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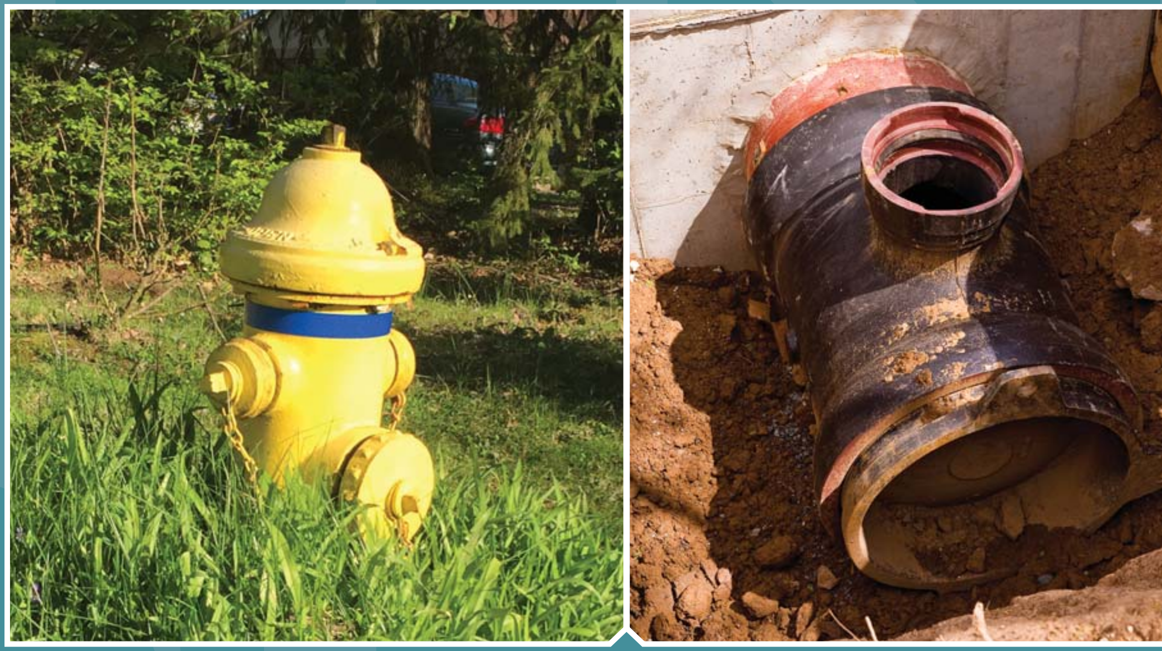
Radiological Contaminant Persistence and Decontamination in Drinking Water Pipes



Office of Research and Development
National Homeland Security Research Center

Radiological Contaminant Persistence and Decontamination in Drinking Water Pipes

U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

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NOTICE

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Battelle

LIST OF ABBREVIATIONS

ABC	Analytical Balance Corporation
AR	annular reactor
ASTM	ASTM International
AWWA	American Water Works Association
BG	background or not detectable above background
°C	degrees Celsius
CCA	chemical cleaning agent
cfu	colony forming units
cm	centimeters
EPA	U.S. Environmental Protection Agency
%E	percent error
EDTA	ethylenediaminetetraacetic acid
FE	flushing evaluation
ft/s	foot/second
g	gram
in.	inch
HPC	heterotrophic plate counts
L	liter
lpm	liter per minute
µL	microliter
µg	microgram
mg	milligrams
mm	millimeters
mL	milliliters
min	minute
NHSRC	National Homeland Security Research Center
%P	percent persistence
PDEDP	pipe decontamination experimental design protocol
PE	persistence evaluation
PVC	polyvinyl chloride
QAPP	Quality Assurance Project Plan
QC	quality control
%R	percent recovery
RPD	relative percent difference
rpm	revolutions per minute
WECE	water exposure control experiment

EXECUTIVE SUMMARY

The objective of this study was to use the Pipe Decontamination Experimental Design Protocol (PDEDP) to evaluate the persistence of cesium, cobalt, and strontium on concrete and polyvinyl chloride (PVC) and explore possible decontamination approaches. The PDEDP is an approach for evaluating the persistence characteristics of contaminants on drinking water pipe materials and various decontamination approaches.

During this study, conditions within operational drinking water pipes were simulated using annular reactors (i.e., ring-shaped reactors). The annular reactors consist of a glass outer cylinder and a rotating polycarbonate inner cylinder with 20 flush mounted rectangular coupons that are made of materials that simulate drinking water pipe materials. For this study, concrete-lined and PVC coupons (samples) were used. Shear stress was applied to the coupon surfaces by setting the reactors' inner cylinder rotation to 100 revolutions per minute, which produces shear forces similar to 1 ft/s flow in a 6 inch pipe. During normal operation, the flow of drinking water through the reactor was maintained at approximately 0.2 liter per minute so that the residence time of the water in the reactor was approximately 5 minutes. Prior to use of any pipe material coupons, a biofilm was grown on all of the coupons. Each contaminant was studied separately and coupons were not shared between experiments.

The study included five components for each contaminant studied:

- Surface extraction method validation - The surface extraction method validation confirmed that cesium, cobalt, and strontium could be extracted from the coupons after direct contamination of the coupons.
- Surface contamination method validation - The surface contamination method validation confirmed that coupons could be contaminated with all three contaminants by exposing them to a solution of contaminated water.
- Persistence evaluation – Pipe material coupons were contaminated and then exposed to fresh tap water in annular reactors operating at 100 rpm (simulating 1 ft/s flow). The results of the persistence evaluation showed that cesium was not persistent on concrete pipe materials. Conversely, cobalt and strontium were persistent on

concrete; cobalt more so than strontium. Similarly to concrete, cesium was not persistent on PVC pipe materials. In addition, cobalt and strontium were not persistent on PVC pipe materials.

- Decontamination evaluation for flushing – Pipe material coupons were contaminated and then exposed to fresh tap water in reactors operating at 200-250 rpm (simulating 1.6-2.5 ft/s flow). The results from the flushing evaluation for cesium, cobalt and strontium confirmed the results that were observed during the persistence evaluations.
- Decontamination evaluation for chemical cleaning agents – Pipe material coupons were contaminated and then exposed to a solution containing one of the following cleaning agents in reactors with no rotation: ethylenediaminetetraacetic acid (EDTA), tartaric acid, calcium chloride, ammonium acetate. EDTA was an effective chemical cleaning agent for cobalt on concrete. Tartaric acid also performed well for cobalt on concrete however, it formed a yellow precipitate on the surface of the coupons. Ammonium acetate and calcium chloride were both moderately effective as chemical cleaning agents for strontium on concrete. None of the contaminants were persistent on PVC pipe materials so chemical cleaning agents were not evaluated on PVC. Cesium was not persistent on concrete so chemical cleaning agents were not evaluated for cesium.

1.0 INTRODUCTION

The U.S. Environmental Protection Agency's (EPA) National Homeland Security Research Center (NHSRC) conducts research to protect infrastructure, and to detect, respond to and recover from terrorist attacks on the nation's water and wastewater infrastructure. The potential for contamination of water infrastructure with radiological contaminants is one area of concern. Previous to this study, EPA's Persistence and Decontamination Experimental Design Protocol (PDEDP), a procedure to quantitatively determine the persistence of contaminants on various drinking water pipe materials, had been developed. The objective of this project was to test the PDEDP using surrogates for radiological contaminants and, if the radiological contaminants persists, to test techniques for decontaminating the pipe surfaces.

Annular reactors (AR) (i.e., ring-shaped reactor) were used to simulate the flow of contaminants past drinking water pipe materials. The drinking water pipe materials included concrete and polyvinyl chloride (PVC). Concrete (or cement-mortar) is a common lining on the interior of iron drinking water pipes. PVC can be used in home plumbing and distribution system pipes. The contaminants spiked into the ARs included stable cesium (Cs)-133, cobalt (Co)-59, and strontium (Sr)-88. These contaminant surrogates were selected because of the likelihood of the presence of the actual contaminants in water systems due to a radiological incident (e.g., Radiological Dispersal Device, Nuclear Power Plant accident, or direct contamination of the system). The following report includes a summary of the experimental design as well as the results, with one section dedicated to each pipe material and contaminant combination that was tested.

2.0 SUMMARY OF PIPE DECONTAMINATION EXPERIMENTAL DESIGN PROTOCOL (PDEDP)

The PDEDP includes five sequential experimental steps. These steps are included

1. Surface extraction method validation
2. Surface contamination method validation
3. Contaminant persistence evaluation
4. Contaminant flushing evaluation

5. Chemical cleaning agent evaluation.

Summaries of the experimental set up, each step of the experimental design, and details of the analytical methods are provided below. Each contaminant was studied separately using the PDEDP and fresh coupons were used for each experiment.

2.1 Experimental Reactor System

The conditions within operational drinking water pipes were simulated in annular reactors (AR) (BioSurface Technologies Corporation, Bozeman, MT). The ARs consist of a glass outer cylinder and a rotating polycarbonate inner cylinder with 20 flush mounted rectangular coupons that are made of materials that simulate drinking water pipe materials. Tap water flows into the top of the reactor, through the annular space, and then exits through the bottom. The rotating inner drum keeps the water in the annular space well mixed.

For this testing, concrete and PVC coupons (BioSurface Technologies Corporation, Bozeman, MT) were used. For the concrete-lined coupons, the cement in the concrete (or cement-mortar matrix) met the requirements of the C150-07 ASTM International Standard Specification for Portland Cement (1) and the thickness of the concrete was approximately 1.3 millimeter (mm), which is slightly less than as specified in American Water Works Association (AWWA) C104-03 Standard for Cement-Mortar Lining for Ductile-Iron Pipe and Fittings for Water (2). The concrete coupons were made from a polycarbonate backing with the concrete applied at the above thickness. Concrete was separated from the polycarbonate during sampling and only the concrete was analyzed. The PVC coupons were made entirely of PVC so no separation was required.

The coupons had surface areas of 14 mm × 148 mm. Shear stress was applied to the coupon surfaces by setting the inner cylinder rotation to 100 revolutions per minute (rpm), which produces shear forces similar to 30.5 centimeter (cm)/second (s) (1 foot (ft)/s) flow in a 15.2 cm (6 inch (in.)) pipe (3). For the flushing evaluation, the cylinder rotation was set as high as 250 rpm, corresponding to shear similar to 75 cm/s (2.5 ft/s) flow in a 15.2 cm pipe. During normal operation, the flow of drinking water through the annular space of the AR (connected directly to the tap) was maintained at approximately 0.2 liter per minute (lpm) so the residence time of the water in the AR was approximately 5 minutes. This water flow prevented the depletion of chlorine levels in the water and minimized re-deposition of sheared contaminants on the coupons.

The pH and temperature of the drinking water was measured daily using a multi-parameter water monitor (Rosemount Analytical Model WQS, Rosemount Analytical, Irvine, CA). The free chlorine concentration of the drinking water was measured daily using a Hach® analyzer (Hach CL17 or DR5000, Hach Company, Loveland, CO). The ARs were always operated in the dark by covering them completely with aluminum foil. Because some contaminant was likely to adsorb onto the non-coupon components of the AR and affect the amount of contaminant that was available for coupon contamination, the concentration of the bulk contamination solutions was measured to ensure that an adequate concentration of contaminant was maintained to achieve coupon contamination.

2.2 Coupon Biofilm Growth

Biofilm was grown on all of the coupons before the method validation (surface contamination extraction and surface contamination), contaminant persistence and decontamination (flushing and chemical cleaning agent) steps. The biofilm was grown by submerging the required number of coupons into a sterile container that allowed recirculation of dechlorinated tap water fortified with 1 gram (g) of yeast extract as a nutrient for biofilm growth. Dechlorination of the tap water enhanced biofilm growth and reduced the time necessary to establish a biofilm. The container was kept in the dark to better simulate biofilm growth in an enclosed pipe and water was recirculated using a pump for at least four days with an additional 1 g of yeast added after every two days.

The biofilm growth on the coupons was measured using heterotrophic plate counts (HPC). Coupons to be measured for HPC were centrifuged within a Triton™ X solution (Sigma-Aldrich, St. Louis, MO), mixed using a vortex mixer (Sigma-Aldrich, St. Louis, MO), and then decanted. Two tenfold dilutions of that decanted solution were prepared and plated in triplicate on tryptic soy agar plates using a pipette (Rainin L200, L19304, Rainin Instrument LLC, Oakland, CA). After incubation for 48 hours at 35-37 degrees Celsius (°C), the distinguishable colonies on each plate were counted and surface density of HPC was calculated.

Throughout the concrete and PVC experiments, 15 sets of coupons were used and the HPC densities were determined for nine of the 15 sets. On average, the HPC densities were 2.3

× 10^6 colony forming units (cfu)/cm^2. The standard deviation of the HPC densities was 1.6 × 10^6 cfu/cm^2. While there was not a target HPC density for the coupons, the consistent growth of biofilm (densities within one log of one another) provided a means to simulate pipe conditions encountered in the field on pipe material coupons.

2.3 Persistence and Decontamination Experimental Design Protocol (PDEDP)

The generation of persistence and decontamination data from this experimental design included contamination of coupons by exposing them to bulk solutions of the surrogate radiological contaminants. Thereafter, the persistence of each contaminant on the coupons and/or the application of a decontamination approach were investigated to determine both the propensity of each contaminant to persist on the coupons and the effectiveness of decontamination approaches in removing the contaminant from the coupon surface. The usefulness of results from such experiments relies on the accuracy of the contaminant measurements. In order to be confident in these measurements, two important questions needed to be answered about the approach to contaminant measurement:

- When a contaminant has adsorbed to the coupon surface, how well can it be extracted from that surface?
- When a coupon has been exposed to a bulk solution at a given concentration, how much of the contaminant is adsorbed to the coupon surface?

To answer these two questions, two method validation steps were conducted as the first two steps of the experimental design (section 2.3.1 and 2.3.2). First, the surface contamination extraction method was validated. Second, the coupon surface contamination method was validated.

2.3.1 Method Validation Step 1: Surface Contamination Extraction

The validation required 20 half coupons of the selected material type with a biofilm developed as described in Section 2.2. These coupons were removed from the biofilm growth container and allowed to air dry until water droplets were not visible on the surface, but the surface was still damp. This drying step ensured the contaminant was added to the coupon surface and not added to the water remaining on the coupon surface following the biofilm growth period.

Each coupon (including blanks) were cut in half with metal snips and five drops of the contaminant solution were applied directly to each half coupon using a micropipette (Eppendorf Research Plus, Eppendorf International, Hauppauge, NY) approximately 10 mm apart. The volume of each drop was 15 microliter (µL) for a total addition of 7.5 microgram (µg) for each contaminant. Five non-contaminated coupons were also extracted as blanks.

For each of the half coupon segments (contaminated and non-contaminated), the concrete was removed from the polycarbonate backing and placed into a plastic sample container (Thermo Scientific # 03-342-23, Thermo Fisher Scientific, Inc., Waltham, MA). To prepare the concrete for analysis, each concrete sample was dried at 50 °C then ground to a powder using a glass stir rod (Thermo Scientific # 11381E, Thermo Fisher Scientific, Inc., Waltham, MA). The concrete samples remained in their individual sample containers throughout the drying and grinding process to minimize cross contamination and sample loss. Dilute nitric acid and deionized water were used to clean the glass stir rod before each sample was ground. After the samples were ground, they were shipped to the analysis laboratory where it was digested for metals analysis (see Table 1 and section 3.2.1 for analytical method details).

Table 1. Contaminant Analytical Techniques, Limit of Quantitation

Contaminant	Analytical Technique	Approx. Limit of Quantitation
Cesium	ICP-MS	0.001 mg/L
Cobalt	ICP-MS	0.001 mg/L
Strontium	ICP-MS	0.001 mg/L

In the case of the PVC coupons, the entire coupon half was placed into a plastic test tube filled with 25 milliliter (mL) aqueous 0.5% nitric acid which fully submerged the coupon. After inserting the PVC coupon, the test tube was sealed with a cap and sonicated at 40 kilohertz for 5 minutes, the nitric acid was then decanted into another similar test tube and replaced with 25 mL of fresh nitric acid, and then sonicated for another 5 minutes. The two aliquots of decanted nitric acid were combined for analysis. The pipe coupon was then removed from the container and rinsed one last time with 0.5% nitric acid. Like the concrete, this solution was shipped to the analysis laboratory (see Table 1 and section 3.2.1 for analytical method details).

The percent recovery (%R) was calculated using the following equation

$$\%R = \frac{C_R}{C_o} \times 100$$

where C_R is the mass of contaminant recovered from the coupon surface and C_o is the mass of contaminant originally dispensed onto the coupon surface.

2.3.2 *Method Validation Step 2: Surface Contamination*

Step 2 involved validating a method to contaminate the surface of the coupons in a way that simulates an actual intentional contamination of a water distribution system. The surface contamination method to be validated incorporated:

- Preparing coupons with biofilm
- Exposing the coupons to contaminated water in the AR without flow (batch mode)
- Extraction of the contaminant from the coupon using the method validated in Step 1.

To begin the validation, 10 coupons were prepared with a biofilm. Five of the coupons were loaded in the AR and five were reserved as blank coupons. The bulk contamination solution for each contaminant was prepared at approximately 100 mg/L (10 g/L for strontium) and added to the AR through the opening at the top of the AR. Following addition of the bulk contamination solution, rotation of the AR was initiated as described in Section 2.1, but the water was not permitted to flow through the AR in order to increase the contact time between the contaminated water and the coupons. Two hours following the addition of the bulk contamination solution, the coupons were removed, dipped once into approximately 25 mL of uncontaminated ASTM deionized water (rinse step) and then treated following the contaminant extraction method validated as described in Section 2.3.1 and the extracts analyzed as described in Section 3.2. The rinse step was to ensure that the contaminant is extracted from the surface of the coupon and was not an artifact of the residual contamination solution on the surface of the coupon. The bulk contamination solution was sampled at the start, middle and end of the contamination time period to confirm the contaminant availability for adsorption.

2.3.3 Contaminant Persistence Evaluation

This section describes the approach to evaluating the persistence of a contaminant on various pipe coupon materials. Table 2 provides an overview of the persistence evaluation. For each combination of coupon material and contaminant, biofilm was grown on 20 coupons as described in Section 2.2. Two coupons with biofilm were the non-contaminated blank coupons and the rest of the coupons were contaminated with a bulk solution following the surface contamination method described in section 2.3.2. Immediately following the coupon contamination step, three coupons were removed to serve as control coupons. The amounts of contaminant on the surfaces of these control coupons were compared with the amounts remaining on the coupons that were left in the AR for various lengths of time following the removal of the control coupons.

After removal of the control coupons, a stopped flow scenario was evaluated by stopping the rotation of the AR, stopping the flow of water through the AR, and replacing the contaminated water with uncontaminated drinking water. Stopping flow simulates a no-flow environment in a water system that could occur when a “do not use” order is issued. This stopped flow scenario was conducted for 24 hours after which three persistence evaluation coupons were removed. After that 24 hour period, the flow of drinking water and AR rotation was resumed to normal operating conditions (AR rotating at 100 rpm and fresh tap water flow through the AR). Following the stopped flow scenario, sets of three persistence evaluation coupons were collected from the AR at four different time increments (4 hours, 1 day, 3 days, and 7 days) following the resumption of flow. Following the removal of each of these sets of coupons, they were extracted and the amount of contaminant on the coupon surfaces compared with the amount on the control coupons collected just after the coupon contamination step.

Table 2. Persistence Evaluation (PE)

PE Step	Description	Coupons removed (20 total)
PE 1	Developed biofilm (confirmed with heterotrophic plate count) on 20 coupons; remove two coupons as blank control coupons	2

PE 2	Stopped flow through AR, filled AR with contaminated bulk solution, inserted 18 coupons into AR, operated AR at 100 rpm, waited 2 hours	0
PE 3	Sampled bulk contamination solution at start, half-way point, and end of contamination period	0
PE 4	Following 2 hour contamination period, removed three coupons as contaminated control coupons	3
PE 5	Stopped AR rotation to simulate stopped flow. Replaced bulk contamination solution with uncontaminated water and remained at stopped flow for 24 hours; collected three coupons	3
PE 6	Restarted the AR rotation and flow through the AR. Removed three coupons each at 4 hours, 1 day, 3 days, and 7 days after restart of AR rotation and flow	12
PE 7	Measured amount of contaminant remaining on coupons and compared to amount remaining on contaminated control coupons	0

This comparison was made by calculating the percent persistence (%P) of the contaminant on the coupons as described by the following equation.

$$\%P = \frac{C_{PE}}{C_C} \times 100$$

where C_{PE} is the mass of contaminant recovered from the coupon surface and C_C is the average mass of contaminant originally measured from the surfaces of the control coupon surfaces.

The uncertainty of each of the individual measurements required to calculate the %P (i.e., uncertainty in the measurements required to determine the control and experimental results) was used to determine the propagation of uncertainty in the %P calculation. The combined experimental uncertainty in the %P calculation (ΔP) was determined using the method of propagation of errors and is defined below:

$$\Delta\text{P} = \sqrt{\left(\frac{SD_{PCC}}{P_{CC}}\right)^2 + \left(\frac{\text{SD}_{PTC}}{P_{TC}}\right)^2} \times \%\text{P}$$

where SD_{PCC} and SD_{PTC} are the standard deviations of the contaminated control coupons and test coupons, respectively, being compared. Similarly, P_{CC} and P_{TC} are the average %Ps of the contaminated control coupons and the test coupons, respectively, being compared. In addition, t-tests were used to determine the probability that the data from the various experimental conditions were significantly different from one another at the 95% confidence interval.

2.3.4 Contaminant Flushing Evaluation

This section describes the evaluation of pipe decontamination using flushing. Table 3 provides an overview of the flushing evaluation. As was the case for the persistence evaluation, a biofilm was grown on 20 coupons of the desired material and 18 were loaded in the AR and contaminated using the validated surface contamination method. Three contaminated coupons were removed to serve as the control coupons. The amounts of contaminant on the surfaces of these control coupons were compared with the amounts remaining on the coupons that were left in the AR and exposed to flushing conditions.

Following coupon contamination, the AR inner cylinder rotation was raised from 100 rpm to 200 rpm which corresponded to a water velocity of 0.5 ms^{-1} (1.6 ft/s) in a 15.2 cm (6 in.) pipe (3). This increased rotational speed was held for one day. Sets of three coupons were collected from the AR at three different time increments (2 hours, 4 hours, and 1 day) following the coupon contamination. Then, the rotational speed was increased again to 250 rpm (2.5 ft/s in a 6 in pipe) and held for another day, with the collection of three coupons after 4 hours and after 1 day of 250 rpm conditions. Following the removal of each set of three coupons, the coupons were extracted and the amounts of contaminant on the coupons were compared with the amounts on the control coupons collected just after the surface contamination step.

A water control exposure experiment was run in parallel with the flushing experiments. Contaminated coupons were prepared in the manner described above, but they were exposed only to fresh drinking water with no AR rotation (stagnant water) and sampled at the same time intervals as in the flushing experiment. The difference between the samples exposed to flushing and those in the water control exposure experiment show the effect that flushing had on adhered contaminant.

Table 3. Evaluation of Flushing as a Decontamination Approach

Step	Description	Coupons removed (20 total)
F 1	Developed biofilm (confirmed with heterotrophic plate count) on 20 coupons of same material; removed two coupons as blanks	2
F 2	Injected enough contaminant into AR to achieve desired bulk concentration within AR; inserted 18 coupons and operated AR at 100 rpm, waited 2 hours	0
F 3	Sampled bulk contaminant solution at start, half-way point, and end of contamination time	0
F 4	Following 2 hour contamination period, replaced contaminated bulk solution with uncontaminated water and removed three coupons as contaminated control coupons	3

F 5	Increased AR rotational velocity to 200 rpm from original velocity of 100 rpm	0
F 6	Removed three coupons each at 2 hours, 4 hours, and 1 day following increase in rotational velocity	9
F 7	Increased AR rotational velocity to 250 rpm from 200 rpm	0
F 8	Removed three coupons each at 4 hours and 1 day following increase in rotational velocity	6
F 9	Measured amount of contaminant remaining on coupons and compared to amount remaining on contaminated control coupons	0

2.3.5 Chemical Cleaning Agent Evaluation

This section describes the evaluation of pipe decontamination using chemical cleaning agents (CCA). Cleaning agents were only evaluated on contaminants deemed persistent in previous steps of the PDEDP. Table 4 provides an overview of the CCA experiments. A biofilm was grown on 20 coupons of the desired material and 18 were loaded in the AR and contaminated using the validated surface contamination method. After contamination, three contaminated coupons were removed to serve as the control coupons. The amounts of contaminant on the surfaces of these control coupons were compared with the amounts remaining on the coupons that were left in the AR and exposed to CCA.

The CCA evaluation was started in a similar way as for the flushing evaluation. However, instead of increasing the rotational velocity of the AR, the rotation of the AR was stopped and the tap water flow through the AR was also stopped to simulate a stopped flow scenario. Stopping flow simulates a no-flow environment in a water system that could occur when a “do not use” order is issued. The CCA was then added and the chemical treatment was performed as a stopped flow treatment. Comparison of the amounts of contaminant adhered to the coupons before and after treatment was made by calculating the %P as described earlier.

Table 4. Evaluation of Chemical Cleaning Agents (CCA) as a Decontamination Approach

Step	Description	Coupons removed (20 total)
CCA 1	Developed biofilm (confirmed with heterotrophic plate count) on 20 coupons of same material; removed two coupons as blanks	2
CCA 2	Injected enough contaminant into AR to achieve desired bulk concentration within AR; inserted 18 coupons and operate AR at 100 rpm, waited 2 hours	0
CCA 3	Sampled bulk contaminant solution at start, half-way point, and end of contamination time	0

CCA 4	Following the 2 hour contamination period, replaced bulk solution with uncontaminated water and removed three coupons as contaminated control coupons	3
CCA 5	Stopped flow through AR and stopped rotation of AR; introduced CCA at desired concentration and pH level	0
CCA 6	Removed three coupons at 2 hours, 4 hours, 1 day, 3 days, and 7 days following introduction of CCA	15
CCA 7	Calculated percent persistence for all coupons by comparing residual contaminant on the surface with contaminated control coupons	0

3.0 QUALITY ASSURANCE/QUALITY CONTROL

3.1 Experimental Controls

Table 5 summarizes the controls included in this study. The controls are important because the results of the persistence and decontamination experiments are dependent on the original concentration of contaminants on the surface of the control coupons. In addition, the AR has available surface area that could become contaminated, thus becoming a source of secondary contamination.

Table 5. Experimental Controls

Component of Pipe Decontamination Experimental Design	Type of Control	Description
Surface Contamination Extraction Method Verification	Five non-contaminated blanks	Allows comparison between coupons that have contaminant applied and those that have not
Surface Contamination Method Verification	Five non-contaminated blanks	Allows comparison between coupons that have contaminant adsorbed from the bulk solution and those that have not
Evaluation of Contaminant Persistence	Two non-contaminated control coupons blanks	Taken from a set of coupons following biofilm growth; allows comparison of coupons that have been contaminated from the bulk solution and those that have not been contaminated
	Three contaminated control coupons	Removed from AR after contamination of coupons, but before persistence testing in clean water; allows comparison of coupons containing a "diminished" amount of contaminant (due to "normal" flow of clean water) with coupons containing "total" amount of contaminant (not influenced by the "normal" flow of clean water)
Evaluation of Flushing Decontamination	Two non-contaminated blanks	Taken from set of coupons following biofilm growth; allows comparison of coupons that have been contaminated from the bulk solution and those that have not
	Three contaminated control coupons	Removed from AR after contamination of coupons, but before flushing at increased velocities in clean water; allows comparison of contaminant remaining on the coupons only due to increased rotational velocity
	Water Exposure Control Experiment (18 coupons)	Contaminated coupons that are exposed only to clean water (no AR rotation) to determine decontamination differences at increased time intervals and increased AR rotational speeds
Evaluation of Chemical Cleaning Agent Decontamination	Two non-contaminated blanks	Taken from set of coupons following biofilm growth; allows comparison between coupons that have contaminant adsorbed from the bulk solution and those that have not
	Three contaminated control coupons and	Removed from AR at specified coupon collection time intervals and placed in container with dechlorinated drinking water; allows comparison of

	other collected coupons	contaminant remaining before and after introduction of the chemical cleaning agent

3.2 Measurement Methods

3.2.1 Cesium, Cobalt, and Strontium

The analytical method that was used for the chemical form all three contaminants is EPA Method 200.8 (4) "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry". Although cesium and strontium are not covered by Method 200.8, the techniques in Method 200.8 were used to digest the cement-mortar samples. Analytical Balance Corporation (ABC) has extensive experience using Method 200.8 to treat and digest water samples, and performed all ICP-MS analyses of aqueous cesium, cobalt and strontium in this study. Calibration standards were prepared in ASTM Type 1 water with external standards and acidified. A six-point calibration curve was generated prior to sample analyses. A calibration blank was also prepared using ASTM Type I water and acidified with the same acid matrix as the calibration standards. The calibration levels bracketed the sample concentration. The limit of quantification for ICP-MS analyses of aqueous (post-digestion) Cs, Sr and Co was approximately 0.001 mg/L. Two continuing calibration check solutions were analyzed after every 10 samples and at the end of the sequence in order to verify instrument sensitivity and calibration throughout the analysis. The results of these samples were always between 90 -110% of the known concentration. A laboratory reagent blank consisting of ASTM Type I water was analyzed and no contamination was found. A laboratory fortified matrix sample was analyzed with each batch of samples. Recoveries for the samples were always within the acceptable range of 85-115%. It should be noted that the radiochemistry method for each contaminant would be used in the event of a contamination incident with radionuclides.

3.2.2 Enumeration of Biofilm Growth

Biofilm growth on the coupons was enumerated using the following steps. A sterile 0.01% solution (by volume) of Triton X-100 (Sigma-Aldrich, St. Louis, MO) in phosphate buffered saline was prepared. The coupon to be analyzed was either cut in half (for the PVC pipe material), or the concrete was chipped off the polycarbonate backing (for the concrete pipe material) then placed in a sterile centrifuge tube (VWR # 89004-364, VWR, West Chester, PA) containing 30 mL of the 0.01% Triton X solution, mixed using a vortex mixer, and then decanted. Thereafter, two tenfold dilutions of that decanted solution were prepared using the 0.01% Triton X solution as the diluent. Each of those solutions were plated in triplicate by dispensing 100 µL onto agar plates (Teknova #T0134, Teknova, Hollister, CA). Using a spreader, the aliquot was evenly distributed on the plate and placed in an incubator for at least 48 hours at 35-37 °C. After incubation, the distinguishable colonies on each plate were counted. In order to be considered a viable plate count, the number of colonies on a given plate were required to be between 30 and 300. The density of colony forming units (cfu/cm^2) was determined by dividing the average number of colonies by the plated volume, multiplying by the dilution factor and the sample volume and then dividing by the coupon area.

3.3 Quality Control

Quality control samples for the contaminant reference methods, including continuing calibration checks, laboratory blanks, and laboratory fortified matrix samples are described in Section 3.2.1. The data quality objectives for each of these samples are provided in Table 6. The acceptable ranges were established to limit the error introduced into the experimental work.

Table 6. Data Quality Objectives for ICP-MS Analysis

Method	Sample Type	QC Requirement	Corrective Action
ICP-MS analysis of cesium, cobalt, and strontium (EPA Method 200.8)	Initial calibration verification (secondary source)	90-110% of known concentration	Rerun analysis
	Continuing calibration check	90-110% of known concentration, every batch of 10 samples	Repeat sample analysis; if still outside of range repeat calibration
	Calibration and laboratory reagent blank	+/-10% of detection limit; include with each batch of 10 samples	Determine and correct cause of contamination
	Laboratory fortified matrix spike	85-115% of known concentration; every batch of 10 samples	Repeat sample analysis; if still outside of range repeat calibration
	Laboratory duplicate sample	<20% RPD	Repeat sample analysis; if still outside of range repeat calibration
	Matrix and digestion spike	80-120%	Repeat sample analysis; if still outside of range repeat calibration
	Digestion blank	+/-10% of detection limit	Repeat sample analysis; if still outside of range repeat calibration

ICP-MS, inductively coupled plasma - mass spectrometry: RPD, relative percent difference

3.4 Audits

3.4.1 Performance Evaluation Audit

A performance evaluation audit was conducted to assess the accuracy of the ICP-MS reference method (EPA Method 200.8). A performance evaluation sample containing 105 mg/L cesium, 40 mg/L cobalt, and 49 mg/L strontium was provided for analysis. Accuracy of the measurement was expressed in terms of the percent error (%E), as calculated from the following equation:

$$\%E = \frac{\left| d - C_R \right|}{C_R} \times 100$$

where C_R was the standard or reference concentration of the performance evaluation sample and *d* was the measurement obtained using the reference method. Ideally, if the reference value and the measured value were the same, there would be a percent error of zero. The results of the reference method indicated %E of 2% for cesium, 7% for cobalt, and 19% for strontium. All of these values are within the acceptable %E of 25%, which is an internal Battelle standard for accuracy.

3.4.2 Technical Systems Audit

The Battelle QA Manager conducted a technical systems audit at the Columbus, OH testing location to ensure that the evaluation was performed in accordance with the quality assurance project plan (QAPP) for this study. As part of the audit, the Battelle QA manager reviewed the reference sampling and analysis methods used, compared actual evaluation procedures with those specified in the QAPP, and reviewed data acquisition and handling procedures. No significant adverse findings were noted in this audit. The records concerning the audit are permanently stored with the Battelle QA manager.

3.4.3 Deviation

There was one deviation to the quality assurance project plan during this project. During Method Validation Step 2: Surface Contamination, the bulk solution used for contamination was 100 mg/L for cesium and cobalt. For strontium, 100 mg/L did not provide enough strontium to the surface of the coupon for strontium detection above the background. A 10 g/L strontium solution was used successfully. The QAPP listed the bulk contamination solution to be 1 mg/L for all three contaminants. A 10 g/L strontium solution was employed in Step 2 and all subsequent steps where strontium used. There was no negative impact as a result of this deviation.

3.4.4 Data Quality Audit

At least 10% of the data acquired during the evaluation were audited. The Battelle QA manager traced the data from the initial acquisition, through reduction and statistical analysis, to final reporting, to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit were checked.

3.4.5 QA/QC Reporting

Each assessment and audit was documented in accordance with the Testing and Evaluation Contract QAPP. Once an assessment report was prepared by the Battelle QA manager, it was routed to the work assignment leader and Battelle Testing and Evaluation Program manager for review and approval. The Battelle QA manager then distributed the final assessment report to the EPA contracting officer’s representative, QA manager, and Battelle staff.

4.0 RESULTS

Testing of the PDEDP included use of non-radioactive cesium, cobalt, and strontium with concrete lined and PVC AR coupons. The results are divided into separate sections for each combination of contaminant and coupon type. In order to further evaluate the data, t-tests were performed to determine what time periods exhibited significant differences from one another at the 95% confidence interval. The null hypotheses of the t-tests were that the difference in amount of contaminant remaining on the coupons across the various sample collection time periods was zero. The probabilities (p) generated by the t-test were the probabilities of the null hypothesis being confirmed. Therefore, p-values less than 0.05 indicated a small likelihood the difference between the two data sets was zero, and thus, are considered to be significantly different from one another.

4.1 Method Validation Step 1: Surface Contamination Extraction

The objective of this component of testing was to determine if the three contaminants could be extracted from the coupon surfaces. Concrete and PVC coupons were spiked with 7.5 µg of cesium, cobalt, or strontium. For concrete coupons, the concrete was removed from the polycarbonate backing using the method described in Section 2.3.1, but the results were reported for only the concrete. The PVC was rinsed with dilute nitric acid and the rinse analyzed directly. Table 7 gives the results including the amount of contaminant spiked onto the coupons, the amount extracted, the total recovery, and the standard deviation.

Table 7. Surface Contamination Extraction

	Amount spiked (µg)	**Avg. amount recovered (µg)**	**Total Recovery**	**SD**
Cs concrete	7.5	1.3	18%	4%
Co concrete		0.8	11%	6%
Sr concrete		BG	BG	BG
Cs PVC		7.1	95%	17%
Co PVC		4.7	62%	4%
Sr PVC		7.6	101%	15%

Five replicates were spiked and extracted at each concentration level.
BG-indicates that the spiked Sr was not detectable above the background; this experiment was not repeated because Method Validation Step 2 revealed successful detection extraction from the concrete coupon (see section 4.2).

4.2 Method Validation Step 2: Surface Contamination

This testing indicates whether or not a contaminant will adsorb to the pipe coupon surface after the coupon is exposed to a bulk water solution. Table 8 gives the results from the surface contamination method validation on concrete and PVC after a two hour exposure to 100 mg/L of each contaminant in the ARs. Excluding strontium on concrete, an average of between 3.1 µg and 33 µg of contaminant was adsorbed to the coupon surfaces out of a total of 100,000 µg of contaminant (0.003-0.03%) that was available in the bulk solution. The results show that cesium, cobalt, and strontium (on PVC only) reproducibly adsorbed to the surface of the concrete and PVC coupons and could be recovered.

Strontium was not detectable on the concrete above the background levels when a 100 mg/L solution was used. Therefore, strontium contamination was performed with a 10 g/L strontium solution in this step and all subsequent steps of the PDEDP. Using a 10 g/L solution resulted in an average of 385 µg of recoverable strontium from concrete. Overall, the ratio of target contaminant on the concrete to the target contaminant measured in the background concrete coupon samples was 29, 41, and 7 for cesium, cobalt, and strontium (10 g/L contamination solution), respectively. For the PVC coupons, the ratios were 63, 152, and 26 for cesium, cobalt, and strontium (all 100 mg/L contamination solutions), respectively.

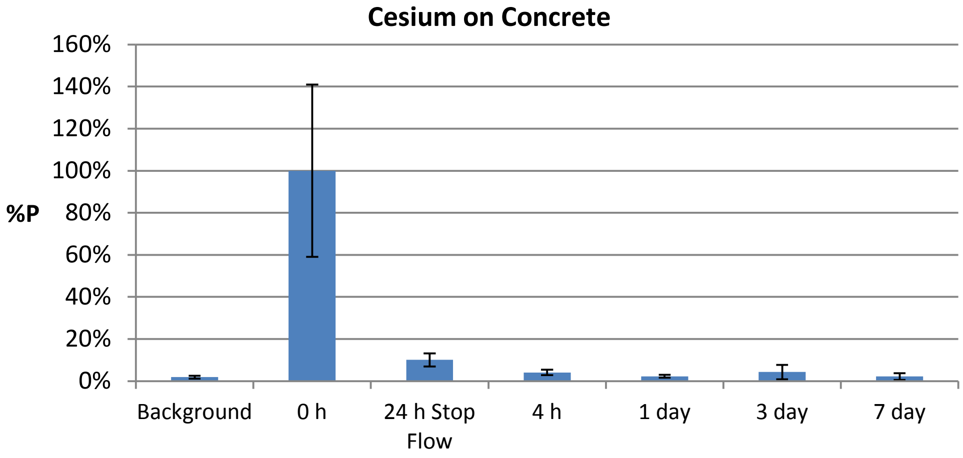
Table 8. Contaminant Surface Contamination

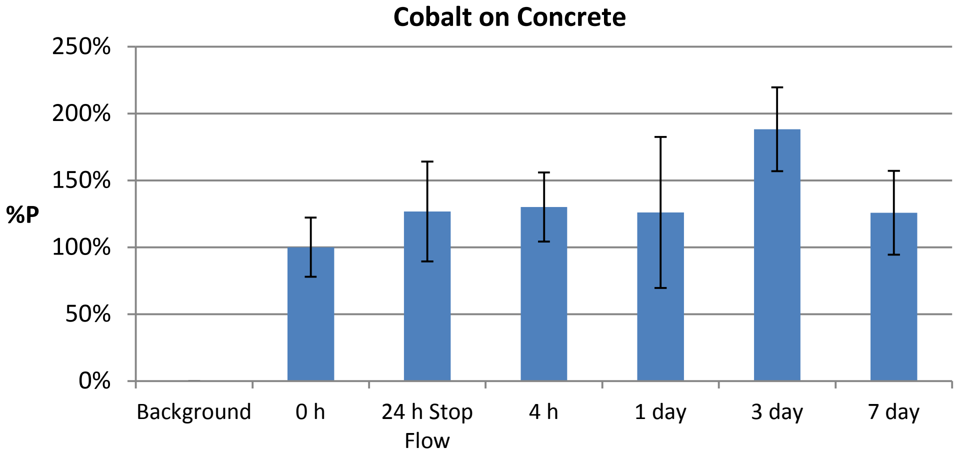
Contaminated Coupon	Amount Recovered from Concrete (µg)			Amount Recovered from PVC (µg)		
	Cesium	Cobalt	Strontium[a]	Cesium	Cobalt	Strontium
#1	3.6	25	410	19	18	30
#2	2.8	24	422	16	16	42
#3	2.7	20	444	14	14	19
#4	4.4	69	348	15	15	23
#5	2.0	27	305	15	19	21
Avg.	3.1	33	385	16	16	27
St. Dev.	0.9	20	58	2.0	2.1	9.4
%RSD	30%	61%	15	12%	13%	35%

[a] Sr experiments included use of a 10 g/L contamination solution.

4.3 Contaminants on Concrete Persistence Evaluation

Figure 1 shows the results from the persistence evaluation for each contaminant on the concrete coupon surfaces. The vertical axes show the percent of each contaminant remaining on the coupons after each time period (shown across the horizontal axis) during which fresh tap water is flowing through the AR and the AR is rotating at 100 rpm. The columns at the far left side of the graphs (0 hr) represent the initial contamination level (as measured on the contaminated control coupons) and each successive column represents the time periods and experimental conditions defined by the PDEDP. The error bars on the graphs are the standard deviations of the contaminant remaining on the three coupons sampled.





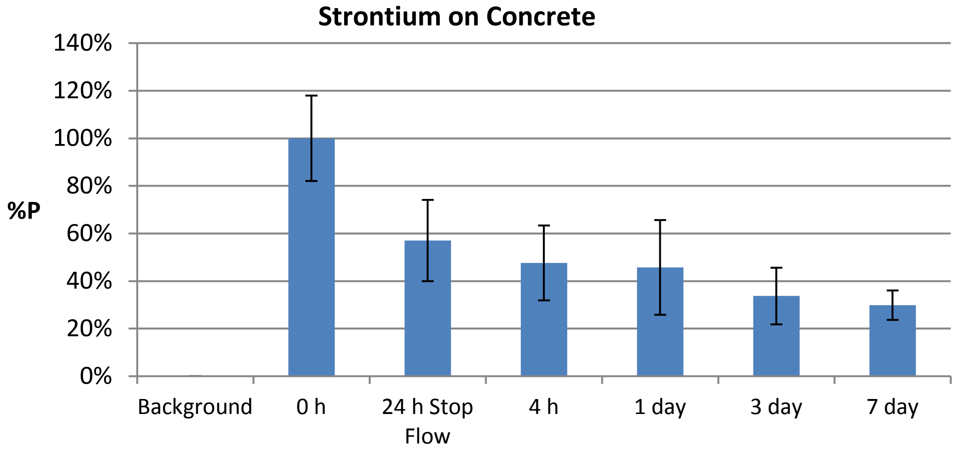


Figure 1. **Persistence evaluation - percent persistence (%P) of cesium, cobalt, and strontium on concrete.**

Based on observation of the graphs in Figure 1, the amounts of residual cesium and strontium decreased throughout the experiment while the residual cobalt remained steady or possibly exhibited a slight increase. In order to further clarify the data, t-tests were performed to determine what time periods exhibited significant differences from one another at the 95% confidence interval. The null hypotheses of the t-tests were that the difference in amount of contaminant remaining on the coupons across the various time periods was zero. The probabilities (p) generated by the t-test were the probabilities of the null hypothesis being confirmed. Therefore, p-values less than 0.05 indicated a small likelihood that the difference between the two data sets was zero, and thus, are considered to be significantly different from one another.

Table 9 gives the p-values for comparison of each possible set of coupons collected at the various time periods. The data that exhibited significant differences are highlighted in gray. For cesium, the initial contamination level was significantly different from each of the subsequent sample collection times. Therefore, the residual cesium in Figure 1 decreased during stopped flow and 4 hours later. The decrease steadied thereafter as the residual amounts became relatively small. Statistically, the day 3 cesium sample was the same as the 24 hour sample, but it was still significantly different than the 0 hour sample. For cobalt, there were only two significant differences, both of which provided indication of an increase between the initial contamination and the 3 day sample. For strontium, the only significant differences were between the zero hour sample and the rest of the time intervals. These data indicate that after the initial contamination (0 hr), strontium concentration at all of the subsequent time intervals was significantly smaller than at time zero. However, the concentration of strontium on the coupons at all time intervals past time zero were statistically the same.

In summary, the cesium does not persist on the concrete coupons as the residual percent persistence (%P) values decrease to less than 5% within 4 hours after the stopped flow. Strontium is slightly more persistent in that the %Ps decrease to approximately 30% over the course of the experiment. Cobalt is very persistent as there is no significant decrease in %P throughout the course of the experiment.

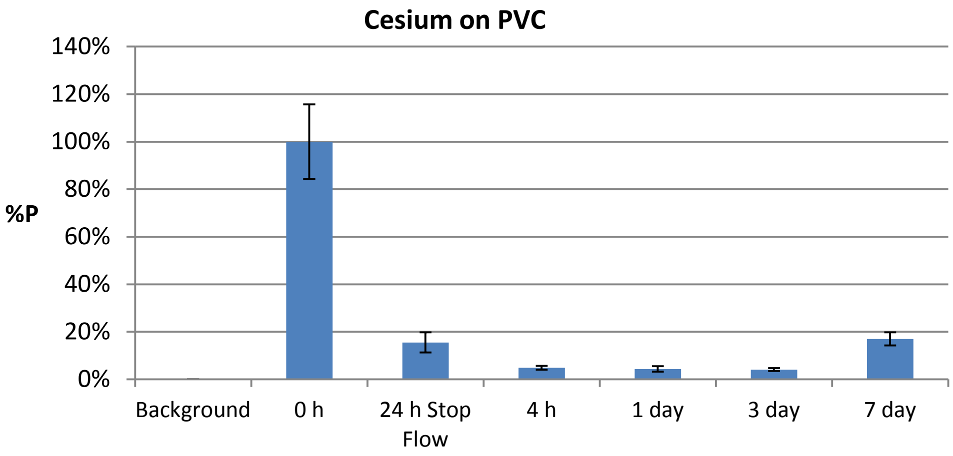
Table 9. Contaminants on Concrete – Probability Value Matrix for Persistence Evaluation

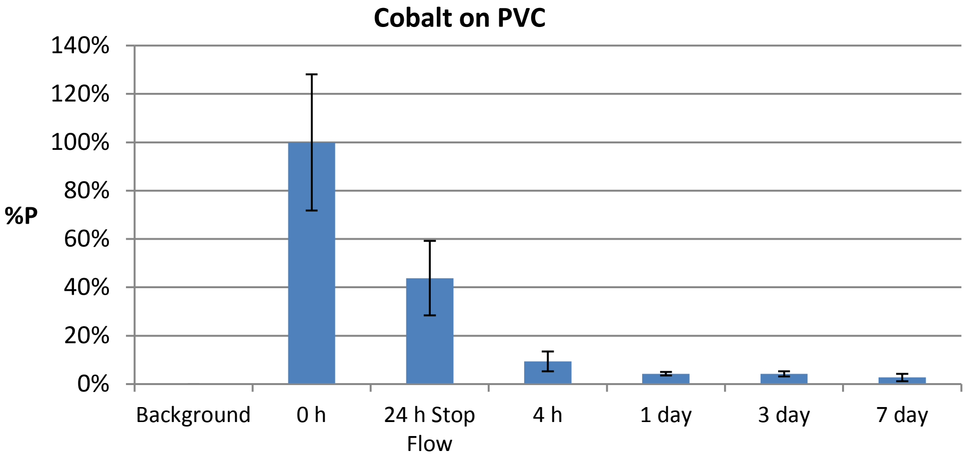
	Persistence Evaluation Times	**probability (p) values (< 0.05 - significant difference)**				
		24 h stop	**4 h**	**1 day**	**3 day**	**7 day**
Cesium	**0 h**	0.0327	0.0290	0.0280	0.0279	0.0277
	24 h Stop Flow		0.0023	0.0046	0.0778	0.0027
	4 h			0.0219	0.9141	0.1486
	1 day				0.3845	0.9480
	3 day					0.3818
Cobalt	**0 h**	0.2831	0.0812	0.4888	0.0021	0.2093
	24 h Stop Flow		0.8843	0.9841	0.0657	0.9691
	4 h			0.9098	0.0093	0.8170
	1 day				0.1744	0.9958
	3 day					0.0315
Strontium	**0 h**	0.0184	0.0084	0.0217	0.0013	0.0016
	24 h Stop Flow		0.4632	0.4573	0.0959	0.0753
	4 h			0.8974	0.2463	0.1490
	1 day				0.3989	0.2748
	3 day					0.6058

Light shading indicates significant differences

4.4 Contaminants on PVC Persistence Evaluation

Figure 2 shows the results from the persistence evaluation for each contaminant on the PVC coupon surfaces. The vertical axes show the percent of each contaminant remaining on the coupons after each time period (shown across the horizontal axis) during which fresh tap water is flowing through the AR and the AR is rotating at 100 rpm. The columns at the far left side of the graphs represent the initial contamination level (0 hr as measured on the contaminated control coupons) and each successive column represents the time periods and experimental conditions





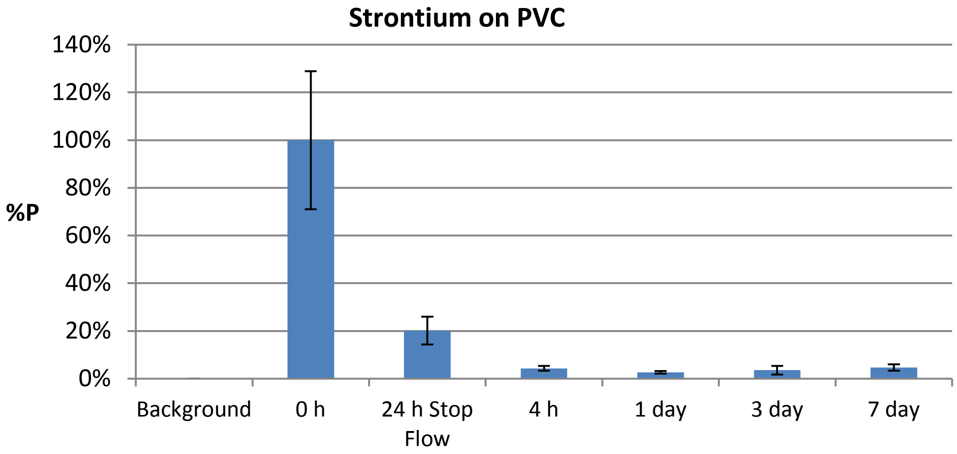


Figure 2. Persistence evaluation - percent persistence (%P) on PVC for cesium, cobalt , and strontium.

defined by the PDEDP. The error bars on the graphs are the standard deviations of the remaining contaminant measured on the three coupons sampled.

Based on observation of the graphs in Figure 2, the amounts of all three contaminants decreased throughout the experiment relative to the 0 hour and 24 hour samples. There was a slight increase at the end of the cesium experiment while the residual levels of the other two contaminants steadied over the final days of the experiment. In order to further clarify the data, t-tests were performed to determine what time periods exhibited significant differences from one another at the 95% confidence interval. The null hypotheses of the t-tests were that the difference in amount of contaminants remaining on the coupons across the various time periods was zero.

Table 10 gives the p-values for comparison of each possible set of coupons collected at the various time periods. The data that exhibited significant differences are highlighted in gray. For all three contaminants, the initial contamination level was significantly different from each subsequent sample collection interval. In addition, the 24 hour stopped flow sample was significantly different than the subsequent samples, indicating that a decrease in residual contaminant concentration continued past the 24 hour stopped flow sample. However, beyond the sample collected 4 h after the stopped flow, only strontium exhibited a continued significant concentration decrease. Interestingly, the cesium exhibited a significant increase in %P when comparing the 3 day to the 7 day sample. There is no clear reason for this apparent increase in average residual contaminant. In summary, none of the three contaminants persist on the PVC coupons as the residual %Ps decrease to less than 5% within 4 hours after the stopped flow. The only exception observed here was the 7 day cesium sample.

Table 10. Contaminants on PVC – Probability Value Matrix for Persistence Evaluation

	Persistence Evaluation Times	**probability (p) values (< 0.05 - significant difference)**				
		24 h stop	**4 h**	**1 day**	**3 day**	**7 day**
Cesium	**0 h**	0.0002	0.0000	0.0000	0.0000	0.0000
	24 h Stop Flow		0.0320	0.0241	0.0293	0.5350
	4 h			0.4647	0.0742	0.0000
	1 day				0.6914	0.0001
	3 day					0.0006
Cobalt	**0 h**	0.0330	0.0194	0.0194	0.0193	0.0186
	24 h Stop Flow		0.0415	0.0383	0.0380	0.0346
	4 h			0.1463	0.1416	0.0827
	1 day				1.0000	0.2193
	3 day					0.2222
Strontium	**0 h**	0.0259	0.0209	0.0203	0.0202	0.0209
	24 h Stop Flow		0.0277	0.0243	0.0186	0.0261
	4 h			0.0452	0.5326	0.7045
	1 day				0.4699	0.0857
	3 day					0.4161

Light shading indicates significant differences

4.5 Contaminants on Concrete Flushing Evaluation

Figure 3 shows the %P results from the flushing evaluation and water exposure control experiment for all three contaminants on the concrete coupon surfaces. The bars at the far left side of the graphs (0 h) represent the %P of the average initial contamination level measured on the three contaminated control coupons (by definition the %P is 100%). The remaining bars represent the %P of cesium, cobalt, and strontium after exposure to the rotational velocities noted along the horizontal axis. The error lines on the graphs represent the propagated error around the calculation of %P as described in Section 2.3.3. The water exposure control experiment included the contamination and collection of coupons in a manner identical to that of the flushing evaluation, but the AR was not rotating (see section 2.3.4).

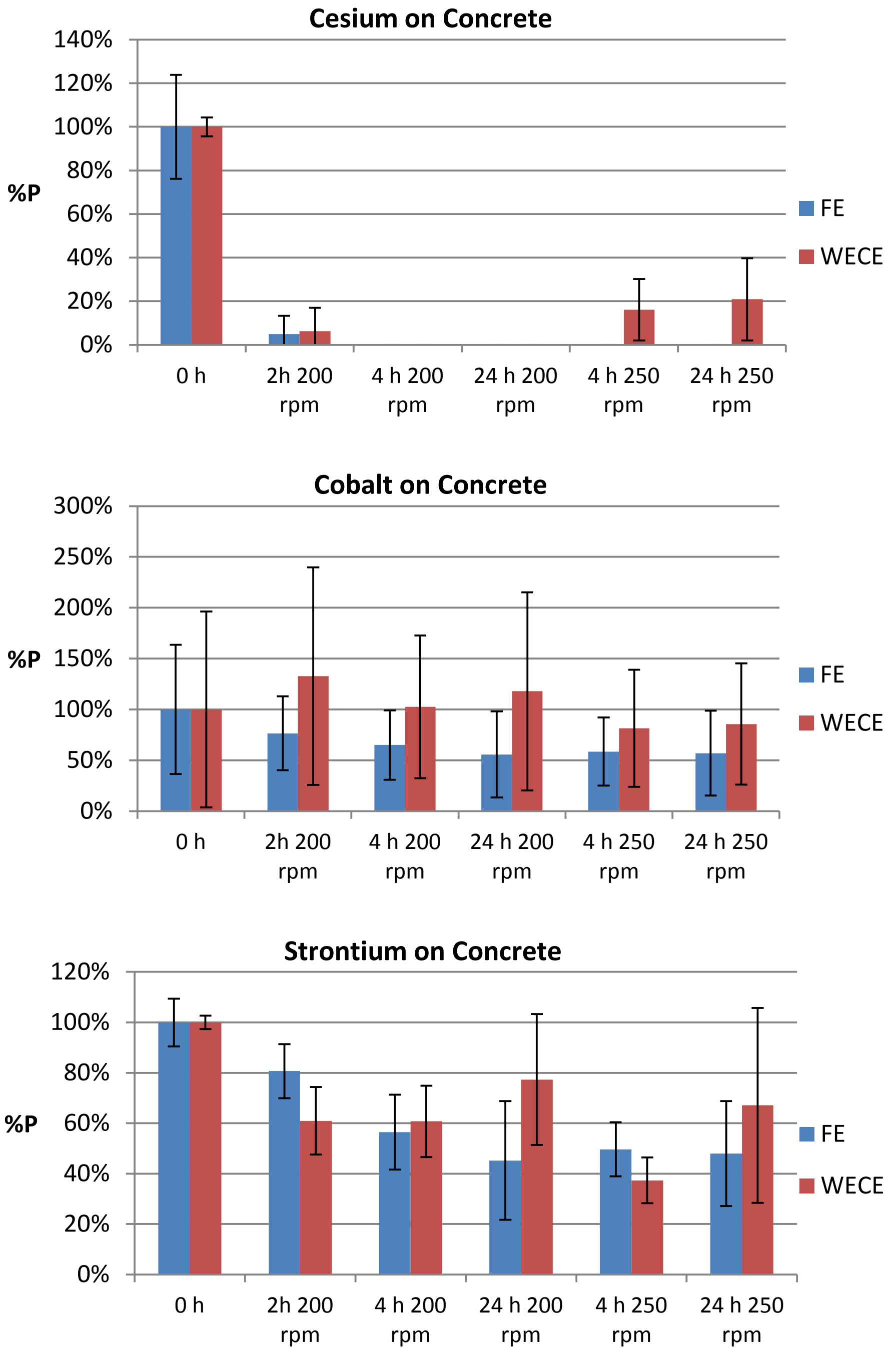


Figure 3. Flushing evaluation (FE) and water exposure control experiment (WECE) percent persistence (%P) on concrete for cesium, cobalt, and strontium.

Upon observation of Figure 3, the data confirm the results determined during the persistence evaluation. The cesium does not persist under flushing conditions. In fact, the water exposure control experiment results indicate that cesium exposed to stagnant water also does not persist as there is very little detectable residual cesium near the end of the experiment. Strontium persists to a larger extent, with the %P decreasing to approximately 40% over the course of the experiment. Strontium also persisted in stagnant water. Cobalt is the most persistent with no significant decrease observed. Also, the cobalt water exposure control experiment result suggests that cobalt on concrete is persistent in stagnant water.

Statistical analyses were performed using t-tests to further clarify any differences between the time intervals during each flushing scenario. Table 11 gives the p-values for comparisons of all possible pairs of coupons collected at the various flushing conditions. The significant differences are highlighted in gray. These results show that for cesium and strontium, only the initial contaminated samples are significantly different from the rest of the samples indicating that the decrease in residual contaminant steadies after the 2 h, 200 rpm sample is collected and remains statistically unchanged for the rest of the experiment. No significant change in cobalt concentration was observed during the course of flushing.

Table 11. Contaminants on Concrete – Probability Value Matrix for Flushing Evaluation

	Persistence Evaluation Times	**probability (p) values (< 0.05 - significant difference)**				
		2h 200 rpm	**4 h 200 rpm**	**24 h 200 rpm**	**4 h 250 rpm**	**24 h 250 rpm**
Cesium	**0 h**	0.0034	0.0094	0.0094	0.0094	0.0094
	2h 200 rpm		0.4226	0.4226	0.4226	0.4226
	4 h 200 rpm			NA	NA	NA
	24 h 200 rpm				NA	NA
	4 h 250 rpm					NA
Cobalt	**0 h**	0.4656	0.3106	0.2517	0.2500	0.2587
	2h 200 rpm		0.4062	0.4061	0.2802	0.4160
	4 h 200 rpm			0.7077	0.7109	0.7366
	24 h 200 rpm				0.9087	0.9668
	4 h 250 rpm					0.9459
Strontium	**0 h**	0.0484	0.0200	0.0464	0.0034	0.0378
	2h 200 rpm		0.0804	0.1042	0.0177	0.0932
	4 h 200 rpm			0.5242	0.5436	0.5928
	24 h 200 rpm				0.7845	0.8862
	4 h 250 rpm					0.9068

Light shading indicates significant differences
NA: Not Analyzed

4.6 Cesium and Cobalt on PVC Flushing Evaluation and Water Exposure Control Experiment

Figure 4 shows the %P results from the flushing evaluation and water exposure control experiment for cesium and cobalt only on PVC. Strontium was not tested during flushing since adhesion to PVC was low during the persistence evaluation when strontium was spiked at the higher concentration of 10 g/L.

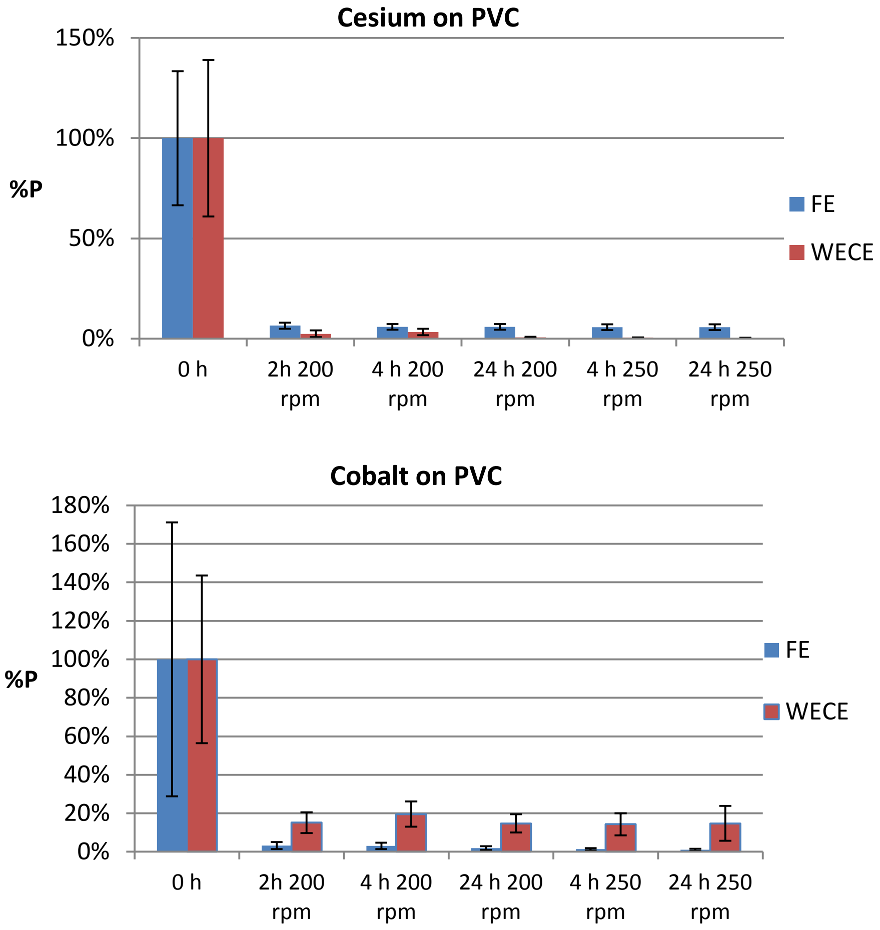


Figure 4. Flushing evaluation (FE) and water exposure control experiment (WECE) - percent persistence (%P) on PVC for cesium and cobalt.

The results in Figure 4 also confirmed the persistence evaluation results. The cesium did not persist either in the flushing evaluation or during the water exposure control experiment. Interestingly, the %P decreased more in the stagnant water of the water exposure control experiment. Cobalt also did not persist, but it does seem that the flushing provides an enhancement of decontamination compared with the water exposure control experiment. Table 12 gives the p-values for comparisons of all possible pairs of coupons collected at the various flushing conditions. The significant differences are highlighted in gray. These results show that for cesium, only the initial contaminated samples are significantly different from the rest of the samples, indicating that the decrease in residual contaminant steadies after the 2 h, 200 rpm sample is collected and remains statistically unchanged for the rest of the experiment. For cobalt, Figure 4 shows a clear difference between the average values of the initial contaminated coupon and the subsequent sample collection times. However, there is not a statistically significant difference between the time zero concentration and the rest of the coupons because of a large uncertainty in the measurement of the initial coupon.

Table 12. Contaminants on PVC – Probability Value Matrix for Flushing Evaluation

		probability (p) values (< 0.05 - significant difference)				
	Persistence Evaluation Times	**2h 200 rpm**	**4 h 200 rpm**	**24 h 200 rpm**	**4 h 250 rpm**	**24 h 250 rpm**
Cesium	**0 h**	0.0207	0.0204	0.0205	0.0204	0.0204
	2h 200 rpm		0.1734	0.0474	0.0824	0.0824
	4 h 200 rpm			1.0000	0.7250	0.7250
	24 h 200 rpm				0.6495	0.6495
	4 h 250 rpm					1.0000
Cobalt	**0 h**	0.0794	0.0792	0.0776	0.0768	0.0764
	2h 200 rpm		0.8419	0.1135	0.0691	0.0447
	4 h 200 rpm			0.1007	0.0572	0.0326
	24 h 200 rpm				0.1835	0.0765
	4 h 250 rpm					0.1835

Light shading indicates significant differences

4.7 Cobalt on Concrete Chemical Cleaning Agent Evaluation

Data from the persistence evaluation and flushing evaluation experiments strongly suggested that cobalt was persistent on concrete under routine and flushing flow conditions. Therefore, two separate experiments were performed to evaluate 0.1 M tartaric acid (pH 3) and 0.1 M ethylenediaminetetraacetic acid (EDTA) as decontaminating agents for cobalt adhered to concrete. The coupons were contaminated, the control coupons were removed, and then the CCA was added to the AR with no flow or rotation and coupons were then collected over the course of the next 7 days.

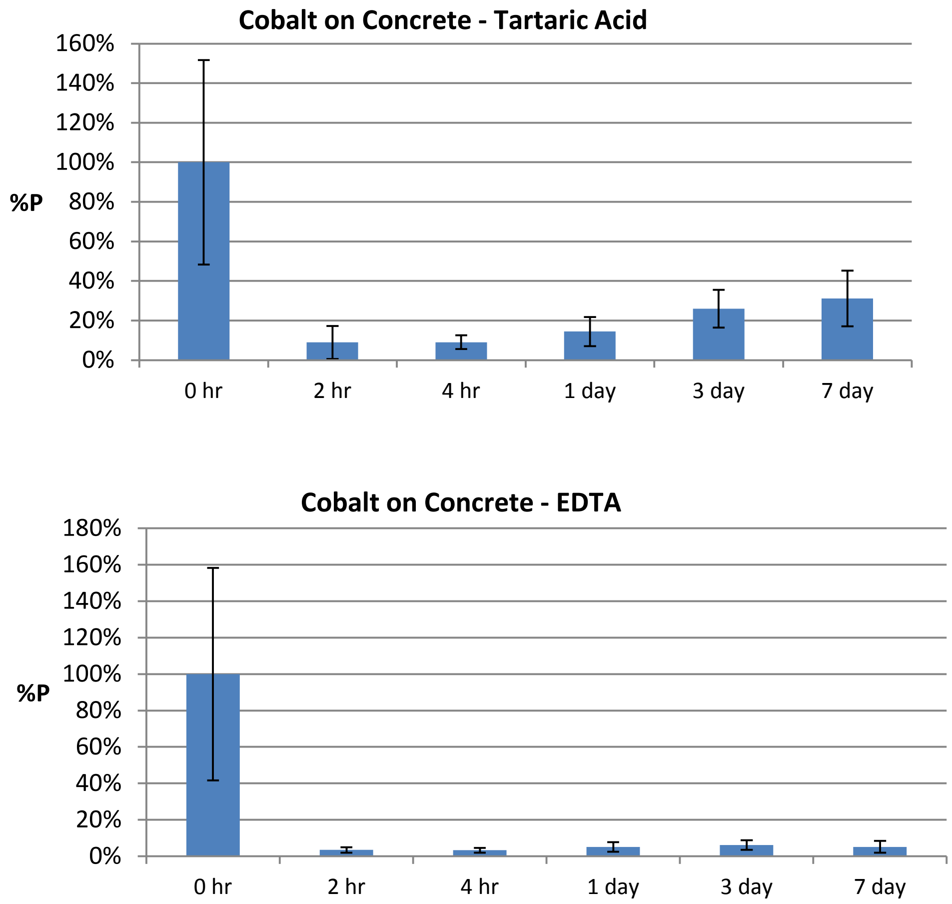


Figure 5. Chemical cleaning agent evaluation - percent persistence (%P) on concrete for tartaric acid and EDTA.

Observation of the graphical results indicate that EDTA is an effective CCA for cobalt on concrete. Tartaric acid also appears to have good CCA characteristics. However, a yellow precipitate formed on the concrete coupons application of tartaric acid, making it a less than desirable CCA from a practical standpoint. Also, the concentration of cobalt increased at later time intervals, which may result from the observed precipitation.

When comparing the CCA decontamination results in stagnant water to the effect of stagnant water alone, the effectiveness of the CCA is clear. In Figure 1 (pg. 21, section 4.3), the effect of stagnant water alone on the removal of cobalt from cement-mortar is shown. Cobalt concentration effectively remained the same over the course of 24 hours. When exposed to

EDTA, the adhered cobalt concentration decreased by approximately 95% within 2 hours and remained at that level up to 7 days. Figure 1 also shows that the cobalt concentration remained the same or increased over the course of 7 days after exposure to flow, which suggests that further treatment with stagnant water alone would be ineffective.

Statistical analyses were performed using t-tests to further clarify any differences among the data from each CCA treatment scenario. Table 13 gives the p-values for comparisons of all possible pairs of coupons collected at the various time intervals.

Table 13. Cobalt on Concrete – Probability Value Matrix for Chemical Cleaning Agent Evaluation

	Evaluation Conditions	probability (p) values (< 0.05 - significant difference)				
		2 hr	**4 hr**	**1 day**	**3 day**	**7 day**
Tartaric Acid	**0 hr**	0.0447	0.0497	0.0533	0.0724	0.0758
	2 hr		0.9973	0.3695	0.0589	0.0279
	4 hr			0.1999	0.0000	0.0419
	1 day				0.0532	0.0526
	3 day					0.3972
EDTA	**0 hr**	0.0558	0.0556	0.0574	0.0587	0.0571
	2 hr		0.4002	0.2204	0.0231	0.3535
	4 hr			0.1858	0.0177	0.3116
	1 day				0.4090	0.9900
	3 day					0.5596

Light shading indicates significant differences

The significant differences are highlighted in gray. For the tartaric acid, the first two time points (2 h, 4 h, and 1 day) were significantly different than the initially contaminated coupon even though there was a relatively high level of uncertainty in the initial measurement due to one measurement that was close to an outlier. Later in the experiment, there were some significant differences that were driven by the increase in concentration mentioned above. For EDTA, the contaminated control samples were almost significantly different than many of the rest of the samples collected. However, there was some uncertainty in that measurement that caused the p-values to be just above what would be considered significantly different at the 95% confidence interval. Within the first two hours, the cobalt concentration dropped to levels near the detection limit and remained there the rest of the experiment. The data suggest that EDTA is a strong CCA for cobalt from concrete.

4.8 Strontium on Concrete Chemical Cleaning Agent Evaluation

Data from the persistence evaluation and flushing evaluation experiments suggested that strontium was persistent on concrete under routine and flushing flow conditions. Therefore, two separate experiments were performed in order to evaluate 0.1 M calcium chloride and 0.2 M ammonium acetate (pH 3) as decontaminating agents for concrete lined pipes. The coupons were contaminated, the control coupons were removed, and then the CCA was added to the AR with no flow or rotation and coupons were then collected over the course of the next 7 days.

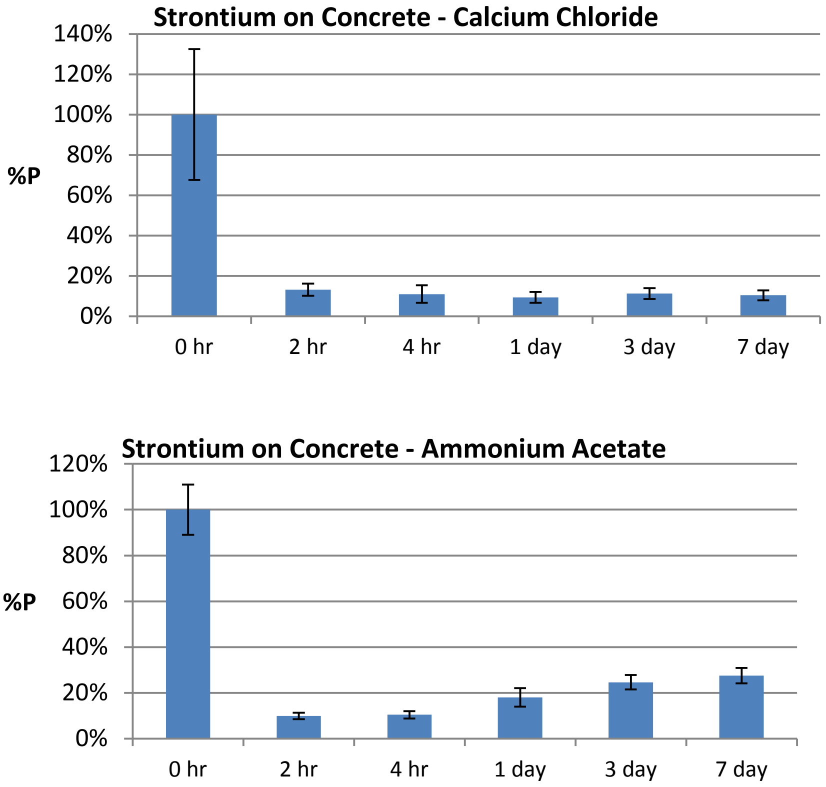


Figure 6. Chemical cleaning agent evaluation - percent persistence (%P) and strontium remaining on concrete for calcium chloride and ammonium acetate.

Observations of the graphical results indicate that calcium chloride is a moderately effective CCA for strontium on concrete. The %P dropped to approximately 10% within the first 2 hours and then stabilized. Ammonium acetate dropped the strontium concentration, which then increased over the following several days.

Figure 1 (pg. 21, section 4.3) shows that after exposure to stagnant water for 24 hours, strontium concentration decreased by 43%, with no further reduction (or a slight reduction) when shear was applied. These results indicate that continued exposure to stagnant water would not improve decontamination effectiveness. When coupons were exposed to calcium chloride and ammonium acetate, a strontium reduction of 90% occurred within two hours. This result held constant for calcium chloride, but continued exposure to ammonium acetate led to some strontium reaccumulating after 7 days of exposure. Once again, these results show the benefit of CCAs compared to stagnant or flowing water.

Table 14. Strontium on Concrete – Probability Value Matrix for Chemical Cleaning Agent Evaluation

	Evaluation Conditions	probability (p) values (< 0.05 - significant difference)				
		2 hr	**4 hr**	**1 day**	**3 day**	**7 day**
Calcium chloride	**0 hr**	0.0224	0.0193	0.0202	0.0213	0.0210
	2 hr		0.4113	0.0537	0.0688	0.0241
	4 hr			0.5389	0.9087	0.8063
	1 day				0.1766	0.4124
	3 day					0.3124
Ammonium Acetate	**0 hr**	0.0020	0.0019	0.0006	0.0016	0.0017
	2 hr		0.6793	0.0569	0.0035	0.0026
	4 hr			0.0613	0.0029	0.0021
	1 day				0.0770	0.0296
	3 day					0.2423

Light shading indicates significant differences

As with the persistence and flushing evaluations, statistical analyses were performed using t-tests to further clarify any differences among the data from each flushing scenario. Table 14 gives the p-values for comparisons of each possible set of coupons collected at the various time intervals. The significant differences are highlighted in gray. For both CCAs, samples at each time interval were significantly different from the contaminated control at the 95% confidence level. The calcium chloride results then steadied at the 2 hr concentration while the ammonium acetate exhibited significant differences at later time points, driven by the increase in residual strontium concentration at those time intervals. It is not clear why this increase occurred. The data suggest that calcium chloride removed 90% of the adhered strontium and is a good candidate for decontamination. Application of ammonium acetate yielded similar results, although the unexplained apparent increase in strontium after application may negate its effectiveness.

4.9 Water Quality Measurements

Throughout this evaluation the pH, temperature, and free chlorine concentration of the tap water was measured daily. The pH of the tap water was on average 7.4 +/-0.2. The average free chlorine concentration of the tap water was measured to be 1.3 mg/L +/-0.3mg/L. The average temperature of the tap water was 15.5 °C +/-6°C (this includes summer and winter months).

5.0 RESULTS SUMMARY

The objective of this study was to collect data pertaining to the persistence of surrogate radiological contaminants on concrete-lined and/or PVC pipe coupons and possible decontamination approaches. Several key points are summarized below.

5.1 Collection of Surrogate Radiological Persistence Data

Use of the AR proved to be an effective means of reproducibly simulating the flow of water past pipe materials, contaminating the coupons with cesium, cobalt, and strontium, and simulating a water distribution system. The surface extraction and surface contamination method validation steps were necessary to demonstrate whether or not the radiological surrogates could be studied (if it cannot be extracted it will be difficult to study its persistence) and if it is a viable threat (if a contaminant will not partition onto a pipe from an aqueous solution, it may not be a decontamination concern). These method validation steps were demonstrated with a limited number of replicates for cesium, cobalt, and strontium. Each of these method validations could be more rigorously tested. Tests could include more replicates or additional separate experiments that optimize certain components of the extraction such as sonication time and extraction acid.

5.2 Persistence and Decontamination Testing

The surface extraction method validation confirmed that cesium, cobalt, and strontium could be extracted from the surface of concrete after direct contamination of the coupon. The surface contamination method validation confirmed that a coupon could be contaminated with cesium, cobalt, and strontium by exposing it to a solution of contaminated water. The results from the persistence evaluation are summarized below:

- Cesium was not persistent on concrete or PVC pipe materials
- Cobalt was very persistent on concrete, but less persistent on PVC
- Strontium was persistent on concrete, but not on PVC.

Results from the decontamination portion of the study are as follows:

- Flushing was not effective for cobalt or strontium on concrete
- EDTA was an effective chemical cleaning agent for cobalt on concrete.
- Tartaric acid was an effective chemical cleaning agent for cobalt on concrete, but it formed a yellow precipitate on the surface of the coupons.

- Ammonium acetate and calcium chloride were both moderately effective as chemical cleaning agents for strontium on concrete.
- None of the contaminants were persistent on PVC pipe materials, so chemical cleaning agents were not evaluated on PVC.

5.3 Future Research Needs

The water system decontamination research area is one with many factors to be explored. Listed below are possible areas for further study:

- Biofilm is a factor that impacts surface adsorption of contaminants. Additional work could be performed to determine more information about the role of biofilm in persistence and decontamination of contaminants from pipe material.
- Broadening of the adsorption/decontamination data set by expanding on the list of chemical contaminants and examining biological contaminants.
- Use of additional pipe materials as well as additional decontamination agents.
- Scaling up of AR experiments to experiments with real pipe in order to study how well the AR experiments translate into a large scale scenario.
- Comparison of the PDEDP with an experimental design that does not include flowing water (5). Such a design may be easier and cheaper to implement.

6.0 REFERENCES

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