

# Characteristics of Melting Incinerator Ashes Using a Direct Current Plasma Torch

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## Abstract

Fly ashes both from municipal solid waste incinerator (MSWI) and medical waste incinerator (MWI) are classified as hazardous materials because they contain high amounts of heavy metals. In present these contaminant ashes have become a major environmental problem. In this study, we determine the ability of these contaminating heavy metals to be incorporated into a glass-matrix and in various mineral phases after a high temperature melting process using a direct current plasma torch. After the melting process, the leaching characteristics of heavy metals in fly ash and vitrified slag were investigated using the toxicity characteristic leaching procedure (TCLP), and the products also were characterized by X-ray diffractometry (XRD) for crystal structure determination, and scanning electron microscopy (SEM) for microstructure/morphology observation. After vitrification, there were prominent changes in microstructures and crystalline phases between produced slags and raw ashes. TCLP results indicate the leaching level of heavy metals in slags decreases obviously and additives such as silica and liquid ceramic (LC) contribute to high effect on immobilization of heavy metals in a host glass matrix.

**Keywords:** Fly ash; Heavy metal; Melting; Plasma torch

## Introduction

Over the past two decades, incineration has been increasingly applied for treating municipal solid waste (MSW). The dominating purpose of burning MSW is to cut down the volume and mass of MSW, because of the increasing difficulty of finding suitable sites for controlled and uncontrolled landfill waste disposal operations [1,2]. The capacity of incinerating MSW was about 16.4 Mt, up to 16% of all MSW in 2011 in China [3]. Recently, incineration has also been the most widespread adopted technology for the disposal of medical waste (MW) since the nationwide outbreak of severe acute respiratory syndrome (SARS) in 2003 in China. Incinerating MW can not only neutralize its infectivity, which is the most hazardous MW property, but also sharply reduce its volume [4,5].

However, during incinerating MSW and MW, a great quantity of fly ashes from the air pollution control (APC) systems, which were set up for wiping off hazardous materials in the flue gas, were discharged. These APC fly ashes were classified as hazardous wastes owing to containing significant amounts of toxic materials such as heavy metals and persistent organic pollutants (POPs), e.g. dioxins and furans [6-9], and the fly ash from medical waste incinerator (MWI) was much more deleterious than that of municipal solid waste incinerator (MSWI) [8,9].

With growing public concerns and rigorous regulatory requirements, how to safely handle the ash is gaining more and more attention by the scientific community and by the general society. It is well known that inappropriate treatment and final disposal of the ash can induce adverse impacts on both public health and the environment [10]. Therefore, developing a safe and reliable immobilization technology, to transform the ash into a stable form, is very necessary. Many alternative methods for hazardous fly ash treatment have been suggested and developed. One of these methods is the melting technology which reduces the volume, yields the glassy leaching-resistant slag, and destroys toxic organic compounds effectively [11-14].

Among several melting methods, plasma melting technology has attracted increasing interest for hazardous waste treatment. Compared with a fuel type melting furnace, a thermal plasma system has the advantages of high temperature and high energy density, which allows

fast heat transfer at the reactor boundaries and correspondingly shorter treatment time. In the past decade, thermal plasma technology has been extensively used for the treatment of various hazardous wastes [13-20].

In this study a direct current (DC) plasma appliance has been developed for the vitrification of fly ashes from both MWI and MSWI. The transformation of the mineralogical species of fly ashes and the leachability of major heavy metals during melting process were investigated, in order to ascertain the mechanism of fixing metal in molten slag. Also the density and the microstructure of original ash and vitrified slag were surveyed.

## Experimental Methods

### Thermal plasma system

The plasma torch used in this experiment consists of four major parts: cathode, first anode, linked part and second anode, as shown in Figure 1. Compared with conventional thermal plasma torches, this torch has a special design with two nozzles shaped copper anodes set at different axial distances from the cathode tip [21,22]. This configuration can not only extend jet length but also enhance the arc stability. In this work, argon was used as working gas at a flow rate varied from 12 to 14 L/min. The double arcs plasma torch was operated in direct current mode with typically 20-30 V/100 A for the first arc and 50-60 V/100 A for the second arc. The temperature of the plasma jet near the torch exit is over 11000K, and the heat flux of the plasma jet is around 65 kW/m<sup>2</sup> at 14cm downstream from the exit [20-24].

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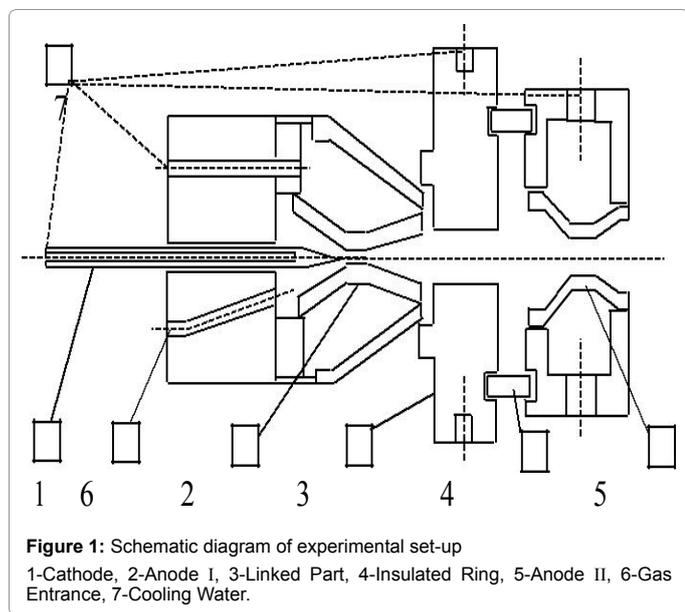
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A plasma melting furnace based on this plasma torch has been developed in our lab. A crucible filled with fly ash was vitrified by atmospheric thermal plasma jet. The crucible had a capacity of 30-60 g of fly ash, which could be completely vitrified within about 15 min. using this plasma melting furnace, prior study on treating MWI fly ash has shown satisfactory results [11].

### Fly ash

Three representative fly ash samples were used in this investigation, named FA1, FA2 and FA3, respectively. Both FA1 and FA2 were collected from fabric filters in air pollution cleaning devices installed in MSWI, but the former was obtained from a grate type incinerator, then the latter was from a circulated fluidized bed incinerator. FA3 was sampled from a medium-scale MWI with handling capacity of 10 tons/d, equipped with a simplified stoker furnace. These three incinerators are all located in Zhejiang province in Southeast China.

The elemental composition of samples tested by X-ray Energy Disperse Spectroscopy (EDS) (GENENIS 4000, EDAX Inc. USA) is shown in Table 1. The elementary composition of these three samples was very similar, and their primary elements were carbon, oxygen, silicon, chlorine and calcium. Nevertheless, the loss of ignition (LOI) was far different, and LOI of FA3 was as high as 18.2%, which was much higher than that of FA1 and FA2. That was to say the proportion of organic components in MWI ash was much higher, compared with MSWI ash, which went against melting process.



**Figure 1:** Schematic diagram of experimental set-up  
1-Cathode, 2-Anode I, 3-Linked Part, 4-Insulated Ring, 5-Anode II, 6-Gas Entrance, 7-Cooling Water.

The heavy metal in ash samples was extracted using mingled acid solution then tested by Atomic Absorption Spectrophotometer (AAS) (SOLAAR 969, Thermo Inc., America). The concentrations are also listed in Table 1. As can be seen, the amount of Zn and Pb in all samples far exceeded that of Cd, Cr, Cu and Ni, and Zn was especially so.

## Results and Discussion

### Metal leaching test

**Fly ash and molten slag:** The leaching capability of heavy metals was evaluated by the toxicity characteristic leaching procedure method (TCLP, USEPA method 1311). Acetic acid solution (pH 2.88 ± 0.05) was used as the leaching liquid.

The liquid-to-solid ratio was 20:1 and agitation time was 18 hr with rotary tumbler at (30 ± 2) r/min. After extraction, the leachates were examined by AAS (Table 2). The results show that the heavy metals' leaching characteristics of FA1 were very similar to FA3, but as for FA2, the leachability was quite different. For example, the concentration of Zn in FA2 was near to 5 mg/L far exceeding that of FA1 and FA3, and the leaching content of 0.3033 mg/L of Cd was beyond threshold value of Cd according to the Environmental Protection Administration of China.

After melting treatment, TCLP was also adapted to examine the

Element	FA1	FA2	FA3
C	8.69	25.35	13.54
O	30.80	33.15	23.90
Na	2.26	1.29	1.75
Mg	2.61	1.23	3.01
Al	3.59	8.83	4.28
Si	7.50	13.87	6.17
P	1.12	0.73	0.63
S	3.58	0.99	1.51
Cl	11.96	1.26	17.23
K	2.79	1.44	1.50
Ca	22.95	7.89	21.66
Fe	2.15	3.24	0.56
LOI	7.17	10.3	18.2
<b>heavy metals concentration (mg/kg)</b>			
Pb	2943.5 (713.7)*	1964.2 (70.1)	1237.4 (214.1)
Cd	142.2 (15.0)	68.4 (14.8)	74.7 (13.3)
Cr	74.3 (21.4)	93.7 (7.7)	117.3 (34.3)
Zn	9743.8 (1511.4)	7512.5 (221.6)	8053.4 (780.2)
Cu	465.2 (43.2)	542.7 (75.9)	227.7 (21.1)
Ni	74.9 (34.9)	69.2 (33.7)	55.9 (31.2)

LOI - loss of ignition

\*Values in parentheses are standard deviation of means of triplicate

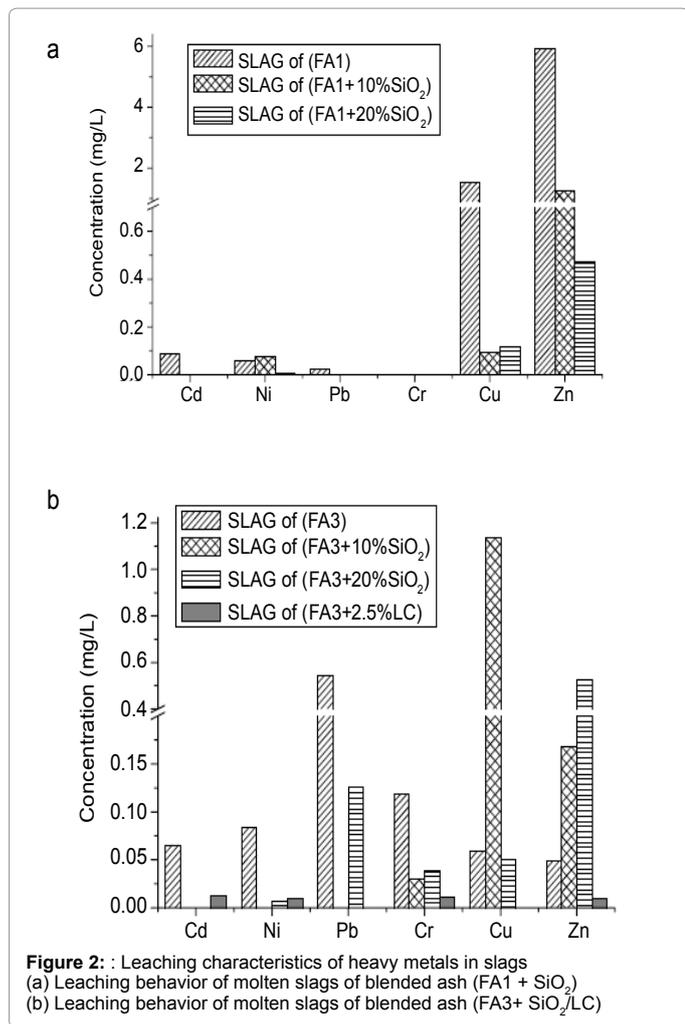
**Table 1:** Elemental composition of fly ashes (wt%).

	Pb	Cd	Cr	Zn	Cu	Ni
FA1	0.3254 (0.070)*	0.1323 (0.0254)	0.2464 (0.0735)	0.1422 (0.0077)	0.0483 (0.0028)	0.2293 (0.0585)
FA2	0.2868 (0.1005)	0.3033 (0.0291)	0.4725 (0.2133)	4.7465 (1.230)	0.2859 (0.1407)	0.2851 (0.0753)
FA3	0.3106 (0.0786)	0.1361 (0.0195)	0.2491 (0.0128)	0.0758 (0.0034)	0.1109 (0.0136)	0.1973 (0.0141)
S1	0.0243 (0.0151)	0.0865 (0.0044)	BDL	5.9382 (0.011)	1.533 (0.026)	0.0504 (0.0236)
S2	BDL	BDL	BDL	0.0843 (0.0098)	0.2972 (0.0221)	0.308 (0.0258)
S3	0.4946 (0.1657)	0.0559 (0.0397)	0.1067 (0.0622)	0.0537 (0.0238)	0.0544 (0.0236)	0.0763 (0.0388)
China limit	3	0.3	10	50	50	10

BDL-below detection limit

\*Values in parentheses are standard deviation of means of triplicate

**Table 2:** The leaching concentrations of heavy metals in fly ashes and vitrified slags (mg/L).



metals' leaching abilities in the produced slags, named S1, S2 and S3, respectively. And the concentrations are listed in Table 2. It is indicated that the slags show well effect on retaining heavy metals. Particularly, we can find that resistance to dissolution was most effective for Cr, Cd and Pb which were highly toxic. Compared with FA2, the extracted amounts of S2 swiftly decreased, especially for Cd, Pb, Cr and Zn. As for S1 and S3, the amounts of several heavy metals were even higher than those in raw ashes, such as Pb, Zn and Cu. The reason was that the high content of Chlorine in FA1 and FA3 impeded the stabilization of heavy metals [25-27] and the high value of basicity of FA1 and FA3 led to poor efficiency of vitrification [28]. It should be noted here, the total elemental mass balances were not considered in this study for some volatile metals such as Cd and Pb may evaporate to the atmosphere during molten stage. Therefore, when using thermal melting technology to treat fly ash, a secondary air pollution control system should be designed to catch volatile metals [29].

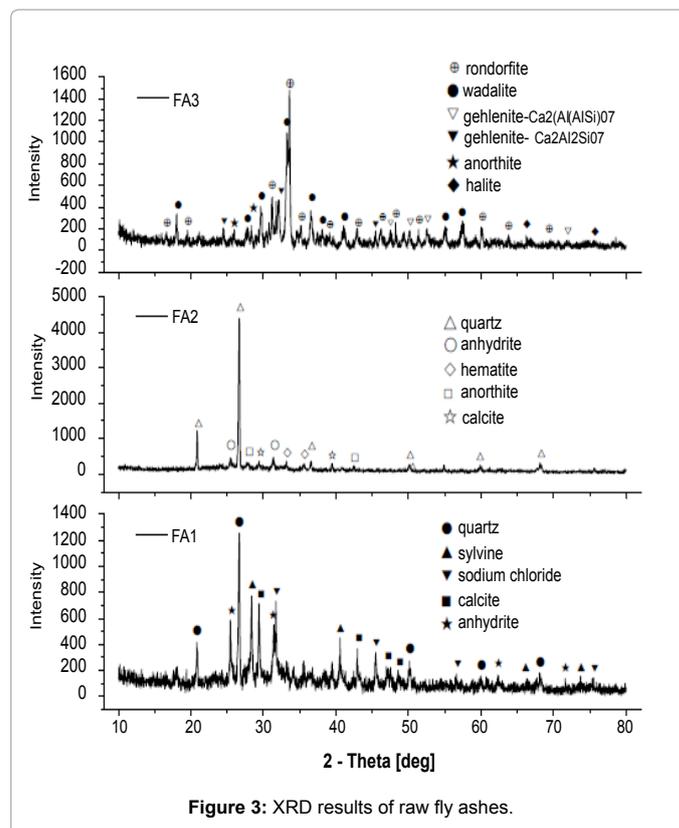
**Additive for melting:** The experiments on improving the melting performance of FA1 and FA3 were conducted by adding SiO<sub>2</sub> (analytic grade) (Western-Union Chem-Industrial Corp., Shanghai) into the raw fly ashes at the proportion of 10 wt. % and 20 wt. %, respectively. Liquid ceramic (LC, composed of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) (Beijing Dingxin Aihua Science-Technologies Corp.) was also introduced into FA3 by 2.5 wt. %, as another additive for comparison. Then these samples were placed into the plasma melting furnace for vitrification and the vitreous slags,

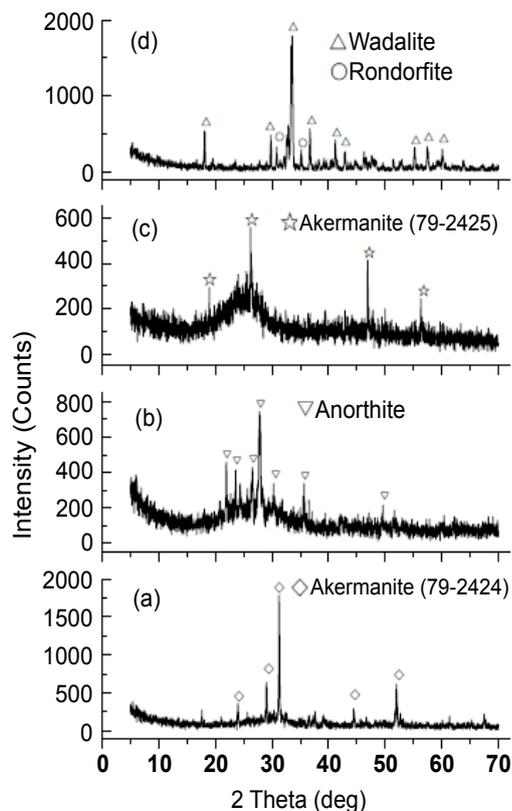
named SlagFA1 and SlagFA3, respectively, were analyzed to evaluate their physical and chemical properties.

The leaching content of heavy metals is shown in Figure 2. As can be seen, for both SlagFA1 and SlagFA3, the leaching amounts decreased significantly when SiO<sub>2</sub> was used as additive to raw fly ashes. For SlagFA1 (Figure 2a), the leaching level of Cu and Zn was noticeably reduced. The amount of Cu dramatically decreased from 1.53 mg/L to 0.09 mg/L (10 wt% SiO<sub>2</sub>) and 0.11 mg/L (20 wt% SiO<sub>2</sub>). And the amount of Zn remarkably decreased from 5.9 mg/L to 1.26 mg/L (10 wt% SiO<sub>2</sub>) and 0.47 mg/L (20 wt% SiO<sub>2</sub>), respectively. For SlagFA3 (Figure 2b), the molten slags of blended ashes exhibited much better effect on retaining heavy metals than that of fly ash alone. The immobilizing of Cd, Cr, Pb and Ni was significantly improved, except for Cu and Zn. For Cu, no noteworthy trend of the leaching concentrations could be observed with a variety of SiO<sub>2</sub> values, and for Zn, the leaching value decreased as the portion of SiO<sub>2</sub> increased. While 2.5 wt% of LC was introduced into FA3, the produced molten slag showed extraordinary effect on immobilization of heavy metals. Similar results were reported by other researchers [30,31]. In general, chemical stability is consistent with the progressive formation of a more compact and interconnected glass network structure with the addition of the glass formers. Therefore, addition of SiO<sub>2</sub> and LC strengthened the chemical stability of the glass-like slags.

### XRD of fly ash and slag

The X-ray diffraction (XRD) investigations were carried out with a Rigaku Model D/max-rA diffractometer using Cu K $\alpha$  radiation, operated at 40kV and 100mA in the 2 $\theta$  range from 5° to 80°. Crystalline phases were identified by comparing intensities and positions of Bragg peaks with those listed in the Joint Committee on Powder Diffraction Standards data files.





**Figure 4:** XRD results of molten slags. (a)S1; (b) S2; (c) SlagFA3 (FA3+10 wt% SiO<sub>2</sub>); (d) S3.

Figure 3 shows the XRD results of the raw ash samples. As can be seen, the main phases were quartz (SiO<sub>2</sub>), hematite (Fe<sub>2</sub>O<sub>3</sub>) and calcium salt (CaSO<sub>4</sub> and CaCO<sub>3</sub>) in FA2. This crystal characterization had disadvantage over fastening metals but was conducive to vitrification. As for FA1 and FA3, their crystalline phases were much complex including halite (NaCl), sylvine (KCl) and rondorfite (Cl-bearing) and this kind mineral phase led to poor effect of melting raw materials [32].

The crystal phases of molten slags are exhibited in Figure 4. The XRD pattern of each slag was completely different from that of raw ash. Compared with S1 and S3, both S2 and SlagFA3 show no noticeable crystalline peaks and confirm the amorphous glass structure which contributed to holding heavy metals in the silicate glass framework [33].

### SEM of slag

The produced vitrified slags were ground to powder then their microstructure characterizations were investigated using Scanning Electron Microscopy (SEM). The SEM micrographs are shown in Figure 5. These SEM images indicate that these three fly ashes can be transformed into extremely compact and uniform vitreous slags under appropriate vitrification, thus making them more inert to chemical etching and higher mechanical strength for reclamation.

### Volume reduction

Archimedes method was utilized to measure the density of raw ashes and molten slags. After thermal melting treatment, the densities of samples significantly increased from 0.62-0.84 g/cm<sup>3</sup> (fly ashes) to

1.89-3.11 g/cm<sup>3</sup> (slags). Thus the reduction of volume reached 60-73%.

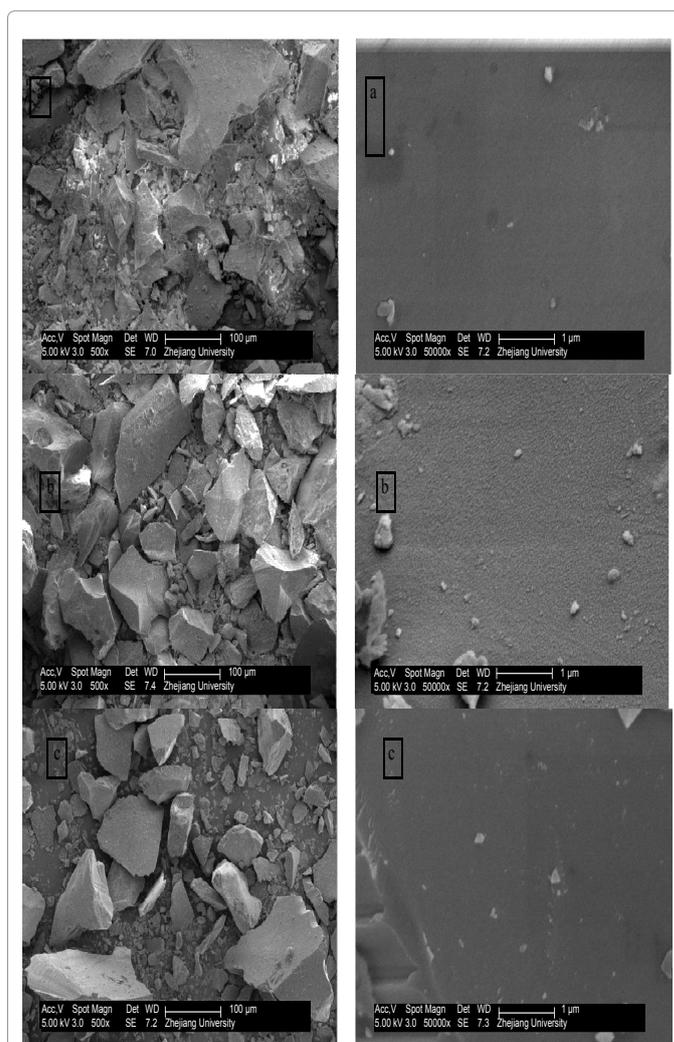
### Conclusions

A lab-scale DC thermal plasma melting system was used to dispose the hazardous fly ashes. After the melting process, the crystalline phases and microstructures of raw fly ashes were changed drastically, and the produced slags exhibited a glass-like monolithic morphology and interconnected compact microstructure, the reduction of bulk volume was in range of 60-73%. Compared with the raw ashes, the molten slags manifest well leaching-resistance of heavy metals, especially for Cd, Pb and Cr. The high chlorine content and low basicity in raw ash hampered solidification of heavy metals. Nevertheless, additive of SiO<sub>2</sub> and LC conducted to the formation of silicate glassy for immobilization of heavy metals and enhanced vitrification treatment significantly.

In conclusion, the thermal plasma torch is an alternative and promising technology for vitrification of hazardous fly ash.

### Acknowledgment

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**Figure 5:** SEM of molten slags obtained from various fly ashes (a) S1; (b) S2; (c) SlagFA3 (FA3+10 wt% SiO<sub>2</sub>).

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