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Solidification of Heavy Metals in Waste Incineration Fly Ashes with Silica-Alumina Composite

Yiqiong Lu[1,2*], Miao Li[3]

[1] School of Environment and Natural Resources, Renmin University of China, Beijing 100086, China
[2] Department of Work Safty and Environmental Protection, China Energy Investment Corporation Limited, Beijing 100011, China
[3] Development Research Center of the Ministry of Water Resources of P.R.China, Beijing 100038, China

Corresponding Author Email: yiqiong.lu@chnenergy.com.cn

ABSTRACT

This paper replaces the ordinary Portland cement with water-quenched granulated blast furnace slags (WQGBFSs), a silica-alumina composite, for solidification of waste incineration fly ashes (WIFAs), and explores the solidification effects of solidified bodies cured for different ages of heavy metals under the excitation of sulfates. The test blocks were subjected to analysis through X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and thermogravimetry and differential scanning calorimetry (TG-DSC). The results show that the silica-alumina composite outshines the ordinary Portland cement in solidification of heavy metals like Pb and Cd; the test block containing 15 % WIFAs, 70 % WQGBFSs and 15 % flue gas desulfurization gypsum (FGDG) reached the compressive strength of 43.67MPa after being cured for 28d, and had much lower leaching concentrations of heavy metals (e.g. Pb, Cd, Hg and Cr) than the limits in the drinking water standard; the main hydration products of the cementitious system are the calcium silicate hydrate (C-S-H) and ettringite (Aft); the hydration products have strong solidification effects of heavy metal ions.

1. INTRODUCTION

The production of domestic waste in China is growing at an alarming annual rate of 8~10 %, due to the rapid growth of the economy and living standards. Most of the waste is disposed of through incineration, which has a prominent waste reduction effect. However, the incineration of domestic waste will produce fly ash, equivalent to 3~5% of the original waste in mass. When the fly ash passes through the flue, it will be enriched with heavy metals like Pb, Cd, Cr and Hg. All these heavy metals are defined as hazardous wastes at home and abroad, posing a severe threat to the eco-environment. Hence, the fly ash produced by the incineration of domestic waste should be stabilized and solidified. In recent years, much research has been done on the solidification of this type of fly ash.

Galiano et al. [1] introduced the solidification of municipal solid waste incineration (MSWI) fly ash, which contains hazardous metals such as Pb, Cd, Cr, Zn or Ba, through geopolymerization. Different reagents such as sodium hydroxide, potassium hydroxide, sodium silicate, potassium silicate, kaolin, metakaolin and ground blast furnace slag were used to explore the potential of geopolymers as waste solidifiers.

Alba et al. [2] discussed the stabilization/solidification process with Portland cement applied to municipal solid waste incineration residues. Two types of residues were considered: fly ash produced in an electrostatic precipitator, and air pollution control (APC) residues from a semi-dry scrubber process. Cement pastes with different percentages of the two types of residues were characterized based on their physical

properties, the effect of the hydration products and their leaching behavior. The results show that the Portland pastes prepared with APC residues set faster than those prepared with fly ash residues; heavy metals like Zn, Pb and Cd and sulphates were immobilized within the pastes, whereas chlorides were only partially retained.

Yu et al. [3] explored the solidifying effect of cement addition on municipal solid waste incineration fly ash, the interaction of the fly ash with cement and water, and the leaching of heavy metals from cement-solidified fly ash. Mi Kufová et al. [4] dealt with certain problems arising in the solidification process of municipal solid waste fly ash by cementation, described the stabilization efficiency of two kinds of binders, namely, slag cement and waste containing alumina and silica, and tested the leachability and compressive strength of original and solidified samples.

Yakubu et al. [5] evaluated the potential of municipal solid waste incineration fly ash samples to solidify/stabilize the heavy metal (Cu, Pb, Zn, Cr, Cd, As and Mn) contents, when leached under different pHs. It was assumed that the concentration of a heavy metal in the leachate is negatively correlated with its solidification/stabilization. The research results show that the raw fly ash contained high levels of heavy metals, which exceed the acceptable limits; extremely acidic conditions favored heavy metal leaching compared to extremely alkaline conditions; the extent of solidification/stabilization of heavy metals was generally low under highly acidic conditions (pH$\leq$4), but increased with the increasing pH; all the metals solidified/stabilized in pH media of 5~11, except Zn which was detected in the entire pH range. Hence, the pH environment is affected by changes in landfill

conditions, and heavy metal leaching will increase at pH≤4.

Shao et al. [6] tested the fly ash stabilization and solidification by an alkali activated blast furnace slag-based cementitious material. Diaz-Loya et al. [7] introduced the municipal solid waste incineration fly ash to industrial construction, where human exposure potential is limited, the chemical properties of the samples were fully analyzed by X-ray fluorescence (XRF), X-ray diffraction (XRD) and inductive coupled plasma (ICP), and leachability of the contaminants before and after the activation was monitored by EPA's Toxicity Characteristic Leaching Procedure (TCLP). Su et al. [8] investigated the effects of magnesium potassium phosphate cement (MKPC), a novel agent for solidification/stabilization of heavy metals, on different heavy metals.

Anastasiadou et al. [9] attempted to increase the mechanical properties of fly ash with different amounts of ordinary Portland cement (OPC) as a binder, and proved with the solidified matrix that the cement is able to immobilize the heavy metals found in fly and bottom ash. Hou et al. [10] tested and analyzed the chemical composition, content and leachability of heavy metals in municipal solid waste incineration fly ash. The results show that the leachability of Pb and Cr exceeds the leaching toxicity standard, making the fly ash a hazardous waste that must be solidified. Therefore, these scholars examined the effects of cement in solidifying municipal solid waste incineration fly ash.

Rémond et al. [11] analyzed the physical, chemical and mineralogical features of municipal solid waste incineration fly ash, and introduced these features into a model; then, the simplified quantitative mineralogical composition was proposed for the ash; the performance features like setting time, compressive strength and shrinkage were studied for ash-containing mortars. Cyr et al. [12] evaluated the functional and environmental properties of ternary and quaternary binders using cement, metakaolin, and two industrial by-products from combustion processes (i.e. municipal solid waste incineration fly ash and sewage sludge ash).

Aubert et al. [13] examined the features of a treated ash and its use in concrete. The leaching tests carried out on the concrete confirm that the ash treatment can obtain materials with no major environmental risk. Shi and Kan et al. [14] verified the feasibility of applying municipal solid waste incineration fly ash as an auxiliary cementitious material, and tested the water demand of the fly ash for normal consistency, setting time, volume stability, as well as flexural and compressive strength; the results show that the addition of common mineral admixtures enhanced the strength of solidified body, and the immobilizing effect of heavy metals.

Wang et al. [15] investigated the feasibility of clinker production of municipal solid waste incineration fly ash based on cement. The tested fly ashes were washed and reused as raw material, with dosage of 1 % of cement raw material (w/w). The fly ash washing process was optimized to maximize the extraction of chloride and sulphate. The cement thus obtained is qualified for actual use. Tang et al. [16] studied the solidification/stabilization of fly ash containing heavy metals using the Portland cement as a binder, and demonstrated the significant impacts of the cement/fly ash ratio and curing time on the mechanical properties of cement.

Iretskaya et al. [17] introduced a new phosphorylation process leading to hydroxylapatite formation, which can effectively remove the heavy metals in municipal solid waste incineration fly ash. Massardier et al. [18] compared the retention properties of different polymers and those of concrete and polymer-concrete double barrier materials, and opened new perspectives for the use of plastic waste for fly ash solidification.

Drawing on the above studies, this paper replaces the ordinary Portland cement with water-quenched granulated blast furnace slags (WQGBFSs), a silica-alumina composite, for solidification of waste incineration fly ashes (WIFAs), and probes deep into the solidification mechanism.

2. METHODOLOGY

2.1 Materials

(1) WQGBFS

The WQGBFSs were supplied by a steel plant in Tangshan, China. The original WQGBSFs were dried, removed of iron and then ground to the specific surface area (SSA) of 400 $m^2 \cdot kg^{-1}$. As shown in Table 1, about 90 % of the WQGBFSs were SiO_2, CaO and Al_2O_3. The remaining part consists of small amounts of FeO, MgO, Na_2O, K_2O, Fe_2O_3, etc. The X-ray diffraction (XRD) pattern of the WQGBFSs is displayed in Figure 1. The alkalinity coefficient and mass coefficient of the WQGBFSs are $Mo=(CaO+MgO)/(SiO_2+Al_2O_3)=1.78>1$ and $K=(CaO+MgO+Al_2O_3)/(SiO_2+MnO_2+TiO_2)=2.43>1.2$, respectively, indicating that the WQGBFSs are alkaline and highly active, as specified in *Granulated Blast Furnace Slag Used for Cement Production* (GB203.78).

(2) Flue gas desulfurization gypsum (FGDG)

The FGDG was provided by a thermal power plant in Hebei Province, China, and dried at 40°C. CaO and SO_3 are the top two components in the FGDG, followed in descending order by SiO_2, MgO and Al_2O_3. The main chemical components and XRD pattern of the FGDG are displayed in Table 2 and Figure 2, respectively. It can be seen that the FGDG mainly consists of $CaSO_4 \cdot 2H_2O$. After 5min grinding, the SSA of the FGDG reached 480m^2/kg.

(3) WIFAs

The WIFAs were collected from a municipal waste incineration power plant in Hebei Province, China. The chemical components, heavy metal leaching results and XRD pattern of the original WIFAs are shown in Table 3, Table 4 and Figure 3, respectively.

Table 1. Chemical components of the WQGBFSs

Component	CaO	SiO₂	Al₂O₃	MgO	Fe₂O₃	TiO₂	MnO	SO₃
Content (%)	46.45	21.69	15.51	8.42	2.50	1.86	0.70	0.85

Table 2. Chemical components of the FGDG

Component	CaO	Cl	Na₂O	K₂O	SO₃	SiO₂	MgO	Al₂O₃	Fe₂O₃	ZnO	P₂O₅
Content (%)	35.47	0.338	0.027	0.162	37.4	2.07	1.1	1.03	0.332	0.006	0.023

Table 3. Chemical components of the WIFAs

Component	CaO	Cl	Na₂O	K₂O	SO₃	Al₂O₃	Fe₂O₃	ZnO	P₂O₅	Cr₂O₃	PbO
Content (%)	40.54	16.72	5.64	3.57	6.13	1.93	0.87	0.403	0.438	0.0152	0.0835

Table 4. Heavy metal leaching results of the original WIFAs (mg/L)

Element	Cd	Pb	Hg	As	Zn	Cu	Cr
Content (%)	2.36	3.45	0.005	0.003	28.71	4.93	<0.01
Standard for potable water	0.005	0.01	0.01	0.01	1	1	0.01
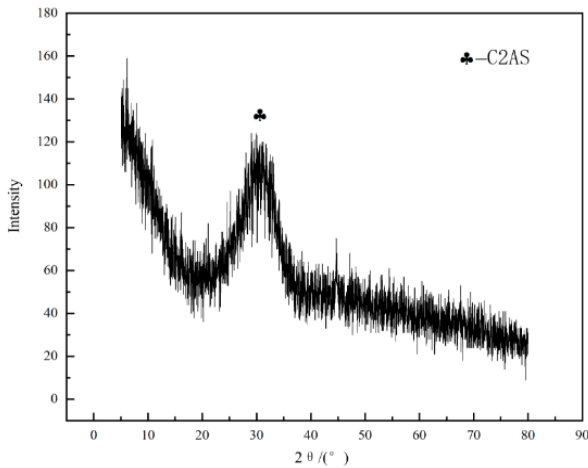
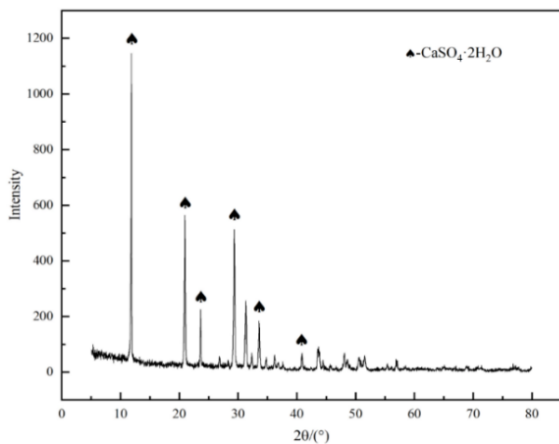**Figure 1.** The XRD pattern of the WQGBFSs

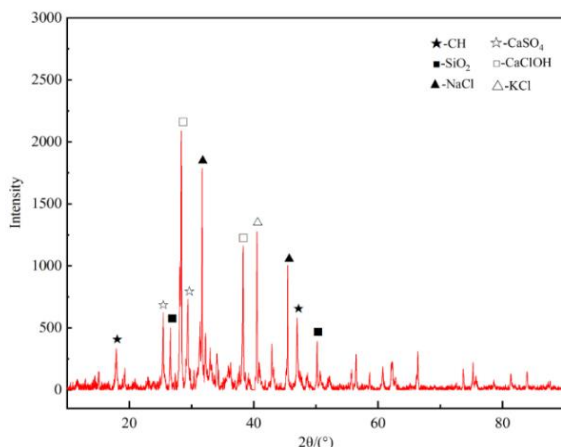**Figure 2.** The XRD pattern of the FGDG

Figure 3. The XRD pattern of the WIFAs

2.2 Experimental plan

Before replacing cement with the WQGBFSs for WIFAs solidification, 30mm×30mm×50mm test blocks were prepared by the mix ratios in Table 5, and cured at the temperature of 35±1℃ and the humidity of 95 %. The compressive strength and leaching toxicity of each test block were measured at preset ages.

Table 5. Mix ratios of test blocks

Serial number	WIFAs	WQGBFSs	FGDG	Water-binder ratio
A	10	75	15	0.3
B	15	70	15	0.3
C	20	65	15	0.3

2.3 Heavy metal leaching test

The leaching toxicity was measured by the Chinese national standard *Solid Waste: Extraction Procedure for Leaching Toxicity: Horizontal Vibration Method* (HJ557-2009). First, each sample was crushed until all the particles could pass through a sieve of 3mm pore size. Next, 10g dry sample was weighted and placed in a 250mL extraction flask, and the extractant was added to the flask at the liquid-to-solid ratio of 10:1 (L/kg). After that, the flask was fixed vertically on a horizontal vibrator, and vibrated for 8h at room temperature. Then, the flask was removed and allowed to stand for 16h. The leach liquor was filtered by a pressure filter with a 0.45µm microporous membrane. The filtered liquor was collected, and shaken evenly for analysis.

According to *Identification Standards for Hazardous Wastes* (GB5085.3-2007), the heavy metal contents in the leach liquor were measured by an ICAP-9000 inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Jarrel-ASH, US).

3. EXPERIMENTAL RESULTS AND ANALYSIS

3.1 Effects of WIFAs content on compressive strength of test blocks and leaching concentrations of heavy metals

The mechanical properties of the test blocks have a significant effect of the long-term stability of the solidified body, and the solidification effect of chloride ions and heavy metal ions. Figure 4 shows the effects of WIFAs content on compressive strength of test blocks at different ages. Table 6 presents the effects of WIFAs content on the leaching concentrations of heavy metals of the solidified body.

As shown in Figure 4, with the growing content of the WIFAs, the compressive strengths of 7d and 28d test blocks both increased first and then declined, while the compressive

strength of 3d test block continued to grow. The changing trends can be explained as follows: the WIFAs have an abundance of CaO; with the addition of the WIFAs, the CaO content surges up in the cementitious system, which facilitates the hydration reaction; thus, the compressive strength of the test block will increase in the early phase. With the extension of the curing age, the hydration products are distributed unevenly across the cementitious system, as the hydration is accelerated by the CaO. As a result, numerous pores appear inside the test block, reducing the compressive strength.
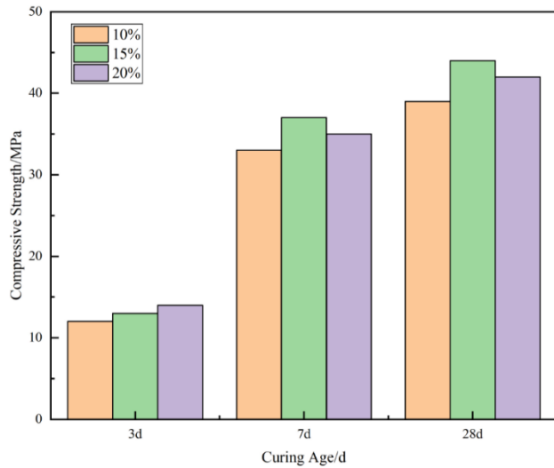

Figure 4. Effects of WIFAs content on compressive strength of test blocks at different ages

Table 6. Leaching concentrations of heavy metals in 28d test block (μg/L)

Element	Cd	Cr	Hg	Pb	Zn	Cu
Leaching concentration (%)	0.02	13.21	0.07	1.98	2.02	20.05

As shown in Table 6, the silica-alumina composite with WQGBFSs and FGDG as the main materials exhibited a good solidification effect of the heavy metals in the WIFAs. Compared with the original WIFAs sample, the 28d test block achieved much lower leaching concentrations of heavy metals, which is far below the limits on these heavy metals in the drinking water standard.

3.2 Analysis of hydration mechanism

(1) XRD analysis of test blocks

Figure 5 displays the XRD patterns of silica-alumina composite test blocks at different ages. It can be seen that the main component in the test blocks cured for 3d, 7d and 28d was calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$), hydrocalumite ($Ca_4Al_2O_6Cl_2 \cdot 10H_2O$, $Ca_2Al(OH)_6Cl \cdot 2H_2O$) and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$), respectively. The convex hulls near 30° are the diffraction peaks of the low crystallinity or amorphous calcium silicate hydrate (C-S-H) produced through hydration of the silica-alumina composite in the cementitious system. The Ca^{2+} ions produced through the hydration can be replaced by heavy metal ions with the same valence number, such that some heavy metal ions enter the silicon-oxygen tetrahedra and aluminum-oxygen tetrahedra in the C-S-H to balance the electrical charges.

With the occurrence of hydration, a large amount of hydrocalumite was formed in the cementitious system. This is because the WIFAs contain lots of chlorides, which can react with the CaO in the WQGBFSs and the WIFAs. In addition, a certain amount of ettringite (Aft) is formed in the cementitious system, under the excitation of SO_4^{2-} in the FGDG.
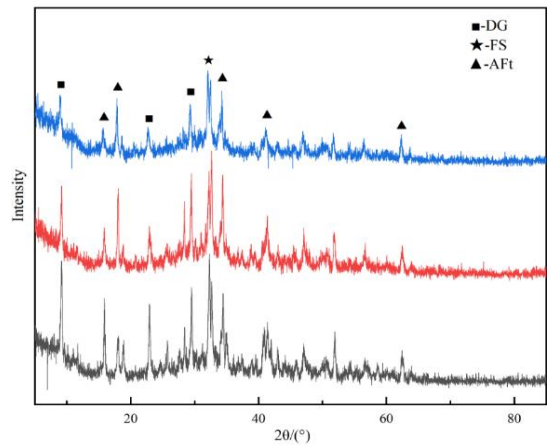

Figure 5. The XRD patterns of test blocks at different ages

(2) Fourier transform infrared spectroscopy (FT-IR) analysis of test blocks

Figure 6 provides the FT-IR patterns of the test blocks cured for 3d, 7d and 28d, respectively. Obviously, the three test blocks had basically the same peak shape. Specifically, the peaks at 3,411.87cm^{-1} and 1,623.57cm^{-1} are the characteristic peaks of the hydroxyl (O-H) bond in the C-S-H gel and the AFt. The former is the stretching vibration absorption peak of H_2O, which is relatively strong because ettringite has 26 water molecules in its chemical formula, and the latter belongs to the asymmetric stretching vibration band of CO_3^{2-}, which is possibly caused by the carbonization during sample preparation.

The peaks at 1,127.22 cm^{-1} and 983.58 cm^{-1} are the characteristic absorption peaks of silicates, which results from the asymmetric stretching vibration of Si-O bond in silicon-oxygen tetrahedra. The 983.58 cm^{-1} peak is also the characteristic peak of C-S-H gel. With the increase of hydration time, the transmittance near 1,127.22 cm^{-1} decreased, indicating the gradual formation of silicates like C-S-H gel.
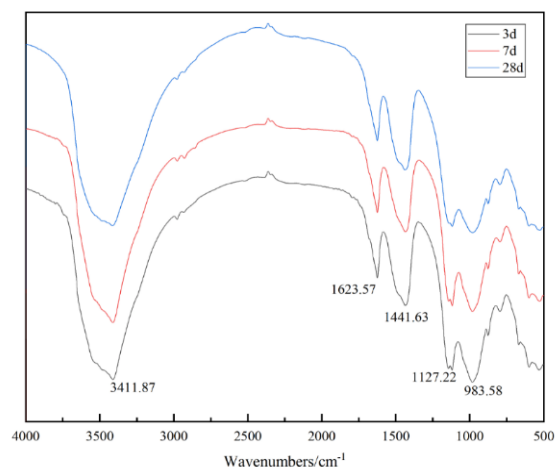

Figure 6. The FT-IR patterns of test blocks at different ages

(3) Thermogravimetry and differential scanning calorimetry (TG-DSC) analysis of test blocks

Figure 7 offers the TG-DSC curves of 28d silica-alumina composite test blocks. It can be seen that the test block lost much of its weight at around 70℃, corresponding to the endothermic peak of 123.6℃. The weight loss caused by this endothermic peak accounts for a large proportion of the total weight loss. This is mainly attributable to the loss of CO_2 and the dehydration of CSH gel, ettringite and Friedel's salt. The WIFAs test block had an endothermic peak at around 365.7°C, corresponding to the dehydroxylation of the Friedel's salt. This means the reaction generates aluminate hydration product.
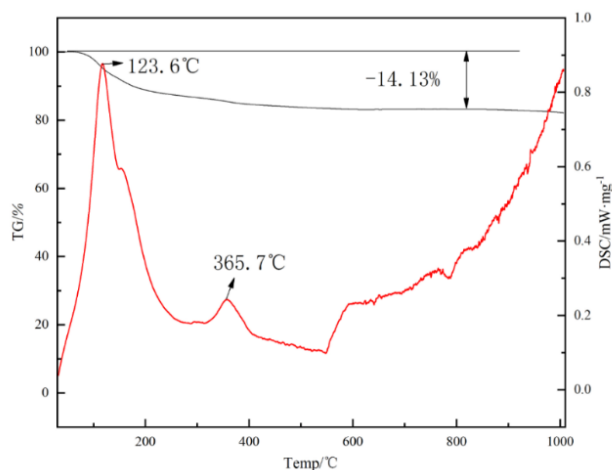

Figure 7. TG-DSC curves of 28d silica-alumina composite test blocks

4. CONCLUSIONS

(1) The silica-alumina composite has a significant solidification effect on the heavy metal ions in the WIFAs. The test block containing 15% WIFAs, 70% WQGBFSs and 15% FGDG reached the compressive strength of 43.67MPa after being cured for 28d, and had much lower leaching concentrations of heavy metals than the limits in the drinking water standard.

(2) The WIFAs greatly boost the hydration of the silica-alumina composite. In the cementitious system, the main hydration products are the C-S-H gel and the AFt. The C-S-H gel and various sulfate-containing double salts have strong solidification effects of heavy metal ions.

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