Technical Improvements to an Absorbing Supergel for Radiological Decontamination in Tropical Environments

Nuclear Engineering Division

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Technical Improvements to an Absorbing Supergel for Radiological Decontamination in Tropical Environments

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TECHNICAL IMPROVEMENTS TO AN ABSORBING SUPERGEL FOR RADIOLOGICAL DECONTAMINATION IN TROPICAL ENVIRONMENTS

ABSTRACT

Argonne National Laboratory (Argonne) developed a superabsorbing gel-based process (SuperGel) for the decontamination of cesium from concrete and other porous building materials. Here, we report on results that tested the gel decontamination technology on specific concrete and ceramic formulations from a coastal city in Southeast Asia, which may differ significantly from some U.S. sources. Results are given for the evaluation of americium and cesium sequestering agents that are commercially available at a reasonable cost; the evaluation of a new SuperGel formulation that combines the decontamination properties of cesium and americium; the variation of the contamination concentration to determine the effects on the decontamination factors with concrete, tile, and brick samples; and pilot-scale testing (0.02–0.09 m² or 6–12 in. square coupons).

1 BACKGROUND

Argonne National Laboratory (Argonne) developed a superabsorbing gel-based process for the decontamination of cesium from concrete and other porous building materials. [1–3] Argonne was able to develop a technology using commercial spray technology, commercial biocompatible polymers, common chemical reagents, and commercial wet-vacuum technology. The process operations begin with spraying a superabsorbing polymer hydrogel dissolved in a high salt solution onto the contaminated surface. The hydrogel retains its consistency in relatively high temperatures and humidity for periods longer than several hours. The hydrogel is removed using a wet vacuum, and the resultant material can be dehydrated to significantly reduce the waste volume requiring disposal. [1]

Then, we reported on results that tested the gel decontamination technology on specific concrete and ceramic formulations from a coastal city in Southeast Asia,* which may differ significantly from some U.S. sources. [2] We employed bench-scale testing in an attempt to produce an optimized formulation for immediate pilot-scale testing and deployment. The goal was to deploy a hydrogel-decontamination technology that meets the decontamination requirements for the environmental conditions and building materials for such a city.

* The specific city is purposely unidentified.

Follow-on work sought to fill in the gaps identified in this previous work. [3] Four tasks were completed. [4] In the first task, the depth profile of the contamination was measured and we confirmed the dominating role that porosity plays in the decontamination of brick. Then, we tested a dryer gel product to potentially improve the convective action of the gel and subsequently the removal of pore water from the porous brick structure; we saw no improvement in decontamination factors. Next, we sought to reduce the number of unit operations in the application of the SuperGel technology. We eliminated the first step in the process (i.e., apply wash solution to the surface of the material) and, instead, increased the hydration of the gel to 100% and found no difference in the percent removal of cesium. In the next task, we examined contaminated concrete samples by x-ray absorption fluorescence spectroscopy to help identify the chemical speciation of residual cesium and americium on samples. Finally, we completed coupon testing of concrete, tile, and brick for the decontamination of americium and made significant progress toward increasing the decontamination of americium from concrete using diphosphonic acid and carbonate ions in the gel. Results from the tile coupons were excellent. Decontamination from brick coupons continued to be problematic due to the high connected porosity.

To reduce the uncertainty with the operational deployment, we have completed four additional tasks and report on these herein. In Task 1 (see Section 2.0), we studied both monosodium titanate (MST) and cellulose acetate as sequestering agents for americium. The original formulations employed crystalline silico-titanate (CST) for cesium (as IONSIV™-IE910, UOP LLC). The cellulose acetate has much poorer affinity for americium than MST. However, MST is no longer commercially available. Similarly, CST has been removed as an off-the-shelf item and has to be custom ordered at a much higher cost. Therefore, we proposed to evaluate other americium and cesium sequestering agents that are commercially available. We performed partitioning coefficient measurements and concrete coupon testing.

In Task 2 (see Section 3.0), we evaluated a SuperGel formulation that combines the decontamination properties of cesium and americium. The SuperGel is compatible with the KCl or NH_4Cl , and Na_2CO_3 and 1-hydroxyethylidene diphosphonic acid (HEDPA) reagents, thereby expanding its applicability to the decontamination of trivalent actinides (and lanthanides, by inference, since they are similarly trivalent in water and display nearly identical behavior as hard Lewis acids), and likely to divalent cations as well, since the HEDPA has a high affinity to those oxidation states in solution.

In Task 3 (see Section 4.0), we varied the concentration of contamination to determine any effects on the decontamination factors. Concrete, tile, and brick samples were tested.

In Task 4 (see Section 5.0), we expanded the decontamination testing beyond our benchtop experiments that used small quantities of substrate material. This pilot-scale test involved larger test samples ($0.02\text{--}0.09\text{ m}^2$ or 6–12 in. square coupons) contaminated to levels consistent with previous testing. The SuperGel would be applied using a variety of methods that can be employed in the field, including industrial sprayers and vacuums rated for radioactive materials.

2 REPLACEMENT SEQUESTERING AGENTS TO MST AND CST (TASK 1)

2.1 INTRODUCTION

We had previously studied both MST, a synthetic zeolite designed for the removal of radionuclides from liquid high-level nuclear waste, and cellulose acetate as sequestering agents for americium. [3] We found that cellulose acetate has much poorer affinity for americium than MST. However, MST is no longer commercially available. Moreover, CST is no longer an off-the-shelf item and has to be custom-ordered at a much higher cost. Therefore, we evaluated other americium and cesium sequestering agents that are commercially available. This study determined the sorption behavior of soluble cesium and americium from solution onto synthetic and natural ion-exchange materials.

2.2 METHODS

2.2.1 Materials

An in-house stock solution of ^{137}Cs was used for the sorption experiments. Americium-241 was purchased from Eckert & Ziegler Isotope Products (1 $\mu\text{Ci/mL}$, June 1, 2008) and diluted into deionized water before spiking (usually 10 μL) into each stock solution tested. To test for cesium sorption, we employed:

- CST (IONSIVTM-IE910, Universal Oil Products)
- KMS-2 [$\text{K}_{2x}\text{Mn}_x\text{Sn}_{3-x}\text{S}_6$ ($x = 0.5\text{--}0.95$), Northwestern University], a layered sulfide mineral that is not available in the market but uses a synthesis method that the inventors believe may be cost-effective in the long term
- vermiculite concentrate, a natural smectite with general formula $(\text{Mg,Fe,Al})_3(\text{Al,Si})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (W.R. Grace & Co.)
- illite (Xuzhou Zhonglian Chemical Technology Co., Ltd.)
- chabazite [$(\text{Ca,Na}_2,\text{K}_2,\text{Mg})\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}$, ZC500H, -50 mesh, St. Cloud Mining Co.; Winston, New Mexico]

As negative controls, we used diatomaceous earth (SiO_2 , crystalline form, Celite Corporation) obtained from Separmatic Filter (Menomonee Falls, Wisconsin).

We completed sorption experiments for ^{241}Am onto various potential replacement sequestering agents for MST. These included:

- clinoptilolite, a natural zeolite with general formula $(\text{Na},\text{K},\text{Ca})_2\text{-}_3\text{Al}_3(\text{Al},\text{Si})_2\text{Si}_{13}\text{O}_{36}\cdot 12\text{H}_2\text{O}$ (St. Cloud Mining Co., New Mexico)
- montmorillonite, a natural smectite with general formula $(\text{Na},\text{Ca})_{0.33}(\text{Al},\text{Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2\cdot n\text{H}_2\text{O}$ (Fischer Scientific USA as K-10)
- vermiculite (same as above)
- birnessite, an manganese oxide mineral with general formula $(\text{Na}_{0.3}\text{Ca}_{0.1}\text{K}_{0.1})(\text{Mn}^{4+},\text{Mn}^{3+})_2\text{O}_4\cdot 1.5\text{H}_2\text{O}$ (synthesized by Ohio State University, Prof. N. Basta)

The pH of the solution was adjusted in some experiments by addition of sodium hydroxide (diluted from pellets, 99.998%, Aldrich) or nitric acid (0.1 M). Solutions of ammonium chloride (NH_4Cl , 99.5 + %, A.C.S. reagent, Sigma-Aldrich), potassium chloride (KCl, Analytical AR Reagent, Mallinckrodt), sodium carbonate (Na_2CO_3 , anhydrous, granular AR ACS Primary Standard, Mallinckrodt), and etidronic acid (hydroxyethane diphosphonic acid, Aldrich) were prepared with deionized H_2O ($\sim 18\text{ M}\Omega\cdot\text{cm}$ resistivity at 25°C). Standard buffer solutions (pH = 4.01, 7.01, and 10.01) were used to calibrate a pH meter (Hanna Instruments).

Material was weighed into 1.5 mL microcentrifuge tubes (Ambion). All experiments were carried out in triplicate, and duplicate aliquots were taken from each sample. Gamma counting was recorded with a Minaxi γ Auto-Gamma 5000 Series Gamma Counter (United Technologies Packard, Model A5550) using 12×75 polypropylene tubes.

Following Kandil et al.,¹ illite and vermiculite were washed with deionized water (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 398 K for 22 hours. Samples were then placed in a dessicator.

2.2.2 Determination of pH Dependence

We performed pH-dependent measurements on the partitioning of cesium onto potential replacement materials. The procedure was as follows: weigh 10 mg of CST, illite, KMS-2, or vermiculite and place it into 1.5 mL microcentrifuge tubes. Add 1.0 mL of the following solutions: 0.01 M KCl to CST, and 1.0 M HNO_3 solution at pH 4 to illite, KMS-2, and vermiculite. Add 10 μL HNO_3 to samples and agitate in a rotating mixer for 60 min until the pH is lowered to pH 3 or 4.

2.2.3 Kinetic Experiments

We completed kinetic experiments to determine the sorption of cesium and americium onto the various sequestering agents as a function of time in deionized water. The distribution coefficient, K_d , is calculated according to the equation:

$$K_d = (C_0 - C_f) / C_f * V/m$$

where C_0 and C_f are the initial and equilibrium radionuclide activity, V is the volume of solution in milliliters, and m is the mass of the sorbent in grams. We prepared solutions for ^{137}Cs and ^{241}Am sorption tests and calibrated pipets to the specified volume. We then placed 10 mg of sorbent material in each microcentrifuge tube and added 1.0 mL of radioactive spiked solution. Each microcentrifuge tube was capped and gently mixed on a rotator mixer for one hour. The timer was started once the radioactive spike was added to the solution. Samples were mixed for the indicated contamination time up to 24 h. Triplicate test tubes were centrifuged for five minutes at 6000 rpm. We took duplicate 400 μL aliquots from each microcentrifuge tube for gamma analysis [Minaxi Gamma Counter, model A5550, 3 in. well-type Na(I) crystal] of the region from 500–900 keV (γ -energy for ^{137}Cs is 662 keV). The control consisted of a blank microcentrifuge tube mixed and sampled as described above for each time period.

2.2.4 Sorption of Cesium from Solution

We tested the sorption of cesium from a mixed formulation solution of 1 M K^+ , 0.5 M CO_3^{2-} , and 0.025 M HEDPA onto natural mineral sorbents: chabazite, montmorillonite, and vermiculite. Tests were run in triplicate at 10 mg/mL and sampled for gamma analysis with duplicate aliquots. A triplicate set of blanks containing no sorbent was run under the same test conditions. Samples were agitated gently in a rotisserie shaker (Barnstead/Thermolyne Labquake Shaker Rotisserie) for one hour. Sample aliquots were either 100 or 400 μL and were counted for the 662 keV photopeak of Cs-137 using a NaI spectrometer (Packard Minaxi AutoGamma, Model A5550, 4π crystal) for ten minutes.

2.2.5 Solid-to-Liquid Ratio

We completed tests of the equilibrium partitioning coefficient (K_d) as a function of the sorbent clay slurry concentration and type of sorbent. Sorption was in the presence of 0.5 M KCl or NH_4Cl using 10–125 mg sorbent/mL salt solution after mixing for 10 and 30 min (triplicate tests and duplicate aliquots for analysis).

We summarize the test matrix for cesium and americium sorption in Tables 2-1 and 2-2, respectively.

TABLE 2-1 Test matrix for sequestering agent sorption tests for trace cesium solution.

Test Series	#1 – Kinetic tests	#2 – Effect of pH	#3 – Effect of K ⁺	#4 – Effect of NH ₄ ⁺	#5 – Effect of CO ₃ ²⁻	#6 – Effect of HEDPA
Sorbent	control (none), SiO ₂ , CST, vermiculite, illite	control (none), SiO ₂ , KMS-2, CST, vermiculite, illite	control (none), SiO ₂ , KMS-2, CST, vermiculite, illite, chabazite	control (none), SiO ₂ , KMS-2, CST, vermiculite, illite, chabazite	control (none), SiO ₂ , CST, vermiculite, illite, chabazite	control (none), SiO ₂ , CST, vermiculite, illite, chabazite
Solution	deionized water at pH = 8 (adjust with ultrapure NaOH or HNO ₃)	pH = 4, 6, 8, 10 (deionized water, pH adjusted with ultrapure NaOH or HNO ₃)	[KCl] = 0, 1e-4, 0.001, 0.01, 0.1, and 0.5 M	[NH ₄ Cl] = 0, 1e-4, 0.001, 0.01, 0.1, and 0.5 M	[Na ₂ CO ₃] = 0, 1e-4, 0.001, 0.01, 0.1, and 0.5 M	[HEDPA] = 0, 1e-4, 0.001, 0.01, 0.1, and 0.5 M
Time	5, 15, 30, 60 min, and overnight (record actual time); Note: for tests at t = 5 and 15 min freeze in ice bath until ready to sample	1 h	1 h	1 h	1 h	1 h
Clay mass to solution volume ratio	10 mg/mL	10 mg/mL	10 mg/mL; 10, 40, 75, 100, 125 mg/mL for 0.5 M KCl only	10 mg/mL; 10, 40, 75, 100, 125 mg/mL for 0.5 M NH ₄ Cl only	10 mg/mL	10 mg/mL

TABLE 2-2 Test matrix for sequestering agent sorption tests for trace americium solution (clay mass-to-solution-volume ratio = 10 mL/g).

Test Series	#1 – Kinetic tests	#2 – Effect of K ⁺	#3 – Effect of NH ₄ ⁺	#4 – Effect of CO ₃ ²⁻	#5 – Effect of HEDPA
Sorbent	control (no sorbent), birnessite, montmorillonite, clinoptilolite, vermiculite	control (no sorbent), birnessite, montmorillonite, clinoptilolite, vermiculite	control (no sorbent), birnessite, montmorillonite, clinoptilolite, vermiculite	control (no sorbent), birnessite, montmorillonite, clinoptilolite, vermiculite	control (no sorbent), birnessite, montmorillonite, clinoptilolite, vermiculite
Solution	deionized water at pH = 8 (adjust with ultrapure NaOH or HNO ₃)	[KCl] = 0, 1e-4, 0.001, 0.01, 0.1, and 0.5 M	[NH ₄ Cl] = 0, 1e-4, 0.001, 0.01, 0.1, and 0.5 M	[Na ₂ CO ₃] = 0, 1e-4, 0.001, 0.01, 0.1, and 0.5 M	[HEDPA] = 0, 1e-4, 0.001, 0.01, 0.1, and 0.5 M
Time	5, 15, 30, 60 min, and overnight (record actual time); for tests at t = 5 and 15 min, freeze in ice bath until ready to sample	1 h	1 h	1 h	1 h

2.3 RESULTS

We have been surveying replacement sequestering agents for MST and CST that offer high affinity for Am and Cs, are readily available, are non-toxic, and are inexpensive. Results are given below.

2.3.1 Properties of Candidates for Sequestering Agent Replacements

We studied a number of natural and synthetic ion-exchange materials and sorbents by perusing the literature first. We searched for studies that reported on the sorption of cesium or americium onto solid sorbents with an emphasis on studies using high ionic strength solutions since the SuperGel is reconstituted in molarity levels of salt. Sorbent properties were reviewed as a function of important sorption properties: pH, equilibration time, material surface area or size, cation exchange capacity, and solution composition. We did not include every study or sorbent we reviewed, because the list would have been prohibitively long. Instead, we selected representative materials as a means of representing the data from many authors. For instance, we did not report on every study on montmorillonite clay; but instead, we reported on studies that represent the rest of the literature as typical values. In Table 2-3, we summarize the literature on sorbents for cesium. In Table 2-4, we summarize it for sorbents for americium.

TABLE 2-3 Summary of the properties of sorbent candidates for cesium in solution.

Sorbent Material	Concentration of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
Magnetite, Goethite, Hematite, Limonite, Ilmenite, Diaspore (Al(OH)O), Enstatite, Quartz, Dolomite, bauxite called Mixed Minerals (MM)	Tracer, concentration or activity not stated	Almost 100% adsorption Cs and Sr at 200 mg solid loading (no liq. Volume given)	35g/kg Cs (0.25mmol/g) loading capacity and 25 g/kg for Sr(0.27mmol/g)	80-100 mesh (0.044-0.74 mm) without pretreatment	pH 1-14 and as function of nitric, perchloric, and sulfuric acids. Used 10mg-5g solid in liquid (volume not stated)	Adsorption of 137Cs and 90Sr radionuclides on MM from aq. solns. is reported by describing the effect of equilibration time. H ions, and adsorbent and adsorbate concn. Optimum physicochem. conditions were identified.	Ahmad 1989
soil	?	99% removal				mix Cs137 contaminated soil with chloride and heat (800-1000°C) for 2h	Spalding
askanite, gumbrin, nontronite, bentonite, kaolin, phlogopite, biotite, muscorite, talcum, vermiculite, glauconite, hydrophlogopite, hydromuscovite, hydrogoethite, or virianite	details in paper?	66.5 to 99.9%			details in paper	Increased sorption of 137Cs from 37.1 with only sand to following with addition of ~1 wt % minerals: 99.9-askanite, 99.9-gumbrin, 99.9-nontronite, 97.0-bentonite, 95.6-kaolin, 99.7-phlogopite, 97.3-biotite, 94.5-muscorite, 87.2-talcum, 99.8-vermiculite, 98.3-glauconite, 99.6-hydrophlogopite, 88.9-hydromuscovite, 66.5-hydrogoethite, and 98.9-virianite; NH4NO3, NaNO3, and Cs(NO3)2 also desorbed 137Cs from minerals and the desorption increased as the radius of the displacing ion approached the ionic radius of 137Cs.	Bakunov 1989
layered metal sulfides, KMS-1 (synthesized material)	30 - 5e3 ppb	150 to 21,000	226 mg Cs/g or 1.7 mmol Cs/g		t=12h, pH=1-12, V/m=50-1000 mL/g, RT, molar ratios of Na/Cs :0-2e4, Ca/Cs: 0-3e3 and Mg/Cs: 0-1e3	Kd_Sr(II) > Kd_Cs(I) for >1000 mL/g; Kd_Sr ~ Kd_Cs at <250 mL/g; fast absorption kinetics for Cs(I) replacing K+ in <5min at low Cs concs; high stability in aq solns over wide pH range; Cs+ replaces K+; excellent sorbent for Sr2+; high selectivity for soft heavy M (Hg2+, Pb2+, Cd2+)	Manos 2009

TABLE 2.3 (Cont.)

Sorbent Material	Concentration of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
zeolites, sirconium-titanium silicates			1.86 to 4.1 mmol Cs/g			most efficient Cs sorbents; refs therein [Moller et al. 2001, J. Mater. Chem; Chang et al. 1998 Ind. Eng. Chem. Res.; Bortun et al., 2000, Chem. Mater.; Clearfield et al. 1998 J. Mol. Struct.]	Manos 2009
perlite						The present invention relates to treatment of chem. and radioactive waste contg. cesium and/or rubidium by introducing it to the ceramic matrixes sintered contg. expanded perlite. The process includes primarily the stages consisting in prepg. a soln. of salt of cesium and/or rubidium; adding the expanded perlite in desired quantity in order to absorb the totality or near total of the prepd. soln.; elimination solvent from the mass obtained; precalcination the compd. of perlite obtained to form the powder of intermediate compd. prepd. at the preceding stages and carrying out the perlite contg. cesium and/or rubidium.	Rehspringer 2004
bentonite clays (Na-form by treatmt w Na ₂ CO ₃ , from Khakassiya deposit, Russia)	5.2e-5M	15 to 90%	27	29 m ² /g; 3.16um + 50nm colloids	IS=0.001 to 0.1M, [Cs]=5.2e-5M, pH=1.5 to 10	Table 1 gives mineral composition of bentonite used (70-80% montmorillonite); at pH >6 and I = 0.001M, >90% sorbed; dec sorption at higher I and acidic conditions; bentonite equilibrated soln: 300ppm Na ⁺ , 50ppm CO ₃ /HCO ₃ , 45ppm SO ₄ (refer to Table 2), NaClO ₄ for I adjustmt, pH adjusted w HCl or NaOH; sorption of Cs predominantly ion-exchg - strong dep on ionic strength; also contains data for Pu	Sabodina 2006

TABLE 2.3 (Cont.)

Sorbent Material	Concentration of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
hydrous manganese oxide (synthesized matl)	1e-2 to 1e-8 M + trace Cs134	1e3 mL/g		120-170 mesh	0.1g sorbent/10mL soln, t=0-2h, pH=3.85		Mishra 2007
hydrous stannic oxide (synthesized matl)	1e-2 to 1e-8 M + trace Cs134	1e3 mL/g		120-170 mesh	0.1g sorbent/10mL soln, t=0-2h, pH=3.85		Mishra 2007
bentonite (Na _{0.3} (AlMg) ₂ Si ₄ O ₁₀ (OH) ₂ ·4H ₂ O) and pink granite	tracer to 0.01M Cs/Sr. tracer to 10 ⁻⁵ M Am.	K _d (Cs-bentonite)=~600mL/g; K _d (Cs-granite)=24mL/g at pH7-8, increases at pH>9. K _d (Am-bentonite)=~4000mL/g at pH7-8. K _d (Cs-bentonite)=~110mL/g at 0.5M Na ⁺ /Ca ²⁺ .	0.72 and 0.33 mmol/g for Cs and Sr sorption capacity by Langmuir	Bentonite fine powder; granite 70-100 mesh	400:1 to 20:1 volume to mass ratio for borehole water with pH 2-10. 0.01M to 0.5M salt	Studied ability of backfill and host granite host rock to sorb radionuclides. 30 min to reach equilibrium for bentonite and Cs. 60 min for granite.	Murali 2002
cements		0.1-100				reported K _d as 1e-4 to 0.1 m ³ /kg	McKinley 1993
soil/surface sediments		10,000				reported K _d as 10 m ³ /kg	McKinley 1993
montmorillonite, No. 11 (sodium saturated form, Santa Rita, NM deposits)	10-10-0.1N + trace Cs137	50,000 [low Na+Cs] 10 [hi Cs+Na]	116	<100 mesh	V/m=100mL/g, 100 mg clay/10mL, [Na]=0.2-0.002N, t=12h, pH=?	exchg capacity due to isomorphous substitutions in crystal lattice (per Ref therein, Lewis-1955, p 54-55); Montmorillonite characterized from Santa Rita, NM as (Na,Ca) _{0.3} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ ·nH ₂ O per http://rruff.info/Montmorillonite/R110052	Wahlberg 1962

TABLE 2.3 (Cont.)

Sorbent Material	Concentration of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
montmorillonite, No. 11 (potassium saturated form, Santa Rita, NM deposits)	10-10-0.1N + trace Cs137	30,000 [low Cs+K] 10 [hi Cs+K]	116	<100 mesh	100 mg clay/ 10mL, [K]=0.2-0.002N, t=12h	exchg capacity due to isomorphous substitutions in crystal lattice (per Ref therein, Lewis-1955, p 54-55)	Wahlberg 1962
montmorillonite, No. 11 (Mg saturated form, Santa Rita, NM deposits)	10-10-0.1N + trace Cs137	7,000 [low Cs+Mg] 10 [hi Cs+Mg]	116	<100 mesh	V/m=100mL/g, 100 mg clay/ 10mL, [Mg]=0.2-0.002N, t=12h	exchg capacity due to isomorphous substitutions in crystal lattice (per Ref therein, Lewis-1955, p 54-55)	Wahlberg 1962
montmorillonite, No. 11 (Ca saturated form, Santa Rita, NM deposits)	10-10-0.1N + trace Cs137	3,000 [low Cs+Ca] 10 [hi Cs+Ca]	116	<100 mesh	V/m=100mL/g, 100 mg clay/10mL, [Ca]=0.2-0.002N, t=12h	exchg capacity due to isomorphous substitutions in crystal lattice (per Ref therein, Lewis-1955, p 54-55)	Wahlberg 1962
montmorillonite, No. 21 (sodium saturated form, Burns, MI deposits)	10-10-0.1N + trace Cs137	20,000 [low Na+Cs] 10 [hi Na+Cs]	130	<100 mesh	V/m=100mL/g, 100 mg clay/ 10mL, [Na]=0.2-0.002N, t=12h	exchg capacity due to isomorphous substitutions in crystal lattice (per Ref therein, Lewis-1955, p 54-55)	Wahlberg 1962
montmorillonite, No. 21 (potassium saturated form, Burns, MI deposits)	10-10-0.1N + trace Cs137	30,000 [low Cs+K] 10 [hi Cs+K]	130	<100 mesh	100 mg clay/ 10mL, [K]=0.2-0.002N, t=12h	exchg capacity due to isomorphous substitutions in crystal lattice (per Ref therein, Lewis-1955, p 54-55)	Wahlberg 1962
montmorillonite, No. 21 (magnesium saturated form, Burns, MI deposits)	10-10-0.1N + trace Cs137	2,000 [low Cs+Mg] 10 [hi Cs+Mg]	130	<100 mesh	V/m=100mL/g, 100 mg clay/ 10mL, [Mg]=0.2-0.002N, t=12h	exchg capacity due to isomorphous substitutions in crystal lattice (per Ref therein, Lewis-1955, p 54-55)	Wahlberg 1962
montmorillonite, No. 21 (calcium saturated form, Burns, MI deposits)	10-10-0.1N + trace Cs137	3,000 [low Cs+Ca] 10 [hi Cs+Ca]	130	<100 mesh	V/m=100mL/g, 100 mg clay/10mL, [Ca]=0.2-0.002N, t=12h	exchg capacity due to isomorphous substitutions in crystal lattice (per Ref therein, Lewis-1955, p 54-55)	Wahlberg 1962
illite, No. 35 (sodium saturated form, Fithian, IL deposits)	10-10-0.1N + trace Cs137	200,000 [low Cs+Na] 2 [hi Cs+Na]	15	<100 mesh	V/m=100mL/g, 100 mg clay/ 10mL, [Na]=0.2-0.002N, t=12h	exchg capacity due to isomorphous substitutions in the crystal lattice and to broken bonds at edges of clay particles (per Ref therein, Grim-1953, p 132-133)	Wahlberg 1962

TABLE 2.3 (Cont.)

Sorbent Material	Concentration of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
illite, No. 35 (potassium saturated form, Fithian, IL deposits)	10-10-0.1N + trace Cs137	2,000 [low Cs+K] 3 [hi Cs+K]	15	<100 mesh	V/m=100mL/g, 100 mg clay/ 10mL, [K]=0.2-0.002N, t=12h	exchg capacity due to isomorphous substitutions in the crystal lattice and to broken bonds at edges of clay particles (per Ref therein, Grim-1953, p 132-133)	Wahlberg 1962
halloysite, No. 12b (sodium saturated form, Bedford, IN deposits)	10-10-0.1N + trace Cs137	150,000 [low Cs+Na] 1 [hi Cs+Na]	19	<100 mesh	V/m=100mL/g, 100 mg clay/ 10mL, [Na]=0.2-0.002N, t=12h	exchg capacity due to dissociation of structural hydroxyl groups at surface of crystals and to broken bonds at edges of clay particles (per Ref therein, Grim-1953)	Wahlberg 1962
halloysite, No. 12b (potassium saturated form, Bedford, IN deposits)	10-10-0.1N + trace Cs137	400 [low Cs+K] 1 [hi Cs+K]	19	<100 mesh	V/m=100mL/g, 100 mg clay/ 10mL, [K]=0.2-0.002N, t=12h	exchg capacity due to dissociation of structural hydroxyl groups at surface of crystals and to broken bonds at edges of clay particles (per Ref therein, Grim-1953)	Wahlberg 1962
halloysite, No. 12b (magnesium saturated form, Bedford, IN deposits)	10-10-0.1N + trace Cs137	40,000 [low Cs+Mg] 3 [hi Cs+Mg]	19	<100 mesh	V/m=100mL/g, 100 mg clay/ 10mL, [Mg]=0.2-0.002N, t=12h	exchg capacity due to dissociation of structural hydroxyl groups at surface of crystals and to broken bonds at edges of clay particles (per Ref therein, Grim-1953)	Wahlberg 1962
halloysite, No. 12b (calcium saturated form, Bedford, IN deposits)	10-10-0.1N + trace Cs137	30,000 [low Cs+Ca] 1 [hi Cs+Ca]	19	<100 mesh	V/m=100mL/g, 100 mg clay/ 10mL, [Ca]=0.2-0.002N, t=12h	exchg capacity due to dissociation of structural hydroxyl groups at surface of crystals and to broken bonds at edges of clay particles (per Ref therein, Grim-1953)	Wahlberg 1962
kaolinite, No. 4 (sodium saturated form, Macon, BA deposits)	10-10-0.1N + trace Cs137	700 [low Cs+Na] 1 [hi Cs+Na]	10	<100 mesh	V/m=100mL/g, 100 mg clay/ 10mL, [Na]=0.2-0.002N, t=12h	exchg capacity due to dissociation of structural hydroxyl groups at surface of crystals and to broken bonds at edges of clay particles (per Ref therein, Grim-1953)	Wahlberg 1962

TABLE 2.3 (Cont.)

Sorbent Material	Concentration of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
kaolinite, No. 4 (potassium saturated form, Macon, BA deposits)	10-10-0.1N + trace Cs137	700 [low Cs+K] 1 [hi Cs+K]	10	<100 mesh	V/m=100mL/g, 100 mg clay/ 10mL, [K]=0.2-0.002N, t=12h	exchg capacity due to dissociation of structural hydroxyl groups at surface of crystals and to broken bonds at edges of clay particles (per Ref therein, Grim-1953)	Wahlberg 1962
kaolinite, No. 4 (magnesium saturated form, Macon, BA deposits)	10-10-0.1N + trace Cs137	400 [low Cs+Mg] 2 [hi Cs+Mg]	10	<100 mesh	V/m=100mL/g, 100 mg clay/ 10mL, [Mg]=0.2-0.002N, t=12h	exchg capacity due to dissociation of structural hydroxyl groups at surface of crystals and to broken bonds at edges of clay particles (per Ref therein, Grim-1953)	Wahlberg 1962
kaolinite, No. 4 (calcium saturated form, Macon, BA deposits)	10-10-0.1N + trace Cs137	400 [low Cs+Ca] 1 [hi Cs+Ca]	10	<100 mesh	V/m=100mL/g, 100 mg clay/ 10mL, [Ca]=0.2-0.002N, t=12h	exchg capacity due to dissociation of structural hydroxyl groups at surface of crystals and to broken bonds at edges of clay particles (per Ref therein, Grim-1953)	Wahlberg 1962
illite	details in patent?	details in patent?			details in patent?	Cesium uptake by plants depends on adsorption/desorption reactions in the soil, as well as root uptake processes controlled by the plant. In this study, sorption and desorption of Cs ⁺ on ref. illite (IMt-1) was investigated in the presence of oxalate to gain understanding of mechanisms by which plant root exudates may influence Cs ⁺ bioavailability in micaceous soils. Cesium sorption on illite decreased significantly as oxalate concn. increased from 0.4 to 2 mM. Cesium desorption from illite increased significantly with increasing oxalate concn. Desorption of Cs ⁺ by exchange with Na ⁺ , Ca ²⁺ and Mg ²⁺ was significantly enhanced in the presence of oxalate as selectivity for Cs ⁺	Wendling 2004

TABLE 2.3 (Cont.)

Sorbent Material	Concentration of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
Illite (<i>Cont.</i>)						decreased with respect to these ions in the presence of oxalate. On the other hand, oxalate had little effect on the Cs+/K+ selectivity coeff. This suggests that oxalate treatments increase the relative proportion of exchange sites that are not highly selective for Cs+ and K+; e.g. "planar" sites. The results indicate that oxalate plays an important role in Cs+ binding on illite and, therefore, plant rhizosphere chem. is likely to alter Cs+ bioavailability in micaceous soils.	
14	titanium silicate (synthesized using TiOSO ₄)	2e-10 and 7e-5 M	6 to 4e4 mL/g	120 to 726 m ² /g	I=0.1 M Na+, t=2h, 1/100 to 1/1000 g/mL	Ref therein 20,21 Cs and Sr sorption onto crystalline TiSi	Lujanienė 2009
	chazabite, clinoptilolite, HTiSi, KTiGe, KTiSiGe, KTSgel, KTSsol, NaTi	trace Cs-137?	1e3 to 2e5 mL/g		pH=11, 1:200 and 1:1000 g/mL, groundwater simulant: [Na]=3e-4M, [Mg]=2e-4M, [CO ₃ 2-]=1e-4M, [OH-]=2e-3M, [NO ₃ -]=2e-4M, [SO ₄ 2-]=2e-4M	Table 3 summarizes K _d _Cs for sorbents, KTiSiGe > KTiGe ~ HTiSi ~ KTSsol, lowest w NaTi	Behrens 1998
	chazabite, clinoptilolite, HTiSi, KTiGe, KTiSiGe, KTSgel, KTSsol, NaTi	trace	7 to 300 mL/g		pH=14, 1:200 g/mL, defense waste simulants: [Na]=5M, [Al]=0.4M, [K]=0.03-0.1, [CO ₃ 2-]=0.04-0.2M, [OH-]=2M, [NO ₃ -]=2M	Tables 4 and 5 summarizes K _d _Cs for sorbents, NaTi > HTiSi > KTSgel	Behrens 1998
	crystalline silicotitanate (CST, Ionsiv IE-910, manufactured by UOP)	6 ug/L Cs-137	5e3 to 9e4 mL/g		pH=12-13, t=0.5,2,6h, [Na]=2M, [Al]=0.01-0.2, [CO ₃ 2-]=0.2-0.6M, [TOC]=0.1-1M, four 3:1 diluted Hanford complexant conc simulant solutions (Table 1 for additional minor components)	Table 6 includes time dependency of K _d 's for various solutions; lower K _d s with organic complexants (untreated solutions)	Marsh 1995

TABLE 2.3 (Cont.)

Sorbent Material	Concentration of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
potassium hexacyanoferrate crystals (KCoFC, prepd at ORNL) and composite (KCoFC-PAN, prepd by F. Sebesta, Czech Techn. Univ.)	6 ug/L Cs-137	2e2 to 9e4 mL/g		150-600 micron crystals	pH=12-13, t=0.5,2,6h, [Na]=2M, [Al]=0.01-0.2, [CO32-]=0.2-0.6M, [TOC]=0.1-1M, four 3:1 diluted Hanford complexant conc simulant solutions (Table 1 for additional minor components)	Table 6 includes time dependency of K _d 's for various solutions; lower K _d s with organic complexants (untreated solutions)	Marsh 1995
nickel hexacyanoferrate composite (NiFC-PAN, prepd by F. Sebesta, Czech Techn. Univ.)	6 ug/L Cs-137	2e2 to 9e4 mL/g			pH=12-13, t=0.5,2,6h, [Na]=2M, [Al]=0.01-0.2, [CO32-]=0.2-0.6M, [TOC]=0.1-1M, four 3:1 diluted Hanford complexant conc simulant solutions (Table 1 for additional minor components)	Table 6 includes time dependency of K _d 's for various solutions; lower K _d s with organic complexants (untreated solutions)	Marsh 1995
K-Ni hexacyanoferrate (KNiFC-CsTreat prepd by Japan)	10ppm Cs-134	1e4-1e6 depending on solution	2.58 meq/g K and 3.34 meg/g Ni	<100 mesh (<149 um)	10 mg/mL. Effect of pH, Na+, K+, NH4+, Ca2+ ions, particle size, kinetics. Samples equilibrated for 5 d for tests.	Uptake kinetics for smaller than 100 mesh was at equilibrium by 1st time pt (<<1 dy). K _d insensitive to Na or Ca and increases with pH, but drops gradually with K+ (K _d =50,000 at 1 M). Drop is linear above ~0.1M NH4+ but still 7-8000 ml/g at 1 M NH4+.	Mimura 1997
resorcinol/formaldehyde resin (BSC-210, manufactured by Boulder Sci. Co., converted to Na form)	6 ug/L Cs-137	1e3 to 7e3 mL/g			pH=12-13, t=0.5,2,6h, [Na]=2M, [Al]=0.01-0.2, [CO32-]=0.2-0.6M, [TOC]=0.1-1M, four 3:1 diluted Hanford complexant conc simulant solutions (Table 1 for additional minor components)	Table 6 includes time dependency of K _d 's for various solutions; lower K _d s with organic complexants (untreated solutions)	Marsh 1995

TABLE 2.3 (Cont.)

Sorbent Material	Concentration of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
Superlig 666 (proprietary macrocycle, prepd by IBC Adv. Technol., Inc.)	6 ug/L Cs-137	30 to 4e3 mL/g			pH=12-13, t=0.5,2,6h, [Na]=2M, [Al]=0.01-0.2, [CO32-]=0.2-0.6M, [TOC]=0.1-1M, four 3:1 diluted Hanford complexant conc simulant solutions (Table 1 for additional minor components)	Table 6 includes time dependency of Kd's for various solutions; higher Kds with organic complexants (untreated solutions)	Marsh 1995
SuperLig 644 (polymeric resin containing poly (hydroxyarlyne) groups) ligand	Cs137 = ~200 uCi/mL; 6.7×10 ⁻⁵ M total Cs	400-2000mL/g depending on Na/Cs ratio.	0.72 to 3.46 mmole/g resin, depending on the Hanford tank composition	20–70 mesh granules and was used received	General composition was 5M Na+, K (0.12M), Al (0.7), NO3- (1.0M), NO2- (0.87M), and free OH- (1.9M) but varied between tank solutions.	volume/resin mass ratio (phase ratio) was typically ~100:1.	Hassan 2002
potassium hexacyanoferrate crystals (KCoFC, prepd at ORNL)	6 ug/L Cs-137	7e1 to 9e4 mL/g		150-600 microns	pH=14, t=0.5,2,6 h, [Na]=4M, [Al]=0.4M, [CO32-]=2M, [TOC]=0.1-0.7M, four Hanford Tank 101-SY simulant solutions (Table 1 for additional minor components)	Table 6 includes time dependency of Kd's for various solutions; lower Kds with organic complexants (untreated solutions)	Marsh 1995
nickel hexacyanoferrate composite (NiFC-PAN, prepd by F. Sebesta, Czech Techn. Univ.)	6 ug/L Cs-137	3e1 to 3e3 mL/g			pH=14, t=0.5,2,6 h, [Na]=4M, [Al]=0.4M, [CO32-]=2M, [TOC]=0.1-0.7M, four Hanford Tank 101-SY simulant solutions (Table 1 for additional minor components)	Table 6 includes time dependency of Kd's for various solutions; lower Kds with organic complexants (untreated solutions)	Marsh 1995

TABLE 2.3 (Cont.)

Sorbent Material	Concentration of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
Ammonium molybdophosphate-polyacrylonitrile (AMP-PAN) composite sorbents (prepd by F. Sebesta, Czech Techn. Univ.)	100 mg AMP-PAN in 15mg/L Cs in 10 mL solution.	>10 ⁵ mL/g in 1-2 HNO ₃ and/or 1-2M NaNO ₃ ; 4000mL/g in 0.5M KNO ₃ and 2000mL/g in 1M KNO ₃ in 1-2MHNO ₃	22.5, 19.8 and 19.6 mg Cs/g sorbent for 5, 10 and 20 BV/hr	0.3–0.6 mm diameter		AMP-PAN/SF02 sorbent was composed of 85.7 wt% AMP and 14.3 wt% PAN. 1.5 cm ³ column BV at flowrates of 5, 10 and 20 bed volumes per hour	
crystalline silicotitanate (Ionsiv IE-910, CST, manufactured by UOP)	6 ug/L Cs-137	2e3 to 4e3 mL/g			pH=14, t=0.5,2,6 h, [Na]=4M, [Al]=0.4M, [CO ₃]=2M, [TOC]=0.1-0.7M, four Hanford Tank 101-SY simulant solutions (Table 1 for additional minor components)	Table 6 includes time dependency of K _d 's for various solutions; slightly lower K _d s with organic complexants (untreated solutions)	Marsh 1995
resorcinol/formaldehyde resin (BSC-210, manufactured by Boulder Sci. Co., converted to Na form)	6 ug/L Cs-137	6e2 to 3e3 mL/g			pH=14, t=0.5,2,6 h, [Na]=4M, [Al]=0.4M, [CO ₃]=2M, [TOC]=0.1-0.7M, four Hanford Tank 101-SY simulant solutions (Table 1 for additional minor components)	Table 6 includes time dependency of K _d 's for various solutions; slightly lower K _d s with organic complexants (untreated solutions)	Marsh 1995
polymeric macrocycle (Superlig 666, proprietary, prepd by IBC Adv. Technol., Inc.)	6 ug/L Cs-137	6e2 to 4e3 mL/g			pH=14, t=0.5,2,6 h, [Na]=4M, [Al]=0.4M, [CO ₃]=2M, [TOC]=0.1-0.7M, four Hanford Tank 101-SY simulant solutions (Table 1 for additional minor components)	Table 6 includes time dependency of K _d 's for various solutions; slightly lower K _d s with organic complexants (untreated solutions)	Marsh 1995
silicotitanate (IONSIV IE-911, UOP)	trace Cs-137	710 mL/g			pH>14, t=72 h, [Na]=5M, [K]=0.5M, Na/Cs=8e4 (Attachment A for detailed contents of DSSF waste simulant)	12-14% increase in Cs loading with 25-fold dilution of waste (5M to 0.2M Na)	Brown 1996

TABLE 2.3 (Cont.)

Sorbent Material	Concentration of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
crystalline silicotitanate (IONSIV IE-910, UOP)	trace Cs-137	910 mL/g			pH>14, t=72 h, [Na]=5M, [K]=0.5M, Na/Cs=8e4 (Attachment A for detailed contents of DSSF waste simulant)	12-14% increase in Cs loading with 25-fold dilution of waste (5M to 0.2M Na)	Brown 1996
zeolite (aluminosilicate, IONSIV TIE-96, UOP)	trace Cs-137	21 mL/g			pH>14, t=72 h, [Na]=5M, [K]=0.5M, Na/Cs=8e4 (Attachment A for detailed contents of DSSF waste simulant)	double Cs loading with 25-fold dilution of waste (5M to 0.2M Na)	Brown 1996
polymeric macrocycle (SuperLig 644, IBC Advanced Technol.)	trace Cs-137	500 mL/g			pH>14, t=72 h, [Na]=5M, [K]=0.5M, Na/Cs=8e4 (Attachment A for detailed contents of DSSF waste simulant)	40-45% decrease in Cs loading with 25-fold dilution of waste (5M to 0.2M Na)	Brown 1996
resorcinol-formaldehyde resin (BSC-187-210, Boulder Sci.)	trace Cs-137	220 mL/g			pH>14, t=72 h, [Na]=5M, [K]=0.5M, Na/Cs=8e4 (Attachment A for detailed contents of DSSF waste simulant)	40-45% decrease in Cs loading with 25-fold dilution of waste (5M to 0.2M Na)	Brown 1996
phenol-formaldehyde resin (Duolite CS-100, Rohm & Hass)	trace Cs-137	88 mL/g			pH>14, t=72 h, [Na]=5M, [K]=0.5M, Na/Cs=8e4 (Attachment A for detailed contents of DSSF waste simulant)	40-45% decrease in Cs loading with 25-fold dilution of waste (5M to 0.2M Na)	Brown 1996
kaolinite	1 kBq/mL	3,287	170	<2um	[CaCl2]=0.01M, pH~7, t=24h, 1g clay/L	CEC in mol_c/kg	Bellenger (2008)
montmorillonite	1 kBq/mL	4,514	940	<2um	[CaCl2]=0.01M, pH~7, t=24h, 1g clay/L	CEC in mol_c/kg	Bellenger (2008)

TABLE 2.3 (Cont.)

Sorbent Material	Concentration of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
illite	5 kBq/mL	155,000	300	<2um	[CaCl ₂]=0.01M, pH~7, t=24h, 1g clay/L	CEC in mol_c/kg	Bellenger (2008)
quartz	1 kBq/mL	0		<200um	[CaCl ₂]=0.01M, pH~7, t=24h, 10g/L	CEC in mol_c/kg	Bellenger (2008)
calcium carbonate	1 kBq/mL	33.8			[CaCl ₂]=0.01M, pH~7, t=24h, 10g/L	CEC in mol_c/kg	Bellenger (2008)

TABLE 2-3 Notes and citations:

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15. Marsh et al. (1995), "Effects of soluble organic complexants and their degradation products on the removal of selected radionuclides from high level waste, Part III," Los Alamos National Lab Report, LA-13000, 64 pgs.
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17. Marsh et al. (1995), "Effects of soluble organic complexants and their degradation products on the removal of selected radionuclides from high level waste, Part II," Los Alamos National Lab Report, LA-12943, 47 pgs.
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19. Bellenger and Staunton (2008), "Adsorption and desorption of ^{85}Sr and ^{137}Cs on reference minerals with and without inorganic and organic surface coatings," J. Environ. Radioactivity 99, 831–840.

TABLE 2-4 Summary of the properties of sorbent candidates for americium in solution.

Sorbent Material	Concentration of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
antimonysilicate (INOES Silicas Ltd.)	trace	1000-1,000,000			[H+]=0.01-1M, t=3d, V/M=500mL/g	XRD pattern similar to hydrous antimony pentoxide (antimonic acid, Sb ₂ O ₅ ·4H ₂ O) a typical pyrochlore structure	Al-Attar (2003)
antimonysilicate, calcium form (synthesized)	trace	100,000			[Ca+]=0.01M, t=3d, V/M=500mL/g	XRD pattern shows high crystallinity and pyrochlore structure	Al-Attar (2003)
antimonysilicate, sodium form (synthesized)	trace	1,000,000			[H+]=0.01-1M, t=3d, V/M=500mL/g	XRD pattern shows high crystallinity and pyrochlore structure	Al-Attar (2003)
birnessite, acid form (synthesized)	trace	10-10,000			[H+]=0.01-1M, t=3d, V/M=500mL/g		Al-Attar (2003)
birnessite, calcium form (synthesized; similar to natural mineral)	trace	6,000,000			[Ca+]=0.01M, t=3d, V/M=500mL/g	XRD pattern similar to natural Ca-rich birnessite reported by Drits et al 1997	Al-Attar (2003)
birnessite, sodium form (Na ₄ Mn ₁₄ O ₂₇ ·9H ₂ O, synthesized)	trace	1,000,000-30,000,000	310		[Na+]=0.01-1M, t=3d, V/M=1000mL/g		Al-Attar (2003)
titanosilicates (Na ₂ Ti ₂ O ₃ SiO ₄ ·2H ₂ O, (Na,K) ₂ TiSi ₅ O ₁₃ nH ₂ O, Na ₉ Si ₁₂ O ₃₈ (OH)12H ₂ O, Na ₃ (Na,H)Ti ₂ O ₂ [Si ₂ O ₆] ₂ ·2H ₂ O), synthesized materials)	trace	10,000-10,000,000	310-760	5-25 microns	[Na+]=0.01-1M, t=3d, V/M=1000mL/g, pH=?	titanosilicates not tested in acidic media due to low acid resistance, reported theoretical CEC in meq/g	Al-Attar (2003)

TABLE 2-4 (Cont.)

Sorbent Material	Conc. of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
apatite	2-5e-9M	10,000		0.04-0.06mm	pH=8, t=5d, [HCO ₃ ⁻]=123mg/L, [Na]=65mg/L, V/m=40-100mL/g, actual grdwater solution composition (Table II)	Fig 1b, no change in K _d as inc pH from 4-9	Allard (1984)
attapulgitite (or palygorskite, magnesium aluminium phyllosilicate, (Mg,Al) ₂ Si ₄ O ₁₀ (OH)·4(H ₂ O))	2-5e-9M	10,000		0.04-0.06mm	pH=8, t=5d, [HCO ₃ ⁻]=123mg/L, [Na]=65mg/L, V/m=40-100mL/g, actual grdwater solution composition (Table II)	Fig 1a, slight inc in K _d for as inc pH from 4 to 6, then constant	Allard (1984)
biotite	2-5e-9M	1,000-10,000		0.04-0.06mm	pH=8, t=5d, [HCO ₃ ⁻]=123mg/L, [Na]=65mg/L, V/m=40-100mL/g, actual grdwater solution composition (Table II)	Fig 1a, inc in K _d as inc pH from 4 to 7, then constant	Allard (1984)
calcite	2-5e-9M	5,000-50,000		0.04-0.06mm	pH=8, t=5d, [HCO ₃ ⁻]=123mg/L, [Na]=65mg/L, V/m=40-100mL/g, actual grdwater solution composition (Table II)	Fig 1b, K _d incs with pH from 7-9	Allard (1984)
corundum (aluminium oxide, Al ₂ O ₃)	2-5e-9M	10-5,000		0.04-0.06mm	pH=8, t=5d, [HCO ₃ ⁻]=123mg/L, [Na]=65mg/L, V/m=40-100mL/g, actual grdwater solution composition (Table II)	Fig 1b, K _d incs with pH from 4-7, K _d _max ~pH 7-9	Allard (1984)

TABLE 2-4 (Cont.)

Sorbent Material	Conc. of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
fluorite	2-5e-9M	8,000		0.04-0.06mm	pH=8, t=5d, [HCO ₃ ⁻]=123mg/L, [Na]=65mg/L, V/m=40-100mL/g, actual grdwater solution composition (Table II)	Fig 1b, no change in K _d as inc pH from 4-9	Allard (1984)
gibbsite (aluminium hydroxide, Al(OH) ₃)	2-5e-9M	60-60,000		0.04-0.06mm	pH=8, t=5d, [HCO ₃ ⁻]=123mg/L, [Na]=65mg/L, V/m=40-100mL/g, actual grdwater solution composition (Table II)	Fig 1b, K _d incs with pH from 4-6, K _d _max ~pH 6-9	Allard (1984)
limonite (hydrous basic iron oxide, FeO(OH) nH ₂ O)	2-5e-9M	500-20,000		0.04-0.06mm	pH=8, t=5d, [HCO ₃ ⁻]=123mg/L, [Na]=65mg/L, V/m=40-100mL/g, actual grdwater solution composition (Table II)	Fig 1b, K _d incs with pH from 4-9, K _d _max ~pH 7	Allard (1984)
magnetite (iron oxide, Fe ₃ O ₄)	2-5e-9M	10-20,000		0.04-0.06mm	pH=8, t=5d, [HCO ₃ ⁻]=123mg/L, [Na]=65mg/L, V/m=40-100mL/g, actual grdwater solution composition (Table II)	Fig 1b, K _d incs with pH from 4-7, K _d _max ~pH 7-9	Allard (1984)
montmorillonite ((Na,Ca) _{0.3} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ nH ₂ O)	2-5e-9M	10,000		0.04-0.06mm	pH=4-9, t=5d, [HCO ₃ ⁻]=123mg/L, [Na]=65mg/L, V/m=40-100mL/g, actual grdwater solution composition (Table II)	Fig 1a, no dep of K _d for pH range of 4-9	Allard (1984)

TABLE 2-4 (Cont.)

Sorbent Material	Conc. of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
clay (Suez Gulf, Egypt, predominantly quartz-48%, kaolinite-11%?, 40% Ca-montmorillonite)			2.35 mol/g	200 mesh	V/m=100 mL/g,	CEC based upon MB dye adsorption where MB=320g/mol for dehydrated dye (C16N18N3SCI)	
olivine (magnesium iron silicate, (Mg,Fe) ₂ SiO ₄)	2-5e-9M	100-10,000		0.04-0.06mm	pH=8, t=5d, [HCO ₃ -]=123mg/L, [Na]=65mg/L, V/m=40-100mL/g, actual grdwater solution composition (Table II)	Fig 1a, inc in Kd as inc pH from 5 to 9	Allard (1984)
pyrite (iron sulfide, FeS ₂)	2-5e-9M	100-10,000		0.04-0.06mm	pH=8, t=5d, [HCO ₃ -]=123mg/L, [Na]=65mg/L, V/m=40-100mL/g, actual grdwater solution composition (Table II)	Fig 1b, Kd incs with pH from 4-8.5, Kd_max ~pH 6	Allard (1984)
quartz	2-5e-9M	50-1,000		0.04-0.06mm	pH=8, t=5d, [HCO ₃ -]=123mg/L, [Na]=65mg/L, V/m=40-100mL/g, actual grdwater solution composition (Table II)	Fig 1a, inc in Kd to max as inc pH from 4 to 7, then dec to 500 as inc pH to 9	Allard (1984)
	2-5e-9M			0.04-0.06mm	pH=8, t=5d, [HCO ₃ -]=123mg/L, [Na]=65mg/L, V/m=40-100mL/g, actual grdwater solution composition (Table II)	sorption mechanism based upon solution chemistry (hydrolysis) rather than sorbent properties (influence of pH on sorption did not vary for range of minerals)	Allard (1984)

TABLE 2-4 (Cont.)

Sorbent Material	Conc. of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
hematite		100,000		6.1 pCi/mg/min in natural groundwater; 3.9 pCi/mg/min in simulated water	natural and simulated groundwater		Conca (2000)
montmorillonite		10,000		3.8 pCi/mg/min in natural groundwater; 3.2 pCi/mg/min in simulated water	natural and simulated groundwater		Conca (2000)
titanium silicate (synthesized using TiOSO ₄)	3.2e-11 M	50-2,000		120 to 726 m ² /g	I=0.1 M Na+, 1/100 to 1/1000 g/mL		Lujaniene (2009)
goethite	3e-11 M	(45-95%)			pH=3.5-8, [sorbent]=?, [Na]=0.1M		Lujaniene (2010)
hematite	3e-11 M	(35-95%)			pH=3.5-8, [sorbent]=?, [Na]=0.1M		Lujaniene (2010)
magnetite	3e-11 M	(75-95%)			pH=4-8, [sorbent]=?, [Na]=0.1M		Lujaniene (2010)
Triassic clay (Northern Lithuania)	3e-11 M	(75-100%)			pH=3.5-8, [clay]=64.3 m ² /L, [Na]=0.01-0.1M	clay composition: 56-71% smectite (14% montmorillonite, 20% illite, 1-9% chlorite minerals) cemented by limonite (FeO(OH)nH ₂ O, surface coated with 1.6% siderite (FeCO ₃), 2.3% hematite (α-Fe ₂ O ₃), 0.1% goethite (α-FeOOH), 19.8% calcite	Lujaniene (2010)

TABLE 2-4 (Cont.)

Sorbent Material	Conc. of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
bone char	10 ⁻⁸ -10 ⁻⁷ M	9-800			pH=14, t=0.5,2,6 h, [Na]=4M, [Al]=0.4M, [CO32-]=2M, [TOC]=0.1-0.7M, four Hanford Tank 101-SY simulant solutions (Table 1 for additional minor components)	Table 8 summarizes time dependency of K _d 's with various solutions; significantly lower K _d 's in presence of organic complexants (untreated solutions); complexation of Am in highly alkaline solns with simpler organic cmpds (such as oxalate and acetate formed from radiolysis of EDTA); converted [Am] to molarity	Marsh (1995)
bone char (Stauffer Chem. Co.)	10 ⁻⁷ M	0.3-5,000			pH=12-13, t=0.5,2,6 h, [Na]=2M, [Al]=0.01-0.2, [CO32-]=0.2-0.6M, [TOC]=0.1-1M, four 3:1 diluted Hanford complexant conc simulant solutions (Table 1 for additional minor components)	Table 9 summarizes time dependency of K _d 's with various solutions; significantly lower K _d 's in presence of organic complexants (untreated solutions); complexation of Am in highly alkaline solns with simpler organic cmpds (such as oxalate and acetate formed from radiolysis of EDTA); converted [Am] to molarity	Marsh (1995)
clinoptilolite (natural zeolite containing quartz, feldspar and clay from Castle Creek and purified form)	10 ⁻⁸ -10 ⁻⁷ M	2-600		<200 mesh	pH=14, t=0.5,2,6 h, [Na]=4M, [Al]=0.4M, [CO32-]=2M, [TOC]=0.1-0.7M, four Hanford Tank 101-SY simulant solutions (Table 1 for additional minor components)	Table 8 summarizes time dependency of K _d 's with various solutions; significantly lower K _d 's in presence of organic complexants (untreated solutions); complexation of Am in highly alkaline solns with simpler organic cmpds (such as oxalate and acetate formed from radiolysis of EDTA); converted [Am] to molarity	Marsh (1995)

TABLE 2-4 (Cont.)

Sorbent Material	Conc. of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
crystalline antimonite acid composite (CsbA-PAN, prepd by F. Sebesta, Czech Techn. Univ.)	10 ⁻⁷ M	0.4-5,000			pH=12-13, t=0.5,2,6 h, [Na]=2M, [Al]=0.01-0.2, [CO ₃]=0.2-0.6M, [TOC]=0.1-1M, four 3:1 diluted Hanford complexant conc simulant solutions (Table 1 for additional minor components)	Table 9 summarizes time dependency of K _d 's with various solutions; significantly lower K _d 's in presence of organic complexants (untreated solutions); complexation of Am in highly alkaline solns with simpler organic cmpds (such as oxalate and acetate formed from radiolysis of EDTA); converted [Am] to molarity	Marsh (1995)
diphonix resin (Eichrom Industries)	10 ⁻⁷ M	0.4-4,000			pH=12-13, t=0.5,2,6 h, [Na]=2M, [Al]=0.01-0.2, [CO ₃]=0.2-0.6M, [TOC]=0.1-1M, four 3:1 diluted Hanford complexant conc simulant solutions (Table 1 for additional minor components)	Table 9 summarizes time dependency of K _d 's with various solutions; significantly lower K _d 's in presence of organic complexants (untreated solutions); complexation of Am in highly alkaline solns with simpler organic cmpds (such as oxalate and acetate formed from radiolysis of EDTA); converted [Am] to molarity	Marsh (1995)
hydrous titanium dioxide (SNL/HTO, amorphous form, prepd by Sandia)	10 ⁻⁸ -10 ⁻⁷ M	20-800		fine powder	pH=14, t=0.5,2,6 h, [Na]=4M, [Al]=0.4M, [CO ₃]=2M, [TOC]=0.1-0.7M, four Hanford Tank 101-SY simulant solutions (Table 1 for additional minor components)	Table 8 summarizes time dependency of K _d 's with various solutions; significantly lower K _d 's in presence of organic complexants (untreated solutions); complexation of Am in highly alkaline solns with simpler organic cmpds (such as oxalate and acetate formed from radiolysis of EDTA); converted [Am] to molarity	Marsh (1995)

TABLE 2-4 (Cont.)

Sorbent Material	Conc. of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
Ionsiv IE-96 (zeolite, UOP)	10 ⁻⁸ -10 ⁻⁷ M	0.3-400			pH=14, t=0.5,2,6 h, [Na]=4M, [Al]=0.4M, [CO32-]=2M, [TOC]=0.1-0.7M, four Hanford Tank 101-SY simulant solutions (Table 1 for additional minor components)	Table 8 summarizes time dependency of K _d 's with various solutions; significantly lower K _d 's in presence of organic complexants (untreated solutions); complexation of Am in highly alkaline solns with simpler organic cmpds (such as oxalate and acetate formed from radiolysis of EDTA); converted [Am] to molarity	Marsh (1995)
monosodium titanate (MST slurry, BSC-265-0106, Boulder Sci. Co.)	10 ⁻⁷ M	0.2-8,000			pH=12-13, t=0.5,2,6 h, [Na]=2M, [Al]=0.01-0.2, [CO32-]=0.2-0.6M, [TOC]=0.1-1M, four 3:1 diluted Hanford complexant conc simulant solutions (Table 1 for additional minor components)	Table 9 summarizes time dependency of K _d 's with various solutions; significantly lower K _d 's in presence of organic complexants (untreated solutions); complexation of Am in highly alkaline solns with simpler organic cmpds (such as oxalate and acetate formed from radiolysis of EDTA); converted [Am] to molarity	Marsh (1995)
Na nanotitanate (8104-170 and 8225-127, Allied Signal, Inc.)	10 ⁻⁸ -10 ⁻⁷ M	6-800		<100 mesh (8104-170) and <40 mesh (8225-127)	pH=14, t=0.5,2,6 h, [Na]=4M, [Al]=0.4M, [CO32-]=2M, [TOC]=0.1-0.7M, four Hanford Tank 101-SY simulant solutions (Table 1 for additional minor components)	Table 8 summarizes time dependency of K _d 's with various solutions; significantly lower K _d 's in presence of organic complexants (untreated solutions); complexation of Am in highly alkaline solns with simpler organic cmpds (such as oxalate and acetate formed from radiolysis of EDTA); converted [Am] to molarity	Marsh (1995)

TABLE 2-4 (Cont.)

Sorbent Material	Conc. of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
nickel hexacyanoferrate composite (NiFC-PAN, prepd by F. Sebesta, Czech Techn. Univ.)	10 ⁻⁸ -10 ⁻⁷ M	40-1000			pH=14, t=0.5,2,6 h, [Na]=4M, [Al]=0.4M, [CO32-]=2M, [TOC]=0.1-0.7M, four Hanford Tank 101-SY simulant solutions (Table 1 for additional minor components)	Table 8 summarizes time dependency of K _d 's with various solutions; significantly lower K _d 's in presence of organic complexants (untreated solutions); complexation of Am in highly alkaline solns with simpler organic cmpds (such as oxalate and acetate formed from radiolysis of EDTA); converted [Am] to molarity	Marsh (1995)
potassium hexacyanoferrate (KCoFC)	10 ⁻⁸ -10 ⁻⁷ M	20-600			pH=14, t=0.5,2,6 h, [Na]=4M, [Al]=0.4M, [CO32-]=2M, [TOC]=0.1-0.7M, four Hanford Tank 101-SY simulant solutions (Table 1 for additional minor components)	Table 8 summarizes time dependency of K _d 's with various solutions; significantly lower K _d 's in presence of organic complexants (untreated solutions); complexation of Am in highly alkaline solns with simpler organic cmpds (such as oxalate and acetate formed from radiolysis of EDTA); converted [Am] to molarity	Marsh (1995)
sodium nanotitanate (8104-170 and 8225-127, Allied Signal, Inc.)	10 ⁻⁷ M	0.3-8,000		<100 mesh (8104-170) and <40 mesh (8225-127)	pH=12-13, t=0.5,2,6 h, [Na]=2M, [Al]=0.01-0.2, [CO32-]=0.2-0.6M, [TOC]=0.1-1M, four 3:1 diluted Hanford complexant conc simulant solutions (Table 1 for additional minor components)	Table 9 summarizes time dependency of K _d 's with various solutions; significantly lower K _d 's in presence of organic complexants (untreated solutions); complexation of Am in highly alkaline solns with simpler organic cmpds (such as oxalate and acetate formed from radiolysis of EDTA); converted [Am] to molarity	Marsh (1995)

TABLE 2-4 (Cont.)

Sorbent Material	Conc. of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
titanium dioxide, hydrous (SNL/HTO, amorphous form, prepd by Sandia)	10 ⁻⁷ M	20-8,000		fine powder	pH=12-13, t=0.5,2,6 h, [Na]=2M, [Al]=0.01-0.2, [CO3 ²⁻]=0.2-0.6M, [TOC]=0.1-1M, four 3:1 diluted Hanford complexant conc simulant solutions (Table 1 for additional minor components)	Table 9 summarizes time dependency of K _d 's with various solutions; significantly lower K _d 's in presence of organic complexants (untreated solutions); complexation of Am in highly alkaline solns with simpler organic cmpds (such as oxalate and acetate formed from radiolysis of EDTA); converted [Am] to molarity	Marsh (1995)
bentonite		5,000				ref therein: McKinley and Hadermann 1985	McKinley (1993)
bentonite		29,400				ref therein: KBS 1983	McKinley (1993)
bentonite/sand		300					McKinley (1993)
cements		500-5000				converted K _d to mL/g, reported as 0.5 to 5 m ³ /kg	McKinley (1993)
coastal marine water		1,000,000				ref therein: Ashton and Summerling 1988	McKinley (1993)
pelagic clay		2,000,000				ref therein: IAEA 1985	McKinley (1993)
sediment		2,000,000				ref therein: Bushman et al. 1991	McKinley (1993)
soil/surface sediments		100,000				converted K _d to mL/g, reported as 100 m ³ /kg	McKinley (1993)

TABLE 2-4 (Cont.)

Sorbent Material	Conc. of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
bentonite	trace	100-5,000		fine powder	pH=3-8, bentonite:water=1:50 to 1:400, [Eu] or [Cs+Sr]=1e-2 to 1e-8 M, BW water analysis (ug/mL): Na+=1.4e3, Mg2+=97, Ca2+=77, K+=42, Cl-=1e3, CO32-=high, etc	bentonite characterized as predominantly montmorillonite; pH<4 no hydrolysis of Am or sorption	Murali (2002)
crushed YMP tuff	7e-9M	1000		75 to 100 microns	J-13 well water from NTS, 3e-3M NaHCO3; column tests at 0.15 mL/h for column density of 1 g/mL	typically 1% breakthru;	Thompson (1989)
basalt (igneous rock)	2e-9M	2,000-6,000			synthetic groundwater, pH=7-8		Triay (1991)
clinoptilolite (M ₈ Al ₈ Si ₂₈ O ₂₇ 24H ₂ O, natural zeolite from Castle Creek, purified form: 98% clinoptilolite, 2% smectite and quartz)	1e-12M	4,900	100	75-500 um	pH 7.5 buffer (sodium carbonate-sodium bicarbonate), t=21d, V/m=100mL/g	reported CEC as ~1meq/g	Triay (1991)
granite (igneous rock)	2e-9M	4,000-7,000			synthetic groundwater, pH=7-8		Triay (1991)
romanechite (manganese oxyhydroxide, BaMn ²⁺ Mn ₈ ⁴⁺ O ₁₆ (OH) ₄ , from Casa Grande, AZ)	1e-12M	330,000		75-500 um	pH 7.5 buffer (sodium carbonate-sodium bicarbonate), t=21d, V/m=100mL/g		Triay (1991)

TABLE 2-4 (Cont.)

Sorbent Material	Conc. of Element	K _d in mL/g (or other units or % sorbed)	CEC (meq/100g)	BET Area (m ² /g) or Size (microns)	Solution Conditions	Notes	Reference
YMP tuff (G4-1502, 71% clinoptilolite, 15% opal-CT, 4% quartz, 3% alkali feldspar, 2% smectite)	1e-8M	2,000			J-13 groundwater, pH=7-8		Triay (1991)
YMP tuff (GU3-433, 76% alkali feldspar, 15% cristobalite, 2% mica, 1% hematite)	2e-7M	30,000			J-13 groundwater, pH=7-8		Triay (1991)
YMP tuff (GU3-688, 68% alkali feldspar, 27% cristobalite, 4% quartz, 1% smectite)	1e-12M	12,000		75-500 um	J-13 groundwater, pH=7-8, alkalinity=1mN (HCO ₃ ⁻), t=21d, V/m=100mL/g		Triay (1991)
layered metal sulfides						Manos (2009) indicates that clays composed of aluminosilicate anionic slabs with alkali or alkaline earth counter cations are excellent cationic exchangers for range of inorganic ions (ref 1–13)	
Wellenberg colloids	1.5e-5M	60,000-400,000			(a) 2e-2M NaHCO ₃ , pH 8.6 and (b) 0.02M NaCl, 1e-5M HCO ₃ , pH 8.6		

TABLE 2-4 Notes and citations:

1. Penrose et al. (1990) reported that plutonium and americium were associated with siliceous colloids in an alluvial aquifer at Los Alamos National Laboratory. W. R. Penrose, et al. (1990), "Mobility of plutonium and americium through a shallow aquifer in a semiarid region," *Environ. Sci. Technol.* 24(2), 228–234.

TABLE 2-4 Notes and citations (Cont.):

2. At the Nevada Test Site, transition metals and lanthanide radionuclides associated with inorganic colloids were recovered from groundwater 300 m from a nuclear detonation cavity (Buddemeier and Hunt 1988). Americium and lead were transported in the vadose zone with organic and inorganic colloids. R.W Buddemeier and J.R Hunt (1988), "Transport of colloidal contaminants in groundwater: radionuclide migration at the Nevada Test Site," *Appl. Geochem.*, 3, 535–548.
3. Under most geologic conditions, transport of radionuclides via iron oxide or clay colloids dominates over transport of radionuclides by true polymerized radiocolloids (McCarthy and Zachara 1989). J.F McCarthy and J.M Zachara (1989), "Subsurface transports of contaminants," *Environ. Sci. Technol.* 23(5), 496–502.
4. Generation and mobilization of colloids have become an important issue for contaminant transport (Kersting et al. 1999), particularly facilitated transport of radionuclides as intrinsic colloids, for example, colloidal Pu(V) or as radionuclide-bearing pseudocolloids such as ²³⁹Pu, ²³⁷Np, ²⁴³Am, and ²⁴⁷Cm from high-level radioactive wastes or ¹³⁷Cs, ⁹⁰Sr, and ⁶⁰Co from low-level radioactive wastes (Triay et al. 1996; Buddemeier and Hunt 1988; Kaplan et al. 1994; McCarthy and Degueudre 1993). A.B. Kersting, et al. (1996), "Migration of plutonium in ground water at the Nevada Test Site," *Nature* 397, 56-59; I. Triay, C. Degueudre, A. Wistrom, C. Cotter, and W. Lemos (1996), "Progress report on colloid-facilitated transport at Yucca Mountain," Los Alamos report LA-12959-MS; D.I Kaplan, P.M Bertsch, D.C Adriano, and K.A Orlandini (1994), "Actinide association with groundwaters colloids in a coastal plain aquifer," *Radiochim. Acta* 66/67, 181–187; J. F. McCarthy and C. Degueudre, (1993), in *Environmental Particles 2* (eds., J. Buffle and H.P. van Leeuwen), Ann Arbor, Lewis, pp. 247–315.
5. Triay et al. (1996) studied the generation and stability of colloids in Yucca Mountain groundwater and found that colloids of clays, silicon, and iron oxides were generated in the groundwater and irreversible sorption of radionuclides onto these colloids occurred.
6. Conca (2000) authored the analysis/modeling reports published by the Yucca Mountain Project of DOE that provide data for Am on colloids of hematite, goethite, montmorillonite, and silica in natural and synthetic groundwater. J. Conca, "Unsaturated zone and saturated zone Transport properties (U0100)," UNT Digital Library, Las Vegas, Nevada, <http://digital.library.unt.edu/ark:/67531/metadc782188>, accessed October 3, 2016.
7. Al-Attar (2003), "Uptake of RNs on microporous and layered ion exchange materials," *J. Materials Chem.*, 13, 2963–2968.
8. Allard (1984), "Mechanisms for the interaction of AmIII and NpV with geologic media," *Mat. Res. Soc. Symp. Proc.*, 26, 899–906.
9. Lujaniene et al. (2009), "Application of inorganic sorbents for removal of Cs Sr Pu and Am from contaminated solutions," *J. Radioanal. Nucl. Chem.* 282, 787–791.
10. Lujaniene et al. (2010), "Effect of natural clay components on sorption of Cs Pu and Am by the clay," *J. Radioanal. Nucl. Chem.* 286, 353–359.
11. Marsh et al. (1995), "Effects of soluble organic complexants and their degradation products on the removal of selected radionuclides from high level waste, Part II: Distribution of Sr, Cs, Tc, and Am onto 32 absorbers from four variations of Hanford Tank 101-SY simulant solution," Los Alamos National Lab Report, LA-12943, April 1995, 1–47.
12. Marsh et al. (1995), "Effects of soluble organic complexants and their degradation products on the removal of selected radionuclides from high level waste, Part III: Distribution of Sr, Cs, Tc, and Am onto 33 absorbers from four variations of a 3:1 dilution of Hanford Complexant Concentrate (CC) simulant solution, Part IV: The effects of varying dilution ratios on the distributions of Sr, Cs, Tc, Pu, and Am onto 12 absorbers from Hanford Complexant Concentrate (CC) simulant solution," Los Alamos National Lab Report, LA-13000, Sept. 1995, 1–64.

TABLE 2-4 Notes and citations (Cont.):

13. McKinley and Scholtis (1993), "A comparison of radionuclide sorption databases used in recent performance assessments," J. Contam. Hydrol., 13, 347–363 (Table 3, data from Refs 1–6; Table 4, data from Ref. 9, Vieno and Suolanen, 1991).
14. Murali and Mathur (2002), "Sorption chars of Am, Sr, Cs on bentonite and granite," J. Radioanal. Nucl. Chem., 254(1), 129–136. (Refer to Refs 18 and 19 for Am complexing agents.)
15. Thompson (1989), J. Radioanal. Nucl. Chem. 130, 353–364; data from Refs. 1 and 2.
16. Allard and Beall (1979), J. Environ. Sci. Health A14, 507, Refs. 7 and 8; Allard et al. (1980), Nucl. Technol. 49, 474.
17. Triay et al. (1991), "Sorption of Am in tuff and pure minerals using synthetic and natural groundwaters," Radiochim. Acta, 52/53, 141–145.
18. Allard and Beall (1979), J. Environ. Sci. Health A14, 507, Refs. 7 and 8; Allard et al. (1980), Nucl. Technol. 49, 474.
19. Thomas (1987), Los Alamos Natl Lab, LA-10960-MS, Ref. 13.

As much of the literature does not provide data on Am- and Cs-clay sorption properties with K^+ or NH_4^+ present in our decontamination solution, we had to down-select the sorbents that might be expected to have a sufficiently high affinity and rapid uptake of Cs or Am in the SuperGel formulation. Based on our review of the literature, clays provide high partitioning coefficients and are abundant in nature, and thus meet important requirements for the decontamination technology, since abundant materials are available worldwide and they are cost-effective. Transition metal oxide minerals (e.g., magnetite goethite, hematite, hydrous manganese, and stannic oxides) are not selective toward cesium at a high ionic strength due to competitive adsorption onto the charged surface sites. Many clays are similarly non-selective except at low-ionic strength (e.g., montmorillonite or bentonite). Illite and vermiculite, because of their very large K_d values, are interesting. Zeolites have a higher selectivity than many sorbents due to their specific cage openings that aid selectivity by providing some physical discrimination as some ions can pass into the pores and others cannot. Chabazite and the synthetic crystalline silico-titanate are interesting. Soil sediments are interesting because of their immediate availability around the world but the studies focus on dilute groundwaters. Moreover, since transition metal oxides dominate the mineral surfaces within soils, there is good reason to believe that the K_d values for Cs^+ will be low in high salt solutions. The presence of various clays within soils suggests that certain soils may be candidates for use as sequestering agents. But tests would need to be conducted to understand what types of soils would be suitable. The hexacyanoferrates are interesting due to their high K_d at high-ionic strength. However, there is a question about its availability for immediate deployment in case of an emergency.

Similar to the data on cesium sorption, the experimental parameters used for the sorption experiments in the literature for Am^{3+} are limited or insufficiently defined. Moreover, the partitioning coefficients reported in the literature for many naturally occurring materials vary widely due to their heterogeneous composition (many mineral phases and adsorbed phases) and poor characterization of their composition. However, the individual, pure mineral phases in the naturally occurring clays offer predictable sorption behavior but may not be available in bulk quantities. Some materials such as synthetic antimony silicates, birnessite (a layered manganese oxide), and titanosilicates in 0.01 M Ca^{2+} or Na^+ and up to 1M H^+ ; romanechite (manganese oxyhydroxide), bentonite (montmorillonite), and smectites are reported to have high partitioning coefficients for americium ($K_d \sim 10^3\text{--}10^7$ mL/g) in moderately salty waters and may warrant investigation if they can be readily available for large-scale use. Many sorbents were tested for sorption of Am^{3+} from Hanford nuclear waste tank solutions. Of these, clinoptilolite, synthetic titanates, and cyanoferrates performed well in the high ionic strength solutions. Soils and sediments from various regions around the world also sorbed Am^{3+} remarkably well. Sorption of Am^{3+} onto natural biotite (mica group phyllosilicate), calcium, aluminum, and transition metal oxides and hydroxides from groundwaters was good.

The companies that we contacted for availability of birnessite, clinoptilolite, illite, vermiculite, and romanechite are in Appendix 2. The suppliers for clinoptilolite and chabazite are in Appendix 3 and the bulk pricing for vermiculite concentrate is in Appendix 4.

The materials tests for cesium sorption were CST, KMS-2, illite, vermiculite, diatomaceous earth, and chabazite.

2.3.2 pH Dependence on Cesium Sequestering Agents

We titrated the samples to qualitatively assess the buffering capabilities of the sorbents. Figure 2-1 shows the volume of acid needed to reach pH 4. Each 20 μL results in an input of sufficient protons to produce 0.02 M $[\text{H}^+]$ in an unbuffered solution ($20 \mu\text{L} \times 1 \text{ mol}/10^6 \mu\text{L} = 2 \times 10^{-5}$ moles into a 1 mL solution, or 2×10^{-2} moles/L or pH = 1.7). Note the strong buffering capabilities of KMS-2 and CST followed by vermiculite and illite.

FIGURE 2-1 Volume of 1.0 M HNO₃ needed to adjust pH of unbuffered clay slurry (10 mg/mL initially). The corresponding concentration of protons for an unbuffered solution is given in the bracketed abscissa labels.

2.3.3 Kinetics of Cesium Sorption

We completed experiments on the kinetic sorption of cesium onto various sorbents from an unbuffered solution (Figure 2-2). Even under mild agitation (rotary mixer), the sorption is at equilibrium within 10 min. Of note, the sorption onto chabazite was very good at 5 min but decreased thereafter.

FIGURE 2-2 Sorption kinetics for ^{137}Cs in unbuffered water in terms of activity in the supernatant solution (top) and percent removal (bottom) of cesium from solution.

2.3.4 Sorption of Cesium in the Presence of Salt

We next studied the sorption of cesium onto these materials while in the presence of various salts and reagents that are part of the SuperGel formulation. For these tests, the procedure was as described for the kinetic tests, except all samples were mixed for 1 h prior to sampling.

The results are displayed in Figures 2-3 to 2-6 in terms of activity in the supernatant solution, partitioning coefficient K_d , and percent removal of cesium from solution. Clear from the data is the strong negative effect that the salt concentration has on sorption at and above 0.1 M. The data indicate that CST is the best choice, and vermiculite is the next best choice overall. In the presence of K^+ , CST is clearly superior, with KMS and vermiculite giving comparable results. In the presence of NH_4^+ , vermiculite is best, followed by CST. CST is clearly better in Na_2CO_3 and HEDPA with vermiculite next best. These results beg the question of whether vermiculite would match the sorption of CST in carbonate and HEDPA if we converted them to their potassium form instead of the sodium and hydrogen forms. KMS-2 was removed from further testing because it was not deemed better than the other natural mineral choices.

2.3.5 Sorption of Cesium with Mixed Isotope Hydrogel Formulation

A combined SuperGel wash solution was formulated to contain potassium ions for cesium desorption and carbonate and diphosphonic acid for americium dissolution and chelation at concentrations of the ions and acid that allow optimal substrate decontamination while remaining compatible with the gel. We tested the sorption of cesium from K_2CO_3 /HEDPA solutions onto montmorillonite, vermiculite, and chabazite. Results for sorption of Cs-137 on the natural materials follow the trend: chabazite > vermiculite > montmorillonite with an average K_d of 32, 21, and 12 mL/g, respectively (refer to Figure 2-7). The relative standard deviations (RSDs) for the replicate tests and aliquots were low: 4.4%, 4.7%, and 4.7%, respectively, for the chabazite, vermiculite, and montmorillonite tests.

The sorption test results for chabazite with the combined cesium and americium decontamination solution formulation were compared with single-component solutions (Figure 2-8). The sorption of Cs-137 onto chabazite in the mixed formulation exhibits the same behavior as for the solutions of KCl or NH_4Cl alone, as it is adversely affected by high concentrations of potassium or ammonium ions. For Cs-137 sorption onto chabazite in solutions containing K^+ ions, the sorption remains high up to 0.1 M K^+ ($K_d > 300$) and drops by a factor of 6 at 0.5 M K^+ ($K_d = 51$) and decreases by an additional factor of 1.5 at 1 M K^+ . At the 1 M K^+ concentration, decontamination of the Cs-137 from the concrete would be more effective while still permitting effective capture or uptake by the sorbent. In contrast, the Cs-137 sorption behavior onto chabazite does not appear to be adversely affected by Na^+ , CO_3^{2-} , or HEDPA in solution concentrations of up to 0.5 M ($K_d > 1000$).

FIGURE 2-3 Effect of KCl on the equilibrium sorption of cesium onto various sequestering agents in terms of activity in the supernatant solution (top), partitioning coefficient K_d (middle), and percent removal (bottom) of cesium from solution.

FIGURE 2-4 Effect of NH_4Cl on the equilibrium sorption of cesium onto various sequestering agents in terms of activity in the supernatant solution (top), partitioning coefficient K_d (middle), and percent removal (bottom) of cesium from solution.

FIGURE 2-5 Effect of Na₂CO₃ on the equilibrium sorption of cesium onto various sequestering agents in terms of activity in the supernatant solution (top), partitioning coefficient K_d (middle), and percent removal (bottom) of cesium from solution.

FIGURE 2-6 Effect of HEDPA on the equilibrium sorption of cesium onto various sequestering agents in terms of activity in the supernatant solution (top), partitioning coefficient K_d (middle), and percent removal (bottom) of cesium from solution.

FIGURE 2-7 Sorption of Cs-137 onto clays from a solution of 1 M K^+ , 0.5 M CO_3^{2-} , and 0.025 M HEDPA after 1 h of gentle agitation at 10 mg/mL slurry concentration.

FIGURE 2-8 Sorption of Cs-137 onto chabazite from 0.0001-0.5 M solutions of NH_4Cl , KCl , Na_2CO_3 , and HEDPA or a combined solution of 1 M K^+ , 0.5 M CO_3^{2-} , and 0.025 M HEDPA. Tests were allowed to equilibrate for 1 h under gentle agitation at 10 mg/mL slurry concentrations.

Results of Cs-137 sorption onto montmorillonite (Figure 2-9) compare the combined formulation solution of 1 M K^+ , 0.5 M CO_3^{2-} , and 0.025 M HEDPA with NH_4Cl solutions that cover the concentration range of 0.0001 to 0.1 M. The low K_d for Cs onto montmorillonite ($K_d = 12$) follows the trend for chabazite of decreasing K_d with an increase in the ammonium ion.

The sorption test results for vermiculite with the combined cesium and americium decontamination formulation were compared with single-component solutions (Figure 2-10). For Cs-137 sorption onto vermiculite in solutions containing K^+ ions, the sorption remains high up to 0.1 M K^+ ($K_d > 200$) and drops by a factor of 6 at 0.5 M K^+ ($K_d = 34$) and decreases by an additional factor of 1.6 at 1 M K^+ . When comparing the K_d 's from 0.5 M Na_2CO_3 solution to the mixed formulation of 0.5 M K_2CO_3 + 0.025 M HEDPA solution sorption tests, we found that the K_d of 300 for Cs in 0.5 M Na_2CO_3 is much higher than that for the mixed formulation solution ($K_d = 21$), indicating that the Na^+ is less competitive with cesium for sorption sites than K^+ or NH_4^+ .

FIGURE 2-9 Sorption of Cs-137 onto montmorillonite from 0.0001-0.1 M solutions of NH_4Cl or a combined formulation solution of 1 M K^+ , 0.5 M CO_3^{2-} , and 0.025 M HEDPA. Tests were allowed to equilibrate for 10 min or 1 h under gentle agitation at 10 mg/mL slurry concentrations.

FIGURE 2-10 Sorption of Cs-137 onto vermiculite from 0.0001-0.5 M solutions of NH_4Cl , KCl , Na_2CO_3 , and HEDPA or a combined solution of 1 M K^+ , 0.5 M CO_3^{2-} , and 0.025 M HEDPA. Tests were allowed to equilibrate for 1 h under gentle agitation at 10 mg/mL slurry concentrations.

2.3.6 Sorption of Cesium as a Function of Solid-to-Liquid Ratio

We completed tests of the K_d as a function of the sorbent clay slurry concentration and type of sorbent. Sorption was in the presence of 0.5 M KCl or NH_4Cl using 10–125 mg sorbent/mL salt solution after mixing for 10 and 30 min (triplicate tests and duplicate aliquots for analysis) in a rotisserie mixer. For KCl (Figure 2-11), the K_d 's are low for all materials, with montmorillonite performing better than vermiculite. However, for NH_4Cl (Figure 2-12), the K_d 's are much higher, with vermiculite performing much better than montmorillonite.

FIGURE 2-11 Sorption of Cs-137 onto clays from solution of 0.5 M KCl after 10 min and 30 min of gentle agitation.

FIGURE 2-12 Sorption of Cs-137 onto clays from solution of 0.5 M NH_4Cl after 10 min and 30 min of gentle agitation.

2.3.7 Kinetics of Americium Sorption

The kinetic tests (Figure 2-13) show that sorption is rapid, reaching equilibrium or peak values within ~10 min. Beyond 60 min, the sorption appears to decrease but still remains high. The sorption increases as

montmorillonite>birnessite> vermiculite>clinoptilolite

We suspect that appreciable hydrolysis of the Am^{3+} ion in these solutions promotes the formation of americium hydroxide $[\text{Am}(\text{OH})_n^{3-n}]$ species in solution, which may form colloids. Colloids of this type may not follow the reported sorption chemistry for the dissolved species.

FIGURE 2-13 Kinetics for sorption of Am-241 onto various sorbents from deionized water.

Following the kinetic tests, we completed equilibrium sorption experiments. From KCl solutions (Figure 2-14) at higher concentration (>0.01 M), the sorption onto clinoptilolite improves with increasing salt. At 0.5 M salt clinoptilolite, birnessite, and vermiculite all sorb americium well, with K_d 's of 10,000 mL/g. Sorption onto montmorillonite appears to suffer greatly at high salt content. The improvement in K_d as salt concentration increases would suggest a salting out effect, although one would expect the potassium to interfere with sorption, as it would have affinity for sorption sites.

FIGURE 2-14 Sorption of Am-241 onto various sorbents from KCl solution.

From carbonate solution (Figure 2-15), birnessite performs best at high salt content (0.1–0.5 M), with K_d 's exceeding 100,000 mL/g at 0.1 M. Sorption values onto montmorillonite and vermiculite are similar and small, while clinoptilolite is the poorest performer. Again, increasing K_d values as the salt concentration increases would suggest a salting-out effect, with similar lack of interference from the sodium ion as we witnessed for the potassium ion.

FIGURE 2-15 Sorption of Am-241 onto various sorbents from Na₂CO₃ solution.

From HEDPA solution, the sorption decreases with higher acidity (Figure 2-16). In our region of interest (0.025 M) the extrapolated K_d 's are <1000 mL/g for birnessite and montmorillonite and <100 mL/g for vermiculite and clinoptilolite. The decrease in K_d values with increasing acidity is likely due to a combination of the competition of hydrogen for sorption sites as is common among the clays, which prefer sorption at near neutral pH values, and the chelation effect of the diphosphonic acid anion for the americium cation. The increase in HEDPA would produce a significant concentration of bound americium ions unavailable for sorption onto the clays.

FIGURE 2-16 Sorption of Am-241 onto various sorbents from HEDPA solution.

3 MIXED ISOTOPE TESTING (TASK 2)

3.1 INTRODUCTION

The ideal technology would be generic enough to decontaminate a variety of radionuclides without changing the formulation. The SuperGel appears to have that type of generality due to its compatibility with KCl, NH₄Cl, Na₂CO₃, and HEDPA reagents. Tests included the decontamination of cesium and americium from concrete, brick, and tile.

3.2 METHODS

3.2.1 Superabsorbent Retention Capacity

We determined the retention capacity of the gel in solution of 0.025 M HEDPA and 0.25 M K₂CO₃ with and without a sequestering agent (Table 3-1). We used Ahlstrom fabric sealed with a Polystar 242 heat sealer. One end was folded, and the other two were sealed to form a pouch. After filling the bag with the polymer and sequestering agent, the end was sealed. Empty bags were weighed to determine the blank correction mass. The bags were soaked for 1 h in excess solution (~50 g for each test), and then the swollen bags were removed and blotted dry on a lint-free wipe before weighing. The gel polymer mix was 99:1 cross-linked to linear copolymer (cross-linked potassium acrylate-acrylamide copolymer and linear sodium acrylate-acrylamide copolymer). Tests with sequestering agent contained 10% sequestering agent relative to dry mass of polymer.

We calculated the superabsorbent retention capacity (SRC), which is given as (grams of absorbed fluid / grams of dry polymer):

$$(W3 - W2 - W1) \div W1$$

where W3 = weight of wet polymer and tea bag; W2 = weight of wet blank tea bag; and W1 = weight of dry polymer mixture.

TABLE 3-1 Polymer hydration capacity for mixed isotope solutions (“powder” refers to polymer plus clay contents. HEDPA=etidronic acid or hydroxyethane diphosphonic acid, “Mont” = montmorillonite, “Verm” = vermiculite).

Sample ID	Powder + T-bag (g)	T-bag (g)	Hydrated Contents (g)	Hydration Capacity Solution per Dry Polymer (g/g)			Solution
				<u>Blank Correction</u>		0.6293	
2517-42-1	0.160	0.160	0.8450				None
2517-42-2	0.160	0.160	0.7450				None
2517-42-3	0.162	0.162	0.7800		<u>Average</u>	<u>STD DEV</u>	None
2517-42-4	1.158	0.161	23.5840	21.8623	21.8	0.3	0.025 M HEDPA/0.25 M K ₂ CO ₃
2517-42-5	1.158	0.160	23.2760	21.5317			0.025 M HEDPA/0.25 M K ₂ CO ₃
2517-42-6	1.154	0.161	23.7350	22.1064			0.025 M HEDPA/0.25 M K ₂ CO ₃
2517-42-7	1.241	0.162	24.4480	20.9246	19.5	1.2	0.025 M HEDPA/0.25 M K ₂ CO ₃ /1% Mont
2517-42-8	1.253	0.162	22.6490	19.0345			0.025 M HEDPA/0.25 M K ₂ CO ₃ /1% Mont
2517-42-9	1.253	0.160	22.2390	18.6246			0.025 M HEDPA/0.25 M K ₂ CO ₃ /1% Mont
2517-42-10	1.255	0.161	14.6987	11.7133	12.6	0.9	0.025 M HEDPA/0.25 M K ₂ CO ₃ /1% Verm
2517-42-11	1.252	0.160	15.6987	12.6533			0.025 M HEDPA/0.25 M K ₂ CO ₃ /1% Verm
2517-42-12	1.256	0.162	16.6987	13.5406			0.025 M HEDPA/0.25 M K ₂ CO ₃ /1% Verm
2517-42-13	1.254	0.160	17.6987	14.4565	15.4	0.9	0.025 M HEDPA/0.25 M K ₂ CO ₃ /0.5% Mon/0.5% Verm
2517-42-14	1.256	0.160	18.6987	15.3407			0.025 M HEDPA/0.25 M K ₂ CO ₃ /0.5% Mon/0.5% Verm
2517-42-15	1.254	0.161	19.6987	16.2995			0.025 M HEDPA/0.25 M K ₂ CO ₃ /0.5% Mon/0.5% Verm

3.2.2 Concrete Coupon Testing from Mixed Isotope Gel Formulation

Concrete coupons were prepared for decontamination experiments. All sides except the face were sealed with 5-minute epoxy (Devcon 5-min epoxy 14270). After preparing the stock Cs-137 solution, we coated the faces of the coupons with 100 μL Cs-137 solution and allowed them to dry before wrapping the coupons with plastic wrap for counting. The plastic wrap was polyvinylidene chloride with low permeability to gases and vapors. The coupons were wrapped under ambient conditions (temperature = 22°C and RH = 40%). Coupons were counted on a high-purity germanium detector (Detector 1, EG&G Ortec HPGe, position 10 cm, 300 second live time). Samples were aged for 24 h in the lab at room temperature. Eight mixed-isotope gel formulations were prepared at 100% hydration for a 99:1 cross-linked: linear PAM/30% PAA gel formulation (see results in Section 3.3). Approximately 3 g gel was applied to the contaminated coupon face and left in contact for 60 min. The gel was removed from the coupon, allowed to dry before wrapping, then analyzed by gamma spectrometry (under same conditions as contamination). All tests were performed in triplicate with background controls.

3.2.3 Cesium and Americium Decontamination Using Mixed-Isotope Gel Formulation

We tested the decontamination of cesium and americium by using a 99:1 cross-linked: linear PAM/30% PAA gel prepared at 100% hydration employing 0.025 M HEDPA and 0.5 M K_2CO_3 . Tests were run on six replicates for each urban material: coupons of concrete, brick, and tile. All sides of the coupons except the face were sealed with 5-min epoxy (Devcon 5-min epoxy #14270) for the decontamination experiments. The faces of the coupons were contaminated with 100 μL Cs-137 stock solution and allowed to dry before a 100 μL of Am-241 stock solution was added. Coupons were placed into individual Ziploc[®] plastic bags for counting on a high-purity germanium detector (Detector 1, EG&G Ortec HPGe, position 20 cm, 600-sec live time). Samples were aged for a week at 40°C (however, the humidity control was lost due to a malfunction of the chamber during the aging process, and the relative humidity of the coupons during the aging process is thus unknown). After one week, approximately 3 g gel was applied to the contaminated coupon face, returned to the humidity chamber at 40°C (with open water containers), and left in contact for 60 min. The gel was removed from the coupon, allowed to dry before wrapping, then analyzed by gamma spectrometry (under same counting conditions as the contamination coupons). All tests were run with background controls.

3.3 RESULTS

3.3.1 Retention Capacity

Tea bag tests were completed on gel reconstituted in 0.025 M HEDPA and 0.25 M K_2CO_3 with and without sequestering agent (Table 3-1). To compare, the tea bag hydration capacities for 1 M KCl, 1 M NH_4Cl , and 0.025 M HEDPA/0.25 M Na_2CO_3 are 19.5, 19.8, and 24.2 g/g, respectively, in the SuperGel formulation. Vermiculite lowers the hydration capacity to 13–15 g/g, but the montmorillonite has only a minor effect compared to HEDPA/ K_2CO_3 (capacity = 21.9 g/g).

3.3.2 Decontamination of Cesium from Concrete Using Mixed Isotope Hydrogel Formulations

Concrete coupons were prepared for decontamination experiments. Eight mixed-isotope gel formulations were prepared at 100% hydration for a 99:1 cross-linked: linear PAM/30% PAA gel formulation (Table 3-2).

TABLE 3-2 Gel formulations of 99:1 cross-linked: linear PAM/30% PAA prepared at 100% gel hydration using different wash solutions.

Gel ID	Gel Wash Solution Formulation							
	NH_4^+	K^+	Na^+	CO_3^{2-}	Cl^-	HEDPA	Mont.	Verm.
2517-40-1	1 M				1 M			
2517-40-2		1 M			1 M			
2517-40-3			0.5 M	0.25 M		0.025 M		
2517-40-4	1 M			0.5 M		0.025 M		
2517-40-5		1 M		0.5 M		0.025 M		
2517-40-6		1 M		0.5 M		0.025 M	1%	
2517-40-7		1 M		0.5 M		0.025 M		1%
2517-40-8		1 M		0.5 M		0.025 M	0.5%	0.5%

Results of cesium removal from the concrete coupon decontaminations with the various gel formulations are shown in Figure 3-1. Average decontamination values and triplicate coupon results are represented in the graph, with values for all the tests ranging between 54 and 88%. These cesium-contaminated coupons were aged for 24 hours under ambient conditions (22°C, 40% RH). The lowest removal of Cs from the concrete was observed with gel #3 containing 0.5 M Na^+ , 0.25 M CO_3^{2-} , and 0.025 M HEDPA (average Cs removal of $63.7 \pm 17.2\%$), and the highest removal was by gel #2 containing 1 M K^+ and 1 M Cl^- (average Cs removal of $83.3 \pm 2.5\%$). The coupon test results using an unpaired t-test for the results from the gel tests were compared for the lowest and highest decontamination. Statistically, there was no difference

between the test results from gel #3 and #2 (Two-sample t-test, T-value = 1.96, p = 0.122). Also, the results for the 1 M KCl prepared gel (#2) were consistent with earlier reported results for the same gel under similar contaminant aging conditions ($83.3 \pm 2.5\%$ from Figure 3-1 and $79.0 \pm 9.2\%$ from 2346-7 and 2346-22 testing).

3.3.3 Cesium and Americium Decontamination Using Mixed Isotope Gel Formulation

A mixed-isotope SuperGel was formulated to contain potassium ions for cesium desorption and carbonate and diphosphonic acid for americium dissolution and chelation. Concentrations of the ions and the acid in the gel were combined and formulated to allow optimal substrate decontamination while remaining compatible with the gel. Contaminated coupons were aged for one week at 40°C in the humidity chamber (a malfunction of the humidity chamber occurred during testing, and relative humidity conditions are thus unknown).

Figure 3-2 shows results of americium and cesium removal from the concrete coupon decontaminations with the 99:1 cross-linked: linear PAM/30% PAA gel prepared at 100% hydration using 0.025 M HEDPA and 0.5 M K_2CO_3 gel formulation. Average decontamination values and data from the six coupon replicate tests are represented in the graph. Results for removal of Am-241 from the urban substrate materials in Figure 3-2 follow the trend: tile >> concrete > brick with an average removal of 86%, 31%, and 9.8%, respectively. The standard deviation for the replicate tests was low: 7.2, 6.3, and 5.9% for the concrete, brick, and tile coupon tests, respectively.

Results for removal of Cs-137 from the urban substrate materials in Figure 3-2 follow the trend: tile >> concrete >> brick with an average removal of 73%, 45%, and 9.8%, respectively. The standard deviation for the replicate tests was also low: 3.4%, 4.0%, and 4.7% for the concrete, brick, and tile coupon tests, respectively. The decontamination results for cesium from tile and concrete coupons are much lower than expected based upon previously reported results. Although the gel formulations used for the comparison are different, the potassium-ion concentration and the contaminant coupon aging conditions are the same (K^+ is assumed to replace Cs^+ from the substrate). Previously reported results for Cs removal using a 100% hydrated gel prepared with 1 M KCl from 7-day aged tile and concrete coupons were $91 \pm 1\%$ and $59 \pm 4\%$, respectively. These lower decontaminations shown in Figure 3-2 for cesium removal from concrete and tile are attributed to differences in aging conditions of the coupons, whereby humidity conditions were not maintained at 90% due to the humidity chamber failure. The 40°C temperature was maintained throughout the contaminant aging process for the testing in Figure 2-2 and may have accelerated the bonding of the contaminant to the substrate material and removed pore water, making the decontamination difficult for a one-hour processing time with the 100% hydrated gel.

FIGURE 3-1 Decontamination of Cs-137 from concrete coupons using 100% hydrated gel formulations (99:1 cross-linked: linear PAM/30% PAA) prepared from different wash solutions. Average cesium removal values are shown in increasing removal efficiency for each gel, and triplicate coupon results are represented to the right of each average. Coupons were aged with its contamination for 24 h at 22°C and 40% RH.

FIGURE 3-2 Decontamination of Am-241 (on left in blue) and Cs-137 (on right in red) from concrete, brick, and tile coupons using 100% hydrated gel formulation (99:1 cross-linked: linear PAM/30% PAA in 0.025 M HEDPA and 0.5 M K₂CO₃). Average cesium removal values are shown as data labels in the figure. Individual coupon replicate results are shown to the right of each average in increasing removal efficiency for each substrate. Coupons with its contamination were aged for one week at 40°C (relative humidity was not available).

4 EFFECT OF VARIATION IN CONCENTRATION OF AMERICIUM AND CESIUM CONTAMINATION (TASK 3)

4.1 INTRODUCTION

The tests in Section 3 were performed at a single concentration of cesium and americium contamination. To be thorough, we proposed testing of cesium and americium within a range of concentrations consistent with three zones of contamination defined by the Liberty Rad Ex exercise (Figure 4-1). Coupons were prepared spanning the specified contamination range for cesium and americium. Concrete, tile, and brick samples were tested.

4.2 METHODS

Coupon decontamination for cesium covered the estimated maximum surface activity for streets and exterior building walls in the decontamination zones following a radiological dispersal device incident. While the zone definitions and mitigation activities were changed from previous reporting [5] and updated with assumptions from the National Tier 2 Full-Scale Radiological Dispersion Device Exercise (also known as Liberty RadEx) sponsored by the U.S. Environmental Protection Agency (EPA), [6] our coupon contaminant surface activities cover the decontamination zones used for current remediation efforts (0.24 and 0.112 mCi/m² for Zones 2 and 3, respectively). Decontamination strategies vary with deposited radioactivity. For example, in Zone 1, the plan is for demolition of 90% of contaminated structures and decontamination of the remaining 10%. For Zones 2 and 3, the reverse is expected, 10% demolition and 90% decontamination. The plume profile model (Figure 4-1) shows the expected zones and radiation dose limits within each for release of Cs-137 in the exercise.

For our tests, concrete coupons were contaminated with Cs-137 activity levels spanning two orders of magnitude and covering the maximum and minimum activities for the decontamination zones (Figure 4-2). Stable cesium was added to trace Cs-137 spiked solutions to achieve high contamination levels while minimizing testing dose levels. As stable isotopes are unavailable for americium and the disposition and chemistry of lanthanide analogues would need verification, only tracer tests with Am-241 were performed at a concentration corresponding to Zone 3 levels.

FIGURE 4-1 Plume profile used in Liberty RadEx for a hypothetical RDD release. [6,7]

FIGURE 4-2 Activity levels for coupons contaminated with Cs-137 and cold cesium carrier.

Using four different wash solutions, we tested the decontamination of cesium and americium with a 99:1 cross-linked: linear PAM/30% PAA gel prepared at 100% hydration. Tests were run in triplicate, with each gel formulation using the concrete material. All sides of the coupons except the face were sealed with 5-minute epoxy (Devcon 5-min epoxy #14270) for the decontamination experiments. The faces of the coupons were contaminated with 100 μ L Cs-137 spiked stock solutions (prepared at low, medium, and high concentration with non-radioactive cesium as appropriate) or 100 μ L of Am-241 stock solution (only one concentration, since non-radioactive Am is unavailable). Coupons were allowed to dry and then bagged into individual Ziploc[®] plastic bags for counting on a high-purity germanium detector (Detector 1, EG&G Ortec HPGe, position 20 cm, 600-sec live time). Samples were aged with its contamination for seven days at room temperature. After one week, approximately 3-g gel was applied to the contaminated coupon face and left in contact with the contaminated coupon surface for 60 min. The gel was removed from the coupon, allowed to dry before wrapping, then analyzed by gamma spectrometry (under same counting conditions as the contamination coupons).

4.3 RESULTS

Results of cesium and americium removal from the concrete coupon decontaminations with the 99:1 cross-linked: linear PAM/30% PAA gel prepared at 100% hydration using 0.025 M HEDPA and 0.5 M K₂CO₃ gel formulation are shown in Tables 4-1 and 4-2, respectively. The results for cesium decontamination appear consistent with our previous testing that shows ~70% removal of cesium in a single decontamination application.

TABLE 4-1 Cesium (Cs) removal at low, medium, and high contaminant concentrations from concrete using 100% hydrated gel formulations (99:1 cross-linked: linear PAM/30% PAA with various wash solutions). Individual coupon replicate results are shown with average and standard deviations for removal efficiency for each gel formulation.

Coupon ID	Gel Wash Solution	Mass of Gel (g)	Cs Removal (%)	Average Removal (%)	Std Dev Removal (%)
<i>low Cs</i>					
2517-91-LC1	1 M NH ₄ Cl	3.1	78.6	76.1	2.2
2517-91-LC2		2.7	75.3		
2517-91-LC3		3.2	74.4		
2517-91-LC4	1 M KCl	2.4	71.6	71.3	7.2
2517-91-LC5		3.1	78.4		
2517-91-LC6		2.8	64.1		
2517-91-LC7	0.5 M K ₂ CO ₃	3.1	77.0	78.7	8.9
2517-91-LC8		3.4	70.8		
2517-91-LC9		2.6	88.4		

TABLE 4-1 (Cont.)

Coupon ID	Gel Wash Solution	Mass of Gel (g)	Cs Removal (%)	Average Removal (%)	Std Dev Removal (%)
<i>low Cs (Cont.)</i>					
2517-91-LC10	0.5 M K ₂ CO ₃ /0.025 M HEDPA	3.3	77.2	64.5	11.0
2517-91-LC11		3.3	58.7		
2517-91-LC12		3.0	57.8		
<i>medium Cs</i>					
2517-84-MC1	1 M NH ₄ Cl	3.2	70.3	67.7	4.4
2517-84-MC2		2.5	62.7		
2517-84-MC3		3.0	70.2		
2517-84-MC4	1 M KCl	3.2	69.2	63.6	4.9
2517-84-MC5		2.6	60.7		
2517-84-MC6		2.3	60.8		
2517-84-MC7	0.5 M K ₂ CO ₃	3.0	79.0	76.1	7.3
2517-84-MC8		2.9	67.9		
2517-84-MC9		2.8	81.6		
2517-84-MC10	0.5 M K ₂ CO ₃ /0.025 M HEDPA	3.4	47.3	60.8	12.2
2517-84-MC11		3.6	64.4		
2517-84-MC12		3.4	70.8		
<i>high Cs</i>					
2517-89-HC1	1 M NH ₄ Cl	3.2	87.5	87.0	0.51
2517-89-HC2		2.7	86.4		
2517-89-HC3		3.6	87.0		
2517-89-HC4	1 M KCl	3.1	57.6	67.4	13.9
2517-89-HC5		4.1	61.3		
2517-89-HC6		4.0	83.3		
2517-89-HC7	0.5 M K ₂ CO ₃	3.3	67.0	66.6	13.1
2517-89-HC8		3.1	79.4		
2517-89-HC9		3.2	53.2		
2517-89-HC10	0.5 M K ₂ CO ₃ /0.025 M HEDPA	3.8	75.0	61.0	12.2
2517-89-HC11		3.4	53.8		
2517-89-HC12		4.0	54.3		

TABLE 4-2 Americium (Am) removal from concrete using 100% hydrated gel formulations (99:1 cross-linked: linear PAM/30% PAA with various wash solutions). Individual coupon replicate results are shown with average and standard deviations for removal efficiency for each gel formulation.

Coupon ID	Gel Wash Solution	Mass of Gel (g)	Am Removal (%)	Average Removal (%)	Std Dev Removal (%)
2517-92-Am1	0.5 M K ₂ CO ₃	2.6	15.7	18.6	2.9
2517-92-Am2		2.2	18.5		
2517-92-Am3		2.5	21.5		
2517-92-Am4	0.5 M K ₂ CO ₃ /0.025 M	3.3	66.7	73.0	5.8
2517-92-Am5	HEDPA	3.4	78.1		
2517-92-Am6		3.1	74.3		

Importantly, the decontamination results for americium are much improved with this combined formulation. We observed 73% decontamination for the combined SuperGel formulation (appropriate for both Cs and Am decontamination), where before we had only achieved ~50% decontamination of Am from concrete. We suspect that the increased carbonate concentration used in the present tests, the new counter ion to the potassium cation needed for cesium ion exchange, might explain the improved results.

5 PILOT-SCALE TESTING (TASK 4)

5.1 INTRODUCTION

To this point, our research has been focused on benchtop experiments with small test surfaces of urban materials. It is vitally important that we complete pilot-scale tests to assess the variability of the tests' data with larger sample areas. Pilot-scale tests involved larger test samples (0.02–0.09 m² or 6–12 in. square coupons) contaminated to levels consistent with previous testing and dissemination of the wash solution and gel using actual methods expected in the field. Testing at the pilot-scale level was performed at Idaho National Laboratory and Argonne National Laboratory.

5.2 METHODS

5.2.1 Idaho Testing of Combined Formulation

5.2.1.1 Materials

Concrete coupons were prepared in a single batch of concrete made from Type II Portland cement. The ready-mix company (Burns Brothers Redi-Mix, Idaho Falls, Idaho) provided physical data on the cement clinker used in the concrete mix (tricalcium silicate = 57.6%; dicalcium silicate = 21.1%; tricalcium aluminate = 4.5%; tetracalcium aluminoferrite = 8.7%; minor constituents = 8.1%) and meets the ASTM C1501 requirement for Type I and II Portland cement.

To make the concrete coupons, the wet concrete was poured into 0.9-m square plywood forms (approximately 4-cm thick) with the surface exposed. The surface was then “floated” to get the smaller aggregate and cement paste to the top (the surface used for this evaluation), and then was cured for 21 days. Following curing, the 4-cm thick squares were cut with a laser-guided rock saw to the desired concrete coupon size of approximately 15 cm × 15 cm. The coupons had a surface finish that was consistent across all the coupons. All of these coupons were contaminated with 2.5 milliliters (mL) of unbuffered, slightly acidic aqueous solution containing approximately 20 nanocurie (nCi)/mL Am-243 which corresponds to an activity level of approximately 50 nCi per coupon (± 5 nCi). This was delivered using a compressed air line connected to a syringe to produce a fine mist. Coupons were contaminated approximately two weeks before use.

5.2.1.2 Pilot-scale Demonstration

The SuperGel (0.5 M K_2CO_3 , 0.025 M HEDPA, in 99/1 cross linked to linear at 100% hydration) was applied approximately 6-mm thick to the ten coupons using a 4-in. spatula (Figure 5-1), was allowed to dwell on the surface for 90 minutes, and then was removed with a wet vacuum (Little Green, Bissell, Grand Rapids, Michigan).

FIGURE 5-1. Test wall containing the nine concrete samples used in the testing at Idaho National Laboratory using the mixed-isotope formulation of the SuperGel.

5.2.2 Argonne Testing of Combined Formulation

5.2.2.1 Materials

Argonne received seventeen $6 \times 6 \times 1$ in. coupons from the sponsor. These coupons were left in their original package for six months before testing. Prior to testing, each coupon was vacuumed (Rigid Shop-Vac) to remove the cement dust from the surface before application of epoxy to seal the coupon side surfaces. Details on the preparation of these concrete coupons are unknown but they were intended to be replicas of the small coupons used in the tests described in Sections 3 and 4.

Coupon surfaces were sealed prior to the decontamination testing by epoxying coupon sides (Figure 5-2) using a wooden applicator stick. Epoxy was not applied to the bottom surface of the coupons. The bottom of each coupon was labeled with a unique identifier.

FIGURE 5-2 Photograph of epoxied coupon side surfaces.

Contaminated coupons were prepared from a working stock solution of Cs-137 (~500,000 cpm/mL). We contaminated each coupon by distributing 4.0 mL of Cs-137 solution to the face of each coupon in quadrants, yielding ~ 1.0 μC per sample. The Cs-137 solution was soaked up immediately, and the coupon surface appeared to be dry. In a few cases, some areas remained wet with droplets and were allowed to air dry for 20–30 min. We observed no visual differences between these test samples and the others that dried upon contact with the solution. When all coupons were dry, each coupon was double-bagged in a polyethylene (Ziploc®) bag.

We prepared the gel formulation in 1.0 M KCl using a 99:1 cross-linked to linear ratio of Hydrosorce polymers with 10% by mass of polymer in CST (IONSIV 911). A 1.0 M KCl solution was prepared and mixed using an impeller mixer until KCl pellets were dissolved. Dry materials (cross-linked/linear polymers, CST) were weighed and mixed together and were slowly added to 1.0 M KCl solution while mixing for 30 min. The gel was prepared at least four days before the demonstrations, covered with plastic wrap, and placed in the refrigerator.

5.2.2.2 Gamma Analyses

Gamma measurements were performed on contaminated, decontaminated, control, and background coupons using Argonne's low-background counting facility. The gamma analyzer was set to count the 667 keV photopeak of Cs-137 against an HPGe detector at a distance of 13.3 cm from the detector face to the contaminated concrete surface. Coupons were counted for 60 or 180 sec. The coupons from pilot tests #1 and #2 were counted in triplicate by rotating the coupon $\frac{1}{3}$ clockwise between each measurement and centering the coupon about the detector face each time. The counting statistics for the triplicate counts on individual coupons indicated very consistent results, with typically less than 1% RSD. Thus, coupons for pilot test #3 were only counted once.

5.2.2.3 Density and Porosity Measurements

We measured the density and porosity of the concrete used in the demonstration. Using a hammer and chisel, we removed several pieces from the corner of one coupon for measurement using a Micropycnometer (Quantachrome, MPY-5) run with pure helium gas. The true volume of concrete $V_{concrete}$ (excluding pore volume) was calculated using the following expression:

$$V_{concrete} = V_c - V_R[P_1/P_2 - 1] \quad (1)$$

where P_1 is the gas pressure initially in the system, P_2 is the gas pressure after release into the cell, V_c is the volume of the cell (8.300 cm³), and V_R is the reference volume (6.605 cm³).

Calibration spheres (stainless steel, $V_{spheres} = 2.145$ m³) were run to check the calibration of the unit prior to measuring the concrete density. The following values were measured and were in good agreement:

Run #1: $P_1 = 17.050$, $P_2 = 8.824$, $V_{spheres} = 2.143$ cm³.

Run #2: $P_1 = 17.126$, $P_2 = 8.863$, $V_{spheres} = 2.142$ cm³.

The concrete pieces were placed in the sample cell and weighed ($m_{concrete}$). Two measurements were taken, and the average value and range were reported. The true density ρ_{true} was computed by $m_{concrete}/V_{concrete}$.

To measure the bulk density, Archimedes method was used. Deionized water at room temperature was measured to a volume of 15 mL into a graduated cylinder. The same concrete pieces used in the pycnometer were wetted with deionized water to ensure removal of air bubbles from the internal porosity. The surface water was removed by quickly blotting onto a lint-free wipe. After dropping the pieces into the graduated cylinder, water was removed and weighed until the water line measured exactly 15 mL. The mass of water was used to calculate the volume of water displaced by the concrete pieces. This value for volume represented the geometric volume of concrete V_{geom} . The bulk density ρ_{bulk} was determined by $m_{concrete}/V_{geom}$ and the pore density as ρ_{bulk}/ρ_{true} .

5.2.2.4 Pilot-scale Demonstrations

We performed three demonstrations of the decontamination process for removing Cs-137 from large concrete test samples. These tests are outlined in Table 5-1. Details for each of the pilot-scale demonstrations are described in the following text.

In Argonne Pilot Test #1, the rough backside of nine coupons was contaminated as described in Section 5.2.2.1. Coupons were selected for pilot test #1 based upon pore surface. Some of the coupons had large deep pores (Figure 5-3) and were not selected for the first demonstration. Technical problems with the humidity chamber resulted in a variation in the aging conditions for the coupons. For three days, the coupons inside the humidity chamber were held at 90% relative humidity and 40°C, but over the weekend the humidity may have dropped

below 90%. When we returned to the lab on Monday morning, the humidity read 70% at 40°C. These issues with the humidity chamber forced us to shut down the chamber for the remaining two days. The coupons were left inside the chamber with open water containers placed in the bottom of the chamber; the temperature in the chamber was allowed to return to ambient (22°C).

TABLE 5-1 Summary of Argonne pilot-test conditions for cesium-137 contaminated concrete coupons.

Argonne Pilot Test #	Contamination Surface for Cs-137	Contaminant Aging Test Conditions	Contaminant Aging Time (days)	Decon Gel Application
Pre-demo	6 × 6 in. rough concrete	22°C, 76% RH	3	Hand trowel
1	6 × 6 in. rough concrete	40°C, 90% RH 40°C, 70–90% RH* 22°C, 70–90% RH*	3 2* 2*	Hand trowel
2	6 × 6 in. smooth concrete	22°C, 64% RH*	7*	Hand trowel
3	6 × 6 in. smooth concrete	40°C, 90% RH	7	Spray gun

* Technical issues were noted with the humidity chamber and the system remained unoperational for the noted duration of tests. The low water vapor permeability of the low-density polyethylene bags used for the coupon tests [8] was used as the basis for assuming that the relative humidity for the coupons was the average relative humidity for the day when the coupons were placed into the bags.

FIGURE 5-3 Photograph showing large pores on surface of concrete coupon.

Non-radioactive and radioactive dry runs with a 6 × 6 in. test sample were performed to evaluate best practices and to ensure a smooth demonstration. A test sample was securely attached to the test stand, and the gel prepared above was applied to the face of the test sample with a plastic trowel.

On the day of the demonstration, test samples were removed from the humidity chamber or double-bag containment and placed onto the test stand. The test samples were placed numerically in rows from left to right. The gel was applied to all test samples, except Sample 5 (control sample), using a trowel spackling tool (Figures 5-4 and 5-5). Gel was applied to the face of each test sample beginning with Sample 1 through Sample 9 and was completed in four min. After one h, the gel was removed from the coupons with the 3-in.-diameter hose of the HEPA vacuum (Figure 5-6). The hydrogel was removed cleanly with very little residue (Figure 5-7), although it should be noted that the suction from a portable wet/dry vacuum is stronger. Test samples were removed from the test stand, double-bagged, and surveyed for transfer to the gamma counting room.

FIGURE 5-4 Photograph of demonstration test stand and setup: attached coupons, trowel for 1.0 M KCl gel application (on left side of test stand), and HEPA-Vac for gel removal (on floor to right of cart).

FIGURE 5-5 Photograph of test sample decontamination using 1.0 M KCl gel formulation for pilot test #1.

FIGURE 5-6 Photograph showing 1.0 M KCl gel removal with HEPA-Vac.

FIGURE 5-7 Photograph of completed demonstration from pilot test #1.

In Argonne Pilot Test#2, we repeated the demonstration by contaminating the smooth coupon face (Figure 5-8). Eight unused samples were contaminated on the smooth front side, as described above. The contaminated control coupon (coupon #5) from Pilot Test #1 was reused. Because the humidity chamber was still not operational and undergoing repairs, it was not used for aging the coupons. The Cs-137 contaminated coupons remained within double-bag containment at ambient temperature for one week.

The 1.0 M KCl gel formulation was used for the decontamination. The test procedure was the same as described for Pilot Test #1. The SuperGel was applied by hand using a trowel. The test stand with gel applied to the coupons is shown in Figure 5-9. After one hour, the gel was removed from the coupons with the 3-in. diameter hose of the HEPA vacuum.

FIGURE 5-8 Photograph showing smooth side of concrete coupon used in pilot test #2.

FIGURE 5-9 Photograph of coupon decontamination (smooth side) using 1.0 M KCl gel formulation for pilot test #2.

In Argonne Pilot Test#3, the nine coupons used in Test #1 (contaminated on the rough, backside) were reused. To start, the front-side (smooth) face was gamma counted to establish the background due to the residual contamination on the (rough) backside. The front side was then contaminated as described above and gamma counted again (except for coupon #5). Contaminated coupons were aged for one week in the humidity chamber at 90% relative humidity and 40°C. Decontamination of the coupons was performed in a tented shelter (Figure 5-10). The gel was applied using a viscous spray unit (GRACO 55:1 Bulldog, 5-gallon stationary single-post ram package with GRACO airless gun) (Figures 5-11 and 5-12). After one hour, the gel was removed from the coupons with the 3-in. diameter hose of the HEPA vacuum (Figure 5-13).

FIGURE 5-10 Tented contamination shelter for Argonne pilot test #3 with test stand in back of the shelter and double-bagged coupons on cart in front opening of shelter.

FIGURE 5-11 Sprayer wand ready to start gel application on contaminated coupons secured within test stand in tented shelter.

FIGURE 5-12 Sprayer applying gel to contaminated coupons.

FIGURE 5-13 Removal of gel from contaminated coupons using HEPA vacuum during pilot test #3.

5.3 RESULTS

5.3.1 Density and Porosity Measurements

The true density of the concrete pieces received from the sponsor for the Argonne Pilot Tests ($m_{\text{concrete}} = 4.0872 \text{ g}$) was measured by pycnometer with the following values:

$$\begin{aligned} \text{Run \#1: } P_1 &= 16.983, P_2 = 8.067, V_{\text{concrete}} = 0.9999 \text{ cm}^3. \\ \text{Run \#2: } P_1 &= 17.112, P_2 = 8.128, V_{\text{concrete}} = 0.9994 \text{ cm}^3. \end{aligned}$$

This gave a true density of 2.596 g/cm^3 .

Two measurements using Archimedes method on 2.5949 g of concrete yielded masses of displaced water of 1.1484 g and 1.083 g for an average volume of water of 1.1157 g . With the density of water of 0.999 g/cm^3 , a bulk density of 2.33 g/cm^3 was calculated. Using these two density values, we calculated a porosity of 11%, compared to 24% for the small coupons used throughout the program. This low porosity for the large concrete coupons seems contradictory to observations made during contamination of the coupons, whereby the contaminant solution beaded up on the surface on the small coupons and took almost an hour to dry versus the immediate uptake of the contaminant solution by the large concrete coupons. Without details on

the fabrication of the coupons it is difficult to conjecture the discrepancy in density between small lab samples and these pilot scale test samples. Perhaps hydrophobic polymer was included in the small coupon tests that were not in the larger coupons. Such polymers are added often to concrete to control properties. Such a polymer could permit higher decontamination factors than more dense coupons.

5.3.2 Idaho Testing of Combined Formulation

Idaho National Laboratory (INL) conducted tests on the removal of americium-243 from U.S. concrete samples (Table 5-2). Even though the contaminated substrates were U.S.-made concrete (6 × 6 in. coupons) with a very different composition than that of concrete reported in previous sections of this report, this is valuable data since it provides another test set for the mixed isotope hydrogel formulation.

TABLE 5-2 Preliminary Results from INL Pilot Test on U.S. Concrete Coupons.

	Pre-Decon Activity (nCi/Coupon)	Post-Decon Activity (nCi/Coupon)	%RSD
	52	10	80%
	56	21	62%
	51	18	65%
	42	16	62%
Avg	50	17	67%
SD	6	5	9%

5.3.2 Argonne Testing of Combined Gel Formulation

The pre-test for Argonne Pilot Test #1 was performed on a single concrete coupon to establish safe work procedures. Therefore, this coupon was aged under ambient lab conditions and was not maintained under the test conditions for the pilot test #1 coupons. This pre-test coupon was only aged for 3 days in double-bag containment at 22°C and 76% RH (ambient conditions). Decontamination of the coupon resulted in 52.4% cesium removal from its rough surface.

Pilot Test #1 demonstration coupons were aged for 7 days within the humidity chamber. The chamber failed to maintain the set humidity during the coupon aging process, but testing was continued within the chamber while we attempted to maintain high humidity conditions by using open containers of water (refer to Table 5-1). The contamination and decontamination data for the coupons are shown in Figure 5-14. Triplicate gamma counting was performed on the

individual coupons and showed very little variability, with a RSD of 0.2–1.7%. The positive control coupon validated the gamma counting and decontamination test processes, i.e., no effect on the control coupon activity was found (RSD of 0.7% for the control counts before and after decontamination). Background counts of a clean coupon were also performed and gave low count rates expected for the counting facility. Decontamination results for removal of cesium from Pilot Test #1 on concrete coupons with a rough surface are shown in Figure 5-15. The average cesium removal was 31.7 % ($\pm 3.7\%$ standard deviation) for coupons that were aged for 7 days at 22–40°C and 70–90% RH. The RSD between the coupons tested was only 12% despite the variability in test aging conditions.

FIGURE 5-14 Activity of coupons from Argonne Pilot Test #1 before (dark color) and after (light color) decontamination. Triplicate counts shown for individual coupons; control coupon activity shown on right.

FIGURE 5-15 Decontamination results for Cs-137 from Argonne Pilot Test #1.

The smooth surfaces of concrete coupons were contaminated with Cs-137 in the Pilot Test #2 demonstration. Coupons were aged for 7 days within double-bag containment at ambient room conditions. At the time of this demonstration, the humidity chamber was not operational and undergoing repairs. The contamination and decontamination data for the coupons are shown in Figure 5-16. Triplicate gamma counting was performed on the individual coupons and showed very little variability (RSD of 0.2-3.0%). The positive control coupon validated the gamma counting and decontamination test processes, i.e., no effect on the control coupon activity was found (RSD of 4.0% for the control counts before and after decontamination). Background counts of a clean coupon were also performed and gave low count rates expected for the counting facility. Decontamination results for removal of cesium from Pilot Test #2 on concrete coupons with a smooth surface are shown in Figure 5-17. The average cesium removal was 50.5 % ($\pm 5.7\%$ RSD) for coupons that were aged for 7 days at 22°C and 64% RH. The RSD for the decontamination for all eight coupons tested was only 11%. While cesium was removed 1.6 times greater from the smooth concrete surface than the rough surface, the coupon aging conditions were not the same between pilot test #1 and #2. An additional pilot test was performed on concrete coupons at the required temperature and humidity for cesium contaminant on the smooth surface.

FIGURE 5-16 Activity of coupons before (dark color) and after (light color) decontamination from Argonne Pilot Test #2. Triplicate counts shown for individual coupons; control coupon activity shown on right.

FIGURE 5-17 Decontamination results for Cs-137 from Argonne Pilot Test #2 (individual coupons and average of eight coupons and control coupon).

The smooth surfaces of concrete coupons were contaminated with Cs-137 in the Pilot Test #3 demonstration. The coupons were aged for 7 days within the humidity chamber at 40°C and 90% RH. The contamination and decontamination data for the coupons are shown in Figure 5-18. Triplicate gamma counting was performed on the individual coupons and showed very little variability (RSD of 1.7%). The positive control coupon validated the gamma counting and decontamination test processes, i.e., no effect on the control coupon activity was found (RSD of 1.8% for the control counts before and after decontamination). Background counts of a clean coupon were also performed and gave low count rates expected for the counting facility. Decontamination results for removal of cesium from Pilot Test #3 on concrete coupons with a smooth surface are shown in Figure 5-19. The average cesium removal was 36.8% ($\pm 4.0\%$ standard deviation) for coupons that were aged for 7 days at 40°C and 90% RH. The relative standard deviation for the decontamination for all eight coupons tested was low, 11%, which is typical of what had been seen with other tests.

FIGURE 5-18 Activity of coupons before (dark color) and after (light color) decontamination from Argonne Pilot Test #3. Triplicate counts shown for individual coupons; control coupon activity shown on right.

FIGURE 5-19 Decontamination results for Cs-137 from Argonne Pilot Test #3 (individual coupons and average of eight coupons and control coupon).

While it was initially assumed that the short aging time (pre-test with only one coupon) and surface roughness of the coupons (large pores in the coupon face) were a key factor in lower decontamination results when compared with the small coupon testing results, higher temperatures (40°C) and low humidity for aging the contaminant may also be important. The average cesium removal was slightly higher (but within the standard deviation of the results) from the smooth concrete surface than the rough surface when the coupon aging conditions were most similar (Table 5-3 for pilot tests #1 and #3). When coupon surfaces were the same (smooth), the lower temperature and humidity aging conditions for the contaminant on the concrete gave 13.7% higher cesium removal (Table 5-3 for pilot tests #2 and 3).

Future work could entail characterization of the composition of these 6 × 6 in. coupons was identical to the 2 × 2 in. coupons previously provided, of the pore structure on each side of the coupon and testing of surface absorption, and permeability as a function of aging conditions.

TABLE 5-3 Summary of cesium removal results on Singapore concrete from Argonne pilot tests.

Argonne Pilot Test #	Contaminant Aging Conditions	Coupon Contamination Surface	Number of Contaminated Coupons Tested	% Cs Removal Average (Standard Deviation)
Pre-demo	Time: 3 days Containment: double-bag Temp: 22°C ^a Relative Humidity: 76% ^b	rough	1	52.4
1	Time: 7 days Containment: chamber ^c Temp: 22 ^a –40°C Relative Humidity: 70 ^c –90%	rough	8	31.7 (± 3.7)
2	Time: 7 days Containment: double-bag Temp: 22°C ^a Relative Humidity: 64% ^b	smooth	8	50.5 (± 5.7)
3	Time: 7 days Containment: chamber Temp: 40°C Relative Humidity: 90%	smooth	8	36.8 (± 4.0)

^a Assumed average ambient laboratory temperature.

^b Assumed average relative humidity for day coupons that were bagged; information obtained from local city weather history records.

^c Chamber failure occurred.

6 CONCLUSIONS

Argonne National Laboratory improved the superabsorbing gel-based process (SuperGel) for the decontamination of cesium from concrete and other porous building materials from a coastal city in Southeast Asia. To mitigate a potential problem in obtaining bulk quantities of crystalline silico-titanate materials (IONSIV-910) for capture of cesium, we perused the literature for other sequestering agents. There was little information in the literature describing the sorption characteristics of cesium from salty waters except for the work done related to the underground, high-level liquid waste storage tanks in the United States that contain molarity concentrations of sodium. We chose to test the clays illite and vermiculite with the zeolite chabazite. Chabazite and vermiculite did not produce K_d values as high as crystalline silico-titanate in NH_4^+ salt solutions but did exceed the K_d values for crystalline silico-titanate in

K⁺ solutions. Both chabazite and vermiculite are available in bulk quantities from the United States but their availability worldwide would have to be determined.

Similarly, we explored sequestering agents for Am³⁺ and found that the literature does not include separation from salty solutions except for the studies on liquid nuclear waste solution. We decided to test birnessite and clinoptilolite and compare these results to those for sorption onto montmorillonite and vermiculite. From KCL, Am³⁺ sorbed well onto all but montmorillonite. In the acidic HEDPA solutions, all sorbents had K_d values < 20 mL/g. In Na⁺, birnessite performed well above (K_d > 10,000 mL/g) the others (K_d < 200 mL/g). The availability of bulk birnessite needs further evaluation.

Next, we tested the SuperGel formulation that was compatible for both cesium and americium decontamination. This formulation combined the K⁺ or NH₄⁺ salts needed for cesium decontamination with the CO₃²⁻ and HEDPA needed to decontaminate americium effectively. We tested different combinations of these reagents and found that 64 to 83% Cs-137 could be removed with no difference in percent removal of cesium as a function of concentration of cesium for coupons aged for 24 hours with contamination. The most effective combination was the 1 M K⁺ or NH₄⁺ as the carbonate salt in 0.025 M HEDPA. We tested the removal of americium and cesium from concrete, brick, and tile aged one week with contamination. For cesium tests, we removed 73% from tile, 45% from concrete and 9.8% from brick. For americium tests, we removed 86% from tile, 31% from concrete, and 9.8% from brick. The lower percent removal values from previous tests is attributed to dry conditions during the aging process.

We conducted tests on U.S.-made 6 × 6 in. coupons (1 in. thick) contaminated with Cs-137 and aged for three days using the combined gel formulation (0.5 M K₂CO₃, 0.025 M HEDPA, in 99/1 cross linked to linear at 100% hydration). From four replicates, they removed 67±9% of the cesium.

Then, we ran several tests on concrete samples (6 in. × 6 in.) provided by the sponsor and aged the Cs-137 for seven days before applying the hydrogel reconstituted in 1 M KCl. We removed 32% of cesium from the rough backside of the concrete samples aged at 70–90% relative humidity and 22–40°C, 50.5% from the smooth side aged at 64% relative humidity and 22°C, and 37% of cesium from the smooth side aged at 90% relative humidity and 40°C.

Additional tests with mixed isotope formulation are recommended to understand better the variance of decontamination efficacy with material property and large coupon tests should be conducted with the mixed isotope formulation.

APPENDIX A CLINIPTOLOLITE SUPPLIERS IN UNITED STATES

U.S. Companies Producing or Selling Clinoptilolite			
Company	Mine Site	Zeolite Type	Web Site
Bear River Zeolite LLC P.O. Box 643 47 Cox Gulch Road Thompson Falls, MT 59873 406-827-3523	Idaho	K-rich Clinoptilolite	http://www.bearriverzeolite.com/
KMI Zeolite Inc. 3100 Sandy Valley Road Jean, NV 89019 Phone: 702-723-5415	California	Clinoptilolite	http://www.kmizeolite.com/
St. Cloud Mining Co. P.O. Box 196 761 Saint Cloud Road Winston, NM 87943 (575) 743-5215	New Mexico	Clinoptilolite	http://www.stcloudmining.com/
Steelhead Specialty Minerals Rock Pointe Corporate Center 1212 North Washington Street Suite 12 Spokane, WA 99201 (509) 328-5685	California	Clinoptilolite	www.steelheadspecialtyminerals.com
Teague Mineral Products 1925 Highway 201 South Adrian, OR 97901-9407 (541) 339-3940	Oregon	Clinoptilolite	http://teaguemineralproducts.com/
Zeotech Corp. 6 Mangham Court Peralta, NM 87042 (505) 866-0301	Texas	Clinoptilolite	http://www.zeotechcorp.com/

**APPENDIX B COMPANIES CONTACTED FOR AVAILABILITY OF BIRNESSITE,
CLINOPTILONITE, ILLITE, AND ROMANECHITE**

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Company	Product	Amount/Cost	Comment	Contact	Link
Minerological Research Company	all		mineral collectors	408-923-6800	http://minresco.com/
Pala International	none		mineral collectors	760-728-9121	www.palaminerals.com
Cowboy Mining Company	none	\$80 per ton-flatbed holds 22 1/2 tons	Have Na bentonite	800-243-7455	www.cowboymining.com/
Kimble Company			Does not distribute these minerals.	800-501-0002	www.kimblecompanies.com/
Messer Clay Company			Does not distribute these minerals.	606-255-0388	www.messerclaycompany.com/
American Colloid Company	all		Spoke to geologist/mining manager: see file for USA Zeolite Sources-said to try Boral, KMI, and St. Cloud for clinoptilolite (below).	Dave Carroll - Geologist/Mining Manager	www.colloid.com/
Boral	illite		Spoke to Carl and will get back to me.	800-5boral5	www.boralbricks.com
KMI Zeolite Inc. (on list from American Colloid)				Conrad Wagner 866-725-7253	http://kmizeolite.com/

Company-----	Product	Amount/Cost	Comment	Contact	Link	
St. Cloud Mining Co. (on list from American Colloid)	clinoptilolite	\$450 per ton	Largest supplier of clinoptilolite in U.S.; however, it is made to order. Sent us 2 types each with 3 mesh sizes plus a sample of chabazite.	Joe McEnaney 203-761-1291 cell 203-209-6084	http://stcloudmining.com/	
University of Wisconsin	birnessite		Initially offered to supply gram quantities	Joel Pedersen 608-263-4971	joelpedersen@wisc.edu	
The Ohio State University	birnessite		Is sending 20-25 g.	Nicholas Basta 614-292-6282	basta.4@osu.edu	Professor of Soil and Environmental Chemistry, School of Environment and Natural Resources, 410C Kottman Hall, The Ohio State University Columbus, Ohio 43210
Chevron	all		Does not know of commercial deposit, samples available for purchase. Chevron noted that we will not find these samples in pure form.	Eric Daniels	ericdaniels@chevron.com	
Specialty Vermiculite Corp.	vermiculite	\$120 per ton	Sent 50 lb sample to Menomonee Wisc. for demo.	Deb Sobel	dsobel@spvcorp.com	SPV Corp. 2666 Gaynor Ave. NW Grand Rapids, MI 49544

Company	Product	Amount/Cost	Comment	Contact	Link
U.S. Geological Survey	all		Sent e-mail with contact information. Said we should contact Christy Minerals for clinoptilolite (below).	Robert Virta 703-648-7726	rvirta@usgs.gov Mineral Commodity Specialist National Minerals Information Center U.S. Geological Survey Reston, VA 20192
Christy Minerals (referred by Robert Virta USGS)	illite		Sent 2 illitic samples that formed a mud-like slurry and were deemed unusable	Jeff Porter 636-585-2214, # 239	jporter@christyminerals.com
Chevron	all		Pure illite is not easy to obtain. Birnessite, a manganese oxide that can be made synthetically, and clinoptilolite (a zeolite) are possibly available elsewhere. Purity is often not high.	Douglas McCarty	DMcCarty@chevron.com Chevron ETC 3901 Briarpak Houston, TX 77042

APPENDIX C SUPPLIERS OF CLINOPTILOLITE AND CHABAZITE

Sample	Company	State	Product Type	Zeolite Type	Calculated CEC*	Company Reported CEC	Montmoril- lonite	Opal C-T	Calcite	Quartz	Feldspars
R01-0134	St. Cloud Mining, Inc.	NM	Zeolite (var. Clinoptilolite) 6 × 14 mesh	Clinoptilolite	>120	80–120				3–10%	Trace
R01-0137	American Abs. Products (closed?)	OR	Zeolite 6 × 14	Clinoptilolite	>120						
R01-0138	Moltan Co L.P.	NV	Zeolite / Diatomaceous Earth	Clinoptilolite/ Mordenite	50–80		10–30%	3-10%			Trace
R01-0287	Ash Meadows (ZEOX Corp)	CA	Clinoptilolite	Clinoptilolite	>120					Trace	
	KMI Zeolite Inc.	CA		Clinoptilolite	>160	160–210				<5%	
	Bear River Zeolite	ID		Clinoptilolite	150	140–165		15%			
	Steelhead Specialty Minerals	ID		Clinoptilolite							
	Teague Mineral Products	ID / OR		Clinoptilolite							
	GSA Resources (ZEOX Corp)	AZ		Chabazite		250					
	UOP LLC	AZ		Chabazite/ Mordenite	210						

Sample	Company	State	Product Type	Zeolite Type	Calculated CEC*	Company Reported CEC	Montmorillonite	Opal C-T	Calcite	Quartz	Feldspars
R01-0139	Zeotech Corp.	TX	Kitty Crystals	Clinoptilolite	50–120		10–30%	3–10%	Trace		
	Daleco Resources Corp	TX		Clinoptilolite							

Type	CEC (Theoretical)	CEC (Practical)	Pore Diameter
Clinoptilolite	230 meq/100 g	180 meq/100 g	3.9–5.4 Angstroms
Mordenite	220 meq/100 g	175 meq/100 g	2.9–5.7 Angstroms
Chabazite	390 meq/100 g	310 meq/100 g	3.7–4.2 Angstroms

* Implied CEC based on estimated percentage of zeolite present.

APPENDIX D PRICE FOR VERMICULITE IN BULK

**Enoree List Pricing
Effective thru April 30, 2012
(whereupon pricing will then be reviewed)**

For information, please contact Customer Service at (800) 342-2017 between the hours of 8:30am and 5:00pm EST.

VCX Vermiculite Ore Concentrate

<u>Products</u>	<u>Unit Of Sale</u>	<u>Price Per Unit</u>	<u>Price Per Ton</u>
<u>Bulk Shipments:</u>			
VCX 205 Bulk	Ton	\$120.00	\$120.00
<u>Packaged Goods:</u>			
VCX 205 50# Bags (60/Pallet)	Bag	\$3.84	\$154.00
VCX 205 3000# Tote	Tote	\$212.00	\$141.00

Terms and Conditions of Sale:

1. All sales are subject to SPV's Standard Conditions of Sale (see reverse side).
2. Payment Terms: Net 30 Days.
3. All pricing is FOB SPV's plant in Enoree, SC.

Notes:

1. Minimum order is 60 bags or 1 pallet.
2. For additional information on ordering, packaging or delivery, please contact the SPV Customer Service Center or your sales representative.
3. The palletizing configurations included with this pricing are:

50# Bags: 60 Bags stretch wrapped on a 40" X 48" wood pallet.

3000# Tote With Pallet: 1 Tote on a 48" X 48" wood pallet.

4. Typical volumes per load are:	Unit Of	Unit Volume	Ton Volume
Description:	<u>Sale</u>	<u>Per Shipment</u>	<u>Per Shipment</u>
Bulk Rail Shipments:	Ton	95	95
Bulk (LCL) Shipments:	Ton	21	21
50# Bags	Bag	840	21
3000# Tote	Tote	14	21

5. Tote Charge & Return Policy: SPV will provide a returnable tote sack as packaging for this product. A tote sack charge of \$25.00 each and \$12.00 each per pallet will be charged on your invoice. This deposit will be credited back to your account once the totes and pallets are returned freight prepaid to the SPV plant that originally shipped the product i.e., Specialty Vermiculite Corp., Hwy 221, Enoree, SC 29335. The totes are to be folded, stacked and banded on a pallet upon return to facilitate counting. Naturally, SPV reserves the right to inspect the returned pallet and totes prior to issuing the credit, with only totes that are returned clean, folded, and in reusable condition being eligible for credit. Deposits on damaged totes/pallets or totes not originally supplied by SPV will not be refunded.

6. A "Block and Brace" charge of \$40.00 will be added for intermodal shipments.

7. For disposable tote and pallet, add \$20 per unit (\$13 for tote and \$7 for pallet).

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