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Chemical durability of lead silicate glass in HNO_3, HCl and H_2SO_4 aqueous acid solutions

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ABSTRACT

Acid dissolution of silicate glasses with different lead contents was rigorously investigated. Aqueous solutions containing 0.5, 1, and 2 N HNO_3, HCl and H_2SO_4 were used to measure the durability of the glass probes. Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Inductively Coupled Plasma (ICP), X-ray Diffraction (XRD) and weight loss analyses were used to evaluate the morphological/compositional changes of the probes, the ash deposit, and the aqueous solutions produced due to the dissolution of the glass specimens. Empirical results showed that any increase in the lead content of the probes deteriorated the durability of the glasses by accelerating the hydrolysis of the silica network. ZrO_2 and TiO_2 additions had inverse effect and improved the chemical durability and the practical lifetime of the lead glasses.

1. Introduction

Lead silicate glass (LSG) is significantly used in many different areas from radiation protection, video-screen manufacturing and electrode glass production to ophthalmic biotechnology [1–8]. Because of its toxic nature, the study of dissolution of LSG in both environmental and industrial solutions is of considerable importance. Chemical durability of LSG when soaked in water, acetic acid, sulfuric acid and nitric acid has been investigated by previous authors [6–9,10,11].

Silicon content has a substantial effect on the durability of the LSG [9,12]. Pure silica has, for example, silica tetrahedrons directly connected to each other with oxygen atoms located at corners. Addition of a modifier like PbO causes partial breakage of the direct interconnections [2,13–15]. In such a case, indirect connection of the silica tetrahedrons via Pb ions deteriorates the chemical durability of the LSG glass [6–9].

When a glass probe contacts an acidic aqueous solution, the H^+ ions of the medium replaces the modifier cations in the glass network:

$$\equiv Si-O-M-O-Si\equiv + 2H^+ \leftrightarrow 2(\equiv Si-O-H) + M^{2+}. \quad (1)$$

Leaching removes the modifier and produces a modifier-depleted silica-rich layer near the LSG surface [5,8,9,16,17]. Water molecules then penetrate easily and react with the network. The amount of the modifying cations in the silica network thus significantly affect on the chemical durability of the silicate glass. Simultaneous presence of two or more cations like Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Ti^{4+}, and Zr^{4+} in the glass enhances for example the chemical durability of the LSG [18,19].

The present study focuses on the effect of lead, titanium and zirconium oxide on the chemical durability of LSG samples utilized in

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Table 1
Chemical composition of lead silicate glass samples used in this investigation.

Sample	(wt%)						
	PbO	SiO_2	ZrO_2	TiO_2	Al_2O_3	As_2O_3	Alkaline (Na, K)
S1	55.6 ± 0.41	34 ± 0.23	2.7 ± 0.02	1 ± 0.02	2.3 ± 0.02	0.3 ± 0.002	4.1 ± 0.04
S2	65.4 ± 0.43	26.9 ± 0.21	2.4 ± 0.02	1 ± 0.02	2.2 ± 0.02	0.3 ± 0.02	1.8 ± 0.02
S3	68.5 ±0.39	24 ± 0.22	2.4 ± 0.02	1 ± 0.02	2.2 ± 0.02	0.3 ± 0.02	1.6 ± 0.02
S4	68.5 ± 0.45	27.5 ± 0.19	–	–	2.2 ± 0.02	0.3 ± 0.02	1.5 ± 0.02

aqueous acidic environments. Quantitative weight loss data combined with SEM, XRD and ICP results are used to characterize the LSG surface morphology and to reveal the mechanism of the LSG dissolution the reaction products obtained.

2. Experimental procedure

2.1. LSG probe preparation

LSGs with chemical compositions given in (Table 1) were produced from technical grade silica >99.9 (Iran, Hamedan), Pb_3O_4 (Iran) and reagent grade Na_2O, K_2O, ZrO_2, TiO_2 to As_2O_3 (Aldrich Chemical Co.) powders. Each batch of the mixed materials weighed 500 g and was melted in an alumina crucible under atmospheric pressure at temperatures from 1200 to 1300 °C in an electric furnace (Exciton Co., Iran) for 2 h. For achieving an acceptable homogeneity, the glass melt was water quenched. The quenching was twice repeated. The produced frit was then ground to <60 grit and was well mixed in a ceramic mortar. This was also twice repeated. The ground powder was then melted and then poured in a stainless steel mold to yield a solid piece. The solid was then annealed at about 10 °C above the glass transition temperature for 12 h. The furnace was then turned off and cooled overnight to prevent from later cracking. Transformation temperatures were determined by differential thermal analysis.

2.2. Leaching

LSG cast probes were cut into $15 \times 15 \times 3$ mm rectangular blocks with a diamond hacksaw. One side of each probe was polished with rough SiC paper to 3000 grit. An anti-acid paste (Sikagard 63N, Sika and Sweis) was used to isolate all other surfaces. Before dissolution, the probe was degreased by rinsing in a 2-propanol cleaning solution for 3 min. The probes were then washed with deionized water and dried at 60 °C for 4 h. They were weighed by a (Mettler Toledo AG204) electric balance having ±0.0001 g accuracy. The effective surface area per volume of each probe being exposed to the solution was around $0.133\ cm^{-1}$.

HNO_3 (Ruth, Germany), HCl (Ruth, Germany) and H_2SO_4 (Merck, Germany) were used for LSG dissolution. Dissolution tests were carried out with 0.5, 1 and 2 N acid concentrations for 65 h. The pH values were continuously controlled with a pH meter (Sana, SL-901, Iran) equipped with (Sentec, England) electrode.

2.3. SEM, XRD and ICP analyses

Characterization of the surface of the glasses after dissolution experiments was carried out by using a scanning electron microscope (Philips, XL30) equipped with energy dispersive spectroscopy (EDS). X-ray diffraction pattern (XRD, Philips, PW 1800, Cu K_α radiation) helped the identification of the layers that precipitated on the surface of the glasses when the dissolution process had proceeded. The atomic emission spectroscopy with an inductively coupled plasma measurements (ICP-Perkins Elmer Model Optima 2100 DV) determined the concentration of Pb^{2+}, Si^{4+} ions in solutions after dissolution.

2.4. Weight loss determination

Precise weight measurements combined with the EDS and the ICP analyses of both the ash layer deposited and the solution enriched with the dissolved ions (Table 3) provided important information about dissolution of the LSG in different acid environments (Table 4). The quantities determined were defined as:

$$\begin{aligned} &w_0 = \text{Weight of the probe before contacting the solution}(g), \\ &w_1 = \text{Weight of the probe and the ash deposit after drying} \\ &\quad \text{of the pulled out probe}(g), \\ &w_2 = \text{Weight of the probe after removing of the ash deposit}(g), \\ &w_1 - w_2 = \text{Weight of the ash deposit}. \end{aligned} \tag{2a}$$

Assuming that the weight of H^+ is negligible in comparison with the weight of Pb^{2+} entering into the solution, one can write:

$$w_0 - w_1 = \text{Weight of the elements dissolved in the solution}. \tag{2b}$$

The specific weight loss, W, was determined by dividing $w_0 - w_2$ to the total surface area S of the LSG [20]:

$$W = (w_0 - w_2)/S, \tag{3}$$

where W is the specific weight loss (g/cm^2) and S is the surface area of the sample (cm^2).

By using the ICP results, the weight fractions of $Pb^{2+}$and Si^{4+} cations in solution (X'_i) were determined from the following relation:

$$X'_i = X''_i / \sum Xi, \tag{4}$$

where X''_i is the ppm value of Pb^{2+} and Si^{4+} entering into the solution and $\sum Xi$ is the sum of the ppm values of the whole cations entering into the solution. The concentration of Pb and Si in the solution and the weight per surface area of the Pb^{2+} and the Si^{4+} in the dissolution products are calculated by application of the ICP and the EDS results by using the following correlations:

$$C_{Pb} = X'_{Pb} \times M_l \times V, \tag{4a}$$

$$C_{Si} = X'_{Si} \times M_l \times V, \tag{4b}$$

$$W_{Pb} = (C_{Pb} \times V + f_{Pb} \times m')/S, \tag{5a}$$

$$W_{Si} = (C_{Si} \times V + f_{Si} \times m')/S, \tag{5b}$$

where M_l is the weight of the solution, V is the volume of the solution, W_{Pb} and W_{Si} are the total weight loss of Pb and Si per surface area of LSG, C_{Pb} and C_{Si} are the concentrations of Pb^{2+} and Si^{4+} cations in the solution, f_{Pb} and f_{Si} are the weight fractions of Pb and Si in the ash deposit, m' is the weight of the ash deposit and S is the sample surface area. Pb and Si were the only main LSG components reported to be extracted from the surface of the samples. The surface concentration of the samples obtained by EDS analysis are given in Table 2. Table 3 indicates the wt% of Pb and Si in the dissolution products evaluated from the following relationships:

$$\begin{aligned} &\text{wt\%Pb} = 100 m_{Pb}/(m_{Pb} + m_{Si}) \\ &\text{wt\%Si} = 100 m_{Si}/(m_{Pb} + m_{Si}), \end{aligned}$$