Radioactive Contamination Tenacity on Building Substrate – 17417

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ABSTRACT

Radiological decontamination is an essential enterprise that has become more important over the last four decades due to unfortunate accidents and the threat of terrorist actions. Decontamination can be an effective, beneficial alternative for the cleanup of radiological contamination events; however, the costs and benefits need to be balanced against those for complete removal and demolition of contaminated areas or facilities. Demolition and removal are often the first options considered in such circumstances as decontamination may be thought of as slow and costly. Decontamination has advantages, including significant waste reduction over demolition. In areas with buildings of cultural or societal importance, demolition may not be an option.

Three decontamination evaluation test series are the focus of this article: SIMCON 1 and 2 (i.e., simulated contamination), and Urban RDD (radiological dispersal device, i.e., a dirty bomb detonation). These test series revealed that different contaminants respond differently during decontamination. This was found to be true with both SIMCON and Urban RDD simulant tests. SIMCON 2 especially demonstrated that chemically different contaminants respond differently to different decontamination methods: cesium appears to be less tenacious (more easily removed) than zirconium using chemical methods. These differences were underscored by the Urban RDD tests where americium and cobalt tended to precipitate on high pH surfaces (such as concrete), making them easier to remove, while cesium and strontium were essentially unaffected by surface pH and were imbibed more strongly into the substrate pore structure.

While authorities argue over the contributions of contaminant chemistry and substrate morphology, the clear answer is that each has a contribution to the tenacity of a contaminant. Knowing how these characteristics interact will make us better at decontamination in the field. This knowledge refutes the efforts of perhaps well-meaning marketers to define our decontamination problems by what products they are trying to sell; often a "one size fits all" type approach. Knowing even a little bit about the character of the decontamination problem will save time and money and increase the efficacy of decontamination.

INTRODUCTION

Contamination simulation tests, gauging the efficacy of different decontamination methods, have been conducted at the Idaho National Laboratory since 1991. The simulation methods were designed to replicate substrates and contaminants found in the nuclear industry or that would be found in an urban contamination event. The

problems were defined by field conditions, not by laboratory convenience. The results of the tests, with the characteristics of contaminant and substrate, lead to fundamental insights into the nature and mechanisms of radiological contamination. These conditions and methods have been described previously [1,2,3] and are divided into three groups:

1. Fixed contamination on stainless steel (SS) substrates
2. Loose contamination on SS substrates, and
3. Urban RDD contamination.

The work detailed in this report focuses on fixed, urban RDD contamination created by spraying radioactive contaminants (Cs-137, Sr-85, Co-60, and Am-243) on concrete, limestone, marble, and granite substrates. Figure 1 shows a coupon being contaminated in the lab.

Figure 1. Spraying a building material coupon with a radioactive contaminant.

While the original purpose for these simulated contamination tests was to determine the effectiveness of individual decontamination methods on an empirical basis, a fundamental understanding of radiological contamination mechanisms was advanced as well. Data analysis was performed after testing, including a data mining effort. The overarching goal of the data mining process is to extract information from a data set and transform it into an understandable structure for further use. Aside from the raw analysis steps, it may involve data processing, modeling, and visualization, among others.[4] In the case of the decontamination data considered here, many of the secondary conclusions (those not associated with which decontamination method performed well) are qualitative. For example, it was found that different contamination-fixation mechanisms produce very different

results. In some cases, data relationships previously established only by anecdote can be quantified.

More advanced data mining involves a method of pairing data in such a way that the relationships between the different data are highlighted. In the case of these simulated contamination data, the primary measure in the data is the percent removal, or results of the effectiveness tests, which will be analyzed in terms of:
- Decontamination method;
- Contaminant species (i.e., radionuclide); and
- Substrate.

Essentially, this effort identifies and quantifies some important aspects of the resultant data that were not the original experiments' focus or intent, and were not readily apparent without data processing.

Having gone through these additional analysis steps, we come away with a new appreciation of how contaminants behave during decontamination. This understanding enables a paradigm shift with respect to how we go about performing decontamination and what results we can expect.

RADIONUCLIDE DECONTAMINATION DIFFERENCES

Unravelling which characteristics result in which contaminants becoming tenaciously attached to which substrate is a difficult puzzle. Our approach is to simplify the puzzle by grouping related data, using data mining to examine the resultant data set, and reducing the number of data fields so that individual differences can be examined separately. This approach emphasizes relationships and reveals dependencies.

While the SIMCON 1 and 2 data are instructive, the Urban RDD data have more interesting relationships and better rule association qualities. Using this data we have compared various contaminant characteristics for a single substrate (concrete), several decontamination methods, and a number of substrates. During this examination we became aware of what we consider a primary effect: Contaminant interaction with a substrate is very pH dependent. There are other dependencies which are vital to the understanding of the whole system, but this report focuses on that primary relationship.

During the tests and evaluation of the data there were a number of characteristics examined: cation-exchange capacity, isoelectric potential, substrate microstructure, and substrate/contaminant surface pH chemical interaction. A complete examination of these characteristics is beyond the limitations of this report. Summarily, we found that, for cationic radionuclides that do not interact chemically with the substrate surface (i.e., pH-promoted precipitation), and for substrates of similar permeability, the net surface negative charge (cation exchange capacity and isoelectric potential) of the material substrate – along with the contaminant charge density – plays a role in determining the tenacity of the affixed contaminant. Special characteristics – for instance, granite microstructure, which is layered like clay – also seem to promote the sequestration of radionuclides within the substrate.

Evaluation of Contaminants on Concrete

A box and whisker diagram summarizing and comparing concrete decontamination efficiencies for the four radionuclide species studied is shown in Figure 2. The figure shows the relative relationship between americium, cobalt, cesium, and strontium over 64 different tests, using three different chemical decontamination technologies: Rad-Release II, Argonne SuperGel, and DeconGel 1108. The data are well grouped for each radionuclide, and they exhibit a declining trend in median removal percentage, from americium to cobalt to cesium to strontium. These data begin to paint a picture of the relative tenacity of these different chemical species. It suggests differences in the chemical nature of each radionuclide is a major factor in decontamination efficacy.
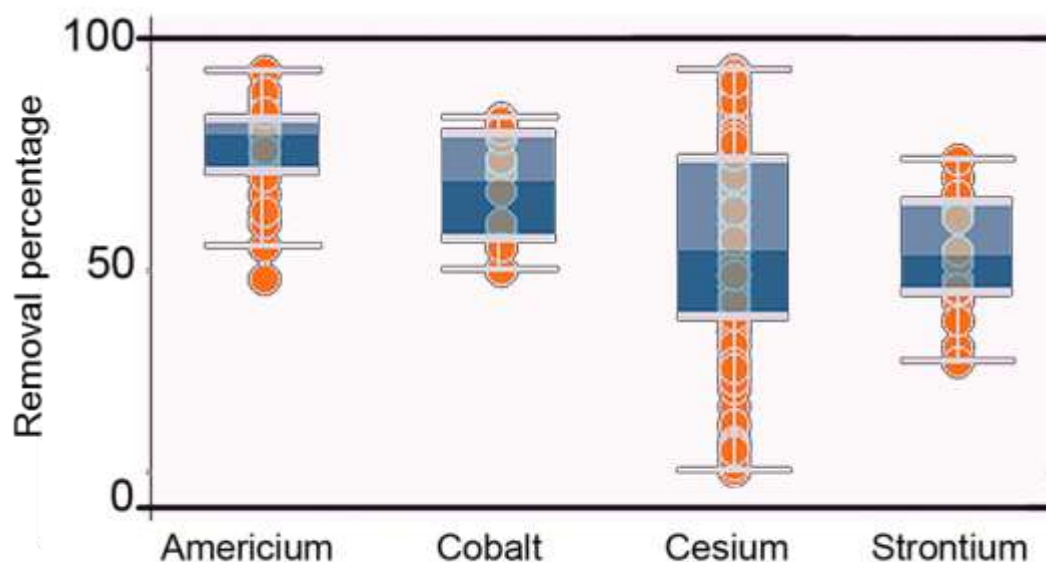

Figure 2. Tableau analysis of concrete decontamination results for four radioactive species.

A second observation to be taken from Figure 2 is that there is considerable variability in decontamination technique efficacy for each radionuclide. Cesium exhibits the most variability. The lack of uniformity indicates that individual radionuclide tenacity must be viewed in terms of its interactions with a given substrate. Historically, the characteristics listed in Table I have been related to cation/substrate interaction. It is instructive to consider these relationships in more detail. The decontamination results listed in column two of Table I are the average (the simple mean) of results for the three chemical decontamination methods: DeconGel 1108, Rad-Release II and Argonne SuperGel. The other physical properties listed in Table I –ion radius, solubility product, and ionic potential – exert the strongest influence on ion-substrate interactions, and thus, tenacity.

TABLE I. Decontamination efficacy and physical characteristics for four radionuclides.
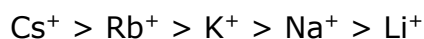
Radionuclide	Decon result [% removal]	Ionic radius [cm][a]	Solubility product, k_{sp} (pH = ~8)	Ionic potential [nm^{-1}]
Americium	75%	180 X 10^{-10}	3.2×10^{-18} mol^4/dm^{12} [as Am(OH)$_3$][b]	16.7
Cobalt	70%	126 X 10^{-10}	5.9×10^{-15} mol^3/dm^9 [as Co(OH)$_2$][c]	15.9
Cesium	55%	244 X 10^{-10}	1.2×10^{2} mol^2/dm^6 [as CsOH][d]	4.1
Strontium	54%	195 X 10^{-10}	6.4×10^{-3} mol^3/dm^9 [as Sr(OH)$_2$][e]	10.3

[a]Cordero et al. [5]; [b]Rai et al. [6]; [c]Generalic [7]; [d]Etacude [8]; [e]Krishnan [9]

A long held belief in decontamination literature is that the absorption strength of a contaminant on a substrate is a key ingredient in determining its resistance to removal. Researchers have found a strong correlation between the constant partition coefficient, K_d, and resistance to contaminant removal, particularly for Cs and Sr, when in contact with natural mineral substrates and urban surfaces such as concrete.[10, 11] K_d is defined as the ratio of the quantity of the adsorbate (i.e., metal or radionuclide) adsorbed per unit mass of solid to the quantity of the adsorbate remaining in solution at equilibrium. The parameter K_d is in fact a convolution of two more fundamental properties of any given cation-substrate system:

1. the strength of adsorption, usually expressed in the form of an equilibrium constant such as that used in the Langmuir adsorption isotherm equation; and
2. the number/concentration of sites available for adsorption, usually expressed in the form of a cation exchange capacity (CEC).

Based on these considerations and laboratory observations, the relative adsorption affinity of metals has been described as follows:[12]

$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$

$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$

$Hg^{2+} > Cd^{2+} > Zn^{2+}$

$Fe^{3+} > Fe^{2+} > Fe^+$
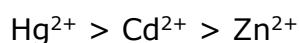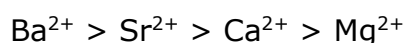
The relationship between ionic potential (charge density) of the radionuclides tested may be a factor in resistance to removal (decontamination), it does not adequately

explain the decontamination results presented in Table I and Figure 2. Table I shows the ionic potential values for the radionuclides used in these tests, the order of *weakness* of ionic potential (weakness indicating ease of removal) being:

$$Cs^+ > Sr^{2+} > Co^{2+} > Am^{3+}$$
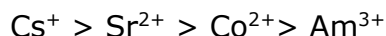
However the removal percentages (decontamination efficiencies) from concrete for the contaminants listed in Table I are ranked as follows:

$$Am^{3+} > Co^{2+} > Cs^+ > Sr^{2+}$$
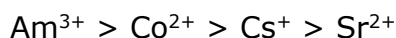
This indicates almost the exact opposite order than might be expected on the basis of the contaminants' ionic potentials and indicates that other factors influence the outcome. Chemical solubility and precipitation at higher pH, as discussed earlier, exert a stronger influence on tenacity than does ionic potential.

Contaminant Behavior on Alkaline Surfaces

A wide range of physicochemical characteristics influence whether any given radiochemical contaminant is more tenacious (more difficult to remove) than another. However, we can begin to understand these characteristics when we observe that two of the contaminants studied, Cs^+ and Sr^{2+}, are mobile, cationic species, and thus, may penetrate significant distances into the porous materials typical of urban structures. Amphoteric species such as americium, on the other hand, may become less soluble on basic (i.e., high pH) media. Because of the abundance of calcium hydroxide and calcium carbonate in concrete, the pH of the surface of concrete is very alkaline.[13] Thus, while the Am(III) contaminant simulant may be applied as an Am^{3+} cation, it is likely in the form of a sparingly soluble oxyhydroxide when sorbed, due to neutralization by the basic surface of the concrete. Such surface-precipitated species are less likely to penetrate deeply into concrete.

To better illustrate the difference in behavior on alkaline concrete, Figure 3 shows a comparison between E_H–pH speciation, or Pourbaix diagrams, for the cesium-water and americium-water systems. A clear observation from these Pourbaix diagrams is the dependence of americium speciation on pH.[14] The vertical axis of each Pourbaix diagram describes the prevailing redox in the aqueous system under consideration. The dashed diagonal lines, labelled "a" and "b" and angled down to the right, describe the region of stability of the aqueous phase. Below the lower dashed line (a), the water is reduced, leading to hydrogen evolution. Above the upper dashed line (b) the water is oxidized, leading to oxygen evolution. Within the two dashed lines lie the solution conditions for an aqueous system which are of relevance to the RDD simulant decontamination test results shown in Table II.

From low to high pH, the cesium (left pane) and americium (right pane) systems shown in Figure 3 exhibit vastly different chemistries. The cesium ion remains unchanged in its character throughout the pH range. It remains in solution as a positive Cs^+ cation with a highly soluble character. As a cationic alkali metal species, it behaves as one of the most soluble species in the periodic table. By

contrast, at higher pH the americium cation, Am^{3+}, either hydrolyzes to form $Am(OH)_3$ or hydrolyzes and oxidizes to form $Am(OH)_4$, depending on the prevailing redox conditions of the system. Both of these species are much less soluble than the original Am^{3+} ion that predominates at low pH. In other words, as pH increases, the solubility of americium is greatly decreased.
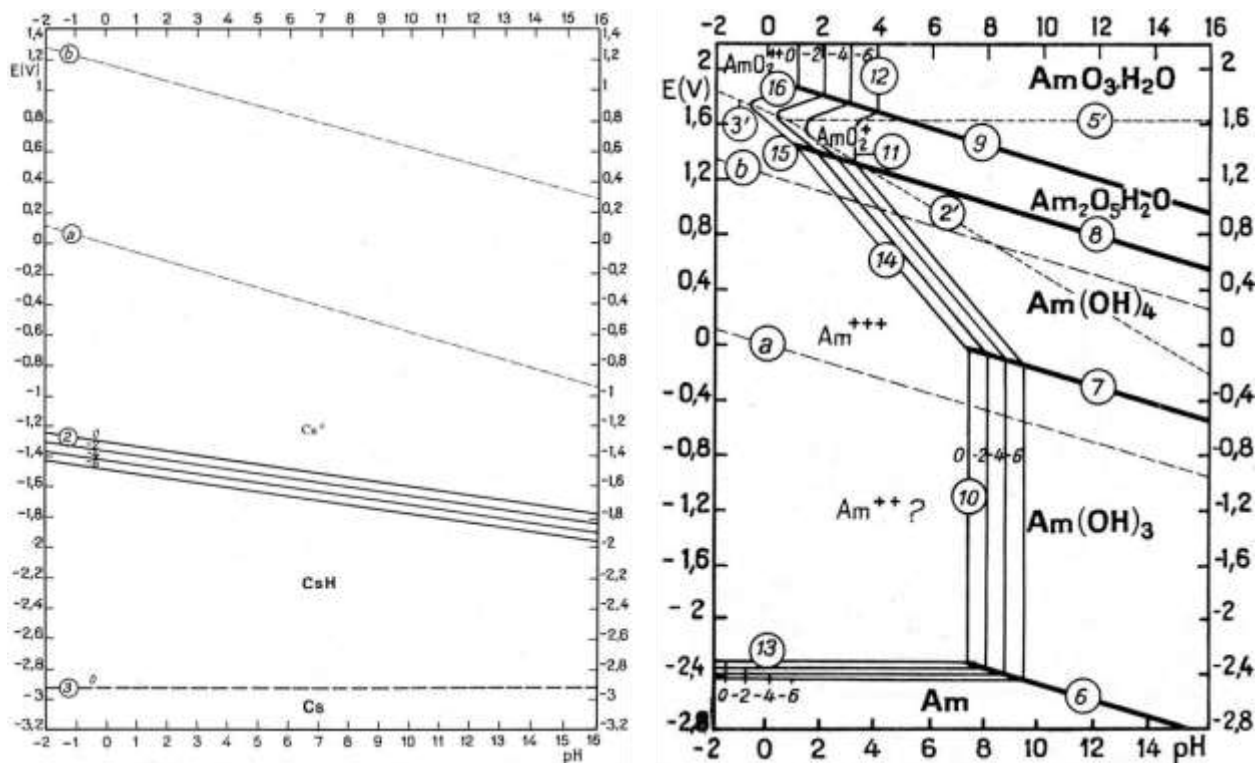

Figure 3. Pourbaix diagrams for cesium (left) and americium (right).[14]

The two other principle chemical species included in the tests have similar characteristics to americium and cesium. Figure 4 shows the Pourbaix diagrams for cobalt (left pane) and strontium (right pane). Examining these two diagrams reveals that cobalt undergoes chemical speciation changes analogous to americium. At high pH it forms insoluble $Co(OH)_2$ or $Co(OH)_3$ species, depending on the redox conditions of the system. However, in contrast to americium, at pH > 13, the soluble anion $HCoO_2^-$ may be formed. Cobalt solubility decreases with increasing pH, goes through a minimum, then increases again from pH 7-13. Strontium (like cesium) has virtually no change in its speciation, remaining a double positive charge cation, Sr^{2+}, up to pH 14, retaining soluble alkaline earth character.

The tenacity of different radiochemical species through a range of chemical decontamination methods to a large degree reflects their soluble/insoluble character as summarized in the Pourbaix diagrams. The more soluble radionuclides exhibit greater tenacity during the application of surface decontamination techniques. This behavior is indicative of the role played by substrate penetration, most likely via interconnected pores, in determining ease of contaminant removal. The two alkali/alkaline earth metals, cesium and strontium, have high solubility

across the pH range, whereas cobalt and americium have hydroxides and oxyhydroxides forming at even moderate pH levels, in some cases down to pH 4. The solubility of the hydroxy species under alkaline conditions is exceedingly low, as described by the solubility product data shown in Table I. In practice, this means that the likelihood of species with low solubility penetrating into the surface of the substrate is very slight. Such species are not mobile at high pH. They precipitate upon contact with the basic surface of the substrate, allowing for highly efficient removal by simple decontamination techniques, e.g., strippable coatings.
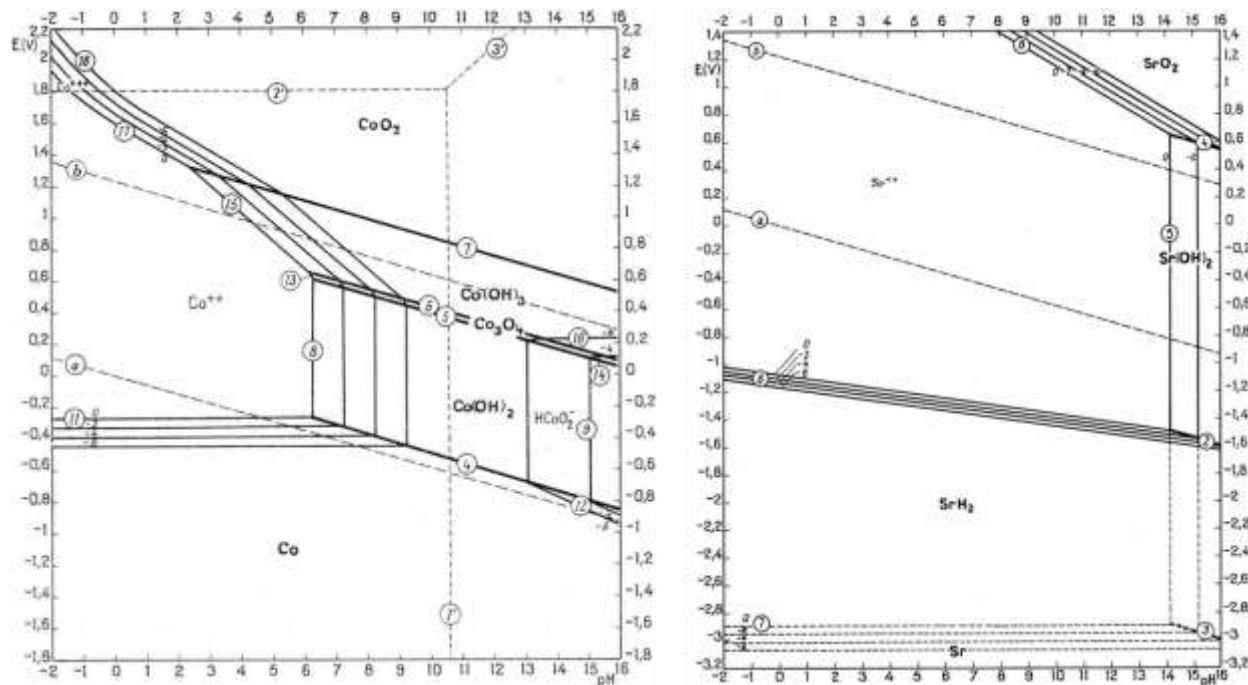

Figure 4. Cobalt (left) and strontium (right) Pourbaix diagrams.[14]

CONCLUSIONS

Our evaluation of urban decontamination testing found that chemical speciation of radioisotopes has a profound effect on their tenacity during decontamination. We call it a primary influence because, if the radionuclide precipitates on the surface, no other characteristics really influence subsequent fixation or permeation. For many radionuclides, decontamination outcomes can be predicted based on this one characteristic. For the case of urban terrorist RDD remediation, this approach helps greatly. There are only about nine radionuclides that likely would be used: Am-241, Cf-252, Co-60, Cs-137, Ir-192, Pu-238, Po-210, Ra-226, Sr-90.[15] Of those nine, only Cs-137, Sr-90, and Ra-226 are alkali or alkali metal species, which would exhibit permeation beyond the surface.

This greatly simplifies RDD remediation scientists' and engineers' job, because preservation of an urban environment through decontamination is typically the preferred alternative. The six radionuclides that are actinides or transition metals should exhibit surface precipitation. In that case simple strippable coatings should

perform very well. For the alkali/alkaline earth species, including cesium, radium and strontium, a decontamination system that includes a mechanism to reverse their permeation (or removes substrate) should be used.

The general nuclear industry case often becomes more difficult than the single radionuclide RDD scenario. Spent fuel processing facilities, for instance, are contaminated with a messy mixture of many different radionuclides. The key in such environments is flexibility of approach: use decontamination methods that utilize both near surface and penetrating technologies. In previous WM Symposia reports we have described some of these robust, versatile methods.

The INL is currently developing a computer program to quantify insights gained from the decontamination simulation studies. This program will predict and simulate human judgement, providing a decontamination "coach". It will incorporate not only chemical characteristics, but also surface effects and substrate permeability. The program is in the conceptual phase and does not yet have a sponsor. Once fully developed, the software should enable more efficient and accurate decision making by those responding to a contamination event.

ACKNOWLEDGEMENTS

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