adequate phosphorous fertilizer was necessary and desired by agricultural development for nutrient supplement to meet the demand of crops, vegetables and etc., i.e., up to 2.6×10⁸ tons phosphorous ores were mined all over the world in 2017 [3]. But SS utilization on agriculture was strictly limited by various regulations due to the high content pathogens and heavy metals [4]. So, only 48 % SS was used for agriculture and landscaping in China [5]. Necessary procedures needed to be operated on SS for recovering phosphorous effectively.

SS incineration was one of the effective SS processing technologies. After SS incineration, organisms and pathogens were decomposed efficiently. Some heavy metals were released from SS and then was collected in bag filters. In this way, the volume and toxicity of SS was reduced a lot and
phosphorous was recovered and the chemical energy in SS was reused for generating electricity as more as possible [6-7]. As a result, worldwide scholars were gradually involved in studies of SS incineration. Considerable phosphorous fixation rate was obtained by pyrolysis compared with combustion and gasification [8]. It was elucidated that rising temperature contributed to the transformation of AlPO₄ into Ca₃(PO₄)₂ and adding CaO improved total phosphorous (TP) in SS ash [9].

Although incineration had remarkable benefits for SS disposal, the feasibility of SS incineration was limited by 80 % moisture in mechanical dewatered SS [10]. It’s better to be burnt with coal to reduce the difficulty of combustion. The added complex mineral components in coal could also affect phosphorous. It was concluded that there might be an about 20 % CaO difference in various coals, which could affect phosphorous capture [11].

Above all, when improving combustion characteristic by adding coals into SS there were little reports about the effect of coal on phosphorous during combustion. Thus, this paper began with sole SS combustion and subsequently focused on phosphorous transformation and migration regulation during its co-combustion with coal.

2 Experimental materials and methods

SS used in the experiment was collected form a waste water treatment plant in Chinese Jinan, while Xiheishan coal (XHS) and Xiaolongtan coal (XLT) were selected as the high-rank fuels. The samples were grinded to 45-105 μm. The sample properties and ash compositions were listed in table 1 and table 2 respectively.

**Table 1.** Proximate and ultimate analysis of samples

| Sample | Proximate analysis/% (mass, ad) | Ultimate analysis/% (mass, ad) | P/% (mass, ad) |
|--------|---------------------------------|-------------------------------|---------------|
| SS     | 4.42 30.15 63.03 2.40 17.78 1.91 9.61 2.05 1.21 | 3.62 |
| XHS    | 4.53 33.28 15.18 47.01 55.48 4.39 19.64 0.64 0.15 | 0 |
| XLT    | 8.29 43.55 14.71 33.45 51.84 4.58 17.83 1.68 1.07 | 0 |

*: by difference.

**Table 2.** Ash composition of samples

| Sample/%(m/m) | SiO₂ | Fe₂O₃ | Al₂O₃ | P₂O₅ | CaO | MgO | SO₃ | K₂O | Others |
|---------------|------|-------|-------|------|-----|-----|-----|-----|--------|
| SS            | 30.22| 22.24 | 16.82 | 13.05| 8.31| 3.25| 3.08| 1.88| 1.15   |
| XHS           | 50.92| 5.77  | 27.52 | 0    | 0   | 5.83| 5.39| 0.89| 3.68   |
| XLT           | 3.30 | 17.65 | 4.33  | 0    | 46.2| 1.99| 25.56| 0.24| 0.73   |

The combustion experiment was operated by drop tube furnace, as displayed in figure 1. 800 °C, 900 °C and 1000 °C were set as the experimental temperature. The mass ratios of SS to coal were 3:7, 5:5 and 7:3 for the investigation of coal contents.

TP was examined by spectrophotometry [12-13]. The principle was that in acid environment orthophosphate reacted with ammonia molybdate and potassium antimony tartrate to generate a kind of yellow complex, which was reduced to blue complex by ascorbic acid. The blue complex was quantitatively determined by spectrophotometer at a specific wavelength (700 nanometers).

The phosphorous species in raw SS was examined by SMT method (the Standards, Measurements and Testing). This method divided phosphorous into organic phosphorous (OP), non-apatite inorganic phosphorous (NAIP) and apatite phosphorous (AP) [14].

To compare the results under various experimental conditions, ratio of enrichment (RE) was defined as

\[
RE = \frac{C_{M1} \times M_2}{C_{M2} \times M_1} \times 100 \%
\]
Where \( C_r \) referred to the concentration of phosphorous in SS ash or SS char; \( M_r \) referred to the mass of SS ash or SS char obtained from thermal treatment; \( C_t \) referred to the phosphorous content in SS; \( M_t \) referred to the mass of SS fed in experiment.

![Schematic drawing of dope tube furnace](image1)

**Figure 1.** Schematic drawing of dope tube furnace

![Phosphorous fixation rate in SS char and SS ash](image2)

**Figure 2.** Phosphorous fixation rate in SS char and SS ash

### 3. Results and discussions

#### 3.1 Effect of temperature on phosphorous fixation rate in SS ash

The variation trend with temperature of phosphorous fixation rate was illustrated in figure 2. Phosphorous fixation rate increased in SS ash when temperature rose as rising temperature contributed to \( \text{CaCO}_3 \) decomposition and subsequently accelerated the reaction between phosphorous and calcium. But all ratio of enrichment in SS were below 100 %. To explain it, the SMT method was utilized. The results of SMT method illustrated that there were 18.28 % OP, 24.16 % NAIP and 57.57 % AP in raw SS. And the content of OP accounted for the inevitable emission of phosphorous.

#### 3.2 Effect of temperature on phosphorous fixation rate during co-combustion of SS with coals

As shown in figure 3, the function of temperature and coal species on phosphorous were investigated. Except for the positive effect of XLT on phosphorous (about 15 % increment), XHS contributed slightly to phosphorous capture in particular at 1000 °C. The reason was the difference in crystal phase structure among the three kinds of coals. The Ca- and Mg-containing minerals content were rather higher in XLT (48.19 % CaO and MgO) than that in XHS (5.83 % MgO) based on the data in table 2.

In addition, phosphorous fixation rate XLT was positively correlated with temperature rising, whereas that for XHS acted oppositely. For XHS, the higher Ca- and Mg-containing compounds as well as Si- and Al-containing minerals were the main factors affecting TP in ash. In 800 °C most magnesium preferred to capture phosphorous, while more magnesium reacted with silicon and aluminum into Mg-Al-Si compounds with temperature increasing. That’s why there was a downward tendency of TP when it comes to temperature for XHS. For XLT, the highest content of calcium components in samples made an obvious influence to phosphorous fixation rate in the whole experimental temperature range (800-1000 °C).
3.3 Effect of coal content on phosphorous fixation rate during co-combustion of SS with coals

Different SS/coal mixtures were combusted in 1000 °C furnace and the results were gathered in figure 4. Effect of XHS content could be ignored, whereas phosphorous fixation rate was positive correlated with XLT content. The calcium and magnesium contents in XHS were too low to bring any effects on phosphorous. For XLT, the high calcium minerals content had the excellent ability in capturing phosphorous. Therefore, phosphorous fixation rate in SS/XLT ash rose from 69.64 % to 93.29 % as XLT proportion was added (30-70 %).

4. Conclusion

During combustion, most escaped phosphorous was oxidized and then captured by calcium. Calcium was the main compound capturing phosphorous vapor. In the experiment, TP in SS ash was increased by the rising temperature as higher temperature decomposed CaCO$_3$ quickly.

The effect of coal depended on its mineral composition. For XHS calcium and magnesium in coal prompted TP, while the excess aluminum and silica competed Ca and Mg in 1000 °C. For XLT adding coal contributed to phosphorous capturing because of its unique high calcium proportion among the three coals.

During SS/coal co-combustion, increasing temperature contributed to TP increment. As far as the effect of coal content, XLT acted best for phosphorous capture. TP was positively correlated with coal content and rose from 69.64 % to 93.29 % as XLT was added.

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