

Sorption of Radionuclides to Building Materials and its Removal Using Simple Salts – 15452

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ABSTRACT

Decontamination after a nuclear or radiological release requires a detailed understanding of the materials hosting the contamination, the chemistry of the radionuclide, and the chemical properties of the decontamination agent. We have been studying the sorption chemistry of cesium onto urban building materials and roadways to develop simple decontamination methods that can be deployed for wide-area decontamination efforts. Our results include sorption/desorption of these radionuclides onto specific minerals found in some concrete and brick, and from monolithic coupons of concrete, asphalt, marble, tile, and brick as a function of time, age of contamination, and salt composition of the decontamination solutions. For example, we found that both the fine and coarse aggregate of concrete sorb cesium very well, and its desorption is much improved using 0.5M ammonium-based salts than at lower concentrations. Decontamination of cesium from asphalt was much improved when a surfactant was added to the salt to improve the wettability of the decontamination solution (40% removal compared to <20% when only salt was present in the solution). Decontamination of powdered cesium is significantly higher when salt is present (>80% removed) compared to tap water washes (40% removal) although we found no difference in the decontamination from asphalt. We have also tested the re-adsorption of these radionuclides from the decontamination solution onto solid supports to facilitate waste disposal and minimize collateral environmental contamination. For example, in ammonium solutions, montmorillonite clay sorbs cesium poorly, but vermiculite clay can remove >90% of the cesium at 0.5M NH_4^+ . With these results, we have been able to recommend simple salt solutions that can be effective on certain radioactive contaminations. These methods may be applicable to self-help activities in addition to wide-area decontamination efforts.

INTRODUCTION

Nuclear decontamination is a well-established field in the nuclear industry, practiced during routine operations [1] or in decommissioning of a nuclear facility [2]. Decontamination methods include various chemical and physical means of removing radioactivity so that the facility (and/or material therein) may continue in operation, handled with minimally incurred radiation dose, or disassembled for transport and disposal. While facility decontamination can be a very complicated undertaking, it is considered a small-scale operation compared to cleanup after a large, uncontrolled releases of radioactivity to the environment, as was the case with the Chernobyl nuclear reactor accident in 1986 and, most recently, with the reactor accidents at Fukushima. These accidents highlight the limited experience and lack of effective methods for performing wide-area decontamination, whether in a rural or urban environment. The threat of a malicious release of radioactive material as a dirty bomb or improvised nuclear weapon is an additional concern.

Decontamination of urban building materials after a nuclear or radiological release requires a detailed understanding of the materials hosting the contamination, the chemistry of the radionuclide, and the chemical properties of the decontamination agent. Washing cesium with water is generally ineffective as studies on water washes using a fire hose have demonstrated [3,4]. Sandalls [5] first reported the use of ammonium nitrate wash to remove cesium from building materials, employing its ion exchange properties that are very similar to cesium (cationic charge density and hydrated radii). Ahn et al. [6] employed ammonium-loaded clay suspensions to decontaminate cesium from brick and slate but found that the ammonium provided only marginal improvement in decontamination factors to the clay suspension alone. DeWitt et al. [7] found that ammonium concentrations generally above 0.2M improved decontamination factors only marginally on concrete, asphalt and clay tiles. Real et al. [8] reported dramatic improvements

in the removal of cesium after deposition as an aerosol from clay tile and concrete using ammonium solutions. Specific to decontamination after release from a radiological dispersal device, Drake and MacKinney [9] discussed the U.S. Environmental Protection Agency's mission to develop decontamination technologies and tools. Demmer et al. discussed research results [10] and advent of benchmark testing methods [11]. Most recently, the EPA has reported results from testing ionic formulations on concrete, granite, marble, limestone and asphalt [12-14], and Kaminski et al. [15] reported the development of a system for washing buildings and roadways with potassium or ammonium salt solution and containing the waters for recycle. We have been studying the sorption of cesium onto urban building materials and roadways to develop simple decontamination methods that can be deployed for wide area decontamination efforts.

METHODS

All chemicals used were reagent grade or better, and all solutions used deionized water (~18 MΩ•cm resistivity at 25 °C). The ammonium chloride solutions were prepared by adding the salt to tap water from the lab sink. The cesium-137 stock solution was analyzed by ICP-MS for potential contaminants. The results verified the purity of the stock solution (Table I). Cesium-137 in solution and sorbed to aggregate or coupons surfaces was monitored by gamma-ray spectroscopy (Minaxi NaI detector or Ortec HPGe detector) for the area within the 662 keV photopeak.

TABLE I. ICP-MS and gamma* analysis results of Cs-137 stock solution

Element	Concentration ($\mu\text{g/L}$)	Estimated Accuracy
Lithium	< 7.2	$\pm 13\%$
Boron	< 25.5	$\pm 18\%$
Sodium	120	$\pm 11\%$
Magnesium	< 3.1	$\pm 10\%$
Aluminum	< 28.8	$\pm 10\%$
Silicon	< 7.4	$\pm 10\%$
Potassium	133	$\pm 12\%$
Calcium	248	$\pm 10\%$
Iron	66.7	$\pm 10\%$
Rubidium	0.14	$\pm 10\%$
*Cs-137	17.8	$\pm 2\%$

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, approximately 5 g of concrete material (one of the following: cement pieces, fine aggregate or coarse aggregate) was weighed into a polystyrene test tube. An aliquot of 4.75 mL of deionized water was added to the sample. The sample was spiked with 0.25 mL of the Cs-137 stock solution and gently mixed for 60 minutes. Then, the sample was centrifuged and the supernatant was

removed before adding 5 mL of deionized water to rinse entrained liquid. The rinse was immediately removed. The contaminated sample was wrapped in plastic for gamma analysis and counted 18 cm from the detector face.

Decontamination of the sample was performed by adding five mL of a wash solution to the test tube, and the sample gently mixed for 60 minutes. After decontamination, the samples were centrifuged and the wash solution was removed. A rinse of five mL of deionized water was added to the sample and removed immediately. The decontaminated aggregate samples were analyzed 18 cm from the detector face. Single samples were run for all tests in this section unless specified otherwise.

Coupons

Concrete monolithic coupons were prepared by adding 83 mL of deionized water per kg of concrete mix. It was mixed for three minutes and allowed to rest. It was mixed again for another three minutes before it was scooped into 1.5” tall x 1.25” diameter pieces of PVC pipe. It was pressed to remove voids in the concrete. The top surface was smoothed with a spatula to give it a smooth surface. The monoliths were covered with plastic and kept moist by misting occasionally with water and removed from the mold after 10 to 15 days and kept in a moist environment. The monoliths were ready for use after 40 days of curing. Then, a thin layer of epoxy was applied to the sides of the monoliths to prevent sorption of solution.

For the flow testing, additional coupons (red brick, limestone, granite, concrete, and asphalt) were supplied by EPA (Table II) as part of material used in a broader testing program. Note that the asphalt depicted in Fig. 1 has aggregates to the surface.

TABLE II. 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



Figure 1. Typical coupons of concrete (left) and asphalt (right).

Substrate coupons were contaminated by using a pipette to spread 100 μL of a dilute Cs-137 stock solution on the coupon surface. The coupons were left until they were visibly dry, at which point they were wrapped in plastic and left overnight for gamma counting in the morning.

Coupons were contaminated with powdered CsCl after spiking with Cs-137 tracer and evaporating to dryness. To do this, the powdered CsCl was placed on a plastic the coupon face was lightly ground into the powder.

Static soak tests

The first set of tests was performed on concrete coupons. After contamination and overnight aging, the coupons were suspended on a Teflon® grid for 1 hour in 6 mL of solution (deionized water, tap water, and ammonium salt solutions) in a Petri dish. As selected time intervals, 200 μL aliquots were withdrawn for gamma analysis. The 1-hr soak times may not prove practical for many applications, so shorter times were investigated. In the next set of scoping tests, we exposed the five materials to 0.1 M and 0.5 M ammonium chloride solutions. For each substrate, three contaminated coupons were placed in 10 mL of 0.1 M ammonium chloride, and three coupons were placed in 10 mL of 0.5 M ammonium chloride. (The coupons were placed contaminated side down on a Teflon® grid to eliminate any wetting problems.) Each coupon was exposed to the wash solution for three minutes, after which it was rinsed for 2-3 seconds with deionized water and left to dry overnight. Solution aliquots were also removed from each Petri dish for gamma counting.

Flow test

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 2 x 4 in. (5 x 10 cm) sheet of Parafilm™ to prevent the wash water from dripping across the backside of the Teflon® holder.

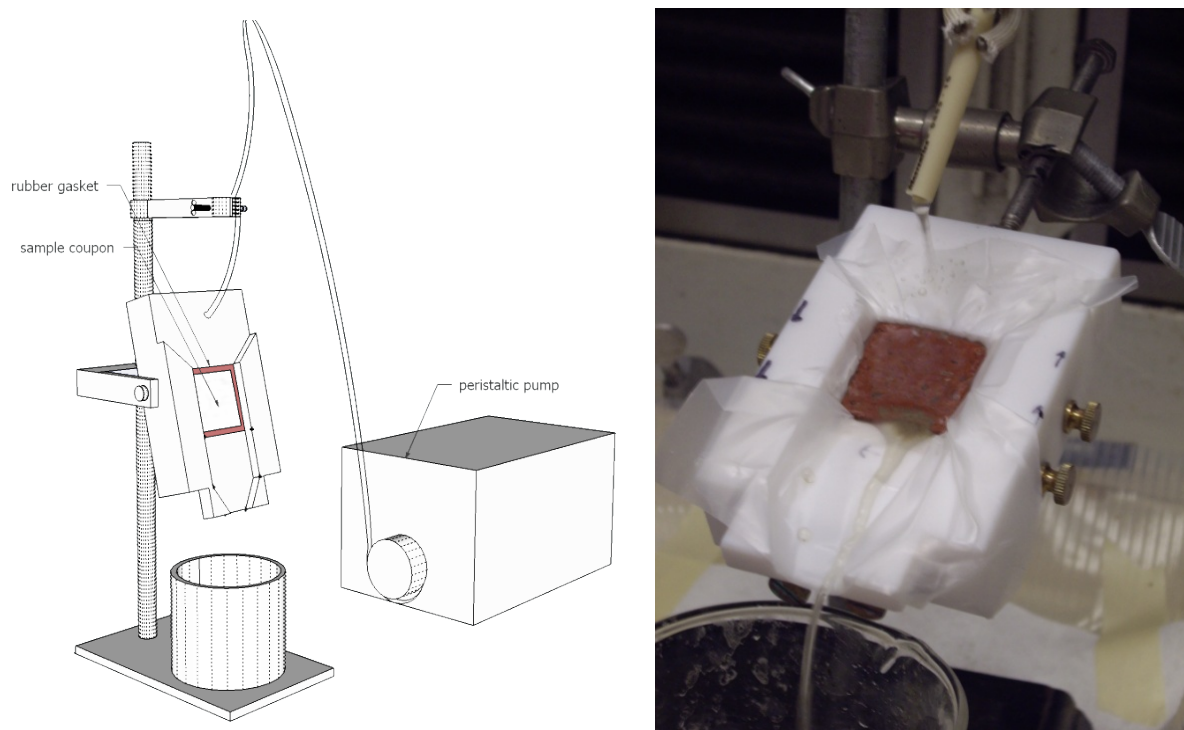


Figure 2. Schematic of flow system (left). A wash solution is pumped into the hood and flows over a brick coupon and into the collection beaker (right).

Sorption tests onto clays

Grace vermiculite (Specialty Vermiculite Co.) and bentonite (K10, Aldrich) slurry at concentrations of 40, 50, 75, 100, and 125 mg/mL were tested in 0.5 M NH_4Cl . All slurries were performed in duplicate, and aliquots were taken at 10, 30, and 60 min for gamma counting. The 125 μL of 1.2 M NH_4Cl spike solution was added directly before the Cs stock spike, and the NH_4^+ was not allowed to pre-equilibrate with the clay.

RESULTS AND DISCUSSION

Concrete aggregate batch tests

Ammonium chloride was shown to be an effective wash solution for removing cesium from concrete. We examined the decontamination of concrete coarse aggregate as a function of ammonium chloride concentration and observed an increase in cesium removal as the ammonium chloride concentration increased (Figure 3). In separate batch tests, the fine aggregate showed similar sorption behavior to the coarse aggregate while the concrete pieces could be much more easily decontaminated of the cesium even at very low ammonium or other salt concentrations. The data on the fine aggregate and concrete pieces will not be discussed further.

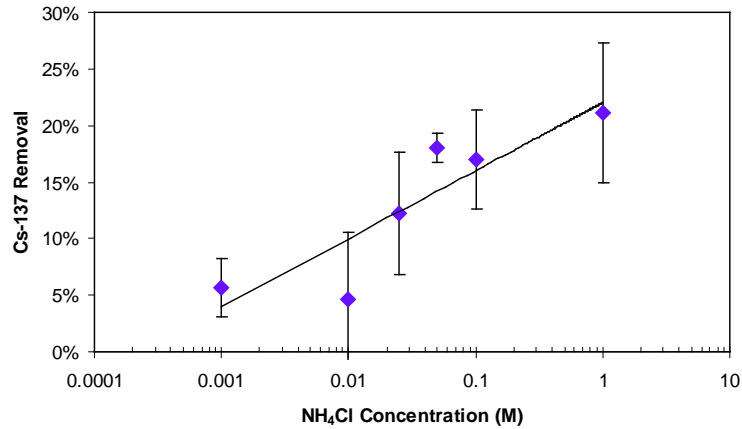


Figure 3. Decontamination of Cs-137 (in % removed) from coarse aggregate as a function of ammonium chloride concentration.

Static soak tests

The purpose of the test was to determine the effect of salt concentration on coupon decontamination as a function of soak time. The results (Fig. 4) show that the higher salt concentration produces high decontamination (percent Cs-137 removed), as expected. At 10 mM and 0.5 M, the decontamination continued to improve for soak times up to the 60 min limit we applied in these tests.

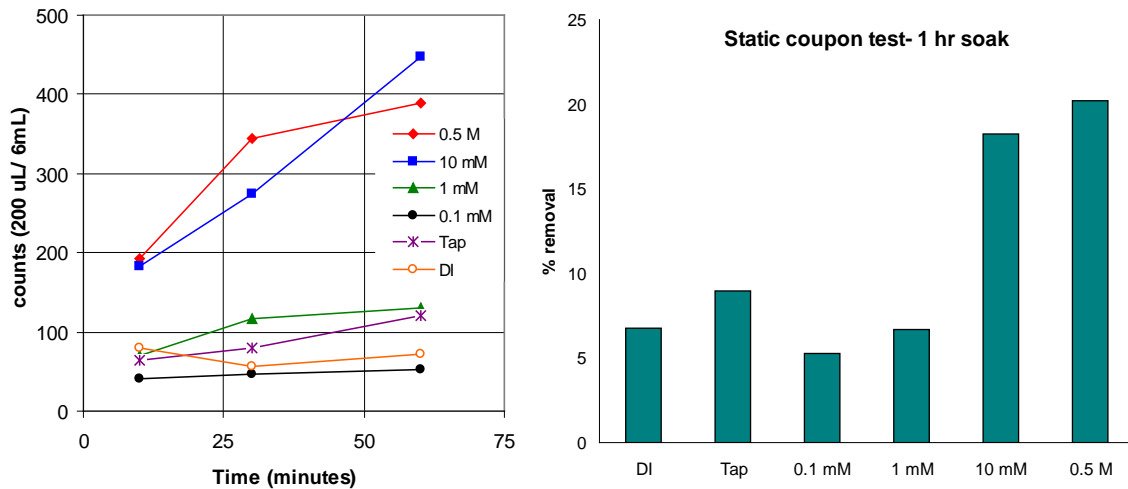


Figure 4. Activity of Cs-137 in solution (left) and % removal from the surface of concrete coupons into various salt solutions.

From these initial tests and despite the large error bars (Fig. 5), it is clear that the higher salt solution desorbs cesium better from all the coupon materials, as expected.

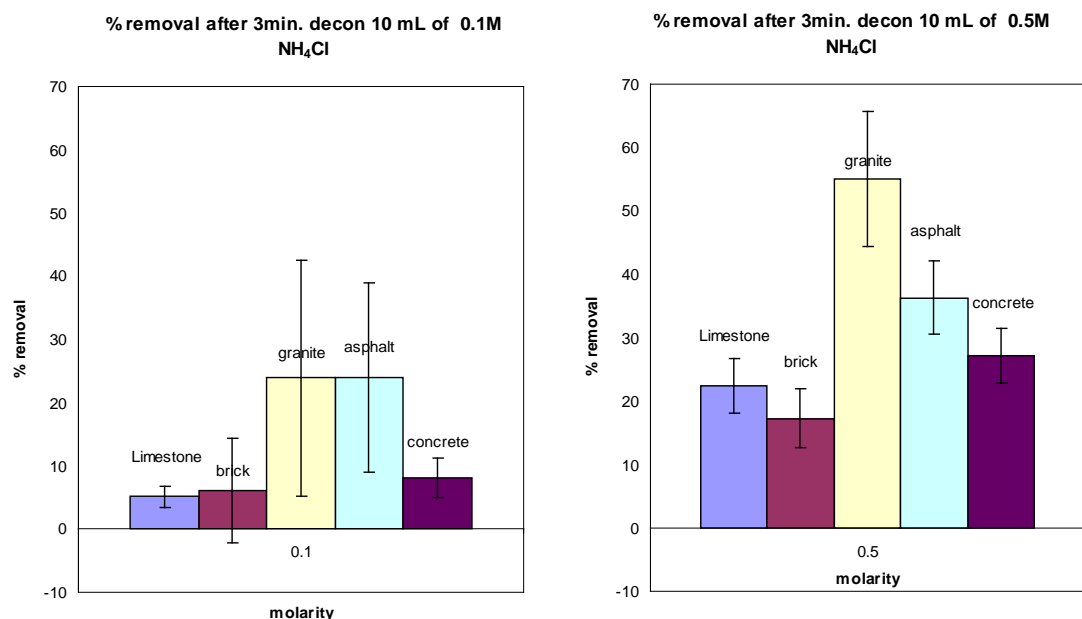


Figure 5. Desorption of cesium (percent removed) from the five substrates into 0.1 M (left) and 0.5 M (right) NH_4Cl after a three-minute soak period.

To investigate the effect of wet versus dry deposition, we completed flow tests (100 mL/min) comparing decontamination of cesium deposited in dry form and in soluble or wet form on concrete coupons (Fig. 6). The decontamination of dry cesium with tap water or 0.5 M NH_4Cl was much improved over decontamination of wet cesium using 0.5 M NH_4Cl . For dry deposition, we achieved 75-80% decontamination with the NH_4^+ and highly variable decontamination of 32-70% with tap water. We then performed successive decontaminations of the cesium after dry and wet deposition (Fig. 6). Decontamination of cesium was little improved with successive steps, even in the dry deposition cases. Note that this behavior may result from solubilized cesium becoming immediately bound to the concrete during the time scale of the experiment. This may point to the need, in some cases, for higher flow rates to minimize the time cesium has to bind to the substrate.

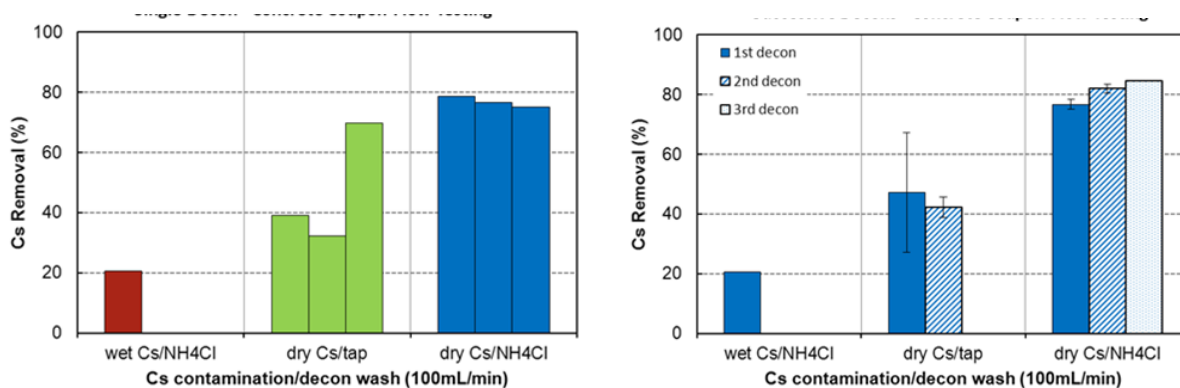


Figure 6. Single (left) and successive decontaminations (right) of cesium from concrete coupons for dry and wet deposition.

Identical tests were completed on asphalt coupons after dry and wet deposition of cesium as those reported above for concrete (Fig. 7). First, the inclusion of a wetting agent (sodium dodecyl sulfate) markedly improved decontamination and we suspect this was due to the visibly improved coverage of the asphalt surface by the wash water during the flow tests. Flow tests with tap water or salt produced isolated rivulets down the coupon surface. Comparing wet and dry contamination, we note that even tap water can be very effective against dry deposition. Successive decontamination experiments were also completed on the samples of asphalt that had been prepared by dry deposition of cesium. The decontamination improved slightly, from 93% to an average of 95% total removed after two decontaminations.

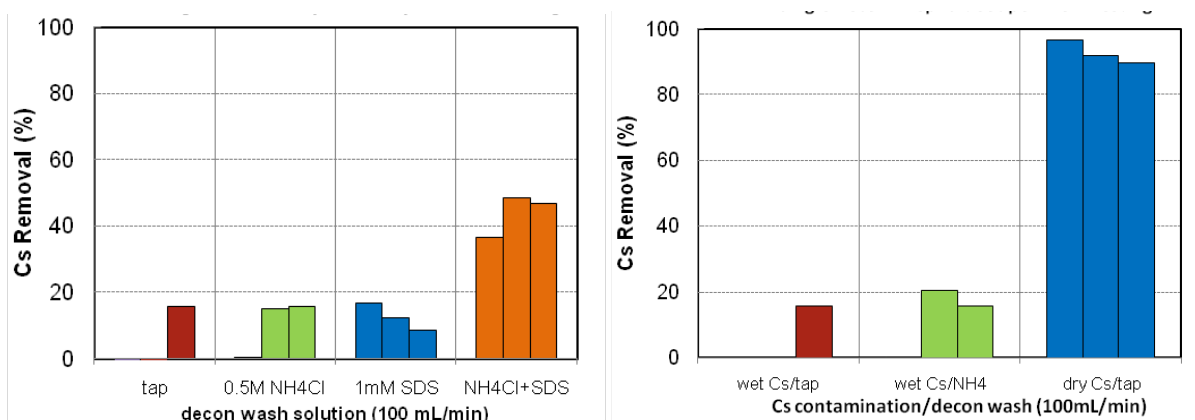


Figure 7. Decontamination of Cs-137 from asphalt coupons in flow tests following wet deposition of cesium (left) into several wash solutions and its removal for dry and wet deposition of cesium.

Sorption tests onto clays

Assuming we can deploy a salt water wash to the building materials, then we must have methods to contain the runoff and avert potential downstream contamination (e.g., sewer systems, water reclamation plants, rivers and drainage basins). To counter cesium mobility, we investigated the use of common solid sequestering agents to remove cesium from solution and provide a means of filtering the wash waters for reuse or disposal. Based on a literature review, the clays of vermiculite and montmorillonite were found to be potentially superior to other clays, rocks, or other common materials. Using the 0.5M NH_4Cl wash solution, we found that Cs-137 may be removed better using the vermiculite clay than montmorillonite (Fig. 8), although high slurry loadings may be necessary and a series of slurry treatments. That is, the wash water would need to be mixed and separated with the clay in successive stages in order to remove cesium to permit water reuse. The exact values cannot be computed since the reuse limits have not been established. However, to remove 99% of cesium using vermiculite would require 2 stages of mixing at a slurry concentration of 100g/L.

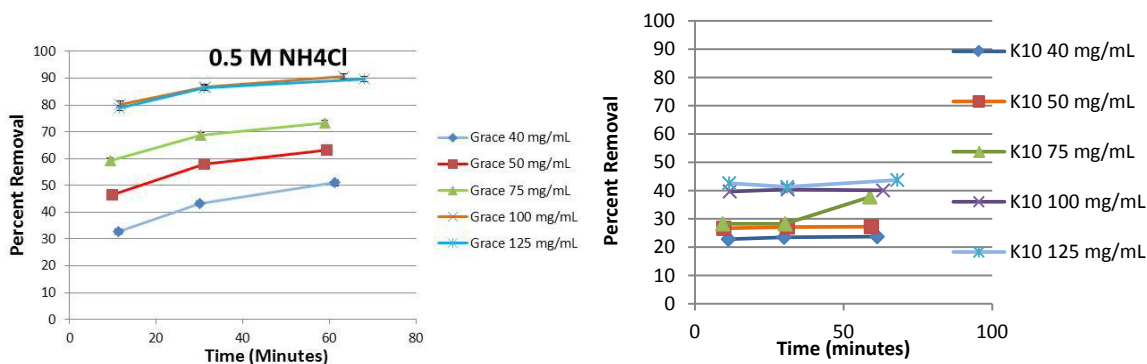


Figure 8. Percent cesium removal from batch tests as a function of Grace vermiculite (left) and K10 montmorillonite (right) slurry concentrations in 0.5 M NH₄Cl.

CONCLUSIONS

We have established the concentration of ammonium salt solutions needed to maximize removal of Cs-137 from a common concrete formulation by showing that improved decontamination factors can be obtained more consistently with 0.5M NH₄Cl than even 0.1M. The results are consistent between the concrete, asphalt, granite, brick, and limestone surfaces we tested. In addition, we saw a dramatic improvement in the decontamination of cesium that was deposited dry onto asphalt and concrete surfaces and the difficulty in removing cesium from such coupons once it had dissolved. This supports previous studies and highlights the importance in being able to perform decontamination activities quickly to maximize removal. Once removed, we found that vermiculite clay is effective in selectively sorbing cesium even from high ammonium salt solutions.

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