THE FORMATION MECHANISM OF THE VITRIFIED SLAG IN A PLASMA ARC REACTOR FOR HAZARDOUS WASTE TREATMENT*

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ABSTRACT

Various hazardous wastes with additives have been vitrified to investigate the formation mechanism of the glassy slag by a 30 kW DC plasma-arc reactor developed by the Institute of Mechanics, Chinese Academy of Sciences. The average temperature in the reaction area is controlled at 1500°C. The chemical compositions of three sorts of fly ashes are analyzed by XRF (X-Ray Fluorescence). Fly ashes with vitrifying additives can be vitrified to form glassy slag, which show that the ratio of the whole oxygen ions to the whole network former ions in glass (R) is appropriate in the range of 2~3 to form durable vitrified slag. In this experiment, the arc power is controlled below 5 kW to inhibit waste evaporation. To enhance the effects of heat transfer to wastes, ferrous powder has been added into the graphite crucible, which aggregates as ingot below the molten silicate after vitrification. The slag fails to form glass if the quenching rate is less than 1 K/min. Therefore, the slag will break into small chips due to the sharp quenching rate, which is more than 100 K/sec.

INTRODUCTION

Amounts of toxic and hazardous waste are produced every year. The thermal treatment technology for wastes without secondary pollution has been widely studied by many researchers. Previous studies of plasma treatment of hazardous wastes have been done for years, including mixed medical wastes, incineration ashes, radioactive wastes, etc. The plasma pyrolysis with vitrification (PP/V) technology is a promising and environmentally friendly technology (1, 2). Due to the relatively high temperature heated by electricity, the toxic and hazardous wastes are destroyed completely in a plasma reactor. The hazardous organic wastes such as PCBs, PCDDs and PCDFs are pyrolyzed into some harmlessly simple molecules, and the off-gases are combustible and easily cleaned (3-5). Noncombustible inorganic wastes with a high content of heavy metals are mixed with proper vitrifying additives and melted, and then rapidly quenched to form a durable and leach-resistant glassy slag. The vitrified slag with a very low leaching rate can effectively stabilize and immobilize heavy metals. As a consequence, the vitrified slag is an environmentally friendly material for landfilling and it can also be reused as glass-ceramic material for construction (6-8). PP/V technology is a state-of-the-art technology and recently attracts more and more attentions in the world.

The following factors are very important to form a glassy slag: proper vitrifying materials; high enough molten temperature; sufficient reaction time; high enough viscosity of the materials and fast quenching rate. In the plasma treatment process, both operating parameters and the mechanism of the heavy metals transferring from the raw material into the vitrified slag are very important, but are not well understood and need further research.

A 30 kW DC plasma-arc reactor is designed to treat hazardous wastes in the Institute of Mechanics, Chinese Academy of Sciences (IM, CAS). Various hazardous wastes, such as chemical waste, medical and fly ash mixtures, have been destroyed and vitrified with this reactor. Three sorts of fly ashes collected by fabric filter are employed as the experimental materials. Many batch tests of fly ashes are carried out to investigate the formation mechanism of the vitrified slag. The mechanism to form vitreous slag is analyzed in terms of Zachariasen's random network theory of glass.

EXPERIMENTAL FACILITY

A schematic description of the 30 kW DC plasma-arc reactor is shown in Fig. 1. The system is composed of seven sub-systems: power supply, argon gas supply system, plasma arc generator and reactor of 30 kW, data acquisition system, measurement system, cooling system and off-gas scrubbing system. The reactor can work with different plasma gases of nitrogen, hydrogen, and argon, and has five connecting ports with the same flange to mount the electrodes and the quartz windows. It is convenient to change the position of the plasma arc by moving the electrodes. Reaction process in the graphite crucible can be observed and recorded from the windows. A picture of a tungsten cathode with a working gas of argon is shown in Fig. 2, where a dark filter is used to avoid strong arc light. The temperature of wastes is measured by a W-Rh thermocouple placed in the central bottom of crucible. The probe is protected by graphite sheath from molten silicate corrosion. Its position can be easily adjusted up and down. The temperature is controlled at approximately 1500°C in this experiment.



Fig. 1 A schematic diagram of the plasma system



Fig. 2 The working tungsten cathode

Three sorts of fly ashes, sampled from three different power plants, are marked with FA-1, FA-2 and FA-3. The chemical compositions of them, analyzed by XRF (X-Ray Fluorescence), are shown in Table I. It shows that the fly ashes contain a high content of heavy metals and a great deal of network formers from Table I.

Fly ashes	FA-1	FA-2	FA-3
composition	Wt.%	Wt.%	Wt.%
SiO ₂	40.46	51.5307	55.11
Al ₂ O ₃	49.04	31.7748	27.42
Fe ₂ O ₃	2.18	7.4025	4.36
CaO	4.24	1.8477	2.46
TiO ₂	1.90	1.6349	1.22
K ₂ O	0.44	1.0677	1.53
MgO	0.24	0.3910	0.61
Na ₂ O	0.08	0.2305	0.39
P ₂ O ₅	0.16	0.3433	0.13 0.05
SrO	0.00	0.1133	
ZrO ₂	0.00	0.1170	0.05
SO ₃	0.26	0.9172	0.52
Cr ₂ O ₃	0.01	0.0713	0.01
MnO	0.02	0.0481	0.03
V ₂ O ₅	0.02		—
С	0.92	2.4808	6.10
BaO	0.03		—
PbO ₂	0.01		—
ZnO		0.0293	—

Table I. The Chemical Compositions of Fly Ashes

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 SiO_2 is chosen as a vitrifying additive to adjust the proper proportion of network former. The experimental process is as follows: 1) put the waste mixture into graphite crucible after fly ash mixed with additives; 2) close the plasma reactor door; 3) pump out the air in the reactor; 4) inject argon into the reactor as the plasma gas; 5) start the arc by moving the cathode; 6) heat the mixture for 15min; 7) shut off power supply; and 8) cool the molten slag at a high enough quenching rate, which is controlled at 50 K/min in this study.

THE FORMATION MECHANISM OF A GLASSY SLAG

When a molten slag is cooled at a slow quenching rate, its viscosity increases very fast as its temperature decreases. The high viscosity will greatly reduce the molecular mobility of the molten slag, which resists forming crystals by regular molecular rearranging. On the other hand, if the slag keeps liquid phase below the liquidus, the deeper the slag is supercooled, the faster the crystalline phase nucleates and grows. Glassy slag can be obtained if the quenching time is shorter than the time required for nucleation and growth of the crystalline phase (9, 10). Consequently, when cooled at fast enough quenching rate, the vitrified slag would become kinetically stable and neither nucleation nor growth of the more stable crystalline phases would occur.

The viscosity of a slag or glass depends strongly on two factors: composition and temperature. The change of viscosity with temperature is very large, which can be represented by an Arrhenius equation (12). So the quenching rate is very important to form durable vitrified slag.

According to Zachariasen's random network theory of glass, it can be explained that the viscosity of molten slag is relatively high since the glass-forming materials such as SiO_2 , As_2O_3 can form a three-dimensional extended network losing long-range order. In the silicon-oxygen tetrahedron, bridging oxygen connects two silicon-oxygen tetrahedra and makes the structure compact, which also leads to three-dimensional extended networks and high viscosity. On the contrary, non-bridging oxygen breaks the connection between two silicon-oxygen tetrahedra and decreases the viscosity. The ratio of the whole oxygen ions to the whole network former ions in glass (R) represents the ratio of network former and network modifier. R has a strong influence on the properties and formation of the glassy slag. Quartz glass with R of 2 is very chemically stable. As a result, the smaller the R is, the more bridging oxygen is present, and more stable and compact glass forms.

A three-dimensional extended network has four fundamental structure parameters: X (the number of non-bridging oxygen), Y (the number of bridging oxygen), Z (the coordination number of the cation of network former), and R. The relationships among them are represented by the following two equations (13):

$$X+Y=Z (Eq. 1)$$

$$X+0.5Y=R$$
 (Eq. 2)

In the silicate molten slag, the cation of the network former is usually silicon, so Z=4. If X is bigger than 2, the three-dimensional extended network would fail to form. If X equals 2, R equals 3. In general, R is appropriate in the range of $2\sim3$ to form good vitrified slag.

All three sorts of fly ashes contain a great deal of Al2O3 termed as intermediate oxide, which acts

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both-side function. If Al_2O_3 is minor, it would act as network former, otherwise as network modifier. Consequently, SiO_2 is chosen as vitrifying additive to adjust the proper proportion of network former of fly ashes. The fundamental network structure parameters of fly ashes adjusted by adding SiO_2 are shown in Table II.

Sample	NO.1	NO.2	NO.3	NO.4	NO.5	NO.6
	FA-1	FA-1: SiO ₂ =1:1	FA-2	FA-2: SiO ₂ =1:1	FA-3	FA-3: SiO ₂ =1:1
Parameters						
R	4.42	2.7	3.43	2.48	3.12	2.4
Х	4.85	1.4	2.85	0.97	2.24	0.8
Y	-0.86	2.6	1.16	3.02	1.76	3.2

Table II. The Fundamental Network Structure Parameters of Fly Ashes

RESULTS AND DISCUSSIONS

The wastes in the graphite crucible are rapidly heated by the intensive thermal energy generated by electricity. The waste mixture has a low thermal conductivity of approximately 0.7 W/(m×K). The high heat flux to the upper layer of wastes leads to relatively high Biot number. Due to high Biot number, the upper layer of waste has been heated to a temperature higher than the evaporation temperature, but the lower layer of waste still remains in solid state. Consequently, high arc power results in a serious waste evaporation problem. In this experiment, the arc power of less than 5kW is appropriate to effectively avoid evaporation. To enhance the effects of heat transfer to wastes, ferrous powder has been added into the graphite crucible, which aggregates as an ingot below the molten silicate after vitrification as a consequence of gravity.

The mixtures with different contents of vitrifying additives, such as sand, calcium oxide and disodium oxide, are vitrified into vitreous slag in different molds. Two of them are shown in Fig. 3. The results show that when the mixture contains more sand, vitreous slag forms more easily. The slag sample 1 and slag sample 2 are shown in Fig. 4 and Fig. 5, respectively. The slag sample 1, 3 and 5 did not form amorphous structures. On the contrary, the slag sample 2, 4 and 6 formed amorphous structures. Table 2 shows that sample 1, 3 and 5 have the R number more than 3, but sample 2, 4 and 6 have the R number in the range of $2 \sim 3$. The slag sample $1 \sim 6$ show that R is appropriate in the range of $2 \sim 3$ to form a vitreous slag as analyzed above. The R number more than 3 accounts for the failure of vitrification process of sample 1, 3 and 5. Fly ash with vitrifying additive forms vitrified slag. Further detailed analysis of slags by XRD, SEM and TCLP will be performed in the next step. It is found that the slag fails to form glass if the quenching rate is less than 1 K/min. Therefore, the slag will break into small chips due to the sharp quenching rate, which is more than 100 K/sec.



Fig. 3 The vitrified slag from vitrifying additive mixture



Fig. 4 The slag sample 1

Fig. 5 The vitreous slag sample 2

CONCLUSIONS

Three sorts of fly ashes with SiO_2 additive have been vitrified to investigate the formation mechanism of a glassy slag by a 30 kW DC plasma-arc reactor. Due to high Biot number, the upper layer of waste has been heated to a temperature higher than the evaporation temperature, but the lower layer of waste still remains in solid state. Consequently, high arc power results in a serious waste evaporation problem and the arc power less than 5kW is appropriate in this experiment. Ferrous powder has been added into the graphite crucible to enhance the effects of heat transfer to wastes and aggregates as ingot in the below of molten silicate after vitrification.

The high viscosity of a melt depends largely on two factors: composition and temperature. Glass formation requires fast enough quenching rate. It is found that the slag fails to form glass if the quenching rate is less than 1 K/min. Therefore, the slag will break into small chips due to the sharp quenching rate, which is more than 100 K/sec.

The R number has a strong influence on the formation and properties of the glassy slag. The vitrification results of the mixture of waste with vitrifying additives show that the mixture contains of more sand, vitreous slag forms more easily. Sample 1, 3 and 5 have the R number more than 3 that accounts for the failure of vitrification process. Sample 2, 4 and 6 have the R number less than 3 and form amorphous state. The slag sample $1\sim6$ show that the R number is appropriate in the range of $2\sim3$ to form a vitreous slag. Fly ashes with vitrifying additive can form vitrified slag.

Footnotes

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References

- 1. Pfender, E., Thermal Plasma Technology: Where Do We Stand and Where Are We going? Plasma Chemistry and Plasma Processing 19 (1), 1-31, (1999).
- Sheng H.-Z., Xu Y.-X. and Cao Y.-X., Plasma Based Pyro-incinerator for Hazardous Waste Disposal, Proceedings of the 2002 International Conference on Incineration and Thermal Treatment Technologies, New Orleans, Louisiana, USA, (May 2002).
- Hongzhi Sheng, Yaojian Li, Xiaolin Wei, Yongxiang Xu, Junguo Tian, Rui Wang and Zhiqin Huang, Plasma Pyrolysis of Hazardous Waste from Chemical Plant, Proceedings of the 4th International Conference on Combustion, Incineration/Pyrolysis and Emission Control, Kyoto, Japan, (September 2006).
- 4. Seok-Wan Kim, Hyun-Seo Park and Hyung-Jin Kim, 100 kW Steam Plasma Process for Treatment of PCBs(Polychlorinated Biphenyls) Waste, Vacuum, 70, 59-66, (2003).
- Hongzhi Sheng, Xiaolin Wei, Yu Zhang and Yongxiang Xu, Destruction of Hazardous Wastes in a Plasma-Arc Reactor and a Plasma-Enhanced Pyrolysis Reactor, Proceedings of the 2005 International Conference on Incineration and Thermal Treatment Technologies, Texas, USA, (May 2005).
- Lapa N., Santos Oliveira J.F., Camacho S.L. and Circeo L.J., An Ecotoxic Risk Assessment of Residue Materials Produced by the Plasma Pyrolysis/Vitrification (PP/V) Process. Waste Management 22, 335-342, (2002).
- 7. Kjell E. Haugsten and Bengt Gustavson, Environmental Properties of Vitrified Fly Ash from Hazardous and Municipal Waste Incineration, Waste Management 20, 167-176, (2000).
- J.P. Chu, I.J. Hwang, C.C. Tzeng, Y.Y. Kuo and Y.J. Yu, Characterization of Vitrified Slag from Mixed Medical Waste Surrogates Treated by a Thermal Plasma System, Journal of Hazardous Materials 58, 179-194, (1998)
- 9. Allen M.Alper, Phase Diagrams Materials Science and Technology, Volume I, Academic Press (1970).
- 10. Saeid Davatolhagh, Bond-ordering Representation for the Glass Transition, dissertation, Ohio State University, (2001).
- 11. YongQuan WU, Theoretical Studies on the Micro-structure of Molten Silicates and Its Relation with the Macro-Propertities, dissertation, ShangHai University, (November 2003).
- 12. Wanqing Huang, Laboratory Research for High-Temperature Waste Vitrification, dissertation, University of Idaho, p4-19, (2000).
- 13. Xiulan Wu, Guoping Chen and Ying Ji, Production Prescription and Process Control of Silicate, Chemical Industry Press, p111-120, (August 2004).