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COLLOID FORMATION DURING WASTE GLASS CORROSION

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The long-term behavior of nuclear waste glass in a geologic repository may require a technical consideration of the role of colloids in the release and transport of radionuclides. The neglect of colloidal properties in assessing the near- and far-field migration behavior of actinides may lead to significant underestimates and poor predictions of biosphere exposure from high-level waste (HLW) disposal. Existing data on colloid-facilitated transport suggests that radionuclide migration may be enhanced, but the importance of colloids is not adequately assessed [1]. Indeed, the occurrence of radionuclide transport, attributed to colloidal species, has been reported at Mortandad Canyon, Los Alamos and at the Nevada Test Site [2]; both unsaturated regions are similar to the proposed HLW repository at Yucca Mountain. Although some developments have been made on understanding the transport characteristics of colloids [3], the characterization of colloids generated from the corrosion of the waste form has been limited [4]. Colloids are known to incorporate radionuclides either from hydrolysis of dissolved species (real colloids) or from adsorption of dissolved species onto existing groundwater colloids (pseudocolloids) [5]; however, these colloids may be considered secondary and solubility limited when compared to the colloids generated during glass alteration [6].

Glass alteration results from complex interactions between waste form and groundwater or between waste form and humid air and is governed by the near-field chemistry (glass composition, groundwater composition, engineered barrier systems, time of barrier breachment, etc.). As the glass is altered under repository conditions, new phases are formed which are waste form dependent. Under certain conditions, these altered glass phases are a source of colloidal material, whereby colloidal-sized particles may detach from the reacted surface and become solution-borne colloids [7-9]. The actinides can thereby be present in solution at higher concentrations as an insoluble glass alteration phase than as real or pseudocolloids.

The formation of actinide-bearing colloids is best understood from the investigation and characterization of colloids in the near-field (waste form colloids) [6,7]. Long-term drip tests designed to simulate repository conditions have resulted in the formation of clay colloids and brockite, a thorium orthophosphate, in the leachant [7]. Brockite is known to incorporate rare earths, uranium, americium, and possibly plutonium into its crystal structure. Initial release rates of actinides from the glass were low, but increased rates were observed when the reaction progress had incorporated spalling of the reaction layer [7].

The reactivity of high Pu loaded glasses has exhibited further evidence of waste form reaction phases spalling actinide-bearing colloids [8]. Glasses doped with various concentrations of Pu were reacted under accelerated conditions [8]. Plutonium was found associated with colloidal material suspended in solution as a plutonium oxide particle attached to an Fe-rich clay. Some clay was also found to have incorporated substantial amounts of Pu. While the incorporation of actinides in alteration phases may retard the initial release of actinides; spalling of the reacted layer has been shown to release these materials as colloids [6-9].

The structure and composition of colloidal particles are commonly determined with analytical transmission electron microscopy and ultrafiltration for glass reaction tests [6-9]. These techniques have been combined with small particle handling techniques and autoradiography to determine the sites for actinide adsorption on waste glass derived colloids

[6]. Americium and plutonium were identified in the brockite inclusions rather than the clay colloid matrix [6]. Techniques used to examine colloids often have a deleterious effect on the colloidal system and it is a challenge to find a technique which can extract representative information on the nature of colloidal particles. Presently, dynamic light scattering and electrophoretic mobility measurements are nonintrusive methods that can be used to characterize physical characteristics of actinide-bearing colloids [10,11].

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