Leaching behavior of cathode ray tube (CRT) glasses

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The leaching behavior of cathode ray tube (CRT) funnel and neck glasses were compared in 0.001 N HCl and 0.001 N NaOH at 70 and 90°C. We measured the weight loss and leached amount of each component and observed the surface changes by scanning electron microscopy (SEM). In acid solution funnel glass showed t²-dependent leaching, whereas neck glass only demonstrated congruent dissolution after 8 weeks. In basic solutions leaching behavior was almost equivalent for both types of glass. Dissolution halted after one or two weeks as a result of the deposition of a protective layer. This layer was formed by saturation of Pb and was subsequently dissolvable by refreshing the leachant solution.

1. Introduction

Cathode ray tubes (CRTs) used in color televisions are composed of panel glass, funnel glass, and neck glass. Panel and funnel glasses are bonded with seal glass. Except panel glass, these glasses contain lead oxide (PbO). Further, funnel, neck, and seal frit glasses contain about 23, 32, and 75 mass % PbO, respectively. These materials are recycled to produce new CRT glass; however, with the advent of flat-panel displays, demand for CRTs is decreasing along with any initiatives for their reuse. New uses of CRT cullet are being investigated, such as in bricks and tiles,¹ glass ceramics,² high-strength mortars³ and X-ray-shielding cement.⁴ In some cases, the Pb component of CRT glass makes it difficult to treat the waste as a recyclable resource. To avoid Pb leaching from products, various methods for Pb removal, such as reduction melting⁵-⁷ and volatilization under vacuum heating,⁸ have been investigated. Though Pb recovery is an effective technique for preventing the depletion of natural Pb resources, these methods consume a significant amount of energy. A considerably better way to use CRT glass as a Pb resource is to use them as flux in Pb smelting instead of silica.⁹ For such a use, large quantities of CRT glass needs to be temporarily stored. This is because in Japan, the possible annual consumption of funnel glass used as flux in Pb smelting is expected to increase to about 12000 Mg (ton) from the current 6000 Mg.¹⁰ However, this increased amount would still be significantly lower than the amount of waste CRT generated in Japan, which was about 30000 Mg in 2012.¹¹ If the CRT glass disposed of in landfills is to be used as a stock for flux in Pb smelting, the leaching behavior of CRT glass must be investigated in order to prevent potential environmental problems that would arise from the leaching of Pb and other heavy metals into groundwater.

We have studied funnel glass leaching¹² and made the following observations. Under acidic conditions, leaching starts via ion exchange between alkali and hydronium ions in a diffusion-controlled reaction; this mechanism is similar to that observed for other types of Pb glass. In addition, the leached amount is proportional to the square root of the experiment duration. Furthermore, we found that the diffusion-controlled leaching continued for more than half a year at 90°C. Under neutral and basic conditions, leaching occurred during the first several days and then stopped. Further, a Pb-rich layer was observed under basic conditions.

The acid resistance of Pb glass has been studied extensively¹³-²⁵ owing to concerns regarding the harmfulness of Pb glass in tableware. The leaching behavior of the three types of Pb-containing CRT glass, i.e., funnel, neck, and seal frit glass, is expected to vary because of the difference in the composition of the glass types. Seal glass has a particularly high Pb content, which may weaken the acid resistance of this glass. Musson et al. evaluated the Pb leachability of CRT glass by employing the Toxicity Characteristic Leaching Procedure¹³ and found that in acid, the leachability of Pb derived from color TVs is much higher than that of Pb derived from black and white TVs, which contain no seal glass. We have also confirmed that seal glass showed much dissolution in acidic condition. Hence the part of seal glass should not be landfilled but separately processed.

Concerning the neck glass, to the best of our knowledge, no study has been undertaken to compare the leaching behaviors of funnel and neck glasses. In the present study, we examined the difference between the leaching behaviors of funnel and neck glasses. In order to test the long-term leaching behavior of the

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2. Experimental

CRT funnel and neck glass were provided by Nippon Electric Glass (Malaysia) Sdn. Bhd., where funnel glass is commercially produced from recycled cullets. The empirical formulae of the funnel and neck glasses were 6.2Na2O·4.3Al2O3·3.5CaO·1.9MgO·0.4SrO·0.8ZrO2·0.2Sb2O3 (mol %) and 48.1SiO2·32.2PbO·10.4K2O·2.8Na2O·2.5CaO·1.8SrO·1.1ZrO2·0.6Sb2O3 (mass %), respectively, which were analyzed at NSG Techno-Research Co., Ltd., by wet analysis. This corresponded to 65.5SiO2·7.9PbO·4.8CaO·0.4SrO·0.2Fe2O3 and 48.1SiO2·32.2PbO·10.4K2O·2.8Na2O·2.5CaO·1.8SrO·1.1ZrO2·0.6Sb2O3 (mol %), respectively. The composition of the funnel glass was similar to that of other published examples.26)

Sample preparation for funnel glass has been described elsewhere.25) The surface area (SA) of the sample was approximately 400 mm² and the volume of the leaching solution (V) was 40 cm³, giving an SA/V ratio of 10 m⁻¹. The neck glass was delivered in a tube shape, which required cutting and heating at 620°C in order to flatten and anneal it. The material was subsequently trimmed to 17 x 9 x 2 mm and ground to a flat surface. The final grinding was performed in oil so as to avoid compositional change through leaching in water.

The leaching test was carried out based on the MCC-1 test used for nuclear waste glass.27) This static leaching test method was conducted in a Teflon vessel at 70 and 90°C for 1, 3, 7, 14, 28, 56, 91, 182, 248, and 364 days. The experimental conditions agree with those reported in our previous study.12) After the test in alkaline condition at pH 11.0, the leachant solution was acidified with one drop of HCl so as to dissolve all hydroxide precipitates after removal of the sample from the vessel. We measured the weight of the sample before and after the test and calculated the total mass loss (ML) from the weight change.

The analysis of each element in the leachate was conducted by inductively coupled plasma (ICP) spectrometry (SPS7800; Seiko Instruments Inc.) and atomic absorption spectrometry (AAS; AA-680, Shimadzu). Surface was observed by a scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (SEM/EDS, JSM-5900LV JEOL). The cross section of the samples was observed by field emission SEM (FE-SEM at NSG Techno-Research Co., Ltd.).

3. Results

3.1 Mass loss

The total mass loss (ML) in 0.001 N HCl, distilled water and 0.001 N NaOH solution at 90°C for neck glass is shown in Fig. 1. The x-axis of each figure corresponds to the square root of the leaching time. The results for funnel glass at 248 and 364 days in 0.001 N HCl were 5.2 and 5.6 mg cm⁻², which were nearly on the extension line of the previous results.12) Similar results were observed for both the funnel and neck glasses. In 0.001 N HCl solution, the ML increased in proportion to the square root of the leaching time. In distilled water, or 0.001 N NaOH solution, the ML was initially larger than in 0.001 N HCl, with subsequent plateauing of ML after 7 or 14 days. The ML in distilled water was approximately one-half of that in 0.001 N NaOH. The neck glass revealed larger ML in 0.001 N HCl, but slightly smaller ML in 0.001 N NaOH when compared to funnel glass. Similar trends were observed at 70°C, the ML values of which are described in Fig. 2.

3.2 Leaching in acidic solution

The normalized elemental mass loss for element i (NLi) plots against the square root of leaching time and these are shown in Fig. 3 for the neck glass leached at 90°C in acidic conditions. The lines on these figures are drawn as a visual aid. The results for funnel glass at 248 and 364 days was on the extension line of the previous results12) again. Alkali and Pb elements were soluble in comparison to other elements. The NLi difference between the soluble and insoluble components for the neck glass was much larger than that for the funnel glass. Moreover, the NLi values for funnel glass were approximately proportion to t¹/₂, whereas those for neck glass were not. The soluble elements in the neck glass demonstrated higher leaching rates at the beginning, which
subsequently decreased over time. In contrast, $N_L_{Si}$ and $N_L_{Al}$ values tended to be proportional to $t^2$. The leaching rates from 56 to 91 days were similar for all elements.

The $N_L$ values at 70°C demonstrated leaching trends similar to that observed at 90°C for both funnel and neck glasses, as shown in Figs. 4 and 5. Data for each element follows a similar trend, although the leaching rate at 90°C was four times larger than that at 70°C.

Surface changes post-leaching in acid solution were observed by SEM and are shown in Figs. 6 to 8. As described in our previous report, the surface of funnel glass displays distinctive hollows when corroded at 90°C, a characteristic which may result from residual stress after grinding. In comparison, the surface of the sample leached at 70°C was characterized by depositions (Fig. 6). Temperature influence upon surface attributes was more apparent for the neck glass (Figs. 7 and 8). At 90°C the surface was homogeneously corroded with shallow hollows. In contrast, at 70°C the surface was covered with deposits. These contrary results imply that the leaching mechanism is temperature dependent.

Cross-sections of some samples were obtained by FE-SEM. Both the funnel and neck glass exhibited a dark layer (approximately 600 nm thick) after leaching in acid solution at 90°C for 91 days [Figs. 9(d), 9(e)]. EDS analysis indicated that Si and Al were enriched in this altered layer, leading us to suspect the
After leaching at 70°C for 7 days, the dark layer formed on the funnel glass was thinner than 100 nm [Fig. 9(a)], whereas the layer formed on the neck glass was thick [Fig. 9(b)].

### 3.3 Leaching in alkaline solution

Figures 10 and 11 display the $N_{Li}$ values for funnel and neck glass leached in alkaline conditions at both 70 and 90°C. Values at 70°C were about 70% of those at 90°C, except for Mg in Fig. 10, for which there were no notable differences in $N_{Li}$ values. Alkali elements and Si were relatively soluble in alkaline solution, whereas Al and Pb exhibited lower leachability. Pb precipitated as some insoluble compounds and was only dissolved by acid washing. In the absence of HCl the amount of Pb detected in the leachate solution remained low, as reported in our previous study.12) The rate of leaching leveled off after 14 days, in agreement with the mass loss results.

SEM observations of neck glass samples revealed particles and precipitate on the surface (Fig. 12). After 7 days of leaching the surface bore evidence of moderate particle deposition by EDS analysis. Al and Pb content was richer at the surface after leaching and was represented in elevated concentrations in the particles. Similar trends were observed in samples treated at 70°C, as well as for funnel glass. Analysis of cross-sections by FE-SEM did not reveal a layer of hydrated silica gel, although precipitation was evident on the surface (Fig. 13).

To investigate the effects of saturation, we refreshed the leachant solution every 7 days with a hot NaOH solution prepared in a separate Teflon vessel. The sample was moved to this vessel in order to eliminate the effects of temperature change. The resultant normalized mass loss of each element is shown in Fig. 14, indicating the consistent leaching of material at each refresh step.

### 4. Discussion

#### 4.1 Leaching in acid solution

The reported model for leaching under acidic condition describes the initiation of glass dissolution as an ion exchange...
Fig. 9. FE-SEM micrographs of the cross-sections of funnel and neck glasses after leaching in 0.001 N HCl solutions. (a) Funnel and (b) neck glass leached at 70°C for 7 days. (c) Neck glass leached at 90°C for 7 days. (d) Funnel and (e) neck glass leached at 90°C for 91 days.

Fig. 10. Normalized elemental mass loss for funnel glass against the square root of the time after leaching in 0.001 N NaOH solution at 90 and 70°C.

Fig. 11. Normalized elemental mass loss for neck glass against the square root of the time after leaching in 0.001 N NaOH solution at 90 and 70°C.
mechanism between \( H^+ \) in the solution and alkali ions in the glass. Formation of a hydrated silica-rich layer on the surface is described, which subsequently dissolves.\(^{28}\) In the model, the leached amount is expressed by the sum of the diffused quantities of soluble elements (with a \( t^{1/2} \)-dependence indicative of diffusion control) and the dissolved amount of the surface silica-rich gel layer (resulting from \( t^2 \)-dependence). With extension of the leaching period the diffusion rate of soluble elements from bulk glass and the dissolution rate of the hydrated layer are thought to converge. At the point where these two rates are equivalent a congruent dissolution process occurs. If a protective layer is not formed on the surface, congruent dissolution develops after a certain period.

We considered this model valid in view of our FE-SEM cross-section observations and EDS analysis results, which show that a silica-rich altered layer is formed on the surface after leaching (Fig. 9). In the case of funnel glass, the first step of the diffusion-controlled reaction lasted for at least one year at 90°C. Differences in thickness of the hydrated layer, shown in Figs. 9(a) and 9(d), imply that the growth of the altered layer is mediated by a slow diffusion-controlled ion exchange reaction.

The neck glass exhibited contrary behavior, with congruent dissolution occurring after 56 days. The leach rates of soluble elements such as alkalis and Pb were initially large (Fig. 3) and a thick hydrated layer formed quickly, even after 7 days at 70°C [Fig. 9(b)]. Based on these observations the authors deduce greater mobility of alkali and Pb ions in neck glass compared to funnel glass. Since the covalency of Pb-oxygen bond is more than that of alkalis to oxygen, its diffusion in bulk glass is much less than that of alkalis. We infer that Pb must move quickly in the hydrated layer.

Funnel and neck glass compositions are relatively similar when compared on a molar basis, except where the Pb content and alkali ratio are concerned. The cause of the difference of leaching behavior might be the different network structure or merely the different Pb content, but we did not examine this matter in the present study.
The leaching rate at 70°C was four times smaller than that at 90°C for both the neck and funnel glasses (Figs. 4 and 5). Extrapolation of the Arrhenius law to lower temperatures indicated that the leaching rate would be 1/100 at 30°C. The leaching activity of each element is deemed to be equivalent at the lower temperature range, as displayed in Figs. 4 and 5. In contrast, SEM measurements suggest that an alternate leaching mechanism is operative at this temperature (see the Results section). In order to ensure the validity of the Arrhenius relationship tests at lower temperature were required.

4.2 Leaching in alkaline solution

In alkaline solution trends in leaching behavior were similar for neck and funnel glass at different temperatures, as shown in Figs. 10 and 11. A hydrated layer was not detected by FE-SEM measurement of cross-sections derived from either glass. Under alkaline conditions the leaching of glass is usually initiated by cutting of the silica network via OH⁻ attack, causing dissolution that precludes formation of a hydrated layer. In place of the altered layer we observed particle precipitate by FE-SEM (Fig. 13). Given that Pb(OH)₂ and Mg(OH)₂ have low solubility, these elements would be the main component of precipitates on funnel glass observed by EDS analysis of sample cross-sections. The solubility of Pb²⁺ at pH 11 was much lower than 1 mg/L at room temperature.

The leaching of all elements, including soluble species, had virtually ceased after 7 or 14 days (Figs. 10 and 11). In the previous report, we concluded that the Pb-rich layer becomes a dense protective layer that greatly decreases the dissolution rate. The protective layer and the precipitate, shown in Fig. 12, may not be composed of the same material in view of the incomplete coverage of the surface after 7 days of leaching.

However, Fig. 14 indicates that leaching resumes in fresh alkaline solution. Hence, this protective layer is thought to derive stability from solutions saturated with Pb ions. The protective layer and other elements in glass continue to dissolve in refreshed leachate solutions until the Pb concentration is raised again to the saturated value. To prevent the progress of Pb leaching that occurs under alkaline conditions the supply of fresh water available to the glass should be suppressed. At lower temperatures a corresponding drop in the solubility product constant occurs, with concomitant reduction in the amount of leaching.

5. Conclusion

Pb Leaching tests from CRT funnel and neck glass samples were performed at 70 and 90°C using the MCC-1-based method, from 1 to 364 days in 0.001 N HCl and 0.001 N NaOH solutions. We examined the differences in leaching behavior between these types of glass, as well the subjectivity of leaching in these systems to temperature changes.

In HCl solution the funnel glass demonstrated increasing ML and NLi values that were almost proportional to the square root of the leaching time ($t^{1/2}$) over a period of 364 days at 90°C. A diffusion-controlled leaching process, similar to that of other silicate glasses, is implied by these findings. In contrast, the NLi or NLIs of Pb rich neck glass were not proportional to $t^{1/2}$. The difference between the NLi values of soluble components, such as Pb and alkalis elements, and those of insoluble elements such as Si and Al, were much greater in neck glass than in funnel cullet. Soluble elements dissolved quickly during the first several days and decreased with time, whereas the insoluble elements dissolved at a rate nearly proportional to $t$. The NLi values began to converge for all elements after 56 days, which indicates that congruent dissolution occurred. At 70°C similar leaching behavior was observed for both neck and funnel glass, although a fourfold increase in leaching period was required in order to attain an amount of leaching equivalent to that observed at 90°C. SEM observations of the surface revealed contrasting images for different leaching temperatures, thus implying that the leaching mechanism differs depending on the temperature profile utilized. Our SEM observations of the sample cross-sections indicated that a silica-rich layer was formed on the surface. On funnel glass the thickness of this layer was markedly reduced at 70°C after 7 days, in comparison with the result at 90°C after 91 days. On the neck glass a silica-rich layer formed quickly and its thickness remained similar under both sets of conditions.

In NaOH ML and NLi values quickly rose (within 7 or 14 days) with subsequent cessation of further dissolution for both glasses. Leaching activity trended in the same direction at both 70 and 90°C, yielding two thirds of the total leaching amount at the lower temperature. A protective layer was formed on the surface due to saturation of Pb ions in the leachate solution. However, the layer was dissolved in a refreshed solution.

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