



# Article Solidification/Stabilization of MSWI Fly Ash Using a Novel Metallurgical Slag-Based Cementitious Material

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Abstract: Four industrial wastes, i.e., blast furnace slag, steel slag, desulfurization ash, and phosphoric acid sludge, were used to prepare a low-carbon binder, metallurgical slag-based cementitious material (MSCM). The feasibility of solidification/stabilization of municipal solid waste incineration (MSWI) fly ashes by MSCM were evaluated, and the immobilization mechanisms of heavy metals were proposed. The MSCM paste achieved 28-day strength of 35.2 MPa, showing its high-hydration reactivity. While the fly ash content was as high as 80 wt.%, the 28-day strength of MSCM-fly ash blocks reached 2.2 MPa, and the leaching concentrations of Pb, Zn, Cr, and Hg were much lower than the limit values of the Chinese landfill standard (GB 16889-2008). The immobilization rates of each heavy metal reached 98.75-99.99%, while four kinds of MSWI fly ashes were solidified by MSWI at fly ash content of 60 wt.%. The 28-day strength of binder-fly ash blocks had an increase of 104.92–127.96% by using MSCM to replace ordinary Portland cement (OPC). Correspondingly, the lower leachability of heavy metals was achieved by using MSCM compared to OPC. The mechanisms of solidification/stabilization treatment of MSWI fly ash by MSCM were investigated by XRD, SEM, and TG-DSC. Numerous hydrates, such as calcium silicate hydrate (C-S-H), ettringite (AFt), and Friedel's salt, were observed in hardened MSCM-fly ash pastes. Heavy metals from both MSWI fly ash and MSCM could be effectively immobilized via adsorption, cation exchange, precipitation, and physical encapsulation.

Keywords: metallurgical slags; cementitious material; fly ash; solidification/stabilization; heavy metals

# 1. Introduction

The incineration of municipal solid wastes can remarkably reduce the volume of wastes, save a large amount of land for landfill disposal, as well as recover energy to generate electric power. Thus, it has become the most widely adopted method in China to dispose municipal solid wastes. In the years of 2011–2020, the number of municipal solid waste incineration (MSWI) plants in China rose by 303%, and the incineration capacity increased from 32,485 to 124,076 kilotons, accounting for 51.2% of treated municipal solid wastes in 2020 [1]. However, the incineration of municipal solid wastes produces secondary solid residues, including MSWI fly ash with high contents of toxic heavy metals [2–4]. MSWI fly ash, classified as hazardous waste in many countries, must be carefully disposed to meet certain standards before its landfill, owing to the severe negative impact on the environment and human health [4,5].

The cement-based solidification/stabilization is a typical process to immobilize toxic heavy metals in MSWI fly ashes [6–8]. The ordinary Portland cement (OPC) is a widely



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). used cementitious binder to dispose MSWI fly ashes due to low cost, large quantities, and acceptable heavy metal immobilization efficiency [9,10]. However, the compressive strength of OPC-fly ash blocks may decrease remarkably at the high content of MSWI fly ash [11]. Long-term safety of OPC solidified MSWI fly ash has caused great attention. It has been reported that the leachability of heavy metals in OPC-fly ash blocks increased significantly after six years of natural aging [12]. Additionally, the manufacture of OPC has aroused some environmental issues, e.g., massive CO<sub>2</sub> emission, intensive energy consumption, and emission of acid gas [13,14]. Therefore, it is necessary to find a low-cost, highly efficient, and environmentally friendly cementitious binder to replace OPC.

In recent years, cementitious materials produced from metallurgical slags have been used as alternative low-carbon binders to dispose various hazardous wastes [15,16]. Metallurgical slags, such as blast furnace slag (BFS) and steel slag (SS), are used as major raw materials to produce these cementitious binders. Thus, these binders are more environmentally friendly than OPC with various merits of lower carbon footprint, waste reuse, and lower cost. On the other hand, it has been reported that these cementitious materials can achieve higher mechanical strength of solidified fly ash blocks and lower leachability of heavy metals than the OPC [17]. Therefore, the replacement of OPC with cementitious materials produced from metallurgical slags has caused great concerns in the solidification/stabilization of MSWI fly ash.

Currently, most cementitious materials are fabricated by using BFS, SS, and desulfurization gypsum as major raw materials, and are widely used as cheap binders in building construction, mine backfill, and solidification/stabilization of hazardous wastes [18,19]. Thus, the BFS and desulfurization gypsum have become widely used raw materials with high utilization ratios and increased sale prices in China. Therefore, it is very meaningful to produce a low-cost metallurgical slag-based cementitious materials for the solidification/stabilization of hazardous wastes by using industrial wastes with low utilization ratios. Phosphoric acid sludge (PAS) with a high content of  $P_2O_5$  is a precipitate obtained from the production of wet phosphoric acid [20,21]. Soluble phosphoric salts remain in PAS. However, it contains a high content of F element, resulting in the PAS as a refractory solid waste. The desulfurization ash (DA) is collected during the dry desulphurization of flue gas [22,23]. Its main phases are anhydrous calcium sulfate and calcium sulfite. Additionally, heavy metals, such as Pb and Zn, are usually concentrated in DA [22]. Currently, both PAS and DA have low utilization ratios, and most of them are piled in factories in China.

In this paper, four industrial wastes, i.e., BFS, SS, DA, and PAS, are used as raw materials to produce a novel metallurgical slag-based cementing material (MSCM) for the solidification/stabilization of MSWI fly ash. The feasibility of solidification/stabilization of MSWI fly ash by using novel MSCM to replace OPC was fully investigated. The aims of this work include: (1) to evaluate the solidification/stabilization performance of MSWI fly ashes collected from four cities by MSCM; (2) to compare the solidification/stabilization of MSWI fly ash by using MSCM and OPC as the binder, respectively; (3) to investigate the immobilization mechanisms of heavy metals in MSCM-fly ash blocks with XRD, SEM and TG-DSC.

## 2. Materials and Methods

#### 2.1. Materials

The blast furnace slag (BFS), steel slag (SS), and desulfurization ash (DA) were collected from Wuhan Metal Resources Company in Hubei Province, China. The phosphoric acid sludge (PAS) was provided by China City Environment Protection Engineering Limited Company. The received BFS, with a specific surface area of 530 m<sup>2</sup>/kg, was directly used without further treatment. The granular SS, with a particle size of <10 mm, was ground to be a specific surface area of 550 m<sup>2</sup>/kg using a ball mill (SM500 × 500). The DA, with a specific surface area of 573 m<sup>2</sup>/kg, was dried at 105 °C for 4 h. The PAS with high water content was firstly dried at 105 °C for 10 h, then ground to be a specific surface area of 520 m<sup>2</sup>/kg. The OPC used was 32.5<sup>#</sup> ordinary Portland cement. Four kinds of MSWI fly ashes were collected from MSWI plants in Wuhan, Baoding, Beijing, and Tangshan cities in China and were nominated as FA1, FA2, FA3, and FA4 in this study, respectively.

The chemical compositions and heavy metal contents of raw materials to prepare MSCM are given in Table 1, respectively. The XRD patterns of raw materials are shown in Figure S1. The main crystalline phases of DA were calcite, anhydrite, and calcium sulfite. Typical crystalline lines of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) were not observed. The PAS contained calcite and calcium sodium phosphate as the main crystalline phases. As shown in Table 1, the P<sub>2</sub>O<sub>5</sub> content of PAS reached 21.76 wt.%, indicating that soluble phosphorous salts can immobilize heavy metals by forming insoluble metal phosphates [24]. As given in Table 1, the contents of CaO, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> in raw materials to prepare MSCM were high, contributing to the formation of hydration products. Heavy metal (Zn, Cr, Pb and Hg) contents were very low for BFS and PAS. However, as shown in Table 1, the DA had high contents of Pb and Zn, and the Cr content was also high in SS. The results indicated that toxic Pb, Zn, and Cr elements from prepared MSCM would be incorporated into MSCM-fly ash blocks. Thus, heavy metals from both MSCM and MSWI fly ash should be considered together to evaluate the immobilization rates of heavy metals.

Table 1. Main chemical compositions and heavy metal content of raw materials to prepare MSCM.

De Matala	Components (%)								Heavy Metal Contents (mg/kg)				
Raw Materials	Fe <sub>2</sub> O <sub>3</sub>	$Al_2O_3$	SiO <sub>2</sub>	CaO	MgO	K <sub>2</sub> O	$P_2O_5$	SO <sub>3</sub>	F	Zn	Cr	Pb	Hg
Blast furnace slag (BFS)	1.07	15.73	35.03	36.61	8.59	0.01	0.36	0.09	_	16.67	36.91	0.06	0.32
Steel slag (SS)	26.32	4.3	14.17	38.96	8.22	0.01	1.29	0.18	-	39.75	442.30	1.26	0.17
Desulfurization ash (DA)	5.65	0.83	2.12	32.23	0.83	3.2	0.83	17.44	-	192.20	27.45	2412.81	2.35
Phosphoric acid sludge (PAS)	0.48	1.14	4.73	44.52	1.56	0.32	21.76	0.39	14.67	50.95	3.84	4.22	0.01

#### 2.2. Preparation of Binder-MSWI Fly Ash Blocks

The MSCM was produced by optimizing the mass ratio of PAS:SS:DA:BFS at 20 wt.%:32 wt.%:12 wt.%:36 wt.% with the results given in Table S1 At this mass ratio, pure MSCM paste achieved the highest hydration reactivity owing to the highest 28-day comprehensive strength. The MSCM-fly ash pastes were prepared by mixing the proportional fly ash and MSCM. Then, the water was added into the mixtures at water to solid ratios (w/s) of 0.35~0.55 to achieve similar flowability of different MSCM-fly ash pastes. After the mixing, the pastes were casted into steel molds (30 mm  $\times$  30 mm  $\times$  30 mm), and demolded after 24 h. The samples were cured at 20 °C and relative humidity of 90% in a standard curing box for three, seven, and twenty-eight days. The compressive strengths of the samples were measured according to the Chinese national standard, "Test method for strength of cement mortar" (GB/T 17671-1999). Three samples were tested to obtain the average value.

To investigate the effect of fly ash contents, eight groups of MSCM-fly ash blocks (D1, D2, D3, D4, D5, D6, D7, and D8) were prepared by using FA2 as typical MSWI fly ash at the mass proportions of 10 wt.%, 20 wt.%, 30 wt.%, 40 wt.%, 50 wt.%, 60 wt.%, 70 wt.%, and 80 wt.%, respectively. For comparative purposes, pure MSCM paste (0 wt.% of fly ash) was also prepared and assigned as the D0 sample in this study. To study the solidification/stabilization of different MSWI fly ashes by the MSCM, the mass proportions of fly ash were set at 40 wt.% and 60 wt.%, respectively, as given in Table 2. Additionally, the solidification/stabilization of FA1 was compared using MSCM and OPC as the binders, respectively. Two pastes, D0 (100 wt.% MSCM + 0 wt.% FA2) and D4 (60 wt.% MSCM + 40 wt.% FA2), were used to investigate the immobilization mechanisms of heavy metals. In this work, the proportions of binders and MSWI fly ash to prepare different fly ash blocks are summarized in Table 2. After the specified curing period, the crushed blocks

were put into anhydrous ethanol to stop the hydration reactions. The powers were collected and dried at 50  $^{\circ}$ C overnight for leaching tests and characterization measurements.

Fly Ash Blocks	Binder	Mswi Fly Ash	Proportion of Binder (wt.%)	Proportion of Mswi Fly Ash (wt.%)
D0	MSCM	FA2	100	0
D1	MSCM	FA2	90	10
D2	MSCM	FA2	80	20
D3	MSCM	FA2	70	30
D4	MSCM	FA2	60	40
D5	MSCM	FA2	50	50
D6	MSCM	FA2	40	60
D7	MSCM	FA2	30	70
D8	MSCM	FA2	20	80
H1-1	MSCM	FA1	60	40
H1-2	MSCM	FA1	40	60
H2-1	MSCM	FA2	60	40
H2-2	MSCM	FA2	40	60
H3-1	MSCM	FA3	60	40
H3-2	MSCM	FA3	40	60
H4-1	MSCM	FA4	60	40
H4-2	MSCM	FA4	40	60
OF-1	OPC	FA1	60	40
OF-2	OPC	FA1	40	60

Table 2. The proportions of binders and MSWI fly ash to prepare different fly ash blocks.

#### 2.3. Leaching Tests and the Characterization

According to the "Solid waste leaching toxicity method-acetic acid buffer leaching method" (HJ/300-2007), the acetic acid buffer method was conducted to leach heavy metals from as-received MSWI fly ashes and cured block samples. Dried block samples were first crushed to below 3 mm before the leaching tests. Samples of 100 g were mixed with buffered acetic acid (pH of 2.64) at a liquid to solid ratio of 20 L/kg. Then, the mixtures were tumbled using an end-over rotator for 18 h at a speed of 30 rpm. After the leaching, 10 mL of the extract was extracted and further filtered through 0.45  $\mu$ m glass fiber filter. The concentrations of heavy metals in the filtrated leachate were determined using inductively coupled plasma-mass spectrometers (ICP-MS, Shimadzu 2030, Shimadzu Corporation, Kyoto, Japan). The heavy metal immobilization rate in the binder-fly ash blocks was calculated as follows:

$$S(\%) = \left(1 - \frac{C_0 \times L}{\sum_i \left(r_i \times \beta_i \times M\right)}\right) \times 100\%$$
(1)

where, *S* was the immobilization rate of the heavy metal; *C*<sub>0</sub> was the heavy metal concentration in the leachate (mg/L); *L* was the volume of the leachate (L); *M* was the mass of the dried samples for the leaching test (kg);  $\gamma_i$  was the mass proportion of PAS, SS, DA, BFS, and fly ash in the block (%);  $\beta_i$  was the heavy metal content in PAS, SS, DA, BFS, and fly ash (mg/kg). Thus, the incorporation of heavy metals in raw materials for preparing MSCM into the blocks was fully considered to calculate the immobilization rates of heavy metals.

The X-ray powder diffraction (XRD) patterns of the samples were recorded by an X-ray diffractometer (D/Max-RC, Rigaku, Tokyo, Japan) with a Cu K $\alpha$  radiation at a scanning speed of 0.04 °/s and a diffraction angle of 5~80°. The thermogravimetric analysis (TGA, Rigaku Thermo plus, Tokyo, Japan) was performed on approximately 10 mg of crushed MSCM-fly ash blocks to determine the decomposition of the phases at high temperatures. The morphology and microstructures of cured pastes were observed by a field emission scanning electron microscope (SEM, Carl Zeiss, Oberkochen, Germany).

### 3. Results and Discussion

#### 3.1. Characterization of MSWI Fly Ashes

The chemical compositions and XRD pattens of four MSWI fly ashes are given in Table S2 and Figure 1, respectively. All of four fly ashes had high contents of CaO, indicating the presence of reactive portlandite and lime. Except for the FA4, the other three fly ashes had high contents of Cl, Na<sub>2</sub>O, and K<sub>2</sub>O. The result was consistent with the presence of chloride salts (NaCl, KCl and CaClOH), as confirmed by XRD analysis. The mineral phases of FA4, mainly existing as quartz and calcium silicate, were quite different from FA1, FA2, and FA3.



**Figure 1.** XRD patterns of as-received four MSWI fly ashes (FA1 (**a**), FA2 (**b**), FA3 (**c**), and FA4 (**d**)) (1—Halite(NaCl); 2—Sylvine (KCl); 3—Calcium chloride hydroxide (CaClOH); 4—Fluorite (CaF<sub>2</sub>); 5—Portlandite (Ca(OH)<sub>2</sub>); 6—Lime (CaO); 7—Calcite (CaCO<sub>3</sub>); 8—Anhydrite (CaSO<sub>4</sub>); 9—Quartz (SiO<sub>2</sub>); 10–Calcium silicate (CaSiO<sub>3</sub>)).

The heavy metal contents and corresponding leaching concentrations of the received MSWI fly ashes are given in Table 3. It can be seen from Table 3 that both contents and leachability of heavy metals in four MSWI fly ashes were quite different from each other. Generally, the Pb and Zn had high contents in all MSWI fly ashes. In particular, the Pb-leaching concentration of FA1 and FA2 reached 46,400 and 8160  $\mu$ g/L, respectively, which were much higher than the permitted level (250  $\mu$ g/L) of the Chinese standard for pollution control on landfill sites of municipal solid waste (GB 16889-2008). Additionally, the FA1 and FA4 had high Zn-leaching concentrations of 5080 and 11,100  $\mu$ g/L, respectively. Therefore, it was essential to control environmental hazards of MSWI fly ashes prior to the landfilling. In this study, it was found that the chemical compositions, mineral phases, and heavy metal leachability were quite different for four kinds of MSWI fly ashes. Thus, it was quite necessary to evaluate the solidification/stabilization performance of different MSWI fly ashes by MSCM.

	Н	eavy Metal (	Content (mg/k	g)	Heavy Metal Leaching Concentrations (µg/L)				
MSWI FIY ASh	Zn	Cr	Pb	Hg	Zn	Cr	Pb	Hg	
FA1	10,136.1	23.8	1323.8	34.7	5080	162	46,400	37	
FA2	2526.0	42.4	1502.0	6.46	127	144	8160	11	
FA3	3829.1	58.1	563.6	23.3	360	107	164	28	
FA4	2799.6	85.4	267.2	3.1	11,100	282	108	7.8	
Limited levels of GB 16889-2008					100,000	4500	250	50	

Table 3. Heavy metal contents and leaching concentrations of four MSWI fly ashes.

## 3.2. Solidification of MSWI Fly Ash with Different Proportions

In this work, the MSWI fly ash (FA2), collected from Baoding City, Hebei Province, China, was selected to investigate the effect of fly ash contents on solidification/stabilization performances of MSCM-fly ash blocks. For comparative purposes, the strength and heavy metal leaching concentrations of hardened MSCM pastes were also measured. As shown in Figure 2, the compressive strength of MSCM pastes had reached 26.9 and 35.2 MPa after curing for 3 and 28 days, respectively. In particular, the three-day strength reached 76.42% of 28-day strength, demonstrating the fast early-strength development of MSCM pastes. It indicated that the MSCM, prepared from four industrial wastes (BFS, SS, DA, and PAS), achieved high cementitious reactivity.



Figure 2. The compressive strength of MSCM-fly ash blocks at different FA2 contents and curing time.

As exhibited in Figure 2, the 28-day compressive strength of MSCM-fly ash blocks decreased rapidly from 34.1 to 2.2 MPa as the FA2 content rose from 10 wt.% to 80 wt.%. Rémond et al. [25] also concluded that the mechanical strength of OPC-fly ash pastes would reduce significantly as the MSWI fly ash content exceeded 15 wt.%. In this case, the 28-day strength of the blocks could reach 2.2 MPa, while the FA2 content was as high as 80 wt.%. It was worth noting that the mechanical strength of MSCM-fly ash blocks could well meet the strength requirements of sanitary landfills (~2.0 MPa).

Figure 3 showed the leaching concentrations of Zn, Cr, Hg, and Pb in MSCM-fly ash blocks at different FA2 contents and curing times. As shown in Figure 3, hardened MSCM pastes (0 wt.% FA2) had very low-leaching concentrations of Zn, Cr, Hg, and Pb. The immobilization rates of Zn, Cr, Hg, and Pb for the D0 sample (MSCM paste) were above 99.60%, as given in Table 4. As listed in Table 1, the DA contained high contents of Pb (2412.81 mg/kg) and Zn (192.20 mg/kg), and SS had a high amount of Cr (442.30 mg/kg), resulting in the increased heavy metal contents of prepared MSCM. Nevertheless, the



low-leaching concentrations confirmed that heavy metals in the MSCM could be effectively immobilized into the hydration products.

**Figure 3.** Leaching concentrations of Zn (**a**), Cr (**b**), Pb (**c**), and Hg (**d**) in MSCM-fly ash blocks at different FA2 contents and curing times.

**Table 4.** The immobilization rates of Zn, Cr, Hg, and Pb in MSCM-fly ash blocks after curing for 28 days.

FA2 Blocks	Zn	Cr	Pb	Hg
D0	99.63%	99.98%	99.98%	99.96%
D1	99.77%	99.98%	99.99%	96.51%
D2	99.97%	99.98%	100.00%	97.13%
D3	99.92%	99.98%	99.99%	99.14%
D4	99.82%	99.98%	99.99%	98.80%
D5	99.88%	99.95%	99.99%	98.53%
D6	99.99%	99.94%	99.98%	98.82%
D7	99.99%	99.94%	99.96%	99.38%
D8	99.99%	99.84%	99.77%	99.72%

As exhibited in Figure 3, while the FA2 content even reached 80 wt.%, the leaching concentrations of Zn, Cr, Hg, and Pb in MSCM-fly ash blocks were far below limit values of the Chinese landfill standard (GB 16889-2008).The Pb and Cr concentrations especially

decreased from 8160 and 144  $\mu$ g/L for the original FA2 to 148 and 4.9  $\mu$ g/L for FA2 blocks, respectively, with the addition of 20 wt.% MSCM. The results indicated that the solidification/stabilization of MSWI fly ash by the MSCM could comply well with the landfill site requirements. As listed in Table 4, the immobilization rates of Zn, Cr, Hg, and Pb were above 99.70%, while the FA2 content was 80 wt.%. It seemed that almost 100% of heavy metals from both MSWI fly ash and MSCM had been immobilized into solidified blocks. Based on the above results of strength and heavy metal leachability, it can be concluded that novel MSCM was a cost-effective, low-carbon, and highly efficient cementitious material for the solidification/stabilization treatment of MSWI fly ash.

As shown in Figure 3, the leaching concentrations of Zn, Cr, and Pb decreased by extending the curing times. However, the Hg concentrations became higher after three days of curing treatment. It may be attributed to the degree of hydration reactions of MSCM-fly ash pastes. The leachability of heavy metals in fly ash blocks was highly related to alkalinity, the amount and type of hydrates, as well as the densification of the blocks [26]. The hydration reactions of BFS, SS, and DA in MSCM-fly ash pastes resulted in the generation of various hydrates, such as C-S-H gel, Aft, and Ca(OH)<sub>2</sub>. As the curing time was extended, the densification and alkalinity of the blocks should increase due to higher amounts of formed C-S-H gel and Ca(OH)<sub>2</sub>, immobilizing heavy metals by physical encapsulation and chemical precipitation [6,7]. Additionally, these hydrates can also immobilize heavy metals via multiple pathways, such as adsorption and cation exchange [6,10]. Thus, it was reasonably observed that more heavy metals (Zn, Cr, and Pd) were immobilized in the blocks at extended curing times.

## 3.3. Solidification of Four Kinds of MSWI Fly Ashes

In this work, the solidification/stabilization of four kinds of MSWI fly ashes was evaluated by using the MSCM as the binder. As listed in Table 5, the 28-day compressive strength of four kinds of fly ash blocks decreased from 16.4–24.1 MPa at 40 wt.% fly ash to 8.9–13.0 MPa at 60 wt.% fly ash. Nevertheless, the strength was still much higher than the strength requirements of sanitary landfills (~2.0 MPa). The decreased strength at higher fly ash contents may be partially attributed to the higher porosity of fly ash blocks [27]. As shown in Table 5, the H4-1 and H4-2 samples for the solidification/stabilization of FA4 achieved the higher strength compared to other fly ash blocks. It may be attributed to the lower content of Cl and higher contents of  $Al_2O_3$  and  $SiO_2$  for the FA4, as seen in Table S2. According to the above results, it can be concluded that the hydration reactivities of MSWI fly ashes collected from four cities were quite different because of different chemical compositions and mineral phases.

**Table 5.** Compressive strength, leaching concentrations, and immobilization rates of heavy metals in MSCM-fly ash blocks after curing for 28 days.

Fly Ash	Compressive	Lea	ching Conce	entrations (µ	g/L)	Immobilization Rate (%)			
Blocks	Strength (MPa)	Zn	Cr	Pb	Hg	Zn	Cr	Pb	Hg
H1-1	21.2	2.59	2.27	18.72	1.52	99.99	99.95	99.95	99.68
H1-2	12.5	3.31	4.11	25.64	4.72	99.99	99.89	99.94	99.33
H2-1	16.4	4.95	1.17	9.78	8.54	99.99	99.93	99.97	98.21
H2-2	8.9	7.65	3.48	23.3	4.21	99.99	99.92	99.95	99.40
H3-1	22.3	2.42	2.09	5.24	6.74	99.99	99.96	99.96	98.58
H3-2	9.6	3.18	3.47	9.15	8.79	99.99	99.93	99.96	98.75
H4-1	24.1	2.11	2.71	5.18	7.85	99.99	99.95	99.96	98.35
H4-2	13.0	3.49	3.96	13.52	7.65	99.99	99.93	99.90	98.92

As given in Table 5, the leaching concentrations of Zn, Cr, Pb and Hg were just in the range of  $1.17-25.64 \mu g/L$  for all MSCM-fly ash blocks, much lower than the limited values of the Chinese landfill standard (GB 16889-2008), as listed in Table 3. Taking the FA1 as an example, the leaching concentrations of Pb and Zn reached 46,400 and 5080  $\mu g/L$  for

original FA1, respectively. By solidifying FA1 with the addition of 40 wt.% MSCM (H1-2 sample), the Pb and Zn concentrations decreased significantly to only 25.64 and 3.31  $\mu$ g/L, respectively. For all MSWI fly ashes, the immobilization rates of Zn, Cr, and Pb exceeded 99.90% and that of Hg reached above 98.70% at 60 wt.% fly ash. Based on the above results, it is suggested that the solidification/stabilization of MSWI fly ashes from different cities by using novel MSCM as a low-carbon binder could achieve high strength of fly ash blocks and low leachability of heavy metals.

## 3.4. Comparison of MSWI Fly Ash Solidification by MSCM and OPC

In this case, the solidification/stabilization treatment of FA1 by MSCM and OPC was compared. Due to high-leaching concentrations of Zn, Pb, and Hg, as seen in Table 3, the FA1 was selected as the typical MSWI fly ash for the comparison. For the solidification/stabilization treatment by OPC, the OF1 and OF2 samples represented OPC-fly ash blocks with 40 wt.% FA1 and 60 wt.% FA1, respectively. As shown in Figure 4, the 28-day strength of H1-1 and H1-2 samples reached 21.2 and 12.5 MPa, respectively. Nevertheless, the strengths of OF1 and OF2 samples were just 9.3 and 6.1 MPa, respectively, at the same FA1 contents. The results indicated that the strength of binder-FA1 blocks had an increase of 104.92–127.96% by using MSCM to replace OPC as the binder. It also suggested that the MSCM, prepared from industrial wastes, achieved higher cementitious reactivity in the solidification/stabilization of MSWI fly ash than OPC.



Figure 4. The compressive strength of FA1 blocks solidified by MSCM and OPC, respectively.

Figure 5 showed the leaching concentrations of heavy metals in FA1 blocks solidified by MSCM and OPC, respectively. Except for the Hg element, the leaching concentrations of Zn, Cr, and Pb decreased at longer curing times while either MSCM or OPC was used as the binder. For all heavy metals, the MSCM-FA1 blocks achieved lower leaching concentrations than OPC-FA1 blocks. Taking Zn and Pb elements as examples, the leaching concentrations decreased from 55.91 to 3.31  $\mu$ g/L and from 39.14 to 25.64  $\mu$ g/L, respectively, by using MSCM to replace OPC to solidify FA1 at 60 wt.% content. Accordingly, it is well suggested that the MSCM could achieve higher mechanic strength and lower leaching concentrations of heavy metals than widely used OPC in the solidification/stabilization of MSWI fly ash.



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**Figure 5.** The leaching concentrations of Zn (**a**), Cr (**b**), Pb (**c**), and Hg (**d**) in FA1 blocks solidified by MSCM and OPC, respectively.

# 3.5. Solidification Mechanisms of MSWI Fly Ash

# 3.5.1. Formation of Hydration Products

Generally, the immobilization of heavy metals in MSWI fly ash was highly related to hydration products formed through numerous reactions of components in binder-fly ash pastes. In this study, pure MSCM paste (100 wt.% MSCM + 0 wt.% FA2, D0 sample) and MSCM-fly ash paste (60 wt.% MSCM + 40 wt.% FA2, D4 sample) were prepared to investigate the formation of hydrates. As shown in Figure 6a, the hydrates, including portlandite, calcium silicate hydrate (C-S-H), and ettringite (AFt), appeared in the hardened MSCM paste. After 60 wt.% MSCM was mixed with 40 wt.% FA2, the stratlingite (C-A-S-H) and Friedel's salt were formed as new hydrates, as shown in Figure 6b, resulting in a denser microstructure in MSCM-fly ash blocks. However, no typical diffraction peaks of portlandite and AFt were observed in D4 samples, which indicated the occurrence of further hydration reactions of these hydrates with the components in FA2. Since the AFt can significantly promote developing the strength of harden paste, the disappearance of AFt in the D4 sample could well explain the decreased strength of MSCM-fly ash blocks at higher FA2 contents, as shown in Figure 2. As shown in Figure 6b, the diffraction peak intensities of KCl and NaCl became lower at longer curing times. It seemed that soluble chloride salts were partially consumed to form Friedel's salt, as confirmed by XRD [28].



**Figure 6.** XRD patterns of D0 (**a**) and D4 (**b**) samples after curing for 3, 7 and 28 days (1—Calcium silicate hydrate (CaO·SiO<sub>2</sub>·nH<sub>2</sub>O); 2—Portlandite (Ca(OH)<sub>2</sub>); 3—Gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O); 4—Ettringite (3CaO·Al<sub>2</sub>O<sub>3</sub>·3CaSO<sub>4</sub>·26H<sub>2</sub>O); 5—RO phases; 6—Sylvine (KCl); 7—Calcium silicate (CaSiO<sub>3</sub>); 8—stratlingite (2CaO·Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>·8H<sub>2</sub>O); 9—Halite (NaCl); 10—Friedel's salt (3CaO·Al<sub>2</sub>O<sub>3</sub>·CaCl<sub>2</sub>·10H<sub>2</sub>O); 11—Calcite (CaCO<sub>3</sub>)).

The microstructures of D4 samples after three days, seven days, and twenty-eight days of hydration are shown in Figure 7. After curing for three days, colloidal C-S-H gels were generated in the MSCM-FA2 block. In addition, the ettringite (AFt) with the typical structures of cloudy filaments or needle rods also appeared [26,27]. By extending curing time to seven days, the amounts of C-S-H gels seemed to increase, and the C-A-S-H appeared. However, the filament- or rod-like AFt phase disappeared, which was consistent with minerals phases determined by XRD. At the curing time of 28 days, more C-S-H and C-A-S-H were coated on the particle surface, promoting the strength development of the FA2 block.



Figure 7. SEM micrographs of D4 samples after curing for 3 (a), 7 (b), and 28 days (c), respectively.

Figure 8 showed the DTG curves of D4 samples after curing for three, seven, and twenty-eight days. The endothermic peaks at 118 °C (3 days), 93 °C (7 days), and 100 °C (28 days) could be assigned to dehydration of free water in hydrates, such as C-S-H gels and AFt [29]. The endothermic peaks between 250 and 350 °C were related to the decomposition of C-S-H gels or C-A-S-H to release crystal water [30]. The change of endothermic peaks located at 250~350 °C might be attributed to the crystalline structure changes due to the incorporation of heavy metal ions in C-S-H or C-A-S-H hydrates [31,32]. The calcite was detected at endothermic peaks of 853 and 867 °C after curing for three days. The peaks at approximately 650 °C could be attributed to the crystal transformation of calcium silicates (e.g.,  $C_3S$  and  $C_2S$ ) [33].



Figure 8. DTG curves of D4 samples after curing for 3, 7, and 28 days.

#### 3.5.2. Immobilization Mechanisms of Heavy Metals

The immobilization mechanisms of heavy metals in MSWI fly ash were quite complex for cement-based solidification/stabilization treatment, including adsorption, isomorphous replacement, chemical precipitation, surface complexation, and physical encapsulation [34,35]. In this case, the hydration of pure MSCM pastes resulted in the formation of C-S-H gel, Aft, and Ca(OH)<sub>2</sub>, which could immobilize heavy metals via adsorption, cation exchange, and physical encapsulation [35–38]. In MSCM-fly ash blocks, new phases, such as C-A-S-H and Friedel's salt, appeared due to the interference of fly ash. The C-A-S-H was the zeolite-like mineral composed of oxygen-silicon tetrahedron, achieving strong capacity of adsorption and ion exchange due to the ultra-large specific surface area [35]. Cation metal ions, such as  $Pb^{2+}$  and  $Cr^{3+}$ , could be effectively adsorbed by the C-A-S-H. Additionally, generated Friedel's salt could participate into the immobilization of heavy metals in MSCM-fly ash blocks [39]. In this study, the precipitation of insoluble metallic phosphates (e.g.,  $Pb_3(PO_4)_2$ ,  $Pb_{10}(PO_4)_6(OH)_2$  might also contribute to the immobilization of cation heavy metal ions due to the high content of  $P_2O_5$  (21.76 wt.%) in phosphoric acid sludge [40,41]. Therefore, heavy metals in MSCM-fly ash blocks could be effectively immobilized via multi-pathways in the hydration process.

## 4. Conclusions

In this work, four industrial wastes, i.e., blast furnace slag, steel slag, desulfurization ash, and phosphoric acid sludge, were used to prepare a low-carbon binder, metallurgical slag-based cementing material (MSCM). Then, the solidification/stabilization of MSWI fly ashes were evaluated by using MSCM as the binder.

- (1) The MSCM exhibited high-hydration reactivity, achieving 3-day and 28-day strengths of 26.9 and 35.2 MPa for pure MSCM pastes, respectively. While the FA2 content was as high as 80 wt.%, the 28-day strength of MSCM-FA2 blocks reached 2.2 MPa, and the leaching concentrations of Zn, Cr, Hg, and Pb were far below the limit values of the Chinese landfill standard (GB 16889-2008). The immobilization rates of Zn, Cr, and Pb were above 99.90%, and that of Hg was above 98.70% for tour kinds of MSWI fly ashes.
- (2) The 28-day strength of MSCM-fly ash blocks reached 8.9–13.0 MPa at fly ash content of 60 wt.%. The 28-day strength of binder-FA1 blocks had an increase of 104.92–127.96% by using MSCM to replace OPC. Additionally, the MSCM-FA1 blocks could achieve much lower leaching concentrations of heavy metals than OPC-FA1 blocks. Compared to widely used OPC, the MSCM had the merits of lower cost, lower CO<sub>2</sub> emission, and higher efficiency in the solidification/stabilization of MSWI fly ash.
- (3) The XRD, SEM, and TG-DSC analysis confirmed the formation of numerous hydrates, e.g., C-S-H gel, AFt, Ca(OH)<sub>2</sub>, C-A-S-H, and Friedel's salt, in the hydration process. Heavy metals in MSWI fly ash could be effectively immobilized via adsorption, cation exchange, precipitation, and physical encapsulation.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/min12050599/s1, Figure S1: XRD patterns of blast furnace slag (a), steel slag (b), desulfurization ash (c), and phosphoric acid sludge (d); Table S1: The comprehensive strength of pure MSCM pastes with different proportions of raw materials; Table S2: Main chemical compositions of four kinds of MSWI fly ashes.

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