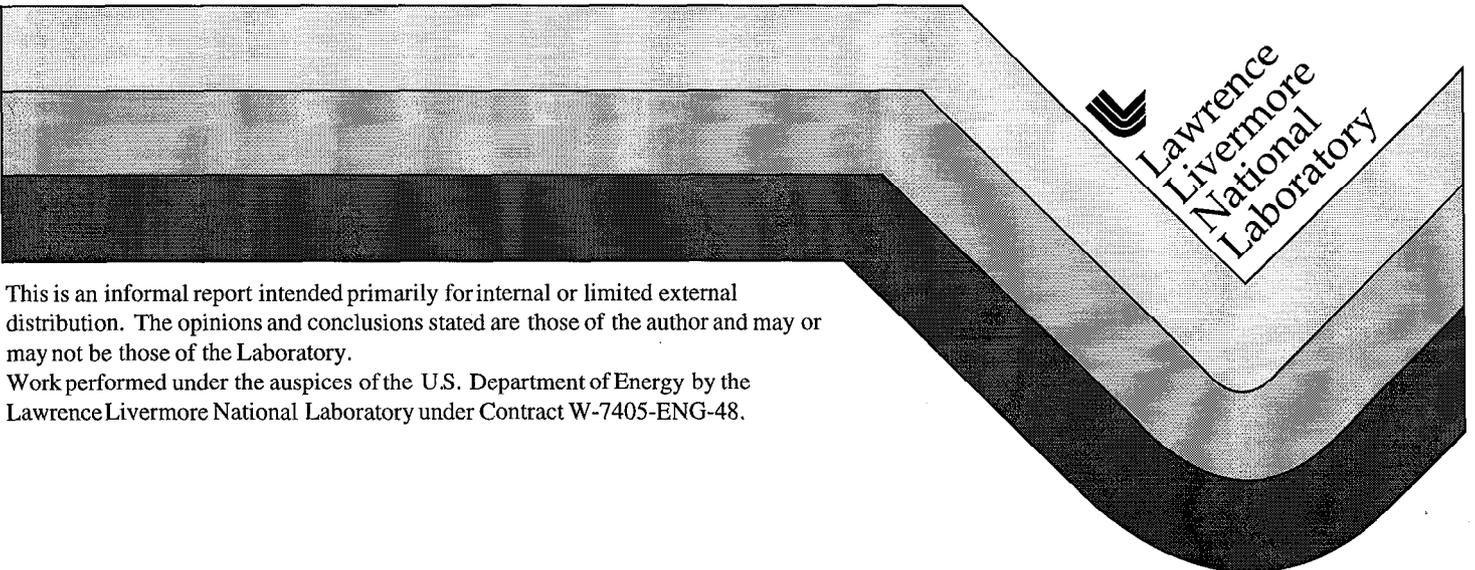


Interim Report on Interaction of Waste Glass Colloids with Corrosion Products

David A. Wruck

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Interim Report on Interaction of Waste Glass Colloids with Corrosion Products

David A. Wruck
Analytical and Nuclear Chemistry Division
Lawrence Livermore National Laboratory
Livermore, CA 94550

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Thermodynamic data for aqueous reactions of key radionuclides are needed for geochemical modeling studies of the Yucca Mountain Project. This report summarizes progress through February 1999 in a study of waste glass colloid interaction with corrosion product solids. Experimental work was recorded in LLNL YMP scientific notebook #00213.

Waste glass colloids are formed during simulated weathering (aqueous leaching and drip tests) of nuclear waste glasses (Bates et al. 1992, Ebert and Bates 1993, Menard et al. 1998). A large fraction of the Pu and Am released from the glasses is associated with the colloids. Previous work has indicated the waste glass colloids are formed as secondary silicate phases, such as smectite clays, at the glass surface. There is also evidence that the Pu and Am are associated with phosphate inclusions within the silicate matrix. This is significant for colloidal transport of the radionuclides, because included material is likely to remain associated with the colloid as it moves (nonexchangeable Pu and Am). In contrast, Pu and Am cations adsorbed on the clay surface or interlayers are expected to be exchangeable with the surrounding medium.

The purpose of the present task is to investigate more directly the exchange behavior of the Pu associated with the waste glass colloids. The goal is to obtain results that will be used to improve models of colloidal transport of Pu from the repository. Fe_2O_3 was selected as a model compound because it is likely to be present as a corrosion product in the repository and hydrous ferric oxides show relatively strong and nonselective sorption of cations in the +3 and +4 oxidation states. Resulting thermodynamic data will include distribution coefficients of Pu among colloidal, aqueous and Fe_2O_3 solid phases for conditions representative of the repository near-field. The major experimental subtasks are (1) synthesis of waste glass colloidal suspensions and (2) batch experiments in which the suspensions are equilibrated with Fe_2O_3 solids of defined particle size.

A 4.8 g sample of SRL 131A simulated nuclear waste glass was obtained from Argonne National Laboratory (ANL). SRL 131A is a borosilicate glass doped with the radionuclides Tc-99, U-natural, Np-237, Pu-239 and Am-241. Table 1 lists the specific activities calculated from reported radionuclide concentrations in the glass (Ebert and Bates 1993, Wolf and Bates 1996). The sample was in the form of 32 disks, each 0.9 mm thick by 10 mm in diameter, which were previously used in 14-, 28- and 56-day leach tests at glass surface to solution volume ratio (S/V) of 340 m^{-1} (Ebert and Bates 1993).

Table 1: Specific activity of radionuclides in SRL 131A.

Nuclide	Microcuries per g
Tc-99	3.9
U-natural	0.016
Np-237	0.068
Pu-239	5.5
Am-241	11

A 19 mg portion of the glass was dissolved to prepare samples for liquid scintillation counting, alpha spectrometry and gamma spectrometry. The results of the analyses were generally consistent with Table 1. The Am-241 alpha activity was 11.4 ± 0.2 microcuries per g. The Pu-239+240 alpha activity was 7.09 ± 0.14 microcuries per g, which is consistent with the reported Pu concentrations if about 10% Pu-240 is present. The ratio of Pu-240 to Pu-239 can be determined by gamma spectrometry after Pu separation from a larger sample of the glass. It is not necessary to know the exact isotopic composition, however, because activities will be ratioed in the sorption experiments.

The recommended colloid synthesis procedure, based on discussions with Carol Mertz of ANL, is the 70-day static leach test at 90°C and $S/V 2000 \text{ m}^{-1}$ (Ebert and Bates 1993). To obtain $S/V 2000 \text{ m}^{-1}$ the glass disks will be broken and ground to powder, the powder sieved and the 100 to 200 mesh fraction retained, and leaching performed with 10 mL solution per g of powdered glass. At ANL the leachant solution was prepared by prereaction of J-13 groundwater with pulverized tuff at 90°C . In this work a solution of similar composition was prepared from reagent grade chemicals (Table 2). The glass and leachant solution will be reacted at 90°C in closed vessels (Parr bombs).

Table 2: Composition of leachant solution (mM).

Na	4.0
Si	1.0
Ca	0.1
HCO_3^-	2.0
NO_3^-	0.5
Cl^-	0.5
SO_4^{2-}	0.4
F^-	0.2

After preparation, the colloidal suspensions will be separated from the glass and analyzed for particle size distribution and radionuclides. The bulk of the activity will remain in the glass.

Expected actinide concentrations in the suspensions are: U-natural, 5 dpm/mL; Np-237, 50 dpm/mL; Pu-239, 300 dpm/mL; Am-241, 700 dpm/mL. Thus, the experiments will require low-level counting of samples with multiple radionuclides.

An analytical method with good sensitivity and selectivity is alpha spectrometry of electrodeposited sources (Kressin 1977). An electrodeposition cell was constructed. A Pu-242 tracer solution was prepared, and Pu recovery was investigated as a function of Fe concentration in the buffer electrolyte solution. The main drawback of the method is the lengthy sample preparation (several hours per sample).

An alternative analytical approach is liquid scintillation counting combined with gamma spectrometry. The total alpha activity is determined by liquid scintillation, and the Am-241 and Np-237 activities are determined by gamma spectrometry. The remaining alpha activity is assigned to Pu-239. Sample preparation is relatively simple, but long gamma count times are required. There is an uncertainty in the total alpha activity due to background from natural U and the Tc-99 and Pa-233 beta emissions, so the method is unreliable when Pu accounts for a small fraction of the alpha activity.

In the batch sorption experiments the colloidal suspensions will be equilibrated with Fe₂O₃ powders which have been sieved to obtain a well-defined particle size. The pH will be adjusted to values in the range 7 to 11, and the distribution of Pu among the bulk solid, colloidal and dissolved components will be determined using the methods discussed above. If Pu uptake by the bulk solid phase is significant, it will be compared to Pu uptake from aqueous solution under similar conditions. This is to see if the distribution can be understood as simultaneous equilibrium reactions between the solution and the colloidal solid and the solution and the bulk solid, or if direct sorption of colloids onto the bulk solid is significant.

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