

# Chemical recycling of inorganic wastes by using phase separation of glass

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A chemical recycling process using phase separation of glass was applied to a granulated blast furnace slag with high CaO content. Glasses were prepared by adding  $B_2O_3$  to the slag in order to promote phase separation, and the glasses were heat-treated above glass transition temperature. In the subsequent acid-treatment, however, gelation due to the elution of  $SiO_2$  phase containing CaO occurred, not obtaining high  $SiO_2$  solids. Then, pretreatment was introduced to reduce CaO content in slag, where the raw slag was briefly washed in acid. The slag glasses prepared from the pretreated slag were commonly phase-separated by heat-treatment regardless of  $B_2O_3$  content. After subsequent acid-treatment, colorless insoluble solids were successfully recovered. The end products consist of 70–90 mass%  $SiO_2$ , and coloring ions such as Mn, Fe and Cr were almost completely removed from the slag glasses. Reutilization as raw materials for glass is expected.

Key-words : Blast furnace slag, Waste recycling, Chemical recycling, Phase separation, Glass

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## 1. Introduction

In 2002, Okayama Prefecture formulated a guideline for the industrial waste management, in which industrial wastes, such as sludge, mining slag, soot dust, and cinders, with exceptionally large amount of generation and final disposal were designated as resources that should be recycled. Most of these wastes have been reused as aggregates for asphalt and concrete substituting for sand and gravel, and the amount of landfill disposal of these wastes is becoming non-negligible; as for industrial wastes, the total emission and landfill disposal in 2004 were 12,224 kt and 510 kt, respectively.<sup>1)</sup> In contrast, those of nonindustrial wastes in 2004 were 739 kt and 111 kt, respectively. The recycling rate of industrial wastes in Okayama Prefecture is much higher, but the absolute amount of landfill disposal is also larger than that of nonindustrial wastes. The remaining life of landfill facilities is decreasing, and the building of novel waste recycling methods is, therefore, urgent for the sustainable development.

The authors have developed a waste recycling method, in which by using phase separation of glass,  $SiO_2$ -rich colorless substance was successfully recovered from an Fe-containing simulated municipal waste slag.<sup>2),3)</sup> It is well known that alkali borosilicate glasses separate into silica-rich and alkali borate-rich glass phases.<sup>4),5)</sup> In the previous studies,<sup>2),3)</sup>  $B_2O_3$  was added to a simulated waste slag ( $SiO_2 : CaO : Al_2O_3 : Fe_2O_3 : Na_2O = 43 : 25 : 17 : 8 : 7$  mass%), obtaining slag glasses, and it was confirmed after phase separation that Fe ions as well as Na and Ca ions were preferentially introduced into the borate-rich phase. After immersing in hydrochloric acid, the borate-rich phase were dissolved in acid, and colorless substances not containing Fe, Na and Ca ions and abundant in  $SiO_2$  were recovered by filtration.

Most of the industrial wastes, such as inorganic sludge and mining slag consist of  $SiO_2$ , CaO, and  $Al_2O_3$  as major inorganic constituents, and it is also the case for municipal waste slags. It is therefore expected that  $SiO_2$ -rich substance is also

recovered by the phase separation of glass prepared from industrial wastes. A recycling method of waste glass using phase separation had been already developed by Akai et al.,<sup>6)</sup> in which as a practical example, colorless glass ( $SiO_2$  content = ca. 95 mass%) was obtained from a colored soda lime glass containing 73 mass%  $SiO_2$ . It is worth noting that  $SiO_2$  content in the final products recovered from the simulated waste slag is also ca. 95 mass%<sup>3)</sup> even though the initial composition of the wastes is quite different. It is therefore suggested that phase separation allows us to produce high silica glasses having a small compositional dispersion from various wastes with different compositions. Granulated blast furnace slag is formed when molten iron blast furnace slag is quenched rapidly by immersing in water, and it has high CaO content. In the present study, granulated blast furnace slag was chosen, and the recovery of colorless high  $SiO_2$  substance was attempted.

## 2. Experimental

Recycling procedure of slag used is shown in Fig. 1. In the present study, a granulated blast furnace slag discharged from an iron-making factory in Okayama Prefecture was used.  $B_2O_3$  was added to the slag changing proportion, and the mixtures were melted at 1500°C for 30 min in a Pt crucible. The melts were press-quenched, obtaining slag glasses. The slag glasses were heated at the temperatures between glass transition and crystallization temperatures, which were determined by differential thermal analyses (DTA). The heat-treated slag glasses were ground into coarse particles (< 600  $\mu m$ ) and soaked in hydrochloric acid (2.5 N). After vacuum filtration, the insoluble residues were rinsed in water and dried, obtaining the final products. As described below, gelation of slag glasses occurred in acid treatment when using the untreated slag. Then, pretreatment was introduced to prevent the gelation, in which slag was washed in acid to reduce CaO content in slag.

Composition was determined by X-ray fluorescence

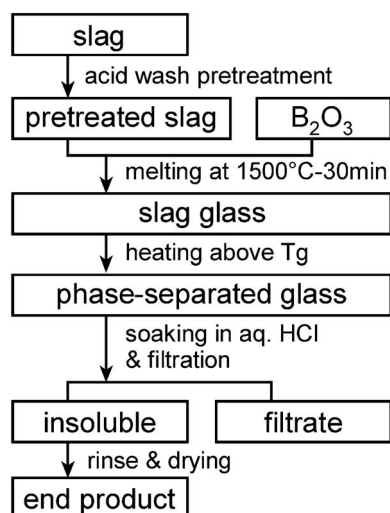


Fig. 1. Slag recycling procedure used in the present study.

(XRF) analysis, where boron atoms are undetectable with the XRF apparatus used in this study. Differential thermal analysis (DTA) was done to obtain glass transition and crystallization temperatures,  $T_g$  and  $T_x$ . Phase separation was confirmed by scanning electron microscope (SEM) observation, where the specimens were etched briefly in 2.5 N hydrochloric acid. Transparency was evaluated by optical absorption obtained from diffuse reflectance measurement.

### 3. Results and discussion

#### 3.1 Compositional change of granulated blast furnace slag

Chemical composition of the granulated blast furnace slag used in the present study was listed in **Table 1**. The main components are CaO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, and their contents are 50, 25, 12 mass%, respectively, which make up about 87% of the total. The coloring components in the slag are MnO, Fe<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>, and their contents are all less than 0.5 mass%. As shown below, however, the slag is colored light-brown.

The slag glasses prepared from the mixtures of slag 8 g and B<sub>2</sub>O<sub>3</sub> 2 g were heat-treated at different temperatures between  $T_g$  and  $T_x$  for various periods. After acid-treatment, however, the slag glasses turned into gel and failed to obtain solid bodies in the case of using the untreated slag. **Figure 2** shows the analytical composition of gels. SiO<sub>2</sub> content in the gels obtained from the untreated slag is 40–70 mass%, which is much less than that in the solid bodies (ca. 95 mass%) recovered from the simulated municipal waste slag.<sup>3)</sup>

Gelation of blast furnace slag in acid has been reported,<sup>7)</sup> and it was therefore suggested that no phase separation occurred in the slag glasses. Even in the case that phase separation took place, if the SiO<sub>2</sub>-rich glass phase contained large amount of CaO, the SiO<sub>2</sub>-rich phase with high basicity would be also leached out and precipitated as gel. As shown in Table 1, CaO content of the untreated slag is quite high, and hence CaO content should be reduced to decrease the basicity of the slag and the SiO<sub>2</sub>-rich glass phase separated.

Then the slag was washed in acid to reduce CaO content. In the acid-washing pretreatment, 1 g of the granulated blast

Table 1. XRF-analytical Composition of the Granulated Blast Furnace Slag used in this Study

component	untreated slag (mass%)	pretreated slag (mass%)
CaO	50.4	39.1
SiO <sub>2</sub>	25.1	34.7
Al <sub>2</sub> O <sub>3</sub>	11.9	16.6
P <sub>2</sub> O <sub>5</sub>	4.31	3.96
MgO	3.77	2.14
S	2.21	1.38
Other components less than 1 mass%: K <sub>2</sub> O, TiO <sub>2</sub> , MnO, Fe <sub>2</sub> O <sub>3</sub> , SrO, BaO, ZrO <sub>2</sub> , Cr <sub>2</sub> O <sub>3</sub>		

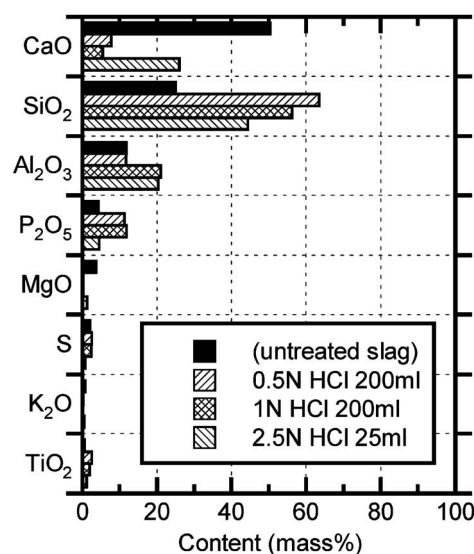


Fig. 2. XRF-analytical composition of the gels precipitated after acid-treatment, in which 10 g of slag glass prepared from 8 g of untreated slag and 2 g of B<sub>2</sub>O<sub>3</sub> was soaked in hydrochloric acids. The composition of the untreated slag is also shown for comparison.

furnace slag was washed in 1 ml of 2.5 N hydrochloric acid in relative ratio. The composition of the pretreated slag is also shown in Table 1. CaO content in the pretreated slag is successfully reduced by 10 mass%, and in the meanwhile, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents increase by 10 and 5 mass%, respectively. No gelation was observed in the acid treatment of the slag glasses prepared from the pretreated slag.

**Figure 3** shows the composition of the insoluble end products obtained from the slag exposed to the acid-washing pretreatment. SiO<sub>2</sub> content in the untreated and pretreated slags is 25 and 35 mass%, respectively, and in the insoluble end products, however, remarkable increase in SiO<sub>2</sub> content is observed at every mixing ratio. With increasing B<sub>2</sub>O<sub>3</sub> ratio, SiO<sub>2</sub> content increases from 70 mass% ( $s : b = 9.5 : 0.5$ ) to 90 mass% ( $s : b = 6 : 4$ ) and CaO content decreases from 12 mass% ( $s : b = 9.5 : 0.5$ ) to 1 mass% ( $s : b = 6 : 4$ ), suggesting that CaO is preferentially introduced into B<sub>2</sub>O<sub>3</sub>-rich glass phase after the phase separation.

As for the other components, Al<sub>2</sub>O<sub>3</sub> content in the insoluble end products decreases with increasing B<sub>2</sub>O<sub>3</sub> content in the slag glasses, which is similar to the case of CaO. The reduction rate of Al<sub>2</sub>O<sub>3</sub> is, however, not as high as that of

CaO. These results suggest the preferential introduction of Al ions into  $B_2O_3$ -rich glass phase after phase separation, and the priority of Ca ions, however, seems to be much higher than Al ions. In the case of  $P_2O_5$ , the content increases after the recycling processes, and the content in the end products is almost constant regardless of  $B_2O_3$  content. It is therefore suggested that P ions are preferentially incorporated into  $SiO_2$ -rich phase rather than  $B_2O_3$ -rich phase, and the removal of  $P_2O_5$  was quite difficult in the present recycling process using phase separation.

### 3.2 SEM observation of phase-separated slag glass

Figure 4 shows the SEM photographs of the surface of the slag glasses after heat-treatment, where the slag glasses were prepared from the slag exposed to the acid-washing pretreatment, and each heat-treatment temperature was chosen at the midpoint between  $T_g$  and  $T_x$ . In every slag glass prepared

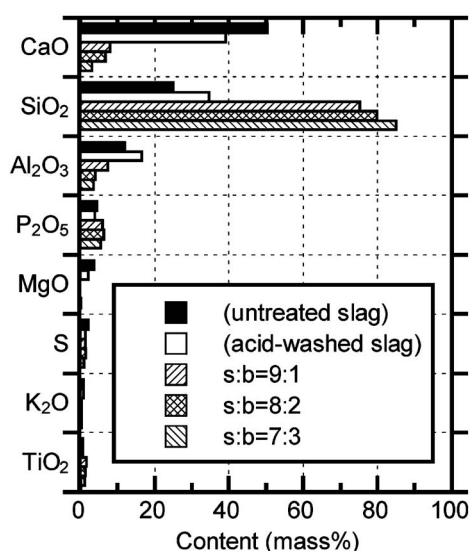


Fig. 3. XRF-analytical composition of the insoluble end products obtained from the slag exposed to the acid-washing pretreatment. The ratio s: b indicates the weight ratio between the acid-washed slag and  $B_2O_3$  in the slag glasses. The composition of the untreated and acid-washed slags is also shown for comparison.

from the pretreated slag, phase separation is confirmed, and the morphology of the surfaces is, however, different between the slag glasses. Difference in phase separation mechanism may be responsible for the difference in surface morphology, that is, the granular aggregates confirmed in the 10 mass%  $B_2O_3$ -containing slag glass (Fig. 4a) are formed by the nucleation and growth mechanism, and the continuous structures observed in the 30 and 50 mass%  $B_2O_3$ -containing slag glasses (Figs. 4b and 4c) are characteristic in spinodal decomposition. In addition, the etched region seems to be decreasing with increasing  $B_2O_3$  content. It is supposed in the low  $B_2O_3$ -containing slag glasses that the amount of CaO incorporated into  $B_2O_3$ -rich glass phase is saturated, and  $SiO_2$ -rich phase has no choice but to accept the residual CaO, leading to the increase in basicity of  $SiO_2$ -rich phase. Consequently, as well as  $B_2O_3$ -rich phase,  $SiO_2$ -rich phase with high basicity is etched by acid, resulting in the larger etched region in the slag glasses containing small amount of  $B_2O_3$ . The compositional change of  $SiO_2$  content in the end products (Fig. 3) is also explainable by the elution of  $SiO_2$ -rich phase containing CaO.

### 3.3 Optical absorption of recovered solids

According to XRF analyses, the coloring components, MnO,  $Fe_2O_3$  and  $Cr_2O_3$  decrease in content after the recycling processes. The amount of these components is, however, less than 0.5 mass% and is hence not shown in Fig. 3. Then, the effect of removal of these components was evaluated by optical absorption. Figures 5 and 6 show the optical absorption spectra and photographs of typical specimens, respectively. Absorption of  $Fe^{3+}$  ions is observed at  $\sim 3$  eV in the  $B_2O_3$ -free slag glass (Fig. 5a), and  $Fe^{3+}$  absorption decreases in intensity along with  $B_2O_3$  addition (Fig. 5b). The  $B_2O_3$ -free slag glass (Fig. 6b) is reddish-brown in color, and decoloration progresses along with  $B_2O_3$  addition (Fig. 6c). The optical absorption in visible region disappears completely in the recovered end products (Figs. 5c and 5d). In the end product after rinsing in water and drying (Fig. 5c), optical absorptions due to  $H_2O$  and Cl are observed in IR and UV regions, respectively. After calcination at  $1000^\circ C$ , these absorptions are successfully bleached, obtaining transparent substance from IR to UV region (Fig. 5d), and the powdered end products appear in white color due to light scattering (Fig. 6d).

(a) s:b = 9:1,  $702^\circ C$ -16h (b) s:b = 7:3,  $663^\circ C$ -16h (c) s:b = 5:5,  $650^\circ C$ -16h

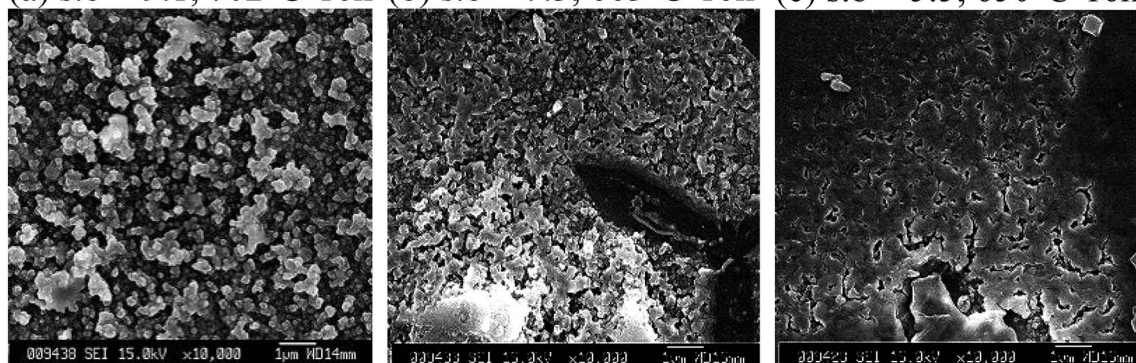


Fig. 4. SEM photographs of the surface of the slag glasses after heat-treatment. The glass surfaces were briefly etched by 2.5 N hydrochloric acid.

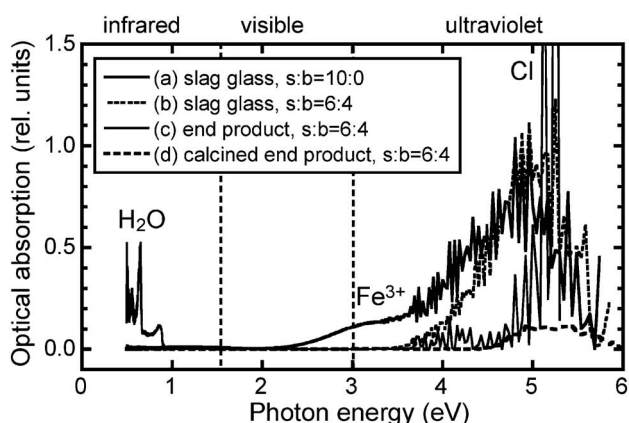


Fig. 5. Optical absorption spectra obtained from diffuse reflectance measurement of slag glasses (a, b) and insoluble end product (c). Calcined end product (d) was obtained by heat-treatment of the end product (c) at 1000°C for 10 min.

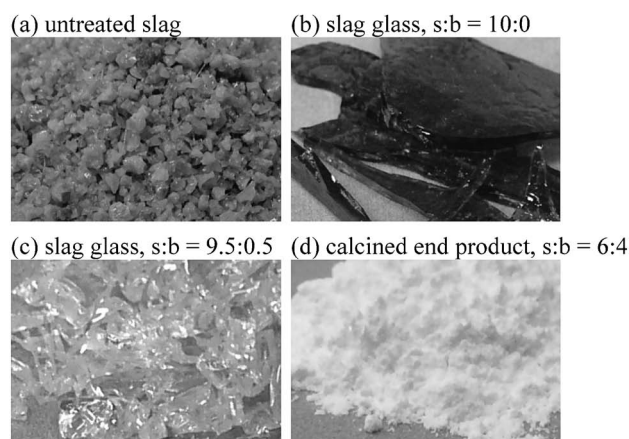


Fig. 6. Photographs of untreated slag, slag glass and end product after calcination (1000°C-10 min).

Boron content in the end products has not been clarified, and hence the decisive conclusion should be avoided, but reutilization as raw materials for glass is expected if the chemical composition of the end products is controlled by changing  $B_2O_3$  ratio in slag glasses. In that event, not only

granulated blast furnace slag but also various inorganic wastes will be recycled as raw materials for sheet glass, rock wool and humidity conditioner.

#### 4. Conclusion

The recycling process using phase separation of glass has been applied to the granulated blast furnace slag. When using the slag without pretreatment, the slag glasses prepared by the addition of  $B_2O_3$  turned into gels at acid-treatment, not obtaining high silica glass. It was supposed that elution of glass phases with high CaO content was responsible for the gelation. Then, the pretreatment was introduced, where the granulated blast furnace slag was washed in acid, and CaO content in the slag was successfully reduced from 50 to 40 mass%. After heat-treatment of the slag glasses prepared from the pretreated slag, phase separation was commonly confirmed in SEM observation regardless of  $B_2O_3$  content in the slag glasses. Through the subsequent acid-treatment, the coloring components, MnO,  $Fe_2O_3$  and  $Cr_2O_3$  were almost completely removed from the slag glasses, obtaining colorless solids with  $SiO_2$  content of 70–90 mass%. It was finally concluded that the recycling process using phase separation of glass was applicable to the CaO-abundant inorganic wastes with high basicity, which demonstrated the possibility to practical use in chemical recycling of wastes.

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