Integrated Wash-Aid, Treatment, and Emergency Reuse System (IWATERS) for Strontium Contaminations – 17390

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ABSTRACT

The Integrated Wash-Aid, Treatment, and Emergency Reuse System (IWATERS) is being developed to mitigate the release of radioactivity to the urban environment by disseminating, collecting, and processing decontamination wash water. Previously, IWATERS was designed for the treatment of surfaces contaminated with radioactive cesium. Experiments were performed to investigate the expansion of IWATERS for strontium contamination. Bench-scale tests were performed to investigate various counter-ions and chelators to promote ion exchange of strontium from building surfaces. Desorption results for Cs, Sr, and Eu from concrete aggregate and concrete, brick, and asphalt coupons using low- and high-pressure flow with Ca^{2+} and Ba^{2+} rich wash water are reported along with those from non-porous surfaces such as glass and vinyl siding. Several sorbents were tested for their ability to specifically separate Sr^{2+} from these high ionic strength wash waters. Alkali metal and alkaline earth salts were found to be effective counter-ions for decontamination of Sr^{2+}, which may facilitate the use of common sorbents, even if their K_d values are <100 mL/g. In practice, low K_d values require the use of large quantities of sorbent. Computer simulations were run using the GoldSim Contaminant Fate Module software package to optimize the efficiency of IWATERS for strontium and account for the technical limitations of the sorbents. This modeling allows greater flexibility to design the wash water recycling system for various end-user specifications including options from rain barrel designs for treating runoff from roofs and facades to larger options like drainage basins for larger-scale wash down activities.

INTRODUCTION

We have been developing a decontamination system for wide-area mitigation and remediation activities. This Integrated Wash-Aid, Treatment, and Emergency Reuse System (IWATERS) (Fig. 1) is designed for soluble and particulate contaminants and we first reported its development [1, 2] for use with cesium contaminations. The components of the system are:

- Worker-friendly wash aid additives in tap water to promote the ion exchange of radionuclides from the surface
- Capture and containment of the contaminated runoff
- Use of sequestering agents to remove the dissolved radionuclides from the wash water
- Filtration and reuse of the wash water for continued operations

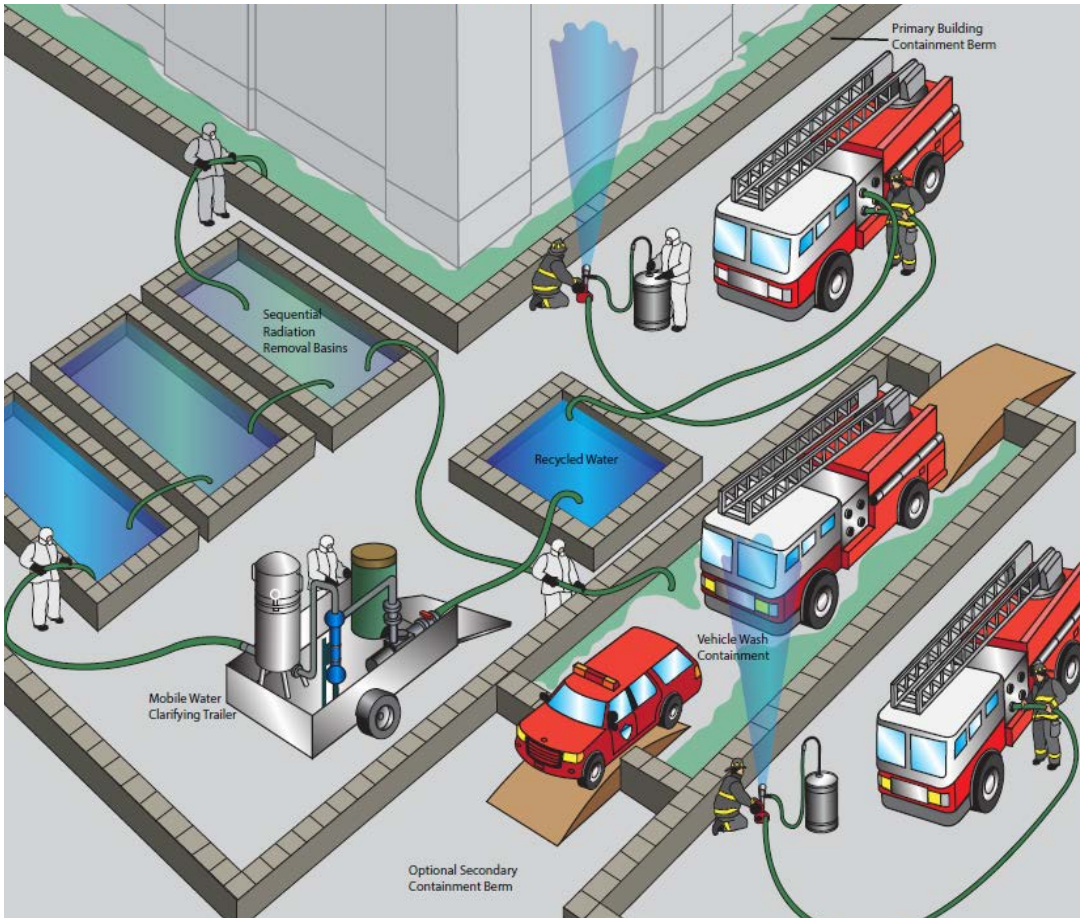

Figure 1. Artist’s rendition of potential deployment of the IWATERS for building and vehicle contaminations. Additives are drawn via an eductor into a firehose to promote ion exchange of contaminants from the surfaces. This contaminated water (green) is contained and transferred through several filtration beds containing solid sorbent materials (i.e., sequestering agents) before being clarified in a mobile filtration trailer and recycled for continued decontamination operations. A similar system can be used for vehicle decontamination, as shown in the right side of the drawing..

The logistics for IWATERS was demonstrated first during the Wide Area Recovery and Resiliency Program (WARRP) Capstone Event (September 13-14, 2012 in Denver, CO) and again at the Wide-Area Urban Radiological Containment, Mitigation, and Clean-up Technology Demonstration (June 22 – 25, 2015 in Columbus, OH).

In this paper, we focus on the effect of decontamination wash waters on removal of strontium. Considering the wash water composition, we would prefer one that excludes chelating agents that might complicate water treatment and corrosive or hazardous chemicals. In the IWATERS for cesium contaminations, we recommended potassium or sodium salts with a dilute surfactant to target sorption of cesium by ion exchange. 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 [3] and likely an effective candidate to use in wash waters to promote ion exchange of sorbed radioactive Sr^{2+}. As such, we conducted tests with calcium and barium salts and compared these results to those using potassium and tap water as controls. We report the results on various building materials exposed to low and high-pressure flow. Then, we employ a K_d model to predict breakthrough of Sr^{2+} in reactive filtration beds composed of natural sorbents.

METHODS

All chemicals used were reagent grade or better, deionized water (~18 MΩ•cm resistivity at 25 °C) and tap water from the laboratory supply. The strontium-85 (Sr-85) was from Perkin-Elmer and monitored by gamma-ray spectroscopy (WIZARD^2® NaI detector or Ortec HPGe Detective DX-100T detector) for the 514 keV photopeaks.

Concrete aggregate batch tests

A commercially-available concrete mix (Quikrete®, standard 4000 psi concrete mix purchased from a local home supply store) was separated by sieving into the following: cement powder (<0.15 mm, 15% by mass), fine aggregate (0.15-2 mm, 45% by mass), coarse aggregate (>2 mm, 40% by mass). The fine and coarse aggregate fractions were rinsed with deionized water and dried before testing. Cement pieces were prepared by mixing Portland cement (Quikrete®) with deionized water at a ratio of 2.5:1 cement-to-water. The cement paste was poured into 1.25 inch diameter, 0.25 inch thick molds to prepare cement monoliths. The monoliths were cured in a hydrated environment for at least 30 days prior to use. The monoliths were cracked into small pieces of ~ 2 mm and used for testing.

To contaminate the samples, 0.5 g or 1.0 g of material (one of the following: cement pieces, fine aggregate or coarse aggregate) was weighed into a polystyrene test tube. Radioactive Sr-85 stock solution was added to the sample (1:1 volume:mass ratio). The samples were mixed by a rotisserie mixer for 60 minutes unless otherwise stated. Then, the samples were centrifuged and the supernatant removed before adding an equal volume of deionized water to rinse entrained liquid. The rinse was removed immediately.

Desorption of Sr-85 from the sample was measured by adding an equal volume of a wash solution to the test tube and mixing by rotisserie for 60 minutes, unless otherwise stated. Then, the samples were centrifuged and the supernatant removed. A rinse of deionized water was added to the sample and removed immediately. Triplicate samples were run for all tests and an aliquot from all solutions were analyzed using the NaI well detector.

Coupons

Various coupon materials were tested. These included square cutouts (2.54 x 2.54 cm) of: Painted wood (Wood: Home Depot 1/2 inch pressed plywood, Paint:Glidden Exterior Premium Paint, Semi-Gloss White, GL68II, Titanium dioxide – 10-20%, Texanol ($C_{12}H_{24}O_3$) – 1-5%, Water – 50-60%, Acrylic resin – 20-30%, three coats); Vinyl Siding (Home Depot, Cellwood Progression Vinyl Siding Sample-White, PGD45*Sample 04); Painted metal (Home Depot, 3x6 Rib Steel Roof Panel White, PN#231030); Glass (Window replacement glass, Old Castle Tempered Glass, low E, ASTM E2190 certified, edges beveled); and Architectural roof shingle (Home Depot, PX A42399). Brick, concrete, and asphalt coupons (2.5 cm cubes) were supplied by the National Homeland Security Research Center of the U.S. EPA (Table I) as part of material used in a broader testing program.

TABLE I. Coupon material descriptions and sources.

Material	Description	Name	Locality	Source
Red brick	Red, fine-grained	Paving brick	Made from red Triassic clay	Triangle Brick Company, Durham, NC
Limestone	Light-grey, coarse-grained, ~75% skeletal grains, remainder calcite cement and trace (1%) quartz, dolomite, pyrite, clay	Indiana	South central IN	Cathedral Stone Products, Hanover Park, MD
Granite	Pink with dark banding, medium-coarse texture, biotite	Milford Pink	Milford, MS	Fletcher Granite
Concrete	Cement with sand aggregate	Quikrete® concrete mix	N/A	Local supply store, Raleigh-Durham area
Asphalt	Laboratory-pressed asphalt	N/A	N/A	North Carolina Department of Transportation

Except for concrete, brick, and asphalt coupons, all coupons were washed thoroughly using soap and deionized water (Greenworks Dishwashing Liquid) to remove any oils or contaminants. Coupons were rinsed with deionized water and allowed to dry overnight and labeled with a permanent marker. The coupons were spiked with a solution of Cs-137, Sr-85, and Eu-152 (8000-9000 counts per minute in 100 µL counted at the face of the HPGe detector). (Cs-137 and Eu-152 data not reported here.) The coupons were allowed to dry, wrapped in plastic, and left overnight for gamma counting in the morning.

Low Pressure Flow Testing

Low-pressure flow tests are intended to simulate the use of waters originating from garden hoses or firefighter nozzles. For thes experiments, we constructed a test holder to direct flow over a small coupon. Each coupon was fit into an adjustable Teflon® holder (Fig. 2) clamped to a ring stand at an angle to allow maximum distribution of water. A small peristaltic pump was used to flow water over the coupon at a rate of 100 mL/min. The coupons were placed on top of a 5 x 10 cm (2 x 4 in.) sheet of Parafilm™ to prevent the wash water from dripping across the backside of the Teflon® holder.

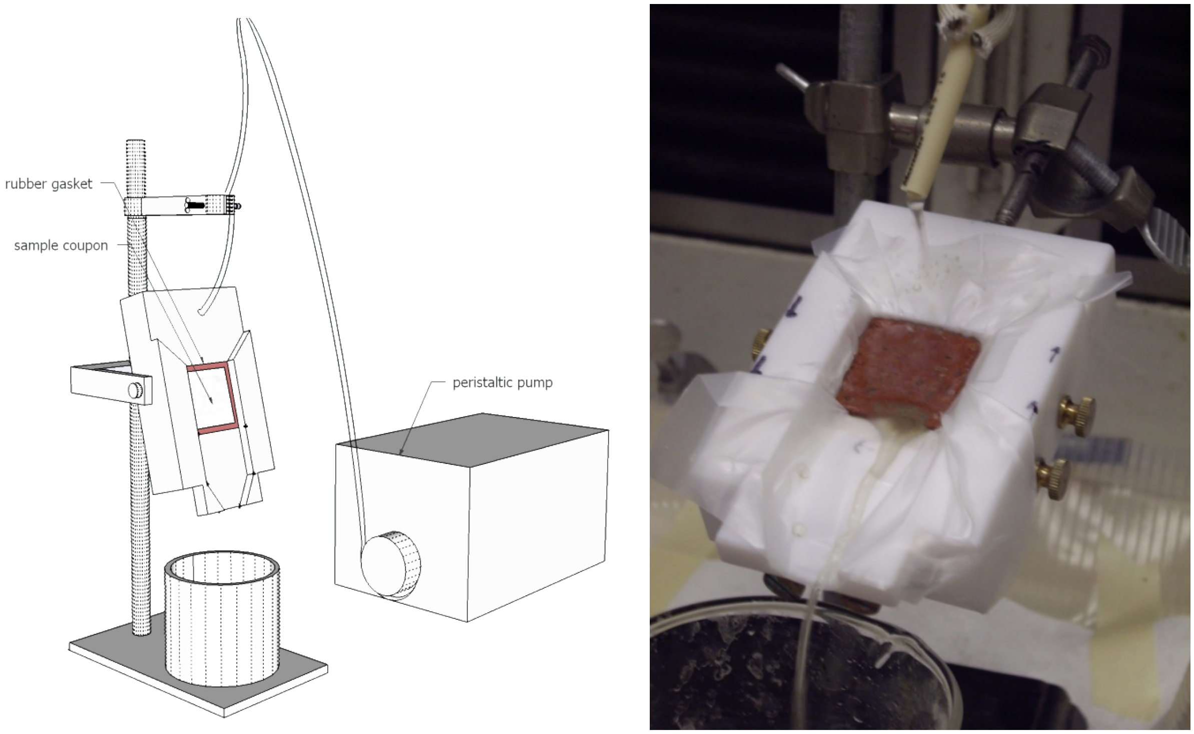

Figure 2. Schematic of flow system (left). A solution is pumped into the hood and flows over a brick coupon and into the collection beaker (right).

High Pressure Wash Testing

Commercial power washers are being used extensively in Japan for remediation after the reactor accident at Fukushima. To better understand the important variables in power washing, we designed and constructed an automated high-pressure containment device (Fig. 3) that allows us to program the wash rate (mm/sec) along specific spray patterns for various wash water compositions, spray pressure, spray angles, and sample orientation. This system will allow us to use commercial spray units of many different types. The supply hoses connect to the fitting at the top (gray and brown cylinders on the blue oval plate) of the unit and the wands insert onto fitting located underneath the top. The sample carousal moves the sample (under computer control) under the wand so the spray angle is maintained.

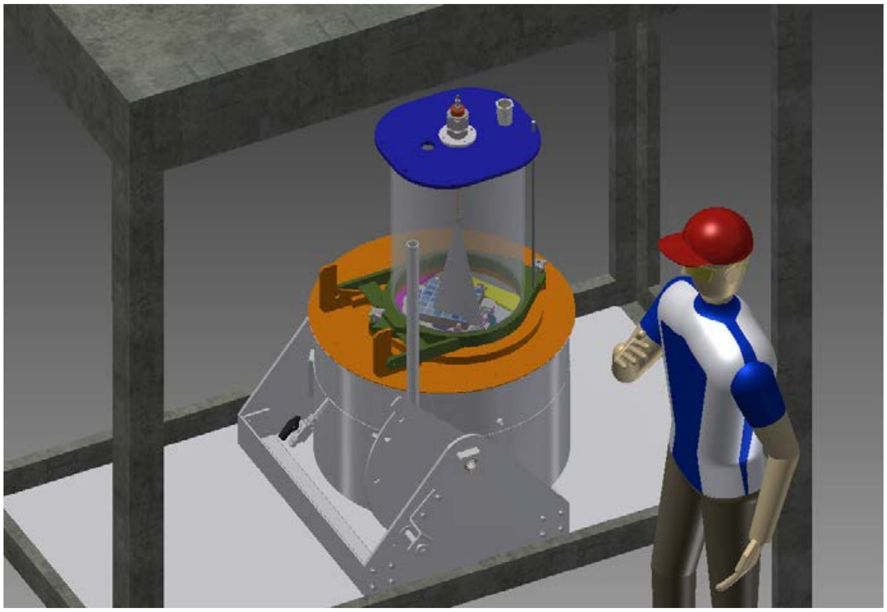

Figure 3. High pressure wash chamber is programmed for a controlled and reproducible spray pattern across a sample or set or samples. The nozzle and wand are shown descending vertically from the top cap (blue). The 6x6 inch sample holder is shown for larger coupons (array of blue squares at center). The nominal spray pattern is shown as the gray-colored fan impinging on the array of blue colored squares (drawing to scale).

GoldSim Modeling

After wash down activities, we seek a simple filtration system that can be constructed from readily available materials to effect removal of the radioactive material from solution and recycle of the wash waters for continued wash down activities. For instance, wash waters from a roof may be collected in the downspouts of the gutter system and passed through a bed of sorbent within a barrel. The GoldSim contaminant fate module was used to model breakthrough and assess the feasibility of using various minerals as sorbent materials in retention barrels. We recently reported simulation results for cesium and strontium from tap water to simulate wash waters originating from fire hydrants [4]. Here, we used the following input values to describe a filtration bed consisting of absorbent material mixed with sand (to improve hydraulic conductivity) in a cylindrical configuration (appropriate in describing a rectangular bed also, ignoring end-effects) with contaminated wash water inlet at the top and outlet from the bottom.

- Length = 150cm
- Ratio Sand to Total Mass = 0.9
- Head Height of water= 50 cm
- Diameter of the bed = 107.6 cm (corr. 10ft^2 bed)
- K_d Sand (inert)= 1.96 mL/g

- K_d Adsorber = 202 mL/g

We performed sensitivity analysis of each of the following variables about the central value given above: K_d Adsorber, K_d sand, Head Height of Water, and Barrel Diameter to determine the effects on the breakthrough of radionuclides from the barrel system defined as 1% of the input concentration level. We report here the results from varying the K_d of the adsorber.

RESULTS AND DISCUSSION

Sorption kinetics and desorption into salts

In the development of decontamination agents in the past, we sought a method of benchmarking decontaminant formulations to better compare reagents to determine the promising formulations for continued testing. Because of the prevalence of concrete in the urban environment, we used the components of concrete to test the ability to sorb and desorb radioactive Cs^+. These materials included the fine (FA), coarse aggregate (CA), and small pieces of cement. Similar experiments follow for Sr-85. We first evaluated the kinetics for sorption of Sr-85 onto the fine aggregate and crushed cement pieces (Fig. 4-5). Equilibrium for sorption under these short periods was reached within 45 minutes onto the fine aggregate and within 60-90 minutes onto the crushed cement. The K_d value was generally < 10 mL/g for both materials.

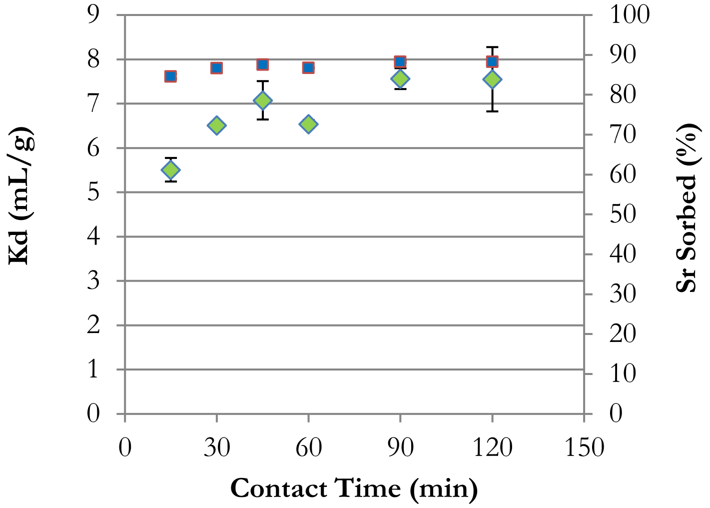

Figure 4. Sorption of Sr^{2+} onto fine aggregate. Triangles are the K_d values and the squares are the % absorbed for a V/m= 1 mL/g.

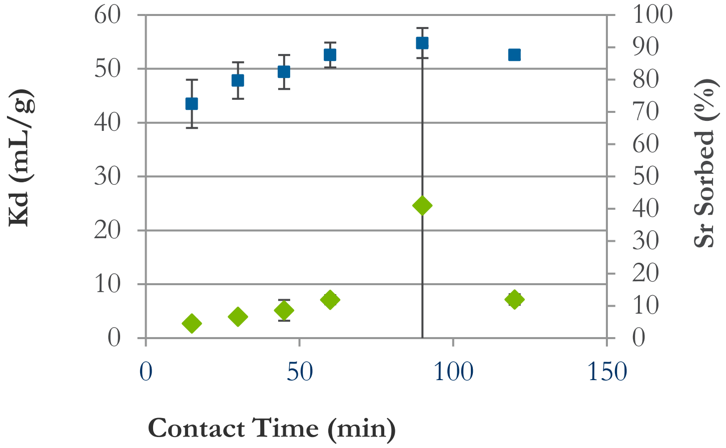

Figure 5. Sorption of Sr^{2+} onto crushed cement. Triangles are the K_d values and the squares are the % absorbed for a V/m= 1 mL/g.

We tested the desorption of the strontium from the coarse and fine aggregate of concrete (Fig. 6) and from crushed brick and cement samples (Fig. 7). The desorption was approximately 70% from the aggregate materials with little or no dependence on the concentration of Ca^{2+} or Ba^{2+} in the range of 0.1M to 1.0 M salt. We added a strong chelator DTPA to the calcium chloride salt (Fig. 7) and found that removal was not improved, as measured with the fine aggregate. Removal from brick was nearly quantitative. However, strontium could not be removed from the cement samples to better than 10%.

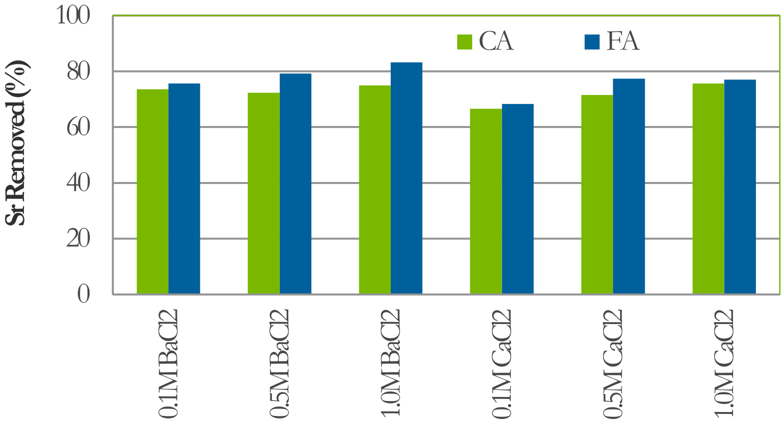

Figure 6. Desorption of Sr^{2+} from coarse and fine aggregates (CA and FA, respectively) of concrete using Ba and Ca salts. V/m= 1.

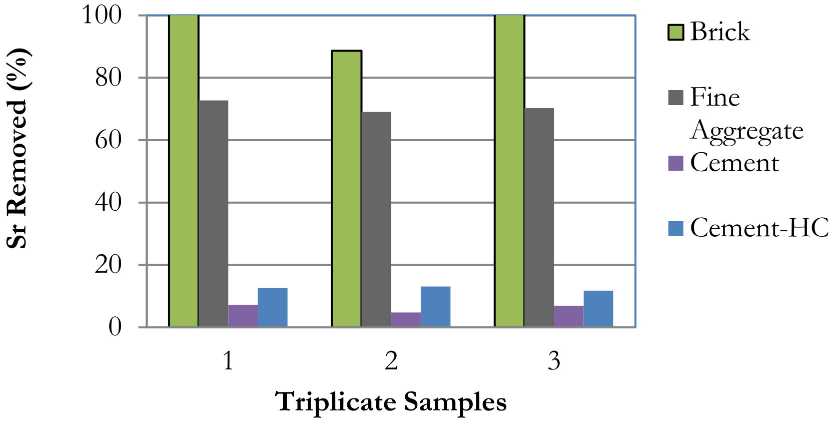

Figure 7. Desorption of Sr^{2+} from fine aggregate, crushed brick, and crushed concrete using 0.1M $CaCl_2$/0.1M DTPA as pentasodium salt. V/m= 1.

Low-pressure flow tests

Based on brief scoping tests (data not shown), we were encouraged to find that the use of calcium salt may not enhance removal of strontium from the building materials over the use of potassium salt, which is the same salt we recommend for the cesium IWATERS. This is potentially important because of the difficulty in separating Sr^{2+} in the presence of Ca^{2+}, which is required if we want to recycle the wash waters. Therefore, we carried out low-pressure flow tests using potassium salts to simulate washing via a garden hose or fire hose nozzle. We found (Fig. 8) that increasing the concentration of K^+ from 0.1 to 0.5 M did not significantly increase the removal of strontium from asphalt, brick, or concrete and the presence of K^+ dramatically improved removal compared to tap water alone for brick only. That is, there was little improvement in the removal of strontium from asphalt, concrete, asphalt composite shingles, and painted wood over tap water. For the non-porous materials glass, painted metal, and vinyl siding, we measured nearly quantitative removal of strontium (and cesium) using simply tap water.

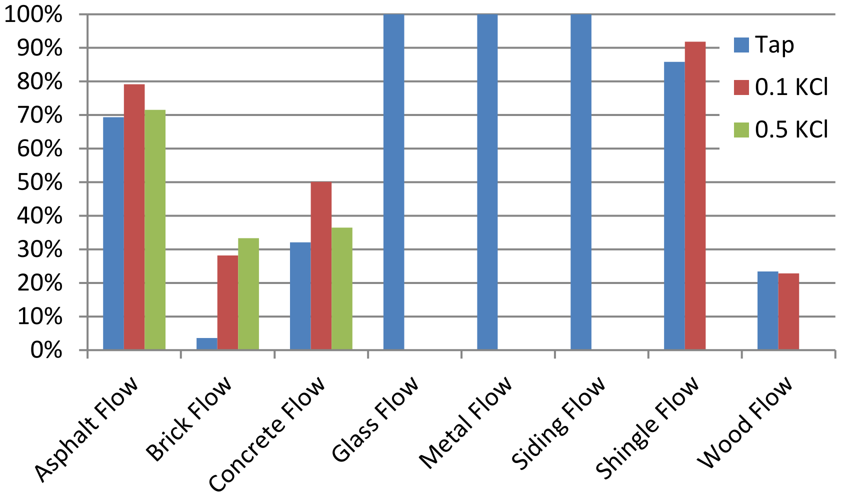

Figure 8. Removal of strontium in low-pressure flow (flow rate = 100 mL/min).

High-pressure wash testing with tap water

We followed up the low-pressure flow tests with high-pressure flow tests using tap water only as the wash water composition (Table II). Recognizing that our low-pressure flow tests exposed the sample to 100 mL total wash water per coupon to remove 30% strontium, we measured much less removal using the high pressure flow tests when using the middle length wand (distance from nozzle to sample = 26 cm) and the short wand (distance from nozzle to sample = 33 cm). Only the longest wand (distance from nozzle to sample = 13 cm) was able to remove 28±7% of the strontium, comparable to that of the low-pressure flow tests. Interestingly, we were able to remove 7±8%, 13±5%, and 18±7% strontium as we *increased* the rate of movement across the sample from 5 to 50 mm/sec.

Table II. High pressure flow test decontamination data.

			Rate	% Removal	
Material	Wand	Nozzle (°)	(mm/sec)	Sr-85	std dev
Concrete	middle	15	5	7	8
Concrete	middle	15	25	13	5
Concrete	middle	15	50	18	7
Concrete	middle	15	5	7	8
Concrete	Long	15	5	28	7
Concrete	Short	15	5	14	13

Initial Modeling for Potential Wash Water Reuse

The GoldSim modeling platform was employed to model the removal of cesium and strontium from wash waters. Our initial model, using the K_d approach to describe the sorption reactions, described the removal of Cs^+ and Sr^{2+} from tap water using rain barrels filled with montmorillonite, and/or vermiculite and sand. The study is detailed in [4]. In the present study, we modeled a more generic filtration bed for the volume of wash water that could be treated given an arbitrary K_d value. This allows us to more generically evaluate the size of potential filtration beds using a variety of materials that might be available. We used the effective K_d (mL/g) of the entire filtration bed. That is, for a bed composed, for example, mostly of relatively inert material such as 90% sand (K_d = 1.96 mL/g) and 10% sorbent (K_d = 30 mL/g), the effective K_d would be 4.8 mL/g. Importantly, for a bed depth of 1.5 m and 0.9 m^2 (10 ft^2) footprint (1.35 m^3 = 1350 L) with fill material with an effective K_d of 30 mL/g, we would expect to process approximately 30,000 liters before reaching 1% breakthrough (Fig. 9). These results are encouraging because it provides strong evidence that a decontamination operation that produces copious volumes of wash water can be filtered to remove the radioactive components using natural materials that may have lower K_d values than synthetic adsorbers that often require long lead times for delivery.

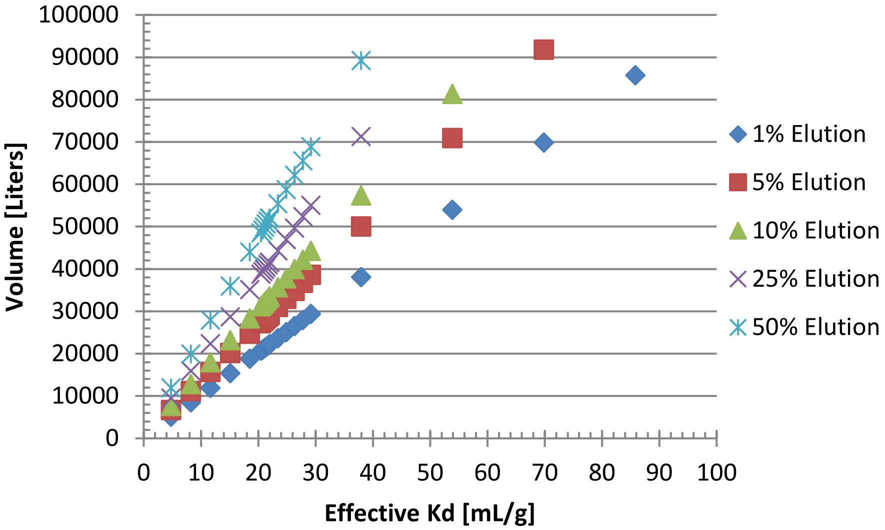

Figure 10. Total cleaned volume of wash solution vs. effective K_d.

CONCLUSIONS

Based on the IWATERS developed for cesium contaminations, we continue to develop the system for strontium contaminations. We tested potassium, calcium, and barium salt solutions to determine the efficacy of removing radioactive strontium from various building materials. In low-pressure flow tests, we found that tap water was effective in removing strontium from asphalt, glass, painted metal, vinyl siding, asphalt shingle and painted wood and addition of potassium salt was no more effective than tap water. K^+ did dramatically improve its removal from brick, but results from concrete were marginally improved.

High-pressure flow tests using tap water on concrete samples failed to remove strontium to the same level as the low-pressure flow tests except for tests using the shortest distance between the wand and the sample (highest pressure). We noted that a faster rate of movement of the sample under the sprayer led to higher percent removal of strontium.

Our modeling shows that a filtration bed composed of a sorbent with modest K_d values of 30 mL/g is capable of treating perhaps 20 times its volume in wash water.

We continue to evaluate wash water compositions to understand and improve the decontamination of strontium from building materials. It appears that a wash water composition of simple salts might be an effective approach and would be compatible with the formulation for the IWATERS for cesium contaminations. Follow-up studies include more detailed experiments to determine the effect of high pressure washing on decontamination, experiments determining the K_d values for various natural and synthetic adsorbents for Sr^{2+} ions in solutions containing alkali metal and alkali earth metal ions. Experimental data from these studies will then be used to model more accurately the predicted breakthrough. With this information, we can recommend a sorbent that would be sufficiently selective for Sr^{2+} ion, so that the wash waters could be recycled for continued wash down operations. Ultimately, we can generate a series of look-up tables that describe the dimensions of the filtration bed required to treat an expected volume of wash water.

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