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Sorption of Anionic Iodine and Molybdenum to Multisorbing Barrier (MSB) Materials - 20030

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ABSTRACT

A multisorbing barrier (MSB) material containing sodium bentonite (NaB), organoclay, and anion resin is being evaluated for containment of anionic radionuclides. Batch tests on the MSB were conducted using two non-radioactive analog isotopes (^{127}I , ^{95}Mo) as surrogates for ^{129}I and ^{99}Tc due to their similar valence and molecular weight relative to the radionuclides. Tests were conducted on the organoclay, anion resin, and NaB individually and on NaB-resin blends with resin contents of 1% and 5% by mass. The anion resin exhibits very strong sorption of ^{127}I and ^{95}Mo relative to the other materials. The organoclay exhibited modest sorption of ^{95}Mo and ^{127}I , and NaB little sorption. The sorption isotherms follow a linear model for NaB, a Freundlich model for the organoclay, and a Langmuir model for the anion resin and NaB-resin mixtures. Combining resin with NaB significantly enhances sorption relative to NaB alone, with a larger resin fraction yielding greater sorption.

INTRODUCTION

Low-level radioactive waste (LLW) and mixed waste (MW) contain long-lived radionuclides such as iodine-129 (^{129}I) and technetium-99 (^{99}Tc) [1, 2, 3]. These radionuclides, which exist predominantly in an anionic speciation (e.g., $^{129}\text{I}^-$ and $^{99}\text{TcO}_4^-$), can be highly mobile in the environment [4, 5, 6, 7]. Because they are anionic, they are sorbed modestly if not at all by conventional engineered barrier materials, which typically have negatively charged surfaces [8, 9]. Consequently, release of $^{129}\text{I}^-$ and $^{99}\text{TcO}_4^-$ can have a controlling influence on performance assessments for on-site disposal facilities for LLW and MW. Reducing the release of $^{129}\text{I}^-$ and $^{99}\text{TcO}_4^-$ using innovative barrier systems has potential to enhance the effectiveness and reduce the cost of on-site disposal facilities.

Sorption, reductive precipitation, and co-precipitation have been studied to remove radionuclides from aqueous solutions [10-18]. For example, active carbon and zeolites, with high surface area and a porous structure, have been used to sorb uranium (U) and radon (Rn) [10, 11]. Reduction reactions induced by zero-valent iron nanoparticles have been shown to immobilize pertechnetate and arsenic [12,

13]. Organoclays with positively charged surfaces have been used to sequester heavy metals, organic contaminants, and $^{99}\text{TcO}_4^-$ [6, 19]. However, these containment techniques have not been deployed in engineered barriers for LLW and MW.

A multisorbing barrier (MSB) is being developed by the investigators to control flow and transport of anionic radionuclides as well as other contaminants of concern (COCs) in LLW and MW disposal facilities (e.g., cationic metal species, volatile and semi-volatile organic compounds, mercury, etc.) by combining low hydraulic conductivity and high sorptive potential. The MSBs being explored are a combination of sodium bentonite (NaB), organoclay, and anion resin.

These components have complementary characteristics that can sorb a variety of COCs while also maintaining very low hydraulic conductivity. This paper describes findings from batch sorption tests using the aforementioned MSB materials and two analog isotopes, iodine (^{127}I) and molybdenum (^{95}Mo), that are surrogates for ^{129}I and ^{99}Tc . These analog isotopes have similar valence and molecular weight as the target radionuclides, but are not radioactive and therefore radiological safety precautions and disposal of radioactive wastes from the experiments were avoided.

MATERIALS AND METHODS

Sorbent Materials

Three commercially available sorbent materials and two blends were evaluated: (i) NaB that contained at least 75% montmorillonite (Colloid Environmental Technologies Co., Hoffman Estates, IL, USA) to achieve low hydraulic conductivity and sorb cationic COCs, (ii) organoclay consisting of bentonite exchanged with the organic cation dimethylammonium (HUESKER, Charlotte, NC, USA) to sorb anions and organic compounds, and (iii) a macroporous and strongly basic anion resin with a bead diameter of 0.8 mm (Zhengguang Resin Co., Ltd., Hangzhou, China). Tests were conducted on these materials alone and on blends of NaB and resin with 1% resin or 5% resin by weight. NaB was used as the clay component because the hydraulic conductivity of NaB to water is very low ($\sim 10^{-11}$ m/s) [6].

Batch Reaction Tests

Batch tests were conducted on the sorbent materials using an aqueous solution prepared by dissolving reagent grade potassium iodide (KI) or sodium molybdate (Na_2MoO_4) in ASTM Type II deionized (DI) water. Target concentrations were in the range 10-1000 $\mu\text{g/L}$ for ^{127}I and 5-500 $\mu\text{g/L}$ for ^{95}Mo . The solid-to-liquid (S/L) ratio was 1:100 (by mass) for all batch tests except those with anion resin (S/L ratio = 1:1000).

For each batch test, oven-dried sorbent was mixed with 40 mL of sorbate solution in a 50-mL polypropylene centrifuge tube. For NaB and organoclay, 0.4 g of oven-dried sorbent was used; 0.04 g of sorbent was used for anion resin. The centrifuge tubes were tumbled at 30 rpm for 24 hr at room temperature ($20 \pm 2^\circ\text{C}$) following the procedure o in ASTM D4646. Afterwards, the solid and liquid were separated by centrifugation at 4000 rpm for 20 min, and a 10-mL aliquot of supernatant was extracted and transferred into a 15-mL polypropylene centrifuge tube for chemical analysis. Initial and final concentrations of ^{127}I and ^{95}Mo were measured by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7900, Santa Clara, USA). Control tests were conducted without sorbent to account for losses. Sorption of ^{127}I and ^{95}Mo to the polypropylene centrifuge tubes and other equipment was negligible.

RESULTS AND DISCUSSION

Sorption isotherms for ^{127}I and ^{95}Mo and the sorbents are shown in Fig. 1. The isotherm data were fit with linear, Freundlich, or Langmuir, isotherm models depending on shape:

$$\text{Linear: } q = K_d C_e \quad (1)$$

$$\text{Freundlich: } q = K_F C_e^{1/n} \quad (2)$$

$$\text{Langmuir: } q = Q_o b C_e / (1 + b C_e) \quad (3)$$

where q is the solid-phase concentration at equilibrium, C_e is the liquid-phase concentration at equilibrium, K_d is the partition coefficient in the linear isotherm, K_F and n are the Freundlich parameters, and Q_o and b are the Langmuir parameters. Eqs. 1-3 were fit to the isotherm data using a least-square-error algorithm.

Sorption isotherms for ^{127}I and ^{95}Mo were linear for NaB and nonlinear for the organoclay and NaB-Resin blends, as shown in Fig. 1. Sorption was lowest for the NaB, especially for ^{95}Mo . Sorption on organoclay was modest and was best described using the Freundlich isotherm model with the parameters shown in Fig. 1. The greatest sorption was obtained with anion resin alone (described subsequently) or with the NaB-resin mixture with 5% resin. Isotherms for the batch tests conducted with anion resin were best described with a Langmuir isotherm model, as shown in Fig. 1. The fraction of anion resin in the NaB-resin mixture had a large influence on sorption - high sorption using 5% resin and low sorption comparable to NaB alone with 1% resin.

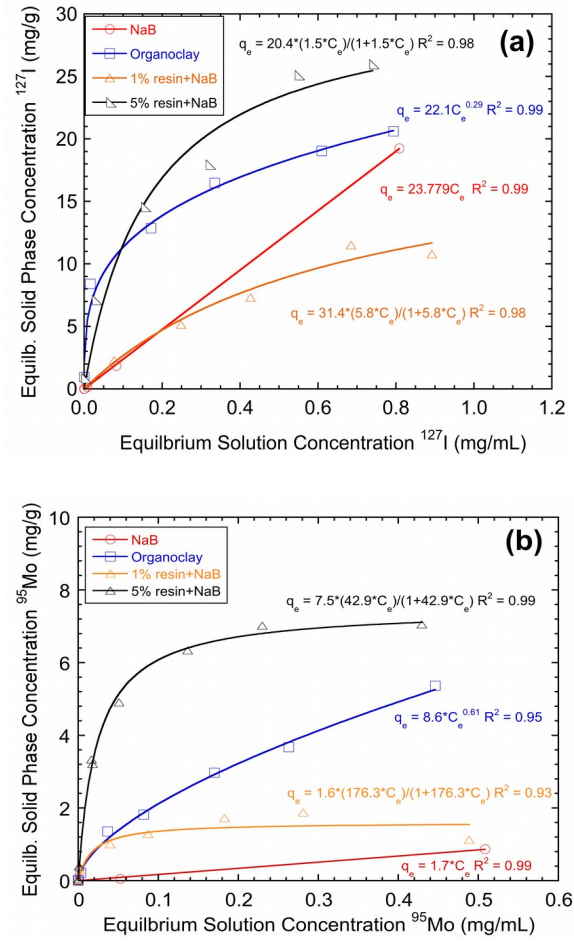


Fig. 1. Sorption isotherms for ^{127}I (a) and ^{95}Mo (b) to NaB, organoclay, and NaB-resin blends.

The strong influence of resin content on adsorption by the NaB-resin mixtures is due to the high affinity of the anion resin for ^{127}I and ^{95}Mo , as shown in Fig. 2. The isotherms for the resin alone are shown in Fig 2 on a separate graph because the solid phase concentrations are 10-30 times higher than for the other sorbents (Fig. 1).

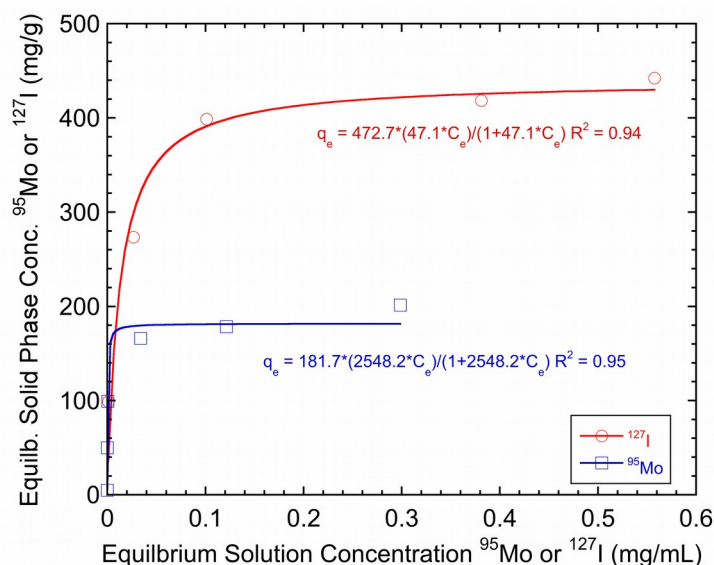


Fig. 2. Sorption isotherms for ¹²⁷I and ⁹⁵Mo on the anion resin.

SUMMARY

Adsorption of ¹²⁷I and ⁹⁵Mo to multisorbing barrier materials was evaluated using batch reaction tests with sodium bentonite (NaB), organoclay, anion resin, and NaB-resin blends as sorbents. Non-radioactive analog isotopes (¹²⁷I, ⁹⁵Mo) having similar valence and molecular weight as the radionuclides ¹²⁹I and ⁹⁹Tc were used to avoid radiological safety precautions and disposal of radioactive waste from the experiments. Sorption isotherms obtained from the batch tests were fit with linear (NaB sorbent), Freundlich (organoclay sorbent), and Langmuir (NaB-resin mixtures and resin alone) isotherm models.

Findings from the batch experiments indicate that high sorptive potential can be achieved by blending a modest fraction (5%) of anion resin with NaB. Moreover, the sorptive potential is highly sensitive to the fraction of anion resin in the mixture, suggesting that custom blends can be created to address site-specific needs for engineered barriers. The organoclay had modest sorptive potential relative to the NaB-resin mixture with 5% resin, but much higher sorptive potential than NaB alone.

These findings indicate that MSB materials have significant promise for creating engineered barriers that can contain ¹²⁹I and ⁹⁹Tc. Engineered barriers with MSB having high sorptive potential can reduce releases of difficult to manage contaminants such as ¹²⁹I and ⁹⁹Tc, potentially leading to more effective containment systems that have lower cost.

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