Acid and heat treatment to reduce lead leaching from cathode ray tube funnel glass

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The effect of acid and heat treatments on chemical durability was investigated for cathode ray tube (CRT) funnel glass. The acid and post-heat treatment suppressed the lead leaching from the CRT funnel glass in an acid solution remarkably due to the formation of a silica-like surface layer. Pb ions were, however, easily leached into alkaline solution after the acid and post-heat treatment. In addition, the dependencies of acid resistance on the conditions of acid treatment and on the temperature of heat treatment were investigated.

Key-words : CRT lead glass, Chemical durability, Leaching suppression, Acid treatment, Environmental safety

1. Introduction

Glasses constituting cathode ray tubes (CRTs) used in color televisions were formerly recycled as resources to produce new CRT glass. The production of new CRTs has, however, stopped almost completely. Hence, new applications of the used CRT (CRT cullet) are now being investigated.¹ Funnel and neck glasses in CRTs contain lead oxide (PbO), which makes it difficult to use these glasses as recyclable resources. The best use of CRT cullet is utilizing it as a flux for refining Pb.² Nevertheless, the demand in Japan for the cullet as a flux is limited to approximately ten thousand tons per year and is much lower than the supply of the cullet.³ Therefore, the cullet must be stored in controlled landfill sites, before use. While in a landfill, Pb ions leach into the groundwater, which causes environmental problems.

The lead elution of CRT glass in landfill conditions was studied by Sugita et al., who found that Pb ions eluted from CRT glass into wet acid soils were adsorbed by the soils, which prevented Pb ions from dissolving in water.⁴ This implies that acid soils act as a natural barrier against lead elusion, until the amount of Pb ions leached from the CRT glass exceeds the adsorption limit. Therefore, it is highly possible that the CRT cullet can be stored in the acid soils for a long period without water pollution, as long as the amount of Pb ions leached from CRT glass is reduced in acid solution, so as not to exceed the adsorption limit. Therefore, it is important to improve the acid resistance of the CRT cullet. The acid resistance of lead glasses has been studied extensively.⁵⁻⁷ D’Souza et al. have shown that the heat treatment after leaching test suppresses further leaching of Pb ions from alkali lead silicate glass into acid solution.⁸ It is expected from their study that the acid treatment followed by the heat treatment reduces the leaching of Pb ions from CRT glass which has complicated composition, similarly to the case of the simple alkali lead silicate glass. In the present study, we have attempted to improve the acid resistance of CRT glass by the heat treatment subsequent to the acid treatment.

2. Experimental procedures

The CRT funnel glass prepared from recycled cullet was provided by Nippon Electric Glass (Malaysia) Sdn. Bhd. The composition of the funnel glass was 51.6SiO₂·23.1PbO·7.7K₂O·6.2Na₂O·4.3Al₂O₃·3.5CaO·1.9MgO·0.5SrO·0.3BaO·0.4B₂O₃·0.3SnO₂·0.2Fe₂O₃ (mass %), according to the wet chemical analysis by NSG Techno-Research Co., Ltd. The sample glass specimens were prepared by grinding the funnel glass plates by #3000 SiC powder in oil. The sample preparation method has been described in detail elsewhere.⁹ The surface area of the specimen was approximately 400 mm². The acid treatment of funnel glass was carried out by soaking the glass specimens in 40 ml of 0.1 N CH₃COOH, 0.1 and 0.001 N HNO₃, and 0.001 N HCl aq. solutions at temperatures from 60 to 110°C for periods from 1 to 7 days in a Teflon vessel. A pressure-resistant stainless outer vessel was used for the acid treatment at 110°C. The specimens were heat-treated at temperatures from 150 to 500°C for 30 min in an ambient atmosphere within an electric furnace, following the acid treatment. Besides these treatments, the sulfur treatment was performed, in which the specimen was heated with 1 g of (NH₄)₂SO₄ in a silica glass vessel at 450°C for 30 min, followed by rinse with distilled water.¹⁰

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Infrared reflection (IRR) spectra of the glass were measured with an infrared spectrometer (Avatar 360, Thermo Nicolet) after the acid treatment by 0.1N acetic acid at 110°C for 7 days and after the subsequent heat treatment at 150°C for 30 min, 250°C for 30 min, 350°C for 30 min, 450°C for 30 min and 500°C for 30 min. The heat treatment and the spectral measurement were repeated alternately.

The static leaching test was carried out in a 0.001 N HCl aq. solution at 90°C for 7 and 28 days in a Teflon vessel, for the glasses after the acid and post-heat treatment, since the average pH of acid rain was ranging from 4.5 to 6.5, and the maximum pH was about 3.6 within a short period in Japan. In addition, the leaching test was carried out in a 0.001 N NaOH aq. solution for comparison. The leaching test method has been described in detail elsewhere. The concentration of Si, Pb, Ca, Mg and Al in the leaching solutions were measured with an inductively coupled plasma spectrometer (SPS7800, Seiko Instruments Inc.) after the leaching test. The concentration of K was measured with an atomic absorption spectrometer (AA-680, Shimadzu). The normalized elemental mass loss of element i (NLi) was calculated by the following equation,

\[ NL_i = \frac{C_i V}{f_i S_A} \] 

where \( C_i \), \( f_i \), \( V \) and \( S_A \) represent the concentration of element i in solution, (g m\(^{-3}\)), the fraction of element i in the untreated (pristine) glass, the volume of solution (m\(^3\)) and the surface area of the specimen (m\(^2\)), respectively.

3. Results and discussion

Figure 1 depicts NLi’s in the acid solution after static leaching test. NLi’s decreased after the acid treatment and after the heat treatment, as compared with NLi’s of the untreated glass. In particular, after the acid treatment and the heat treatment, NLi Pb was decreased to one-third and one-half of that of the untreated glass, respectively. In the previous studies, it was shown that Pb and alkali ions leached out from lead silicate glasses via ion exchange between these elements and hydronium ions in acid solution, to form a hydrated silica-rich layer on the surface, and that the surface of this hydrated layer gradually dissolved into acid solution. Therefore, it was deduced that the reduction of NLi’s after the acid treatment was due to the formation of a hydrated silica-rich layer which retarded the leaching of Pb, alkali and alkaline earth ions. On the other hand, it has been shown that the chemical durability is increased by the heat treatment in soda-lime-silicate glasses, owing to the reduction of the concentration of alkali ions in the surface region during heat treatment. Therefore, it was deduced that the reduction of NLi’s after the heat treatment was due to the reduction of alkali concentration in the surface region.

The acid and post-heat treatment reduced NLi’s drastically, except NLi Ca, as shown in Fig. 1. In particular, NLi Pb was reduced to near or below the detection limit. Figure 2 displays IRR spectra of the glasses. A peak due to Si–O–Pb linkages was observed at about 1010 cm\(^{-1}\) in the spectrum of the untreated sample. This peak disappeared after the acid treatment by acetic acid at 110°C for 7 days. Instead, a shoulder and a peak appeared at about 950 and 1080 cm\(^{-1}\), which were assigned to SiO\(_4\) groups with non-bridging oxygen atoms and to SiO\(_3\) groups with bridging linkages, respectively. These findings indicate that Pb ions were leached out from the glass surfaces during the acid treatment, which is consistent with the mechanism of the reactions between lead silicate glasses and acid solutions proposed in the previous studies.

The heat treatment subsequent to the acid treatment decreased the intensity of the shoulder at 950 cm\(^{-1}\) and increased the intensity of the peak at 1080 cm\(^{-1}\), indicating the formation of Si–O–Si linkages through the condensation of silanol groups by the heat treatment. Furthermore, the former and the latter decreased and increased with an increase in heating temperature, respectively. On
the other hand, $NL_i$'s decreased with an increase in heating temperature except $NL_K$, as depicted in Fig. 1(A). It was deduced from these findings that a silica like surface layer was formed through the formation of $=Si-O-Si= \rightarrow Si-OH \rightarrow Si-OH$ linkages, which acted as a protective layer for acid solutions to reduce $NL_i$'s, since it has been reported that very little silica dissolves at pH < 8. $NL_K$ was, however, unchanged after the heat treatment, probably due to the presence of residual silanol groups in silica like layer.

**Figure 3** depicts the dependence of $NL_i$'s on the conditions of acid treatment, such as the kind of acids, the concentration of acids, the temperature and the period. Lead leaching was sufficiently suppressed, irrespective of the conditions of acid treatment. Careful observation, however, shows that $NL_{Si}$ increased with the progress of acid treatment, more specifically, with the increase of temperature for the acetic acid treatment and with the increase of acid concentration for the nitric acid treatment. The increase of $NL_{Si}$ was attributed to the deterioration of surface layer, since it is known that the roughness of glass surface increased after etching by HCl aq. solution. 17)

The result of static leaching test for the sample subjected to the sulfur-treatment is also shown in Fig. 3. $NL_i$'s of the sample subjected to the sulfur treatment was much smaller than those of the untreated sample, the sample subjected to only the acid treatment and the sample subjected to only the heat treatment, owing to the formation of an alkali-depleted surface layer. 16) Although the sulfur treatment reduced $NL_K$ more than the acid and post-heat treatment, the latter reduced $NL_{Pb}$ much more than the former. Hence, the acid and post-heat treatment was preferable to the sulfur treatment in suppressing Pb leaching. The result of static leaching test in an alkaline solution for the sample subjected to the acid and post-heat treatment was scarcely different from that for the untreated sample, as shown in Fig. 4. In other words, the alkaline resistance of CRT glass was not improved by the acid and post-heat treatment at all. The lack of improvement in alkaline resistance is due to the formation of silica like layer, which is easily dissolved in alkaline solutions. 15) Hence, it is important to maintain acidic environmental conditions for maintaining the silica like layer on the glass. The glass should not be contacted with alkaline materials such as concrete in a landfill.

The leaching of Pb ions in acid solution was reduced for the CRT cullet glass drastically after the acid and post-heat treatment in the present study, as expected from the previous study on the simple lead silicate glasses. 3) In addition, it was remarkable that the leaching of Pb ions was suppressed after the static leaching test in 0.001N HCl aq. solution for 28 days, as shown in Fig. 3. Therefore, the acid and post-heat treatment is a promising method for suppressing the Pb leaching from CRT glass in the landfill condition. Investigating whether the suppression of lead leaching can be sustained for a long landfilling period is a scope for future study.

### 4. Conclusion

Acid and heat treatments of CRT funnel glass was investigated, in order to suppress lead leaching from the CRT funnel glass in landfill conditions. The acid treatment followed by the heat treatment at 500°C suppressed the lead leaching in an acid solution remarkably. Although the suppression of lead leaching was less dependent on the conditions of acid treatment, it increased with an increasing in temperature of the post-heat treatment. It was deduced from infrared reflection spectra measurement that a hydrated silica rich layer was formed via ion exchange between Pb and alkali ions in the glass and hydronium ions in acid solutions during the acid treatment, and that the hydrated silica layer changed to the silica like layer through the condensation reaction of silanol groups during
the post-heat treatment, which acted as a protective layer for acid solutions. Since the protective layer consisted of silica like layer, however, Pb ions were easily leached into alkaline solution. The acid and post-heat treatment was more effective for the reduction of lead leaching in acid solution than the sulfur treatment.

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