

Natural and Synthetic Barriers to Immobilize Radionuclides

W. Um^{1,2}

¹Division of Advanced Nuclear Engineering, Pohang University of Science and Technology, Pohang, Korea

²Pacific Northwest National Laboratory, PO Box 999, P7-54, Richland, WA, 99352, USA

wooyongum@postech.ac.kr

1. Introduction

The fate and transport of radionuclides in the aqueous phase is controlled by various physical, chemical, and biological processes with the surrounding matrix. Because the physicochemical interaction at solid-water interfaces influences the migration of radionuclide in the subsurface environment, an understanding of the sequestration mechanism controlling the distribution of radionuclides of concern between the aqueous and solid phases is required to predict the transport of radionuclides in nature, especially for the proposed nuclear wastes repositories. In the radioactive waste repository facility, natural or synthetic materials are planned to be used as a barrier (or getter) material to immobilize and retard radionuclide release. The getter material can be used to selectively scavenge the radionuclide of interest from a liquid waste stream and subsequently incorporate the loaded getters in a cementitious or various monolithic waste forms. Also, the getter material is to reduce the release of radionuclides from monolithic waste forms by being emplaced as a backfill barrier material around the wastes or waste form to minimize the potential hazard of leached radioactive wastes. The barrier material should be highly efficient to sequester radionuclides and possess physical and chemical stability for long-term exposure to

2. Results and Discussion

Secondary precipitate crystalline as natural barrier materials: The key radionuclides were found to be sequestered into secondary crystalline mineral structures

severe weathering conditions. Because potential leaching of radionuclides depends on various environmental and weathering conditions of the near-field repository, the barrier materials must be durable and not disintegrate under a range of moisture, temperature, pressure, radiation, Eh, pH, and solution conditions [1]. Particularly for temperature extremes, the backfill material should be able to withstand elevated temperatures resulting from the heat generating high-radiation fluxes of solidified high-level nuclear wastes. The barrier materials are most commonly synthetic or natural inorganic materials that selectively adsorb radionuclide and metallic contaminants. In here, both natural and synthetic barrier materials are discussed to increase our understanding of potential retardation of radionuclide transport in the repository.

Table 1. Composition of synthetic glass leachate based on the STORM calculations of glass (LAW44) dissolution.

Glass Leachate	
Constituents	Concentration (M)
NaHCO ₃	2.3 × 10 ⁻¹
Na ₂ CO ₃	4.6 × 10 ⁻¹
H ₃ BO ₃	1.3 × 10 ⁻²
Na ₂ SiO ₃ ·9H ₂ O	1.9 × 10 ⁻²
NaOH	2.5 × 10 ⁻³
KOH	5.2 × 10 ⁻⁴
pH : 9.7 (measured at 25 °C)	
Alkalinity (mg/L as CaCO ₃) : 67 000 (measured)	
Ionic Strength : 1.67 M (calculated without considering precipitates)	

formed when glass waste forms weathered in the subsurface environment and the glass leachate contacted with surrounding sediments. The leachate from the glass waste forms disposed in the integrated disposal facility (IDF) has high ionic strengths and high pH in nature based on predictions using the STORM glass leaching code (Table 1). In the early weathering stage inside the glass-dominated portion of the burial facility, pH values can exceed 9.8. Under such alkaline conditions, several complex geochemical reactions are known to occur in both glass waste forms and surrounding sediments that include dissolution of several carbonate and silicate minerals, precipitation of secondary and tertiary mineral phases, and sequestration of radionuclides into secondary and tertiary mineral phases [2]. Weathering of glass waste form and the reacted sediment with glass leachate showed the formation of sodalite/cancrinite, a feldspathoid mineral with a cage-structure. Radioactive Sr, Cs, and Re (as surrogate for Tc) were found to be incorporated within these secondary mineral precipitates formed on the weathered glass waste surface and the reacted sediments, which can reduce the transport of radionuclides in the repository.

Synthetic nanoporous zirconium oxophosphate and U(VI) removal: Since phosphate-bearing material is regarded as one of the most promising backfill materials because of its high physicochemical stability, as well as having a high affinity for uranium and other radioactive contaminants, uniformly arrayed zirconium-phosphate nanoporous material was synthesized using the cationic surfactant octadecyltrimethyl ammonium bromide (OCTBr) $[C_{21}H_{46}BrN]$ and zirconium sulfate $[Zr(SO_4)_2 \cdot 4H_2O]$ as a pore-structure directing template and an inorganic precursor, respectively. The calcined nanoporous zirconium phosphate material was characterized using various methods and used as an adsorbent for removal of U(VI) in a $NaNO_3$ solution with varying background conditions including pH, ionic

strength, U(VI) concentrations, and carbonate concentrations. Batch U(VI) adsorption results showed that U(VI) adsorption reached steady-state condition within 48 hours and all the dissolved U(VI) (10^{-6} M) was removed by this material at neutral pH and closed conditions to atmospheric $CO_2(g)$. The U(VI) adsorption followed a traditional Langmuir adsorption isotherm, and the distribution coefficient (K_d) calculated from the linear region of the Langmuir isotherm was 105,000 mL/g.

3. Conclusions

The experiments of weathering of glass waste form and the reacted sediments with simulated glass leachates show that radionuclide sequestration can be significantly enhanced by promoting the formation of secondary precipitates (cage structured feldspathoid minerals such as sodalite and cancrinite). In addition, synthetic phosphate-bearing nanoporous material exhibits high stability at temperature and has a very high K_d value for U(VI) removal. Both natural and synthetic barrier materials can be used as additional efficient adsorbents for retarding transport of radionuclides from various contaminated waste streams and waste forms present at U.S. Department of Energy clean-up sites and the proposed geologic radioactive waste disposal facility.

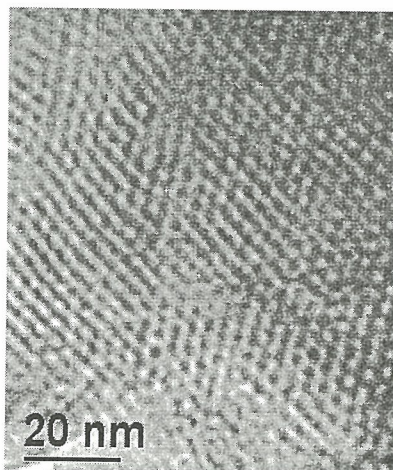


Fig. 1. Transmission electron micrograph image for zirconium oxophosphate calcined at 500 °C.

4. REFERENCES

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