Irreversible Wash Aid Additive for Mitigation of Urban, Radioactive Contaminations – 14328

Michael Kaminski *, Carol Mertz *, Nadia Kivenas *
* Argonne National Laboratory

ABSTRACT

After a large release of radioactive material, urban areas may be contaminated, compromising response efforts by first responders and law enforcement officials. In such an event, it may be important to deploy mitigation efforts in certain areas in order to restore response activities and public services. Argonne, working with the U.S. EPA has explored the state-of-the-art for a wash system. The goal of this system is to rapidly return critical infrastructure components to service following a Cs-137 radiological dispersal device (RDD) release while avoiding spread of Cs-137 beyond its original deposition area and minimizing the amount of Cs-137-contaminated wastewater.

The wash aid system consists of a water-based decontamination agent that employs highly soluble salts and surfactants to effect ion replacement reactions with cesium and improve wettability onto hydrophobic surfaces. The now-mobile cesium carried by the wash water is captured in the wash water by solid sequestering agents suspended in the wash water. Using additional sequestering agent at the street level, one can reduce contamination levels in the water such that the wash water can be recycled for reuse thereby reducing the demand for water for decontamination operations. This wash water can be collected into a temporary reservoir created by collapsible berm systems currently deployed worldwide to control flood waters.

Through a review of the literature and laboratory studies, we down-selected candidate salts, surfactants, and solid sequestering agents that can be integrated into a wash aid to effectively reduce surface contamination and capture the mobile cesium to prevent downstream environmental contamination.

The prototype system employs salt at concentrations between 0.1-0.5M out the fire nozzle while the use of 1 mM surfactant dramatically improves the decontamination of cesium from asphalt. The results suggest that we can remove >95% of dry cesium depending on the chemical form and substrate but decontamination of 40% of the cesium should be expected for depositions that have been solubilized by moisture in the air or by rainwater or other precipitation. Specific clays can be spread across the reservoir to actively sorb the cesium and permit reuse of the wash water. Using 100 g/L slurry concentration, up to 80% of the cesium can be sorbed in a single step and commercial-off-the-shelf systems like the centrifugal separators and bag filters provide a means of recycling the wash waters for reuse. Additional treatments can be performed on site to further reduce cesium concentrations in the wash for reuse.

INTRODUCTION

After a large release of radioactive material, urban areas may be contaminated, compromising response efforts by first responders and law enforcement officials. In such an event, it may be important to deploy mitigation efforts in certain areas in order to restore response activities and public services. Argonne with the U.S. EPA has explored the state-of-the-art for a wash system. The goal of this system is to rapidly return critical infrastructure components to service following a Cs-137 radiological dispersal device (RDD) release while avoiding spread of Cs-137 beyond its original deposition area and minimizing the amount of Cs-137-contaminated wastewater.

Mitigation of a contaminated area can be envisioned using many different approaches. Of those available we chose to develop the technique of 1) washing down the contamination zone, 2) introducing sequestering agents into the wash water to bind the radionuclides, 3) containing the wash water locally, 4) treating the wash water to permit free release or reuse, 5) and disposing of the sequestering agents. Therefore, we completed a perusal of commercial vendors and suppliers to determine the COTS equipment that can be purchased, stockpiled, or is immediately available either locally, regionally, or nationally to deploy the wash aid system. We supplemented the literature data with experiments to determine the wash solution composition to produce the highest decontamination factors, the sequestering agent to selectively remove the cesium in the presence of high salt, the method of collecting the wash water runoff, and the method of filtering the solid sequestering agent form the wash water to permit the water's reuse.

METHODS

Concrete Aggregate Testing

A commercially-available concrete mix (Quickrete®, from a local home supply store) was separated by sieving into the following sizes: 0.15-2mm and >2 mm. The coarse aggregate fraction was >2 mm and comprised 40% of the concrete mix and was rinsed with deionized water (DIW) and dried before testing.

To contaminate the samples, approximately 5 g of concrete material was weighed into a polystyrene test tube. An aliquot of 4.75 mL of DIW 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 analysis. The sample was placed 18 cm from the face of a high purity gamma detector (HPGE, EG&G ORTEC) and counted for a 300 seconds live time and integration of the 662 keV photopeak indicating Cs-137.

Decontamination of the sample was performed by adding five mL of a wash solution to the test tube. The sample was gently mixed with the wash solution for 60 minutes. After decontamination, the samples were centrifuged and the wash solution was removed. A rinse of five mL of DIW was added to the sample and then removed immediately. The decontaminated aggregate samples were analyzed 18 cm from the detector face as described above. Triplicate samples were run.

Decontamination of Cesium from Asphalt Coupons

Asphalt and concrete coupon samples were obtained from the Environmental Protection Agency as part of their sample testing program (National Homeland Security Research Center, Dr. Sangdon Lee). The asphalt was pressed in the laboratory using source materials form the North Carolina Department of Transportation. The concrete mix (Quickrete®) was obtained from a local home supply store. Concrete coupons (1" cubes) were contaminated by using a pipette to spread 100 µL of a dilute Cs-137 stock solution on the material surface. The coupons were left until they were visibly dry, at which point they were wrapped in plastic wrap and counted with the HPGe the next day. To prepare coupons with dry deposition of cesium contamination, cesium-137 chloride was dried uniformly across a piece of Parafilm® and the face of the coupon was ground into the dried salt. The sample was then wrapped in plastic wrap as before and counted. In scoping tests, we pipetted 5 mL of tap water, 0.5M salt, or 1 mM anionic surfactant across the coupon face to assess the decontamination. In flow tests, the coupons were subjected to 100 mL/min flow using a custom-built Teflon® sample holder (Fig. 1). Flow tests used 0.5M salt +1 mM anionic surfactant. These tests were performed in triplicate.

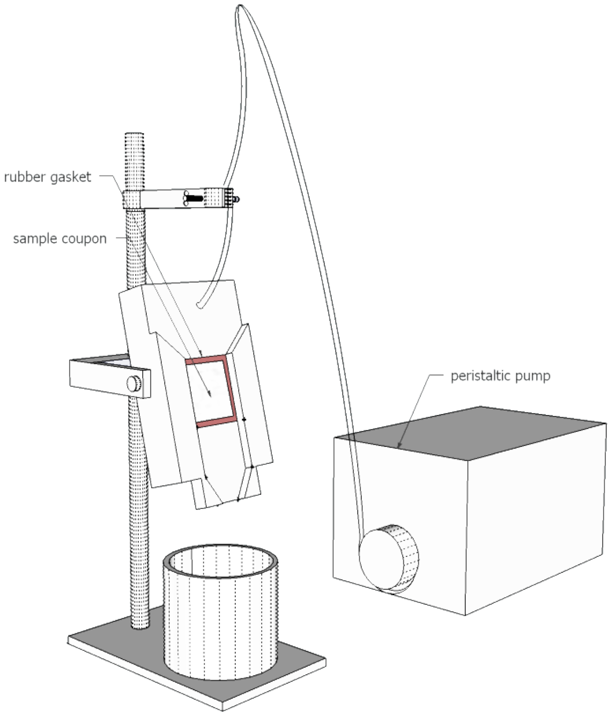

Figure 1. Schematic of flow system the permits passing wash water over a coupon and collecting the runoff for analysis. The peristaltic pump draw fluid from a small glass reservoir (not shown).

Sorption of Salt onto Sequestering Agents

After a review of the literature (not shown), we down-selected several materials as candidates to serve as a sequestering agent for cesium and to serve as controls (SiO_2). These materials include: crystalline silico-titanate, $Na_2(H_2O)_2Ti_4O_5(OH)(SiO_4)_2Na(H_2O)_{1.7}$ a synthetic zeolite sold under the trade name IONSIV®IE-911 (UOP) with properties tailored toward cesium sorption in high sodium solutions; montmorillonite clay, $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$ the most common clay material studied and implemented in the industry for radionuclide sequestration (Fischer Scientific USA as K-10, American Colloid Co.); vermiculite clay, $(Mg,Fe^{2+},Al)_3(Al,Si)_4O_{10}(OH)_2 \bullet 4(H_2O)$ a clay with perhaps the most selectivity for cesium over competing alkali metal cations (W.R. Grace & Co., Cambridge, MA, as VCX™ Vermiculite Ore Concentrate); illite, $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$, a high-capacity clay (Xuzhou Zhonglian Chemical Technology Co., Ltd); and chabazite, $(Sr,Ca,K_2,Na_2)[Al_2Si_4O_{12}] \bullet 6(H_2O)$ a natural zeolite (St. Cloud Mining Co., Winston, New Mexico). The negative control was silica in the form of diatomaceous earth (Celite Corporation). Illite and vermiculite were washed with DIW and centrifuged four times to remove any dust or water-soluble impurities. The supernatant was removed with a disposable transfer pipette after each centrifugation and replaced with new DIW. Each washed sample was placed in a glass petri dish and dried in an oven at 398K for 22 hours. Samples were then placed in a dessicator. All other sorbents were used as received.

Salts were obtained from Sigma-Aldrich and Millinckrodt as 99.5+% A.C.S. reagent grade or analytical AR grade and their solutions prepared with deionized H_2O (~18MΩ•cm resistivity at 25°C) or Chicago tap water.

We completed experiments to determine the kinetics for sorption and the percent of cesium removed as a function of slurry concentration (mass of solid/volume of Cs solution) and salt concentration. This involved mixing 10-100 mg of solid with 1 mL of solution for 60 min (rotary mixer) before centrifuging the sample and withdrawing aliquots for gamma counting of the Cs-137 tracer (Minaxi γ Auto-Gamma 5000 Series Gamma Counter, United Technologies Packard, Model A5550 using 12 x 75 polypropylene tubes). Material was weighed into 1.5mL microcentrifuge tubes (Ambion).

Contaminated Water Filtration

For lab tests, the Lakos Portable Test Rig that included 3/8” Lakos Separator (IL-0037B, 3-6 gpm nominal) operated by a self-priming pump (Dayton® ½ HP, 7000 rpm, 25 GPM maximum, Fig. 2) was used. This system was integrated with a Separmatic pressurized fabric filter system (closed tank system, 16 gal/min, 16 ft^2 filter surface area, 3450 rpm ½ HP centrifugal pump) where the LAKOS unit was the primary filter with the discharge fed directly into the pressurized filter tank of the Separmatic unit (Fig. 2) for final clarification. The discharge from the Separmatic filter would be free of suspended material. These tests were designed to determine the filter efficiency. After filling the 75 gallon feed tank with tap water, salt was dissolved into it to produce a 0.5M solution. Then, 69 lbs. of clay (10% slurry) was added and stirred for 10 min using a dual blade mixer. This was fed into the LAKOS unit using the ½ HP self-priming pump. Samples were collected from the feed into the LAKOS, the discharge from the LAKOS and feed into the Separmatic filter, the discharge from the Separmatic filter, and the purge from the LAKOS unit.

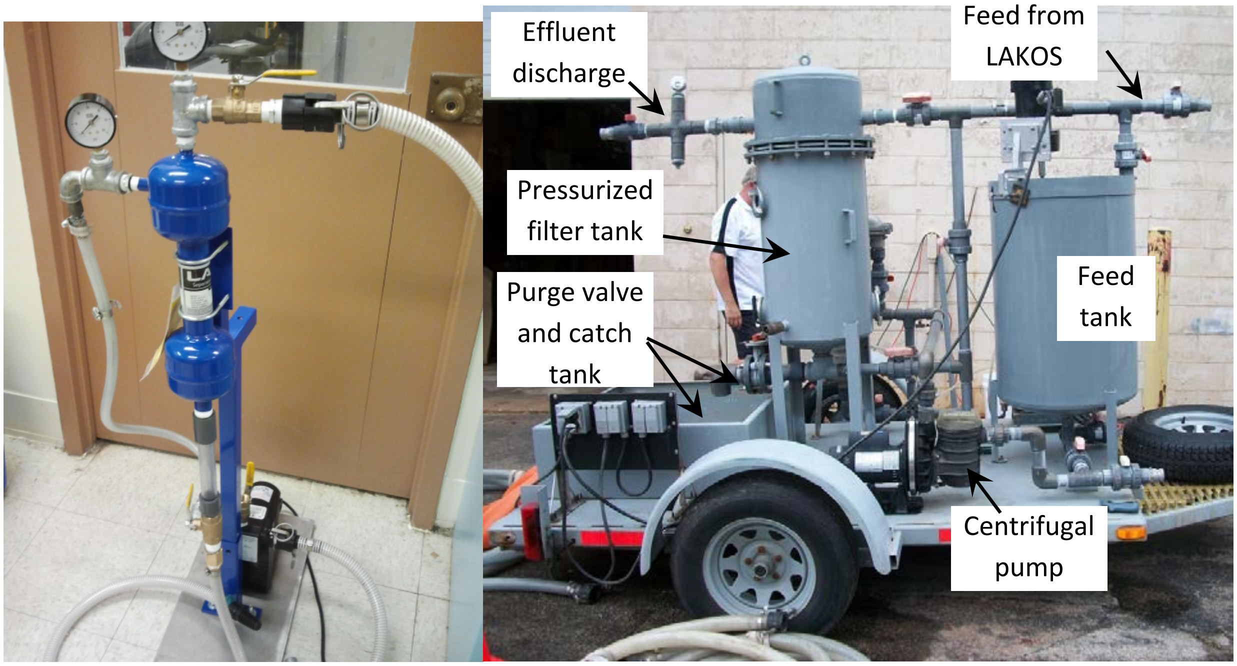

Figure 2. The LAKOS centrifugal filter, portable test rig and the small-scale Separmatic Systems® pressurized filter skid module. The LAKOS was mounted onto the Separmatic skid and connected in series for pilot-scale testing.

RESULTS AND DISCUSSION

The Wash Solution

An important consideration in developing a wash solution for radioactive contamination mitigation outdoors is to avoid introducing additional chemical hazards. Not only would a large volume of mixed waste be produced, which is extremely expensive and difficult to dispose, the outdoor environment of the mitigation operations would preclude worker safety. Our previous work in the development of non-hazardous wash solutions was based on the ability of common salts in high concentration to readily exchange with sorbed cesium. We surveyed commonly available salts distributed in large quantities locally and regionally. Our work in this area (unpublished data) showed that various ammonium and potassium salts were more effective in desorbing cesium from porous building materials such as the aggregates from concrete, crushed tiles, and crushed brick over other alkali metal, alkaline earth, and transition metal salts or chelators and surfactants (unpublished data).

Decontamination factors or the percent of cesium removed from the concrete, for instance, was concentration dependent (Fig. 3) where concentrations of salt above 0.05M were most effective. Further data collected over the last ten years showed that consistent results could be obtained with salts concentrations >0.1M. Tests above 1.0M were not conducted but higher concentrations are more difficult to generate in the field in large quantities.

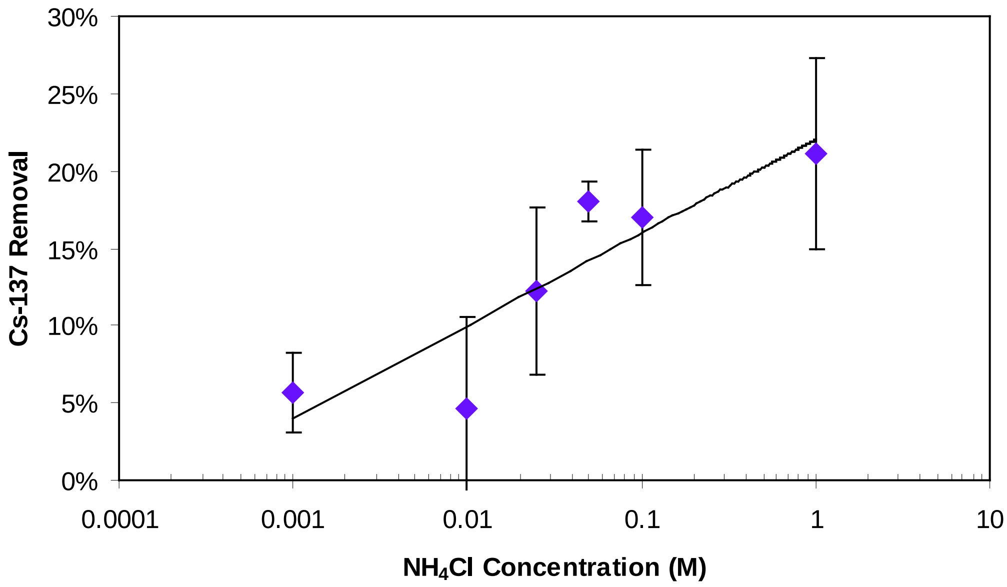

Figure 3. Decontamination of Cs-137 (in % removed) from coarse aggregate of concrete derived from river rock as a function of ammonium chloride concentration.

From these data, we assumed the same cations would be effective toward asphalt (Fig. 4) and found that the use of surfactant to improve the wettability of the wash solution could dramatically improve the removal of cesium sorbed onto the asphalt surface.

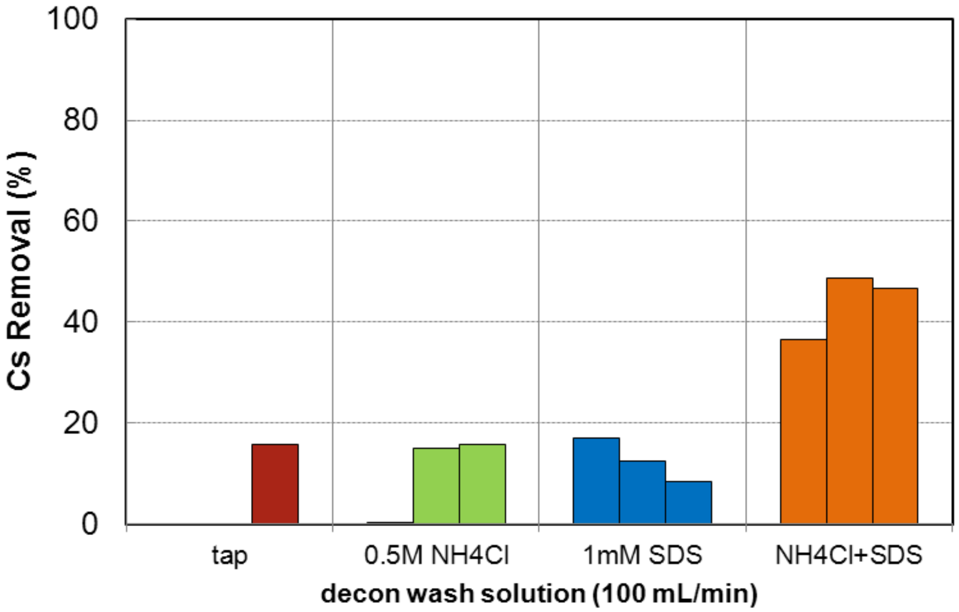

Figure 4. Decontamination of cesium from asphalt coupons. Samples were rinsed by pipetting 5 mL of tap water, 0.5M NH4Cl, or 1 mM SDS in scoping tests across the coupon face. Flow

tests used 100 mL of 0.5M NH_4Cl+1 mM SDS passed over the face of the coupon at a rate of 100 mL/min.

Next, (Fig. 5) the effect of dissolved cesium (wet) deposition or dry cesium deposition was tested. Here, the improved removal of dry deposits into the wash solution was evident with nearly 80% removal of dry cesium salt from concrete and >95% removal from asphalt.

Since large volumes of salt water are needed at this concentration, we do not expect to draw from a reservoir of solution at this concentration. Instead, we expect that a concentrated brine tank can be established at the site and this solution could be drawn into the fire hose using conventional drafting techniques. Drafting employs an eductor nozzle that mixes the hydrant fluid was the brine solution.

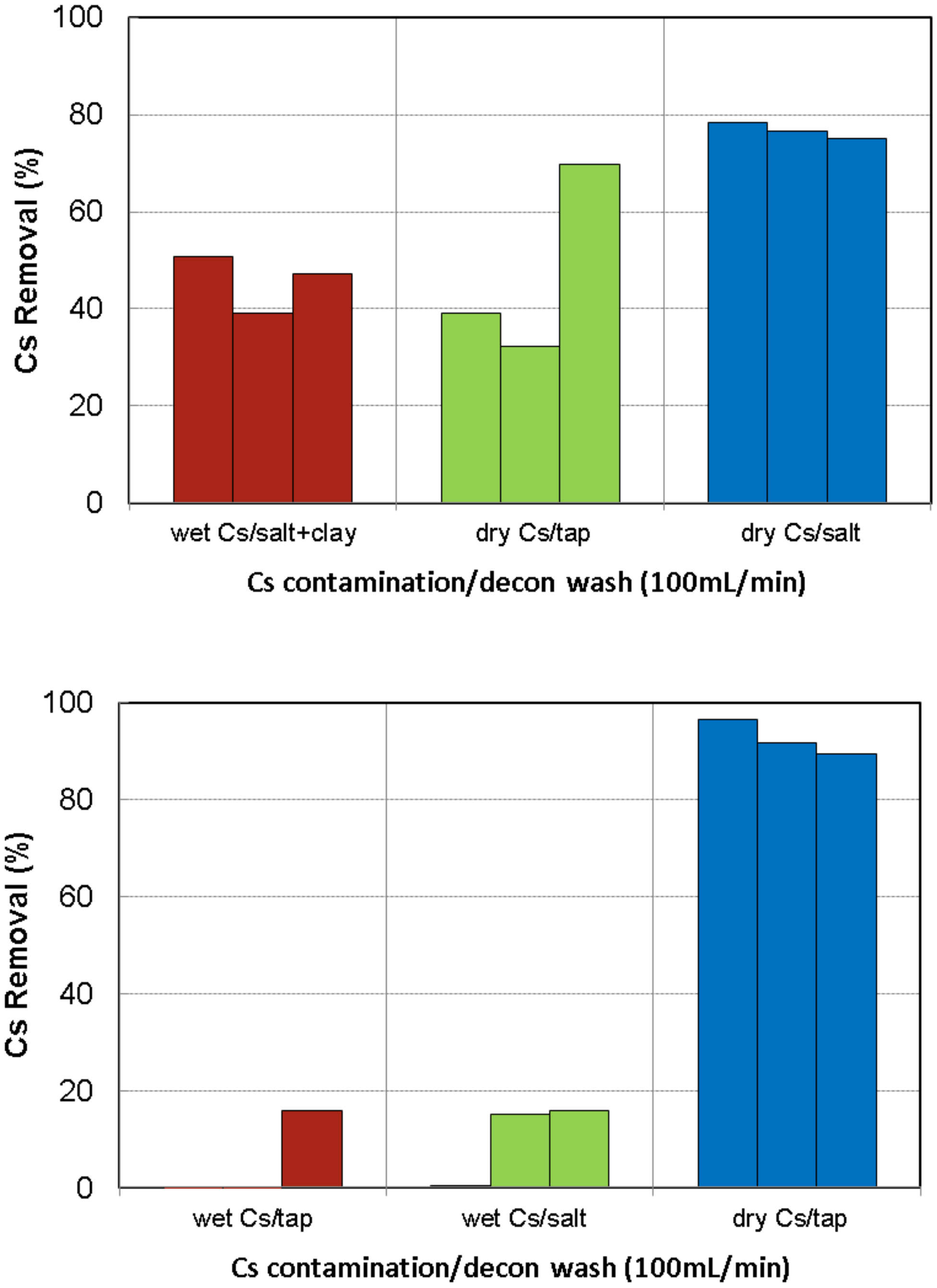

Figure 5. Percent removal of cesium from concrete (top) and asphalt (bottom) coupons in flow tests using either dissolved or powdered cesium salt as the contamination source.

The Solid Sequestering Agent

As the wash waters pass over the contaminated surfaces of the buildings, roadways, and vehicles, the radioactive cesium will accumulate in the wash. Sequestering the radioactivity onto solid substrates as quickly as possible is preferred in order to limit cross-contamination and facilitate the separation of radioactivity from the wash water for its potential reuse or free-discharge. We considered including a solid sequestering agent into the educator system so that both the salt and sequestering agent would bath the contaminated surfaces simultaneously. However, tests showed that this approach is counterproductive (unpublished data). The excess salt cations simply overload the sorption sites on the solid sequestering agents rapidly rendering them ineffective against sequestering the radioactive cesium and simultaneously lowering the effective free salt concentration in the wash water; the lower free salt concentration translates into a lower decontamination factors for cesium.

In this system, the runoff from the contamination zone will be contained within a temporary reservoir. The solid sequestering agent can be spread across the ground within the contamination zone and within the area of runoff accumulation to effect mixing the contaminated runoff immediately with the solid sequestering agent.

The sequestering agent would mix with the incoming cesium-laden wash waters and serve several purposes and thus may require different sequestering agents to meet the differing goals. In all cases, the sequestering agent must have good selectivity for cesium at trace concentrations over 100's of millimolar concentrations of monovalent salt. A material that is readily available in sufficient quantity regionally or locally is preferred, since it is likely that substantial quantities of material will be needed in this function. Next, we may wish to use a sequestering material to create the berms that will form the walls of the reservoir. Even though the reservoir walls should be impermeable to water, an engineering backup may be prudent in case there is permeate. Filling the berm with sequestering agent would provide a means of decontaminating water in situ to mitigate this potential contamination source. After collecting the contaminated wash water (contains contaminated salt water and sequestering agent in suspension), the sequestering agent must be filtered from the wash water. It is highly unlikely that this initial water filtration will reduce cesium concentrations in the water to below discharge standards so additional separation or "cleanup" of cesium will be required. "Cleanup" of cesium can be performed in batch or continuous operations but should be capable of processing very large volumes of water.

Various sorbents were tested further in the presence of different pure salts (in deionized water) and a range of concentrations (0.1mM – 500mM). Clays have been known for many years to be candidate materials for the irreversible sequestration of cesium and other radionuclides [1]. The engineered sorbent based on silicotitanates marked an important development in tailored sorbents due to its remarkable selectivity in the presence of high alkali metal salt [2]. From salt solutions (Fig. 6), illite and SiO_2 sorb cesium poorly except at the lowest salt concentration. Salt >0.1M decreased sorption significantly among the other agents with CST also performing poorly at 0.5M. The best solid in the presence of this particular salt was chabazite followed by vermiculite but with K_d's <100 mL/g at 0.5M salt.

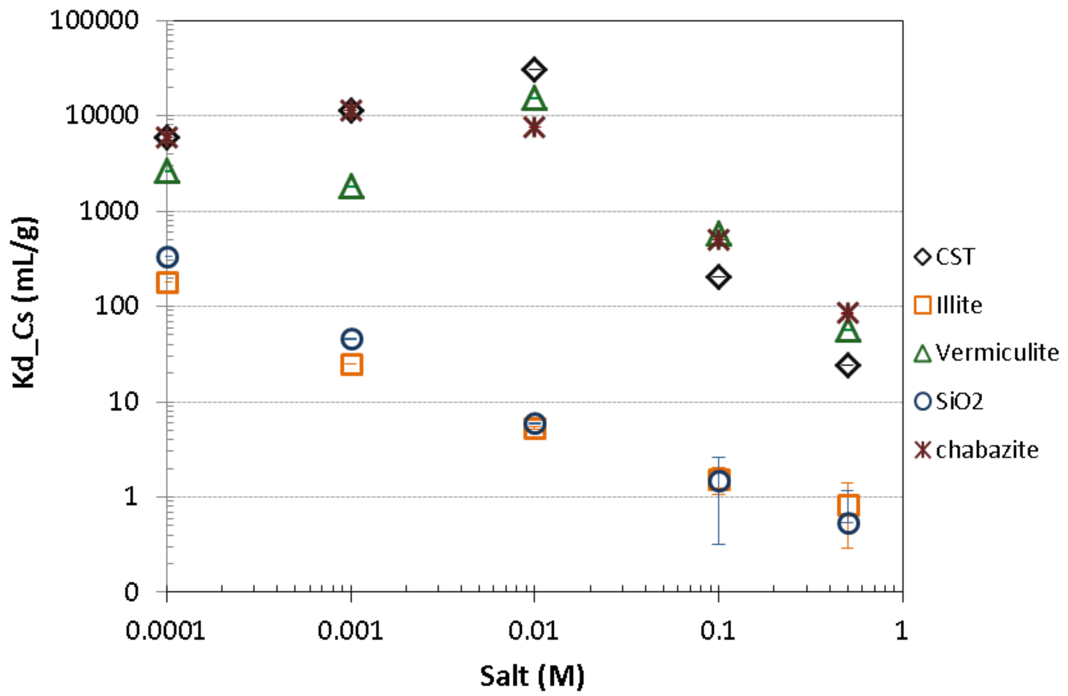

Figure 6. Sorption of cesium onto sequestering agent candidates as a function of monovalent salt concentration in solution (10 mg solid in 1 mL water. Tests in triplicate and samples counted in duplicate. The standard deviation between samples was <5% for most tests except those with very low sorption). CST= modified crystalline silico-titanate.

To understand the effect of slurry concentration on cesium sorption, the slurry concentration was increased at constant salt concentration of 0.5M, since this was our target salt concentration for radiation mitigation. First, considering kinetics (Fig. 7), the vermiculite approached equilibrium after 60 minutes and there was no benefit to increasing the clay slurry concentration above 100 mg/mL for both clays; vermiculite removes 90% of the cesium while K10 montmorillonite removes slightly more than 40% in 0.5M salt at both 100 and 125 mg/mL (data not shown).

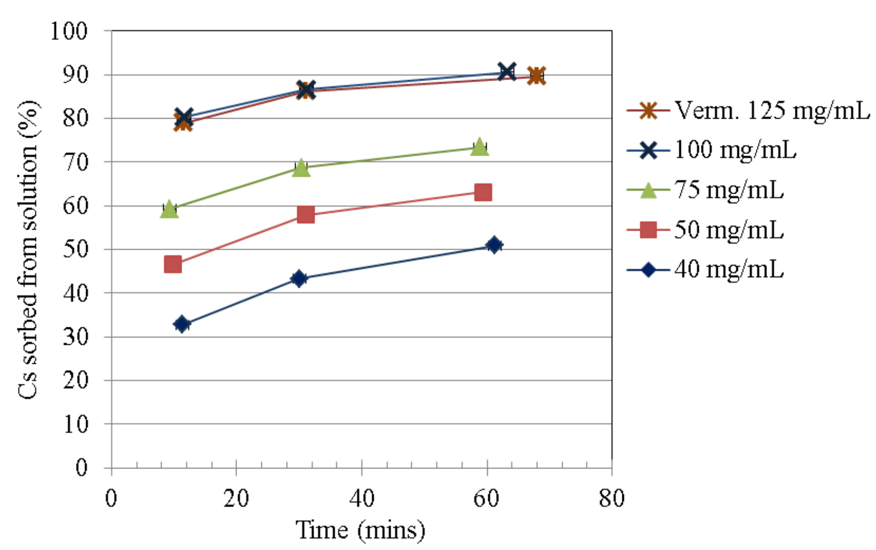

Figure 7. Kinetics for cesium sorption from 0.5M salt solution onto vermiculite and as a function of clay slurry concentration. Standard deviations were <5% except at 75 mg/mL where standard deviations were 14% between duplicate counting samples.

Containing the Contaminated Water for Filtration and Reuse

Although the chemical composition of the wash water was discussed, the utility of the clay as a sequestering agent for dissolved radioactive cesium, and the method of preparing the wash water for dissemination, we have not addressed the method of collecting and capturing the wash waters as they are generated and the method of treating such waters for reuse and disposal. A primary concern that was raised by members of EPA and the Water Environment Research Foundation (private communication) was the potential for contaminating the sewer system and the downstream water reclamation plants. To minimize such contamination, we focused on systems that can retain water at the street level with on-site treatment.

Because of the potential volume of water, 10's of thousands of gallons to millions of gallons, we cannot expect collapsible tanks to be sufficiently large and available to capture the wash waters until they can be processed and discharged. Instead, we searched for methods of creating reservoirs at the mitigation site to prepare and contain voluminous wash waters.

There are several types of collapsible berm concepts. These products are superior to sand bagging because miles of berm can be filled in a much shorter period than with sand bags, once berm units arrive on site. Large sections can be set-up and filled with material available immediate to the site such as sand, dirt, or rocks. Unlike sandbagging, the man-hours required to fill open containers with material is much less since heavy equipment can perform the work. The containers are pre-fabricated and opened accordion-style to create long section in a short period.

Several suppliers are available but because they are world-wide suppliers of berm units, their units are off-the-shelf, and they are the preferred supplier of material to the Army Corp of Engineers and the U.S. Department of Defense, HESCO USA (www.hesco-usa.com) was consulted to develop a berm system for the containment of wash waters. HESCO USA also routinely deploys their personnel into areas containing hazardous materials so they are proficient with the personal protective equipment and procedures for working in such areas and handling hazardous materials.

HESCO offers a variety of off-the-shelf unit sizes, liner material, and basket designs to fit their applications. They are shipped as 5 basket sections, where five individual rectangular containers (baskets) are connected accordion-style as a single section. They also supply a much longer, integrated section (accordion style) that is used for military applications to set up very long (100's of feet) sections quickly. All sections are shipped in collapsed form on pallets ready for installation. Galvanized, steel pins connect all the containers as a continuous unit and front loaders or specialized hopper systems (Fig. 8) can be used to fill the containers. In deployment, the HESCO containers surround the contaminated area whether it be a building, roadway, or at low elevation to contain the wash water runoff.

Figure 8. For the HESCO standard container systems a skid loader (bobcat) is used or they have a specialized hopper system with conveyer that directly feeds material into the bags.

Contaminated Water Filtration and Reuse

With the runoff of contaminated wash water collected in the temporary reservoir, the water can be collected for reuse or further treatment and disposal. This requires separating the sequestering agent from the salt solution. Ideally, the system for separating the contaminated slurry can be constructed rapidly with limited footprint available at the street-level or would be mobile filtration trucks or trailer units. Such mobile units are commercially-available and used to provide potable waters after disasters like floods, hurricanes, and tornadoes. Since they are designed to produce potable water, they often have a series of filter media and chemical additives to make the water safe for consumption. However, that is not the goal. The primary concern here is to employ a system for reuse of wash water or at least removal of the radioactive component (i.e., the clay).

Several methods continue to be explored. Desiring minimal moving parts, the centrifugal separators are effective (www.lakos.com). They employ no moving parts and can remove gross quantities of solids from a concentrated feed. The effluent from this device can then be fed into a second filter system for final clarification. Simple designs such as bag filters might be appropriate. For our initial tests, the LAKOS centrifugal separator was used as a primary separator to feed a diluted slurry to a bag filter designed by Separmatic filters for final clarification. Connecting these two devices in series, several tests were completed using a slurry feed of

100g/L and examining the output effluents from each device. Optical pictures of the various samples are shown in Figure 9. Note that the LAKOS discharge solids concentration is lower than the feed and the purge is concentrated over the feed. However, the LAKOS should remove nearly 90% of the solids but the separation efficiency was ~50%. This may be due to the very high solids content and the difficulty in controlling the purge valve on the LAKOS unit. The use of the automatic purge actuators provided by the vendor might alleviate this problem. Also, for high slurry feed concentrations, the vendor recommends a series of two or more centrifugal separators to effectively reduce the slurry concentration for final clarification. The effluent from the Separmatic unit was very clean with no observable particles.

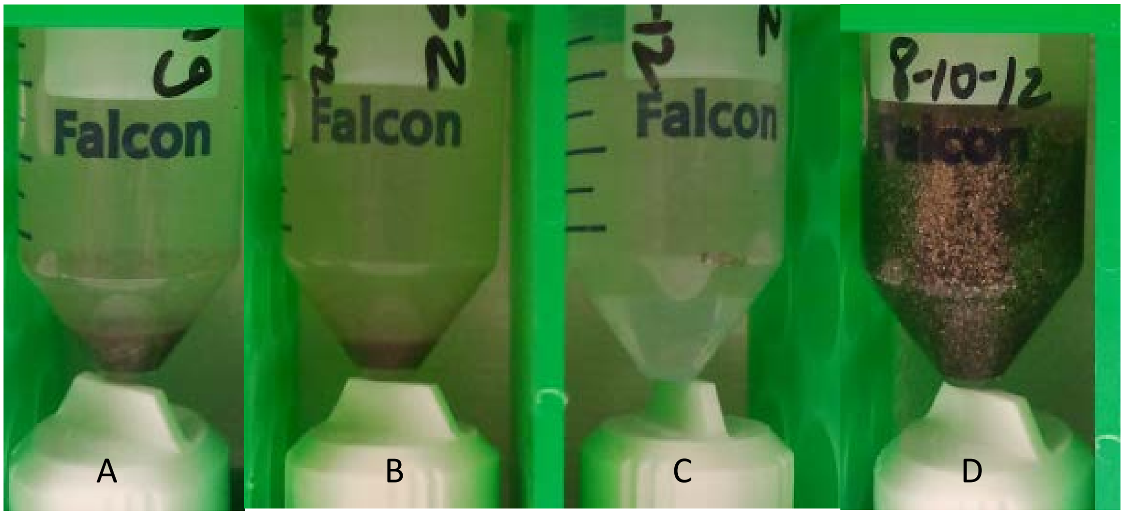

Figure 9. Sample from the feed (10% slurry, A), LAKOS discharge (B), the Separmatic filter discharge (C), and the purge from the LAKOS separator (D).

CONCLUSIONS

It is important that a system is designed to mitigate the effects of a release of radioactive material to an urban center. Working with various experts, stakeholders, local government and federal agencies, Argonne down-selected various technologies and reagents toward producing a rapidly deployable system for washing a large urban area with the goal of reducing radiation levels and restoring critical infrastructure for use. This system of salt and surfactant additives can be rapidly disseminated by firefighters to reduce the contamination levels on the surfaces of buildings, thoroughfares, walkways, and vehicles and collected into reservoirs set up at the street level. The results suggest that we can remove >95% of dry cesium depending on the chemical form and substrate but decontamination of 40% of the cesium should be expected for depositions that have been solubilized by moisture in the air or by rainwater or other precipitation. Specific clays can be spread across the reservoir to actively sorb the cesium and permit reuse of the wash water. Using 100 g/L slurry concentration, up to 80% of the cesium can be sorbed in a single step and commercial-off-the-shelf systems like the centrifugal separators and bag filters provide a means of recycling the wash waters for reuse.

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