Modelling the sulfate capacity of simulated radioactive waste borosilicate glasses

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ABSTRACT

The capacity of simulated high-level radioactive waste borosilicate glasses to incorporate sulfate has been studied as a function of glass composition. Combined Raman, ^{57}Fe Mössbauer and literature evidence supports the attribution of coordination numbers and oxidation states of constituent cations for the purposes of modelling, and results confirm the validity of correlating sulfate incorporation in multi-component borosilicate radioactive waste glasses with different models. A strong compositional dependency is observed and this can be described by an inverse linear relationship between incorporated sulfate (mol% SO_4^{2-}) and total cation field strength index of the glass, $\Sigma(z/a^2)$, with a high goodness-of-fit ($R^2 \approx 0.950$). Similar relationships are also obtained if theoretical optical basicity, Λ_{th} ($R^2 \approx 0.930$) or non-bridging oxygen per tetrahedron ratio, NBO/T ($R^2 \approx 0.919$), are used. Results support the application of these models, and in particular $\Sigma(z/a^2)$, as predictive tools to aid the development of new glass compositions with enhanced sulfate capacities.

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1. Introduction

Sulfur can be a problematic component of certain civil and defence radioactive wastes that are destined to be converted into wasteforms by vitrification. Such sulfur-bearing wastes include, but are not limited to, waste liquors arising from the PUREX process [1,2] and spent ion exchange resins [3]. The presence of sulfur can pose problems for safe, cost-effective waste vitrification due to its low (<ca.1 wt% SO_3) capacity in the alkali borosilicate glasses that are used globally as radioactive waste host matrices [3–10]. Sulfate capacity is defined for the purposes of this study as the non-equilibrium sulfate solubility, i.e. the sulfate solubility as determined under a set of consistent non-equilibrium conditions, as arise in most laboratory-scale and industrial-scale glass melting operations. If the sulfate capacity limit of an oxide glass is exceeded during melting, a molten salt or "gall" layer forms on the melt surface. This is highly undesirable for several reasons. Radionuclides such as ^{135,137}Cs, ^{99}Tc and ^{90}Sr migrate into this water-soluble

sulfate layer during melting [4,6,9,10] and the salt layer can thereby provide a pathway for these radionuclides to readily be released into the environment following contact with water in a geological waste repository. In addition, molten salts can affect processing of the waste: they exhibit low viscosities and their high corrosivities toward melt vessels shorten melter service lifetimes [4,6,9,10]. Consequently, research has focussed on optimising sulfate incorporation levels and establishing melter operating parameters that maintain sulfate levels below their capacity limit in the glass melt [6,9–15]. This, in turn, can restrict the types and concentrations of waste that can be vitrified, ultimately increasing the costs and timescales associated with waste vitrification, interim storage and final geological disposal.

Development of new or modified glass compositions with enhanced sulfate capacities remains a global research priority. Indian scientists have developed SiO_2-B_2O_3-Na_2O-BaO and SiO_2-B_2O_3-Na_2O-PbO glasses for high-level radioactive waste vitrification [1,16,17], some of which can incorporate up to 3 mol % SO_4^{2-} without formation of a salt layer during melting [16]. This level of sulfate incorporation is considerably higher than accepted sulfate capacities in traditional alkali borosilicate glasses, which are

usually less than 1 mol % SO_4^{2-} [6,9–15]. Although the Indian glasses have been the focus of considerable study (see, for example, [1,16,17]) the origins of their high sulfate capacity are not apparent. One plausible explanation may be that their low (1000 °C) melting temperatures play a role, since lower melting temperatures can enhance the sulfate capacity and solubility in some oxide melts [18–20]. However, other possible explanations also exist and further work is required to explain this behaviour. The Indian results for BaO-containing glasses are commensurate with Ooura and Hanada [21], who demonstrated high (1–3 mol % SO_3) sulfate capacities in BaO-containing SiO_2-Na_2O-BaO glasses and linked the alkaline earth contribution with the thermal decomposition equilibrium constant of its sulfate. Other silicate glasses rich in BaO and exhibiting high sulfur capacities have been developed for vitrification of sulfur-rich spent ion exchange resins [3,7,8]. Generally, literature supports the addition of large, basic, low field strength cations as a means of enhancing sulfate capacities in silicate and borosilicate glasses [3,4,6–8,10,16,17,21]. For other oxide glass systems, P_2O_5-Al_2O_3-Na_2O-Fe_2O_3 glasses exhibiting high sulfate capacities have been used as vitrification matrices at the Russian Mayak facility [2]. Some phosphate glasses can accommodate sulfate contents of the order of several percent [2,4]. However, borosilicate glasses are the global material of choice for the majority of radioactive waste vitrification activities and thus we have focussed here on borosilicate glasses.

Glass composition plays a key role in determining sulfate capacity and solubility [2–21] and the relative concentrations of O^0, O^- and O^{2-} (bridging oxygen, non-bridging oxygen and free oxygen, respectively) are major factors in this [4,6,10,18–21]. A number of research papers and reviews have been published concerning prediction or modelling of the capacity and solubility of sulfate and other anionic species in oxide glasses (see, for example [4,6,10,19,20], and references therein). Any mechanistic-based model, in order to be useful, must include a meaningful representation of glass composition and/or structure; and must be able to accommodate a broad range of chemical elements which may be present in the glass in sufficient concentration to have an impact on sulfur behaviour. A range of numerical scales have been developed which can, to varying degrees, fulfil these requirements. These range from simple scales, for example molar concentration of glass forming oxides ($[SiO_2]$, $[P_2O_5]$, $[B_2O_3]$, $[SiO_2 + B_2O_3]$ etc.), to more structurally representative scales such as the ratio of oxygen to glass former ($[O]/[Si]$, $[O]/[P]$ etc.), the ratio of non-bridging oxygen to tetrahedral cations (NBO/T), or the ratio of non-bridging oxygen to bridging oxygen (NBO/BO). However, these scales lack the subtlety to consider, for example, the different effects of chemically similar components, for example, Li_2O and Na_2O or MgO and CaO, or differences in their effects on glass structure (e.g., ionic radii), although in the case of NBO/T this can be accommodated in terms of relative NBO and T contributions. To achieve higher levels of discrimination more detailed scales, with terms for each glass component, are worthy of investigation. This latter category includes the cation field strength and optical basicity scales, which are among the most well-known and widely-utilised of such scales within glass science. Previously, models using these scales were applied to sulfate capacity data for a range of phosphate glasses and a small number of borosilicate glasses [4]. It was observed that cation field strength index, $\Sigma(z/a^2)$ provided the most accurate relationship with sulfate capacity across a wide range of surveyed glass compositions. The aim of the work presented here was to apply and compare the cation field strength index and theoretical optical basicity scales to the study of sulfate capacities in a series of simulated multi-component borosilicate glasses representative of U.S. high-level radioactive

waste glasses from the Savannah River Site, but more widely applicable worldwide. It is important to note that the aim of this work was to investigate the inherent capacity of the glasses studied to incorporate sulfate as dissolved species within their atomic structure under imposed near-sulfate-saturation conditions. It is acknowledged that during real-world waste vitrification, conditions are likely to differ from those studied in the laboratory. For example there may be differences in melting temperature, redox conditions, batch or glass compositions that include the presence of other salts (e.g., halides or nitrates), or organics. Any of these factors can influence sulfate capacity and solubility in glass - but the inherent capacity of any glass to incorporate sulfate under a given set of conditions is a function of glass composition and structure, and that is the focus of the work presented here. The goal was to gain improved understanding of the mechanisms controlling sulfate solubility in glasses, and in particular to build a tool that can assist glass scientists and technologists in predicting the inherent capability of radioactive waste borosilicate glasses to incorporate sulfate.

2. Materials and methods

A total of eleven experimental glasses were prepared in two inter-related series, Series A and B, which are broadly representative of U.S. high-level radioactive waste glasses (see, for example, [9,11–15]). Analysed compositions of all glasses are shown in Table 1. Sulfate was added to the batch as Na_2SO_4 at levels providing what was expected to be a modest excess of Na_2SO_4: 2 wt% SO_4^{2-} equivalent was present in each nominal glass composition. All glasses were expected to exhibit sulfate capacities and solubilities below 2 wt% SO_4^{2-} and thus form a sulfate "gall" layer on the surface of the glass melt, enabling sulfate saturation of the molten glass to be achieved, or at the very least, approached. Batches to make 150 g of glass were prepared using appropriate levels of dried sand (purity > 99.9%) and analytical grade raw materials (Li_2CO_3, Na_2CO_3, Na_2SO_4, Fe_2O_3, $Al(OH)_3$, H_3BO_3, $CaCO_3$ and ZrO_2) which were weighed into sample bags using a calibrated balance, then mixed thoroughly to ensure good batch homogeneity. Batches were transferred into a ZrO_2 grain stabilised (ZGS) Pt crucible with a loose-fitting ZGS Pt lid and then placed in an electric furnace at 1150 °C and melted for 1 h. This methodology was selected to enable direct comparison with data previously obtained for simulated U.S. waste glasses [12,13] that were prepared under the same conditions. After 1 h of melting the crucible was removed from the furnace and the molten glass was poured into a steel mould and allowed to cool without annealing. In most cases a sulfate "gall" layer was observed, which indicates that the sulfate capacity-limit of the glass melt was exceeded. These samples were washed for 5 min under running hot water (ca. 50–60 °C) to dissolve and remove excess sulfate salts. Samples were then carefully dried. Glasses were ground to a fine powder and washed in dilute nitric acid to remove any remaining sulfate phases. X-ray diffractometry was performed on all samples using a PANalytical Empyrean X-ray diffractometer and results confirmed that all samples were X-ray amorphous. Samples B1 and B2 were found to contain very minor amounts of crystalline SiO_2, it is believed that this was due to a few grains of undissolved raw material sand which were observed at the glass/air/crucible boundary in these two glass samples, and the errors that this minor amount of undissolved SiO_2 introduced into sulfate capacity modelling have been incorporated in the estimated uncertainties. Two preparation techniques, sodium peroxide fusion and lithium metaborate/tetraborate fusion, were used to prepare the glass samples, in duplicate, for compositional analysis. Solutions ob-