

## Effect of cooling rate and basicity during vitrification of fly ash Part 2. On the chemical stability and acid resistance of slags

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### Abstract

The object of this study is to investigate how the cooling rate and the basicity during the vitrification process govern the chemical stability and acid resistance of slags. In this experiment, the incineration fly ashes with various basicities were vitrified at 1450 °C and cooled down by air cooling and water quenching, respectively. The amorphous volume fractions (AVF) in slags were estimated by X-ray diffraction analysis with the addition of an internal standard. Scanning electron microscopy was applied to qualitatively examine the microstructures of the original and the acid-immersed slags. It was verified that the addition of SiO<sub>2</sub> and water quenching both significantly affected the crystalline characteristics of the slag. When the basicity was >0.990, the AVF of slags was approximately equal regardless of the cooling rate. When the basicity was <0.674, water quenching greatly enhanced the formation of glassy amorphous phase and the immobilization of metals in slags. In contrast, a lower basicity (<0.511) is required if one wants to vitrify fly ash into slags and cool it down by air. As a whole, the glassy amorphous structure presented better chemical resistance than the crystalline structure to decomposition by an acid.

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**Keywords:** Water quenching; Vitrification; Corrosion; Amorphous volume fraction; Basicity

### 1. Introduction

Incineration is a popular technology to treat municipal solid waste (MSW) in Taiwan due to the diminishing availability of landfill sites. It causes toxic metals contained in MSW to either evaporate into fly ash or remain in bottom ash. In general, about 20–30 wt% of original waste is left as ashes [1]. Fly ash must be detoxified because it contains high concentrations of heavy metals and organic pollutants [2]. Direct landfilling of fly ash is not suitable as it will result in serious contamination of ground-water and soil. Solidification and stabilization by cementation

have been frequently used to treat fly ash worldwide [3]. However, this technology increases the waste volume. In addition, organic toxics, such as dioxins and PAHs, are difficult to stabilize by cementation or other chemicals since the hydration of cementation will be hindered by the high concentrations of alkali chlorides in fly ash [4].

By contrast, vitrification can destroy dioxins, immobilize heavy metals, and reduce the waste volume [5–8]. Useful products, such as glass ceramics or road paving stones, could be made through such a thermal process [9]. Hence, vitrification is regarded as a good technology to treat fly ash or other hazardous materials [10]. From an environmental point of view, the leaching behavior of heavy metals in slags is especially important due to their serious threat to public health. It is well known that leaching concentration of hazardous metals is highly related to

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the structure of slags. A previous study also stated that the leaching concentration of metals in crystalline slags is relatively high in comparison to amorphous slags [11]. It has been reported that the grain boundary precipitation of agglomerates causes the increase of leaching [12], but no direct evidence supports this statement. In part 1 of the current investigation, it was verified that the addition of SiO<sub>2</sub> and water quenching both enhanced the ability of Al and O to disperse uniformly and reduce the formation of crystalline phases in slags. Nevertheless, how these two

factors influenced the chemical stability of slags was not demonstrated. In part 2 of this study, the effect of the amorphous glassy structures on the immobilization of metals and resistance to acid corrosion is further investigated.

## 2. Experimental

The fly ash used in this experiment was sampled from fabric filters in an air pollution control device at a municipal solid waste

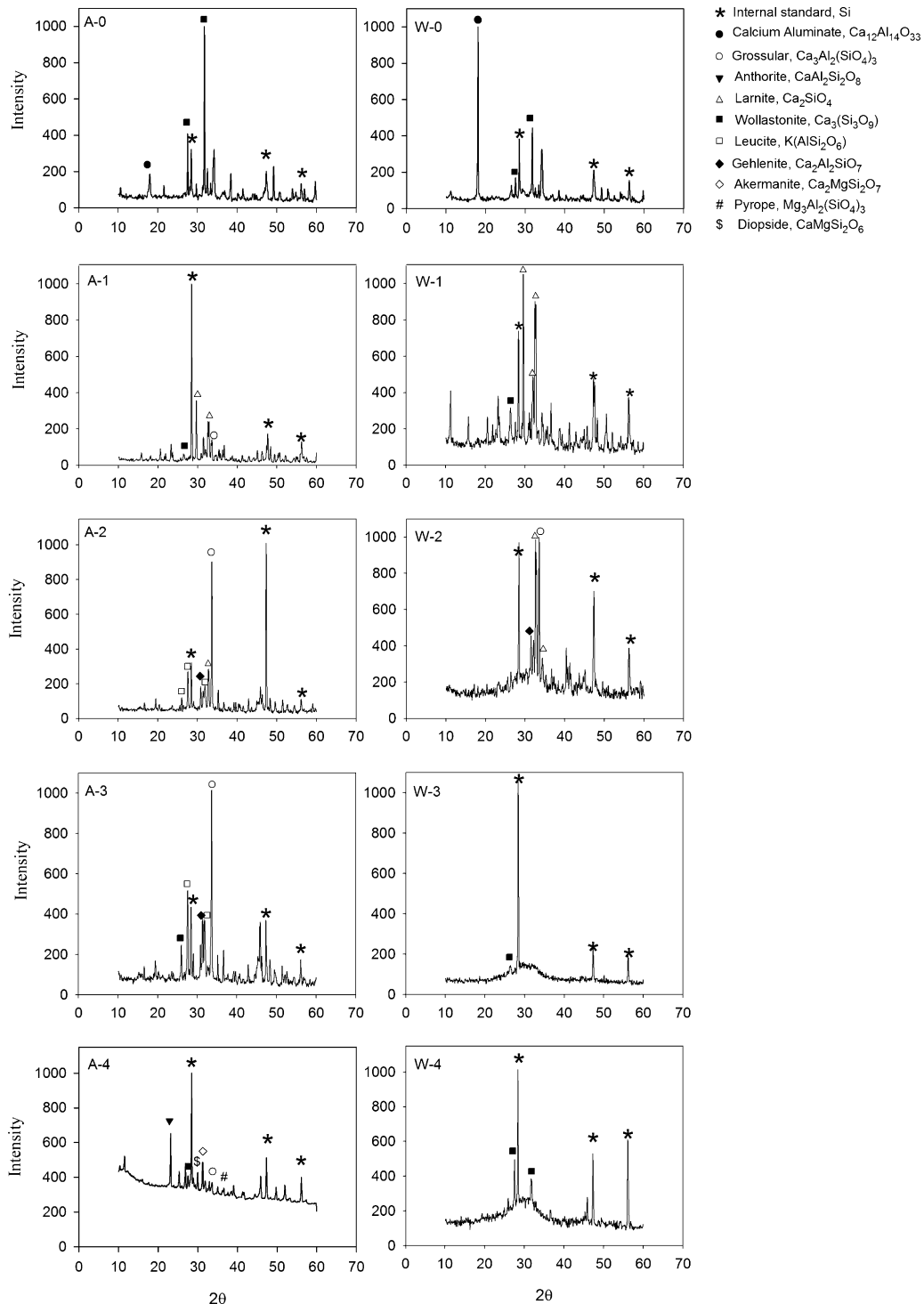


Fig. 1. XRD analysis patterns of slags.

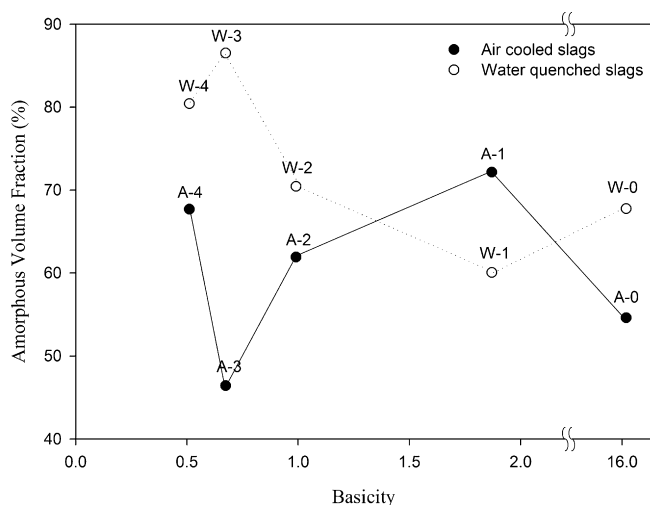


Fig. 2. Behavior of amorphous volume fraction in slags vs. basicity.

incinerator located in Southern Taiwan. To adjust the basicity of the fly ash,  $\text{SiO}_2$  served as an additive with  $\text{SiO}_2$ /fly ash (S/A) mass mixing ratios of 0, 0.1, 0.2, 0.3 and 0.4. Ash mixtures were heated to  $1450^\circ\text{C}$  at  $6^\circ\text{C}/\text{min}$ . Specimens were then cooled down by air cooling and water quenching, respectively. The specimens produced by air cooling and water quenching, were correspondingly labeled in numeric order as A-0 to A-4 and W-0 to W-4, respectively.

The mobility of hazardous metal species in fly ash and slags was evaluated by the toxicity characteristic leaching procedure (TCLP). The extracts of TCLP were digested and diluted to a fixed volume following the detailed procedure given in Method 1311 [13]. The concentrations of metal species in extracts, including Cd, Cr, Cu, Pb, and Zn were determined by atomic absorption spectrometry.

In order to investigate the acid resistance of slags with various crystalline characteristics, the slags were pulverized and immersed in an acid solution of 3 wt% HCl for 7 days.

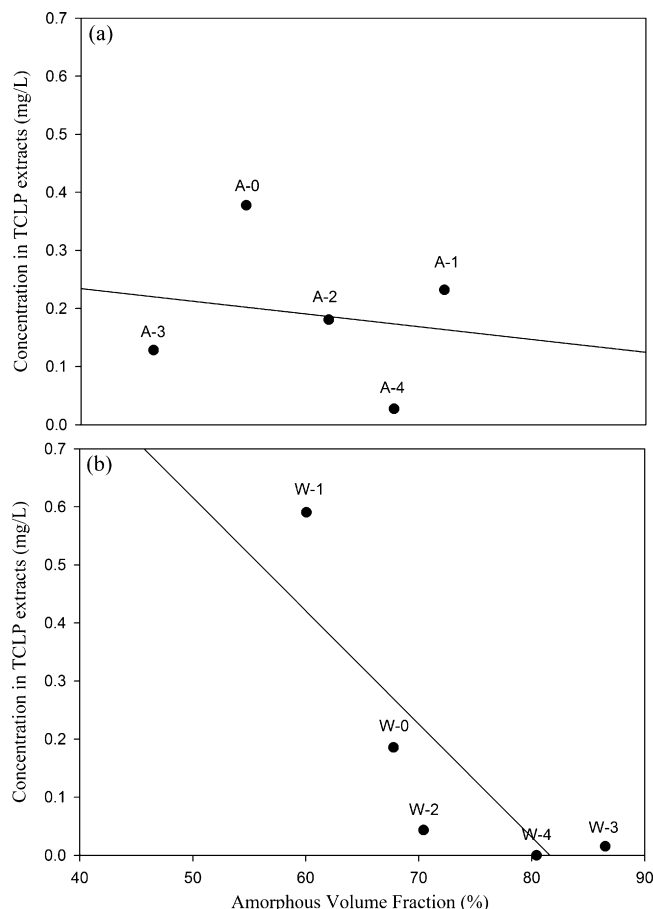


Fig. 3. Leaching behavior of Cd vs. amorphous volume fraction (a) air cooled slags; and (b) water cooled slags.

The specimens were rinsed by de-ionic water and then dried at  $105^\circ\text{C}$  for 1 h. The microstructures of the original slags and the acid-immersed slags were qualitatively examined by scanning electron microscopy—energy dispersive spectroscopy (Jeol JXA-840 SEM-EDS). Specimens were adhered on a metal-

Table 1  
Composition of fly ash and slags ( $n = 3$ )

Crust elements	Ash-0			A-0			W-0		
	Range (%)	Average (%)	R.S.D. (%)	Range (%)	Average (%)	R.S.D. (%)	Range (%)	Average (%)	R.S.D. (%)
$\text{Al}_2\text{O}_3$	0.604–0.711	0.671	8.62	1.16–1.40	1.31	10.4	1.12–1.29	1.22	6.87
CaO	19.4–23.0	21.1	8.44	39.4–43.2	40.7	5.30	34.3–38.0	35.9	5.32
$\text{Fe}_2\text{O}_3$	1.63–2.05	1.82	11.6	2.99–3.16	3.07	2.80	2.61–2.71	2.65	1.86
MgO	0.918–1.03	0.972	6.01	1.63–1.72	1.66	2.86	1.63–1.67	1.65	1.34
$\text{SiO}_2$	0.757–1.60	1.31	36.6	2.05–2.25	2.15	4.65	1.81–2.27	2.10	11.9
Anthropogenic Metals	Range (mg/kg)	Average (mg/kg)	R.S.D. (%)	Range (mg/kg)	Average (g/kg)	R.S.D. (%)	Range (mg/kg)	Average (g/kg)	R.S.D. (%)
Cd	35.2–38.7	36.8	4.80	3.52–4.32	3.80	11.8	6.62–6.67	6.64	0.38
Cr	470–573	508	11.1	332–360	348	4.19	353–370	364	2.64
Cu	253–300	276	8.46	607–645	626	3.06	403–422	412	2.23
Mn	283–352	311	11.7	458–478	471	2.36	455–468	461	1.46
Ni	14.4–28.7	21.2	33.9	123–132	127	3.53	42.7–54.0	48.0	11.9
Pb	2400–2520	2470	2.55	1250–1360	1300	4.56	1170–1310	1230	5.99
Zn	5150–7320	6110	18.1	48.7–60.3	53.3	11.6	54.2–73.3	65.1	15.2

R.S.D. = relative standard deviation.

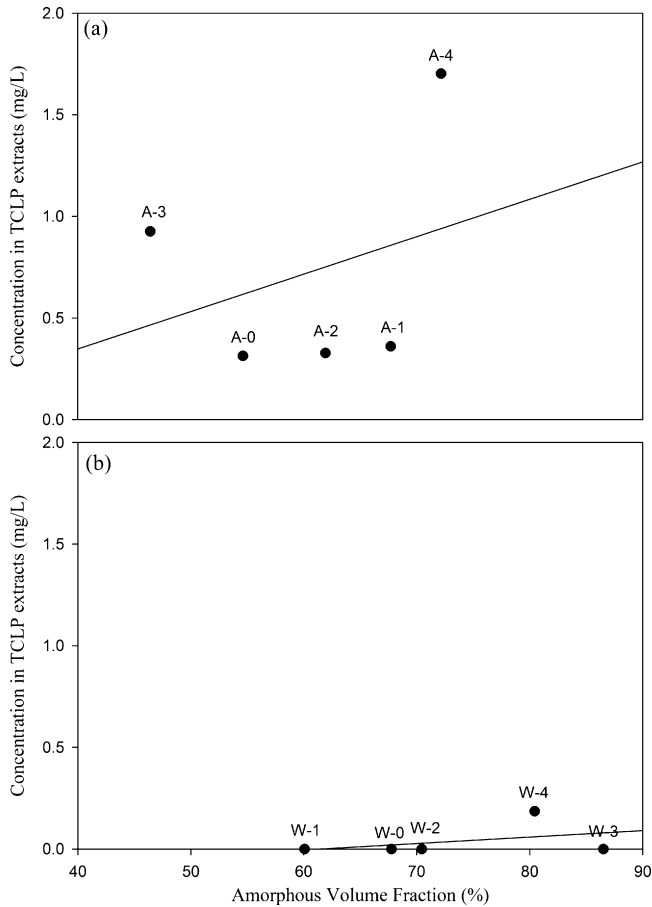


Fig. 4. Leaching behavior of Cr vs. amorphous volume fraction (a) air cooled slags; and (b) water cooled slags.

lic plate, coated with Au using an ion sputter coater, and then scanned by the microscope.

The crystalline phases in slags were determined by X-ray diffraction (XRD) analysis. This was carried out by a powder diffractometer (Geigerflex 3063) with Ni-filtered Cu K $\alpha$  radiation on powders, at a particle size <20  $\mu$ m, at 4°/min, in the 2 $\theta$  = 10–60° range. The XRD analysis patterns, taken from part 1 of this study, are shown in Fig. 1. The crystalline phases in slags were specifically identified and the volume fractions of these phases were quantitatively estimated in part 1 of our study. In this work, the volume fraction of the crystalline phase in slags was measured by an XRD analysis with an internal standard addition [14]. High-purity silica was used to mix with specimens as an internal standard with a Si/sample mass ratio of 0.1. It served as a reference material in the crystalline quantitative analysis. The approximate fraction of the crystalline phase was then determined according to the area of their specific peaks in comparison with the internal standard and the details of the procedure given in previous reports [15]. The amorphous volume fractions (AVF) of slags were calculated by the following equation.

$$AVF = 1 - \sum_{i=1}^{i=n} CP_i$$

CP $_i$ : the volume fraction of *i*th crystalline phase.

### 3. Results and discussion

#### 3.1. Metal composition and amorphous volume fraction of slags

Fig. 2 illustrates the behaviors of amorphous volume fraction in slags with a variety of basicities and different cooling ways. When the basicity >0.990, which is not favorable for vitrification [16], the AVFs were roughly equal, whether by air cooling or water quenching. However, at basicity = 0.674, AVF of water quenched slags elevated to 80–90%, whereas the AVF of air cooled slags ranged from only about 40–50%. This clearly demonstrates that water quenching actually has a significant effect on enhancing the formation of glassy amorphous structures if the basicity is <0.674. A previous study reported that the formation of glassy amorphous structures drastically reduces the specific surface area [17]. Therefore, it could be expected that water quenched slags would have a smaller surface area than air cooled slags, and this would affect the leaching behavior of metals. For air cooled slags, the inverse of AVF at the basicity <0.674 was observed, revealing that AVF will be elevated at lower basicity according to the results of a previous study [18]. Apparently, an even lower basicity (<0.674) is required if one wants to vitrify fly ash well with an air cooling process.

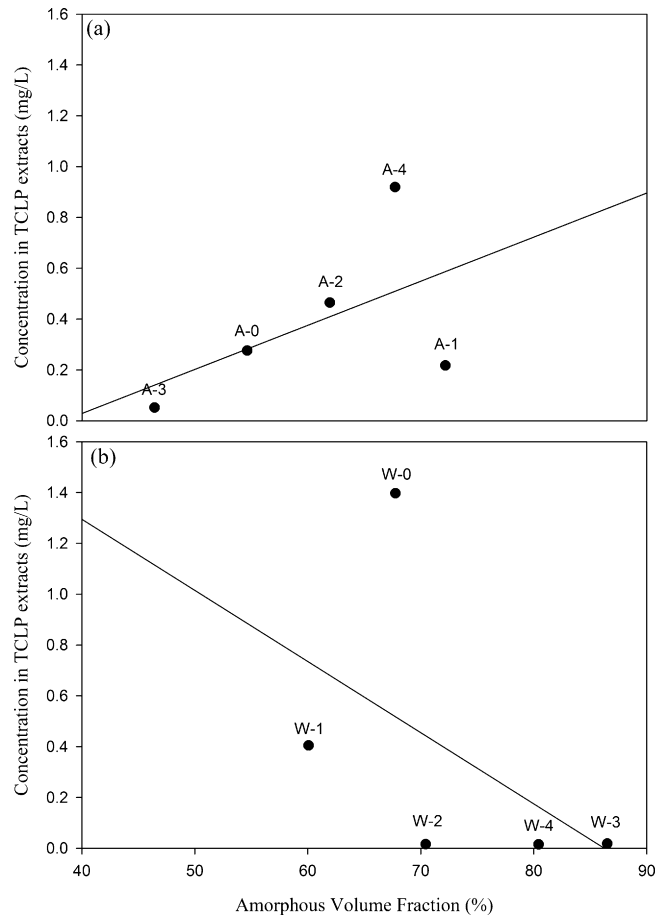


Fig. 5. Leaching behavior of Cu vs. amorphous volume fraction (a) air cooled slags; and (b) water cooled slags.

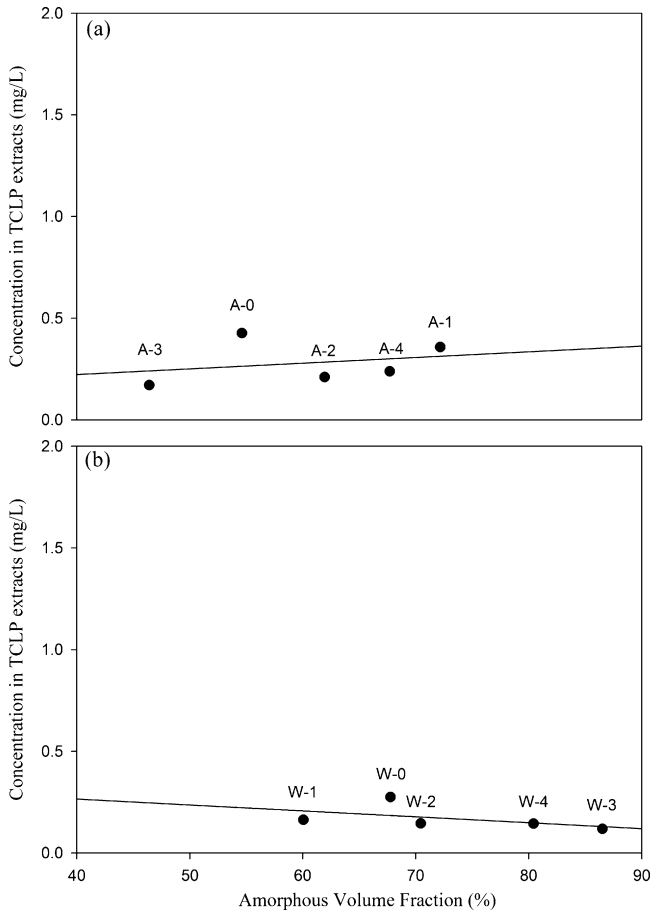


Fig. 6. Leaching behavior of Pb vs. amorphous volume fraction (a) air cooled slags; and (b) water cooled slags.

### 3.2. Metal leaching behavior of slags

The metal leaching behaviors in slags versus the amorphous volume fraction are illustrated in Figs. 3–7. Table 1 (taken from part 1 of this study) shows the compositions of the fly ash and the slags to serve as a reference to evaluate the leaching behaviors of heavy metals. The composition A-0 and W-0 are on behalf of air-cooled and water quenched slags, respectively. The metal content (except for Si) in A-1 to A-4 and W-1 to W-4 decrease proportionally due to the addition of SiO<sub>2</sub>. For Cd, no noteworthy trend of the leaching concentrations with a variety of AVF values could be observed in air cooled slags, whereas the availability of Cd in water quenched slags with higher AVF values was significantly reduced. In Fig. 4, the leaching concentrations of Cr in air cooled slags were relatively higher than those in water quenched slags. A similar result found that Cr would be more mobile with a slower cooling rate due to a more intensive surface oxidation of the slag to form more leachable Cr<sup>+6</sup> [12].

For Cu, it was observed in both slags that the concentration in the extract decreased as the AVF increased. In water quenched slags, leaching of Cu was undetectable while the AVF was elevated to 70%. Fig. 6 shows that the leaching concentrations of Pb in slags were all under 0.5 mg/L, revealing that AVF had no notable influence on the mobility of Pb. After

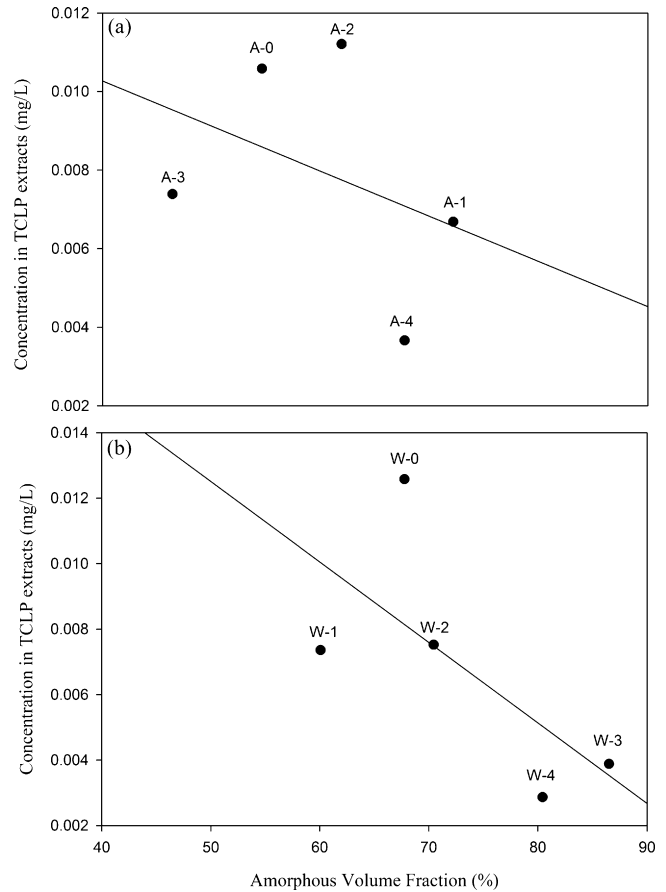


Fig. 7. Leaching behavior of Zn vs. amorphous volume fraction (a) air cooled slags; and (b) water cooled slags.

vitrification, leaching concentrations of Zn were <0.01 mg/L in all slags, indicating that its availability was drastically reduced.

### 3.3. Microstructure of fly ash and slags

The appearance of the fly ash was light gray and powdery. After the vitrification process, air cooled slags agglomerated and turned dark gray. In contrast, water quenched slags were

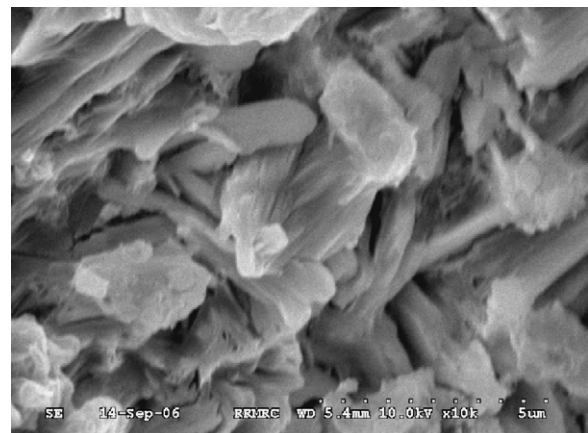
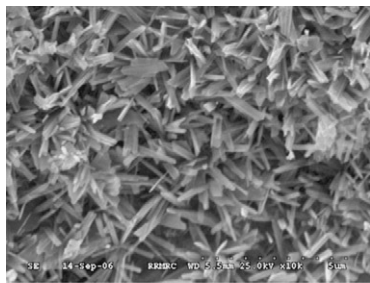


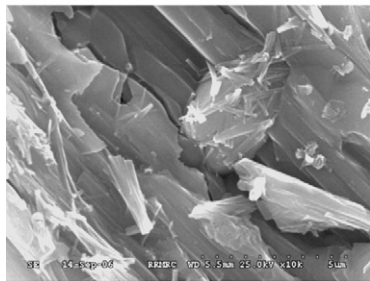
Fig. 8. SEM images of the fly ash.

all fractured into pieces during the cooling process and turned red brown. Fig. 8 shows the SEM images of the fly ash, which demonstrates that its structure is highly porous, uneven, and has a crystalline surface. Therefore, it could be expected that heavy

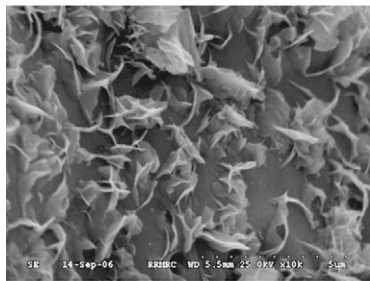
metals adsorbed on the fly ash particles could be easily leached out. Figs. 9 and 10 illustrate the SEM images of slags cooled down by air and water quenching, respectively. After vitrification, the formation of crystalline phases could be commonly



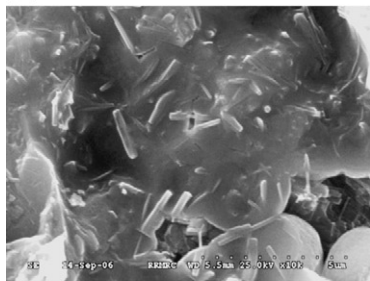
(a)A-0



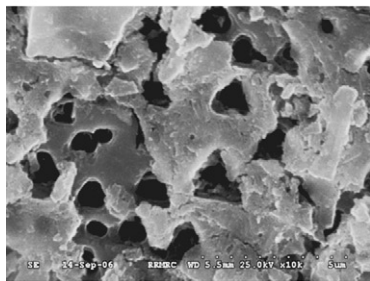
(b)A-1



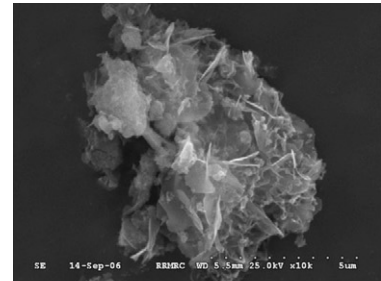
(c)A-2



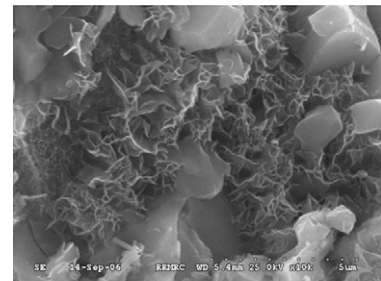
(d)A-3



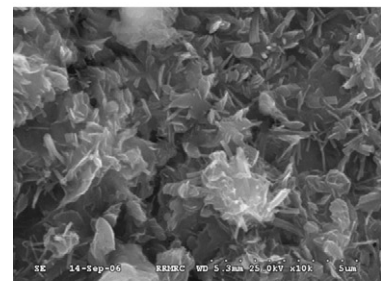
(e)A-4



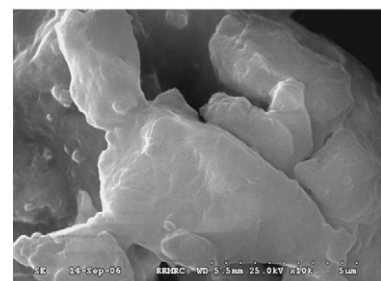
(a)W-0



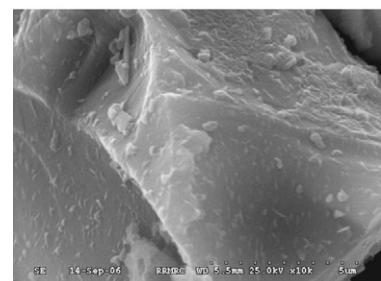
(b)W-1



(c)W-2



(d)W-3



(e)W-4

Fig. 9. SEM images of air cooled slags (a) A-0; (b) A-1; (c) A-2; (d) A-3; (e) A-4.

Fig. 10. SEM images of water quenched slags (a) W-0; (b) W-1; (c) W-2; (d) W-3; (e) W-4.

observed in all air cooled slags. In Fig. 9(a), A-0 had an elongated, highly porous, and fibric radial crystalline structure. The XRD analysis patterns showed that wollastonite,  $\text{Ca}_3(\text{Si}_3\text{O}_9)$ , was the predominate crystalline phase in both A-0 and W-0. The appearance of  $\text{Ca}_3(\text{Si}_3\text{O}_9)$  was fibrous, supporting the observation of the SEM images. In Fig. 9(b) and (c), glassy structures were initially observed in A-1 and A-2, and their characteristics were more obvious with an increase of  $\text{SiO}_2$ . Comparing the shape of crystalline phases in the air cooled slags, it can be seen that a transformation of the crystalline phase occurred. As more  $\text{SiO}_2$  was added, the crystalline phases in A-2 and A-3 were partly embedded or encapsulated in the amorphous structure. As for A-4, a compact and dense structure appeared to enclose the crystalline phase, but a significant amount of pores was also observed.

As for the water quenched slags, shown in Fig. 10, the shape of the crystalline phases in W-0 was needle-like and similar to A-0, but few glass-like agglomerates were observed. As the amount of  $\text{SiO}_2$  increased, both the amount and volume of the glassy amorphous phase also increased. In W-2, the amorphous phase started to encapsulate the crystalline phase, and the appearance of the crystalline phase was similar to A-2. For W-3 and W-4, the crystalline phases almost diminished and were completely embedded into the glassy amorphous structure, with only a few crystalline agglomerates observed on the surface, indicating good effect of vitrification.

As a whole, the morphology of slags pairs, including those of A-0/W-0, A-1/W-1, and A-2/W-2, were roughly similar. Conversely, the appearances of A-3/W-3 and A-4/W-4 were completely different from each other. The similarity of the slag appearance obviously depended on the basicity and the way of being cooled down during vitrification. When the addition of  $\text{SiO}_2$  was insufficient to vitrify the fly ash well, the appearance of slags was similar as long as their basicities were equal, regardless of the method of cooling down. In contrast, water quenching or air cooling govern the crystalline structure of slags with adequate basicity ( $<0.674$ ). This statement is also supported by the results from the XRD analysis reported in part I of this study.

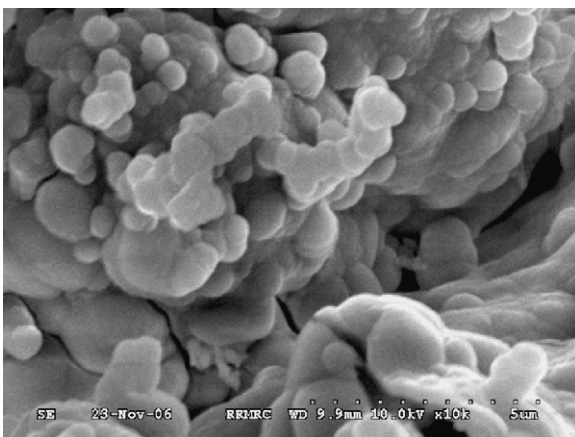
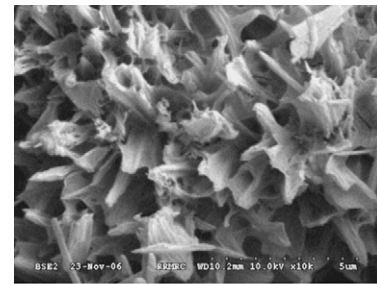
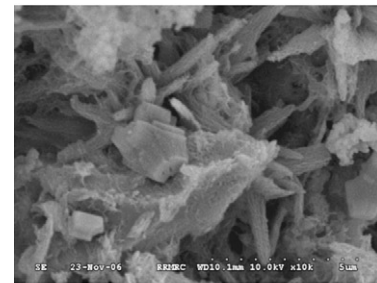


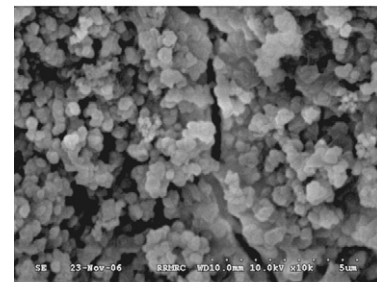
Fig. 11. SEM images of the fly ash after being immersed in a 3% HCl solution for 7 days.



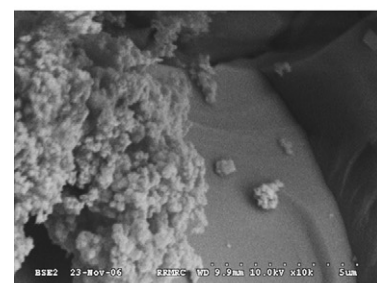
(a)A-0



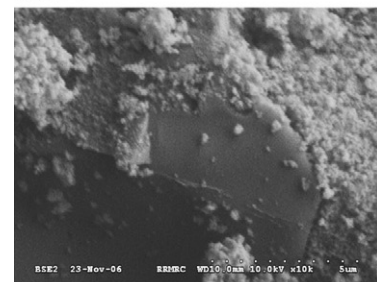
(b)A-1



(c)A-2



(d)A-3

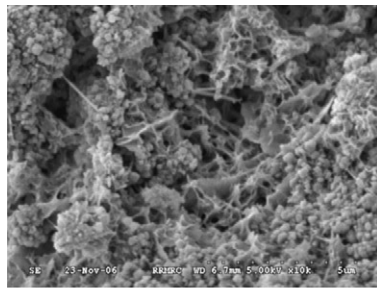


(e)A-4

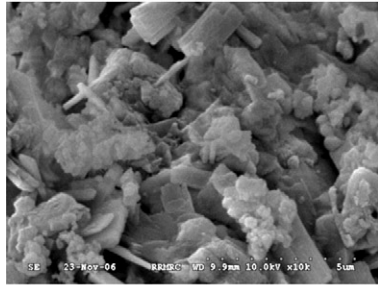
Fig. 12. SEM images of air cooled slags after being immersed in a 3% HCl solution for 7 days (a) A-0; (b) A-1; (c) A-2; (d) A-3; (e) A-4.

### 3.4. Acid resistance of slags

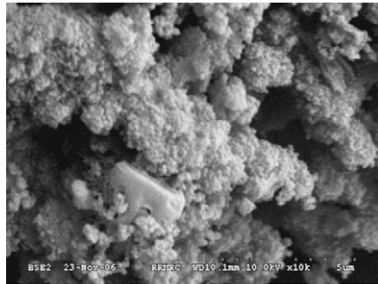
Figs. 11–13 show images of the slags with severe corrosion in an acid solution with 3 wt% HCl. In Fig. 11, the fly ash changed



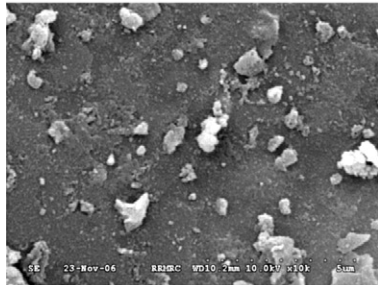
(a) W-0



(b) W-1



(c) W-2



(d) W-3



(e) W-4

Fig. 13. SEM images of water quenched slags after being immersed in a 3% HCl solution for 7 days (a) W-0; (b) W-1; (c) W-2; (d) W-3; (e) W-4.

into a sphere after the harsh corrosion of HCl. In Fig. 12(a)–(c), it can be obviously seen that the fabric crystalline phases were seriously corroded to a powder and the crystalline structure of the slags was destroyed.

However, for A-3 and A-4, a drastic difference between the crystalline and amorphous phases was seen in the SEM photographs. Some porous or powdered structures which appeared on the surface of slags due to the immersion in HCl solution were clearly observed, while the glassy amorphous structures showed stability even after being exposed to the acid solution.

For water quenched slags, Fig. 13(a)–(c) approved that an acid attack resulted in a large number of pores in W-0 to W-2. As for W-3 and W-4, no sign of decomposition was seen on the surface of the amorphous glassy structure. Even for the crystalline phase depositing on the amorphous glassy phase, only slight wear mark was observed, revealing that W-3 and W-4 had a better chemical stability to resist decomposition by an acid. According to the XRD analysis in part 1 of this paper, similar crystalline patterns were found in the slag pairs of A-0/W-0, A-1/W-1 and A-2/W-2. On examining SEM photographs of these slag pairs, the appearances of slags before the corrosion of HCl were found to be in accordance with the XRD analysis. With lower AVF, more crystalline structure could be observed on the surface of slags. In contrast, a more obviously glassy amorphous structure was found with higher AVF. After the corrosion of acid, it was found that all slags were seriously decomposed, except for W-3 and W-4, which contained a higher AVF. Those areas which were seriously corroded had a crystalline structure. This shows that slags with a higher AVF have better ability to resist the acid. However, the glassy amorphous phase will decrease the hardness and bending stress of slags due to the wrecking of the crystalline structure [19]. Therefore, it is difficult to give consideration to both chemical and physical properties.

As the basicity decreased to 0.674, significant differences between air cooled and water quenched slags were distinguished according to the XRD and SEM analysis. By combining the results, it was clearly found that water quenching with a basicity <0.674 could obtain good effect of vitrification. By contrast, a basicity <0.511 would be required to vitrify fly ash well if the slag was cooled down by air.

#### 4. Conclusions

The basicity and cooling down method appeared to greatly affect the crystalline characteristics of the structure in slags. When the basicity was higher than 0.990, no matter how the slags were cooled down, the AVF in slags were approximately equal and the appearance of the crystalline phases was also roughly similar. The XRD analysis in part 1 of this study supported the above statement. When the basicity decreased to 0.674, water quenching significantly enhanced the formation of glassy amorphous structures, while, hazardous metal species in the slags were also well immobilized. In slags, the glassy amorphous structure also presented better resistance to the decomposition by an acid than the crystalline structure. It can be concluded that the addition of SiO<sub>2</sub> and water quenching both are important factors during vitrification that can enhance the formation of an amorphous glassy structure to improve the chemical stability of slags. Such an amorphous structure will weaken a slag, and thus the choosing of an amorphous or a crystalline structure of the slag depends on how the slags are reused. When a highly toxic



waste is treated, the safety of reusing the slag is the most important consideration, in other words, a glassy amorphous structure is suitable. Contrarily, a crystallized structure is preferred when physical strength is an important requirement for recycling.

## References

- [1] C.C. Wiles, Municipal solid waste combustion ash: state of knowledge, *J. Hazard. Mater.* 47 (1996) 325–344.
- [2] Y.M. Kuo, T.C. Lin, P.J. Tsai, W.J. Lee, H.Y. Lin, Fate of polycyclic aromatic hydrocarbons during vitrification of incinerator ash in a coke bed furnace, *Chemosphere* 51 (2003) 313–319.
- [3] F.P. Constantino, R.P. Miguel, V. José, Solidification/stabilization of electric arc furnace dust using coal fly ash analysis of the stabilization process, *J. Hazard. Mater.* B82 (2001) 183–195.
- [4] H.Y. Moon, H.S. Kim, D.S. Choi, Relationship between average pore diameter and chloride diffusivity in various concretes, *Construct. Build. Mater.* 20 (2006) 725–732.
- [5] Y.M. Kuo, T.C. Lin, P.J. Tsai, Immobilization and encapsulation during vitrification of incineration ashes in a coke bed furnace, *J. Hazard. Mater.* B133 (2006) 75–78.
- [6] Y.M. Kuo, T.C. Lin, P.J. Tsai, Metal behavior during vitrification of incinerator ash in a coke bed furnace, *J. Hazard. Mater.* B109 (2004) 79–84.
- [7] Y.M. Kuo, T.C. Lin, P.J. Tsai, Effect of SiO<sub>2</sub> on immobilization of metals and encapsulation of a glass network in slag, *J. Air Waste Manage.* 53 (2003) 1412–1416.
- [8] C.T. Li, Y.J. Huang, K.L. Huang, W.J. Lee, Characterization of slags and ingots from the vitrification of municipal solid waste incineration ashes, *Indust. Chem. Eng. Res.* 42 (2003) 2306–2313.
- [9] Z. Károly, I. Mohai, M. Tóth, F. Wéber, J. Szépvölgyi, Production of glass–ceramics from fly ash using arc plasma, *J. Eur. Ceram. Soc.* 27 (2007) 1721–1725.
- [10] E. Ecke, H. Sakanakura, T. Matsuto, N. Tanaka, A. Lagerkvist, State of the art treatment processes for municipal solid waste incineration residues in Japan, *Waste Manage. Res.* 18 (2000) 41–51.
- [11] Y.J. Park, J. Heo, Vitrification of fly ash from municipal solid waste incinerator, *J. Hazard. Mater.* B91 (2002) 83–93.
- [12] K.E. Haugsten, B. Gustavson, Environmental properties of vitrified fly ash from hazardous and municipal waste incineration, *Waste Manage.* 20 (2000) 167–176.
- [13] Environmental Protection Administration of United States Toxicity Characteristic Leaching Procedure: SW846 Method 1311.
- [14] B.D. Cullity, S.R. Stock, *Elements of X-ray diffraction*, third ed., Prentice Hall, Upper Saddle River, 2001.
- [15] C.Y. Chen, G.S. Lan, W.H. Tuan, Preparation of mullite by the reaction sintering of kaolinite and alumina, *J. Eur. Ceram. Soc.* 20 (2000) 2519–2525.
- [16] K. Park, J. Hyun, S. Maken, S. Jang, J.W. Park, Vitrification of municipal solid waste incinerator fly ash using Brown's gas, *Energy Fuels* 19 (2005) 258–262.
- [17] H. Ecke, H. Sakanakura, T. Matsuto, N. Tanaka, A. Lagerkvist, Effect of electric arc vitrification of bottom ash on the mobility and fate on metals, *Environ. Sci. Technol.* 35 (2001) 1531–1536.
- [18] Y.M. Kuo, J.W. Wang, C.H. Tsai, Encapsulation behaviors of metals in slags containing various amorphous volume fractions, *J. Air Waste Manage. Assoc.* 57 (2007) 820–827.
- [19] F. Peng, K.M. Liang, A.M. Hu, Nano-crystal glass–ceramics obtained from high alumina coal fly ash, *Fuel* 84 (2005) 341–346.