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SURFACE CHEMISTRY AND DURABILITY OF BOROSILICATE GLASS

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ABSTRACT

Preliminary results show that glass durability is dependent on reactions occurring at the glass-solution interface. CSG glass (18.2 wt. % Na_2O , 5.97 wt. % CaO , 11.68 wt. % Al_2O_3 , 8.43 wt. % B_2O_3 , and 55.73 wt. % SiO_2) dissolution and net surface H^+ and OH^- adsorption are minimal at near neutral pH. In the acid and alkaline pH regions, CSG glass dissolution rates are proportional to $[\text{H}^+]_{\text{adsorbed}}^2$ and $[\text{OH}^-]_{\text{adsorbed}}^{0.8}$, respectively. In contrast, silica gel dissolution and net H^+ and OH^- adsorption are minimal and independent of pH in acid to neutral solutions. In the alkaline pH region, silica gel dissolution is proportional to $[\text{OH}^-]_{\text{adsorbed}}^{0.9}$. Although Na adsorption is significant for CSG glass and silica gel in the alkaline pH regions, it is not clear if it enhances dissolution, or is an artifact of depolymerization of the framework bonds.

INTRODUCTION

Important glass-water interactions are poorly understood for borosilicate glass radioactive waste forms. This is because glass-water interactions are a complex function of solution, bulk glass and surface glass compositions. Much of the experimental glass kinetic data are from dissolution of multicomponent glasses in batch reactors. These experiments are too complicated to allow mechanisms controlling glass dissolution to be determined. In batch reactors, solution composition and secondary mineral precipitation are not controlled. Therefore, the effects of glass composition and glass-water surface reactions on dissolution cannot be isolated.

This work compares the surface chemistries and dissolution behaviors of CSG glass (nonradioactive analog for SRL-165 glass) and silica gel at 25°C, in a preliminary effort to determine the surface complexation reactions that control the durability of borosilicate glasses. We chose to compare silica gel with CSG glass because silica is the dominant component in waste glasses and layers enriched in silica are known to form at glass surfaces during dissolution. The surface chemistries are inferred from potentiometric titrations of glass and gel suspensions according to surface complexation theory. Surface complexation theory has been successfully applied to simple oxide dissolution kinetics [1-4]. The dissolution rates are determined from flow-through and pH-stat experiments for CSG glass [5] and silica gel, respectively.

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EXPERIMENTAL METHODS

Potentiometric titrations were performed on suspensions of CSG glass and silica gel using a Mettler DL21 automatic titrator. CSG glass, a nonradioactive analog for SRL-165 waste glass (18.2 wt. % Na₂O, 5.97 wt. % CaO, 11.68 wt. % Al₂O₃, 8.43 wt. % B₂O₃, and 55.73 wt. % SiO₂), and Silicar[®] silica gel were washed repeatedly with distilled and deionized water to remove fines. The CSG glass and silica gel surface areas were determined to be 0.13 and 273 (m²/g) by BET N₂(g) adsorption. Approximately 2.5 grams of CSG glass or 0.5 grams of silica gel were added to 50 ml of 10⁻² M NaNO₃, purged with N₂(g) for at least 60 minutes, and continuously stirred overnight. Acid and alkaline titrations were performed on separate suspensions. The pH electrode was calibrated with the appropriate buffers prior to the background electrolyte blank titration. The net H⁺ or OH⁻ concentrations adsorbed at the solid surface were calculated from the difference between the blank pH and the suspension pH corrected for the hydrolysis of any dissolved species. High purity N₂(g) was slowly bubbled through the reaction vessels during the blank and suspension titrations to ensure a CO₂ free environment. The equilibration time for the adsorption reactions was 10 minutes. A sample was taken at the end of each experiment, filtered, and analyzed for dissolved Na, Ca, B, Al, and Si by ICP-AES.

Silica gel Na⁺-H⁺ ion exchange and dissolution studies were performed with a Mettler DL21 automatic titrator in pH-stat mode at pH 3, 4, 5, 6, 7, 8, 9, 10, and 11. The duration of each pH-stat experiment was approximately 5 hours. For each pH-stat experiment 8 to 10 samples were taken, filtered, diluted with distilled and deionized water, and analyzed by ICP-AES for dissolved Na and Si. The suspension pH was recorded every 10 minutes over the duration of the experiment.

SURFACE COMPLEXATION THEORY

According to surface complexation theory, dissolution rates of oxides and silicates are controlled by the breaking of metal-oxygen framework bonds, which are accelerated by the adsorption of H⁺ and OH⁻ ions at surface reaction sites [1,6]. Surface adsorption reactions are rapid, such that the rate limiting step is the detachment of the cation from the mineral-solution interface. For a simple oxide, the important surface reactions are protonation and deprotonation of surface metal reaction site:

respectively. The $>M$ symbol represents metal surface species, K_{a1} and K_{a2} are conditional constants for the mass balance expressions for respective adsorption reactions, and $[i]$ and $\{i\}$ are the respective concentrations and activities of the i^{th} surface or aqueous species. Note that the deprotonation reaction is equivalent to the adsorption of an OH^- ion at the neutral metal-site producing a negatively charged surface species and water. Breaking of the critical metal-oxygen bonds occurs if a significant number of H^+ or OH^- ions are adsorbed to neighboring metal surface sites. The overall dissolution rate, R , may be expressed as:

$$R = k_H[>\text{MOH}_2^+]^n + k_{\text{OH}}[>\text{MO}^-]^m \quad (3)$$

where k_i is the dissolution rate constant attributed to the i^{th} adsorbing ion. Exponents n and m are experimentally determined reaction orders, and represent the number of ions adsorbed prior to the detachment of the metal ion into the bulk solution.

RESULTS AND DISCUSSION

Qualitatively, the correlation between net adsorption of H^+ at the solid-solution interface and net dissolution rate is good. The net dissolution and adsorption of H^+ depends on the bulk solid composition. The dissolution and adsorption behaviors of CSG glass are distinct from the dissolution and adsorption behaviors of silica gel (Fig. 1). The CSG glass dissolution rates [5] are at minimum at near neutral pH, and increase at more acid and alkaline pHs. This correlates well with an increase in H^+ adsorption from near neutral to acid pH and increasing desorption of H^+ from near neutral to alkaline pH. Unlike CSG glass, the dissolution behavior of silica gel is at a minimum and independent of solution pH from acid to near neutral pH, and increases with increasing pH at $\text{pH} > 8$, correlating well with minimal sorption of H^+ in the acid to near neutral pH and increasing H^+ desorption in the alkaline pH region. The dissolution and net H^+ adsorption behaviors for CSG glass and silica gel are identical to the dissolution behaviors of many alumino-silicate minerals [3,7-14] and quartz [4,15], respectively. Note also, that the release of Al and Si from CSG glass is not congruent. The Al and Si dissolution rates are normalized to their respective mole % in the bulk glass and should be equal at a given pH, if dissolution is congruent. The higher rate of Al removal, indicates that an enriched silica layer forms at the glass-water interface. Only at $\text{pH} > 10$ is dissolution congruent.

Figure 2 shows log-log plots of dissolution rates versus net H^+ adsorption for CSG glass and silica gel. Assuming that the release of Si into solution reflects the net durability of a glass, CSG glass dissolution rates are proportional to $[\text{H}^+]_{\text{adsorbed}}^2$ in the acid pH region and $[\text{OH}^-]_{\text{adsorbed}}^{0.8}$ in the

Fig. 1. Log dissolution rates (R) vs. pH for CSG glass (a) and silica gel (c) and the ΔH° vs. pH for CSG glass (b) and silica gel (d).

alkaline pH region. Silica gel dissolution rate are proportional to $[\text{OH}^-]_{\text{adsorbed}}^{0.9}$. Surface complexation theory interprets microscopic surface reactions from macroscopic changes in the bulk solution composition. Brady and Walther [4,12,14] interpret $[\text{OH}^-]_{\text{adsorbed}}$ to be equal to the $[\text{>SiO}^-]$ and the $[\text{H}^+]_{\text{adsorbed}}$ to be equal to the $[\text{>AlOH}_2^+]$ from the dissolution and adsorption behavior of feldspars and quartz as a function of solution pH. Similar interpretations could be made for CSG glass.

Important surface complexation reactions for CSG glass are the protonation and deprotonation of >AlOH , the deprotonation of >SiOH , and the exchange of alkalis and alkaline earths for H^+ at >SiOH and >AlOH . It is thought that the strong hydration of alkalis and alkaline earths in the bulk solution prevent them from forming inner sphere complexes at the Al- and Si-sites. However, in the acid pH region, exchange of Na^+ for H^+ bonded to tetrahedrally coordinated Al, may be an important mechanism controlling the net dissolution of CSG glass. Recent studies [16-18] have shown that Na^+ adsorption enhances pure silicate dissolution. Note that, the deprotonation of

Fig. 2. Log CSG glass dissolution rate vs. log [H⁺] adsorbed (a) and log [OH⁻] adsorbed (b), and the log silica gel dissolution rate vs. log [OH⁻] adsorbed (c).

>SiOH to a negative >SiO⁻ and the exchange of Na⁺ for H⁺ at >SiOH to >SiO⁻ Na⁺ both result in consumption of OH⁻ from the bulk solution. The surface chemistry of boron oxides is unclear.

Na⁺ - H⁺ Exchange

In order to determine the rate catalyzing adsorption reactions, the alkali and alkaline earth exchange reactions must be better understood. Towards this effort, we investigated exchange of Na⁺ for H⁺ at silanol sites on silica gel from pH 3 to 11 at 25°C. This is the first study that has measured both the dissolved Na, Si, and pH to determine the importance of Na adsorption to silica gel dissolution. In agreement with previous studies [19], no Na adsorption occurs at pH less than 7, where the dominant silanol surface species is the neutral >SiOH. At pHs greater than 8, the Na adsorption is significant and exceeds the net change in [OH⁻] (Fig. 3a). If Na adsorption occurs only at silanol sites as an

Fig. 3. $\Delta[\text{Na}]$ vs. $\Delta[\text{OH}^-]$ removed from solution measured in the ion exchange experiments (a), the silica gel titration (b), and the CSG glass titration.

exchange reaction, then $\Delta[\text{OH}^-]$ must be greater than or equal to $\Delta[\text{Na}]$. In these experiments $\Delta[\text{Na}] > \Delta[\text{OH}^-]$ by a factor of 1.4. Note also, that the extent of Na removal from solution approaches the total concentration of silanol sites for silica gel, 8.303×10^{-6} (moles m^{-2}) [20,21].

Figure 3 (b and c) shows the net Na adsorption from silica gel and CSG glass potentiometric titrations. Unlike the ion exchange experiments, the amount of Na adsorbed at the silica gel-solution interface is approximately 50% of the total $[\text{OH}^-]$ removed from solution, indicating that Na^+ and the background electrolyte counter ion NO_3^- diffuse into the silica gel with increased reaction. The net adsorption of Na at the CSG glass-solution interface reaches a maximum at $\Delta[\text{OH}^-] > 1 \times 10^{-4}$ (moles m^{-2}). Note also, that the $\Delta[\text{OH}^-]$ is two orders of magnitude greater than $\Delta[\text{OH}^-]$ on the silica gel. This may indicate that the number of reactive sites increases with increasing H^+ or OH^- adsorption or that the BET surface area underestimates the reactive CSG glass surface area.

CONCLUDING REMARKS

For glasses and gels, there is a good correlation between the net adsorption H^+ at surface and the net dissolution rate. However, we do not have enough information on the exchange of Na^+ for H^+ at framework reaction sites ($>SiOH$ and $>AlOH$) to determine the rate controlling reactions. Our experiments also show that uptake of Na by silica gel differs from the uptake of Na by CSG glass which contains 18.2 wt % Na_2O . Both Na and OH removal from solution in silica gel suspensions increase with increasing solution pH. Na adsorption at the CSG glass surface reaches a maximum at $1 \times 10^{-4} OH^-$ (moles m^{-2}) and net adsorption of H^+ and OH^- exceeds the total number of surface sites estimated from silica gel by two orders of magnitude.

Bunker and co-workers [22-24] have shown with NMR and Raman spectroscopy that glass durability is controlled by polymerization reactions at the glass-solution interface. Very simply, the greater the number of non-bridging silanol bonds, the less durable the glass. Surface complexation theory assumes that the total number of silanol sites is constant, and that the adsorption or desorption of H^+ from the silanol sites accelerates the dissolution of the glass. Future studies include the combination of potentiometric titrations and NMR experiments to determine the mechanisms controlling the dissolution kinetics of glasses as a function of glass and solution composition.

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