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# Colloids from the aqueous corrosion of aluminium-based nuclear fuel

M.D. Kaminski *, M.M. Goldberg, C.J. Mertz

*Argonne National Laboratory, Chemical Engineering Division, 9700 South Cass Avenue, Argonne, IL 60439, USA*

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## Abstract

Nuclear wastes to be buried in the proposed repository underneath Yucca Mountain, Nevada, may produce colloids and contribute to the release of radioactivity from the repository. As a component of non-commercial nuclear fuels slated for disposal, aluminium-based fuels may release the colloids during aqueous corrosion. This paper reports on the characterization of such colloids, which are predominantly clays >100 nm. Colloid concentrations never exceeded $8 \times 10^{11}$ particles/L, which is well within the range of values used in the repository release models. These colloids carry 99% of the released uranium and highlight the potential importance of the colloid phase in determining radionuclide transport from the uranium–aluminium fuels.

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## 1. Introduction

As part of an environmental assessment of a geologic repository for high-level radioactive waste and spent nuclear fuel, the US Department of Energy (DoE) models radioactivity release from the waste package and subsequent transport through the subsurface. Radioactive colloids generated during the corrosion of the waste represent potentially important sources of radioactive release, yet they are incompletely identified and poorly understood. This knowledge gap propagates into large uncertainties in predictive-model release calculations and was cited as a deficiency by expert evaluation of US efforts in this area [1].

To date, information has appeared in the literature on the nature of the colloids formed during the oxidative corrosion of high-level waste glass [2–6] and references therein] and commercial uranium oxide ($UO_2$) fuels [7]. Fortner et al. [8] describe colloids generated during the corrosion of production reactor fuel owned by the DoE. Still, none of the more than 200 other fuel types in the DoE inventory has been characterized for colloid production and reported in the peer-review literature. As one of the fuels chosen by the DoE for evaluation, aluminium-based spent nuclear fuels represent a potentially significant component of the inventory, due to their high fissile uranium concentration, relative volume in the DoE inventory, and high fission and activation product concentration resulting from high burnup. We focused our research on colloids produced during the aqueous

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* Corresponding author. Tel.: +1 630 252 4777; fax: +1 630 252 4771/5246.

*E-mail address:* kaminski@cmt.anl.gov (M.D. Kaminski).

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corrosion of aluminium-based nuclear fuel. In this paper, we determine the concentration, size distribution, and morphology of the colloids and discuss the significance of this data to the repository.

## 2. Experimental

### 2.1. Materials and testing

The well water was prepared from water sampled from the J-13 well near Yucca Mountain and modified with volcanic detritus or tuff that characterizes the geology of Yucca Mountain, as described in [9]. The ionic strength and pH of the modified water was ~3 millimolal and 7–8, respectively (within the stability regime for montmorillonite clay [2]). The cation concentrations (μg/g or ppm) in the modified groundwater (herein referred to as 'well water') were Na: 70–707, Mg: 0.01–0.21, Al: 0.11–1.36, Si: 27–144, Ca: 2.4–10.1, Fe: 0.01–1.82, U: 0.0008–0.1.

The test scheme was designed to observe colloidal products as a result of direct colloid production (e.g., spallation of oxidized fuel products in the colloidal size range) and that from the precipitation of material (colloidal precipitates formed when the solubility product was exceeded). We dripped well water intermittently (0.75 mL twice weekly) onto the face of a non-radiated uranium aluminide fuel coupon (5 × 4 × 2 mm, see Table 1) placed horizontally inside a perforated Zircaloy cup that was suspended inside a stainless steel test vessel. The water drained off the fuel and passed through a series of gold mesh sieves with 11 μm openings and larger (to trap particulates) and into the base of the sealed vessel. We ran three tests of varied duration at 90 °C (Test 1 = 16 days, Test 2 = 55 days, Test 3 = 183 days). Periodically, we cooled the vessel to room temperature and withdrew all of the reacted well water from the base for analysis. Control tests containing no fuel were run concurrently and analyzed after 83 and 151 days.

Table 1
Composition of U–Al fuel

| Element | Fuel meat (g/g) | Cladding (g/g) |
|---|---|---|
| Na | $2.92 \times 10^{-5}$ | $<4 \times 10^{-4}$ |
| Mg | $2.63 \times 10^{-5}$ | $3.13 \times 10^{-2}$ |
| Al | 0.497 | $9.62 \times 10^{-1}$ |
| Si | $2.5 \times 10^{-4}$ | $3.06 \times 10^{-4}$ |
| K | $9.74 \times 10^{-5}$ | $1.61 \times 10^{-4}$ |
| Ca | $3.9 \times 10^{-4}$ | $8.41 \times 10^{-4}$ |
| Fe | $1.45 \times 10^{-3}$ | $3.44 \times 10^{-3}$ |
| Zr | $1.45 \times 10^{-5}$ | $8.66 \times 10^{-6}$ |
| Au | $9.68 \times 10^{-8}$ | $1.93 \times 10^{-7}$ |
| $^{235}$U | 0.10 | NA |
| $^{238}$U | 0.39 | $4.07 \times 10^{-5}$ |
| Total | 0.99 | 1.0 |

### 2.2. Analysis

The concentration of metals in the reacted well water (or leachate) at the base of the vessel that passed through a 30 kDa filter (Millipore-Ultrafree MC) represented the dissolved fraction. This number was subtracted from the unfiltered leachate concentrations (colloidal/particulate <11 μm + dissolved) to determine the colloidal/particulate fraction. Liquid samples were acidified and analyzed by inductively coupled plasma mass spectrometry, as described elsewhere [10].

Transmission electron microscopy (acc. voltage = 200 kV) and energy dispersive X-ray analysis were used to characterize the morphology and composition of colloids prepared by passing unfiltered sample leachate through a Formvar-coated grid (Ladd Research) or a hydrophilic Butvar-coated grid prepared in-house.

Dynamic laser light scattering was used to determine the concentration and size distribution of the colloids using an argon ion laser at 3–20 mW (Malvern PCS4700C, 515 nm, 500 μm PMT aperture). Samples consisting of approximately 400 μL of unfiltered leachate were stored in cylindrical glass vials at room temperature. We analyzed samples withdrawn at the end of three tests (day 16 for Test 1, day 55 for Test 2, and day 183 for Test 3) at various times after test termination to monitor the effect of storage time on scattering intensity. Precipitates that formed after prolonged storage were removed by centrifugation prior to analysis of the solution. Scattering intensities were measured at an angle of 90°. The unit was checked against polystyrene standards from Duke Scientific (33, 73, 304 nm diameters) and NIST (SRM 1963 and SRM 1691, 100 and 269 nm diameters, respectively) for size agreement. Bimodal standards prepared from 32 and 100 nm standards confirmed the deconvolution of discrete colloid populations. The CONTIN [11] inversion program calculated colloid size distributions based on temporal fluctuations in light scattering intensity.

Average light scattering intensities were correlated with particle concentrations by assuming that light scattering intensities measured at 3 mW for the standard spheres and unknown samples are similar for identical concentrations. The measured intensities produced curves from which concentrations of unknown samples were estimated (Fig. 1). This is an acceptable method of estimation if the unknown colloids are spherical and the refractive index of the standards ($n_{\mathrm{RI}} = 1.6$) is near that of the unknown [12]. As will be shown, clays have a refractive index similar to the standards ($n_{\mathrm{RI}} = 1.53$–$1.64$), comprised a significant fraction of the colloids, and the aggregates were roughly spherical, thus lending credence to this method of estimation.