



Stabilization of a chlorine-rich fly ash by colloidal silica solution

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ABSTRACT

Fly ash from municipal solid waste incinerators (MSWI) consists of various substances, including a lot of heavy metals. In cases where fly ash contains a lot of chlorides, it is very difficult to apply general treatment methods because chlorides could hinder hydration in cementation and cause great loss in vitrification. In this study, we report a promising method for the treatment of fly ash containing a high concentration of chlorides. A colloidal silica solution was induced to stabilize the fly ash. The fly ash used in this research has a chlorine level over 35 wt.% as well as containing heavy metals, such as Pb (1120 ppm) and Zn (5430 ppm). The samples were prepared at a temperature of 600–800 °C for 2 h after mixing with the fly ash and a 4 wt.% colloidal silica solution. The effect of the colloidal silica was evaluated by the leaching test, Toxicity Characteristic Leaching Procedure (TCLP). The solidified products with fly ash and colloidal silica at temperatures of more than 700 °C had an excellent resistance, with Pb²⁺ <0.02 ppm, Zn²⁺ <0.52 ppm, and Cd²⁺, Cr²⁺, Cu²⁺, Mn²⁺ <0.01 ppm, and it could be influenced by the phases containing Ca and Si formed above 600 °C and reduction of a chemically weak phase.

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1. Introduction

Fly ash from municipal solid waste incinerators (MSWI) contains a lot of heavy metals as well as toxic organic substances [1]. Most countries classify MSWI fly ash as a highly hazardous material which must be detoxified before final disposal. Recently, many countries have selected incineration as a MSW treatment method instead of employing landfill, so the generation of fly ash has continuously increased.

There have been several researches about fly ash stabilization. However, most of them dealt with fly ash containing mainly oxides, which could be treated by conventional methods, such as cementation and vitrification, in spite of the slight disadvantages [2–5]. However, in cases where fly ash has a high concentration of chlorine compounds, it is very difficult to apply the existing techniques. Cementation is the most popular and inexpensive method for stabilizing fly ash, but it is difficult to solidify a chlorine-rich fly ash since chlorides hinder the hydration of cement [6,7]. Vitrification can also provide an alternative because it can destroy dioxins at high temperatures and make various heavy metals inert through their incorporation into the glass matrix. This technique is also limited, however, because most chlorides are too volatile at high temperatures over 1000 °C to be confined into the vitreous products [1], which causes secondary pollution.

On the other hand, a colloidal silica solution is inexpensive, highly reactive, and non-toxic. A previous study about the reactivity of colloidal silica revealed its potential as a waste stabilizer [8]. This study dealt with the effect of colloidal silica on the stabilization of a chlorine-rich MSWI fly ash. The leaching test using the Toxicity Characteristic Leaching Procedure (TCLP) was employed to evaluate the effect of the colloidal silica. Also, cementation and chemical treatment with H₃PO₄ were induced as references.

2. Experimental

The fly ash used in the experiments was sampled from a grate-type MSWI (Cheonan, Korea). The fly ash collection system was a bag filter. The particle size was around 50 μm. The chemical composition of fly ash was analyzed using a combination of ion chromatography (IC, DIONEX DX120) and an X-ray fluorescence spectrometer (XRF, PHILIPS PW2400). The specimens for XRF analysis were prepared in the form of pellets to reduce the loss of volatile materials. Table 1 shows the chemical composition of fly ash. The major compositions were Cl, Ca and Na, with 37.4, 23.9 and 18.5 wt.%, respectively. Also, Pb and Zn showed high concentrations, at 5430 and 1120 ppm, respectively.

A colloidal silica solution (Du Pont, LUDOX AS-40) was used after diluting up to 4 wt.%. Zeta-potential which represents the degree of stability in a colloidal solution was measured by MALVERN-ZETASIZER3000. Also, colloid particles were observed in a suspended state in the solution by using a field emission scanning

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Table 1
Composition of fly ash (as received)

Component	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	C
Major compositions Conc. (wt.%)	18.5	2.0	1.0	1.8	0.2	2.8	37.4	2.5	23.9	0.2	9.1
Component	Cr	Mn	Cu	Zn	Cd	Pb					
Heavy metals Conc. (ppm)	47	67	168	5430	39	1120					

Table 2
Specifications of samples

Sample #	Specifications
1	FA ^a (50 wt.%) + 4 wt.% CSS ^b (50 wt.%), drying at 50 °C for 12 h
2	FA (50 wt.%) + 4 wt.% CSS (50 wt.%), heat treatment at 600 °C for 2 h
3	FA (50 wt.%) + 4 wt.% CSS (50 wt.%), heat treatment at 700 °C for 2 h
4	FA (50 wt.%) + 4 wt.% CSS (50 wt.%), heat treatment at 800 °C for 2 h
5	FA (50 wt.%) + Cement (50 wt.%) + water (W/C ratio = 0.8), curing for 7 days
6	FA (50 wt.%) + Cement (50 wt.%) + water (W/C ratio = 1.0), curing for 7 days
7	FA (50 wt.%) + Cement (50 wt.%) + water (W/C ratio = 1.2), curing for 7 days
8	FA (50 wt.%) + 2 wt.% H ₃ PO ₄ solution (50 wt.%); mixing for 30 min, drying at 50 °C for 12 h
9	FA (50 wt.%) + 5 wt.% H ₃ PO ₄ solution (50 wt.%); mixing for 30 min, drying at 50 °C for 12 h
10	FA (50 wt.%) + 10 wt.% H ₃ PO ₄ solution (50 wt.%); mixing for 30 min., drying at 50 °C for 12 h

^a Fly ash.

^b Colloidal silica solution.

electron microscope (FE-SEM, TESCAN MIRA-LMU) and a liquid sampler.

The specimens were prepared by mixing fly ash and 4 wt.% colloidal silica solution manually for 30 min and then treating the mixtures at different temperatures from 50 to 800 °C. References such as cementation and chemical treatment with H₃PO₄ were also prepared under several conditions. In the sample # 5–7, fly ash and cement were mixed well for 5 min at 300 rpm and then deionized water was added and mixed for 5 min. The cementation products were wet-cured at 25 °C for 7 days. In the sample # 8–10, H₃PO₄ was dissolved in water to facilitate homogeneous reactions with heavy metals. The solution was mixed with fly ash for 30 min and the mixture was dried at 50 °C for 12 h. The specifications for the samples are summarized in Table 2.

Chemical stability was estimated by the TCLP method of the U.S. Environmental Protection Agency (EPA). The samples for the leaching test were powdered and sieved to a particle size <50 μm, similar to the size of fly ash, so that a direct comparison becomes possible. The concentrations of heavy metals in the leached solution were measured by inductively coupled plasma – atomic emission spectroscopy (ICP–AES, VARIAN LIBERTY-AX) and the changes after the addition of colloidal silica solution were investigated by X-ray diffractometer (XRD) and FE-SEM.

3. Results and discussion

The major components of fly ash were Cl, Ca and Na as well as unburned carbon. A high concentration of chlorine is due to salty food waste in MSW. As shown in Table 1, fly ash consists of various elements, so it is difficult to expect exact reactions during the exper-

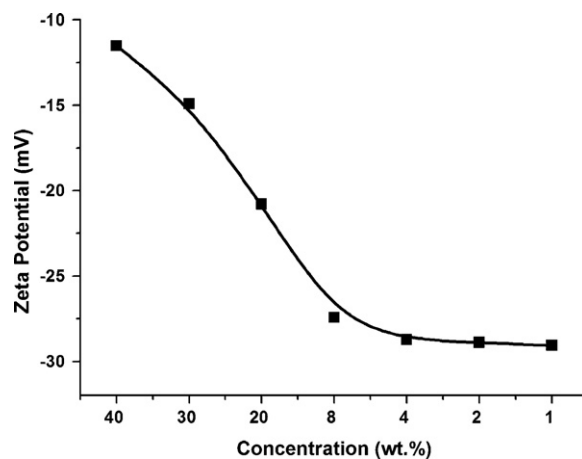


Fig. 1. Changes in zeta-potentials with concentration of the colloidal silica solution.

iment. In this study, the effectiveness of colloidal silica solution was evaluated on the basis of a leaching test, TCLP.

A colloidal solution means that small particles, with which the status is electrochemically stable, are suspended in the solution. Zeta-potential represents the electrical stability among the colloidal particles. To determine the optimum concentration for fly ash treatment, the zeta-potential was measured according to the colloidal silica concentration (Fig. 1). The potentials were stabilized around –28 mV, which means that it is sufficient not only to cause a heterogeneous reaction when the solution is mixed with electrically different materials, but also to have a strong ionic reactivity with positive ions, such as heavy metal ions [9]. In the consideration of economical efficiency and electrical properties, as well as sufficient amount of colloidal silica to stabilize the various heavy metals, a 4 wt.% colloidal silica solution was selected as an additive to detoxify the fly ash. As shown in Fig. 2, the colloidal silica in a

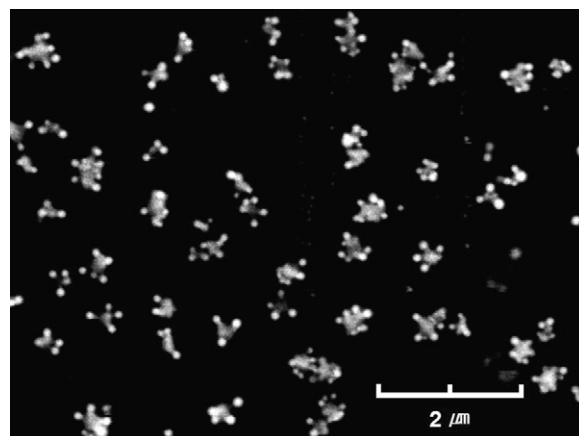


Fig. 2. Colloidal silica particles suspended in the solution.

Table 3
Results of leaching tests by TCLP (ppm)

Samples	Cd	Cr	Cu	Mn	Pb	Zn
Korean regulatory standard (leachate)	0.1	2.0	3.0	10.0	1.0	5.0
Fly ash (as received)	0.78	0.01	3.02	0.09	15.00	55.46
# 1	0.02	N.D. ^a	0.03	0.01	3.36	6.54
# 2	0.01	N.D.	0.03	N.D.	0.18	6.98
# 3	N.D.	N.D.	0.01	N.D.	0.02	0.52
# 4	N.D.	N.D.	0.01	N.D.	0.01	0.50
# 5	N.D.	N.D.	N.D.	N.D.	0.01	0.21
# 6	N.D.	N.D.	N.D.	N.D.	0.03	0.20
# 7	N.D.	N.D.	N.D.	N.D.	0.09	0.21
# 8	0.87	0.01	1.53	0.36	7.79	60.51
# 9	2.35	0.01	1.49	0.69	7.83	122.33
# 10	3.36	0.02	4.01	0.99	10.60	134.05

^a Not detected (detection limit: Cd, Cr, and Cu 0.005 ppm, Mn 0.003).

4 wt.% solution was suspended in a clustered form of particles of several tens of nanometers.

The results of the TCLP are summarized in Table 3. This research was focused on the chemical stability of the mixture of MSWI fly ash and a colloidal silica solution. Comparing the absolute chemical stability among the samples, the particle sizes for the leaching tests were controlled to less than 50 μm , similar to the size of the fly ash. The fly ash, as received, showed weak chemical stability and then the leaching of Pb^{2+} and Zn^{2+} exceeded the Korean regulatory standard by more than 10 times. In cases where the colloidal silica solutions were applied, the leached heavy metal ions decreased as the heat treatment temperature increased as shown in the results for # 1–4. Particularly in the condition of heat treatment at 700 and 800 °C for 2 h, the leaching of Pb and Zn was confined effectively from 15.00 and 55.46 ppm in the as-received fly ash to less than 0.02 and 0.52 ppm, respectively. The results for # 5, # 6 and # 7 are related to cementation and satisfy the regulatory standard very well. However, the cementation products did not develop sufficient strength to solidify fly ash and remained friable powders. This is the expected result and may be influenced by chlorides [6]. Fig. 3 shows a microstructure of sample # 5, which shows that the cement networks were not well developed. In other words, the cement in this research can be used only as a chemical stabilizer but can be unsuitable as a binder of fly ash particles. Therefore, it is necessary to increase the amount of cement in order to achieve effective cementation. Phosphate is known as a heavy metal stabilizer, which creates a chemically stable form with heavy metals

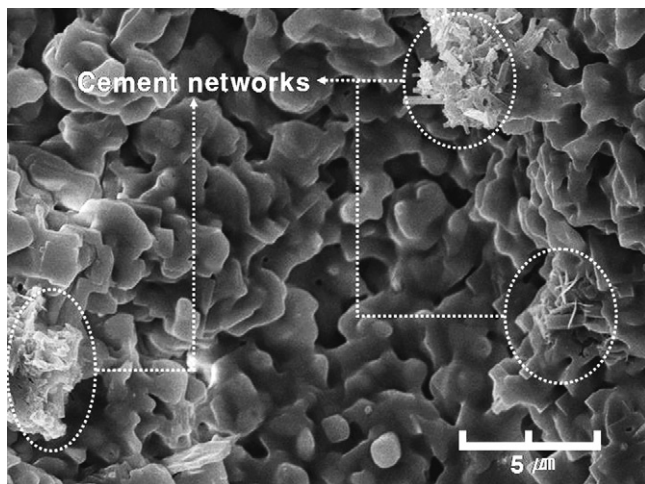


Fig. 3. Scanning electron micrograph of the cementation product (sample # 5).

[10–12]. Samples of # 8–10 were prepared by using H_3PO_4 . However, the leaching was worse than the fly ash before the treatment. Further studies are currently being carried out and it seems that the excessive chlorine ions may be blocking the formation of the stable precipitates.

The leaching results prove that colloidal silica solution could be a promising treatment method for a chlorine-rich fly ash. In addition, some changes might occur when the treatment temperature increases because the heavy metal leaching was reduced sharply. In order to identify the change, an XRD analysis was performed. Fig. 4 shows the X-ray diffractograms of as-received fly ash and in samples # 2 and # 3. As the treatment temperature changed from 600 to 700 °C, the peaks related to Si, such as CaSiO_2 and $\text{CaMgSi}_2\text{O}_6$, increased, while those of CaClOH and $\text{Ca}(\text{OH})_2$ decreased. Fig. 5 shows the microstructures of samples # 2–4. When the mixture of fly ash and colloidal silica was treated at 600 °C for 2 h, an irregular structure was formed, as shown in Fig. 5(a). As the treatment temperature changed, phases like a cross-linked disk appeared at 700 °C and started to melt from the surface at around 800 °C (Fig. 5(b) and (c)).

The products in this research were ground and sieved to a particle size <50 μm in order to compare the chemical stability with fly ash under the same condition. From the results described above, the improvement in the chemical stability could be due to the following reasons when a chlorine-rich fly ash was treated with a colloidal silica solution. Firstly, the reduction of a chemically weak phase would have influenced the stabilization of heavy metals. CaClOH is a water-soluble material so it could make the material matrix weak in an aqueous environment. Second, some phases such as CaSiO_2 and $\text{CaMgSi}_2\text{O}_6$, which could be originated by a colloidal silica solution could prevent the heavy metals from leaching since the chemically strong phases kept the material structure stable from chemical attack. In addition, it is also possible that heavy metals are chemically incorporated into the stable phases. Therefore, the mechanism could be inferred as follows:

- (1) $\text{Ca}(\text{OH})_2$, which decomposes from 512 °C, changes to CaO [13].
- (2) CaClOH is decomposed at a temperature of more than 600 °C.
- (3) Heavy metals are incorporated into stable oxide forms containing Ca or Si, in which Ca could be derived from reactions (1) or (2) and the colloidal silica solution could act as a source of Si.

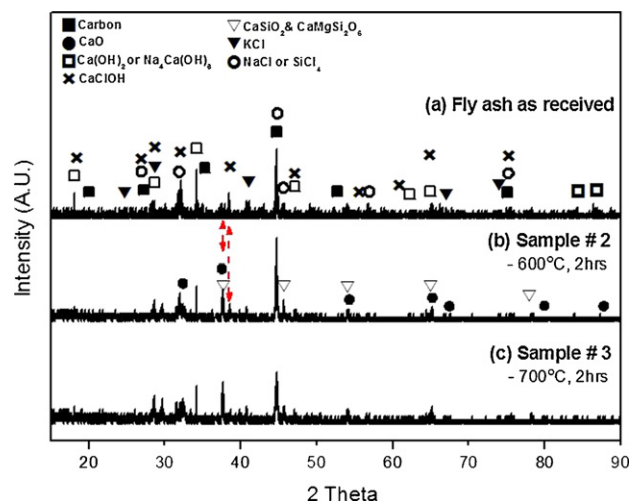


Fig. 4. X-ray diffractograms of the fly ash as received and the product treated by the colloidal silica solution (sample # 3).

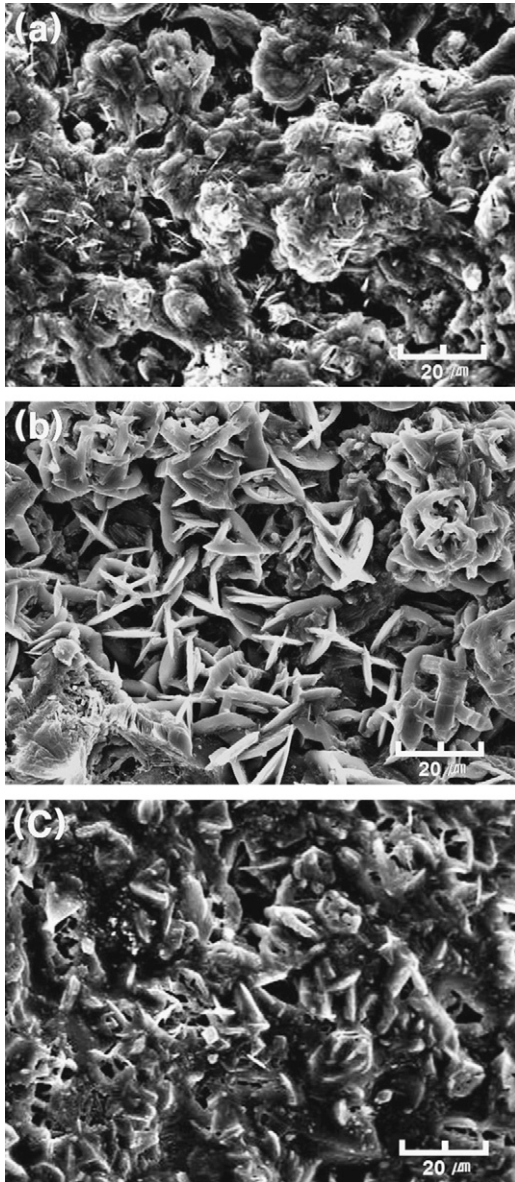


Fig. 5. Scanning electron micrographs after heat treatment for 2 h at (a) 600 °C, (b) 700 °C, and (c) 800 °C.

4. Conclusions

MSWI fly ash containing a large amount of chlorine can be stabilized using a colloidal silica solution. When a conventional cementation method was applied to fly ash with a ratio of 1:1

(Cement:Fly ash), the leaching of heavy metals was effectively restricted within $Pb^{2+} < 0.02$ ppm, $Zn^{2+} < 0.21$ ppm, and Cd^{2+} , Cr^{2+} , Cu^{2+} , $Mn^{2+} < 0.01$ ppm. Nevertheless, hydration reaction was not developed so that the cementation products remained friable powders.

The mixture of fly ash and a 4 wt.% colloidal silica solution was treated at 600, 700, and 800 °C for 2 h, as well as at 50 °C for 12 h and the results of the leaching tests showed that colloidal silica was effective in treating a chlorine-rich fly ash, $Pb^{2+} < 0.02$ ppm, $Zn^{2+} < 0.52$ ppm, and Cd^{2+} , Cr^{2+} , Cu^{2+} , $Mn^{2+} < 0.01$ ppm in the treatments at 700 and 800 °C. From the analyses of the phases and the leached concentrations of heavy metals before and after treatment, the stability improvement is due to a reduction in the chemically weak phase (CaClOH) and the formation of durable phases containing Ca and Si formed more than 600 °C. On the other hand, cementation products induced as references were not suitable for stabilization despite of their good chemical characteristic because they did not develop sufficient strength to solidify fly ash but remained friable powders.

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