



Hydrolysis kinetics of lead silicate glass in acid solution

Rafi Ali Rahimi^{a,b,*}, Sayed Khatibuleslam Sadrnezhaad^{a,c}, Gholamreza Raisali^d, Amir Hamidi^b

^a Materials and Energy Research Center, P.O. Box 14155-4777, Tehran, Iran

^b Material Research School, Nuclear Science & Technology Research Institute (NSTIR), Atomic Energy Organization of Iran, Moazen Street, Rajaei Shahr, Karaj 31485-498, Iran

^c Center of Excellence for Production of Advanced Materials, Department of Materials Science and Engineering, Sharif University of Technology, P.O. Box 11365-9466, Tehran, Iran

^d Radiation Applications Research School, Nuclear Science & Technology Research Institute, Atomic Energy Organization of Iran, End of Kargareh Shomali Street, Tehran 11365-3486, Iran

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ABSTRACT

Hydrolysis kinetics of the lead silicate glass (LSG) with 40 mol% PbO in 0.5 N HNO₃ aqueous acid solution was investigated. The surface morphology and the gel layer thickness were studied by scanning electron microscopy (SEM) micrographs. Energy dispersive X-ray spectroscopy (EDS) and inductively coupled plasma spectroscopy (ICP) were used to determine the composition of the gel layer and the aqueous solution, respectively. The silicon content of the dissolution products was determined by using weight-loss data and compositions of the gel layer and the solution. The kinetic parameters were determined using the shrinking-core-model (SCM) for rate controlling step. The activation energy obtained for hydrolysis reaction was $Q_{che} = 56.07$ kJ/mole. The diffusion coefficient of the Pb ions from the gel layer was determined by using its concentration in solution and in LSG. The shrinkage of the sample and the gel layer thickness during dissolution process were determined.

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1. Introduction

There have been many investigations about the dissolution of lead and boro-silicate glasses in water and aqueous acid solutions [1–10]. It has become clear that the dissolution of all silicate glasses starts by the ion-exchange reaction and goes on simultaneously by the accomplishment of the ion-exchange reaction in the glass/modifier-depleted film interface and the hydrolysis reaction of the silica in the modifier-depleted/gel layer interface. In LSG glasses, the ion-exchange reaction occurs between H⁺ and Pb²⁺ ions [3,4,6,8–10]. Depending on the lead content of the LSG and the concentration of the aqueous acid solution, the ion-exchange reaction results in porous hydrated silica network with one, two, or three siloxane bonds (Si–O–Si bonds between silica tetrahedrons). This dramatically multiplies the active surface area with respect to the initial external surface of the sample [5,11,12]. The hydrolysis reaction is initiated at the weak silica network (silica tetrahedrons with lower siloxane bond) [2,7,13,14] and then goes on to the end.

The modifier elements are dissolved in vast range, but the silica components have limited solubility in solution. By increasing the silicon concentration in solution, re-precipitation of this compound is started [1,5,12–15]. This produces the gel layer on the surface of

the LSG glass. The liquid film, gel layer and the modifier depleted layers are the rate limiting steps during dissolution process. They inhibit transfer of components incorporating in ion-exchange (proton and modifier cations) and hydrolysis reactions (water and the hydrated silica molecules) [1,3].

In present study, by using un-reacted core model and the double-stage kinetic modeling procedure in 0.5 N HNO₃ acid solution (pH 0.3), the prevailing step during hydrolysis of the LSG was disclosed [16]. The analytical techniques (SEM–EDS and ICP) were used to determine the morphology of the sample surfaces and the composition of the gel layer and solution. The fractional weight loss of silicon in dissolution products is applied to the software previously developed for simulation of the kinetic processes [17–20]. The thickness of the gel layer was measured by SEM equipment and the sample shrinkage due to the dissolution process was calculated by the silicon amount extracted from the LSG sample and entered into the dissolution products, i.e. the gel layer and the aqueous acid solution.

2. Experimental procedure

Dissolution experiments were carried out on LSG samples with the composition given in Table 1. Rectangular shape samples with 0.015 × 0.015 × 0.003 m³ dimensions were polished in one side from rough to 3000 mesh, with SiC paper. Their other surfaces covered with anti-acid paste (Sikagard 63N, Sika, and Sweis). The samples were rinsed in 2-propanol for three minutes. They were washed, with deionized water, then dried at 60 °C for 4 h and

* Corresponding author. Address: Material Research School, Nuclear Science & Technology Research Institute (NSTIR), Atomic Energy Organization of Iran, Moazen Street, Rajaei Shahr, Karaj 31485-498, Iran.

E-mail addresses: rrahimi@nrcam.org (R.A. Rahimi), sadrnezh@sharif.edu (S.K. Sadrnezhaad), graisali@aeoi.org.ir (G. Raisali), ahamidi@nrcam.org (A. Hamidi).