The Impact of Additives on the Formation and Leaching Characteristics of the Vitrified Slag

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ABSTRACT

Plasma technology is a state-of-the-art technology to destroy various types of hazardous wastes. The vitrified slag can form in the process of plasma treatment of inorganic wastes and effectively stabilize and immobilize heavy metals, and its leaching rate is very low. In this paper, the impact of additives on the formation and leaching characteristics of the vitrified slag has been studied by a 30 kW DC plasma arc reactor system and rotating agitator, respectively. In the experiment, the mixtures of additives (SiO_2, Na_2CO_3, Na_2SiO_3 and CaO) and two types of fly ashes have been vitrified, and leaching rates of the vitrifies slag have been tested according to Identification standards for hazardous wastes ---- Identification for extraction toxicity (GB 5085.3-2007). XRD (X-ray diffraction) analysis results of the microscopic structures of the vitrified slag show they are amorphous. The impact of additives depend on the ration of O/Si (the ratio of the whole oxygen ions to the whole network former Si ions in the vitrified slag, range of 2~3) and the basicity (range of 0.2~0.8), which are the determinative factors in the formation of the vitrified slag. The bigger ratio of O/Si and the narrower peak width of the spectrum lead to the higher leaching characteristics and more unstable vitrified slag.

INTRODUCTION

With plasma treating waste technology (PTWT), inorganic waste can be heated beyond 1600°C, and turn to liquid state. After melt reacting, the character became even, and then the metal liquid turns to the vitrified slag by fast cooling speed. The PTWT can make kinds of hazardous wastes turn to vitrified slag, for example, hazardous waste from chemical plant, fly ash and polluted soil. The chemical character of vitrified slag is very stable, and the leaching characteristics are very low, so they can keep the hazardous elements for hundreds of years in nature. Some waste can turn to vitrified slag directly, but others need the additives (e.g. SiO_2, Na_2CO_3, Na_2SiO_3 or CaO) [1-5]. We choose the SiO_2, Na_2CO_3 and CaO as the additives in the paper, and research the additives amount to get more stable vitrified slag.

How to get the vitrified slag and what is the condition is not exactly mentioned recent years. In this paper, the condition of the vitrified slag experiments are done in a 30 kW DC plasma-arc reactor, and introduce the impact of the temperature, the ratio of O/Si, cooling speed and basicity (B_{ca}) during the vitrified slag formation. At last it is verified that the vitrified slag are very stable and has low leaching characteristics though the leaching experiment, which settled as the Identification standards for hazardous wastes-Identification for extraction toxicity.

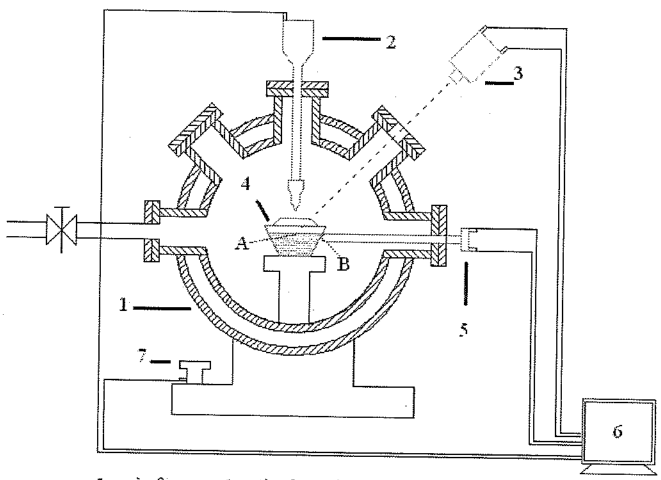
EXPERIMENTAL FACILITY

A complete 30 kW DC hazardous waste treatment system (PAWTS) using plasma technology includes water circulating system, main furnace, power supply system, temperature detecting system, exhaust gas treatment and data acquisition system[6].

Temperature Detecting System

A PtRh-Pt thermocouple was used to detect the temperature of the crucible's outer wall, and an infrared colorimeter was used to detect the temperature in the center of the melt's surface, shown at Figure 1. As the thermocouple is presenting the temperature of crucible's wall rather than the temperature of molten slag, it is defined as indicated temperature. The level of thermoelectric potential is measured by a DAM-E3039F A/D module and the data is stored in computer for further analysis. The type of Infrared colorimeter is CIT-1TD, with a measuring range of 900-3000°C, a precision level of ±1%, and a response time of 67ms. The wave lengths of the two infrared waves are 0.94μm and 1.4μm. It is connected with a PC for real-time sampling.

Figure 1: the detecting spots' arrangement



1 main furnace, 2 cathode, 3 infrared colorimeter, 4 crucible,
5 S-shaped thermocouple, 6 computer, 7 Anode
A the center of the melt's surface by infrared colorimeter
B the crucible's outer wall by S-shaped thermocouple

EXPERIMENTAL RESEARCH OF VITRIFIED SLAG

The X-ray crystallography study of the vitrified slag showed a characteristic of "distant term disorder", which explained its category of amorphous body. The experimental research on 2 kinds of fly ashes and some additives of SiO_2, CaO and Na_2CO_3 showed that the cooling rate and the ratio of O/Si are both most important factors that affect the formation process of the vitrified slag.

One kind of fly ashes from an MSW (Municipal Solid Waste) incineration plant in Henan Province, China and another is from a coal-firing power plant in Heilongjiang Province, China. They were marked with MSW-FA and CF-FA. An X-ray fluorescence (XRF) research was employed and the results are listed in table 1.

Table 1

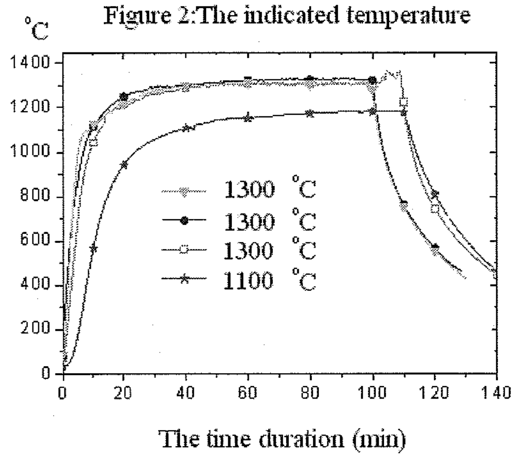
The component of MSW-FA and CF-FA											
component	Al_2O_3	SiO_2	CaO	TiO_2	Fe_2O_3	K_2O	SO_3	MgO	P_2O_5	ZrO_2	SrO
CF-FA	21.41	67.16	0.80	1.14	3.09	3.77	0.14	1.08	0.22	0.08	0.05
MSW-FA	48.04	43.11	3.52	2.15	1.79	0.38	0.27	0.22	0.17	0.14	0.12
component	Cr_2O_3	MnO	Y_2O_3	ZnO	NbO	Ga_2O_3	CuO	BaO	Rb_2O	Na_2O	
CF-FA	0.05	0.02	0	0.01	0	0.05	0.01	0.08	0.02	0.84	
MSW-FA	0.03	0.03	0.01	0.01	0.01	0.01	0.01	0	0	0	

In each experiment, 60g mixed material with different B_{ca} and O/Si was employed. The time duration was set to 1-2 hours, and the forming characteristics with different temperatures and cooling rates were studied.

1. Temperature

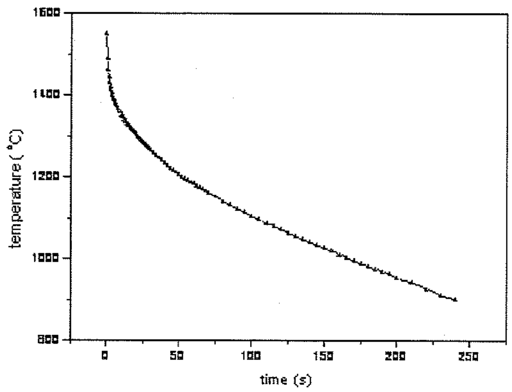
Two setting temperatures were 1100°C and 1300°C. The indicated temperature is shown in Figure 2.

Figure 2:The indicated temperature



The cooling temperature recorded by infrared colorimeter when shut down the arc is shown in Figure 3.

Figure 3: Cooling temperature



The XRD analysis showed that all residues were transformed into vitrified slag, which indicated that temperature was not a main factor to affect the formation of vitrified slag, but temperature had a great influence on whether or not the melting process could be completed in a setting amount of time.

Experimenting temperature must be higher than the eutectic point; otherwise the homogeneous liquid state melt cannot be formed. In this experiment, the vitrified slag was formed after a treatment of fast cooling process of the high temperature melt, there could not be vitrified slag if the temperature is low because the mixed materials could not melt. When the temperature is higher than the waste's eutectic point, it has a medium effect on the vitrified slag's forming.

2. O/Si

O/Si is through the formula below:

$$R = \frac{\sum_{i}^{N} n_i O_i}{\sum_{i}^{N} n_i Si_i}$$

Where:

R O/Si

N the total number of the sample's constituents

n the amount of the oxide constituent i by mol

O_i the number of oxygen atoms of oxide constituent i

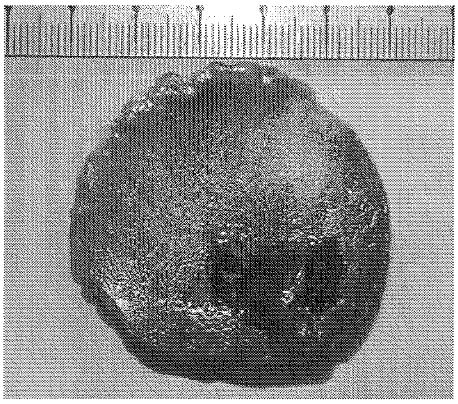
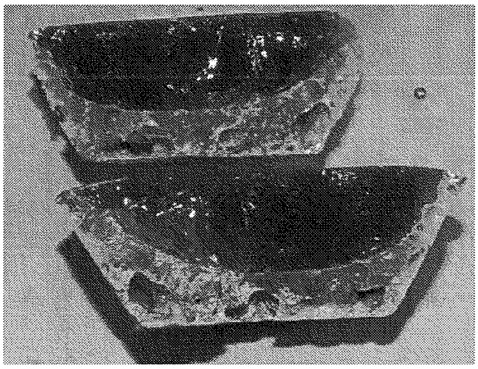
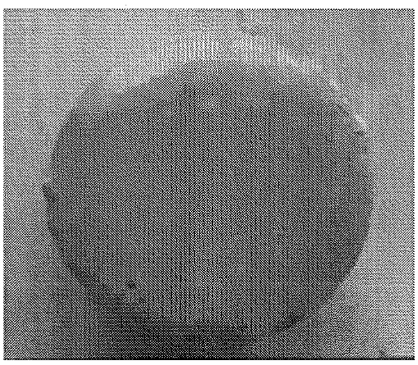
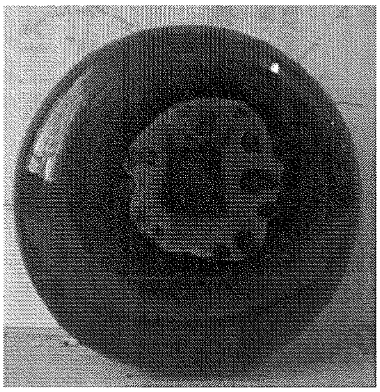
Si the number of silicon atoms of oxide constituent I

Suffix

i the oxide constituent i in the sample

The four slag pictures of different O/Si are shown in Table 2.

Table 2

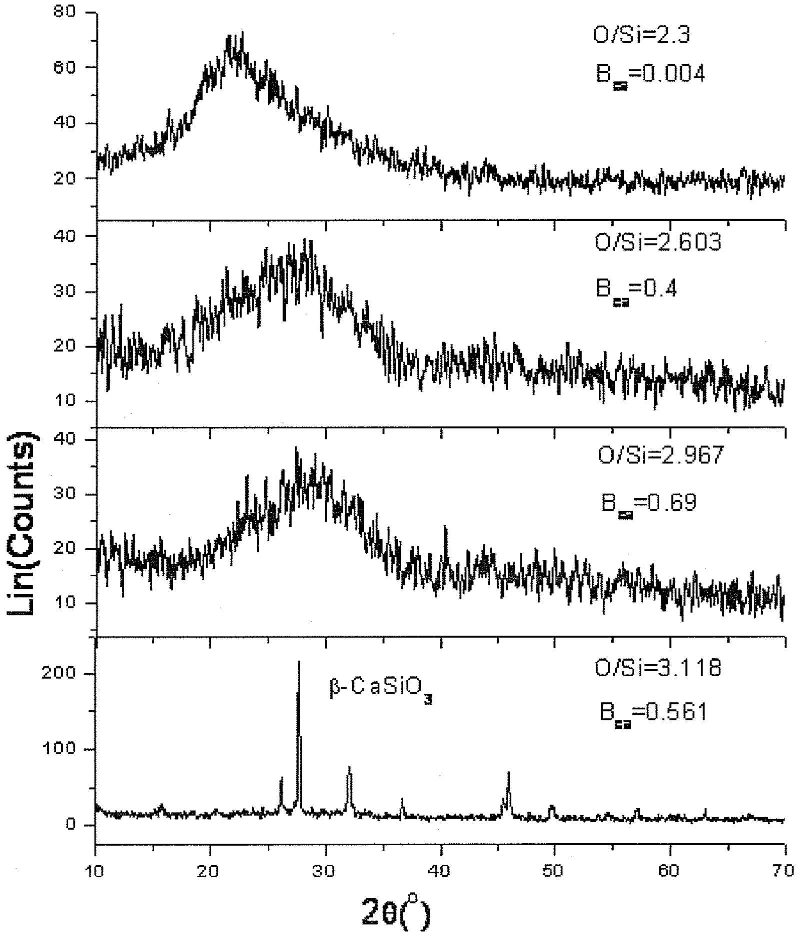
The slag's appearance pictures with different O/Si	
O/Si=3.118	O/Si=2.967
	
O/Si=2.603	O/Si=2.3
	

It was concluded from the slag's appearance that samples with an O/Si less than 3 had formed vitrified slag. The slag's surface of the sample with an O/Si of 3.118 had crystal solids, which showed that it was partially crystallized.

The XRD analysis is shown in Figure 4. It is obvious that the curve of the slag with an

O/Si of 3.118 has several diffract peaks, they are from β-$CaSiO_3$ crystal, hence, the slag is not vitrified. The curves of other 3 samples of slag, whose O/Si are less than 3 have no peak diffract peaks and the curve is extended wide to different diffract directions, which indicates that their micro structures are not "distant term order", namely, the vitrified slag is formed. The conclusion can be reached that the O/Si range to form vitrified slag is 2~3.

Figure 4: The four XRD of different O/Si and Bca



3. B_{ca}

B_{ca} is defined as the molar ration of CaO and SiO_2, which is shown in the formula below:

$$B = \frac{m_{CaO}}{MW_{CaO}} \times \frac{MW_{SiO_2}}{m_{SiO_2}}$$

Where:

B	the basicity	
m_{SiO_2}	the weight of SiO_2	g
m_{CaO}	the weight of CaO	g
MW_{CaO}	the molecular weight of CaO	56 g/mol
MW_{SiO_2}	the molecular weight of SiO_2	60 g/mol

From the figure 4, the slag with its $B_{ca} = 0.561$ did not turn vitrified slag, the others become vitrified slag. Some of vitrified slags B_{ca} are less than 0.561, and some are more than 0.561. It indicated that B_{ca} don`t relate to the formation of vitrified slag obviously.

4. Cooling Rate

There are 2 kinds of cooling methods in the experimental research, normal cooling and water quenching.

Normal cooling: cut off the power supply after the treatment, leave the crucible in the furnace, the slag is naturally cooled to room temperature.

Water quenching: when indicated temperature is lower than 800°C, open the furnace and sink the crucible into water quickly.

Slag photos for each kind of cooling method are shown in Figure 5 and Figure 6. Both methods can form vitrified slag. The vitrified slag by water quenching is more transparent and brittle, namely, closer to normal glass; while the one by normal cooling is harder. It shows that normal cooling could meet the requirements of vitrifying, faster cooling speed might cause differences chemically and physically.

Figure 5: Water quenching

Figure 6: Normal cooling

LEACHING CHARACTERISTICS RESEARCH

The mixed material was added by tracing heavy metal As, Pb, Cr and Zn with the same concentration of 6mg/g, and the vitrified slag was made from the material. The data was provided by Analysis Center of Tsinghua University. The concentration of each heavy metal is As-1.232mg/g, Pb-0.6624mg/g, Cr-6.116mg/g and Zn-1.9944mg/g. The material weight before the experiment is 60g and the weight of the vitrified slag is 55g. The slag was analyzed using ICP-AES method and the concentration of As, Pb, Zn and Cr was acquired. The results are shown in table 3, where the Identification Standards for Hazardous wastes identification for extraction toxicity is also displayed.

Table 3

The tracing heavy metal	Zn	Cr	As	Pb
The leaching solution	ND[1]	ND	ND	ND
Identification Standards for Hazardous	100	5	5	5

[1]ND not detected

It is shown that vitrified slag has a great chemical stability, a very low leaching capability. It can wrap up heavy metals and exist in nature safely in a long duration.

CONCLUSIONS

Based on the study above, the following conclusions can be drawn:

1. The temperature is not a main factor to affect the formation of vitrified slag, but must be higher than the eutectic point.
2. O/Si is the most important parameter, the range of 2~3 is the proper one to form vitrified slag.
3. B_{ca} can be explained as a part of O/Si, it affects the formation of vitrified slag by changing O/Si.
4. The natural cooling rate is enough to form vitrified slag, the faster only affect

appearance or maybe the chemical characteristics.

5. The leaching characteristics of vitrified slag are excellent, and the slag can be buried in nature directly.

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KEY WORDS

plasma, arc, vitrified slag, O/Si, XRD, hazardous wastes