Phosphorus Gasification from Sewage Sludge during Carbothermic Reduction

Elias MATINDE,1) Yasushi SASAKI2) and Mitsutaka HINO1)

1) Department of Metallurgy, Graduate School of Engineering, Tohoku University, Aoba-ku, Sendai 980-8579 Japan.
2) Formerly Department of Metallurgy, Graduate School of Engineering, Tohoku University. Now at Graduate Institute of Ferrous Technology, Pohang University of Science and Technology, Pohang, 790-784, Korea (South).

(Received on February 28, 2008; accepted on April 28, 2008)

The gasification process of phosphorus from municipal sewage sludge during carbothermic reduction process was investigated using a quadrupole mass spectrometer gas analysis and thermo-gravimetric analysis. Two types of sludge, with high and low Fe₂O₃ content, were used to evaluate the possible effect of Fe₂O₃ on the gasification behavior of phosphorus from sewage sludge during incineration processes. The gas species vaporized during the carbothermic reaction were measured by the quadrupole mass spectrometer with comparison to the ion currents for the respective molecular gas species. From the gas analysis, it was observed that PO and PO₂ gas species were dominantly vaporized around 1 073 K. Metallic phase phosphorus gas of P₂ vaporized in the 1 273–1 700 K temperature range. The evolution of another metallic phase phosphorus gas of P₄ was found to be negligibly small. Fe₂O₃ in the sludge has an important role in the phosphorus emission from the sludge during carbothermic reduction reaction, since metallic phosphorous gases react with the reduced iron and form Fe–P alloy.

KEY WORDS: phosphorus gasification; incineration; metallic phosphorous gas; phosphorous oxide gas; carbothermic reduction; municipal sewage sludge.

1. Introduction

Waste recycling and re-utilization for the recovery of valuable chemical elements through high temperature treatment has attracted considerable attention over recent years. Shortage of landfill space and risk of environmental pollution has led to the urgent need for the recycling of sewage sludge waste. Incineration of sewage sludge waste is by far the most preferred method of treatment before disposal. Incineration by gasification-melting processing integrates a gasification process at low temperatures and reducing conditions, and the melting of the resulting residual solid matter. The primary products are molten slag and fly ash residue. During the gasification melting process, the phosphorus in sludge ash vaporizes under reducing conditions and precipitate to accumulate as fine particles in the low temperature sections of the gas treatment facilities, resulting in accretion and, therefore, clogging of the gas treatment equipment. Understanding the fundamental mechanism of phosphorus gasification is important to clarify the thermodynamic conditions of the gasification melting processes under reducing conditions.

Several researchers in the past have carried out a significant number of investigations dealing with the thermodynamics of P₂O₅ reduction by solid carbon. Ryu et al.¹) reported that the reduction rate of P₂O₅ is a first order reaction with respect to phosphorous content and that the reaction is controlled by the liquid phase mass transfer of P₂O₅ in slag containing less than 2.0 mass% of P₂O₅. Ban-ya¹) and Nagabayashi et al.¹) applied a quadratic formalism based on the regular solution model to estimate the equilibrium relation of phosphorus in FeO–P₂O₅–SiO₂–CaO–MgO slags. Suk et al.¹) applied a real time X-ray observation of phosphorus vaporization from steelmaking slag and the suppression of phosphorus reversion to liquid iron during the reduction of CaO–SiO₂–Al₂O₃–MgO–P₂O₅–FeO slag system by solid aluminium and solid carbon. They concluded that the reversion of phosphorus in hot metal could be reduced by incorporating a two-step de-oxidation to reduce the total FeO by carbon and then rapidly vaporizing P₂O₅ into gas phase by Al reduction. However, efforts by most of these researchers were mainly directed at the phosphate thermodynamic behaviour in steelmaking slag, rich in FeO and consisting of relatively low phosphorous levels.

Few data is available for the P₂O₅ thermodynamic behaviour from incinerator ash of municipal sewage sludge with high P₂O₅ content, especially during the solid state reduction at temperatures less than 1 473 K. In this work, a quadrupole mass spectrometer coupled to an electric furnace was used to investigate the vaporization behaviour of phosphorus from incinerator ash of sewage sludge during the solid-state carbothermic reduction reaction. The mass spectra of the vaporized gas species were interpreted qualitatively based on their isotopic abundance ratios. The vapour pressure of vaporized phosphorus gas species were measured by comparison to the ion current (I¹/m/z) intensities for the respective molecular gas species.
2. Experimental

2.1. Material Description

Two types of sludge ash material, identified as A and B, were considered in this investigation. Table 1 shows the chemical compositions of the dewatered sewage sludge samples used in this investigation. In Sample A, ferric salts were used to precipitate phosphorus during the wastewater treatment process. In Sample B, no chemical precipitation agent was used and the phosphorus was allowed to settle naturally. The two samples were selected to evaluate the possible effect of Fe₂O₃ on the thermodynamic behavior of P₂O₅ and therefore, the gasification behavior of phosphorus from sewage sludge ash. Characterization of the sludge by X-ray diffraction analysis in Figs. 1 and 2 show that Sludge A mainly consists of Fe₂O₃, Ca₆Al₂Si₂O₈ (anorthite) and Ca₉Fe(PO₄)₇ (calcium iron phosphate) and the mineral phases detected in Sludge B were mainly SiO₂ (quartz), Ca₃Al(PO₄)₂ (calcium aluminum phosphate), Ca₆(PO₄)₂ (whitlockite) and AlPO₄ (aluminum phosphate). The melting points for Samples A and B were around 1313 K and 1543 K, respectively, from TGA results.

Sludge powder was mixed with varying amount of graphite powder and pressed into tablet using hand press.

Table 1. Chemical composition of Sludge A and B used in the experimental work.

<table>
<thead>
<tr>
<th></th>
<th>Sludge A</th>
<th>Sludge B</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>24.50</td>
<td>21.51</td>
</tr>
<tr>
<td>CaO</td>
<td>9.50</td>
<td>9.45</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>24.30</td>
<td>3.62</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>14.30</td>
<td>13.97</td>
</tr>
<tr>
<td>MnO</td>
<td>0.30</td>
<td>0.04</td>
</tr>
<tr>
<td>MgO</td>
<td>2.30</td>
<td>6.18</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.10</td>
<td>0.60</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>21.10</td>
<td>38.15</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.20</td>
<td>0.14</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.20</td>
<td>3.40</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.70</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Powder X-ray diffraction analysis for Sample A.

Fig. 2. Powder X-ray diffraction analysis for Sample B.

2.2. Apparatus

Thermo-gravimetric and differential thermal analysis (TG-DTA) experiments, with argon gas purging, were carried out to determine the thermal behavior of sludge samples. About 30 mg samples (including carbon weight) were heated in alumina crucibles (5 mm diameter and 4 mm height) from 298 to 1573 K at a rate of 10 K/min. The sample weight loss against a reference Al₂O₃ powder was determined as a function of temperature. The analysis was carried out in argon atmosphere in order to evaluate inert conditions consistent with those applied in the mass spectrometer gas analysis.

A quadrupole mass spectrometer (QMS) was used to analyze gas species vaporized during the non-isothermal carbothermic reduction of sludge ash samples under high vacuum conditions. Since the total weight of sample (sludge with carbon) is fixed to 30 mg, the sludge weight is decreased with increase of carbon content. Figure 3 shows the schematic representation of the experimental set up used in the gas analysis experiments. Sludge ash tablet samples with various carbon contents (10–30 mass%) was placed at the centre of the isothermal zone of the furnace. Then they were heated to 1723 K at a rate of 7 K/min in a resistance furnace under vacuum conditions, and maintained at 1723 K for 2 h. The reacting system was evacuated by use of rotary and diffusion pumps. The vacuum condition in the reacting system varies from about 1×10⁻³ to 5×10⁻³ Pa due to the gas evolution and was not controlled. The evolved gas was drawn to the mass spectrometer by using a variable leak valve. A turbo pump was used to evacuate the QMS system. The total pressure in the QMS was manually controlled to maintain vacuum conditions of about 3×10⁻⁴ Pa by use of the variable leak valve. The gas species vaporized during the course of the reaction were measured by comparison to the ion currents (I = m/z) of their respective molecular gas species. Table 2 shows the analyzed molecular ions and their masses (m/z). Given the complexity of the sludge ash composition and side chemical reactions, only the gas species of our interest were con-

The average diameters of sludge powder A and B are almost the same and are about 300 µm, and that of graphite powder are 9 µm.

Table 2. Analyzed molecular ions and their masses (m/z).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Mass (m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>32</td>
</tr>
<tr>
<td>CO</td>
<td>28</td>
</tr>
<tr>
<td>CO₂</td>
<td>44</td>
</tr>
<tr>
<td>H₂</td>
<td>2</td>
</tr>
<tr>
<td>H₂O</td>
<td>18</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>148</td>
</tr>
</tbody>
</table>

Fig. 3. Schematic representation of the experimental set up used for the gas analysis experiments.
3. Results

Figure 4 illustrates the thermograms obtained during the non-isothermal carbothermic reduction reaction of sludge ash samples A and B. Both samples showed a gradual weight loss in the temperature range 923–1323 K, followed by a significant increase in the weight loss for temperatures above 1323 K. Distinct endothermic reactions were detected from around 1173 K and 1323 K for Sample B and Sample A, respectively. These results suggest that the carbon solution loss reaction becomes dominant above 1323 K.

Figures 5 and 6 illustrate the comparative behaviour of phosphorus oxide gas species vaporized during the solid state carbothermic reduction of sludge samples. The vaporization of PO and PO$_2$ gas species were dominantly detected around 1073 K, with an average PO/PO$_2$ ratio of 0.8–0.9. In this temperature range both samples are in solid state. The intensity of PO and PO$_2$ vaporized from Sample A, with 24.3 mass% Fe$_2$O$_3$, were several times higher than that observed from Sample B, with 3.6 mass% Fe$_2$O$_3$. The intensities of vaporized phosphorus oxide gas species increased with increasing the amount of carbon in the sample. It is also found that the phosphorus oxide gas species were able to vaporize in the solid state from samples without the addition of carbon. When the temperatures reached 1273 K, the phosphorus oxide gas species started to diminish and were replaced by metallic phase phosphorus gas species.

Figures 7 and 8 show the vaporization behaviour of metallic phase phosphorus of P$_2$ and P$_4$, respectively. The P$_2$ gas evolution was negligibly small before temperature reached to 1300 K, but it became dominant at more than 1300 K. The intensity of evolved P$_2$ gas from Sample B is

| Table 2. Expected molecular/fragment ions and their ionic masses (m/z) |
|-----------------|-----------------|-----------------|-----------------|
| 28 C$_7$H$_{14}$O$_4$N$_2$ | 32 O$_2$N$_2$5 | 62 P$_2$N$_2$ | 124 P$_4$N$_2$ |
| 29 C$_8$H$_{14}$O$_4$ | 44 O$_2$N$_2$5 | 63 P$_2$O$_2$ | 142 P$_4$O$_2$ |
| 31 P | 47 PO | 78 P$_2$O | 284 P$_4$O |

Fig. 4. TG-DTA for Samples A and B reduced with 14 and 17 mass% amount of carbon, respectively.

Fig. 5. Gas analysis for PO gas species vaporized during the solid state carbothermic reduction reaction. The solid lines denote Sample A reduced with up to 30 mass% carbon, and dotted lines denote Sample B reduced with up to 30 mass% carbon.

Fig. 6. Gas analysis for PO$_2$ gas species vaporized during the solid state carbothermic reduction reaction. The solid lines denote Sample A reduced with up to 30 mass% carbon, and dotted lines denote Sample B reduced with up to 30 mass% carbon.

Fig. 7. Gas analysis for P$_2$ gas species vaporized during the carbothermic reduction reaction in the melt. The solid lines denote Sample A reduced with up to 30 mass% carbon, and dotted lines denote Sample B reduced with up to 30 mass% carbon.
found to be larger than those from Sample A. This difference simply suggests that Fe₂O₃ may have some effects on the vaporization behaviour of P₂. Compared with other phosphorous gas species, the intensity of evolved P₄ was rather small so that it is very hard to recognize any particular tendencies at this moment.

The vaporization behavior of elemental P is presented in Fig. 9. The vaporization behavior of P was quite peculiar. Namely, P gas from Sample A was dominant at around 1000 K, but those from Sample B became dominant at more than 1600 K.

CO and CO₂ gases were detected during the reduction reaction as illustrated by Fig. 10. Up to 1173 K, both CO and CO₂ gases were evolved. At temperatures above 1273 K, CO₂ evolution stopped and only CO gas was detected. Combined with the TGA results shown in Fig. 4, the behaviour of CO and CO₂ gas evolution can be understood based on the carbon solution loss reaction.

4. Discussion

4.1. Reaction Mechanism

Just as shown in Figs. 1 and 2, phosphorous in the sludge can be existed as a phosphorous compound such as Ca₃(PO₄)₂. The carbothermic reduction of phosphorous compounds can be consisted of several steps and be very complex. In Fig. 4, several peaks in DTA curves are observed. These may correspond to the particular steps of the carbothermic reduction of phosphorous compounds. However, the reliable reaction mechanisms of the carbothermic reduction of various phosphorous compounds are not yet established. Our main concern in the present study is the identification of phosphorous gases as the outcome of carbothermic reduction of sludge. Therefore, in the present study, we qualitatively discuss the carbothermic reaction of sludge as a whole, but not investigate each reduction step of the carbothermic reduction of phosphorous compounds. Thus, the phosphorous in the sludge in solid state is simply represented by P₂O₅(compound) and those in molten state is by P₂O₅(l). P₂O₅(compound) can be one of the phosphorous compounds existed in the original sludge and/or one of the intermediate phosphorous compounds produced during the carbothermic reaction.

In the temperature range of less than 1273 K, the direct contact between C and Fe₂O₃ or P₂O₅(compound) can initiate the following reactions of Fe₂O₃ and P₂O₅.

\[
3\text{Fe}_2\text{O}_3(s) + \text{C} \rightarrow 2\text{Fe}_3\text{O}_4(s) + \text{CO}_2
\]

\[
\text{P}_2\text{O}_5\text{(compound)} + 3\text{C} \rightarrow 2\text{PO}(g) + 3\text{CO}
\]

\[
\text{P}_2\text{O}_5\text{(compound)} + \text{C} \rightarrow 2\text{PO}_2(g) + \text{CO}_2
\]

where (s) and (g) mean solid phase and gas phase, respectively. The reduction of P₂O₅(compound) by CO gas, to produce PO, PO₂ and CO₂, may proceed by the following reaction, since CO₂ gas evolution was observed up to 1273 K as shown in Fig. 9.

\[
3\text{Fe}_2\text{O}_3(s) + \text{CO} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2
\]

\[
\text{Fe}_2\text{O}_3(s) + \text{CO} \rightarrow 3\text{FeO} + \text{CO}_2
\]

\[
\text{FeO(s)} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2
\]

\[
\text{P}_2\text{O}_5\text{(compound)} + 3\text{CO} \rightarrow 2\text{PO}_2(g) + 3\text{CO}_2
\]

\[
\text{P}_2\text{O}_5\text{(compound)} + \text{CO} \rightarrow 2\text{PO}_2(g) + \text{CO}_2
\]

Along with these reactions, the carbon solution loss reaction (9) may occur.
The weight loss and the amount of gas evolution at less than 1273 K are relatively small compared with those at more than 1273 K. This is not only by the small rate constant of the reaction due to low temperature, but also carbon solution loss reaction in this temperature range is less dominant so that the produced CO2 gas cannot be converted to CO gas. The latter will be the main reason of the small reduction rate reaction at less than 1273 K since the rate was suddenly increased after 1273 K.

The vaporization of metallic phase phosphorus gas species was predominant in the temperature range 1373 to 1700 K as shown in Figs. 7 and 8. At this temperature range, the detection of CO2 was negligible as shown in Fig. 10. Namely, the carbon solution loss reaction becomes dominant and produced CO2 can be converted to CO gas. Thus, reduction processes are carried out by the CO gas reduction along with the carbon solution loss reaction, so-called apparent direct reduction. Therefore, the reduction reactions of P2O5 in the melt, and the subsequent vaporization of metallic phosphorus gas species is apparently expressed by

\[
\begin{align*}
2P_2O_5(l) + 10C & \rightarrow P_4(g) + 10CO \\
P_2O_5(l) + 5C & \rightarrow P_2(g) + 5CO \\
P_2O_5(l) + 5C & \rightarrow P(g) + 5CO
\end{align*}
\]

where (l) means the liquid phase. An actual direct reduction may also occur along with the apparent direct reduction. For the initiation of the actual direct reduction, CO bubbles must be formed at the interface between C and melt. Namely, the nominal direct reduction needs extra energy to create new interface. The apparent direct reaction will be more effective because no need to create bubbles. Thus, the apparent direct reaction is possibly more favoured than the nominal direct reduction.

4.2. Effect of Fe2O3

As shown in Figs. 5 and 6, the intensity of PO and PO2 vaporized from Sample A with high Fe2O3 content were several times higher than that observed from Sample B with low Fe2O3 content. Based on the thermodynamic stability, it is expected that Fe2O3 can be rather easily reduced than P2O5(compound). Consequently, Sample A will produce much larger amount of CO gas than that of Sample B. As a result, PO and PO2 can be produced more effectively in the Sample A based on the reactions of (7) and (8).

In the temperature range 1373 to 1700 K, P2 gas production from Sample B is generally much larger than that of Sample A as shown in Fig. 7. As mentioned before, the large amount of PO and PO2 gas were produced from Sample A. However, their evolved amounts are small enough to retain the most of P2O5(compound) in the sample. Thus, the small amount of P2 production in Sample A cannot be explained based on the depletion of P2O5 in the sample.

After experiment, the cross sectional surface of samples are examined, and many iron particles are found in the sample. Figure 11 shows the result of EPMA analysis of the iron particles in Sample A that is quenched at 1473 K. It clearly shows the existence of P element in the reduced Fe particle. This result simply means that produced P2 gas can react with the reduced iron and form Fe–P alloy. If so, only small amount of produced P2 gas is able to leave from the sample with the reduced iron as gas species. Sample A have an enough amount of reduced iron to absorb most of the produced P2 gas. This is the reason that P2 gas production from Sample A is apparently much smaller than that of Sample B. Thus, Fe2O3 in the sludge has an important role to control the emission of P2 from the sludge during carbothermic reduction reaction. For the P4 evolution, the same process is likely to occur. However, the amount of evolved P4 is too small for the reliable discussion.

The peculiar behaviour of P evolution shown in Fig. 9 is plausibly explained based on the Fe2O3 reduction. Compared with Sample B, CO gas evolution is dominant in Sample A due to its high content of Fe2O3. As a result, it is expected that Sample A can produce larger amount of P than that from Sample B at low temperature of less than 1300 K. With increase of temperature, the reaction between the evolved P gas and the reduced iron becomes dominant. The amount of the reduced iron in sample A is much larger than that in Sample B so that most of evolved P in Sample A may react with the reduced iron. However, relatively large amount of P can leave Sample B since the amount of the reduced iron is rather small compared with the sample A.

Consequently, less amount of P gas from Sample A than that from sample B was observed at high temperature.

4.3. Effect of Carbon Content

As shown in Figs. 5 and 6, the intensities of vaporized
phosphorus oxide gas species from Sample A increased with increasing the amount of carbon in the sample. With increase of carbon content, the number of contacting points between carbon and oxides may increase so that the rate of the initiation reactions of (1)–(3) and the following reactions of (4)–(8) can be enhanced. In the case of Sample B, the carbon content is found to have a weak effect on the production rate of PO and PO\(_2\) gas. The Fe\(_2\)O\(_3\) content in Sample B is rather small so that the increase of carbon content may have small effect to increase the contact places between Fe\(_2\)O\(_3\) and carbon.

It is noted that the production of PO and PO\(_2\) gas was detected in the sample without carbon. It has been shown by Kato and co-workers\(^6–9\) that the main components of the gas phase at temperature of 1 643–1 663 K over the melts, Fe\(_2\)O–P\(_2\)O\(_5\)–SiO\(_2\), Fe\(_2\)O–P\(_2\)O\(_5\)–CaO–SiO\(_2\), Fe\(_2\)O–P\(_2\)O\(_5\)–CaO, Fe\(_2\)O–P\(_2\)O\(_5\)–MgO, Fe\(_2\)O–P\(_2\)O\(_5\)–MnO and Fe\(_2\)O–P\(_2\)O\(_5\), under vacuum condition are PO, PO\(_2\), P\(_2\) and Fe. Thus, it is possible that PO and PO\(_2\) gases vaporize from the sludge contained P\(_2\)O\(_5\) under the present vacuum condition. The reaction may be represented by the following dissociation reactions;

\[
\text{P}_2\text{O}_5(\text{compound}) \rightarrow 2\text{PO}(g) + \frac{3}{2}\text{O}_2 \quad \ldots (14)
\]

Thus, the possible reactions in the present study are the following dissociation reactions;

\[
\begin{align*}
\text{P}_2\text{O}_5(\text{compound}) & \rightarrow 2\text{PO}(g) + \frac{3}{2}\text{O}_2 \quad \ldots (14) \\
\end{align*}
\]

The production of PO and PO\(_2\) gases can be controlled by the partial pressure of oxygen in the reacting system. The Gibbs free energy of the reaction (14)\(^{10}\) is expressed by

\[
\Delta G_0 = 192\,750 - 927\degree T (\text{cal/mol}) \quad \ldots (15)
\]

From the Eq. (15) and tentatively assuming the equilibrium condition and the unity activity of P\(_2\)O\(_5\), the following relation is obtained.

\[
(p_{\text{PO}})^2(p_{\text{O}_2})^{3/2} = 10^{-21} \text{ atm} \quad \text{at} \ 1000 \text{ K}
\]

Using this relation, \(P_{\text{PO}_2}\) with the \(P_{\text{O}_2}\) of \(10^{-6}\) atm is calculated to be about \(10^{-10}\) atm. The \(P_{\text{O}_2}\) in the system can be much smaller than \(10^{-6}\) atm, because the vacuum pressure in the present experimental condition is about \(10^{-6}\) atm and the system is always evacuated. It means that rather larger \(P_{\text{PO}_2}\) can be expected. Therefore, the dissociation reaction of (13) or (14) possibly take place in the present experimental conditions.

5. Conclusions

In the present study, the gasification process of phosphorus from municipal sewage waste sludge during carbothermic reduction process has been investigated using quadrupole mass spectroscopic gas analysis and thermo-gravimetric analysis. The results are summarized as follows:

(1) At temperatures of less than 1 273 K, PO and PO\(_2\) are the most stable gas phases evolved. When the temperatures reached 1 273 K, phosphorus oxide gas phases started to diminish and are replaced by metallic phosphorus gas species.

(2) At more than 1 273 K, a metallic phosphorous gas of P\(_2\) is the dominant gas phase up to the maximum sample temperature of 1 673 K.

(3) Metallic phosphorous gases can react with the reduced iron and form Fe–P alloy. Thus, Fe\(_2\)O\(_3\) in the sludge has an important role to control the phosphorous emission from the sludge during carbothermic reduction reaction.

REFERENCES