

# Chemical recycling of municipal waste slag by using phase separation

Tokuro NANBA,<sup>†</sup> Yutaro KURODA,<sup>\*</sup> Shinichi SAKIDA<sup>\*\*</sup> and Yasuhiko BENINO

Graduate School of Environmental Science, Okayama University, 3-1-1, Tsushima-Naka, Kita-ku, Okayama 700-8530

<sup>\*</sup>Faculty of Environmental Science and Technology, Okayama University, 3-1-1, Tsushima-Naka, Kita-ku, Okayama 700-8530

<sup>\*\*</sup>Environmental Management Center, Okayama University, 3-1-1, Tsushima-Naka, Kita-ku, Okayama 700-8530

A chemical recycling method by using phase separation was applied to municipal waste slags. Glasses were prepared from incineration ash and ash-melted slag, where  $B_2O_3$  was added to promote phase separation. The glasses were heat-treated at temperatures higher than their glass transition temperatures, and they were soaked in hydrochloric acid, leaching CaO,  $Fe_2O_3$ ,  $K_2O$ , and S. Transparent and colorless solids containing ca. 80 mass% of  $SiO_2$  were successfully obtained as residues. It was suggested that phase separation took place not in the heat-treatment but in the vitrification process, and further characterizations are however required to investigate the phenomena at microscopic levels in the recycling processes.

©2009 The Ceramic Society of Japan. All rights reserved.

Key-words : Municipal waste slag, Waste recycling, Chemical recycling, Phase separation, Glass

[Received August 17, 2009; Accepted October 15, 2009]

## 1. Introduction

High temperature waste-melting incineration method is one of the municipal waste incineration methods, in which municipal wastes are combusted and melted at temperatures higher than  $1,300^\circ\text{C}$ , being discharged as a slag. The method is widely used in Japan and contributes to energy saving through power generation and heat recovery, decomposition of dioxin, and volume reduction of wastes. The municipal waste slags are reused as alternatives to gravel and sand for paving aggregates and cement materials, and the recycling rate is, however, not 100%. In Japan, the remaining useful life of final disposal sites for non-industrial wastes is not long, 14.8 years at FY 2005,<sup>1)</sup> and hence new resources recycling routes for the municipal waste slags are being developed. Major constituents of municipal waste slags are  $SiO_2$ , CaO, and  $Al_2O_3$ , and the chemical composition is similar to conventional glasses. The slags are however colored in black due to  $Fe_2O_3$  present up to 10 mass%. The authors' research group expected that the slags were used as raw materials for glass if the slags became transparent and colorless by removing  $Fe_2O_3$ . Then, phase separation of glass was focused on for the removal method of  $Fe_2O_3$ .

Vycor<sup>®</sup> glass is well known as a glass of using phase separation. When an alkali borosilicate glass is heated at temperature higher than glass transition temperature ( $T_g$ ), the glass separate into two glass phases; one is alkali borate rich phase which is easily dissolved in acid, and the other one is silica rich phase which is insoluble in acid. Hence, phase separation has been used as a fabricating method of porous glass and high purity silica glass.<sup>2),3)</sup> The authors supposed that phase separation was useful for the removal of  $Fe_2O_3$  from slags. After phase separation, alkali ions are mostly present in borate phase, and the borate phase is hence in higher basicity than the alkali-free silica phase. If Fe ions prefer basic environment, Fe ions in phase-separated

borosilicate glasses will be preferentially distributed into borate rich phase. Then, it is expected that by soaking the phase-separated borosilicate glasses in acid, Fe ions as well as borate phase leach away, obtaining transparent and colorless silica glass.

In the municipal waste slags,  $B_2O_3$  is not present, and hence  $B_2O_3$  should be added to the slags to promote phase separation. The authors' research group started the waste recycling study by using a simulated municipal waste slag prepared from reagents. From a simulated slag containing 45 mass% of  $SiO_2$  and 10 mass% of  $Fe_2O_3$ , transparent and colorless solids containing ca. 95 mass% of  $SiO_2$  were successfully obtained, in which  $Fe_2O_3$  is almost completely removed.<sup>4),5)</sup> In the next experiment, the recycling process developed was applied to a granulated blast furnace slag (25 mass%  $SiO_2$ ) produced at ironworks in Okayama prefecture. Transparent and colorless solids (ca. 80 mass%  $SiO_2$ ) were finally recovered.<sup>6)</sup>

Municipal waste slags have similar composition to granulated blast furnace slags, and it is hence expected that the recycling process by using phase separation is also applicable to municipal waste slags. High temperature waste-melting incineration of municipal wastes is classified into two methods, that is, gasification-melting and ash-melting methods. In gasification-melting method, gases obtained by thermal decomposition of wastes are used as fuel for the incineration of undecomposed carbon residues. In ash-melting method, ashes obtained by incineration are thermally decomposed at higher temperature. In the present study, incineration ash and ash-melted slag produced in a municipal waste incineration plant using the ash-melting method were chosen to investigate the applicability of the recycling process using phase separation.

## 2. Experimental

The recycling procedure is shown in Fig. 1. The incineration ash and ash-melted slag produced at a municipal waste incineration plant in Okayama prefecture were used in the present study.  $B_2O_3$  was added to the wastes, and the mixtures were melted at  $1,500^\circ\text{C}$  for 30 min in  $Al_2O_3$ - and Pt-crucibles in preparing ash

<sup>†</sup> Corresponding author: T. Nanba ; E-mail: tokuro\_n@cc.okayama-u.ac.jp

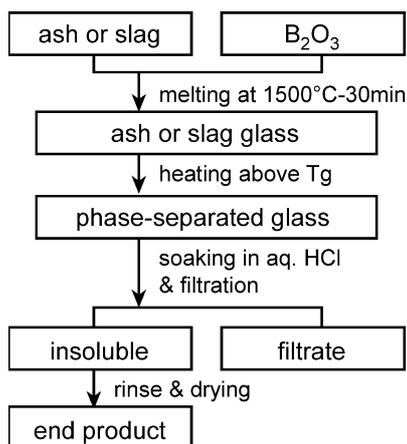


Fig. 1. Waste recycling procedure used in the present study.

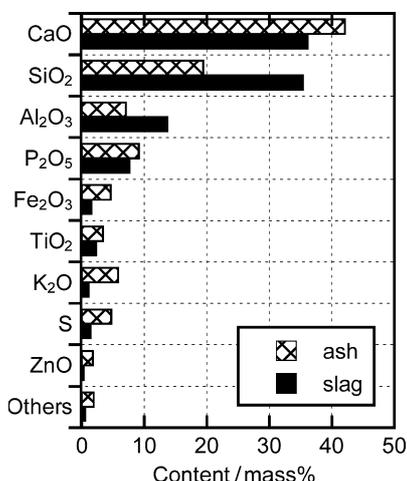


Fig. 2. XRF-analytical composition of the ash and ash-melted slag used in the present study.

and slag glasses, respectively. The melts were quenched to obtain  $B_2O_3$ -containing glasses. Differential thermal analyses (DTA) were done to determine  $T_g$ . The glasses prepared from ash or slag were heat-treated for 8 h at the temperatures higher than  $T_g$  to induce phase separation. The heat-treated glasses were ground into coarse particles  $< 150 \mu\text{m}$  and soaked in 2.5 N hydrochloric acid for 48 h, dissolving out the  $B_2O_3$ -rich glass phase. The insoluble residues were recovered by vacuum filtration. Chemical compositions of the recovered solids were determined by X-ray fluorescence (XRF) spectrometry. Boron is not detectable with the XRF apparatus used in the present study. It is expected that boron is also present in the recovered solids, and it is hence noted that the analytical compositions shown below are not actual, and they should be used as a measure of compositional change. Optical absorption of the recovered solids was estimated from diffuse reflectance measurement.

### 3. Results

**Figure 2** shows the chemical composition of the incineration ash and ash-melted slag used in the present study. The chemical composition of these wastes is different, and the content of  $SiO_2$  and  $Al_2O_3$  in the slag is higher than that of the ash. In the waste incineration plant providing these wastes, an ash-melting process is used, where incombustible wastes are added to the incineration

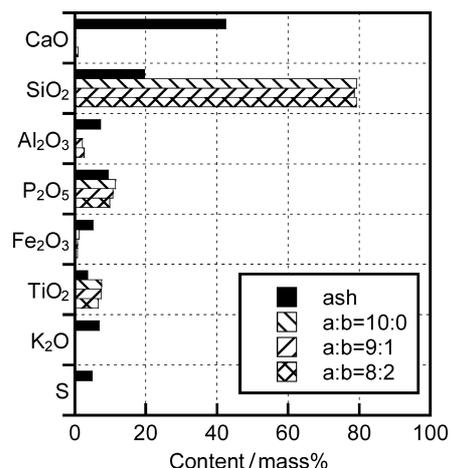


Fig. 3. XRF-analytical composition of the insoluble end products recovered from the incineration ash. The ratio a:b indicates the weight ratio between the ash and  $B_2O_3$  in the ash glasses. The composition of the untreated ash is also shown for comparison.

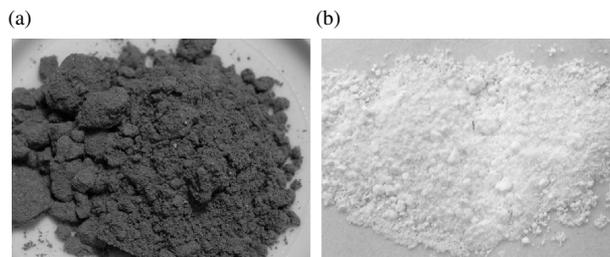


Fig. 4. Photographs of (a) the incineration ash and (b) an end product recovered from the ash (a:b = 9:1).

ash and the mixtures are melted in an electric resistance furnace, producing the final slag. Hence, the compositional difference between the ash and ash-melted slag is due to the addition of incombustible wastes.

**Figure 3** shows the chemical composition of the insoluble solids recovered from the incineration ash.  $SiO_2$  content increases greatly from 20 mass% in the incineration ash to 80 mass% in the insoluble solids recovered from the ash. In contrast, the constituents of  $CaO$ ,  $Fe_2O_3$ ,  $K_2O$ , and  $S$  are almost completely removed from the ash glasses. Little difference in composition is observed between the solids recovered from the ash glasses with different  $B_2O_3$ -mixing ratio. As shown in **Fig. 4**, the incineration ash is gray, and the insoluble end products recovered from the ash are white. It is found from **Fig. 5** that the recovered solids are entirely transparent in visible region.

**Figures 6–8** show the results obtained from the ash-melted slag, in which the notation, s:b indicates the weight ratio mixing the ash-melted slag and  $B_2O_3$ . The results obtained are similar to the case of the incineration ash. As shown in **Fig. 2**,  $Fe_2O_3$  content in the ash-melted slag is smaller than that in the ash, and as shown in **Figs. 7 and 8**, however, the ash-melted slag is black and has larger optical absorption in visible region. The optical absorption in visible region is probably due to the transition metal ions, such as  $Fe^{3+}$ ,  $V^{5+}$ ,  $Cr^{3+}$ , and  $Mn^{2+}$ . In the end products recovered from the ash-melted slag,  $CaO$ ,  $Fe_2O_3$ ,  $K_2O$ , and  $S$  are almost completely removed (**Fig. 6**), and the recovered solids are visually white (**Fig. 7**) and transparent to visible light (**Fig. 8**).

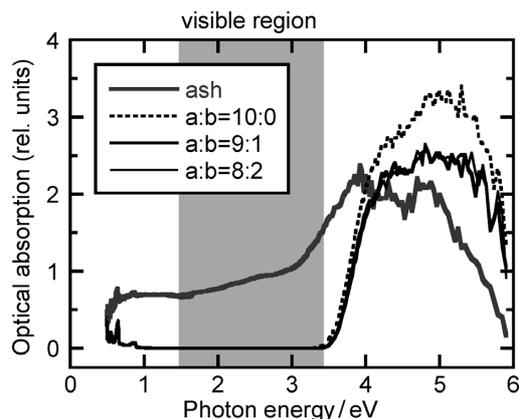


Fig. 5. Optical absorption spectra of the untreated incineration ash and the insoluble end products recovered from the ash. The ratio  $a:b$  indicates the weight ratio between the ash and  $B_2O_3$  in the ash glasses.

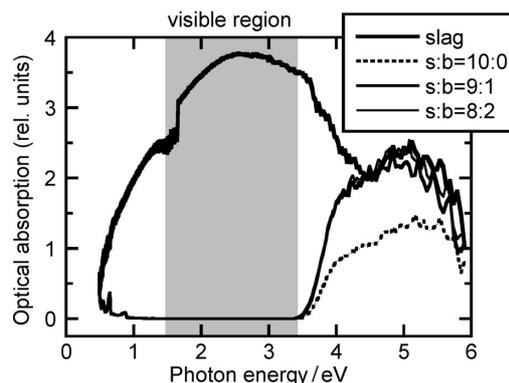


Fig. 8. Optical absorption spectra of the untreated slag and the insoluble end products recovered from the slag. The ratio  $s:b$  indicates the weight ratio between the slag and  $B_2O_3$  in the slag glasses.

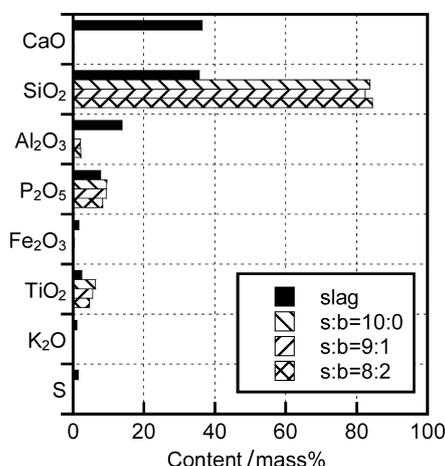


Fig. 6. XRF-analytical composition of the insoluble end products recovered from the ash-melted slag. The ratio  $s:b$  indicates the weight ratio between the slag and  $B_2O_3$  in the slag glasses. The composition of the untreated slag is also shown for comparison.

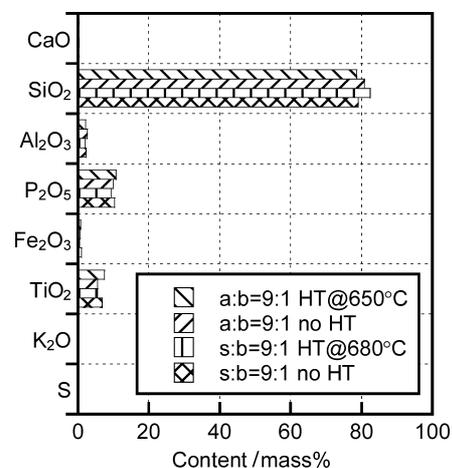


Fig. 9. XRF-analytical composition of the insoluble end products obtained from the ash and slag glasses containing 10 mass%  $B_2O_3$  ( $a:b = 9:1$ ,  $s:b = 9:1$ ). "HT" and "no HT" indicate the results with and without heat-treatment, respectively.

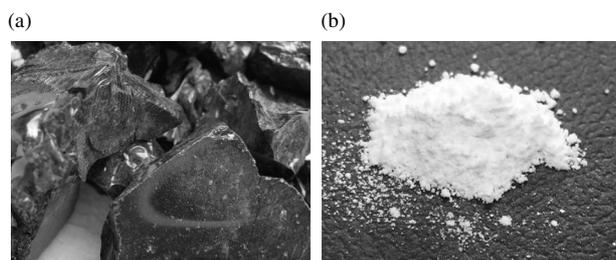


Fig. 7. Photographs of (a) the ash-melted slag and (b) an end product recovered from the slag ( $s:b = 9:1$ ).

#### 4. Discussion

As shown in Figs. 3 and 6,  $CaO$ ,  $Fe_2O_3$ ,  $K_2O$ , and  $S$  are almost completely removed from the ash and slag glasses, obtaining the solids containing ca. 80 mass%  $SiO_2$ , which have no optical absorption in visible region as shown in Figs. 5 and 8. The composition of the recovered solids is nearly independent of  $B_2O_3$  content in the ash and slag glasses. It is noted that the colorless solids are successfully obtained from the  $B_2O_3$ -free glasses,  $a:b$

$= 10:0$  and  $s:b = 10:0$ . When the original ash and slag were directly acid-treated, they were almost completely dissolved into acid and colorless solids were not obtained. It was therefore suggested that vitrification of the wastes was indispensable to obtain insoluble colorless solids.

In the present waste recycling process,  $B_2O_3$  is added to the wastes to promote phase separation. As indicated above, however,  $B_2O_3$  is not indispensable to obtain insoluble colorless solids, suggesting the possibility that phase separation is also needless to obtain insoluble colorless solids. Then the ash and slag glasses are directly acid-treated without the heat treatment for phase separation. As shown in Fig. 9, there is no significant difference in composition between the recovered solids with and without heat treatment. It is therefore concluded that phase separation of the ash and slag glasses does not happen at least in the heat treatment. Then, what is the formation process of the  $SiO_2$ -rich solids from the ash and slag glasses? Two possible processes are thought of; liquid-liquid phase separation in vitrification process and dissolution-precipitation in acid treatment. Scanning electron microscope (SEM) observation was done for various specimens, and evidence of phase separation was not obtained yet.

In the case of a granulated blast furnace slag, which has similar chemical composition to the present municipal waste slag,

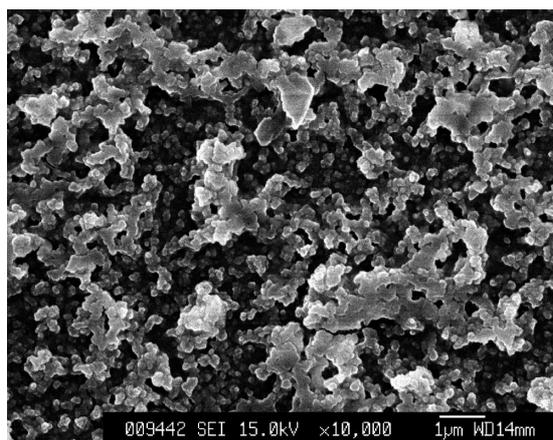


Fig. 10. SEM photographs of the surface of a slag glass (granulated blast furnace slag :  $B_2O_3 = 6:4$  in weight ratio) before heat-treatment.<sup>7)</sup> The glass surface was briefly etched by 2.5 N hydrochloric acid.

phase separation is successfully confirmed by SEM observation.<sup>6)</sup> As shown in Fig. 10, phase separation is recognized in a slag glass prepared from granulated blast furnace slag before heat treatment.<sup>7)</sup> It is therefore supposed that liquid-liquid phase separation takes place in the vitrification process of the incineration ash and ash-melted slag as well as the granulated blast furnace slag. In the recovered solids without being subjected to heat treatment, small and broad optical absorption was observed at 1.8–2.8 eV, which was not observed in the recovered solids being subjected to heat treatment. It is hence suggested that heat treatment is effective to the development of phase separated textures and migration of coloration species.

It is also shown in Figs. 3 and 6 that the contents of  $P_2O_5$  and  $TiO_2$  as well as  $SiO_2$  in the recovered solids increase from those of the incineration ash and ash-melted slag, which is the same with the case of granulated blast furnace slag.<sup>6)</sup> It is therefore suggested that the removal of  $P_2O_5$  and  $TiO_2$  from the  $SiO_2$ -rich phase is quite difficult by using phase separation phenomenon. In the  $B_2O_3$ -rich phase, glass network consists of  $BO_3$  and  $BO_4$  units, and non-bridging oxygens (NBOs) should be present in many of the  $BO_3$  units because large amount of CaO is incorporated into the  $B_2O_3$ -rich phase. According to Uchida et al.,<sup>8)</sup>  $BO_4$  units are classified as a hard base, and  $BO_3$  units containing NBOs are a soft base. It is hence supposed that both hard and soft acids, that is, most of cations including  $Ca^{2+}$ ,  $Al^{3+}$ ,  $Fe^{3+}$  and  $K^+$ , are preferentially distributed into the  $B_2O_3$ -rich basic phase. Meanwhile,  $Ti^{4+}$  and  $P^{5+}$  are also regarded as a hard acid,<sup>9)</sup> but they prefer to be dissolved in the  $SiO_2$ -rich acidic phase. This is explained as follows:  $P_2O_5$  is known as a network former, and  $TiO_2$  is a conditional network former. Both  $PO_4$  and  $TiO_4$  as well as  $SiO_4$  units do not require any charge-compensating cations such as  $Ca^{2+}$  and  $K^+$ , but it is not the case in  $AlO_4$  units. Thus, it is supposed that the distribution of the constituents after phase separation is dependent on acid-base strength, and further experiments are however required to clarify the distribution mechanism.

As above mentioned, the recovered solids have a high  $SiO_2$  content (> 80 mass%) and no optical absorption in the visible region. Furthermore, the composition of the recovered solids is nearly independent of  $B_2O_3$  content in the ash and slag glasses, and the deviation in composition is quite small. Considering the

practical application, the compositional deviation of the recovered solids is an important issue. Composition of municipal wastes varies according to seasons, and it is hence expected that the seasonal fluctuation in composition of the recovered solids is unavoidable. As shown in Figs. 3 and 6, however, the incineration ash and ash-melted slag have different composition; CaO/ $SiO_2$  ratio  $\approx 2$  in the incineration ash and  $\approx 1$  in the ash-melted slag. Nevertheless, significant difference in composition is not observed between the recovered solids from the incineration ash and ash-melted slag. Therefore, the remaining issue for the practical application is a cost saving. If resolving the issues, it is expected that the recovered solids are used as raw materials for sheet glass, rock wool and humidity conditioner.

## 5. Conclusion

The recycling method using phase separation was applied to the incineration ash ( $SiO_2$  content = 20 mass%) and ash-melted slag (35 mass%) produced at a municipal waste incineration plant to examine availability of the recycling method. As a result, transparent and colorless solids containing ca. 80 mass% of  $SiO_2$  were successfully recovered from the incineration ash and ash-melted slag. The chemical composition of the recovered solids was independent of content of  $B_2O_3$ , which was added to the wastes to promote phase separation. The recovered solids without being subjected to the heat treatment for phase separation showed little difference in composition with the heat-treated solids. As the reason for obtaining the solids with high  $SiO_2$  content after acid treatment, two mechanisms were supposed, that is, liquid-liquid phase separation in vitrification process and dissolution-reprecipitation in acid treatment. Conclusive evidences were not obtained yet, and in the case of a glass prepared from a granulated blast furnace slag, however, SEM observation indicated the liquid-liquid phase separation in the vitrification process. It might also take place in the vitrification process of municipal waste incineration ash and slag. Further characterizations are required to obtain the definitive conclusion for the chemical recycling mechanism.

**Acknowledgement** The authors gratefully acknowledge the financial support of Wesco Scientific Promotion Foundation, Japan.

## References

- 1) Ministry of the Environment, "Annual Report on the Environment and the Sound Material-Cycle Society in Japan 2008," 2008 (2008).
- 2) R. J. Charles and F. E. Wagstaff, *J. Am. Ceram. Soc.*, 51, 16–20 (1968).
- 3) W. Haller, D. H. Blackburn, F. E. Wagstaff and R. J. Charles, *J. Am. Ceram. Soc.*, 53, 34–39 (1970).
- 4) T. Imaoka, S. Sakida, T. Nanba and Y. Miura, *Proceedings in Materials Science & Technology 2006*, Cincinnati, USA, (2006) CD-ROM.
- 5) T. Imaoka, S. Sakida, T. Nanba and Y. Miura, *J. Environ. Sci. Tech. Okayama Univ.*, 12, 161–165 (2007).
- 6) T. Nanba, S. Mikami, T. Imaoka, S. Sakida and Y. Miura, *J. Ceram. Soc. Japan*, 116, 220–223 (2008).
- 7) S. Mikami, Undergraduate thesis, Okayama University (2007).
- 8) N. Uchida, T. Maekawa and T. Yokokawa, *J. Non-Cryst. Solids*, 88, 1–10 (1986).
- 9) J. E. Huheey, E. A. Keiter and R. L. Keiter, "Inorganic Chemistry: Principles of Structure and Reactivity (4th Edition)", Harper Collins College Publishers, New York, p.347 (1993).