Volatilization Mechanism of Pb from Fly Ash in Municipal Waste Incinerator

Mototsugu Matsuno¹, Katsuhiro Tomoda¹ and Takashi Nakamura²

¹Sumitomo Metal Mining Co., Ltd, Tokyo 105-8716, Japan
²Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8517, Japan

Fly ash produced by waste combustion is designated as specially controlled waste in Japan due to harmful heavy metals contained in it and is legislated to be processed properly before disposal to landfill. As for technologies for making the fly ash harmless, several methods are recommended for the treatment, but each of them has some problems to be solved. The fly ash from a municipal solid waste incinerator contains large amounts of chlorinated compounds that make the harmful treatment difficult. A complete recycling of waste residue left behind after waste incineration, however, is required to solve the shortage of available final disposal sites. With this background, a new technology needs to be developed, that the heavy metals in the fly ash are removed sufficiently, no harmful heavy metals are leached and the residue ingredients are used effectively. In addition, Japanese government revised the Soil Contamination Countermeasures Law in February 2003 to strengthen the soil environmental evaluation standards. This could also promote the development of above technology. This paper focuses on lead that is particularly emphasized in the law, and proposes an advanced technology to remove lead from the fly ash, discussing the removal mechanism and removing conditions of lead. The newly developed technology is associated with the sintering process using a rotary kiln, and effectively uses only the chlorinated compounds contained in the fly ash to volatilize and remove the heavy metals. The technology achieves satisfactory low level of dioxins as well as prevention of lead leach. The fly ash treated by the technology also has passed a leaching test at pH 4 simulating typical acid rain circumstances.

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Keywords: lead volatilization, HCl, fly ash, waste incinerator, sintering

1. Introduction

Fly ash produced from a municipal solid waste incinerator is designated as specially controlled waste in Japan since it contains large amounts of heavy metals such as lead (Pb) and cadmium (Cd). There is a legal obligation to make it harmless before the landfill disposal. The Ministry of Health, Labor, and Welfare of Japan recommends several basic technologies for making the fly ash harmless and at the same time points out some problems inherent to technology. Therefore a new reliable technology need to be developed.

On the other hand, availability of new waste disposal site becomes very difficult in Japan so that a recycling-oriented technology is urgently required to avoid landfill disposal of wastes.

Technologies for making specially controlled wastes harmless are required, not only to meet the requirements of their disposal to landfill waste site, but also to secure environmental safety satisfying safety standards applied in the areas where the treated wastes can be used effectively, for instance the soil environmental evaluation standard. In any event the conventional technologies are difficult to meet these requirements. This paper focuses on Pb that is emphasized in the soil environmental standards revised in February 2003, and proposes an advanced technology to remove lead from fly ash, discussing the removal mechanism and removing conditions of lead. The developed technology consists of removing heavy metals from the fly ash, through the chloride volatilization method, to allowably low level in the resultant pellets. In this sense, the technology can be differentiated from the existing harmless technologies which simply immobilize heavy metals by adding reagents to the fly ash.

And the technology presented here is also completely different from the volatilization reaction of chloride in oxidizing atmosphere that is adopted by the conventional technologies,¹ and is able to sufficiently volatilize and remove heavy metals in weak HCl atmosphere under which only Cl contained in the fly ash is effectively utilized. Thus the novel technology can be differentiated from the conventional chloride volatilization method which requires the additional chlorine source such as CaCl₂ to achieve high $P_{\text{HCl}}$, aiming at recovering valuable heavy metals in oxidizing atmosphere.

The technology is also able to volatilize and remove heavy metals other than Pb simply by maintaining reducing atmosphere in the bed layer.²⁻⁶

2. Outline of Treatment Method and Testing Method

Figure 1 shows schematically the treatment flow of the newly developed technology. The dimension of the applied kiln in this study is 900 mm in diameter and 12000 mm in length. The kiln was operated under the following conditions: rotation 1 ~ 6 rpm, throughput 100 kg/h (typical) and increased up to 250 kg/h (maximum).

Additive agents such as coke and hematite were added to the fly ash. They were mixed by a mixer and crushed by a vibrating rod mill. Then water was added to the mixture to knead them together. The mixture is extruded to prepare columnar pellets of 10 mm in diameter and 5 to 15 mm in length. After dried, the pellets were charged into a rotary kiln, where the pellets are sintered at temperatures higher than 1000°C. The flue gas is cooled down rapidly to less than 200°C by water spraying to prevent dioxin formation. Secondary fly ash is collected in a bag filter. Since the flue gas contains HCl, the gas is passed through a scrubber to neutralize it, and then entered into an activated carbon absorber to further decrease the concentration of dioxins before venting to atmosphere. Table 1 shows the typical chemical compositions of the fly ash used in the tests. Numbers of test run were conducted in order to indicate the
The applicability of the technology to the wide range of the fly ash compositions.

3. Test Results

3.1 Variations in concentration of Pb, etc in kiln

Figure 2 shows the test results under typical test conditions, giving profiles of various elements as a function of the distance from inlet (left end of the figure) to outlet (right end) of the testing kiln (total length of 12 m).

As can be seen from the figure, Cl gradually decreases as the distance from the inlet (representing a relatively low temperature) increases and shows a rapid decrease at about 950°C. As for K and Na, however, such a rapid decrease can not be seen. This different behavior suggests that some phenomena regarding Cl different from NaCl and KCl volatilization occur in the kiln. On the other hand, Pb shows similar behavior with Cl, giving a rapid decrease at 950°C. This observation suggests some relation between Pb and Cl.

3.2 Amount of Pb remaining in sintered pellets

Figure 3 shows amounts of Pb remaining in sintered pellets for every test run. It can be seen that the volatilization and removal of Pb are fully generated regardless of the testing conditions employed. Among varied conditions, a few test runs show quite higher values than the average because of the insufficient temperature.

3.3 Pb leaching test

Also for the leach of Pb, as a whole stable and low level of Pb is attained as shown in Fig. 4. Since there appears a phenomenon of irregularly exceeding the standard level, the test data including cases of the increased charging amount are rearranged in Table 2 for individual conditions. The data exceeding the standard level were found to be in the condition of accelerating the oxidization, or 4 rpm or higher rotational speed of the kiln.

3.4 Evaluation by Toxicity Characteristic Leaching Procedure (TCLP) and for the test simulating acid rain

Tables 3 and 4 show the evaluation results of leached amount for TCLP and for pH 4 condition. Both cases produced satisfactory results, and it is clear that quite small amount of Pb remaining in sintered pellets is fully stabilized after the treatment.

4. Discussion

The results mentioned above have shown that Pb contained in the fly ash is volatilized and removed to a sufficiently low level. From the fact that Cl is detected in the collected volatilized matter, it is obvious that Pb is volatilized like chloride. As any additive containing Cl is not used in the verification tests, Cl ingredient used in the chloride reaction

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Table 1  Typical chemical compositions of fly ash used in the tests

<table>
<thead>
<tr>
<th>Type of fly ash</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>ZnO</th>
<th>PbO</th>
<th>SO₃</th>
<th>Cl</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (EP ash)</td>
<td>10.2</td>
<td>5.8</td>
<td>1.3</td>
<td>15.8</td>
<td>2.9</td>
<td>12.7</td>
<td>12.0</td>
<td>1.3</td>
<td>0.2</td>
<td>10.8</td>
<td>23.8</td>
<td>0.8</td>
</tr>
<tr>
<td>B (Ca ash)</td>
<td>1.3</td>
<td>3.5</td>
<td>0.8</td>
<td>39.6</td>
<td>4.3</td>
<td>3.9</td>
<td>4.0</td>
<td>0.3</td>
<td>0.1</td>
<td>3.7</td>
<td>13.3</td>
<td>1.9</td>
</tr>
<tr>
<td>C (EP ash)</td>
<td>20.2</td>
<td>13.0</td>
<td>1.5</td>
<td>17.0</td>
<td>3.2</td>
<td>9.1</td>
<td>8.5</td>
<td>2.4</td>
<td>0.8</td>
<td>4.8</td>
<td>13.0</td>
<td>2.4</td>
</tr>
</tbody>
</table>

EP ash: Ash recovered from electric precipitator
Ca ash: Ash to which slack lime was added
is only Cl contained in the fly ash. Therefore Cl which has been regarded as a problem-inducing ingredient in the fly ash is expected to be utilized effectively in the process of volatilization and removal of harmful heavy metals.

4.1 Reaction mechanism by equilibrium calculations
Since chloride is detected in volatilized matter, the volatile compounds containing Pb are determined to be PbCl₂.
Pb in green pellets before sintered is confirmed to be PbO so that PbCl₂ formation reaction is written as follows:
\[ \text{PbO} + 2\text{HCl} = \text{PbCl}_2 + \text{H}_2\text{O} \]
\[ \Delta G^\circ (J) = -189,570 + 94.44T \]  
(1)
\[ \Delta G^\circ (873J) = -107,124 \]
\[ K = \alpha_{\text{PbCl}_2} \times P_{\text{H}_2\text{O}} / \alpha_{\text{PbO}} \times P_{\text{HCl}}^2 = 2.56 \times 10^6 \]  
(2)

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(2)

(*) Rotation of kiln is 4 \text{rm}^{-1} \text{ or more.}
Extraction conditions: A sample of 100 g is dissolved in 1000 mL of water

<table>
<thead>
<tr>
<th>Feed rate (kg/h)</th>
<th>No Pb elution (mg/L)</th>
<th>Feed rate (kg/h)</th>
<th>No Pb elution (mg/L)</th>
<th>Feed rate (kg/h)</th>
<th>No Pb elution (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>&lt;0.01</td>
<td>150</td>
<td>&lt;0.01</td>
<td>200 ~ 250</td>
<td>1 &lt;0.01</td>
</tr>
<tr>
<td>2</td>
<td>&lt;0.01</td>
<td>3</td>
<td>&lt;0.01</td>
<td>200 ~ 250</td>
<td>1 &lt;0.01</td>
</tr>
<tr>
<td>3</td>
<td>&lt;0.01</td>
<td>3</td>
<td>&lt;0.01</td>
<td>2</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>4</td>
<td>&lt;0.01</td>
<td>4</td>
<td>&lt;0.01</td>
<td>2</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>5</td>
<td>&lt;0.01</td>
<td>4</td>
<td>&lt;0.01</td>
<td>2</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>6</td>
<td>&lt;0.01</td>
<td>4</td>
<td>&lt;0.01</td>
<td>2</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>7</td>
<td>&lt;0.01</td>
<td>4</td>
<td>&lt;0.01</td>
<td>2</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>8</td>
<td>&lt;0.01</td>
<td>4</td>
<td>&lt;0.01</td>
<td>2</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

(*) Rotation of kiln is 4 \text{rm}^{-1} \text{ or more.}
Extraction conditions: A sample of 100 g is dissolved in 1000 mL of water

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Elution of Pb (mg/L)</th>
<th>Residual amount (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-1</td>
<td>0.10</td>
<td>0.004</td>
</tr>
<tr>
<td>F-2</td>
<td>0.53</td>
<td>0.032</td>
</tr>
<tr>
<td>L-1</td>
<td>0.15</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>L-2</td>
<td>0.065</td>
<td>0.017</td>
</tr>
</tbody>
</table>

Extraction conditions: A sample of 100 g is dissolved in 2000 mL of acetic-acid solution
These two possible reactions are following.

$\text{NaCl} + \frac{1}{2}\text{SO}_2 + \frac{1}{2}\text{H}_2\text{O} + \frac{1}{4}\text{O}_2 = \text{HCl} + \frac{1}{2}\text{Na}_2\text{SO}_4 \quad (3)$

This value is very low so that the chlorination reaction of Pb possibly occurs.

As shown in Fig. 5, the vapor pressure of PbCl₂ is sufficiently high, thus PbCl₂ is fully volatilized after its formation, which suggests that PbCl₂ is relatively hard to remain in pellets.

As for the source of HCl necessary in the chloride reaction, two reactions related to aluminosilicate and sulfate might occur taking into account the ingredients of the fly ash. These two possible reactions are following.

$\text{NaCl} + \frac{1}{2}\text{SO}_2 + \frac{1}{2}\text{H}_2\text{O} + \frac{1}{4}\text{O}_2 = \text{HCl} + \frac{1}{2}\text{Na}_2\text{SO}_4 \quad (3)$

$\text{NaCl} + 3\text{SiO}_2 + 1.5\text{Al}_2\text{O}_3 + \frac{1}{2}\text{H}_2\text{O} = \text{HCl} + \text{NaAl}_3\text{Si}_3\text{O}_8 \quad (4)$

A comparison of standard free energy of formation for each of the reactions at 900°C shows that the reaction with SO₂ contribution more easily occurs. These reactions, however, are highly temperature-dependent as shown in Fig. 6, and the reaction (4) is likely to occur in the low temperature zone while the reaction (3) does not occur. On the other hand, at temperatures of 900 to 950°C, it can be seen that the values of standard free energy of formation for the reactions are inverted, and at the high temperature zone, the reaction (3) becomes dominant.

On the assumption of $P_{\text{HCl}} = 10^1$ (Pa), the partial pressure of SO₂ necessary in the reaction (4) is calculated to be about $P_{\text{SO}_2} = 10^4$ (Pa).

HCl produced presumably proceeds through the reaction (3) in the low temperature zone and through the reaction (4) in the medium temperature zone. If HCl is produced in the high temperature zone, similar to SO₂, there may occur the migration of HCl to the lower temperature and the migration into the bed layer caused by mechanical entrapment resulted from the rotation of the kiln.

4.2 Basic test relating to the source of SO₂ and to the Pb volatilization

1. The source of SO₂ is CaSO₄, which is contained in the raw material fly ash, and the thermal decomposition of CaSO₄ produces SO₂.

4.2.1 Testing method

As for thermal decomposition of CaSO₄, a basic test was conducted in helium gas atmosphere so as to avoid the influence of oxidation. This condition simulates the actual bed layer. A test at $P_{\text{O}_2} = 3 \times 10^1$ (Pa) was also conducted simulating the oxygen partial pressure in actual gas layer.

The apparatus used consists of a differential thermal balance and a mass spectrometer (TG-MS), schematically shown in Fig. 7. Table 5 shows the main specifications of TG-MS used in the experiments.

Pellets containing CaSO₄ was used as CaSO₄ reagent for thermal decomposition. The sample of fly ash was a powder mixture of fly ash and auxiliary raw materials with the same mixing ratio as that used in the verification test. Aiming at understanding both reactions in internal zone of bed and in gas layer, two types of the atmosphere were chosen: the reducing atmosphere (simulating the bed) of 100% helium as stream; and oxidizing atmosphere (simulating the gas layer) of 3% oxygen-contained helium gas stream.

It should be noted that, different from actual rotary kiln, the test does not form any bed and does not apply counter-flow of gas to the sample. Also note that the gas analysis data is measured in the gas layer.

The variations in the composition of the residue of pellets sintered and the compounds were measured using chemical analysis and X-ray diffractometry (XRD).

4.2.2 Test for producing SO₂ gas

Figure 8 shows the test result of CaSO₄ decomposition and of SO₂ production. The results include both oxidizing and un-oxidizing conditions. The figure clarifies that SO₂ produced increases with the decrease in CaSO₄ in un-oxidizing condition. Taking into account the fact that SO₂ was
produced at more than 600°C, it is supposed that the SO2 contributing reaction is unlikely to occur at least below 600°C. In oxidizing atmosphere, SO2 is produced at higher temperatures than that of un-oxidizing atmosphere.

4.2.3 NaCl decomposition

A basic test was conducted on NaCl decomposition, as a source of HCl produced. Fly ash containing NaCl and moisture was prepared and used as experimental reagent. As shown in Fig. 9 (in un-oxidizing atmosphere), HCl is produced along with the decrease in NaCl, thus the production of HCl caused by the NaCl decomposition was confirmed. The amount of HCl produced, however, was relatively small.

4.2.4 Volatilization and removal of Pb from pellets

The amount of HCl produced and the decrease in Pb in the pellets were also measured to find that HCl production and the decrease in Pb occur almost simultaneously in un-oxidizing atmosphere (see Fig. 10).

4.2.5 Phenomena in oxidizing atmosphere

Figures 8, 9, and 10 also show the data obtained in oxidizing atmosphere. As shown in Fig. 8 (see the case of oxidizing atmosphere), SO2 caused by CaSO4 decomposition occurs in a delayed time compared with the case of un-oxidizing atmosphere, indicating a rapid increase in SO2 at around 950°C. This is due to the delay of CaSO4 decomposition, since the decreasing rate in CaSO4 is smaller than that of un-oxidizing atmosphere. It is, therefore, obvious that the difference in bed atmosphere also gives significant influence on SO2 production. Further it implies that the bed
atmosphere gives influence also on the formation reaction of lead chloride.

On the contrary, as shown in Fig. 9 for HCl produced by NaCl decomposition, the decomposition of chloride is enhanced rather in oxidizing atmosphere. Similarly, as seen in Fig. 10 for the volatilization of Pb in pellets by HCl, the decreased amount of Pb is large owing to the high partial pressure of HCl.

These basic tests indicate that HCl formation reaction from SO\(_2\) and the lead chloride formation occur very easily. Thus, even in the low temperature zone, the SO\(_2\) contribution reaction occurs only if the partial pressure of SO\(_2\) is at a satisfactory level.

### 4.2.6 Evaluation of basic test results

The test results show that the mechanism to produce HCl differs with the kind of atmosphere. It implies that the SO\(_2\)-contributing reaction (the reaction (4)) may firstly occur in the bed layer, and that the SiO\(_2\)-contributing reaction (the reaction (3)) may firstly occur at the contact zone with the gas layer under the presence of a certain level of oxygen partial pressure.

### 4.3 \(P_{\text{HCl}}\) and \(P_{\text{SO}_2}\) in the kiln verification test

To confirm the basic test results, gas analysis was conducted at various positions in the kiln. The result is shown in Table 6.

#### 4.3.1 Sampling method

Gas sampling was made through the sampling holes opened on the kiln at specified positions. For sampling, the kiln was temporarily stopped during the continuous operation when the thickest portion of the bed came to the opposite side of the sampling hole concerned. The sampling device was quickly inserted through the sampling hole into the depth center of the bed to collect sample by sucking the sampling device. For the gas layer, the gas sample was collected at about 50 mm above the bed surface. The sampling was completed in a relatively short period, then the kiln was restarted. By repeating the steps, total sampling work was done.

#### 4.3.2 Analysis of the results

From the data based on the procedures mentioned above in kiln verification tests, the following results were obtained as for HCl:

- a) Small amount of HCl produced was observed at relatively low temperature zone of the charging side.
- b) Significant amount of HCl produced was observed at around 900°C.
- c) At the high temperature zone, however, expected amount of HCl was not observed.
- d) The amount of SO\(_2\) produced was very small at the low temperature zone of the charging side, not reaching an equilibrium pressure necessary for producing HCl.
- e) Very large amount of SO\(_2\) was produced at the high temperature zone, significantly exceeding the amount contained in the raw material. S circulation, therefore, may occur within the kiln needs to be taken into consideration.

The above observations clarify that the partial pressure of SO\(_2\) is low in the low temperature zone, and that SO\(_2\) contributing reaction in the zone is not so active. In order to enhance HCl formation the supply of SO\(_2\) is required obviously. At around 900°C, the amount of HCl formed is satisfactory, and it might be produced through both SO\(_2\)-contributing and SiO\(_2\)-contributing reactions. Due to the fact that the measured values of SO\(_2\) showed very high level, there might occur both SO\(_2\) absorption by the pellets at the charging side and the internal circulation of SO\(_2\) within the kiln in the high temperature zone caused by SO\(_2\) decomposition.

### 4.4 Analysis of reaction in kiln and material balance relating to the gasification

#### 4.4.1 Reaction at the low temperature zone

Based on the results described above, the results of verification test are analyzed as follows:

As shown in Fig. 2, the slow decrease in both Pb and Cl at the relatively low temperature zone suggests that HCl producing reaction is not significant, or that the decomposition of NaCl does not occur and the partial pressure of SO\(_2\) is low. Thus, the decomposition of CaSO\(_4\) observed at temperatures below 700°C under the un-oxidizing condition shown in Fig. 8, presumably begins at a zone of slightly higher temperature than 700°C. As clearly shown in Table 6, since the partial pressure of SO\(_2\) detected in the low temperature zone is lower than the equilibrium partial pressure, SO\(_2\) is not necessarily a controlling variable to produce HCl within the zone. The speculation agrees well with the fact that Cl in charged materials does not decrease significantly in the low temperature zone in the kiln (Fig. 2).
4.4.2 Material balance in the gasification reaction

Based on the kiln test, the material balance relating to the gasified ingredients is expressed in Table 7. Na and K are fed as respective chlorides and oxides. They are partially volatilized as chlorides and then decomposed to produce HCl.

Most of supplied Ca is in a form of oxide, partly with sulfate. Within the kiln, the sulfate is decomposed to produce SO$_2$, while a part of the sulfate reacts with HCl to produce CaCl$_2$.

S is fed as CaSO$_4$, and it is decomposed in the kiln to produce SO$_2$.

In that case, the amount of HCl produced is calculated to be 0.105 kmol at 100 kg/h of charging. If the gas amount is assumed to be 1000 Nm$^3$/h of flue gas at the exit of kiln, HCl concentration in the kiln is calculated to be about 2350 ppm.

The analyzed values of individual ingredients in the kiln, however, are somewhat different from the calculated values, as shown in Table 6, giving higher level in the gas layer than in the bed. The observation suggests that HCl is produced in the bed, and then HCl vapor migrates into the gas layer. Sulfur dioxide (SO$_2$) shows a surprising result (see Table 6), giving a peak of several tens of thousands of ppm significantly exceeding the predicted level at around 950°C, while giving several thousands of ppm at around 700°C at the charging side. These values are much larger than the values simply converted from the amount of S charged continuously. This observation suggests that SO$_2$ produced in the high temperature zone is consumed in the low temperature zone through some possible reactions. At the center portion of the kiln, SO$_2$ concentration was higher in the gas layer than in the bed layer, which could induce SO$_2$ migration from the gas layer into the bed layer at the kiln center. S circulation is established by, for instance, alkali sulfate, and alkali earth sulfate, and CaSO$_4$ was found in the charged material. Although CaSO$_4$ was detected in the charged material by X-ray analysis, no CaSO$_4$ was detected in the sintered material. Since CaSO$_4$ can be produced within the kiln, the CaSO$_4$ may be produced and increased within the kiln, and may be decomposed before the sintered material is discharged. Possible components assumed as the S medium include Na, K, etc. as well as Ca, but these are not confirmed in the present experiment. If all of Ca, Na, and K in the charged materials are converted to respective sulfates, the sum of the partial pressure of SO$_2$ produced by their decomposition becomes about ten thousand ppm, which is far below the observed values. Consequently, the presence of another medium for S circulation is expected, and the possibility of Al, Fe, S$^2-$, etc. should be investigated. The production of S$^2-$ may not be impossible because the oxygen partial pressure in the bed layer in the kiln is as low as $<10^4$ Pa and because the kinetic data suggests.

5. Conclusions

Regarding the advantages of the developed technology giving excellent performance of making harmless and high environmental safety, we made an analysis on the mechanism of volatilization of lead chloride, and obtained the following conclusions:

(1) The basic tests proved that HCl can be produced from NaCl contained in fly ash from waste incinerator.
(2) HCl is produced through decomposition of NaCl by alminosilicate and by the action of SO$_2$.
(3) HCl producing reaction is highly susceptible to the temperature and the partial pressures of SO$_2$ and O$_2$, and the dominating reaction differs with the reaction conditions.
(4) The amount of SO$_2$ produced was measured to be surprisingly large at a temperature of around 900°C, which suggests the presence of S circulation within the kiln in some compound modes. Although the production and decomposition of Na$_2$SO$_4$ and CaSO$_4$ might be associated with this circulation, other causes should be investigated further.

The above-described findings show that stable operation is attained by many reactions, each of which plays the dominant
role responding to the intra-kiln conditions depending on various variables specific to individual incinerator fly ashes, independent of the differences in treatment conditions. These advantageous characteristics make the technology presented versatile as industrial technology.

Acknowledgements

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REFERENCES