Environmental Management Science Program

Project ID Number 60313

Radiation Effects on Transport and Bubble Formation in Silicate Glasses

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June 1, 1998

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Research Objective

To study the fundamental chemistry of radiation damage in silicate/borosilicate glasses and simulated high-level nuclear waste (HLW) forms. Special emphasis is on delineating molecular processes crucial for understanding the aggregation of defects and formation of oxygen bubbles. The knowledge obtained will provide the needed scientific basis for extrapolating long-term behavior of stored radiative waste glass forms.

Research Progress and Implications

This report summarizes the first 6 months of a 3-year project. The following issues have been addressed: (i) the production of radiolytic oxygen, (ii) the chemistry of hydrogenous species, and (iii) the effect of glass composition and microstructure on the formation and accumulation of metastable point defects.

1. Radiolytic oxygen. While the earlier studies indicated that during electron bombardment of silicate glasses the yield of interstitial O_2 was ca. $(1-5) \times 10^{-6}$ eV⁻¹, recent transmission electron microscopy (TEM) studies suggested that upon (c)-radiolysis this yield is 10²-10³ times higher. The latter estimate places the onset of the O_2 bubble formation in the HLW forms from 10¹² rad (1-10 kyr of storage) to 10⁸-10⁹ rad (several years of storage). Questions have been raised about the validity of these TEM measurements (The dose accumulated during the TEM inspection could be considerably higher than the initial (c)-radiation dose.) Our effort is concentrated on measuring the yields of radiolytic gases using less invasive techniques:

Glasses of various compositions were irradiated with 3 MeV electrons to 10⁹-10¹⁰ rad. Two approaches have been used to measure the gas evolution, (i) thermally outgassing the glass samples followed by mass spectrometric analysis of the evolved gases, and (ii) detecting the interstitial O_2 in-situ using laser-induced emission of 1O_2 in the near IR. While the latter approach is still under development, the outgassing experiments have shown that the yield of radiolytic O_2 is actually lower than the lowest earlier estimates. (Since the 0.1-10 keV electrons used in the earlier studies had short penetration depth, some oxygen was produced due to destruction of the charged surface.) In the dose regime studied, the yield of radiolytic O_2 is comparable to the yield of radiolytically desorbed N_2 and by 10-100 times less than the yield of radiolytically generated/desorbed CO_2 .

Particularly low yields of O_2 were observed in the simulated HLW forms, apparently due to uptake of O_2 by metal cations. The implication of our study is that the concentration of O_2 at which the bubbles are formed will accumulate only after 1-10 kyr of the storage. The bubble formation can be further delayed by partial reduction of metal oxides during the glass manufacturing.

2. Hydrogenous species. Mobile, short-lived hydrogen atoms generated by radiolysis of the OH groups anneal the point defects and ameliorate the radiation damage. We undertook a detailed study of the H and D atoms in boron oxide glasses; this study complements our previous work on the H/D atoms in fused silica. Diffusion coefficients of the H/D atoms and the rates of their collisions with transitional metal cations and other defects were measured, and the mechanism of the H atom generation was determined. In particular, it has been shown that in the boron oxide glass (in contrast to silica) the H atoms decay in spur reactions with

other H atoms and/or metastable point defects. The former reaction yields H₂ which coalesces into bubbles at 108-109 rad (compare to 1012-1013 rad for O₂) causing swelling of the glass. Our study resolves several issues concerning the fate of hydrogen in oxide glasses, it also provides a reference system to study radiation-induced volatilization in glasses, in the dose ranges that are readily available to most researchers.

3. Defects in complex glasses. Commercial glasses that exhibit highest leach resistance is microheterogeneous alkali aluminoborosilicate glasses. In such glasses, 1-to-10 nm islets of the boron-rich phase are imbedded in a silica-rich matrix. Since many silicate and borosilicate glasses (including some HLW forms) are phase-separated, the question arises how the radiation damage is distributed between the phases. Using advanced methods of pulsed EPR, we have demonstrated that the radiation damage in borosilicate glasses is concentrated in the boron-rich islets, regardless of their mass fraction. Our work suggests that by using microscopically phase-separated glasses one can achieve the least radiation damage to the bulk of the glass combined with the highest chemical resistance.

Planned Activities

1. We will continue to study the formation and decay of radiolytic O₂, with an emphasis on the role of redox reactions with metal ions and point defects. Our current priority is to improve the accuracy and reliability of the outgassing experiments and to develop optical spectroscopies that would complement these measurements.
2. We have demonstrated the potential of pulsed EPR to sort through many types of paramagnetic defects present in irradiated glasses. These studies will be extended to include alkali silicate, aluminosilicate, and borosilicate glasses doped with transition metal cations.