

Immobilization of Heavy Metals in Municipal Solid Waste Incineration (MSWI) Fly Ash by using Pozzolanic Bottom Ash

Kyushu University Graduate School • Student Member • Dania Labira
 Kyushu University • Member • Mitali Nag
 Kyushu University • Fellow Member • Takayuki Shimaoka

1. Introduction

Municipal solid waste incineration (MSWI) is a common technology used in developed countries for waste treatment. In Japan, about 90% of solid waste generated was processed using incineration technology. The total amount of incineration residues was 8.03 mt/y, including 20 – 30% of fly ash (FA) and 70 – 80% of bottom ash (BA) (MOE, 2022). FA is considered hazardous waste due to the presence of high concentrations of leachable heavy metals such as Zn and Pb. Japanese standard limit of landfill disposal is < 0.3 mg/L for Pb (Nag & Shimaoka, 2023). Common treatments for FA stabilization are melting, sintering, cement solidification, acid extraction, and chelating reagents (Zacco et al., 2014), which is also stipulated by Japanese law. Most of the techniques are efficient but require raw materials and energy consumption.

BA which is also MSWI residue that either disposed in landfills or reused in civil engineering applications. BA in coarse particles contains crystalline silica oxide (mainly quartz), which is non-reactive and suitable for reuse in the construction field (Loginova et al., 2019). This makes BA, particularly in larger particles, reused as bulk fill for road construction, but the residual or finer fraction of BA is unused and then disposed of in a landfill. Due to the essential components contained in BA, it is feasible to reuse BA for heavy metal immobilization, involving carbonation and pozzolanic reactions. Fine particles of BA is rich in pozzolans, such as amorphous silica and alumina, and with the presence of calcium ions can promote heavy metals immobilization involving carbonation and pozzolanic reaction (X. G. Li et al., 2018). Pozzolanic product, i.e., C-S-H gel is able to adsorb or entrap heavy metals, while carbonation reaction produces pH reduction with consequent heavy metal immobilization in FA (Assi et al., 2019; Bosio et al., 2014; Onyelowe et al., 2021).

In the present study, fine fractions of BA are used for heavy metal immobilization in FA. The simplicity of the proposed technology, which only requires wastes produced from the same incineration plant, has objectives: (1) to investigate the role of pozzolans in fine fractions of BA to immobilize heavy metals in FA; (2) reuse residual or fine fractions of BA; (3) obtain a new simple method for FA stabilization, with cost-effective and environmentally-friendly materials; (4) produce new material that is suitable for safe disposal; (5) reduce the amount of MSWI waste going to the landfill; (6) produce new material that may be reused for other purposes such as filler (Rodella et al., 2016).

2. Material and Method

a. Sample preparation

Untreated BA and FA were collected from incineration plant R located in the city of Fukuoka, Japan. To remove the moisture, FA was oven dried at

60 °C for 24 hours, while bulk BA was dried at room temperature. BA was sieved into two different particle size fractions (< 0.25 mm and < 2 mm) and ground by a mechanical milling machine for about 3 minutes till it reached homogenous size with FA.

The experiment was performed as shown in Table 1, by mixing ratio of FA: BA: Water = 10:1:10, mixed for 25 minutes with a magnetic stirring device. Each prepared sample was divided in two halves, one half was placed in the oven for 4h at 120°C (oven-dry), while the other half was dried at room temperature (air-dry). For analysis, the samples were kept open at room temperature and settled for 4, 8, 16, 30, and 60 days after mixing.

b. Sample characterization

The initial condition of raw FA and BA were determined by X-ray fluorescence (XRF) for their elemental composition, by X-ray diffractometry (XRD) for their mineral phase, by inductively coupled plasma optical emission spectroscopy (ICP-OES) for Pb and Zn concentration in their leachate using standard Japanese leaching test (JLT-46). After FA is stabilized by BA, Pb and Zn immobilization efficiency were analyzed by ICP-OES, XRD, and scanning electron microscope coupled with an energy dispersive X-ray (SEM-EDX).

3. Result & Discussion

a. Chemical composition of raw FA and BA

According to XRF result in Table 2, Si, Ca, and Cl were the major elements in FA, the contents of which were over 10 wt.%. In BA, Si, Ca, and Al were the major elements. Among heavy metals, Zn and Pb are the most abundant elements. Considering the environmental toxicity, these two metals were selected as the main target in this study. Similar to Pb²⁺, Zn²⁺ may react with substances like oxygen or acids to form potentially toxic compounds, but Zn in metallic form is relatively harmless (Nag et al., 2022).

Table 1. Experiment condition

	BA	FA	Water	Mixing
Fraction	Mass (g)	Mass (g)	Volume (mL)	Time (mins)
< 0.25 mm	25	250	250	25
< 2 mm	25	250	250	25

Table 2. Chemical composition of raw FA and BA

Sample	Elements (wt%)												
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	P ₂ O ₅	CaO	MgO	Na ₂ O	K ₂ O	Cl	S	F
FA	11.7	2.35	0.69	0.58	0.03	0.54	40.0	2.46	6.53	2.99	24.52	2.13	0.07
BA <0.25 mm	23.5	9.82	3.90	2.29	0.14	2.77	42.5	2.46	1.85	0.75	2.88	0.59	0.03
BA <2 mm	13.3	7.70	6.18	2.11	0.10	2.68	55.5	2.53	1.76	0.58	3.80	0.93	0.03
Sample	Trace elements (ppm)												
	Zn	Cu	Pb	Cr	Ni	Ba	Sb	Sn	Sr	As	V	Cd	Co
FA	14820	1060	3595	120	40	930	1235	10	180	20	0	225	0
BA <0.25 mm	6730	5560	1480	560	240	2830	140	80	410	10	5	120	10
BA <2 mm	4720	1335	555	420	140	3095	150	60	450	4	4	145	10

b. Leaching test of stabilized FA

Pb and Zn concentrations in raw FA were initially 113.73 and 7.41 mg/L, respectively, and the initial pH of raw FA sample was 12.6. The effects of BA fractions (<0.25 mm and <2 mm) on Pb and Zn immobilization were investigated under air-dry and oven-dry with settling times until 60 days as shown in Figure 1. The highest efficiency was achieved using BA $d < 0.25$ mm with air-dry treatment. More than 99 and 96% of Pb and Zn immobilization achieved after 16 days, respectively. Depending on the particle size, BA $d < 2$ mm successfully immobilized Pb and Zn as well, but with slower progress than BA $d < 0.25$ mm. Oven-dry could accelerate the prompt initiation of carbonation, but air-dry exhibits better immobilization of Pb and Zn in a relatively longer settling time accords with previous studies (Assi, Bilo, Zanoletti, et al., 2020). Finest fraction of BA gave a faster immobilization in this study.

c. Mineralogy of stabilized FA

The mineral phases of raw FA and BA identified by XRD are shown in Figure 2(a). In FA sample, halite, sylvite, and calcium chloride hydroxide were the major mineral phases. In BA sample, quartz and Ca-rich minerals such as calcite, lime, and hydrocalumite were the major mineral phases. However, in the stabilized sample shown in Figure 2(b), the peaks originally found in raw ashes such as lime, portlandite, and calcium chloride hydroxide disappeared, while new calcite peaks appeared, suggesting that phases have reacted with CO_2 , and silica and/or alumina contained in the BA, thus carbonation reaction occurred (X. Li et al., 2007). New aluminosilicate minerals (i.e., kozoilite, stilbite), which may be formed from reactions occur in an amorphous matrix (Assi et al., 2020).

d. Microstructural of stabilized FA

As shown in Figure 3(a) and (b), a clear difference between FA before and after stabilization can be seen by FA round particle covered with new structures of C-S-H after stabilization. In the same sample, fibres structures with approximately 1 – 2 μm long and flake structures were found in the stabilized sample shown in Figure 3(c). It is suggested that C-S-H in fibres or needle shape crystals exhibited with a size of 0.5–2 μm long and <0.2 μm wide (Hilal, 2016). At a lower magnification, C-S-H with dense structure or assembled grains-like seems to be easily identified in the same observed sample as shown in Figure 3(d). Calcium silicate hydrate (C-S-H) gel observed by scanning electron microscopy (SEM) is not uniformly distributed on the microscopic scale and exists in various shapes such as fibres, flakes, honeycombs, and tightly assembled grains (Li, 2011), which also accords in this study.

4. Conclusion

MSWI BA has the potential to immobilize heavy metals in FA, particularly Pb and Zn, as it contains pozzolans. The highest Pb and Zn immobilization was using BA

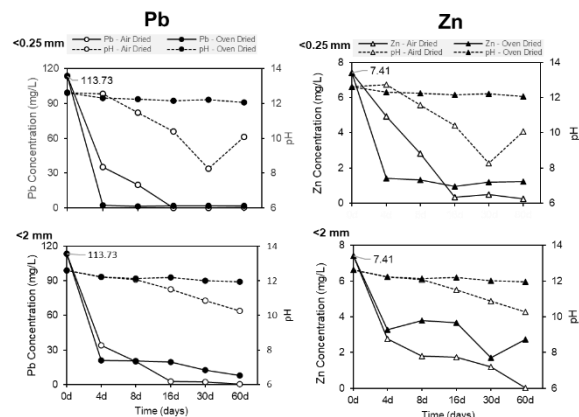


Figure 1. Pb and Zn immobilization in FA by BA (<0.25 and <2 mm)

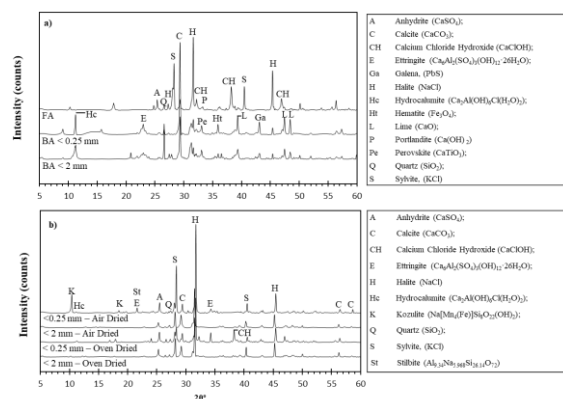


Figure 2. XRD pattern of (a) raw FA and BA; (b) stabilized sample

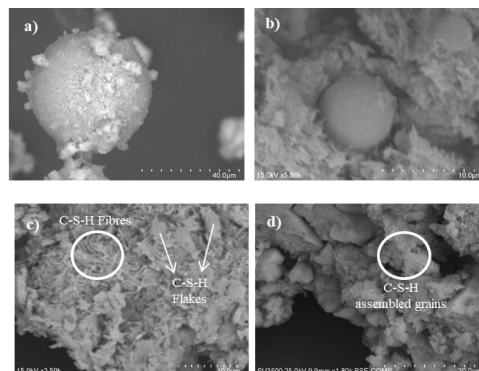


Figure 3. SEM images of (a) raw FA; (b) stabilized FA by BA; (c) C-S-H in stabilized FA 3500 \times ; and (d) C-S-H in stabilized FA 5500 \times magnification

$d < 0.25$ mm in air-dry condition. Oven-dry could accelerate the initiation of immobilization, but air-dry exhibits better immobilization of Pb and Zn in a relatively longer settling time. Pozzolanic and carbonation reactions are thought to be heavy metals immobilization mechanisms. Pozzolanic reaction product, structures of C-S-H gel (calcium silicate hydroxide), was identified by SEM-EDX analysis. Carbonation was contributed, as evidenced by pH reduction in the leaching solution and formation of calcite (CaCO_3). For further optimizations, BA $d < 0.25$ mm and air-dry with different L/S ratio and FA/BA ratio is under study.