Project ID Number: 54982
Project Title: Analysis of Surface Leaching Processes in Vitrified High-level Nuclear Wastes Using In-situ Raman Imaging and Atomistic Modelling

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Students: 3 graduate (PhD) students, and 5 undergraduate students.

DOE Problems Addressed: The vitrification and disposal of radioactive, high-level nuclear wastes requires modeling and monitoring leaching behavior of the complex glasses that are formed. Previous to this research, leaching behavior of materials was quantitatively studied by leachate chemical analysis and by high vacuum surface analysis of the exposed samples. These techniques do not lend themselves to in-situ measurements or to highly radioactive materials.

Research Objective: The work was directed toward the investigation of quantitative remote analysis of the leaching process in glasses, using non-destructive optical methods for evaluating changes taking place on the sample surface.

Research Progress and Implications: After three years of research on this grant, we have examined the feasibility of various surface optical techniques for composition analysis, including Raman and reflection IR spectroscopies. Our results have demonstrated that reflection FTIR analysis can be used for determining the surface composition changes of a glass undergoing corrosion. The results show that glass surface composition during leaching can be measured *quantitatively*. The method uses ergodic analysis of dielectric constants corresponding to identified phonon resonances on the glass surface to determine changes in the glass surface composition with leaching. The process is currently applicable to silicate glasses.

The new methodology developed changes accepted wisdom and has revealed serious inaccuracies in canned software programs available with current instrumentations and previuosly published analyses of IR leaching studies. Since the method is adaptable to fiber optics transmission of the optical signals, it is useable in the storage vaults for continued monitoring of the waste glasses, and it can be used with radioactive materials with little personnel and equipment exposure. Remote sensing of the glass surface composition during storage or in a hot cell provides an invaluable tool for the examination of leaching processes in radioactive materials, and for in-situ tests in the nuclear waste repositories without human intervention.

Development of this program has required the derivation of the Kramers-Kronig transform to a Gaussian function. The analytical and derived equations have been converted into a simple software program which will be made available for analysis of reflection FTIR data.

Ongoing research includes the development of a user-friendly interface for the fitting program, the development of standard characteristics (peak position and peak width) for the IR bands of known molecular complexes and application of the analysis method to complex glasses of the type considered for waste vitrification. The method can be used in-situ and can be adapted to various flow tests proposed for support of the development of ground transport models.

Additional efforts that will not be covered by the grant period:

(1) Development of methodology for using IR transmitting optical fibers for remote applications,
(2) Application of this approach to leaching studies on phase separated and crystallized glasses,
(3) Application of leaching studies to radioactive samples,
(4) Studies of the development of UV Raman facilities for conducting tests of submerged samples.
(5) Interaction with Tank Focus Team members to transfer the technology and developed programs to actual vitrified waste studies.

Publications:

Steven A. MacDonald, Craig R. Schardt, David J. Masiello, and Joseph H. Simmons, “Dispersion Analysis of FTIR Reflection Measurements in Silicate Glasses,” Journal of Non-Crystalline Solids, accepted for publication.

D. J. Masiello, S. A. MacDonald, C. R. Schardt, J. H. Simmons and S. A. McCullough, “Dispersion Functions for Optical Spectroscopy,” Amer. J. Physics, submitted.

Awards:

David Masiello, Undergraduate Scholar’s Best Paper Award, University of Florida, 1999.