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## **Analysis of Surface Leaching Processes in Vitrified High-Level Nuclear Wastes Using In-Situ Raman Imaging and Atomistic Modeling**

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## Analysis of Surface Leaching Processes in Vitrified High-Level Nuclear Wastes Using In-Situ Raman Imaging and Atomistic Modeling

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### Research Objective

The research objective was to test and develop optical methods for real-time, remote and in-situ testing of corrosion processes on the surface of vitrified nuclear wastes.

### Research Progress and Implications

This report summarizes the research conducted in the first 1.5 years of a 3 year grant. At this point, we have identified the conditions for optimal tests and demonstrated that both IR reflection and Raman spectroscopies can be used to determine the dealcalization process in the surface of simple glasses in real time.

### Research Progress

Simple, model silicate glasses containing one and two alkali (Li and Na) oxides were melted and cut into small blocks and the surfaces polished. The blocks were then subjected to static leach tests in deionized water with a surface to volume ratio of  $0.1 \text{ cm}^{-1}$ . Bath temperatures were varied between 20 and  $100^\circ\text{C}$ . Drip tests were also conducted in which de-ionized water flowed at a rate of 0.01 ml/min over the surface ( $3 \text{ cm}^2$ ) of one side of the samples. The samples consisted of glasses with low chemical durability, selected to enhance the surface dealcalization process and allow it to develop in a short time period. They were 20% $\text{Na}_2\text{O}$ -80% $\text{SiO}_2$ , 20% $\text{Li}_2\text{O}$ -80% $\text{SiO}_2$ , 7% $\text{Na}_2\text{O}$ -7% $\text{Li}_2\text{O}$ -86% $\text{SiO}_2$ , and several simulated SRL waste glasses.

Both static leach test and drip test samples were examined after various lengths of exposure by two methods: reflection FTIR spectroscopy and reflection Raman spectroscopy. In the FTIR tests, samples were removed from the bath, were dried and measured. In the Raman tests, samples were measured in-situ without removal from the bath. Both tests showed the expected peaks (corresponding to IR absorption in the FTIR tests, and shifted emission in the Raman tests) typically observed in these materials in the ranges of  $400\text{-}600 \text{ cm}^{-1}$ ,  $800 \text{ cm}^{-1}$  and  $1000\text{-}1200 \text{ cm}^{-1}$ . It was interesting to note that the indicative changes in peak intensities with an alteration of the surface composition consisting of loss of alkali were most obvious in the  $400\text{-}600 \text{ cm}^{-1}$  range for the Raman tests and in the range  $1000\text{-}1200 \text{ cm}^{-1}$  in the FTIR tests.

The FTIR tests consist of measurements of the reflection coefficient of the corroded surface. In these tests, we examined the peaks resulting from absorption processes between 600 and  $1200 \text{ cm}^{-1}$ . These correspond to the bending or asymmetric stretch vibrations of the O-Si-O and the R-O-Si structures in the glass. These peaks have been observed to change with exposure to water in previous studies, however no quantitative analyses were conducted. In past studies, the peaks were observed to shift and change in intensity with leaching, thus defeating any attempt at quantifying the degree of leaching or dealcalization. In the present study, we modeled the FTIR reflection spectra using 5 Gaussian absorption peaks. These peaks were added to form an extinction coefficient and the corresponding wavelength-dependent refractive index was calculated using Kramers-Kronig calculations. The modeled reflection spectra were then fitted to the measured spectra by allowing peak position, peak intensity and peak width to vary. Our results showed an excellent fit of the data with our modelled absorption peaks. It is important to note that using this more appropriate analysis,

the peak positions and peak widths varied very little as a result of leaching of the glass surface. Only the peak integrated areas showed considerable changes with degree of de-alkalization.

Analysis of the  $\text{Na}_2\text{O-SiO}_2$  glass showed a marked decrease in intensity of the Na-O-Si vibration at  $990\text{ cm}^{-1}$  with dealkalization of the surface, and a marked increase in intensity of the O-Si-O vibration at  $1110\text{ cm}^{-1}$ . The time dependence of these intensity changes is currently under analysis to determine if it can be directly correlated (quantitatively) to the amount of surface dealkalization. Studies on the other glasses are slower due to their better chemical durability, but the results are essentially identical. In the  $\text{Li}_2\text{O-SiO}_2$  glass, the same behavior is observed for the O-Si-O peak, while the Li-O-Si peak is observed at  $910\text{ cm}^{-1}$ . In the  $\text{Li}_2\text{O-Na}_2\text{O-SiO}_2$  glass, the alkali peak occurs at  $950\text{ cm}^{-1}$  and corresponds to a mixed alkali vibration.

Raman measurements were conducted on similar samples, except that the tests were all conducted in-situ, without removal of the samples from the leaching bath. At this time, we can only give preliminary results because of an unexpected problem that arose from the setup in the Raman tests which prevents isolating the Raman signal scattered from the sample surface. Consequently, signals scattered from the bulk of the sample were also present and often masked the surface signal. When the surface signal dominates, we have been able to observe variations in intensity in two peaks ( $470$  and  $580\text{ cm}^{-1}$ ) in the  $\text{Li}_2\text{O-SiO}_2$  glass. The variations are less well-defined than the FTIR peaks, but they clearly indicate de-alkalization.

## Implications

Two complementary techniques were used to follow surface dealkalization changes in model silicate and borosilicate glasses: FTIR and Raman spectroscopies. FTIR examines the infrared absorption behavior of the material. Because glass samples strongly absorb IR signals, this is a surface sensitive method, generally limited to a depth of less than a few hundred nanometers. By development of a novel method for analysis of the FTIR data, we have demonstrated that the FTIR method has a potential for a quantitative measure of the glass surface condition, especially de-alkalization and have identified the peaks of principal importance. Further tests will examine the formation of precipitates on the surface. The FTIR method however is limited to observation of relatively dry surfaces since the IR signal is also strongly absorbed by water. Consequently, it cannot be used on submerged samples.

In contrast, the Raman method uses visible light and therefore can be used on submerged samples. In our tests on simple glasses, we have discovered that the geometry of the test is critical because the visible light also penetrates the transparent glass samples and it is difficult to extract surface data from the measurement. However, this problem disappears in simulated, waste-containing samples since they are not transparent. In that case, the tested region of the sample becomes limited to the surface. Preliminary tests show that the Raman approach has great promise for the examination of non-transparent samples whether submerged or not.

## Planned Activities

Planned activities include:

- (1) tests to determine the accuracy of the measurement of surface de-alkalization by FTIR,
- (2) a continuation of FTIR studies in more complex glasses,
- (3) Raman studies in iron-containing glasses to isolate the active region to the sample surface,
- (4) an analysis of the quantitative value of Raman tests,
- (5) extension of studies to the formation of surface precipitates, and
- (6) coordinated Raman and FTIR tests on simulated waste glasses to determine important peaks that relate to the surface chemistry of the materials.

The FTIR tests on model glasses will be completed and analyzed by the end of the second year. The Raman tests on model glasses will be conducted into the first quarter of the third year. The third year will be spent in testing simulated-waste-containing glasses.