

# Removal of lead from cathode ray tube funnel glass by chloride volatilization

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**Abstract** Cathode ray tube funnel glass is an environmentally problematic relict of old television sets. In particular, landfilling of this material is strongly discouraged because of its high lead content. However, recovery of this toxic lead could prevent its release into the environment and allow its reuse. In this research, lead was separated from the glass matrix by a chloride volatilization process. Melting of the funnel glass together with  $\text{CaCl}_2$  resulted in the volatilization of 80 % of lead at 1,000 °C. The use of NaCl as a chlorination agent yielded less volatile lead, while poly(vinyl chloride) and gaseous HCl proved to be ineffective chlorination agents. The differences in the chlorination agent efficiencies could be attributed to differences in the corresponding formation of silicates. Energy-dispersive X-ray spectroscopy showed that diffusion plays an important role in the volatilization of  $\text{PbCl}_2$ .

**Keywords** Recycling · Sodium chloride · Calcium chloride · Polyvinyl chloride · Thermodynamics · Diffusion

## Introduction

Cathode ray tubes (CRTs) were used in the past mainly for television and computer screens. After the introduction of LCD and plasma displays, CRTs lost their competitiveness because of their heavy weight, large size, and radiation emission. In the last several years, CRTs have disappeared from retail stores in developed countries. However, CRT technology was in use for more than 80 years, leaving

numerous devices requiring after-life treatment. The high lead content of the CRT glass and the numerous difficulties involved in lead removal have left landfilling as the only viable disposal option. However, leaching of lead from the CRT glass might result in contamination of the ground water and soil, and therefore (Yamashita et al. 2010), landfilling of this type of waste has been banned (Yot and Méar 2009; Yamashita et al. 2010).

To address this problem, researchers have attempted various methods for separating lead from glass in recent years (Table 1). Yuan et al. (2012) successfully removed lead by performing a leaching procedure after the mechanical activation of the glass by ball milling. Lead was recovered from the leachate as PbS. Miyoshi et al. (2004) achieved the removal of lead from self-made lead glass using subcritical water at 355 °C, although this procedure failed at lower temperatures. Chen et al. (2009) evaporated the metallic lead obtained after reducing PbO with carbon under vacuum conditions. In addition to this metallic lead, foam glass that was acceptable for construction purposes was also obtained. Yot and Méar (2009) used SiC or TiN as reducing agents under an air atmosphere, but did not achieve results as good as those of Chen et al. (2009). Schabbach et al. (2011) did not remove lead from the cone glass, but instead used the glass together with bottom ash rich in Mg and Fe in order to prepare a commercial ceramic glaze with good leaching properties. In this process, the use of waste materials allows the consumption of natural materials to be avoided. However, many of these processes make use of high pressure or vacuum and require expensive pressure control, safety measures, or reactants. In order to achieve an economically viable process, it is necessary to reduce these costs.

In this paper, we describe the removal of lead from CRT glass using a chlorination–volatilization process. In this

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**Table 1** Lead recovery

Author	Method	Lead removal (%)
Yuan et al. (2012)	Leaching after mechanochemical activation	92.5
Miyoshi et al. (2004)	Hydrothermal leaching	93
Chen et al. (2009)	Thermal volatilization of carbon-reduced lead	98.6
Yot and Méar (2009)	Reduction with SiC	40

process, various chlorine-containing waste materials could be used as chlorination agents:  $\text{CaCl}_2$  as a by-product of the Solvay process (Forster 2012) or waste PVC (Park et al. 2009) are cheap alternative materials to SiC or TiN. Moreover,  $\text{PbCl}_2$  has a higher volatility than metallic lead, allowing it to be recovered at lower temperatures and atmospheric pressure. This method has the particular advantage that it utilizes one waste material for the treatment of another.

In the chlorination volatilization process, a chlorination agent is added to the metal-containing material and volatile metal chlorides are separated from the nonvolatile matter. This process was already successfully used to remove lead, zinc, cadmium, and other metals that form volatile chlorides under these conditions from fly ash (Jakob et al. 1995, 1996; Chan and Kirk 1999; Matsuno et al. 2003; Saikia et al. 2007), metal ores (Kanari et al. 2001; Yoo et al. 2005; Lee and Song 2007), molten slag (Wang et al. 2010; Kageyama et al. 2013), and other waste materials. In many cases, the chlorine content of the substrate was sufficient to achieve the desired reduction of the heavy metal content. In other cases, extra chlorine had to be added in the form of a solid or gaseous chlorination agent. Gaseous chlorination agents, mainly HCl and  $\text{Cl}_2$ , are added to the atmosphere at the roasting temperature, while solid chlorination agents (NaCl, KCl,  $\text{CaCl}_2$ , etc.) are mingled with the heavy-metal-containing substrate before the roasting process. In addition, it has been reported that HCl provided by the degradation of waste poly(vinyl chloride) (PVC) could act as a chlorination agent in some cases (Lee and Song 2007; Park et al. 2009).

In all these previously reported chlorination procedures, diffusion has been the limiting factor. Therefore, the temperature at which the process is carried out is another important consideration. Chlorination–volatilization processes can be carried out at temperatures either below or above the melting point or the glass transition temperature, depending on the composition of the material. Materials rich in  $\text{Al}_2\text{O}_3$ , which are characterized by rather high melting points, are roasted in their solid state, while  $\text{SiO}_2$ -containing materials tend to form glasses with broad melting ranges. Glass-forming materials are characterized by their glass transition temperature, at which their viscosity is still high. This hinders diffusion, making the formation of metal chlorides in a heterogeneous material

and the transport of the metal chloride to the surface more difficult. Under these conditions, volatile compounds are depleted at the surface of the melt (Beerkens 2001; MacKenzie and Canil 2008).

The experiments conducted in this work were carried out in the Yoshioka laboratory at Tohoku University (Sendai) from August 2011 to February 2012. In our experiments, we used NaCl,  $\text{CaCl}_2$ , and PVC, as chlorination agents for the lead volatilization between 600 and 1,000 °C. NaCl and  $\text{CaCl}_2$  decrease the melting point and viscosity of glass melts, thereby facilitating faster volatilization of lead (Nakada et al. 2008). PVC, on the other hand, is an organic polymer that is immiscible with the glass melt. It decomposes at the employed temperature range, releasing HCl and organic degradation products. These products have a reducing effect, which might aid the separation of lead from the glass matrix (Nakada et al. 2008; Chen et al. 2009). In order to verify the effects that the different chlorination agents might have on the substrate, we first performed thermodynamic calculations for each agent and compared them with the experimental results. This allowed us to distinguish between thermodynamic and kinetic effects during the process of removing lead from CRT glass.

## Materials and methods

### Materials

Funnel glass from waste television sets with PbO content of 23.1 wt% was used. The glass was ground and sieved to a particle size below 106  $\mu\text{m}$  in order to obtain a homogeneous material. The glass composition was analysed using X-ray fluorescence (XRF) analysis and inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results are given in Table 2. Chlorine was not observed as a part of the glass matrix, and, hence, a chlorination agent had to be provided. The composition was modelled using the thermodynamic calculation software FactSage 6.2 [Centre for Research in Computational Thermochemistry (CRCT), Canada; GTT Technologies, Germany]. The results were of limited reliability, since this program was not able to reproduce this kind of glass. However, it became clear that lead would be incorporated as a silicate



**Table 2** Funnel glass composition

Component	wt%
SiO <sub>2</sub>	57.2
PbO	23.1
Al <sub>2</sub> O <sub>3</sub>	6.22
Na <sub>2</sub> O	5.06
CaO	4.04
MgO	1.77
K <sub>2</sub> O	1.47
Others	1.14

in the glass matrix. Lead silicate is thermochemically more stable than PbO, which makes the removal attempted here more ambitious. The softening point was between 400 and 500 °C, a temperature range in which lead volatilization is not expected.

Concentrated nitric acid (60 wt%), aqueous H<sub>2</sub>O<sub>2</sub> solution (33 wt%), NaOH, NaCl, CaCl<sub>2</sub>, and PVC were purchased from Kanto Kagaku and were of special grade. Fluoric acid (46 wt%) was obtained from Morita Kagaku.

#### Lead volatilization experiment

The experiments were carried out in a horizontal quartz-glass tube (length: 431 mm, inner diameter: 28 mm) heated by an electric furnace (Fig. 1). The reactor was equipped with access to air as the reaction atmosphere and with two traps for the recovery of products, one filled with nitric acid (1 mol l<sup>-1</sup>) and one with NaOH solution (1 mol l<sup>-1</sup>). The use of quartz glass as the reactor materials limited the maximum temperature to 1,000 °C, even if higher temperatures would probably allow higher lead recovery rates.

Prior to the experiment, 0.45 g of glass powder was mixed with a chlorination agent (NaCl, CaCl<sub>2</sub>, or PVC) in a Cl/Pb ratio of 5.7 or 14.2 using a mortar. Then, the sample was added to an alumina boat and placed at the centre of the tube reactor. The sample was then heated to the desired temperature (between 600 and 1,000 °C) with a heating rate of about 1 K s<sup>-1</sup> under air flow (150 ml min<sup>-1</sup>) and maintained at that temperature for 10–120 min. After the experiment, the reactor tube was washed with 1 mol l<sup>-1</sup>

nitric acid in order to collect the products (PbCl<sub>2</sub> and elemental lead) that condensed at cold spots. The resulting solution was combined with the nitric acid trap solution and diluted by 10 or 100 times dependent on the lead concentration. Products were analysed using ICP-AES. No lead was found in the NaOH trap. The residual material in the alumina boat was analysed using X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM) combined with energy-dispersive X-ray spectroscopy (EDX).

#### Analytical methods

A qualitative XRF analysis of the glass was carried out using a JEOL JSX-3200 (Japan Electron Optics Laboratory, Tokyo, Japan).

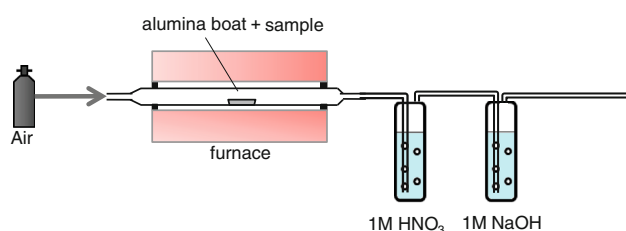
The quantitative analysis was carried out using ICP-AES. Since the trial methods adopted for dissolving the glass for sample preparation resulted in undissolved silicate or PbO, a method involving ultrasonication and the use of fluoric acid and nitric acid was employed. First, 0.3 g of pulverized glass was suspended in 2 ml of deionized water in a Teflon beaker. Then, 30 ml of conc. nitric acid, 20 ml of fluoric acid, and 20 ml of H<sub>2</sub>O<sub>2</sub> were added, and dissolution was effected at a moderate temperature of 40 °C using ultrasonic waves (2510J-MT, Branson) for 1.5 h. Subsequently, the solution was stirred at 80 °C for another hour. The cold solution was topped up to 100 ml, diluted either 10 or 100 times depending on the ion concentration and the sensitivity of the analytical method, and then analysed using ICP-AES (SPS7800, Seiko). The results are given in Table 2.

After the volatilization experiment, the residual glass melt was coated with carbon and pictures were taken using FE-SEM (JEOL JSM-6500F, Tokyo, Japan). In order to obtain information about the lead content at different depths in the sample, EDX was performed.

XRD was carried out using a Rigaku RINT 200 VHF (Tokyo, Japan). The Cu-K<sub>α</sub> line was employed to measure X-ray diffraction pattern between 5° and 89°.

## Results and discussion

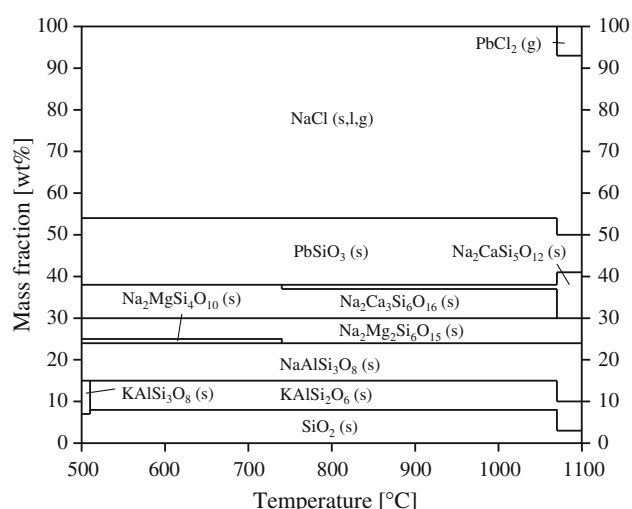
Lead volatilization was conducted using three types of chlorination agents: NaCl, CaCl<sub>2</sub>, and PVC. Lead glass was mixed with each of the chlorination agents before the experiment. As a preliminary consideration, possible applications of the residual glass had to be considered. To minimize the amount of residual glass, gaseous chlorination agents would have been preferable. Therefore, we started the experiments with HCl, which could be provided by the thermal degradation of waste PVC in a future

**Fig. 1** Experimental setup

practical process. This concept would allow for the use of one type of waste material to treat another. However, the results were sobering. The recovery rates for lead were in the range of 1 % or 2 %, and this approach was abandoned in favour of solid chlorination agents. This change in the outline of the concept also meant changing the approach to reusing the residual glass, since sodium and calcium silicate products would now be obtained that could be used as a feedstock for the glass industry.

### Thermodynamic considerations

In order to understand the behaviour of the material, it is necessary to consider the thermodynamic interactions between the glass sample and the chlorination agent used. Interactions between the different components of the glass have a strong impact on the volatilization. The formation of sodium, calcium, and lead silicates can be either driving or inhibiting forces in this process. We tried to simulate the conditions in the glass melt using FactSage 6.2. Unfortunately, the database did not contain data on molten calcium



**Fig. 2** Phase diagram for the thermodynamic equilibrium of the glass (Table 2) with NaCl calculated by FactSage

and lead silicates, leading to results far from reality. Therefore, the calculation was done assuming that all the compounds involved were in their most stable state, although this simplification may lead to additional errors.

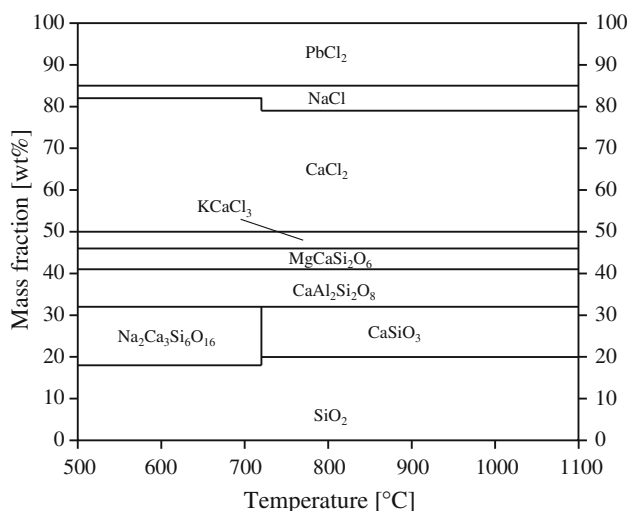
The addition of NaCl (Cl/Pb ratio: 14.2) does not change the structure of the glass-forming components at temperatures below 1,000 °C (Fig. 2). Silicate glass and NaCl might form two phases, since sodium has the lowest tendency to form silicates among the predominant cations involved in this system. However, at about 1,070 °C, PbCl<sub>2</sub> could be released from the system following reaction 1 (Table 3). Since this reaction depends on the calcium content of the glass, it can be maintained until all the Na<sub>2</sub>Ca<sub>3</sub>Si<sub>6</sub>O<sub>16</sub> is consumed, allowing the recovery of 45 % of the lead. On the other hand, reaction 2 does not produce the same result, suggesting that the presence of both sodium and calcium has a positive effect on lead recovery.

The addition of CaCl<sub>2</sub> has a stronger impact on the glass. According to the thermodynamic calculations, lead and potassium chlorides are released from the glass matrix at any temperature because of the strong tendency of calcium to form silicates. On the other hand, some sodium remains in the glass at temperatures below 710 °C (Fig. 3). The removal of these cations results in a calcium-rich glass. Lead chloride is formed by the replacement of lead with calcium in the silicate glass phase (reaction 3 in Table 3). Negative  $\Delta G$  values are obtained at all temperatures. This further underlines the fact that lead volatilization is efficient in the presence of CaCl<sub>2</sub>.

The behaviour of lead glass in the presence of PVC is more complex. For this calculation, the organic phase was composed of C<sub>2</sub>H<sub>3</sub>Cl (Cl/Pb ratio, 14.2) (Fig. 4). As a result, the thermodynamically favoured gases HCl, CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, and H<sub>2</sub> as well as solid graphite are present in the simulation. The reaction of HCl with the glass causes severe depletion of cations and the formation of a large amount of a SiO<sub>2</sub>-rich phase. Besides this, another large phase containing metal chlorides is obtained. Sodium, potassium, and lead are absent in the glass melt, and calcium is only present to some extent between 630

**Table 3** Free energies  $\Delta G$  of relevant reactions at different temperatures with compounds being in their most stable state

Reaction	$\Delta G$ (kJ mol <sup>-1</sup> )			
	600 °C	800 °C	1,000 °C	1,100 °C
1 $4\text{NaCl} + 2\text{PbSiO}_3 + \text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16} + 7\text{SiO}_2 \rightarrow 2\text{PbCl}_2 + 3\text{Na}_2\text{CaSi}_5\text{O}_{12}$	95	52	20	-11
2 $2\text{NaCl} + \text{PbSiO}_3 \rightarrow \text{PbCl}_2 + \text{Na}_2\text{SiO}_3$	55	49	48	40
3 $\text{CaCl}_2 + \text{PbSiO}_3 \rightarrow \text{PbCl}_2 + \text{CaSiO}_3$	-54	-60	-67	-78
4 $2\text{HCl} + \text{PbSiO}_3 \rightarrow \text{PbCl}_2 + \text{SiO}_2 + \text{H}_2\text{O}$	-81	-67	-59	-62
5 $\text{H}_2\text{O} + \text{CH}_4 \rightarrow 3\text{H}_2 + \text{CO}$	5	-45	-96	-122
6 $\text{H}_2\text{O} + \text{C} \rightarrow \text{H}_2 + \text{CO}$	11	-18	-47	-61
7 $\text{PbO} + \text{CO} \rightarrow \text{Pb} + \text{CO}_2$	-54	-57	-59	-60



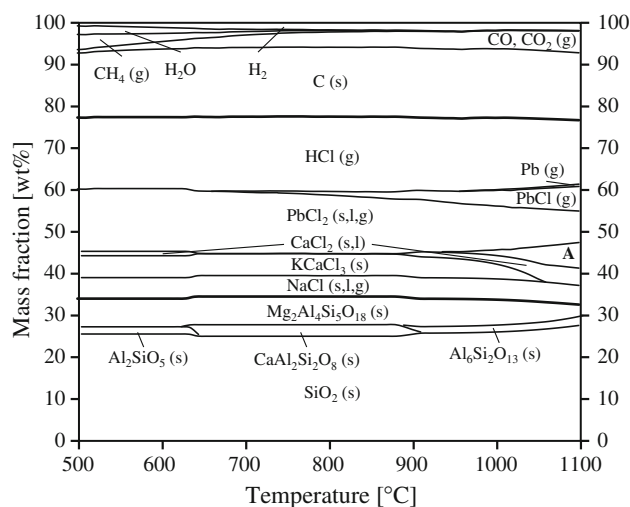
**Fig. 3** Phase diagram for the thermodynamic equilibrium of the glass (Table 2) with  $\text{CaCl}_2$  calculated by FactSage

and 900 °C. The calculation shows that HCl is a thermodynamically effective chlorination agent (reaction 4 in Table 3). The produced  $\text{H}_2\text{O}$  is removed from the equilibrium either by volatilization or reaction with residual organic and carbon from the PVC degradation (reactions 5 and 6 in Table 3). The resulting CO acts also as a reducing agent, leading to the formation of metallic lead (reaction 7 in Table 3). The thermodynamic considerations above show that all three chlorination agents, NaCl,  $\text{CaCl}_2$ , and PVC, should have the ability to release  $\text{PbCl}_2$  from the glass. These calculations do not take into account the kinetic effects, which might lead to a different outcome. This will be discussed in the next section.

#### Lead volatilization

We investigated the lead volatilization using solid chlorination agents under various conditions. The time dependence of these reactions was examined at 1,000 °C with a molar Cl/Pb ratio of 5.69 (Fig. 5a). The highest lead recovery rate was achieved with  $\text{CaCl}_2$  as the chlorination agent, although the reaction with NaCl had a faster start. However, complete lead removal was not achieved in either case. The lead recovery rates in the presence of NaCl and  $\text{CaCl}_2$  were 44 and 52 wt%, respectively. After 1 h of reaction time, the volatilization of lead ended, even though both lead and chloride were still present in the melt. In contrast to the inorganic chlorination agents, the added PVC did not lead to significant volatilization of lead. The recovery rate remained below 1 % after 2 h of reaction time.

When a higher Cl/Pb ratio of 14.2 was used for 1 h, the lead volatilization increased strongly with temperature. The volatilization in the presence of  $\text{CaCl}_2$  had already started at 600 °C and reached 80 % at the maximum



**Fig. 4** Phase diagram for the thermodynamic equilibrium of the glass (Table 2) with  $\text{C}_2\text{H}_3\text{Cl}$  calculated by FactSage. **a** represents KCl (g),  $\text{AlCl}_3$  (g),  $\text{KAlCl}_4$  (g),  $\text{NaAlCl}_4$  (g), and  $\text{MgCl}_2$  (g)

temperature of 1,000 °C. In the presence of NaCl, the volatilization was much slower at low temperatures and only began to accelerate at temperatures close to 1,000 °C, which is in agreement with the thermodynamic calculations. Reaction 1 in Table 3 has a free energy of  $20 \text{ kJ mol}^{-1}$ , leading to an equilibrium constant  $K$  of 0.15 (Eq. 1 with the temperature  $T$  and the gas constant  $R = 8.3144 \text{ kJ mol}^{-1}$ ), which would be sufficient for the continuous removal of  $\text{PbCl}_2$  with the gas stream.

$$\Delta G = -RT \ln K \quad (1)$$

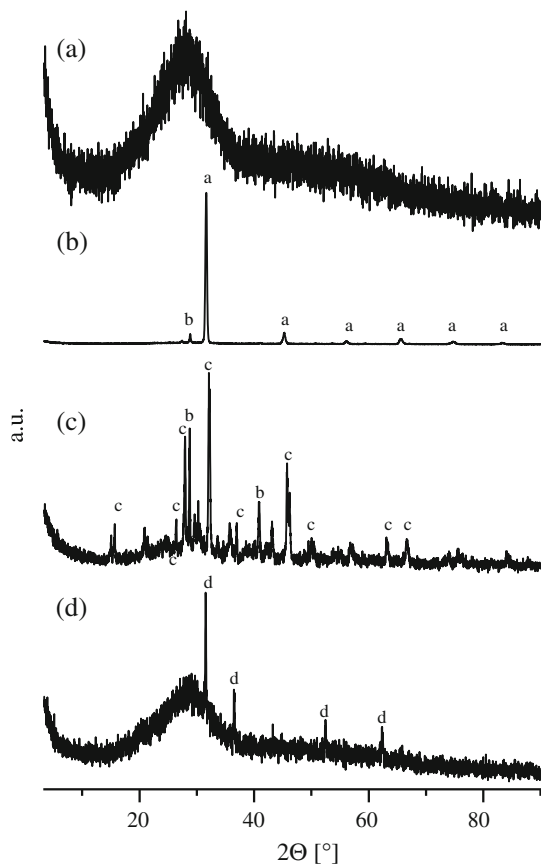
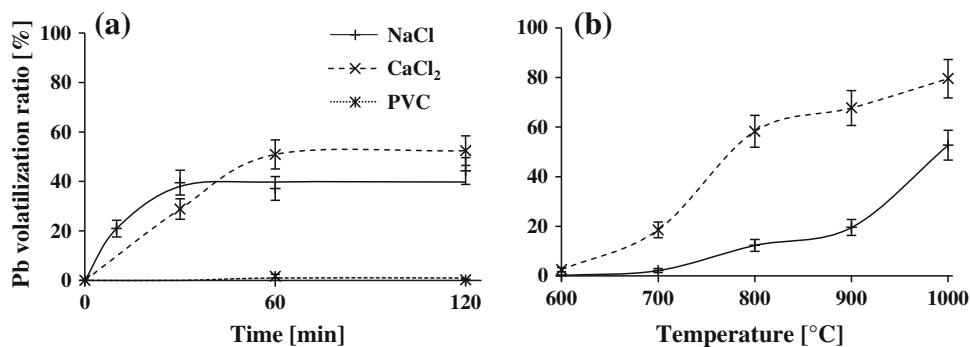
The maximum lead recovery rate of 53 % was higher than expected, since the limitation of Reaction 1 by the calcium concentration allowed only 45 % of the lead to be recovered. The additional lead volatilization probably resulted from reaction 2, since a  $\Delta G$  of  $+48 \text{ kJ mol}^{-1}$  at 1,000 °C results in an equilibrium constant  $K$  of 0.01. This would allow the steady volatilization of  $\text{PbCl}_2$  from the surface of the melt at this temperature.

The reaction with PVC progressed only very little, even at a high Cl/Pb ratio. The results obtained from the calculation were not in agreement with the experimental results, suggesting that kinetic factors had a strong influence on this reaction. As an organic polymer, PVC was barely miscible with the glass. Since the dehydrochlorination of PVC occurs at relatively low temperatures of about 250 °C, the HCl and other gaseous reaction products were provided only for a short time in this process. The reaction products had only superficial contact with the glass melt, and the high viscosity prevented the PVC degradation products from diffusing into the melt. As a result, the reaction between lead and the volatile PVC degradation products occurred only at the surface of the melt. The resulting low reaction rates led to the formation





**Fig. 5** Lead volatilization with different solid chlorination agents: **a** time dependence at 1,000 °C with a Cl/Pb ratio of 5.7 and **b** temperature dependence with a Cl/Pb ratio of 14.2 for 1 h



**Fig. 6** XRD patterns of lead glass after heating for 1 h with **a** no chlorination agent (untreated), **b** NaCl at 1,000 °C (Pb/Cl ratio of 14.2), **c** CaCl<sub>2</sub> at 1,000 °C (Pb/Cl ratio of 14.2), and **d** PVC at 800 °C (Pb/Cl ratio of 5.7). Peaks: **a** NaCl, **b** KCl, **c** CaSiO<sub>3</sub> (Wollastonite), and **d** Pb

of only small amounts of PbCl<sub>2</sub>, and the lead volatilization rate remained at about 1 % (Fig. 5).

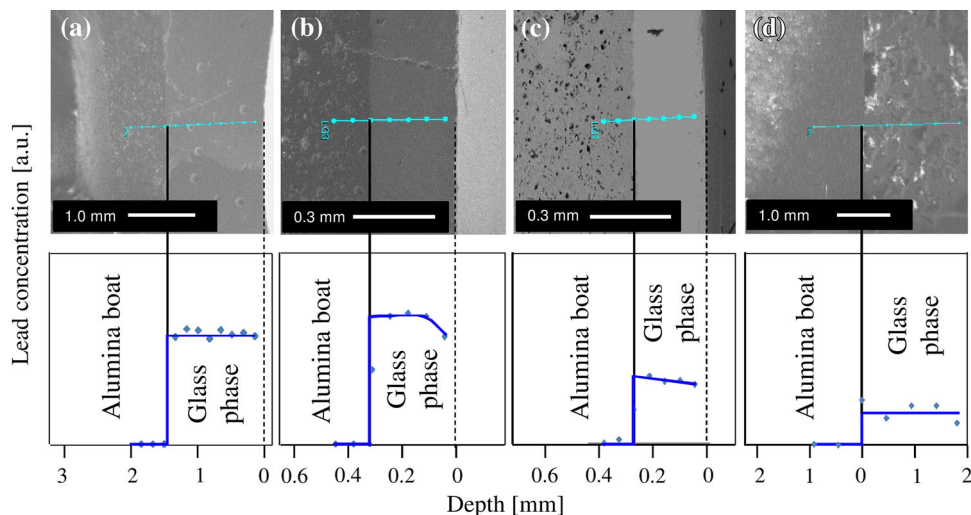
The removal of lead did not change the appearance of the broad XRD pattern of the amorphous glass phase (Fig. 6). The lead glass matrix showed a maximum diffraction signal at 27.7°, and thermal treatment and lead removal did not alter this diffraction pattern of the amorphous glass matrix. However, the chlorination agents did affect the appearance of the

XRD spectra by adding peaks corresponding to crystalline phases. As suggested by the thermodynamic calculation, NaCl barely reacted with the glass (Fig. 6b) and appeared as a crystalline phase next to the barely visible amorphous glass phase. Pure KCl crystals were observed, as well. On the other hand, CaCl<sub>2</sub> had a strong impact on the glass structure (Fig. 6c). The XRD peaks were much smaller than those obtained after the addition of NaCl, and the amorphous glass phase was clearly visible. No CaCl<sub>2</sub> was observed, which indicated that a large amount of chlorine was lost. Instead, wollastonite was observed, suggesting the partial crystallization of CaSiO<sub>3</sub>. Finally, PVC degradation had little impact on the lead glass (Fig. 6d). PVC degradation itself did not leave behind any detectable carbonaceous residue, although some XRD patterns attributable to metallic lead could be observed, indicating that Pb(II) was reduced to metallic lead by the organic degradation products. Thermodynamic calculations have shown that the formation of PbCl<sub>2</sub> is favoured in the presence of HCl, and the reduction of Pb(II) to metallic lead was also predicted. However, the release of HCl from PVC occurs for only a short time at low temperatures (Yoshioka et al. 2005). Thus, it is obvious that the period over which the glass was exposed to HCl was too short to have a significant impact on the glass. Even if PbCl<sub>2</sub> was formed at the glass surface, it immediately volatilized and did not leave any pattern in the XRD results. The residual organic material from the PVC degradation had a longer residence time in the melt, leading to the reduction of Pb(II). Peaks attributable to metallic lead were observed in the XRD results for the lead glass after the reaction with PVC at 800 °C (Fig. 6d). However, no lead patterns were observed after the reaction at 1,000 °C, indicating that only traces of both PbCl<sub>2</sub> and metallic lead were formed at the glass surface and that they volatilized completely at 1,000 °C. Lead below the surface was not affected by the PVC degradation and therefore was not volatilized.

EDX analysis of the samples after treatment at 1,000 °C for 1 h (Fig. 7) further supported these findings. The native lead glass had some air inclusions after melting and had a uniform lead distribution. Inclusions were not observed in the presence of NaCl and CaCl<sub>2</sub>, probably because of the



**Fig. 7** SEM-EDX micrographs and Pb distributions after heating for 1 h at 1,000 °C: **a** lead glass, **b** NaCl (Pb/Cl ratio of 14.2), **c** CaCl<sub>2</sub> (Pb/Cl ratio of 14.2), and **d** PVC (Pb/Cl ratio of 5.7)



reduced viscosity of the melts. In both cases, the lead concentration decreased near the phase boundary of the melt. While the lead concentration remained constant over the cross section in the presence of NaCl and decreased only in a narrow, 100- $\mu\text{m}$  layer close to the phase boundary, a constant reduction in the lead concentration was observed in the presence of CaCl<sub>2</sub>. This also reflects the differences in the lead volatilization occurring in the presence of the two chlorination agents. PbCl<sub>2</sub> was only produced from NaCl near the phase boundary, where it was immediately volatilized, shifting the equilibrium in the direction of PbCl<sub>2</sub>. CaCl<sub>2</sub> reacted with the glass over the entire cross section, forming CaSiO<sub>3</sub> and PbCl<sub>2</sub> that was then volatilized. Large bubbles of gas were formed during the degradation of PVC, giving the melt a spongy appearance. These large bubbles made it more difficult to determine the lead distribution, but it seemed to remain constant over the whole cross section. Even the larger surface formed when the melt expanded because of the gases produced by the PVC degradation did not result in more efficient lead volatilization.

## Conclusion

Volatilization of lead from lead glass in the presence of various solid chlorination agents was investigated. CaCl<sub>2</sub> was the most efficient chlorination agent tested: 80 % of lead could be volatilized at a Cl/Pb ratio of 14.2 and a temperature of 1,000 °C. In this process, the formation of PbCl<sub>2</sub> was thermodynamically preferred.

Unlike when CaCl<sub>2</sub> is used, the formation of PbCl<sub>2</sub> from NaCl is not thermodynamically preferred. PbCl<sub>2</sub> was only formed close to the phase boundary, where it was released into the gas phase and removed from the equilibrium. In this process, about 53 % of lead was recovered.

The degradation of PVC had little impact on the glass composition. HCl was released for only a limited period of time, making the reaction with lead difficult. The carbonaceous residue remained for a longer time, reducing Pb(II) to metallic lead that was volatilized at higher temperatures. Only negligible amounts of lead could be recovered by this process. The use of HCl gas would probably face similar difficulties, since the reaction is limited to the surface of the glass melt. For a sufficient reaction, transport of lead and chloride by diffusion is required. However, diffusion proved to be rather slow under the conditions used.

The residual glass recovered from lead volatilization with CaCl<sub>2</sub> as a chlorination agent still contained about 3 wt% lead. Further improvement of lead recovery and a reduction in the amount of chlorination agent are required. It can be expected that more lead can be removed at higher temperatures at which reduced viscosity of the glass melt might not impede mass transport to the extent observed in this work. Taking this into account, comparable results to those from Miyoshi et al. (2004), Yuan et al. (2012), or even Chen et al. (2009) might be possible. An ecological benefit might be that volatile PbCl<sub>2</sub> could be recovered without producing waste water as in the case of leaching processes. The resulting calcium silicate containing residue might be used as construction material (Giergiczny and Król 2008; Kim et al. 2009).

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