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Evaluating Solid Sorbents for Recycling Wash Waters Containing Strontium and Calcium

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Abstract

A system for rapid reduction of radioactive contamination and recycle of contaminated waters is called the Integrated Wash-Aid, Treatment, and Emergency Reuse System (IWATERS). First developed for cesium contaminations, IWATERS prescribes the use of salt and surfactant additives to decontaminate radionuclides from urban surfaces. The water is collected and recycled after passing through reactive filtration beds containing selective sorbents. To adapt the IWATERS for strontium contaminations, potential additives to enhance its decontamination from urban surfaces are identified. One possible additive is calcium (Ca^{2+}). However, its concentration can have a very strong detrimental effect on the ability of selective sorbents to remove strontium from spent wash water. We recognized that studies on off-the-shelf sorbents that include Ca^{2+} concentrations at relevant levels (greater than millimolar) are absent in the literature. To understand better the effect of Ca^{2+} , we completed a literature review, batch tests, and surface complexation modeling to reveal few sorbent options. Only silico-titanate sorbents exhibited high K_d values in the presence of Ca^{2+} , but have significant drawbacks in cost and availability. Given the state of the art, it is imperative that alternatives to alkaline earth ions in the IWATERS be identified to permit in situ recycle of the wash waters.

Introduction

A release from a radiological dispersal device (RDD) or an improvised nuclear device (IND) has the potential to contaminate a vast area both near the dispersal epicenter and via

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Supplemental Data

Table S1 is available in the ASCE Library (www.ascelibrary.org).

atmospheric deposition of small particles containing the more volatile contaminants (Kumamoto et al. 2015). Rapid mitigation procedures may be necessary to allow first responders to work in a safer environment by reducing overall radiological exposure or to reopen critical infrastructure (e.g., roadways, financial centers, care facilities). For large-area decontamination, few options can rapidly disseminate the decontaminant aside from washing the area down with water. Wash techniques have been specified to remove particulate contaminations and soluble forms of radionuclides (Nisbet and Watson 2015). One such procedure, called the Integrated Wash-Aid, Treatment, and Emergency Reuse System (IWATERS), prescribes the use of wash waters containing salts and other nontoxic, nonhazardous additives to enhance the removal of radionuclides from various surfaces (asphalt, brick, concrete, glass, granite, metal, painted surfaces, wood, etc.) (Kaminski et al. 2014). The IWATERS system includes methods for the wash water to be collected and treated, potentially allowing reuse in decontamination operations, disposal to a municipal wastewater system, or containment for further treatment. Of the various potential radionuclides of interest, we focus here on a variant of the system described in Kaminski et al. (2014) that may be used to mitigate the effects of strontium-90 contamination (Ferguson et al. 2003).

An intentional radiological release in a densely populated urban area may require the use of municipal water supply accessed through fire hydrants as the main water source for cleanup operations such as washing of roadways and building surfaces. Particulate deposits of strontium will be removed with other particles and can be physically filtered using conventional filter processes. Radioactive colloidal material is unknown, but the persistence of soil-derived colloidal material makes this mechanism of transport a potentially interesting problem (Sposito 2008). Instead, we focus on the cationic form of soluble strontium because this may represent a worst-case scenario for deposition. The physical and chemical similarities between Sr^{2+} and Ca^{2+} (ionic radii 1.12 Å and 0.99 Å, respectively) make Ca^{2+} an analog for Sr^{2+} in mineral substitutions (Faure and Powell 2012) and likely an effective candidate as an additive to wash waters to promote ion exchange of sorbed radioactive Sr^{2+} . Moreover, it is present in seawater (~0.01 moles per liter) and persists in drinking water supplies at the tens of ppm level.

During wash-down activities, the strontium in the contaminated wash water may need to be treated on-site to remove the dissolved strontium. Otherwise, copious amounts of contaminated water would need to be stored or transported for off-site treatment. In dilute fresh waters, this treatment can be accomplished using modalities such as ion exchange onto solid sorbents, membrane separation procedures such as reverse osmosis, or precipitation reactions. Reverse osmosis is an energy-intensive procedure that is not selective for particular cations or anions and creates a concentrated discharge stream. Precipitation techniques for dilute radionuclides would require coprecipitants that would add to the solid waste volume. Both the former and latter techniques are not conducive to direct recycling of the water without readdition of salt additives, so the potential for reuse of wash waters for continued mitigation activities may be limited if these procedures are applied for cleanup of the waters. Selective ion exchange may be a preferred method because ion exchange can be better tailored for the removal of specific cations. In addition, the solid ion exchange materials could then be collected and disposed, and the wash waters could be reused using

conventional solid-liquid separation methods. However, the same calcium salts that promote ion exchange of strontium from building surfaces may severely interfere with the separation of the low concentration of radionuclides onto the solid sequestering phase due to the limited ion selectivity of the sequestration agents for certain nonradiological over radiological ions (Kumar and Jain 2013). This selectivity depends on various characteristics, including type of sorbent, ionic strength, temperature, and solution pH.

This paper summarizes reports in the literature regarding the distribution coefficients for sorbents, both synthetic and natural, capable of ion exchange when added to a solution of radioactive strontium in the presence of other salts, with an emphasis on articles citing the use of calcium salts. These adsorbing agents were chosen according to their distribution coefficient with attention also given to the initial salt concentration of the solution. Although there has been extensive investigation of the sequestration of strontium from fresh water solutions, and, more recently, with seawater, this research attempted to extrapolate the effects of those sorbents on strontium in a solution with a high calcium salt concentration. Due to a lack of data in the literature review, this manuscript also reports our own experimental tests and modeling to determine the effect of calcium on strontium sorption onto various sorbents with reported high K_d values.

Methods

Literature Search

Literature searches were performed within the electronic Argonne Research Library and in the Argonne National Laboratory Library. The most commonly used databases in the online library were Web of Science, WorldCat, and SciFinder. Key words such as *sequestration*, *solid-liquid*, *sorbents*, *sorption*, *strontium*, *clays*, and *zeolites* were used to find relevant articles. Of the thousands of articles found, articles were chosen based on the amount of key information given (distribution coefficient K_d values, calcium and major cation concentration) and to cover a variety of sequestration agents. Although there have been similar literature compilations for K_d relationships with salt concentrations, there is no comprehensive compilation for high salt (0.1 M Ca) concentrations (Krupka et al. 1999). The strontium sorbents found over the course of multiple literary searches were grouped into the natural and synthetic categories before comparing their K_d values and subsequently the concentration of competing cations in the solutions. Although there are many ways of comparing the effectiveness of substances for sorption of strontium (e.g., exchange capacity, effect of pH, kinetics, and cost), K_d values (expressed as the ratio of the equilibrium concentration of strontium on the solid and its concentration in the aqueous phase in units of milliliters per gram) are an important first-order determinant for the purposes of this paper and are one of the few physicochemical parameters needed to model the sorption of strontium through a bed of sorbent (Jolin and Kaminski 2016). We report the K_d for 10 synthetic and 10 naturally occurring sorbents chosen based on their generally large K_d values. To provide a more complete picture when comparing sorbents, other factors that can have an effect on the ability of the mineral to sorb strontium were recorded. These factors include solution conditions such as the pH, temperature, competing cations, and their concentrations. Some conditions deviated slightly from paper to paper and therefore were

generalized into a single category. This information is provided in the Supplemental Data to this paper. The pH value ranged from 3 to 9 in a majority of the studies, but when comparing those articles to each other, the highest absorption of strontium was usually observed to occur at neutral to near-neutral values. In terms of cation exchange, $\text{pH} < 9$ is believed to be necessary for partitioning due to the presence of carbonates and the precipitation of CaCO_3 ($K_{\text{sp}} = 3 \times 10^{-9}$) (Lefevre et al. 1993; McHenry 1958). Most experimentation was performed at or near 25°C . The concentrations of the competing cations, however, ranged anywhere from 1 M to 10^{-7} M, and this range was taken into account as comparisons between K_d values were made. The main competing cations in tap waters (Ca^{2+} and Mg^{2+}) are seen in water supplies, though only in small concentrations. The high end of Ca^{2+} was 0.0037 M, except those with seawater ($\text{Ca}^{2+} = 0.01$ M).

Geochemist's Workbench

A model of strontium and calcium sorption was done as an example of the effect of calcium in high concentrations on the ability of sorbents to effectively sequester strontium. The modeled curve is also used to compare with literature and extrapolated values. The surface complexation of calcium and strontium with goethite was modeled using the "React" module of the Geochemist's Workbench software package to explore the effect of a simple ion exchange in the presence of competing salts such as Ca^{+2} . The two-layer surface complexation model of Dzombak and Morel (1990) was used along with the "thermos.com.V8.R6.full" thermodynamic database (Bethke 1996) and the extended form of the Debye-Huckel equation for activity coefficient calculations (Huebner 1970). The model considers two sites on the mineral surface: a strongly sorbing site $> \text{FeOH}(\text{s})$ with a site density of 0.005 mol/mol goethite and a weakly sorbing site $> \text{FeOH}(\text{w})$ with a site density of 0.2 mol/mol goethite. A goethite surface area of $38.0 \text{ m}^2/\text{g}$ was chosen based on the measurements of Carroll et al. (2008). The solution conditions for the model were chosen to reflect surface water conditions and typical V/m ratios for batch experiments reported in the literature: oxygen buffer fugacity of 0.2; carbon dioxide buffer fugacity of $1.0 \times 10^{-3.5}$; pH fixed at either 6, 7, or 8; goethite masses of 10 g/kg water and 100 g/kg water; background solution of 0.001 molar NaCl with charge balanced on Na^+ or Cl^- ; fixed strontium concentration of 1.0×10^{-6} moles/kg water; and 0.1 moles of calcium per liter titrated into the system.

K_d Batch Tests

Traditional batch testing was done in our laboratory to determine K_d values for crystalline silicotitanate (UOP, Ionsiv IE-910, Des Plaines, Illinois, Lot No. 1998040003), Amberlite IRC-748 (Beantown Chemical, Hudson, New Hampshire, CAS#79620-28-3) and Duolite C-467 (Sigma-Aldrich, St. Louis, Missouri). Tests were performed in deionized water ($18.0 \text{ m}\Omega \cdot \text{cm}$) and in the presence of CaCl_2 (calcium chloride dehydrate, 99+% A.C.S. reagent grade, Sigma-Aldrich, St. Louis, Missouri). Tests were performed in triplicate and at calcium concentrations of 0.1, 0.5, and 1.0 M. All tests were done with the established V/m of 100 mL/g . Each batch was sampled at hour intervals for the first 6 h and then $20 \mu\text{L}$ aliquots were taken at 24, 48, and 72 h. Aliquots of control vials (test solutions in test tubes without sorbent) were taken at each sample time and used to compute K_d values with Eq. (1)

$$K_d = [(C_i - C_e)/C_e](V/m) \quad (1)$$

where C_i = initial strontium concentration in solution; C_e = concentration in solution at equilibrium; V = volume of the liquid; and m = mass of the solid in the solution.

Radiostrontium (2.0 mCi Sr-85 in 0.1 M HCl, Perkin Elmer, Naperville, Illinois) was diluted, as appropriate, and activity levels were detected using a Wizard 2 automatic gamma counter (Perkins Elmer, Naperville, Illinois, Model 2480). Samples were counted for a live time of 300 s.

Results and Discussion

From the standpoint of competitive adsorption, to selectively remove strontium from wash water containing calcium, a sorbent would have a high K_d value for strontium in the presence of a relatively high concentration of calcium. However, most reported investigations of K_d values for strontium were conducted in a solution with low or no concentration of competing cations. Overall, there is a lack of data concerning high concentrations of calcium and the associated K_d values. On the other hand, removal of strontium from high ionic strength solutions dominated by sodium ions has been studied. For example, years of studies on separation and purification of strontium from high-level waste stored in underground tanks at Hanford, WA, produced successful precipitation methods (e.g., lead sulfate, ferric hydroxide, calcium carbonate), solvent extraction (e.g., using di-2-ethylhexyl phosphoric acid or novel heterocyclic compounds such as dicyclohexano-18-crown-6), and ion exchange (e.g., antimonic acid, titanates) (see Schulz and Bray 1987; Orth and Kurath 1994). More recently, Morimoto et al. (2011) reported the use of magnesium vermiculite from South Africa that could not retain Sr^{2+} in the presence of 3% sodium ion, but upon removal of the sodium via an upstream tetraethylammonium ion exchanger, Sr^{2+} could be retained well in column experiments. No calcium ions were present in the water in these development studies. Manos and Kanatzidis (2016) reviewed novel synthetic metal sulfide ion exchangers because their soft Lewis base thio donors should be more selective for soft Lewis acid ions such as Cs^+ and Sr^{2+} over the harder Lewis acids of Na^+ and Ca^{2+} . In general, metal sulfides were remarkably selective for Sr^{2+} in the presence of 5 M Na^+ and comparable to the sodium titanates. Although data on the effect of high Ca^{2+} were not available, the removal of Cs^+ (as a surrogate soft Lewis acid) was depressed in the presence of 0.1–1M Ca^{2+} . Still, they measured a $K_d \text{ Cs}^+ > 1,000 \text{ mL/g}$ indicating promise for Sr^{2+} removal in the presence of the high Ca^{2+} ion.

Importantly, recent studies related to mitigation and remediation activities at the Fukushima Daiichi nuclear reactor introduced much-needed data to address the difficult problem of separating strontium from seawater containing high concentrations of Na^+ , Mg^{2+} , Ca^{2+} , and K^+ . Kim et al. (2014) describe a separation scheme specifically designed for an emergency deployment. In it, they use precipitation techniques as the primary operation to reduce strontium via reaction onto barium-modified zeolite. Avramenko et al. (2001) reported their studies using engineered ion exchangers such as the silico-titanate IONSIV IE-911, Duolite

C-467, and novel sorbents still in the development stage to remove Sr^{2+} from seawater. Of these, two barium silicotitanate sorbents in development performed impressively well ($K_d > 4,000 \text{ mL/g}$), and they surmised that the mechanism for Sr^{2+} separation is the formation of insoluble barium sulfate coprecipitates on the sorbent surface. For the ion exchanger materials, they reported $K_d = 70 \text{ mL/g}$ for IONSIV IE-911 and 7 mL/g for Duolite C-467. Sachse and Galarneau (2012) reported the development of macroporous monoliths of zeolite A and measured $K_d = 11 \text{ mL/g}$ for in-flow experiments. Even though these are important developments, the materials are not considered widely available for an immediate mitigation operation and therefore will not be considered in this review. The exception is IONSIV and Duolite ion exchangers due to their superior performance at high salt concentrations.

Focusing on more widely available sorbents that might be used in an emergency scenario, we report experimental and modeling results aimed at filling this data gap for sorbents that are reported to have comparatively high K_d values for strontium (albeit at low calcium concentrations). First, a brief review of the literature for both natural and synthetic sorbents is given. There are numerous K_d values reported in the literature for various soil types, and different soil types are expected to have characteristics that may affect the reported K_d values. Therefore, we highlight data representative of the general literature and do not purport that the data presented signify one correct value.

Review of Natural Sorbents

Of the natural sorbents, the smectite clay FEBEX bentonite (Spain) has a high (~93%) smectite content (Huertas et al. 2000) compared to a typical bentonite (~80%) (Yanagi et al. 1989). When in $0.002\text{--}0.2 \text{ M}$ of sodium, the FEBEX bentonite yielded the greatest K_d value, as high as $5.62 \times 10^5 \text{ mL/g}$ at the lowest sodium concentration (Missana et al. 2008), exceeding the K_d value of any other clay, including kaolin, illite, and vermiculite (Missana et al. 2008; Adeleye et al. 1994; Bellenger and Staunton 2008; Bors et al. 1997). Ca-montmorillonite in a solution with no competing cations and Na-montmorillonite in $0.01\text{--}0.015 \text{ M}$ of Li^+ had a K_d of 600 mL/g and up to $1.0 \times 10^3 \text{ mL/g}$, respectively (Adeleye et al. 1994; Dutta et al. 1999). Na-kaolinite in a solution with no competing cations had a K_d of $1.3 \times 10^3 \text{ mL/g}$, and Na-mica, which was in a solution with calcium as the highest competing cation at $7.27 \times 10^{-4} \text{ M}$, had a maximum of $2.4 \times 10^5 \text{ mL/g}$ (Adeleye et al. 1994; Sylvester and Clearfield 1998). Iron minerals such as bacteriogenic iron oxide, goethite, and nitrate-impacted sediments did not yield comparatively large values, with a K_d range of $19\text{--}133 \text{ mL/g}$ (Langley et al. 2009; Thorpe et al. 2012). Oxidized, multiwall carbon nanotubes (with a functionality of 4 mmol/g of exchangeable protons) in a solution with up to 0.5 M of sodium had a maximum K_d of $3 \times 10^3 \text{ mL/g}$ at 5 ppm strontium (Yavari et al. 2010).

Natural zeolite, when combined with a solution containing $7.27 \times 10^{-4} \text{ M}$ calcium as well as $2.6 \times 10^{-4} \text{ M}$ sodium, $1.12 \times 10^{-7} \text{ M}$ barium, and $2.16 \times 10^{-4} \text{ M}$ magnesium, yielded very high K_d values of 1.36×10^4 to $7.70 \times 10^2 \text{ mL/g}$ (Sylvester and Clearfield 1998; Carroll et al. 2008). Of the soils, a loam from the Tohoku District of Japan had a K_d value of $5.62 \times 10^2 \text{ mL/g}$ (Yanagi et al. 1989). Of the magnetite, sand, and loess tested, K_d values were significantly less when compared to the other natural clays and minerals, indicating that their K_d values were at least one order of magnitude lower and ultimately insignificant (Yanagi et

al. 1989; Missana et al. 2008; Adeleye et al. 1994; Bors et al. 1997; Dutta et al. 1999; Ebner et al. 2001; Rod et al. 2010; Huo et al. 2013; Rhodes 1957; Galamboš et al. 2013; Van Loon et al. 2005; Chirkst et al. 2003; Rajec et al. 1998; Akyüz et al. 2000; Bellenger and Staunton 2008; Chiang et al. 2010; Apak et al. 1996). The last four sorbents were in solutions that did not contain any competing cations. In summary, we find many examples of quite large K_d values ($>1,000$ mL/g) among the natural adsorbents even in the presence of high sodium concentrations, but the presence of Ca^{2+} as the competing cation is at low levels, if present at all.

Review of Synthetic Sorbents

Of the synthetic sorbents, Amberlite, an aminodiacetate, had by far the highest K_d values, at over 5×10^5 mL/g, followed by Duolite, an aminophosphoric acid, which had a K_d of 3.1×10^5 mL/g (Marinin and Brown 2000). For both Amberlite and Duolite, the highest competing ion concentration was 1.5×10^{-2} M of calcium and sodium. Silicon-based sorbents had the next highest K_d values. Na-titanosilicate ranged in K_d from 3.3×10^5 to 8.6×10^5 mL/g, but Na-titanosilicate had a relatively small competing sodium ion concentration of 2.6×10^{-4} M, possibly 10,000 times lower than what would be present in IWATERS-type wash waters. Engineered silico-titanate IE-911 had a K_d of 7.0×10^4 mL/g (Marinin and Brown 2000). A chabazite (a silicate of the zeolite group) named IE-96 had a range of K_d values from 2.6×10^4 to 7.0×10^4 mL/g (Marinin and Brown 2000). Na-zirconium silicate yielded a maximum K_d of 5.2×10^4 mL/g, but values were as low as 2,130 for higher volume-to-mass ratios (Sylvester and Clearfield 1998).

For the ferric arsenate products K-pharmacosiderites, maximum values were upwards of 6×10^5 mL/g (Sylvester and Clearfield 1998) for a $V/m = 1,000$ and 82,300 for $V/m = 200$. KMS-1, a layered sulfide, had a K_d of 4.63×10^4 mL/g while at the largest sodium ion concentration of the top synthetic minerals, at 0.1 M (Manos et al. 2008). Titanates and nonatitanates had the next highest K_d values (Sylvester and Clearfield 1998; Merceille et al. 2012; Lehto et al. 1999). Sylvester's measurements on Nanonatanate yielded a K_d of 3.2×10^4 mL/g, and Na-titanate yielded a K_d of 5.8×10^4 mL/g (Marinin and Brown 2000). Many calcium-based minerals were tested, but most produced very low K_d values (Vojtch et al. 1974; Song et al. 2013; Ivanets et al. 2014; Kulyukhin et al. 2005). Only Ca-alginate beads in a solution without competing cations produced a maximum K_d of 1.6×10^3 mL/g (Song et al. 2013). Zirconium dioxide, with up to 1.2×10^{-2} M of calcium and 2.9×10^{-3} M barium, and a hydrous amorphous $\text{MnO}_2\text{-ZrO}_2$ composite with no competing cations had K_d values of 4.8×10^3 mL/g and 3.0×10^3 mL/g, respectively (Inan and Nostar 2013; Ahmadi et al. 2014). In summary, Sr^{2+} sorption onto synthetic sorbents proved to be an order of magnitude or higher than natural sorbents, although measurements in the presence of greater than millimolar concentrations of Ca^{2+} were equally lacking.

Comparison of Sorbents via K_d Values

To compare the information from the various studies, we have compiled the K_d information (Table 1). We did this with the understanding that K_d itself does not account for the salt concentration or differences in other solution conditions. Of all competing cations, Ca^{2+} is the most significant (Kokotov and Popova 1962). More than 90 sorbents were reviewed, with

Table 1 listing the top 10 of both natural and synthetic types (see the Supplemental Data for a more thorough summary of these sorbents and the test conditions).

Though the greatest K_d values of the natural sorbents were as high as $\sim 10^5$ mL/g (FEBEX bentonite and Na-mica), a couple were 10^4 mg/L and most were less. In contrast, there were a number of synthetic sorbents that had K_d values $>10^4$ mL/g. FEBEX bentonite was the only natural sorbent to have a K_d that matched the synthetic sorbents. In addition, FEBEX bentonite had the highest competing sodium ion concentration, 0.1–0.2 M, of all the minerals in the table, synthetic and natural, which points to the argument that FEBEX bentonite could still be a better sorbent than some of the sorbents with higher K_d values, but measured at lower or zero calcium concentration. A significant drawback is the fact that this is a specific bentonite mined from Spain and other bentonites will vary in their selectivity for strontium. For instance, a bentonite from Japan had a $K_d = 5,000$ mL/g (Yanagi et al. 1989), and ~ 900 mL/g was found from the Slovak region (Galambos et al. 2013).

Interestingly, the synthetic sorbents generally had higher K_d values with respect to their natural unaltered versions in the same subcategories (clays, silicates, etc.), as, for example, $K_d = 100$ and 80 mL/g for manganese oxide-coated and iron oxide-coated, respectively, compared to uncoated montmorillonite ($K_d = 70$ mL/g) (Park et al. 2012). In addition, in many of the research articles, synthetic sorbents that had higher distribution coefficients compared to pure clays or minerals involved the addition or natural occurrence of group I and II metals. Sodium, calcium, and potassium were the elements most commonly seen in these minerals. The addition of these group I and II metals to the natural clays could be an inexpensive modification to increase the K_d values.

Impact of High Calcium Concentration on Strontium K_d Values

Though the literature reports many experiments in dilute calcium solutions, due to a lack of data for higher concentrations of calcium in solution, it is difficult to assess the magnitude of the effect of calcium concentrations on the sorbents. Therefore, this manuscript explores the sequestration potential of the various sorbents in salt water with high competing ion concentrations, with a particular interest in calcium.

In the literature presented previously, some experiments were conducted with different concentrations of calcium. All of these available data have been plotted in Fig. 1, along with logarithmic extrapolation of the K_d value at a calcium concentration of 1.0 M. Importantly, these extrapolated data are a continuation of the slope in the reviewed experimental data and would only be valid if the same mechanism for sorption applied through the entire calcium concentration range and we ignored mass action and changes in selectivity over this concentration range. Certainly, these are poor assumptions and these projected K_d values are a severe overrepresentation. Instead, the purpose of Fig. 1 is to demonstrate the rapid decline in K_d that will undoubtedly happen in the presence of up to 1.0 M calcium. To illustrate this effect, we plotted the results from sorption modeling of Sr^{2+} onto goethite because the Geochemist's Workbench model does take into account mass action and selectivity over the concentration range of interest. We found that competition for sorption sites at calcium concentrations $>1 \times 10^{-4}$ M causes a severe change in slope.

In the present study, we measured the K_d for Duolite-Ca and Amberlite-Ca (Fig. 1). IONSIV IE-911, from the literature, produced a K_d of 70,000 mL/g in the presence of Ca^{2+} with a concentration of 4.24×10^{-4} M. When IE-911 is compared with our own laboratory tests on IE-910 (different in particle size only to IE-911), IE-911 has a higher projected K_d value. The higher concentrations of calcium have a decimating effect on the K_d values for IE-910. Under the lowest concentration conditions (0.1 M), the K_d is reduced by a factor of ~6 and more than a factor of 50 for a calcium concentration of 1.0 M from its projected slope based on data at lower Ca^{2+} concentrations.

To further show the effect of calcium on K_d values, a simulation was run using Geochemist's Workbench with the mineral goethite representing a nonselective ion exchanger (Fig. 1). Goethite, a naturally occurring mineral, has a relatively constant K_d value at lower concentrations of calcium. As the calcium concentration increases toward 1 mmol, there is a decline by a factor of 10 for every power of 10 that the concentration of calcium increases. In the goethite projections, saturation of the binding sites was monitored, and at no point in the model was saturation at 100%. The decline of both the laboratory-tested IE-911 and the goethite model shared similar slopes, leading us to believe similar rates of decline would be encountered in the other minerals as well, drastically lowering the extrapolated K_d values for Amberlite, Duolite, sodium titanate, carbon fibers modified by manganese dioxide (FM), carbon fibers modified by oxyapatite (FP), and others.

In Fig. 2, our own experimental data are plotted with the literature data to illustrate the drastic effect of calcium concentration on K_d values. For comparability, the experimental conditions used to collect the data in this study are similar to those in literature. The main graph shows the literature data and extrapolated values to high or low Ca^{2+} concentration in the solid and dotted lines, respectively. Experimental data collected in this study are presented in the dashed line and the individual data points. The inset, which allows for slope comparison, is a smoothing (a line of best fit over the modeled values) of our experimental data at high calcium concentration to the literature values at low calcium concentration to help the eye of the reader. The experimental data illustrate the expected drop for Amberlite and Duolite, far below the straight-line extrapolations. However, the IE-910/911 continues to sorb strontium effectively even in the presence of higher calcium concentrations, though at a lower K_d value than a simple extrapolation would suggest.

Other Considerations

Though synthetic sorbents tend to have higher sorption, other factors need to be considered when developing procedures for wide-area mitigation methods (Kaminski et al. 2016; Lee and Magnuson 2016). The achievable dose reduction during mitigation is dependent on the speed at which responders can implement them. Mitigation will likely occur early in the response so the availability of sorbents can be a limiting factor in terms of time constraints. Without access to sorbents, the accumulation of wastewater may become unbearable to the environment, and a release of contaminated waste would be detrimental to mitigation efforts while also crippling water supplies for the affected area. Though synthetic sorbents would be able to clean a higher volume of contaminated water, they have other factors that limit their usage. Synthetic sorbents have shelf lives, losing their effectiveness the longer they sit.

Ideally, any municipality would be able to have a stockpile of sorbents that would be ready for use if unfortunate events occurred. This stockpile would require synthetic sorbents to be replaced as they expire, which would be expensive to maintain. The benefit of the synthetic sorbents, a result of their higher exchange capacities and high K_d values, is the lower amount of solid waste that would need to be disposed. Natural sorbents such as clays have the benefit of being cheaper and are typically readily available worldwide, making the maintenance of a stockpile unnecessary. Our results fail to identify a suitable natural sorbent for calcium-rich waters at this time, but associated cleanup activities in Japan may lead to more widely available selective sorbents for the treatment of waters contaminated with strontium.

Conclusions

The practical goal of this research is to enable the IWATERS system to decontaminate highly diverse surfaces of radiostrontium contamination. To accomplish this, an appropriate combination of chemical wash solution and strontium selective sorbent is desirable. Calcium may occur naturally or be added to the chemical wash to improve decontamination. Similarities in physical and chemical characteristics create potential challenges to achieving this goal, due to competitive sorption between calcium and strontium.

The results presented here suggest that 10 synthetic and natural sorbents are promising for IWATERS application due to their high K_d values, if wash waters contain low calcium concentrations ($\ll 0.1$ M). From the literature, synthetic sorbents are the most effective at sequestering radionuclides, though the data include only low calcium concentrations. In the presence of high calcium concentrations, the results for this study show drastically lower K_d values of sorbents, so the amount of solid needed to treat the wash water increases dramatically. Although the synthetic agents outperform their nonmodified natural equivalents, they may also be less accessible and more expensive. It is promising that the research community is developing novel sorbents, but, for now, materials are limited.

The low K_d levels with Ca^{2+} present do not make the use of high concentrations of CaCl_2 as a chemical wash additive an optimal application. However, should site-specific conditions necessitate the use of CaCl_2 or should high concentrations of calcium naturally occur, it is encouraging that these comparatively high calcium concentrations do not preclude preferential removal of strontium, with the amount of additional sorbent being dependent on the calcium concentration.

Even the most promising sorbents will have low K_d values in the range of 10–20 mL/g in the presence of competing calcium salts at 0.1–1.0 M, with the exception of the silico-titanates (IE-910/911). The overall effect of increased calcium concentration is diminished on these engineered silico-titanates, though not nearly as detrimental to the K_d value, holding a value of over 6,500 mL/g at 0.1 M calcium and over 500 mL/g at 1.0 M calcium. With relatively large K_d values at higher calcium concentrations, IE-910/911 may be the most viable sorbent for the IWATERS procedure if a sorbent were required in the near future. However, engineered silico-titanates are not ideal from an availability and cost standpoint, so further investigation of strontium removal approaches may be warranted. Thus, given the state of

the art, use of selective sorbents appears limited at this time. Certainly, techniques that promote the precipitation of strontium in calcium solution are options (Merceille et al. 2012; Weiss and Shipman 1957; International Atomic Energy Agency 1969; Dietz et al. 1991; Maxwell 2008), but, as stated in the “Introduction,” precipitation techniques reduce our ability to directly recycle the wash water for continued operations. However, if calcium can be removed or held to low levels, the amount of sorbent (either synthetic or natural) required may decrease greatly. Also, the addition of +1 alkali metals without addition of alkali earth ions into the chemical wash solution may promote sufficient ion exchange reactions to mobilize strontium into wash waters, which may improve the K_d value of strontium onto the common sequestration materials explored here.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.

(Color) Log plot of calcium concentration versus K_d values. Solid lines (except for goethite) represent the best fit of the data found in the literature. Dotted lines represent an extrapolation of possible K_d values to higher calcium concentrations under the assumption of constant slope from literature values. IONSIV-910 and goethite derive their data from our own experiments and Geochemist's Workbench, respectively.

Fig. 2.

(Color) Log plot of calcium concentration versus literature and our own experimental K_d values. The dotted lines in the main graph represent constant-slope extrapolations, whereas the dashed line for IONSIV-910 represents data from our own study (actual data points shown). The four other individual data points are from our own laboratory on Duolite and Amberlite resins. The inset shows lines connecting the literature data in the main graph with our own experimental data to aid the eye. These data are compared with the modeled K_d values for goethite.

Table 1.

Top 20 natural and synthetic materials and their K_d values

Rank	Sorbent	Synthetic(S) or natural(N)	Reported K_d (mL/g)	[Ca] (mol/L)
1	Amberlite (aminodiacetate)	S	>500,000	4.2×10^{-4}
2	Duolite (aminophosphoric acid)	S	310,000	4.2×10^{-4}
3	Sodium titanosilicate	S	>326,000	7.27×10^{-4}
4	IE-911 (engineered crystalline silicotitanate)	S	70,000; 58,000	4.2×10^{-4} ; 0.002
5	IE-96 (chabazite)	S	139,800–265,500; 1,360	4.2×10^{-4} ; 0.002
6	K-pharmacosiderites (8341–167)	S	82,300–647,000	7.27×10^{-4}
7	K-pharmacosiderites (8341–176)	S	51,900–600,000	7.27×10^{-4}
8	Sodium titanate	S	32,300	0.002
9	Smectite clay (FEBEX bentonite)	N	562,000	0
10	Na-zirconium silicates (8341–147)	S	2,130–103,000	7.27×10^{-4}
11	KMS-1	S	450,000	0
12	Natural zeolite (clinoptilolite)	N	7,700–27,200	7.27×10^{-4}
13	Bentonite (Japanese deposit)	N	5,000	0
14	Goethite	N	1,000	0
15	Na-kaolinite	N	1,300	0
16	Na-mica	N	14,200–240,400	7.27×10^{-4}
17	Nitrate-impacted sediments	N	133	1.67×10^{-3}
18	Na-montmorillonite	N	1,000	0
19	Smectite bentonite (Slovakian deposit)	N	900	0
20	Amorphous silica	N	785	0