

Effects of Ion-Exchange and Hydrolysis Mechanisms on Lead Silicate Glass Corrosion

R. Ali Rahimi* and S.K. Sadrnezhaad†, **

ABSTRACT

Corrosion of lead silicate glass (LSG) contacting 0.5 M aqueous nitric acid (HNO_3) was investigated via scanning electron microscopy, energy-dispersive spectroscopy, inductively coupled plasma analysis, and weight-loss measurement to determine the respective contributions of the ion-exchange vs. the hydrolysis reactions. The LSG having $X_M \equiv \frac{Pb + K + Na}{Si}$ mole ratios of less than 0.7 showed very little weight loss with no Si network deterioration. At $X_M > 0.7$, the mechanism changed into the hydrolysis, which caused the formation of a network-less gel layer resting at the solid/liquid interface. Addition of titania (TiO_2) and zirconia (ZrO_2) had disparate effects: $X_M < 0.7$ improved corrosion resistance; while $X_M > 0.7$ caused detrimental consequences.

KEY WORDS: acid corrosion, glass, titanium, weight loss, zirconium

INTRODUCTION

Low-silica, high-lead glasses are generally used as an absorber of gamma rays in the viewing windows of the hot cells. Lead silicate glass (LSG) is a widely used example. These glasses may deteriorate when contacting highly corrosive acidic environments like nitric acid (HNO_3)-containing solutions. When the

LSG contacts with the acid solution, hydrolysis and ion exchange reactions simultaneously start. Because of the small contact area of the silica lattice with the solution, the hydrolysis reaction is initially slow, but gradually increases. Both ion-exchange and hydrolysis reactions are known, therefore, to affect the corrosion of the silicate glasses.¹⁻⁸ The ion exchange reaction is, however, much faster than the hydrolysis reaction.

A silicate glass provides network places less stable with atoms like lead, sodium, potassium, and boron than with silicon or intermediate elements.⁹⁻¹¹ At the start of the corrosive attack, the ion-exchange mechanism governs the process.¹²⁻¹³ With severe network destruction, hydrolysis becomes prevalent causing silicon removal. In silica-rich glasses, the ion-exchange reaction is the dominant mechanism during the whole corrosion process.¹⁴

Radius differences of hydrogen, lead, and other modifier ions (H^+ 0.012, Pb^{2+} 1.19, Na^+ 1.02, and K^+ 1.38 Å) produce greater space for transfer of protons into the silica network after partial depletion of some lead as well as other modifiers. Interdiffusion of H^+ , Pb^{2+} , and other soluble ions are also affected by the silica content of the LSG, the pH of the solution, titanium and zirconium additives, and the presence of the alkaline elements.¹⁵⁻¹⁷ Quantity and composition of the corrosion products may influence the effectiveness of the competing reactions.

Chemical corrosion of the LSG in hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) as compared to HNO_3 has been described previously.¹⁵ The results have shown that H_2SO_4 is less corrosive than HNO_3 .

Submitted for publication: September 2, 2011. Revised and accepted: December 30, 2011. Preprint available online: June 1, 2012, <http://dx.doi.org/10.5006/0528>.

† Corresponding author. E-mail: sadrnez@sharif.edu.

* Material Research School, Nuclear Science and Technology Research Institute, Atomic Energy Organization of Iran, PO Box 31485-498, Karaj, Iran.

** Department of Materials Science and Engineering, Sharif University of Technology, PO Box 11365-9466, Tehran, Iran.