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Chemical Decomposition of High-Level Nuclear Waste Storage/Disposal Glasses Under Irradiation

Dr. David L. Griscom
Naval Research Laboratory
Code 5612
Washington, District of Columbia 20375
Phone: 202-404-7087
E-mail: griscom@nrl.navy.mil

Celia I. Merzbacher
Naval Research Laboratory
Code 5612
Washington, District of Columbia 20375
Phone: 202-404-7987
E-mail: merzbacher@nrl.navy.mil

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Research Objective

The objective of this project is to employ the technique of electron spin resonance (ESR), in conjunction with other experimental methods, to study radiation-induced decomposition of vitreous compositions proposed for immobilization/disposal of high-level nuclear wastes (HLW) or excess weapons plutonium. ESR is capable of identifying, even at the parts-per-million level, displaced atoms, ruptured bonds, and free radicals created by radiation in such glassy forms. For example, one of the scientific goals is to determine whether ESR-detectable superoxide (O_2^-) and ozonide (O_3^-) ions are precursors of radiation-induced oxygen gas bubbles reported by other investigators. The fundamental understandings obtained in this study will enable reliable predictions of the long-term effects of and decays of the immobilized radionuclides on HLW glasses.

Research Progress and Implications

This report represents the results of an 18-month effort performed under a 3-year research award. Four categories of materials were studied: (1) several actual and proposed HLW glass compositions fabricated at Savannah River Technology Center (SRTC), samples of which had been irradiated to a dose of 30 MGy (1 Gy = 100 rad) to simulate -decay effects, (2) several high-iron phosphate glasses fabricated at the University of Missouri-Rolla (UMR), (3) one other model HLW glass and several simulated natural glasses which had been implanted with 160-keV He^+ ions to simulate-decay damage, and (4) an actual geological glass damaged by decays of trace amounts of contained ^{238}U and ^{232}Th over a period of 65 Myears. Among the category-1 materials were two samples of Defense Waste Processing Facility (DWPF) borosilicate glasses modeling compositions currently being used to vitrify HLW at SRTC. The ESR spectra recorded for the unirradiated DWPF-glass simulants were attributable to Fe^{3+} ions. The 30-MGy irradiation was found to change the Fe^{3+} concentration of these glasses by a statistically insignificant factor (0.987±0.050) and not to create measurable numbers of other defects.

Another glass irradiated to a dose of 30 MGy, an iron phosphate composition containing Li_2O and CeO_2 (modeling PuO_2) as the other two constituents, displayed a much larger -radiation response than the DWPF glass. Specifically, ~$2x10^{18}$ radiolytic superoxide ions (O_2^-) ions per gram were identified and quantified in this glass by ESR. This last observation, coupled with the fact that the ESR properties of even the unirradiated glass closely replicated those of an *iron-free* amorphous peroxyborate composition containing ~1 O_2^- ion for each 9 borons [1], has led to the formulation of a radical new structural model for the air-melted high-iron phosphate glasses, wherein each phosphorus ion is envisioned to be intimately associated with one O_2^- ion [2]. Since high-iron phosphate glasses (composition range ~0.2<[Fe]/[P]<0.67) have displayed many properties favorable for vitrification of phosphate-rich high-level wastes such as are present in large amounts at the Hanford site [3], most of the project effort to date has been devoted to fundamental studies of the lithium-cerium-iron-phosphate and UMR iron-phosphate glasses. The results of ESR, Mössbauer, thermal analysis, and gas-evolution studies carried out in informal collaboration with the UMR and Toyo University (Japan) are reported in [2]. Whether or not the new model based on these data is ultimately confirmed, the ESR technique has proven to be a powerful probe of magnetic structure in the iron phosphate glasses and materials crystallized there from and is expected to lead to valuable new insights concerning the suitabilities of these materials for HLW vitrification.

Those ion-implanted samples which were iron-free displayed ESR spectra attributable to radiolytic O_2^- and/or to nonbridging oxygen ions which had trapped holes. Among these, a borosilicate HLW-glass simulant containing 18 wt% Na_2O additionally displayed a sharp resonance line seeming to exhibit a signature of colloidal sodium (a discontinuity in the ESR linewidth-versus-temperature data at the melting point of Na). However, an alternative possibility still under investigation, is that the sharp line may be due to organic char present as a contaminant on the sample surfaces. ESR signal-to-noise ratios in these experiments were marginal due to the fact that only a layer ~1 μm deep of the 1-mm-thick samples suffered radiation damage. Nevertheless, a high-iron aluminosilicate glass (16.5 wt% FeO, 0% Fe_2O_3) exhibited very strong *ferromagnetic* resonance (FMR) signals of multi-domain metallic iron particles (diameters >20 nm) [4] and single- and multi-domain magnetite (Fe_3O_4) particles induced by the implantations. This result strongly suggests that HLW glasses containing large amounts of Fe^{2+} will disproportionate under the influence of decays of the contained actinides, resulting in separation of the FeO component into metallic iron and Fe_3O_4.

The 65-million-year-old glass displayed a narrow ESR signal, possibly that of O_2^-, which is believed to have resulted from decays. It was not possible to discriminate radiolytic FMR signals, if any, from those of naturally occurring magnetite in this sample.

[1] J.O. Edwards, *et al*., J. Am. Chem. Soc. **91**, 1095 (1969).
[2] D.L. Griscom *et al*., Nucl. Inst. & Methods Phys. Res., (in press).
[3] D.E. Day *et al*., Final report to Pacific Northwest National Laboratory, Contract No. 276822-A-F1, Dec., 1995.
[4] D.L. Griscom *et al*., Earth & Planet. Sci. Lett. **24**, 78 (1974).

Planned Activities

Planned activities include ESR studies of model HLW glasses incorporating short-lived actinides fabricated over a decade ago. Samples of glasses prepared at SRTC and at Pacific Northwest National Laboratory containing ^{244}Cm (half-life 18.1 years) and ^{238}Pu (half life 87.7 years), respectively, have been promised. These will emulate the simultaneous effects of -particle and -recoil damage occurring over periods of 10^3 to 10^6 years in actual HLW glasses or 100 to 1,000 years in ^{239}Pu-containing glasses. Not only will this emulation be superior to simulation by He-ion implantation but it will also yield a 1000-fold improvement in ESR signal-to-noise ratios due to full volumetric irradiation of the samples. Searches for radiolytic alkali-metal colloids and O_2^- and O_3^- ions will be continued. Further studies of high-iron phosphate glasses will be carried out to refine models for their structure and to determine their radiation resistance, and DWPF-glass simulants irradiated to doses >>30 MGy will be investigated to obtain a statistically significant measure of the induced changes in iron valence states.

Other Access To Information

"Radiation effects in glasses used for immobilization of high-level waste and plutonium disposition," W.J. Weber, R.C. Ewing, C.A. Angell, G.W. Arnold, A.N. Cormack, J.M. Delaye, D.L. Griscom, L.W. Hobbs, A. Navrotsky, D.L. Price, A.M. Stoneham, and M.C. Weinberg, J. Mater. Res. 12, No. 8 (1997) 1946-1978.

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