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Project Title: **Chemical Decomposition of High-Level Nuclear Waste Storage/Disposal Glasses Under Irradiation**

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# CHEMICAL DECOMPOSITION OF HIGH-LEVEL NUCLEAR WASTE STORAGE/DISPOSAL GLASSES UNDER IRRADIATION

*U.S. Dept. of Energy Environmental Management Science Program*
*Project Summary/Progress Report*

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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 search for ESR-detectable superoxide ($O_2^-$) and ozonide ($O_3^-$) ions, which could be precursors of radiation-induced oxygen gas bubbles reported by other investigators via the disproportionation reaction, $2O_2^- \rightleftharpoons O_2^{2-} + O_2$. The fundamental understandings obtained in this study will enable reliable predictions of the long-term effects of $\alpha$ and $\beta$ decays of the immobilized radionuclides on the chemical integrity of HLW glasses.

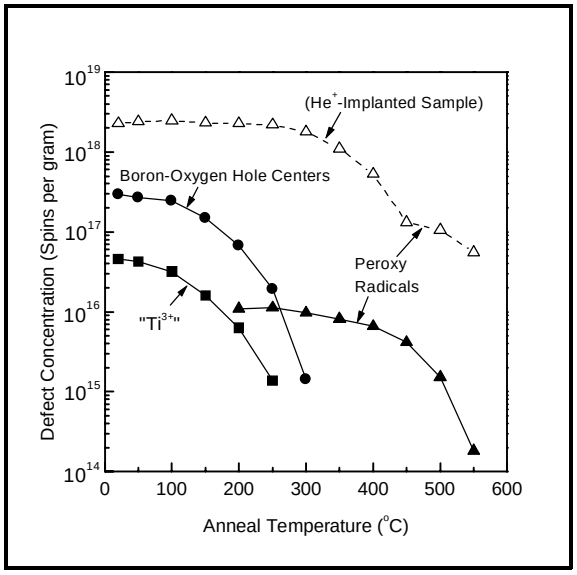
## RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes the results of a 30-month effort performed under a 3-year research award. Four categories of materials were studied: (A) several actual and proposed HLW glass compositions fabricated at Savannah River Technology Center (SRTC), (B) several high-iron phosphate glasses fabricated at the University of Missouri-Rolla (UMR), (C) an iron-free boro-aluminosilicate model HLW glass subjected to $\gamma$ rays (to simulate $\beta$-decay effects) and to implantation by 160-keV $He^+$ ions (to simulate $\alpha$-decay damage), and (D) well-dated geological glasses damaged by $\alpha$ decays of trace amounts of contained $^{238}U$ and $^{232}Th$ over a period of 65 million years. Among materials A 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 and/or precipitated ferrites. The sole effect of a 30-MGy $\gamma$ irradiation (1 Gy = 100 rad) was to change the $Fe^{3+}$ concentration of these glasses by a statistically insignificant factor (0.987±0.050). No induced defect centers were measurable by ESR, possibly due to a suppression effect of the $Fe^{3+}$ ions. (N.B. The presence or absence of radiolytic $O_2$ cannot be directly determined by ESR.)

Another category-A material, an iron phosphate glass containing $Li_2O$ and $CeO_2$, displayed a much larger $\gamma$-radiation ESR response than did the DWPF glass. Specifically, ~$2x10^{18}$ radiolytic superoxide ions ($O_2^-$) ions per gram were identified in this glass by ESR [1]. Since high-iron phosphate glasses in general (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 at the Hanford site [2], the first 15 months of the project were devoted to fundamental studies of (A) the SRTC lithium-cerium-iron-phosphate and (B) various 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 [1]. The ESR results have revealed the unirradiated glasses to possess unusual long-range magnetic structure, which is qualitatively different that of the crystallized materials. This finding, in conjunction with the other types of measurements mentioned, led to the tentative proposal that peroxide ions ($O_2^{2-}$) may have been incorporated

in the *as-prepared* glasses. Whether or not this model proves correct, the present work has inspired a planned polarized-neutron-diffraction study [3] to better elucidate the topology of the glass network.

More recently, samples (C) were examined in detail. ESR spectra were recorded before and after irradiation and after 10-minute postirradiation isochronal anneals. The most numerous paramagnetic states in the unannealed samples following γ irradiation were boron-oxygen trapped-hole centers and $Ti^{3+}$ trapped-electron centers and, following $He^+$ implantation, peroxy radicals (PORs: $O_2^-$ ions bonded into the glass network). Annealing the γ-irradiated samples above 300 °C caused recombination of the trapped electrons and holes, revealing an underlying POR spectrum which annealed in stages at ~400 and 550 °C, similar to the annealing of PORs in the $He^+$-implanted sample (see figure). Normalized to the amount of ionizing energy deposited, the initial POR concentration in the $He^+$-implanted sample was ~100 times that in the γ-irradiated sample. It is thus evident that the PORs induced by $He^+$ implantation result from displacements of oxygens in elastic collision cascades. The absence of trapped electrons and holes in the implanted samples is ascribed to annealing during irradiation associated with the fraction of the implantation energy deposited as heat. One of the fundamental defects to be expected in HLW glasses containing α-particle emitters is therefore the POR [4]. 65-million-year-old glasses displayed narrow ESR signals, possibly due to $O_2^-$ ions, which may have resulted from α decays of contained radionuclides. These geological glasses provided anecdotal evidence for an influence of $Fe^{3+}/Fe_{total}$ on the numbers of $O_2^-$ ions observed. It is argued in [4] that the presence of several wt % $Fe_2O_3$ may suppress the formation of $O_2^-$ ions without impeding production of neutral $O_2$ molecules. Since virtually all HLW streams contain iron oxides, this issue requires further clarification.





[1] D.L. Griscom *et al.*, Nucl. Inst. & Methods Phys. Res. B 141 (1998) 600-615.
[2] D.E. Day *et al.*, Final report to PNNL, Contract No. 276822-A-F1, Dec., 1995.
[3] A.C. Wright *et al.* (to employ neutron source at Institut Laue-Langevin, Grenoble).
[4] D.L. Griscom *et al.*, (submitted to J. Non-Cryst. Solids, Feb., 1999).


## PLANNED ACTIVITIES

Planned activities include ESR studies of seven different model HLW glasses, fabricated, γ-irradiated at four different temperatures, and provided by Pacific Northwest National Laboratory (PNNL). These samples include borosilicate glasses with differing iron contents and two iron phosphate glasses. PNNL will also supply three HLW glass simulants loaded with 1 wt% plutonium which were fabricated 15 years ago. The PNNL glasses containing $^{238}Pu$ (half life 87.7 years) will be shipped as soon as the appropriate site license is issued by the NRC to the Naval Research Laboratory. These samples will emulate the combined effects of α-particle and α-recoil damage occurring in actual HLW glasses over periods of $10^3$ to $10^6$ years or in $^{239}Pu$-containing glasses after 4,000 years. 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 $O_2^-$ and $O_3^-$ ions will be continued, particularly in relation to the possible influence of iron content. Due to the delayed arrival of these samples, a no-cost extension will be requested to complete this work.