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LETTER REPORT

TITLE: Review of: "The Behavior of Actinide Containing Glasses during Gamma Irradiation in a Saturated Tuff Environment," in Scientific Basis for Nuclear Waste Management VIII, Mat. Res. Soc. Symp. Vol. 44, 257-264, 1985, by J.K. Bates and W. M. Oversby.

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PROJECT TITLE: Technical Assistance in Geochemistry

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The subject report documents the effect of gamma irradiation on the dissolution and release of U, Pu, Am, Cs, Np, and Tc, as well as the stable elements Li, Na, B and Mo, from SRL 165 and PNL 76-68 glasses in contact with J-13 water at a temperature of 90°C. The test matrix included the following three conditions for each of the four glass types studied:

1. Two glass discs in J-13 water, SA/V = 0.3 cm^{-1}.
2. Two glass discs in J-13 water, SA/V = 0.3 cm^{-1}, in contact with 0.2 gm of crushed tuff.
3. Crushed glass in J-13 water, SA/V = 1.0 cm^{-1}.

In each case the J-13 water had been previously equilibrated with the tuff at 90°C for a period of two weeks. The purpose of the experiment was to gather information on the possible, but deemed improbable, case where a premature canister failure occurs which allows water, in the presence of air, to reach the canister at elevated temperatures and a high ($2 \pm 0.2 \times 10^5$ rads/hr) gamma dose rate. The experimental vessel was made of 304 L stainless steel and contained ~16 ml of water and ~4 ml of air, in addition to the glass, and in some cases tuff. The four glass compositions studied were:

1. SRL 165 black frit with added 1% U, 0.1% Cs and 0.1% Sr.
2. SRL 165 with added ^{237}Np, ^{239}Pu and ^{241}Am.
3. PNL 76-68 glass ATM-1c containing 3.5% U (PNL-U).
4. PNL 76-68 glass ATM-8 which contains added ^{237}Np, ^{239}Pu, ^{99}Tc and some ^{241}Am (PNL-A).

A total of 112 tests of duration 7, 14, 28 and 56 days were completed.

A critical component in these experiments is the presence of air. Interaction of gamma radiation with nitrogen in the air produces nitric acid, leading to a decrease in the pH of the solutions and an increase in the dissolution of the glass. Sufficient air was included in the

experiments so that the amount of nitric acid produced was not limited by the amount of nitrogen available from the air.

Net dissolution of the glass was monitored by the change in pH and by the normalized mass loss of the solids. Results for the two SRL glasses are identical, within the errors, and are different from the two PNL glasses which are each compositionally distinct and give different results. For the SRL glasses the pH continues to drop over the course of the experiment and the tuff buffers the pH to a higher level. For PNL-A the pH shows a net increase, again with tuff buffering it to a higher level while PNL-U, although displaying an initial increase in pH shows a very small net change after 56 days, with the experiments containing tuff having a lower pH, unlike the other two glasses. The order of mass loss is PNL-U greater than PNL-A greater than SRL.

The rates of release of U, Pu and Am from SRL have begun to slow by 56 days although the total amounts in solution are still increasing. The total amount of Np, U, Pu and Am released from PNL-A is lower at 56 days than at 28, while the amount of Cs has only slightly increased. Results for PNL-U are not shown.

The results agree favorably with those of Bazan and Rego, and Bibler et al. for similar experiments. The variation in dissolution rates for unirradiated samples in the two earlier studies is too great to say with certainty that the irradiation has actually increased the dissolution of the glass. However, it can be said with certainty that the irradiation certainly provides a mechanism (production of nitric acid) that would be expected to increase the dissolution. The authors are correct in stating that no "generic" conclusions can be made from this study and that the effects of radiation will be specific to the dose rate, and the amount of air available, among other factors. This is a well conceived set of experiments that will be more fully described in a longer document stated to be in preparation. Although the experimental conditions are thought to be unlikely in a repository they are possible, and this study does a good job of expanding the data base on the effects of radiation and other geochemical factors such as the presence and abundance of air. Air is often considered important only for its oxygen content and not considered for its other constituents, such as nitrogen, which is often considered to be inert, but which is demonstrated to be potentially important in this case.