Decontamination Method Comparison Testing

Using Simulated Contamination

By

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Abstract

Radiological decontamination of surfaces is challenging. Cleanup tasks are typically visual or even chemically measured, but radioactive contamination is invisible and measured at extremely low levels. Different contamination events have lead to the development of hundreds of decontamination processes. Their selection balances criteria such as cost effectiveness and waste minimization. While testing on the actual system where the contaminations arises (as "field" radioactive specimens) is appropriate, doing so is expensive and time consuming. Simulating contamination with substitute contaminants requires a unique understanding of the system. This provides a less expensive, more controlled and often more informative selection method. However, not all simulation methods are reliable, reproducible, have a useful range nor are relevant to the target activity.

To address these needs, a range of simulated contamination systems have been developed:

- SIMCON 1 – to simulate loose contamination on stainless steel;
- SIMCON 2 – to simulate fixed contamination on oxide coated stainless steel;
- A radiological dispersal device (RDD) or so-called “dirty bomb” contaminant to simulate fixed contamination on urban material surfaces.

Over 400 individual decontamination tests have been performed with these simulants, using a range of contaminants (Cs, Zr, Am, Sr, Co) and substrates (steel, concrete, marble, limestone, granite). Review and data mining of the results of these tests has allowed for the development of an understanding of the

fundamental mechanisms of interaction between contamination and surface and their role in determining decontamination efficiency.

Detailed analysis of the SIMCON results demonstrates that the availability of a deliberately designed contamination simulant system allows for the comparative assessment of a wide range of decontamination methods in a common frame of reference on a “level playing field”. Though somewhat intuitively obvious, the SIMCON methods evaluation unambiguously demonstrated that chemically different contaminants may behave quite differently during a decontamination action. The exact nature of this behavior depends upon the nature of applications (loose or fixed) and the decontamination method itself. If a wide range of decontamination methods are deployed on a well-designed contamination simulant, comparison of the results of the decontamination tests may provide insight into the mechanism of contamination e.g. how it is held (loose, fixed etc.), where it is held (on the surface, in a protective oxide layer etc.) and so forth.

These conclusions are reinforced by detailed consideration of the urban RDD simulant decontamination data. With respect to the contaminants themselves, it is found that cations that exhibit a pH dependent speciation, such as americium or cobalt, can demonstrate radionuclide / material substrate specific chemistry that results in contaminant precipitation at the substrate surface, especially if the material has an intrinsically alkaline surface pH. For example, in the case of Am and Co, this results in the precipitation of Am and Co oxyhydroxide species at the outer surface of materials such as concrete with consequently high percentage removal efficiencies.

For cationic radionuclides such as Cs^+ that do not exhibit any nuclide/material surface specific chemistry the principal material property controlling the tenacity of that nuclide during decontamination from urban material substrates is the permeability of that substrate.

For substrates of similar permeability, net surface negative charge on the material substrate plays a major role in determining the tenacity of non-reactive cations such as cesium; the larger the net negative charge on the substrate surface, the more tenacious the contamination.

Finally, with respect to the decontamination agents themselves, harsh, high concentration chemical agents that utilize multiple decontamination processes (acids, bases, chelants) typically have an effectiveness advantage over more dilute, one component solutions. Strongly acidic solutions achieve the highest overall % removal decontamination results. This is partly because they tend to dissolve small amounts of the substrate surface and liberate imbibed contaminants. Finally, some strippable coating based methods are found to be surprisingly effective; likely because of their chelant/absorbtive character.

Statement of Authorship

I, Rick Demmer, confirm that the work presented in this thesis has been performed, interpreted and written by myself, except where otherwise stated, and has not been submitted in any previous application for a higher degree.

The SIMCON I and II, and Urban/RDD source data presented in this thesis was produced by Rick Demmer at Idaho National Laboratory (aka, Idaho National Engineering Laboratory [1978-1999], Idaho National Engineering and Environmental Laboratory [2000-2004]) between 1992 and 2015. The data was reviewed and interpreted by Rick Demmer whilst registered to study for the degree of Doctor of Philosophy at Lancaster University between 2012 and 2016.

Date....22nd Feb 2016….. Signature of Candidate ....

Director of Studies Declaration

I hereby certify that the candidate has fulfilled the conditions of the resolution and regulations appropriate for the degree of Doctor of Philosophy at Lancaster University and that the candidate is qualified to submit this thesis in application for that degree.

Date..22nd Feb 2016.... Signature of Supervisor

Dedication

This dissertation is dedicated to those who helped me develop these concepts over the last 20 years: to my loving family (especially Linda, Robin and Ron) and friendly (though critical) colleagues in Idaho, Illinois, Ohio, Florida and around the world. When our five-person team was awarded the R&D 100 at Idaho in 2010, I described the “sixth member” as everyone who had strove with us and helped through the five years of development. The rest of the team is always as important as the one who steps up to claim the prize. Thank you for decades of support and encouragement.

Acknowledgements

Over the past 20 years many people have contributed to this research and made this dissertation possible. Naming all of them would be impossible, and I am sure I will leave someone out. If so, please accept my apologies.

I start with our first decontamination development team: Julia Tripp, Russ Ferguson and Kip Archibald. The sponsors of the Urban RDD testing: Dr. Ryan James, Dr. Robert Fox and John Drake. My coworkers over these many years: Don Jenkinson, Mike Jones, Mike Ancho, John Heintzelman, Matt Jones, Marty Kearns, Joey Charboneau, Mike Tollar, Chris Jensen, Tom Sorenson and Steve Hinckley. The Rad-Release Team: Dr. Dean Peterman, Dr. Larry Hull, Dr. Craig Cooper and Karen Wright. My supervisor Professor Colin Boxall. My management at the INL, principally Jack Law and Dr. Terry Todd. And finally to my many friends that encouraged me during this research.

Table of Contents

List of Figures

List of Tables

1. INTRODUCTION

1.1 The Problem of Radiological Contamination

Cleanup has always been a major human activity for as long as we have inhabited this globe. As society has developed, we have moved from simply making things look tidy, to being concerned about cleanliness from a human-health perspective. The cleanup frontier focused on fighting deadly disease when, in 1752, John Pringle noted the parallel of filth/overcrowding and disease; advocating for good sanitation (Porter 1996). Less than 200 years later, a new health threat began with the rise of nuclear energy. As the first nuclear materials were being processed at the desert Hanford Site in Eastern Washington in 1944, radioactive-waste material was being generated and collected; some of which still contaminates that site. Operation of and maintenance on process equipment began to require special remote methods, and decontamination techniques developed specifically for those processes (Geuther and Hansen 1994).

In the early twentieth century, a new type of contaminant, radiological contamination, began to be a significant problem. Radiological contamination is defined as a substance in an undesired location that decays with the emission of ionizing radiation (IAEA Safety Glossary 2007). As Madame Marie Curie began discovering the radioactive nature of radium and polonium in 1900, her laboratory was also becoming contaminated with radioactivity (Women in Science 2014). In the early years of nuclear energy, it must have been a disappointment that radioactive material turned up in unwanted locations; it simply didn't stay where it should have been. This type of contamination defied efforts to control and secure it within specified boundaries and is tenacious in resisting removal. Radiological contamination is one of the byproducts, or legacies, of the scientific exploration and industrial exploitation of nuclear energy in the twentieth century.

The removal of the contaminated residue from nuclear energy is called “decontamination”. In reality, radiological contamination is neither more difficult to control, nor more pernicious than other types of contamination. The fundamental difference with radiological contamination was its ability to be detected by instrumentation, and not by human senses, to a very low level. High quality cleaning applications (such as oxygen service) require cleaning to 100 parts-per-million (ppm) cleanliness standards (ed. Baukal 2013). Very low contaminant levels for high precision chemical analysis (trace analysis) require levels of 0.1 ppm (ed. Flores 2014). But radiological contamination, which can’t be seen or smelled, is easily detected to 1×10^{-13} grams (Johnson, Birkey 2012).

But while easier to detect, radiological contamination suffers from a very high degree of public scrutiny and suspicion that requires increased levels of diligence in control and removal. Radiological contamination is a hazard that causes tremendous fear in the general population. Even scientists who comfortably work with human pathogens are often more concerned with minor amounts of radiological contamination, though it is far less lethal than disease (Dr. Robert Jones 2013, pers. comm. 30 January 2013). This sets the stage for the dilemma of radiological contamination; removing very small quantities of material (far smaller than those required for other hazardous or “dirty” contaminants) so that radiological contamination is maintained below levels of concern.

This seemingly impossible task becomes manageable as more is known about the contamination, its chemical composition, structure, and adherence to the base material. The types of surface and the materials of construction must also be considered prior to selecting a decontamination method. Most piping and tanks used in the nuclear industries are constructed of stainless steel. However, more exotic materials, such as Hastelloy or titanium, are sometimes used. In addition, secondary waste generation, potential for recontamination and waste compatibility with disposal facilities can be important factors.

Decontamination effectiveness can be expressed by a decontamination factor (DF) or by removal percent. DF is defined as the ratio of the concentration of various radionuclides (or exposure, measured in Sieverts) before and after decontamination:

$$\text{DF} = \text{quantity of radiation before decon}/\text{quantity of radiation after decon}$$

DF's vary widely depending on the situation and are most useful when comparing the efficacy of alternate techniques in the same decontamination activity. We have found that, through discussions and presentations of the data for many tests, the public understands the "percent removal" concept and that it is a more informative measure of decontamination achieved by a particular decontamination method:

$$\%\ \text{removal} = 100 \times \frac{(\text{quantity of radiation before} - \text{quantity of radiation after})}{\text{quantity of radiation before}}$$

The percent removal seems to be more intuitive as a concept for decontamination and easier for the public to accept.

Significant progress has been made in the availability and use of non-chemical, or mechanical, decontamination techniques. Mechanical techniques may have unique advantages over chemical techniques for some decontamination tasks. For example, when waste minimization is important, there is a greater potential for waste reduction and ease of waste disposal for these techniques. Some of the techniques also address particular niches that were otherwise unfilled. Many of the mechanical techniques have virtually no interaction with the substrate, and can be used to remove large amounts of surface in a short time. Some of the techniques are quite inexpensive but can be very environmentally friendly. As with chemical decontamination, a thorough investigation of the type, process, and criteria for decontamination should be made prior to any use.

It should also be noted that decontamination has a different context for the decommissioning of nuclear facilities than it has for nuclear operations. Very harsh, aggressive decontamination technologies or processes can often be used during decommissioning activities, activities which would not be acceptable if continued operation of the facility were the goal. Also, cost-benefit analyses can often be performed which can show that decontamination is not cost effective, or necessary, for facility decommissioning.

1.2 Contamination Simulation Thesis

The key thesis of the research presented here is that radiological contamination, which is essentially an accidental assembly of radiological material, can be simulated and shown to be like a reproducible, chemically derived quantity. Simulants in this context can be used to compare different decontamination methods so that effectiveness data can be determined.

Review of twenty years of efforts to simulate contamination allows for several general conclusions to be drawn:

- Decontamination can be an effective, beneficial alternative for many radiological contamination events; decontamination needs to be a balance of recovery versus complete demolition. Decontamination reduces waste greatly over demolition. In areas with buildings of cultural or societal importance, demolition may not be an option.

- Not all highly effective decontamination methods are right for all tasks. A systematic approach should be taken to determine the proper method. The criteria for selecting the method should include effectiveness, waste generation characteristics, waste compatibility and cost.

- A meaningful simulated decontamination test must have an adequate range that allows differentiation of different methods. This usually dictates a "fixed" type of contamination simulant. Developing a fixed, reproducible contamination simulant is not a trivial process; SIMCON 2, developed by the author at INL and described in detail later in this thesis, and Urban RDD simulants are examples of these kinds of systems.

- Knowing how tenacious (how firmly fixed) the contamination allows engineers to select the best, lower cost, least waste methods.

- Different contaminants respond differently during decontamination. This difference is more pronounced with chemical decontamination methods than with mechanical methods.

- The chemical characteristics of a radionuclide, particularly precipitation and speciation, have a fundamental effect on their ability to be adsorbed and retained on a surface.

- Decontamination methods can be grouped by families of similar methods of like effectiveness (i.e., harsh abrasive methods, soft chemical, harsh chemical, etc.). This can simplify the selection of decontamination methods.

- Chemical and physical properties of the substrate have significant effects on the decontamination levels found during testing. The most pronounced characteristics are porosity/permeability and surface pH.

- The microstructure of the substrate (particularly granite, which has a layered, claylike surface) may promote the sequestration of radionuclides on its surface.

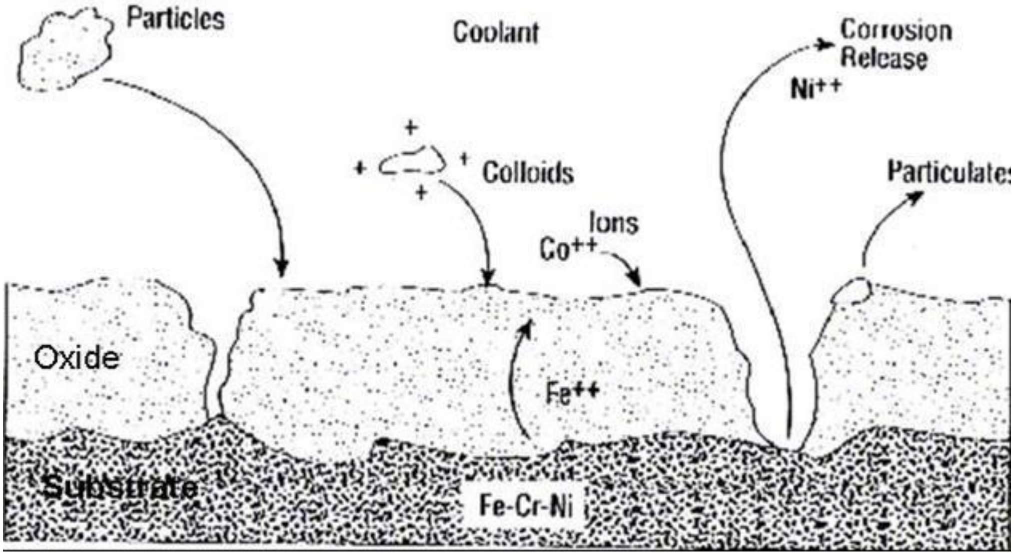
- Acidic solutions seem to have better overall decontamination effectiveness for urban surfaces, but chelation and other adsorptive binding mechanisms greatly enhance decontamination.

These concepts will be explored in this thesis, and the scientific basis for these statements will be developed. This will be done primarily by simulating contamination and using different decontamination methodologies to remove that simulated contamination. This research covers many different types of contamination and hundreds of tests using different technologies. The data from these tests, and the interpretation of the data in terms of the processes used, will explain the contamination, with the focus being to create high-quality test methodologies that can be used to make important decontamination decisions.

1.3 Nuclear Contamination Models

For many years, there has been an accepted model, called CRUD (Chalk River (Canada) Unidentified Deposit or Corrosion Related Unidentified Deposit), for visualizing how nuclear contamination adheres to metal (Wood 1989). Contamination within nuclear reactors may be thought of as occurring chiefly in the oxide formed on the inner surfaces of the metal piping in a reactor's primary coolant system. While some activation of base metal within the core area of the reactor does occur, the majority of the contamination comes from activation products, e.g. metal that becomes suspended in the coolant and passes through the core, where it becomes activated. These suspended materials are often a mixture of metal oxides (and even ions); however, the longer lasting, highly energetic isotope ^{60}Co typically becomes the most significant problem overall. The contaminated-metal-oxide layer, commonly known as CRUD, becomes a trap for suspended and ionic contamination. In addition, some fission products may leak from the fuel and become lodged in this CRUD layer. The visual representation of this contamination model, proposed by the Electric Power Research Institute (EPRI), is shown in Figure 1 (Ocken and Wood 1991).

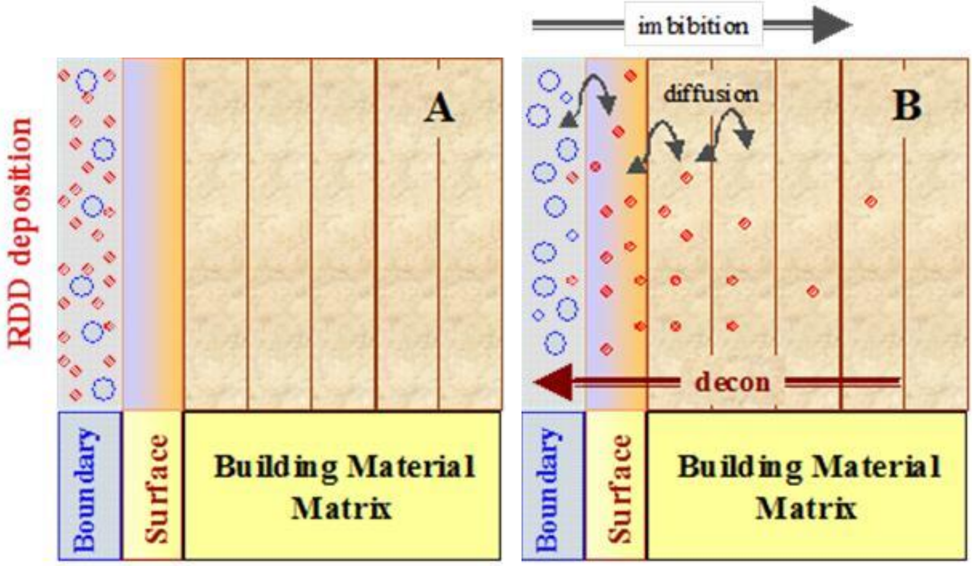
Figure 1. CRUD oxide layer (Ocken and Wood 1991).



This model has served the nuclear decontamination industry well in terms of explaining contamination mechanisms and decontamination methods over the years. For instance, it was long known that an aggressive chemical-decontamination process that utilizes a strongly oxidizing solution (such as alkaline permanganate) followed by a strongly reducing organic acid (such as oxalic acid) was highly effective at removing the tenacious oxide layer from stainless steel substrates. The mechanism is a two-step decontamination approach which removes the tenacious oxide layer and, with it, the contamination. Comparing these observations lead to the understanding that chemicals (such as nitric acid) that promote the growth of the oxide-passivation layer on stainless steels will likely not be highly effective at removing contamination. However, care must be taken as to this generalization because some contamination is simply deposited as a solid on surfaces (such as a leak from a valve), and solutions that would not remove the oxide layer are sometimes highly effective at removing these deposits.

In the case of porous substrates, a different model may be utilized that describes the particular characteristics of the substrate. While similar in some respects to the EPRI CRUD model, this model also makes use of the porosity and cation exchange capacity (CEC) of the material. Porous materials have a quality called “imbibition” that defines their ability to absorb contaminants beyond their surface. This imbibition depends on the porosity, the capillary action drawing the contamination further into the substrate pores, the permeability of the substrate and the other factors that help retain (bind, sequester) the contaminant in the material once it is drawn into the surface (Demmer 2007). The main similarity between metal- and urban-contamination (i.e. porous building material) models is that the largest amount of contamination present typically resides in a boundary layer (similar to the oxide layer) for porous materials. Removing this boundary layer without causing additional imbibition is a significant task. For urban substrates, it is recognized that the boundary layer may consist of loosely bound, weathered material and grime. The INL porous-material conceptual model is shown in Figure 2.

Figure 2. INL RDD deposition model showing contaminant (in red) diffusion.



Interestingly, during the course of evaluating our decontamination data (in Chapter 4), it was discovered that this model lacked an important feature to describe reactions that occur within the boundary layer. The model is focused on diffusion and does not represent contaminants that may be held in the boundary layer due to interactions. The discussion of the behavior of contaminants with alkaline surfaces, in section 4.4.3, will discuss one of those interactions.

Having described extent conceptual models of nuclear contamination, the next section describes the use of these models in developing generic mechanisms of contamination in the context of selected, real world examples.

1.4 Understanding Mechanisms of Radiological Contamination

(Originally presented at the 2014 Waste Management (WM '14) conference, March 2-6, 2014, Phoenix, AZ, USA – revised and updated for presentation here)

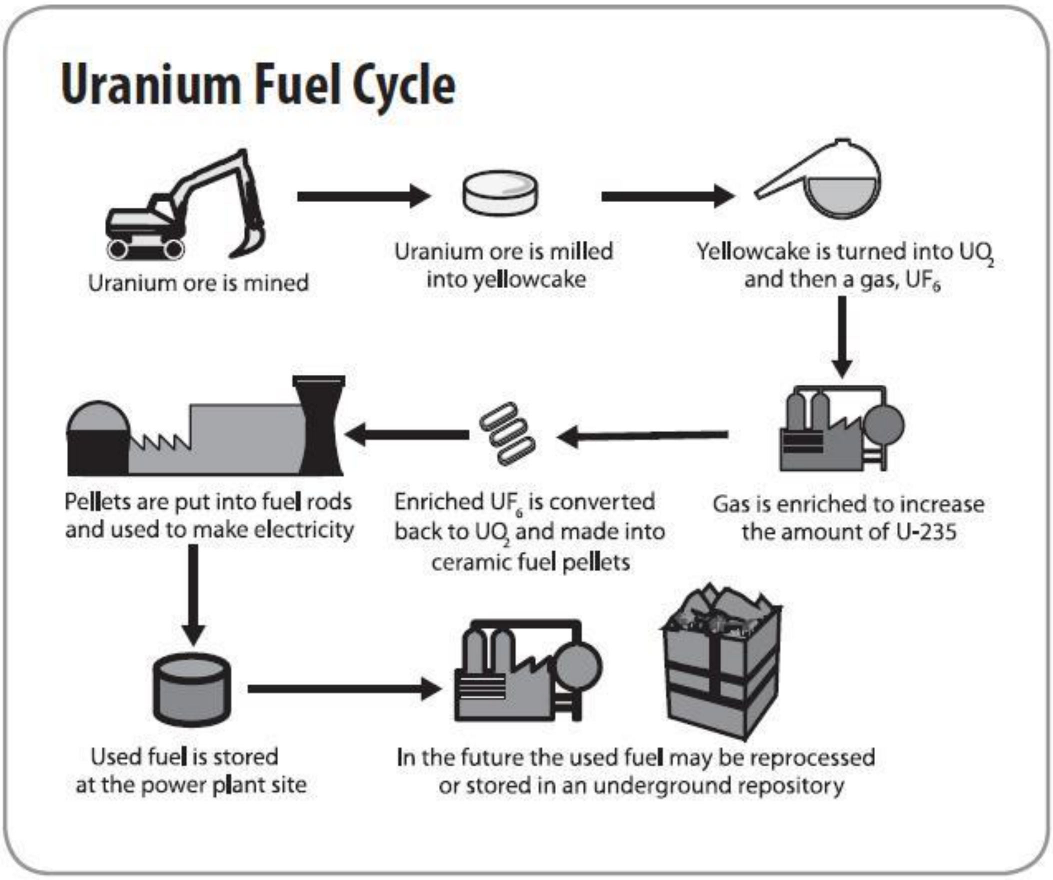
Over the last 50 years, the study of radiological contamination and decontamination has expanded significantly. This section addresses the mechanisms of radiological contamination that have been reported and then discusses which methods have recently been used during performance testing of several different decontamination technologies.

1.4.1 Mechanisms of Radiological Contamination

While much time and attention has been given to understanding different decontamination techniques, significantly less attention has been given to understanding the underlying fundamentals of contamination mechanisms and how to simulate that contamination. Distilling the contamination problem, in terms of that mechanism, is a difficult task and must begin by simplifying the discussion. Not all kinds of contamination can be discussed, because there are so many different mechanisms that could be envisioned. This section will logically work this problem into a few illustrative examples, using previously described concepts and arrive at some specific, common types of contamination.

Contamination of materials occurs because of the physical or chemical transfer of radioactive species onto surfaces where it is unwanted. Some contamination is strongly adhered (difficult to remove) to the surface, termed “fixed” contamination, and some is relatively easy to remove, or “loose” contamination. Generally, loose contamination is simply deposited on the surface by an aerosol method, and it has little interaction with the surface (obvious from its easily removable character). The removal of loose contamination requires little skill, usually a simple wipe with a damp cloth.

Figure 3. Variety of nuclear fuel tasks and facilities in the fuel cycle. (NEED 2014).



Loose contamination is commonly encountered in nuclear facilities operating throughout the fuel cycle and particularly in fuel-fabrication and recycling plants. Some of those tasks and facilities employed in the fuel cycle are shown in Figure 3. In uranium-dioxide-fuel fabrication plants, where fuels are processed as dry powders, materials settle onto horizontal surfaces and may accumulate in nooks and crannies that are not accessible to routine cleaning operations. Ventilation-system surfaces in many different kinds of facilities may also have loose contamination problems. This surface contamination is usually loose, although adherence can be increased by oily films or chemical vapors that are found on the inside of ducts. Since exhaust systems operate at negative pressures, they tend to draw in dust and aerosols that may contain activity. Deposition tends to be heavier in sections of the ducting where the direction or velocity of the fluid changes or at the edges of joints and flanges.

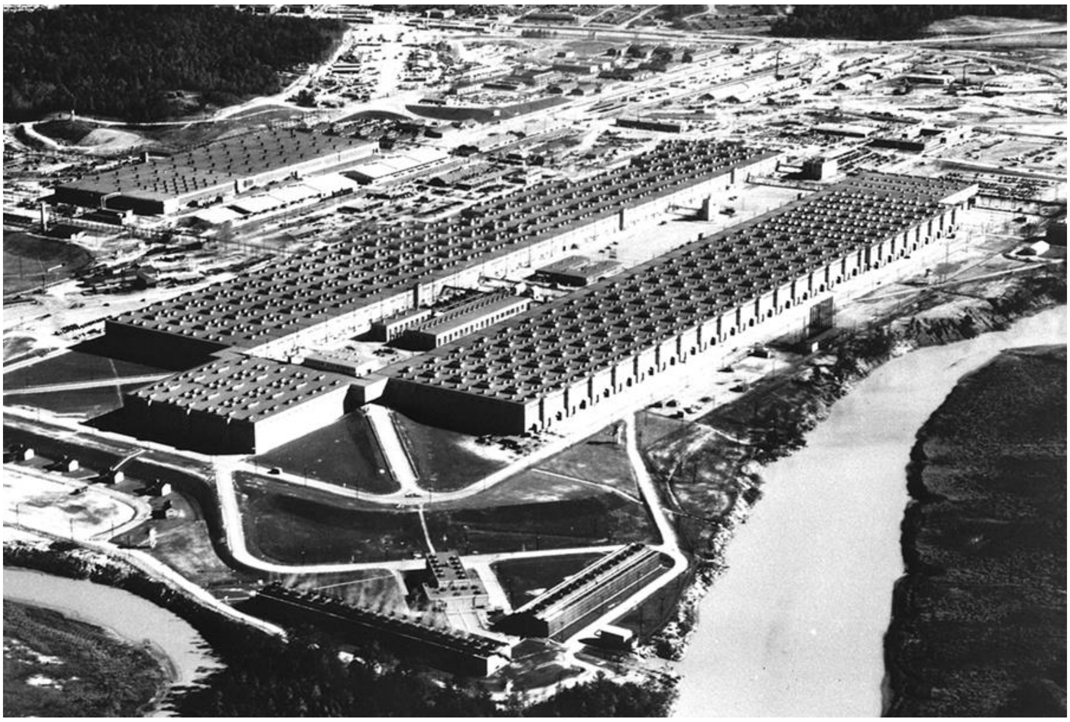
The mechanisms by which contamination is being deposited and trapped may be thought of as one of these primary mechanisms:

1) as solids deposited on the surface (as in the loose contamination case)
2) as trapped in a barrier layer in the near surface
3) as deeply deposited via transport (like capillary action or crevice corrosion) into the bulk of the substrate.

Loose solids, while a vitally important portion of the overall contamination problem, are generally not bound to the surface. Their interaction with the surface of the substrate is very limited. In some cases a positive/negative charge interaction exists between the contaminant and substrate, but this is usually a very weak (covalent) interaction. On the other hand, if contamination resides in the surface, barrier layer, or is transported into the bulk of the material, the mechanism is far more complicated, and the problem becomes more interesting.

One of the tenacious contamination problems commonly encountered in fuel fabrication and recycle complexes are the huge quantities of contaminated metal-processing equipment. In the U.S., the 190,000 m^2 K-25 facility (Figure 4) near Oak Ridge, Tennesee is emblematic of the huge decommissioning challenge posed by these massive facilities. Most of this contamination is due to the overwhelming amount of low-level contamination from the uranium (which has a relatively low radiotoxicity), but may also be from recycled (fission products from irradiated material) contaminants in the feed materials. In the enrichment facilities case the uranium was dissolved in hydrofluoric acid to produce UF_6, and these hydrofluoric acid vapors tend to etch (attack) the surface and allow contamination to lodge in the surface barrier layer of the metal (the metal oxide layer).

Figure 4. K-25 facility near Oak Ridge, Tennesee (Westcott 1945).



Nuclear reactors, on the other hand, present a different mechanism of contamination from enrichment facilities, but share some simularity with other types where contaminants are trapped in the oxide layers. The radioactive contamination in nuclear reactors does not typically come from the fuel or the fission products but, rather, from ^{60}Co corrosion products that are released from the cooling-loop walls (a contaminant in the steel alloys) and from the hard-faced valves. This corrosion product passes through the reactor core and is activated. It then redeposits elsewhere in the reactor cooling loop. There may also be a small amount of fission product from an accidental fuel-cladding breach. These corrosion and fission products become lodged in the surface of the cooling-loop metal because of the growth of high-temperature metal oxide. A common model for this type of oxide-growth/contaminant-trapping contamination fixation (Wood and Spalaris 1989) or “CRUD” layer model previously discussed. Decontamination of this type of contamination problem, which is ubiquitous within the nuclear industry, is most often a matter of controlled removal of that oxide layer. Little to none of the contamination actually moves into the bulk of the metal because it is non-porous.

The Idaho National Laboratory (INL), located in the Northwestern U.S., has been home to over 50 nuclear reactors and many other nuclear facilities; most of these nuclear facilities have also undergone decontamination and decommissioning (D&D). One particularly difficult challenge is decontaminating facilities that treat spent nuclear fuel. The U.S. has four primary locations where nuclear-fuel reprocessing took place: a commercial site at West Valley, New York, and several large scale government-owned facilities at Hanford, Washington; Savannah River, South Carolina; and Idaho itself (Figure 5).

Figure 5. Idaho National Laboratory nuclear fuel reprocessing facility.

These facilities are somewhat unusual in their operation, products, and overall decontamination needs. Most modern spent-fuel-reprocessing facilities make use of a variant of the plutonium/uranium extraction methodology (PUREX). These facilities "pickle," or dissolve, the spent fuel and recover the valuable nuclear material, while separating and disposing of the undesirable fission products as secondary waste. During this process, complicated processing equipment, including hundreds of feet of stainless steel pipes, valves, vessels and other equipment, becomes highly contaminated (Chen, et al. 1997). This happens in part because the contamination adheres to the surface of the equipment, and also leaks through valves. The contamination quantities can be substantial because the entire inventory of fission products and actinides are released during the process, and many tons of fuel may be processed each month; thus, the need for decontamination at these facilities may become very significant.

The work described in this thesis began as a search by its author for decontamination processes which minimize secondary waste and was conducted at the Idaho Nuclear Technology Engineering Center (INTEC) and its predecessor organization, the Idaho Chemical Processing Plant (ICPP). At the start of that search, the then employed decontamination practices produced liquid waste containing large amounts of salt. This is a difficult and costly waste to treat. The search progressed by evaluating a large variety of different chemical and non-chemical methods, a few of which were adopted for use in the processes. In order to test the effectiveness of new decontamination technologies, a new simulated contamination methodology, termed SIMCON, was developed by the author. SIMCON was designed to replicate the type of contamination that developed on stainless steel processing equipment.

This was followed by the development of methods to simulate urban contamination resulting from a RDD. This work was sponsored by DARPA and sought to develop and test cleanup measures that could be deployed against a RDD. While there are a few similarities in the type and mechanisms of contamination produced by many of the processes, the simulants and substrates contaminated in the RDD experiments are vastly different from those used in the SIMCON processes. Additional efforts, sponsored by EPA, have led to the development of a contamination method that simulates fallout from an improvised nuclear device (IND). This IND focused work is particularly innovative as it diverges from creating tenacious contamination to creating a reproducible loose contamination. Examining these different types of contamination (and subsequent decontamination processes), particularly in regards to each other, sheds light on contamination processes that occur throughout the nuclear industry, and even beyond into the urban environment.

Building surfaces display similar processes during contamination, but with less emphasis on surface, barrier layer and greater emphasis on transport. Studies show that the majority (66%) of construction and demolition debris are concrete (Heiser and Sullivan 2009). Common concrete provides a convenient case to study and comprises a majority of existing structural material throughout nuclear facilities. Contamination is transferred to concrete in similar mechanisms as those at play in the metal examples, but typically under less-aggressive conditions. A more typical case for urban contamination is the “fallout” (or rainout) of contamination that had been aerosolized, for example as in a dirty bomb. In some cases, of course, the contamination may be directly applied to concrete, via an accidental release of solution, for example.

The barrier layer of concrete is not composed of a standard oxide “CRUD” layer as described in the nuclear-reactor case. But analogues of the barrier layer exist on building substrate; a degradation layer (calcium hydroxide in the case of concrete) can usually be found, along with typical urban grime such as carbonation, dust, dirt and soot (Gates-Anderson et al. 2007). And while metal surfaces may be somewhat uniformly coated (in the case of processing equipment such as tanks or pipes), that is highly unlikely with urban surfaces that have complex geometries and great deviations in orientation to contamination fallout. However, the overwhelming contamination mechanism for concrete is transport (or imbibition) into deeper layers of the material. This is primarily because of the high porosity of concrete. These various phases of contamination transport are described in the Idaho-developed Urban Contamination Model presented earlier in this chapter.

Another interesting consideration in the case of urban contamination is the method by which the contamination was deposited. In the case discussed above, the contamination was more likely to have been airborne when it was transported to the surface of the concrete; this is certainly the likely case for an intentional (terrorist) contamination dirty bomb event. However, whether contamination is deposited during dry conditions or a wet (rain) event turns out to be one of the primary factors in the ability to successfully decontaminate concrete. Mobility of the contaminant is pivotal. Transport of the contaminant into the surface of urban materials, and the interaction of the contaminant with the physical properties of that material, requires mobility.

Other urban materials have similar considerations with respect to surface/boundary layers and porosity, but may also have additional interesting characteristics. Surface finish (i.e. roughness) can dramatically affect the ability of a contamination to be retained within tiny cracks and crevices. Surface chemistry and ion-exchange-capacity (usually expressed as cation-exchange capacity or CEC) can have an influence on the contaminate interaction with the surface. Certainly the porosity and permeability have a substantial effect on contamination retention. Heterogeneity of the surface may increase surface contaminant retention issues, as in granite where the colored veins are composed of amphiboles and micas that trap cesium within the inner layers of the mineral and “fix” it in place. These are the main mechanisms and characteristics of contamination, though other, smaller effects can still be at work.

The preceding discussion of different contamination mechanisms provides a basis to understand decontamination technologies and to delve more deeply into the cause and effect relationship that we see from these different mechanisms. The results of the experimental work described in this thesis are derived from using the data from effectiveness testing of decontamination technologies and interpreting those results to understand these mechanisms and to identify specific aspects that link contaminant and substrate. These results and the contamination simulation methods are the research and applications of research comparing the performance of various decontamination methods (at a single condition). Whilst they tend toward applied, rather than fundamental research some fundamental insights are provided.

Conclusions about the nature of contamination are often framed within the results of the decontamination processes. Thus the following chapter will discuss details about the variety of decontamination methods used in this thesis and those available throughout the world. This discussion is important, not only to frame the simulation work and results, but to highlight the variety of methods used in the testing.

2 A SURVEY OF DECONTAMINATION METHODS

(Originally published as "Hazardous and Radioactive Waste Treatment Technologies Handbook", June 27, 2001, CRC Press, Chang H Oh, Editor; Chapter 8, Decontamination, J. Tripp, R. Demmer, R. Meservey; revised and updated for presentation here)

Mechanical or "non-chemical" decontamination methods come in a wide variety of types and applications. They can be as simple as brushing a contaminant from the surface and vacuuming it up or as state-of-the-art as using a laser. Most of these methods have their basis in physical or mechanical processes. Abrasive blasting is a simple method that works by brushing or grinding a contaminant from the surface. Laser ablation is a high-technology method that may seem a little mystifying, but uses the simple physical process of thermal shock. These methods, together with performance and cost information, are listed in Table 3.

2.1 Mechanical Methods of Decontamination

The mechanical methods are often used because of liquid-waste concerns with the waste produced by chemical decontamination techniques. Non-chemical methods typically generate less or no secondary waste. Non-chemical waste is usually easier to dispose of than chemical waste. Many have recycling and reuse incorporated into their process for added savings. These systems are more compatible with contaminated materials that can be removed from the process (tools, valves, small equipment, etc.). For in-place equipment, advances are being made to use mechanical techniques inside piping or remotely with manipulators or robots. This section will describe a representative range of such techniques in detail, beginning with CO2 pellet blasting.

Table 1. Relative performance factors for mechanical cleaning techniques.

Technology Family	Performance* Loose Contamination	Performance* Fixed Contamination	Types of Substrate	Initial Cost*	Production Rate*	Decon Item in Place*	Availability*
CO_2 Pellet Blasting	H	M-L	Metal, wood, plastic concrete	H	L	Y	H
Water Blasting	H	M	All	M	H	Y	H
Scabbling	H	H	Primarily concrete, metal	L	H	Y	H
Spalling	H	H	Concrete	L	H	Y	H
Abrasive Grit	H	H	All	M	H	Y	H
Grinding	H	H	All	L	L	Y	H
Milling	H	H	All	M	L	N	H
Vibratory Finishing	H	H	Primarily Metal	L	L	N	H
Hand Scrubbing	H	M	All	L	M	Y	H
Strippable Coatings	M	L	All	L	L	Y	H
Vacuuming	H	L	All	L	H	Y	H
Ultrasonic Cleaning	H	H	Primarily metal	L	L	N	H
Turbulator	H	M	Metal, plastics	L	L	N	H

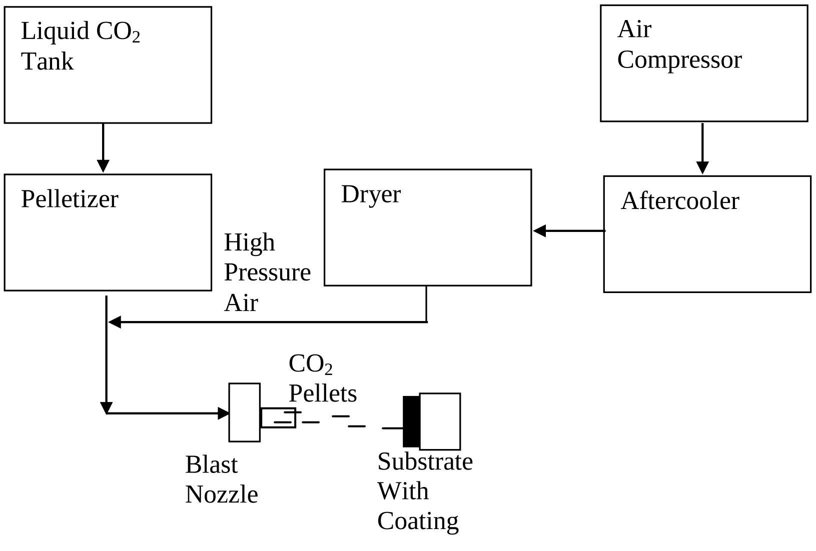
Technology Family	Performance* Loose Contamination	Performance* Fixed Contamination	Types of Substrate	Initial Cost*	Production Rate*	Decon Item in Place*	Availability*
Plasma Cleaning	H	M	Primarily metal	H	L	N	M
Light Ablation	H	M	Metal, concrete	H	L	N	M
Electrokinetic	H	M	Primarily concrete	M	L	Y	M

*All factors are subjective and may change based on application or specific equipment, but should be nearly those quoted here.
Performance factors are based on relative reported cleaning of these methods; High is typically over about 90%, Medium is about 70% and Low is less than %70.
Cost is based on initial cost of equipment, High is over about $100,000, Medium is over about $50,000 and Low is less than $50,000.
Production rate is based on a significantly higher or lower rate than 2.79 m^2 per hour.
Decon in place is based on whether an item can be decontaminated externally without removal.
Availability is based on whether a vendor is currently marketing this equipment or process.

2.1.1 CO_2 Pellet Blasting

A CO_2-pellet-blasting system normally consists of liquid CO_2 at 1379-2068 kPa, transported through a hose to a pelletizer machine, where rapid expansion of the liquid in the chamber converts the CO_2 to a solid state of dry ice or snow. The snow is then compressed into pellets, which are transported through a hose at 276 kPa to a blasting nozzle. At the nozzle, the pellets are entrained in high-pressure air (276-1724 kPa) and propelled from the nozzle onto the contaminated item at 23-305 m/s (Figure 6). The CO_2 pellet penetrates the work piece coating (mechanical abrasion),"mushrooms" under the coating as it strikes the substrate, then sublimes, causing the coating to fall off. This leaves only the coating as waste (a much smaller quantity of secondary waste) while the CO_2 pellet returns to its gaseous state. Pelletizer systems are expensive ($200k–300k), and pellet-blasting operations generally require two people, one to operate the nozzle and one to watch gauges and control the equipment.

Figure 6. CO_2 pellet-blasting system.



In a test at the INL, the best cleaning results on Type 304L stainless steel, construction tools and materials with Cs and Zr contamination required blasting pressures of 862-1034 kPa using a two to three mm pellet size (Figure 7) (Archibald 1993). This test concluded that lower pressures of 275-345 kPa should be used when cleaning soft materials like lead to avoid damage or driving the contaminants into the substrate. In general, CO_2-pellet blasting is effective at removing loose contamination/materials on a variety of surfaces, but is not abrasive enough to remove epoxy paints or tightly adhered contaminants.

Figure 7. Dry ice pellets (Boing 2015).

Ventilation and contamination control are the biggest concerns with all CO_2-blasting systems. Blasting in confined spaces and pits can lead to the heavier carbon dioxide displacing air, causing breathing problems for workers. Worker safety is a major consideration and use of a shrouded blasting nozzle with HEPA filtration addresses this concern. Another concern is line freeze-up, which can be solved with an in-line heater without decreasing blasting effectiveness. Moisture buildup (due to condensation from the air) on the item being cleaned may also be a concern. Use of these systems requires hearing protection due to the high noise level.

2.1.2 CO_2 Shaved Ice

Smaller-scale applications may employ a shaved-dry-ice blaster that uses blocks of readily available dry ice and shaves off ice particles that are subsequently blasted onto a surface. The shaved-ice blasting has been proven as effective as standard pellet blasting for some applications (Archibald 1997). This equipment is much less expensive ($40k) than the typical large pelletizing units such as depicted in Figure 5 (Demmer et al. 1995).

2.1.3 CO_2 Snowflake

CO_2 “snow” machines are used for very gentle cleaning of sensitive equipment, such as telescope optics. This blaster uses compressed carbon dioxide to produce a solid CO_2 snow under pressure for a gentle cleaning action. It has very limited usefulness in nuclear decontamination because of its gentleness and incomplete cleaning ability, but has been used in areas such as cleaning optical lenses. Hughes Aircraft Company developed this machine. The device is a handheld gun-like trigger mechanism that is easily manipulated and requires only a tank of pure carbon dioxide as a supply (Demmer et al. 1995).

2.1.4 Centrifugal CO_2

Centrifugal CO_2-pellet blasting is **s**imilar to the compressed-air/CO_2-pellet-blasting technology. It uses a high-speed rotating wheel to accelerate CO_2 pellets. With the higher speeds available, the centrifuge technology may enable removal of hard oxide layers from steel, thereby removing both zinc coatings from galvanized steel/sheet metal and nickel plating from brass screws. A study by the U.S. Air Force at Warner Robins Air Logistics Center demonstrated the removal of urethane and epoxy-paint surfaces from F-15 aircraft at a rate of 11.1 m^2/h for an 11.2 kW motorized accelerator (Bundy 1993). Some other sources indicate the cleaning potential is roughly equivalent to other CO_2-pellet-blasting techniques (Archibald 1997).

The unit may be remotely operated with the capability of cleaning 18.6-186 m^2/h, depending on the nature of the surface to be cleaned. Cost of the 22.4 kW machine capable of accelerating 907 kg/h of CO_2 at speeds up to 400 m/s is ~$200k (Meservey et al. 1994).

2.1.5 Supercritical CO_2

Supercritical CO_2 (above its critical temperature of 31°C and pressure of 7.38 MPa) is pressurized by an ultra-high-pressure intensifier pump to 3.8×10^4 kPa and forced through nozzles, generating high-velocity CO_2 jets at speeds up to 914 m/s. The nozzles may be mounted in various types of cleaning heads for contaminated surfaces. The CO_2 jets thoroughly penetrate and remove some surface contaminants. The removed contaminants, any of the substrate surface layer that may be removed, and the CO_2 are captured by a vacuum recovery system. A cyclone separator and a HEPA filter collect the solids and the CO_2 is discharged to the atmosphere or recycled (Meservey et al. 1994) and (Bundy 1993).

2.1.6 Cryogenic Cutting Tool

With the cryogenic cutting tool, a very-high-pressure jet of liquid nitrogen (up to 4.1×10^5 kPa) and CO_2 crystals are directed on a work piece as is the case with abrasive blasting. A proprietary ZAWCAD (zero added-waste cutting, abrading, drilling) cryogenic system was developed at the INL for cutting and cleaning various materials with zero added secondary waste (Demmer et al. 1995).

2.1.7 Water Blasting

There are many different methods that use water blasting for decontamination. In one, ultra-high-pressure water (up to 3.8×10^5 kPa) is forced through small-diameter nozzles to generate high-velocity water-jets. The water-jets penetrate and remove surface contaminants, although care must be taken not to damage the substrate. Abrasives may also be added for industrial cutting, milling, or improved decontamination. This operation generates contaminated water as a secondary waste that must be treated. In cleaning concrete, for example, a typical flow rate for one cleaning head would be 11-19 l/min at a surface-treatment rate of about 0.1 m^2/min. Such devices have now been incorporated into remote-controlled deployment devices to allow remote use in hazardous environments.

Superheated water (2068 kPa and 149°C) can also be blasted onto a surface to remove contamination. The lower operating pressures will only remove surface contamination that is soluble or loosely bound to the surface. The wastewater generation rate for a typical commercial unit ranges from 1.5-7.6 l/min.

The high-pressure water lance, or hydrolaser, consists of a high-pressure pump, 6895-68,950 kPa operator-controlled gun with directional nozzle, and associated high-pressure hose. A 13,790 kPa water lance provides a flow of about 30.3 l/min, and a 68,950 kPa unit, a flow of 83.3 l/min. Hydrolasers have been successfully used to decontaminate components, structures, walls and floors, and pipe and tank interiors. A variation of the water lance is the pipe mole, a high-pressure nozzle attached to a high-pressure flexible hose that is inserted in contaminated pipe runs. The nozzle orifices are angled to provide forward thrust of the nozzle and drag the hose through the pipe (Bundy 1993; NEA Group of Experts 1981).

Hot water at low pressure is also used to flush areas to dissolve readily soluble contaminants or to flush loosely deposited particles to a central area for collection. Flushing with hot water is often used following scrubbing, especially on floors. The effectiveness of flushing is enhanced by the use of squeegees to force the water and contaminants to collection or drain areas.

Steam cleaning combines the solvent action of water with the kinetic energy effect of blasting. At relatively high temperatures, the solvent action is increased, and the water-volume requirements are reduced compared to water blasting.

2.1.8 Scabblers/Scarifiers

Mechanical impact methods can be used to remove a contaminated surface. Many vendors market units that use high-speed reciprocating tungsten-carbide-tipped pistons to pulverize protective coatings and concrete substrate in a single-step process. Other types of units, such as diamond-head grinders, needle scalers, etc., use a shrouded head to remove concrete from edges, corners, and wall surfaces (Figure 8). These units are also used for removing relatively thin layers of lead-based coatings and contamination from steel surfaces. Scabblers have limited use on concrete block because the vibration often breaks the block. The solid debris produced by these mechanical scabbling techniques is normally removed and collected by a HEPA-filtered vacuum system. Mechanical scabblers are usually operated manually. The amount of waste generated depends upon the depth of the surface layer that needs to be removed to achieve decontamination. Often, several passes will be required to remove embedded contamination. For example, two different commercial units provide removal of concrete at rates of 49-74 cm^3/min (3.6-5.4 kg/h) and 983 cm^3/min (72.6 kg/h) at a removal depth of 1.6 mm per pass. A seven piston floor unit can remove 29.3 m^2 of concrete surface per hour (Bundy 1993; NEA Group of Experts 1981).

These mechanical decontamination devices can also be attached to remotely operated vehicles or equipment, such that they can be deployed remotely to avoid exposing workers to hazardous environments. In a study conducted at the INL, BROKK Co. demolition robot was tested for service in concrete breaking and scabbling. This used remotely operated, articulated hydraulic boom, allowing the operator to be placed up to 122 m away from the scabbling activities. Large units for floor scabbling are also available from various vendors.

Figure 8. Scabblers being used at the Plum Brook Research Reactor (Boing 2015).

2.1.9 Drilling and Spalling

Drilling and spalling is used to remove concrete surfaces to depths of 2.5-5 cm without removing the entire structure. Spalling is little used because of its inherent safety concerns and sluggish production rates. The process consists of drilling 2.5 cm-diameter holes on a 20 cm pitch to a depth of 5 cm into which a spalling bit is inserted. A tapered mandrel is hydraulically inserted in the expandable bit to spall the concrete. The surface removal rate is about 9.3 m^2/h.

The drill and spall method is good for concrete only (not “cinder” block) and is recommended for removing surface contamination that penetrates 2.5-5 cm into the surface. This technique is good for large-scale, obstruction-free applications (Meservey et al. 1994; NEA Group of Experts 1981).

There are two types of high-pressure-jet spalling devices. One is a compressed-gas-actuated piston that forces small quantities of high-velocity water through a nozzle at a rate of five shots per second. This unit is usually mounted on a heavy transporter, such as a backhoe. The other is a gun that fires glycerin capsules at close range onto a contaminated concrete surface. The glycerin gun can remove a concrete surface at a rate of about 0.93 m^2/h, as compared to the water cannon’s rate of about 0.37 m^2/h. The technique is useful in areas of difficult access. The glycerin gun coats the removed dust and particles with glycerin, which contains the contamination (Meservey et al. 1994).

2.1.10 Abrasive Blasting

This technique projects solid particles, suspended in a fluid medium, at a surface to achieve decontamination by surface abrasion. The medium is typically compressed air or high-pressure water. An option to this basic technique is to utilize a rotating chamber to impart kinetic energy to the particles by centrifugation. The particles can then be discharged onto the contaminated surface without need for supplemental use of a compressed fluid (Wood, Irving, and Allen 1986).

A key factor in achieving successful decontamination without causing deleterious effects on the substrate material is to select the abrasive material and the operating conditions for the application so that just enough surface abrasion occurs to effect the desired decontamination. The prime criteria to be evaluated are hardness of the surface to be decontaminated, the depth of the contamination and degree of degradation of the surface allowed. Any desired action, from general scouring to significant surface abrasion, can be accomplished. Grit blasting is an efficient cleaning method, with high decontamination capabilities.

Abrasive blasting is very versatile and has been heavily used in the nuclear industry in applications ranging from heavily contaminated pipe, with the contamination fixed in the oxide, to lightly contaminated surfaces. Commercial units are readily available. Typical abrasives include sand, glass, plastic, and metallic beads, sponges with imbedded grits, and soft materials such as nutshells, rice hulls and wheat starch (typically used in non-nuclear blasting applications). The En-Vac robotic blasting system is a complete unit to manipulate, vacuum, filter, and recycle (using cyclone separation) an abrasive-blasting process. This system can be used to blast and recover abrasive from many kinds of surfaces including vertical and curved areas. Ice shavings have also been used as an abrasive. Waste production rates, including grit plus filters, could range from 21-484 g/m^2, although some systems recycle some durable grits (alumina, steel shot) for reuse to minimize secondary-waste generation (Meservey et al. 1994; Demmer et al. 1995; Bundy 1993).

2.1.11 Shot Blasting

Shot blasting uses mechanically accelerated iron shot to clean the work surface. After the shot hits the surface to be cleaned, it is recovered by a magnetic system and recirculated. There is some concern that shot blasting may drive contaminants into the surface, making it harder to remove (via injecting (pushing) the contaminant into the pores of the substrate). Therefore, testing of the particular application is advised. Shot can be recycled many times during cleaning, but ultimately erodes and becomes part of the waste stream at the rate of approximately 45 g/m^2. Commercial units are available that have been used to prepare large areas of concrete floors (Figure 9) in one-step for painting, for cleaning rust and marine growth from ship hulls, and for cleaning structural steel elements (Meservey et al. 1994), Bundy 1993).

Figure 9. Centrifugal shot blasting system (OST ID 1851 1998).

2.1.12 Sponge Blasting

The sponge-blasting system decontaminates by blasting surfaces with various grades of patented urethane-foam (solid) media using 758 kPa air as the propellant. The foam may be used either dry or wetted for a variety of surface contaminants, such as oils, greases, lead compounds, chemicals, and radionuclides. Two basic grades of foam cleaning media are used:

> 1) Non-aggressive grade that is used for surface cleaning on sensitive or otherwise critical surfaces
>
> 2) Aggressive grades that are impregnated with abrasives that can remove tough materials such as paints, protective coatings, and rust.

Foam-blasting media are recyclable in a closed-cycle wash unit. The media typically can be recycled eight to ten times. On the first time through, the sponge-blasting unit uses 0.17-0.23 m^3 of media per hour at a surface-cleaning rate of about 0.1 m^2/min. Thus, the solid waste produced (foam media, recycled 10 times, with the absorbed contaminants) is approximately 0.01 m^3/m^2 of surface cleaned. The cleaning heads are similar to those of other blasting technologies and could be readily adapted to a robotic-control system (Meservey et al. DCON-58-IN 1994; Bundy 1993).

2.1.13 Hand Grinding, Honing, Scraping—Automated Grinding

Power-driven grinding equipment can be used to remove the contaminated surface. Operating cost varies with the shape of item being decontaminated and the location. The heat generated by grinding operations can cause organic compounds to vaporize and decompose, requiring special control (Allen 1985; Bundy 1993).

2.1.14 Metal Milling

A metal-milling machine is used to shave off the surface layer of metal in this technique. This method is most suitable only when there are a large number of similar items to be decontaminated because there is a 1/2–3/4-hour set-up time required between differently shaped items. After the equipment is set up and loaded, about 0.23 m^2/h can be milled. The waste generated is the metal surface removed (up to 3.2 mm) (Meservey et al. 1994; Bundy 1993).

2.1.15 Concrete Milling

This equipment comprises a large vehicle used by paving contractors, primarily suitable for large-area horizontal surfaces. The top 0.6-2.5 cm of surface is removed. Operating cost (in 1980 dollars), not including the cost of hauling away the debris, ranges from $1,300-4,100 k/square kilometer (Meservey et al. 1994; Bundy 1993).

2.1.16 Vibratory Finishing

Vibratory finishing employs a rapidly vibrating tub filled with abrasive media, often triangular ceramic or conical plastic impregnated with aluminum oxide, to mechanically scrub contamination. Many other surface materials such as paint, tape, corrosion products, and soil from almost any type item may also be removed by this method. The dislodged contamination and surface material is often removed with a flushing solution. No pretreatment is required except for surfaces coated with epoxy paints. The process will decontaminate a variety of materials, sizes, and shapes at the same time, and the secondary-waste volume produced is small.

Vibratory finishing is an excellent decontamination technique for tools and large quantities of small items, but larger components require extensive disassembly or sectioning. The maximum size of items that can be processed is about 20-30 cm diameter. Up to 136 kg of wrenches, hammers, screwdrivers, and other miscellaneous tools have been successfully decontaminated for reuse within an hour, with minimal operator attention (Wood, Irving and Allen 1986).

2.1.17 Hand Scrubbing

Hand-scrubbing and related manual decontamination operations are probably the most widely and frequently used of the non-chemical techniques. Contaminated surfaces are wiped or scrubbed, by hand or with a power brush or mop, using cleaning/scouring materials and chemical cleaning agents suited to the specific decontamination requirements. Smearable contamination on a smooth or impervious surface may be removed by simple wiping with a dry or damp cloth, whereas the use of an abrasive pad with an aggressive chemical cleaning agent may be required to adequately remove contamination associated with a corrosion layer or embedded in the surface. Organic solvents and detergents can be employed to remove contamination associated with oil, grease, and various types of surface soil. This is a labor-intensive, but versatile, technique. Major concerns and constraints are radiation exposure, possible generation of airborne contamination, and difficulty in removing contamination from crevices and constricted areas (Meservey et al. 1994; Allen 1985).

2.1.18 Strippable and Fixable Coatings

A strippable coating is applied to a contaminated surface by methods such as spraying, brushing, and rolling (as may be used for paint). During application, the coating migrates into surface microvoids to contact contaminants. While the material is wet, it attracts, absorbs, and may chemically bind the contaminants. During the drying or curing process, the contaminants are mechanically locked into a polymer matrix. After the coating dries, it is either manually stripped from the surface (Figure 10) or, in the case of self-stripping coatings, it falls off by itself and is collected by vacuuming. The surface contamination is removed with the coating, producing a dry, hard, non-airborne waste product. Water-based strippable coatings are intended for use in decontaminating smooth and semi-rough porous surfaces, including steel, concrete, aluminum, wood, and painted surfaces. The technology has been used for decontamination purposes in applications involving hazardous and radioactive contaminants. Typical coverage would be 0.74-2.9 m^2/L of polymer, and most coatings dry in 4–24 hours, depending on temperature and humidity (Tripp 1996). A strip coat developed by Los Alamos can sense when uranium or plutonium is present and change color (Archibald et al. 1999). Most commercial strippable coatings may be incinerated for volumetric reduction or ultimate disposal.

Figure 10. ALARA 1146 Strippable Coating Removal (OST/TMS ID 2314 2000).

Strippable coatings may also be applied over clean surfaces prior to contamination to provide a protective sacrificial layer of material or applied to contaminated surfaces to fix contaminants and inhibit airborne contamination such as asbestos (Bundy 1993; Wood, Irving, and Allen 1986; Tripp, 1996). They can be difficult and labor intensive to remove on some porous surfaces.

2.1.19 Vacuuming

Loose solid contaminants can be removed by using a vacuum cleaner. When a significant amount of solids are present, but not loose, they may be broken free by hand scraping or more automated means and then vacuumed by a HEPA-filtered vacuum system. Dust-laden areas are also good candidates for vacuuming to control contamination. Vacuuming is usually used in conjunction with various other contamination-removal techniques (Bundy 1993).

2.1.20 Ultrasonic Cleaning

Ultrasonic cleaning utilizes the scrubbing action of liquid excited by ultrasonic frequencies to remove surface deposits of oils and organic and loosely bound solids from metals, plastic, glass, and other solids. The ultrasonic generator and the contaminated item are located in close proximity within a tank geometrically sized for the application. Basic equipment, widely available commercially, consists of a liquid tank with appropriate plumbing, an ultrasonic generator, and vibrating bars (transducers), which are placed in the tank to provide energy to the liquid. Chemical solvents or liquids with abrasives added may be used as the fluid to increase decontamination effectiveness. The generator converts line frequency (50–60 Hz) to a high frequency of about 18–90 kHz. The transducer converts this impulse to low-amplitude mechanical energy in the fluid. The resulting wave cycles causes the liquid to cavitate and implode. This action serves to scrub the surface being decontaminated. Ultrasonic frequency affects cleaning efficiency by determining the cavity size. Low frequencies generate large, but relatively few cavities with high cleaning power. High frequencies generate a great number of small cavities with good penetrating capability. The most important parameters include ultrasonic frequency, power intensity, cleaning-solution viscosity, temperature, and fluid-recirculation rate. Achievement of optimum results requires a knowledgeable, skilled operator. It produces no abrasion, distortion, or changes in most things and is ideally suited for delicate or valuable parts and materials that are to be reused (Allen 1985).

Ultrasonic cleaning is used mostly for small metal parts that can fit into an ultrasonic bath and is particularly effective for crevices or threaded areas. It is not practical for large items that would require size-reduction. It is ineffective for tightly bound materials such as paints, varnishes, and other materials that are difficult to remove. The technique may generate secondary wastes, which are expensive to manage (such as solvent and detergent solutions requiring processing). The technique is intended for valuable parts which could be recycled "as-is" after cleaning. The technique is also good for removing deposits in difficult-to-access places, and it may be useful for electronic parts and electric motors. Using portable transducers, this technology has been used for cleaning the inside of waste-storage (Meservey et al. 1994; Bundy 1993**;** NEA Group of Experts 1981; Wood, Irving, and Allen, 1986; Allen 1985; and *Decommissioning Handbook* 1994).

2.1.21 Pulsed Acoustical Technique

This new technology, developed by Mississippi State University and the Tennessee Valley Authority, is a type of ultrasonic cleaning. Also known as TCS (tube-cleaning system), this technique uses repetitive high-voltage electrical discharges in fluids (principally water) to produce acoustic shock waves. The results are removal of scale, silt, and other deposits from ducts, tubes and pipes with less worker exposure and less secondary waste produced. The process is applied while the pipe is full of water, and insertion of the TCS tip is made in such a way as to preserve the water pressure during the cleaning. The high voltage spark causes water in the area of the electrode to vaporize, thus causing cavitation in the water, which cleans the pipes of surface contamination. The operator controls the amount of cavitation created in the pipe. There is some evidence that cleaning is accomplished more by a shockwave causing compressive and shear stresses than by the cavitation. In tests, the TCS has been used to clean 2.5 cm diameter pipes in a facility. Further testing and demonstrations are needed (Costley, Mazzola, and Grothaus 1997).

2.1.22 Turbulator

A turbulator (developed and marketed principally by Turco Products) is a large tank with propellers that direct the flow of a cleaning solution over and across a component. Square tanks have two propellers, while rectangular tanks have four propellers arranged at 90-degree angles around the tank. The turbulator is not quite as effective for porous substances as are ultrasonics. It is most effective on non-fixed contamination (i.e. loosely deposited, loosely adhering contamination). It has been used to clean such components as metallic hand tools, pump seals and pistons, valves, seal-injection filters and other filters, and control-drive mechanisms (Meservey et al. 1994).

2.1.23 Microwave Scabbling

This technology directs microwave energy at a concrete surface using a specialized waveguide applicator and heats the concrete and the free water present in the concrete matrix. Continued heating produces thermal and steam-pressure-induced mechanical stresses that cause the concrete surface to burst. The concrete particles from this steam explosion are small enough to be removed by a vacuum system, yet less than 1% of the debris is small enough to pose an airborne contamination hazard. The process is fast, dry, generates little dust, and avoids mechanical impacts. The microwave-applicator head may be manually moved about on the concrete surfaces to be decontaminated. Because the rate and depth of surface removal depend on the applicator translation speed, remote operation would be desirable. At microwave frequencies of 2.5 GHz and 10.6 GHz, continuous concrete removal rates of 1.1 cm^3/s at 5.2 kW and 2.1 cm^3/s at 3.6 kW were obtained. The Japanese reported that up to 2.5 cm of surface could be removed; however, no microwave frequencies or power were reported (White et al. 1992; Yasunaka et al. 1997; Meservey et al. 1994; Bundy 1993; *Decommissioning Handbook* 1994).

2.1.24 Plasma Torch

The plasma torch uses an inert gas, passing through a high-power direct current (DC) or radio frequency (RF) arc discharge, to produce a very-high-temperature gas stream that is capable of melting nearly all uncooled materials. Such torches are used in plasma synthesis and decomposition of materials. Potential uses in decontamination of materials include breaking down oils and polychlorinated biphenyls (PCBs) into less harmful or harmless substances, rapid spalling of concrete, and using the difference in coefficient of thermal expansion to delaminate contaminants from underlying substrates. The torch's inert gas creates no additional waste stream of its own compared to the smoke, CO_2 and NO_x product created by a combustion torch (Meservey et al. DCON-72-IN, 1994).

2.2 Chemical Decontamination

Chemical decontamination is probably the most universally used system for the decontamination of metal surfaces. Solvents can be used to dissolve the contamination film (non-destructive) or the base metal itself. Chemical decontamination can usually be performed with the least amount of process changes, personnel interaction, or direct operator exposure.

The advantages of chemical decontamination solutions include that they are used:

- For inaccessible surfaces
- In situ
- Without excessive labor
- Remotely
- With reduced airborne hazards
- With readily available materials
- With wastes remotely handled
- With recycling of solutions.

The disadvantages of chemical decontamination solutions include that it:

- Is not usually effective on porous surfaces
- Creates large volumes of secondary waste
- Creates possible mixed waste
- Possibly creates corrosion
- Can create safety hazards

- Requires safe chemical makeup and storage
- Engenders criticality concerns.

It should be noted that the generation of mixed wastes, i.e. a mixture of hazardous and radioactive materials, creates special problems for decontamination processes. Because of the difficulty of disposing of mixed wastes, there are generally severe restrictions on their generation. Since mixed-waste disposal sites are few and expensive, all mixed wastes generated must be either treated immediately or stored until such treatment technologies can be developed and made available. Thus, special care must be given when selecting chemical decontamination technologies such that a mixed-waste byproduct is not inadvertently created.

Table 4 shows the relative performance of most chemical decontamination methods. This table gives the relative cleaning efficiency, waste generated, applicability and general chemical type that characterizes each of the chemical decontamination processes. A general discussion is given in the text of each chemical type, with some examples provided.

2.2.1 Water Based Methods

Water can be an excellent decontamination agent for many jobs. It is readily available at all facilities and can be used to dissolve or simply flush away various contaminants. However, if a contaminant is deposited in an oxide layer, particularly in a high-temperature process like a reactor, then pure water will not perform well. Detergents and surfactants are often added to aid in contaminant removal. Water is often combined with another technique, such as scrubbing, or as a flush between chemical treatments.

The method of decontamination by steam provides a mixture of water, steam, and a decontaminating solution. The method is intended for decontamination of tanks and extraction equipment, pipelines, and movable (demountable) equipment. The preparation of the steam mixtures takes place in special devices, using saturated and superheated steam (Tikhonov, Pavlov, and Rodionov 1998).

2.2.2 Organic Solvents

Solvents are used in decontamination for removing organic materials, grease, wax, oil, paint, etc., from surfaces and for cleaning clothes (dry cleaning). Some typical organic solvents are kerosene, 1,1,1-trichloroethane, trichloroethylene, xylene, petroleum ethers, and alcohols. Advantages are that where organic solvents can be properly handled, less secondary waste is generated than in processes using water and detergents. The solvents are more effective than water on organic compounds. Disadvantages of organic solvents are that they are limited to use on specific materials (normally, plastics must be avoided), are hindered by the presence of water, often do not remove water-soluble stains, are generally flammable and toxic, and may contain chlorine; they are not used around stainless steel (Meservey et al. 1994; *Decommissioning Handbook* 1994). Because many organic solvents can generate “mixed waste”, care should be exercised when using chemical-decontamination solutions to avoid the generation of radioactive mixed wastes.

Table 2. Relative Performance Factors for Chemical Decontamination Technologies.

Process or System Name	**Description of Process**	**Type of Chemistry**	**Type of Materials**	**Chemicals Used**	**Relative Efficiency of Process***	**Relative Amount of Waste**	**Type of Waste**
AP	Alkaline permanganate	Oxidation	Stainless and carbon steels	$KMnO_4$, KOH, NaOH	Low	High	Salt solutions, resins
TURCO 4502	Proprietary AP	(same as above)	(same as above)	(same as above)	(same as above)	(same as above)	(same as above)
APAC	AP followed by ammonium citrate (AC)	Oxidation/ reduction	Stainless and carbon steels	$KMnO_4$, KOH, NaOH, ammonium citrate	Medium	High	Salt solutions, resins
APACE	APAC with EDTA	Oxidation/ Reduction/ Complexing	Stainless and carbon steels	$KMnO_4$, KOH, NaOH, ammonium citrate EDTA	Medium	High	Salt solutions, resins
APOX	AP followed by oxalic acid	Oxidation/ reduction	Stainless steel	$KMnO_4$, KOH, NaOH, oxalic acid	Medium	High	Salt solutions, resins

Process or System Name	**Description of Process**	**Type of Chemistry**	**Type of Materials**	**Chemicals Used**	**Relative Efficiency of Process***	**Relative Amount of Waste**	**Type of Waste**
AP-citrox	AP followed by citric and oxalic acids	Oxidation/ reduction	Stainless steel	$KMnO_4$, KOH, NaOH, citric acid, oxalic acid	Medium	High	Salt solutions, resins
Alkaline persulfate, citrox	AP with persulfate followed by citrox	Oxidation/ reduction	Stainless steel	$KMnO_4$, KOH, NaOH, potassium persulfate citric acid, oxalic acid	Medium	High	Salt solutions, resins
APSul	AP followed by sulfamic acid	Oxidation/ reduction	Stainless and carbon steels	$KMnO_4$, KOH, NaOH, sulfamic acid	High	High	Salt solutions, resins
MOPAC (APAC/APOX)	Proprietary system from Siemens, AP followed by citric acid, oxalic acid, EDTA with Fe(III) inhibition	Oxidation/ Reduction/ Complexing	Stainless and carbon steels	$KMnO_4$, KOH, NaOH, citric acid, oxalic acid, EDTA	High	Medium	Salt solutions, resins

Process or System Name	Description of Process	Type of Chemistry	Type of Materials	Chemicals Used	Relative Efficiency of Process*	Relative Amount of Waste	Type of Waste
NP	Nitric acid and potassium permanganate	Oxidation	Stainless steel	HNO_3, $KMnO_4$	Medium	Medium	Salt solutions, resins
LOMI	Proprietary system from EPRI, AP or NP followed by low oxidation metal ion (vanadous formate)	Oxidation/ reduction	Stainless steel, Inconel	AP or NP with Vanadous formate and picolinic acid	High	Medium	Salt solutions, resins
CANDECON	Proprietary system from AECL, may be used with AP and NP	Reduction/ complexing	Stainless steel	Citric and oxalic acids with EDTA	Medium	Low	Resins
NS-1	Proprietary system from Dow Chemical	Complexing	Stainless steel	Unknown, complexing agents and inhibitors	High	High	Salt solutions
CANDEREM	Proprietary system from AECL, may be used with AP and NP	Reduction/ complexing	Stainless steel	Citric acid and EDTA	Low	Low	Resins

Process or System Name	**Description of Process**	**Type of Chemistry**	**Type of Materials**	**Chemicals Used**	**Relative Efficiency of Process***	**Relative Amount of Waste**	**Type of Waste**
HP/CORD	Proprietary system from Siemens, Permanganic acid, reduction with organic acids	Oxidation/ reduction	Stainless steel	Permanganic acid, oxalic acid. hydrogen peroxide	High	Low	Resins
POD	Reduction chemistry, may be used with AP and NP	Reduction/ Complexing	Stainless steel		Medium	low	Salt solutions, resins
OZOX-A	Proprietary system of Kraftwork Union AG	Reduction	Stainless steel	Oxalic acid	Medium	Medium	Salt solutions, resins
OPP	One step oxidizing agent	Oxidation/ reduction	Stainless and carbon steels	Oxalic acid, hydrogen peroxide	Medium	Medium	Salt solutions, resins
Hydrochloric acid	One step, very corrosive system	Dissolution	Stainless and carbon steels	HCl	Medium	High	Salt solutions

Process or System Name	**Description of Process**	**Type of Chemistry**	**Type of Materials**	**Chemicals Used**	**Relative Efficiency of Process***	**Relative Amount of Waste**	**Type of Waste**
Nitric acid	One step	Dissolution /oxidation	Stainless steel	HNO_3	Low	Medium	Salt solutions
Sulfuric acid	One step	Dissolution / oxidation	Stainless and carbon steels	$KMnO_4$, KOH, NaOH, citric acid, oxalic acid, EDTA	High	Medium	Salt solutions, resins
Phosphoric acid	One step	Dissolution	Stainless and carbon steels	H_3PO_4	Medium	Medium	Acid solutions
Sulfamic acid	One step	Reduction	Carbon Steel and Copper	Sulfamic acid	Low	Medium	Acid solutions
Nitric and hydrofluoric acids	One step	Dissolution	Stainless Steel	HNO_3, HF	High	Low	Acid solutions (complexed)

Process or System Name	**Description of Process**	**Type of Chemistry**	**Type of Materials**	**Chemicals Used**	**Relative Efficiency of Process***	**Relative Amount of Waste**	**Type of Waste**
Nitric and sulfuric acids	One step, very corrosive	Dissolution, Oxidation	Stainless Steel	HNO_3, H_2SO_4	High	Medium	Acid solutions
Fluoroboric acid	Proprietary system from ALARON Co. One Step, very corrosive,	Dissolution	Stainless and carbon steels, nickel alloys	HBF_4	High	Medium	Acid solutions (complexed)
Oxalic acid	One step	Reduction/ complexing	Stainless steel	Oxalic acid	Medium	Medium	Acid solutions
Citric acid	One step	Reduction/ complexing	Stainless steel	Citric acid	Medium	Medium	Acid solutions
Ce(IV) process I	Proprietary system from PNNL (Battelle), one step, very corrosive,	Dissolution	Stainless steel	HNO_3, $Ce(NO_3)_4$	High	Medium	Acid solutions

Process or System Name	**Description of Process**	**Type of Chemistry**	**Type of Materials**	**Chemicals Used**	**Relative Efficiency of Process***	**Relative Amount of Waste**	**Type of Waste**
Ce(IV) process II	Proprietary system from PNNL (Battelle), one step, very corrosive	Dissolution	Stainless steel	H_2SO_4, $Ce(NO_3)_4$	High	Medium	Acid solutions
Ce(IV) process III	Proprietary system from PNNL (Battelle), one step, very corrosive	Dissolution	Stainless steel	HNO_3, $Ce(NO_3)_4$, KF	High	Medium	Acid solutions
Ag(II) process	Proprietary system from PNNL (Battelle)	Oxidation	Stainless steel	HNO_3, $K_2S_2O_8$, $AgNO_3$			Acid solutions

- This table adapted from "A Survey of Decontamination Processes Applicable to DOE Nuclear Facilities, ANL-97/19", Chen, 1997.All factors are subjective and may change based on application or specific equipment, typically those quoted here.
- Performance factors are based on relative reported cleaning of these methods; High is typically over about 90%, Medium is about 70% and Low is less than %70.
- Waste factors are based in relation to standard APOX type application; typically contain greater than 20% salt content.
- Cost for chemicals is not typically a significant concern except for processes that are vendor supplied or proprietary.

2.2.3 Oxidizers

The most common chemical decontamination method (next to water flushing) is the use of oxidizing agents. Oxidizers are chemical compounds that remove electrons from other molecules, usually causing them to increase in positive charge (possible exceptions would include anionic species like the radioactive pertechnetate (TcO_4^-)). Molecules in a higher oxidation state are often more soluble. Almost since the beginning of the nuclear industry, it was recognized that an oxidizing solution, usually an alkaline permanganate, was very effective at removing contaminants. In more recent times, the concept of a chromium-rich oxide (CRUD) layer, and the subsequent requirement to dissolve and disrupt this layer, began to gain acceptance in the decontamination profession (Pick 1982). This description seems to explain the alkaline permanganate (AP) systems, as well as other oxidizers. The action of permanganate occurs according to the reaction:

$$2MnO_4- + Cr_2O_3 +2H_2O = 2MnO_2 + 2HCrO_4- + 2H^+$$

$HCrO_4^-$ is more soluble than Cr_2O_3 with the reaction above therefore disrupting and dissolving the Cr_2O_3 surface film. Disrupting the surface film on the metal releases the trapped radionuclide particles and decontaminates the metal. This is often the first step of a two-step alkaline-permanganate/oxalic-acid (APOX) process. The second step uses oxalic acid ($C_2H_2O_4$), or another suitable reductant, to solubilize the strongly held iron oxide, disrupting it. The alkaline systems are often called APAC, for alkaline permanganate/ammonium citrate, or APOX for alkaline permanganate/oxalic acid (Torok 1982). Cycling the decontamination chemistry from oxidative to reductive solutions is more effective than either chemistry alone. A novel method used by Siemens Co. replaces potassium permanganate with permanganic acid, which generates less waste (Bertholdt 1994).

Nitric-acid/potassium-permanganate (NP) decontamination solutions have also been used with success. Percent removals for the NP system utilized at the Ringhals 2 (Sweden) nuclear-reactor system were 84 – 86%, while the AP removal was only 47 – 57% (Pick 1982). NP systems have also been successfully used to decontaminate nuclear fuel reprocessing equipment in the Eurochemic Reprocessing Plant, in France, and in the Tokai Reprocessing Facility in Japan (Van Geel et al. 1971). A newer method of decontamination based on chemical oxidation, using cerrium (IV) nitrate was developed by engineers at Battelle Pacific Northwest Laboratories (PNL), Richland, Washington (Bray 1988). This method uses a controlled milling of stainless steel surface using the strong oxidizing effect of the Ce (IV) ion, which is highly corrosive. A substantial amount of development work was conducted for West Valley Nuclear Services by PNL during the late 1980s for use of this method for decontaminating glass canisters. The corrosion potential of the unspent cerrium (IV) nitrate within the arising waste may be reduced with the addition of a small amount of hydrogen peroxide to produce a non-corrosive cerrium (III) nitrate.

2.2.4 Reductants

Reductants perform a different, complementary, function to that performed by oxidizers. Reduction occurs when a compound donates electrons to a molecule and lessens its positive charge. Some molecules are rendered more soluble as reduced ions. Most organic acids—oxalic, citric, tartaric and formic—are good reductants. They are usually good chelating agents and acids as well (Demmer 1996). Oxalic acid and citric acid are the most commonly used reductants, and have been combined for and CANDEREM processes for the decontamination of heavy and light water reactors (Wood and Spalaris 1989). In the decontamination of ferrous alloys, reduction, the key reduction typically proceeds according to the (oxalic acid) reaction with ubiquitous Fe_2O_3:

$$Fe_2O_3 + C_2H_2O_4 = 2FeO + 2CO_2 + H_2O$$

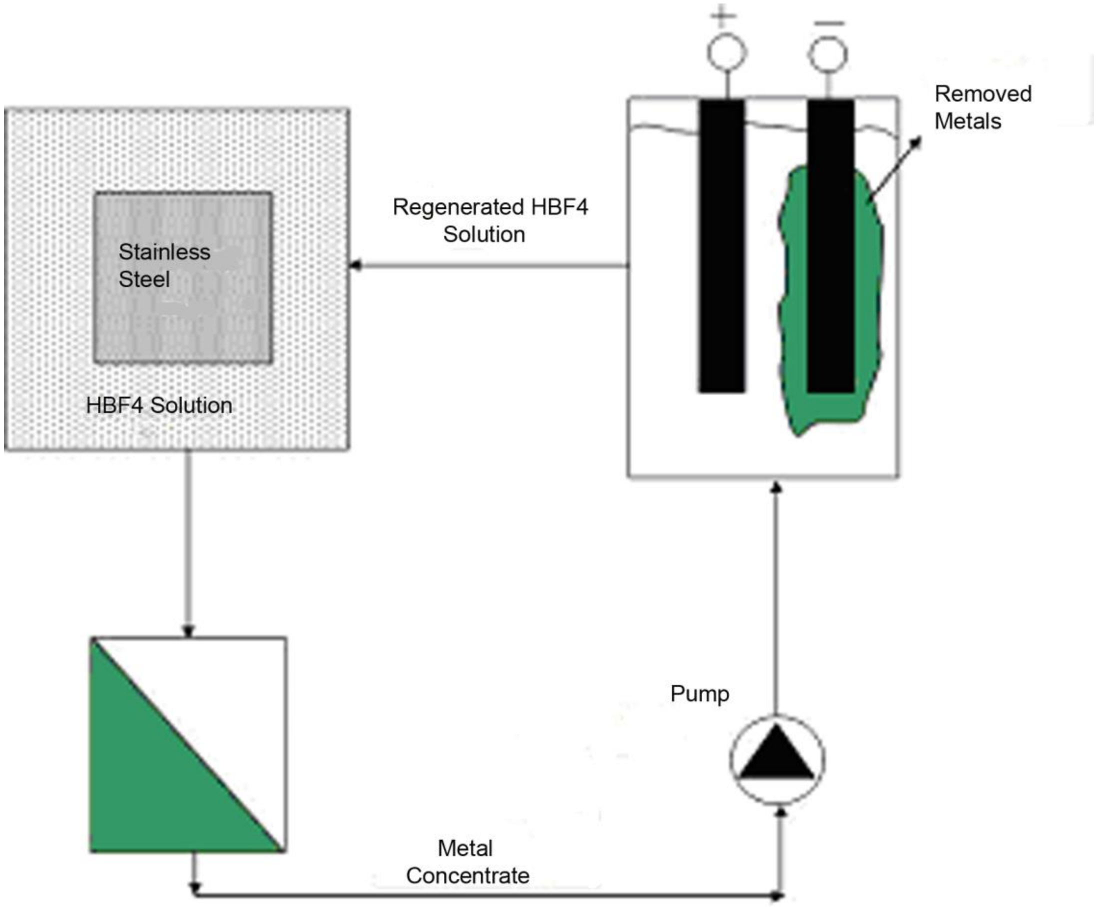
FeO is more soluble than Fe_2O_3, and thus the oxide layer is at least partially dissolved and disrupted. Because it proceeds as a reduction, the process is generally less corrosive, and creates less waste, than an oxidizing chemistry. Reductants are also often used during the treatment of spent oxidizers.

Another example of reduction chemistry based decontamination agents is the low-oxidation metal-ion (LOMI) process (Bradbury et al. 1983). This chemistry uses a vanadous formate, dissolved in picolinic acid to cause the reduction. This is a very powerful reactant, with the vanadous formate being rapidly oxidized by air. It requires isolation of systems, nitrogen blankets, licenses for use and is, in general, complicated and expensive to deploy. It is, however, a very appropriate process when all these ancillary requirements are fulfilled. It shows decontamination results with very-low final waste quantities. LOMI has been used with good results at the Yankee Rowe facility during the decontamination and decommissioning activities of the primary and secondary reactor coolant systems (Bradbury et al. 1983).

2.2.5 Acids

Dissolving materials in acid is an ageless process. The variety of reactions that take place when mineral acids—nitric, sulfuric, hydrochloric, hydrofluoric, phosphoric, etc.—are used in dissolution and decontamination are beyond the scope of this discussion. Some of these reactions are acid-base reactions, complexations and corrosion of the substrate. Virtually all of the mineral acids have been used in decontamination at some time. They produce relatively low secondary waste, but some, particularly hydrochloric acid (HCl), may cause serious corrosion concerns. Nitric acid (HNO_3) is one of the most commonly used acids for decontamination applications, partly because of its compatibility with stainless steels. Solutions of 3.5 M HNO_3 and 0.04 M hydrofluoric acid (HF) have long been used as cleaning/etching solutions on stainless steel (Rankin 1992). Combinations of several organic acids and mineral acids (citric and oxalic acids with nitric acid) have been documented previously (Zohner 1996). Organic acids add an extra dimension because they serve as acids, reductants, and usually chelants.

Figure 11. DECOHA acid recycle.



Fluoroboric acid (HBF_4) is an excellent decontamination reagent, with extremely high decontamination factors. A commercial vendor, ALARON Co., reports decontamination factors of 50 to 100 using the fluoroboric acid process (Rollar 1993). ALARON also uses the electrochemical regeneration/metal ion removal for recycling and regenerating fluoroboric acid that decreases the amount of fluoroboric acid that goes to waste. This DECOHA technology has been proven in laboratory tests and has been used at the damaged reactor at Chernobyl (Beaujean, Fiala-Goldiger and Hanulik 1991). While not a perfect “closed-loop” system, DECOHA offers capabilities that would provide significant recycling benefits (Figure 11). The Electric Power Research Institute (EPRI) has also developed a harsh fluoroboric-acid method, known as decontamination for decommissioning (DFD). This method is currently being used at Big Rock Point for decommissioning (Rollar et al. 1997).

Another effective decontamination method is the TechXtract process, provided by a private decontamination firm, EET, Co. of Bellaire, TX. The TechXtract chemistry is a patented process that combines some 25 different chemicals to incorporate dissolution, oxidation, reduction, hydrolysis, decomposition, wetting, complexation, microencapsulation, and flotation-chemistry principles (Bonem 1996). When complete, the process produces a non-hazardous matrix that does not contain additional, secondary waste characteristics (i.e. low pH), having only any waste characteristics of the original target material. The INEEL has used the TechXtract process to decontaminate both concrete slabs and miscellaneous tools containing fission products (Bonem 1994). EET also performed a successful demonstration on the removal of technetium and uranium with its TechXtract process from nickel-plated components at a gaseous-diffusion plant.

2.2.6 Chelants

Chelating agents (chelants) decontaminate materials by complexing the target contaminant, making it more soluble. Many of the organic acids, as well as some of the mineral acids, have this ability to complex contaminants. Citric and oxalic acids are two very good chelants. Typically, the best chelants are large organic molecules like ethylenediaminetetraacetic acid (EDTA). Usually these chelants will be used in a system—with acids, oxidizers or reductants—to improve overall decontamination performance.

Two commercially available chelant systems have shown good results in tests. CORPEX 921 is one such reagent available from the CORPEX Co. It is has a unique formula which is superior in decontamination to other common chelants previously used. Hanford, Oak Ridge, and Peducah Department of Energy sites have used it to decontaminate nuclear facility processing equipment with good results (Coleman 1997). Thermally unstable complexing solutions (TUCS) are also effective at removing contamination. Ionquest 201 is a strong complexing reagent marketed by the Albright and Wilson Chemical Company. This is a proprietary chemical that is an organic, phosphonic acid. It was developed to extract chemical species, notably uranium and some actinides, from nuclear process streams (Balint 1993). Used with a catalyst, it has been shown to remove contaminants from the surface of metal.

2.2.7 Alkaline Reagents

Alkaline reagents include potassium hydroxide, sodium hydroxide, sodium carbonate, trisodium phosphate, and ammonium carbonate and can be used to remove grease and oil films, neutralize acids, act as surface passivators, remove paint and other coatings, remove rust from mild steel, solubilize species that are soluble at high pH, and provide the right chemical environment for other agents. They are often used alternately with strong acids to clean materials. Alkaline solutions may be used on all nonporous surfaces except aluminum and magnesium, which react with strong bases. Only moderate quantities of waste are produced, and simple neutralization and precipitation has been the traditional method for post-decontamination treatment of the ensuing wastes (Meservey et al. 1994; Tripp et al. 1999).

2.3 Special Chemical Decontamination Processes

Unique and one-of-a-kind decontamination processes have been developed specifically for a few applications. Some of these are situational, that is special situations that are so unusual that they require their own solutions; others are locational, that special facilities or equipment may deserve such special attention. Still other special methods are unusual in that only specialized training and qualification permit their use. Examples of these methods are described below.

2.3.1 Explosive

Explosive decontamination can be used to remove the top 7.5-10 cm of concrete by detonating carefully placed and timed explosive charges. Capital costs are estimated to be under $50k, with operating costs of $0.5/m^2. Safety concerns need to be resolved; care must be taken to contain the dust and to prevent structural damage to both the structure (usually a building) being decontaminated and the surrounding structures. Improvements in the methods of applying explosives and in the uniformity of the detonation are needed. The explosive decontamination can generate toxic vapors (such as carbon monoxide and nitrogen oxides). The technology to control these vapors must be developed and demonstrated (Meservey et al. 1994; Bundy 1993).

2.3.2 Electropolishing

Electropolishing is an electro-chemical decontamination technique that removes a thin layer, approximately 0.5μm, from the surface of contaminated metals. The process establishes an electrical potential between the contaminated item (the anode) and a cathode in an acid electrolyte. Any contamination on the surface or in the pores of the surface is removed and released in the electrolyte by the surface-dissolution process. Electropolishing can achieve very high decontamination factors and could be considered for special applications in a decommissioning program, e.g. salvage of a valuable component the size of which is consistent with available electropolishing tank systems. Electropolishing has been done with various electrolytes, including phosphoric, nitric, sulfuric, and organic acid. The ability to remove contamination from deep cracks, crevices, holes and other areas that are shielded from the cathode is limited unless the geometry is favorable for the use of an internal cathode. The surfaces to be decontaminated must be conductive, and should be free of paint, grease, tape, heavy layers of corrosion products, and any other surface material that might inhibit the electropolishing action. Because of electrolysis of the electrolyte, hydrogen can be generated during the process, creating an explosion hazard which can be eliminated by proper forced ventilation of the area (Bundy 1993; Demmer 1998).

The electropolishing process can now also be applied to large metal surfaces through the use of close-proximity nozzles to spray the electrolyte over the contaminated surface. This and the use of electrolyte-charged sponges can be used to minimize the volume of electrolyte required by eliminating the need to flood or submerge the component; a similar sponge type electrolyte delivery system was used in the Electro-Strip system (Pao 2003).

2.3.3 Supercritical-fluid Extraction

Supercritical-fluid extraction (SFE) uses the properties of a solvent (typically carbon dioxide) under high pressure and temperature to remove contaminants. Under these conditions, the solvent is as efficient at extracting the contaminants as more hazardous solvents. Supercritical extraction by carbon dioxide (SC-CO_2) has enabled the extraction of 75-97% of air-dry uranyl, plutonium, and americium nitrates from stainless steel, rubber, and asbestos surfaces (Skobcov et al. 1997). It has found only limited adoption in radioactive decontamination because of the need for high pressures and temperatures. In comparison with washing of surfaces by acid and alkaline solutions of oxidizers and complexing agents, SFE reduced the amount of secondary waste without using hazardous chemicals and without the risk of flammable and/or corrosive chemicals.

2.3.4 Gels and Foams

Foams and gels are used as a method to enhance chemical decontamination by improving coating contact time and surface area covered per volume. Reagents can be mixed in a gel medium and used for decontamination. This approach significantly reduces the quantity of liquid waste normally generated in a cleaning bath or water jet. The gels that have been tested include organic, inorganic and inorganic modified by organic additives, including glycerophatic, glycerophosphoric, silica and diopside gels. Gels are compatible with most decontaminants. The gel coating can be applied by paintbrush or spray gun or by dipping. Depending on type, the gel is removable by mechanically stripping, dissolution in water, or drying to a powder and removing with a vacuum. The cleaning effectiveness of this method is equivalent to conventional liquid processes and is less costly both in chemical reagents and required labor. They are best for *in situ* removal of smearable contamination over large or oddly shaped objects (Bundy 1993; Meservey et al. 1994; Demmer 1998).

Chemical foams are used to increase solution contact time with contaminated items. Foam is used as a carrier of a chemical-decontamination agent and is applied in a thin layer (0.5-5 cm thick) to a surface in any orientation. The foam is produced by injection of air with a foaming agent into the decontamination solution in a pressurized applicator. The solution is sprayed on the surface, foams, and is subsequently rinsed off. Surfactants can be obtained which have various foam-breakdown times and which can decompose. Decomposition is necessary to prevent foaming problems in downstream waste-processing equipment such as evaporators. Testing has indicated that a liquid-chemical-waste reduction of 70% is possible. Acid solution requirements were reduced by a factor of 20–50. More recently, gels have been preferred for equipment exteriors, and foams are utilized by circulating in pipes and systems *in situ* (Meservey et al. 1994).

2.3.5 Gas-phase Decontamination

This long-term, low-temperature process of gas-phase *in situ* decontamination of equipment employs the fluorinating agents ClF_3 and F_2 in order to remove uranium contamination present on diffusion-cascade equipment. The gaseous diffusion process for uranium enrichment employs an isotopic-separation barrier arranged in diffusion cascades to increase concentration of ^{235}U so the enrichment is adequate for use in commercial nuclear-power reactors (Riddle 1998). The gas phase decontamination process resuspends the remaining (typically ^{238}U) uranium (converting it to a gas) and removes it from the process.

2.3.6 Biological Decontamination

Nature provides an environmental, microbiological resource that has numerous potentially useful bioprocessing applications. The sulfur- and nitrogen-oxidizing microbes are of potential interest for concrete-surface removal applications. The biodecon process is based on the use of naturally occurring microbes. A concrete-degradation phenomenon occurs in nature and is illustrated in degraded concrete pipelines, bridges, and other structures where microbial activity is stimulated by optimum moisture and nutrient conditions. Concrete sewer pipes have been the most frequently attacked structures. A reduced form of sulfur is the usual environmental nutrient. The basis of the effect stems from microbial production of sulfuric acid which, in turn, dissolves the cement matrix of the concrete. Several types of bacteria are known to promote degradation of concrete. Sulfur-oxidizing bacterial strains of *Thiobacillus (T.) thiooxidans* have been selected for the biodecontamination process. *T. thiooxidans* are the most aggressive concrete degraders. Concrete surface materials are loosened as a result of their metabolic processes. These naturally occurring, nonpathogenic, ubiquitous bacteria oxidize reduced forms of sulfur (H_2S, S, $S_2O_3^{2-}$, $S_4O_6^{2-}$) to sulfuric acid. They stick to the surface by producing, at the microscopic scale, a biofilm or adhesive. This acid, at several microsites, loosens the surface. The bioprocess produces no effluents because the microbes produce the acid at numerous microsite locations on the concrete surface. This microbially produced acid is neutralized during the concrete-surface-loosening process. The dissolution of cement at these microsites results in a loosened concrete surface that can be collected for special disposal. The depth of concrete-surface removal has been observed to be between 2–8 mm/year. The *T. thiooxidans* bacteria show no ionizing-radiation effects in the tests conducted thus far and are not expected to show any effects in most biodecontamination cases being contemplated (Johnson et al. 1996).

Microbially induced degradation (MID) has shown to be effective on floors, and small concrete chambers. Walls and ceilings pose other problems. Tests indicate that the process involves the removal of calcium from the concrete. In tests conducted at the INEEL in 1997, surfaces treated with fixed contamination showed significant decontamination. The surface activity before application was 600–900 cpm; after 5 months of treatment, when the surface was scraped to remove the organisms, the surface readings found to be were just slightly above background (Rodgers et al. 1997).

2.4 Emerging Technologies

New methods are constantly emerging that may impact the future of decontamination. Some of these, those listed below for example, have shown promising results and are likely to soon become available as commercial methods.

2.4.1 Laser Ablation

When a focused laser beam irradiates a metal surface, the surface will absorb a fraction of the incoming photons and, when the laser irradiance is sufficiently great, material will be ejected from the surface by a combination of processes that include vaporization and ablation. Decontamination is achieved by removing contaminated surface layers and then capturing the ejected material before redeposition can occur.

Decontaminating a large surface area with a laser in a reasonable amount of time requires that either the laser beam be sufficiently intense to achieve useful irradiance values over a large area or that the laser operate at a very-high repetition rate. In either case, the laser beam needs to be rastered quickly across the surface to achieve large area decontamination.

Some laser coating-removal systems are designed to strip relatively soft coatings from a substrate without damage to the substrate. A prototype paint-removal system was built by BDM International Company and tested by the U.S. Air Force. The system removes a 0.05 mm thick coating of paint at a rate of about 0.23 m^2/min. Other systems are designed to remove contaminants that are embedded within the metal surface itself. Laser-light ablation for removal of metal surfaces uses a high-power, pulsed laser beam. The system generates irradiance levels sufficient to remove microns of metal from a surface and an off-gas system prevents the material redeposition. Monitoring the laser-generated plasma produced during laser surface ablation may assist process control.

Many laser-based technologies developed for decontamination rely on carbon-dioxide lasers that may be difficult to transport to remote locations and have instrumental characteristics more compatible with the removal of surface coatings, such as paints, than removal of the metal substrate itself. Only short-pulse lasers can ablate materials without causing surface melting, which could trap contaminants within the bulk. Of course, lasers capable of removing metal substrate can also remove coatings such as paints and oils (*Decommissioning Handbook* 1994; Tripp 1996; Bundy 1993; Archibald et al. 1999).

Lawrence Livermore National Laboratory (LLNL) has reported on a portable laser that is able to clean a five-foot swath on 183 m of wall in about 1 hour. This laser cleans by photoacoustic stress waves, using a 100-watt neodymium-doped yttrium aluminum garnet (Nd:YAG) beam, pulsing up to 1,000 times/second (1000 Hz). When the beam hits the painted surface, part of the beam energy is converted into sound waves. The sound hits the underlying hard surface and rebounds. When the echo interacts with incoming sound waves created by the laser, the result is a miniature explosion that pulverizes and removes the paint as a fine dust. Each laser, with its accompanying safety equipment and pointing devices would cost about $250,000.

A collaboration between Ames Laboratory and the Idaho National Laboratory resulted in the development of an acousto-optic, q-switched, fiber-optically delivered Nd:YAG laser cleaning system that can remove both surface contamination and metal substrate. This patented technology has been licensed to ZawTech International, Inc., for commercialization (Ames 1998).

International Technical Associates (INTA) have used lasers for paint and concrete surface removal (up to 6 mm). They use a Nd:Yag or a pulsed CO_2-gas laser. Their products include a system specifically designed for the removal of graffiti, paint, organic corrosion, and contamination products from a wide range of surfaces such as asphalt and concrete. For this particular application INTA uses a spectral analysis camera in a computerized feedback loop to control the amount of coating removed. They have another product to remove paint from aircraft without harm; even when the skin is made of graphite-epoxy composite (Lovoi 1994).

2.4.2 Flashlamps and Photochemical Destruction

Radiological decontamination using high-energy xenon flashlamps is an emerging light-ablation technology. Flashlamps are used to clean organic contamination from valuable objects such as artwork, ship hulls, and precious metals. Several flashlamp-based systems are in use in locations around the world. The primary application for flashlamp cleaning is surface areas that need a high degree of decontamination with the absolute minimum of waste generation. These systems tend to be rather slow and may not be considered large-scale production techniques. The technology produces only the material that is removed from the surface as waste. All the vaporized material is collected in a filtration system (Bundy 1993).

A related technique of photochemical degradation matches the ultraviolet (UV) light frequency to specific hydrogen donors. When the UV light is pulsed, the hydrogen donor and the contaminant react, a photolysis reaction causes the organic compound to break down and become mineralized. Effective for many organics, this technology shows great promise in hard-to-reach places but is virtually useless when contaminant is in dense particulate matter like soil. The UV light must reach the contamination to be successful. Photochemical degradation is potentially applicable to all surfaces, although best results can be expected on smooth surfaces.

In ultraviolet/ozone treatment, UV light is absorbed by oxygen molecules to form ozone, which dissociates to form atomic oxygen. The contaminant molecules are also excited and/or dissociated by the absorption of UV. The excited contaminant molecules and the free radicals react with atomic oxygen to produce simpler, volatile molecules, such as CO_2, H_2O, and N_2O. Used widely in the semiconductor industry, this technique has not yet been proven in the nuclear industry, but may work well for metal cleaning (Meservey et al. 1994].

2.4.3 Cold-plasma Surface Cleaning

Plasma surface-cleaning methods by a glow-discharge are commonly and effectively used for cleaning high-bonding-energy contaminants from surfaces of metals, metal oxides, and glasses. Plasma cleaning is done in vacuum chambers for accelerators and magnetic fusion devices. Plasma processes of etching and deposition are also used in material processing and microelectronic manufacturing in industry. Extrapolating these plasma-cleaning techniques for decomposing and destroying oil and PCB contaminants in metal process equipment is feasible. Based on known plasma-assisted etching rates, decontamination rates by reactive plasmas are expected to be higher than that by gas-phase decontamination methods. Moreover, the plasma cleaning process provides a means of separating and recovering uranium from mixed-uranium contaminants, recycling process equipment, reducing the volume of generated secondary wastes, and helping to minimize the final waste-deposition cost. Though additional radio frequency or microwave power is required, the plasma cleaning techniques will be cheaper by approximately a factor of ten and faster than the gas cleaning techniques. Together with a scrubber, the supporting equipment used for the gas-phase decontamination system, including thermal-management system, vacuum system, computer control and monitors can be used for the waste generated in plasma cleaning methods (Bundy 1993).

A device developed at Los Alamos National Laboratory (Svitil 1997) allows plasma to survive at room temperature outside a vacuum. Named the plasma car wash this device runs on 300 watts, weighs less than 36.3 kg, and, in assembled design, resembles a domestic leaf blower. It essentially consists of a tank of pressurized gas (the type of gas used depends on the application) that is pumped into a 15.2 cm-long tube housing two concentric cylindrical electrodes. As the gas shoots between the electrodes, the electric field pulls off its electrons, creating the charged ions of the plasma. The plasma then boosts the energy of other gas molecules in the tube, which shoot from the nozzle and react with other molecules they encounter—such as paint in graffiti—by either pulling them apart or stealing their electrons. Most plasmas operate at extremely high temperatures, but the plasma car wash may be able to operate at temperatures below 204°C.

Plasma etching can be done using a fluorine-plasma discharge. Volatile fluorides are produced, along with chemically reactive fluorine atoms that promote rapid etching. The contaminated metal surfaces are exposed to energetic ions, electrons, and photons, greatly enhancing the decontamination rate. The plasma etching and fluorination technology can be developed for *in situ* decontamination (Bundy 1993).

Water-based reactive plasma uses a water vortex to generate reactive plasma to destroy hazardous and inert organic-fluid wastes. A plasma jet, discharging through the high-velocity-water vortex, will heat feed materials in excess of 2500K. Water is dissociated into $O+$, O_x, $+ OH$, H, and H_2 reactive species which attack and destroy organics. A base can be added to the vortex to remove halogens (O’Brien et al. 1993).

2.4.4 Electrokinetic

The electrokinetic technique uses an electrical field to cause contaminants to move through concrete pores into the surrounding solution. At the Idaho National Laboratory, concrete-decontamination testing was performed by Dry-Tec of North America. Copper-coated steel rods were used as the cathodes and titanium bars as the anodes. These were positioned across a concrete slab. When the electrical circuit was connected, a controlled, cyclical voltage was applied to the system to cause osmotic migration of water in the concrete from the anode to the cathode. As the moisture was either pushed or pulled out of the concrete, contamination was also pushed or pulled through the concrete. This method is probably limited more to small areas than large production applications. The test results indicated some migration of contaminants, with further testing needed to refine the technique (Tripp 1996).

Oak Ridge National Laboratories (ORNL) developed a portable electromigration decontamination technology, which can be used on a localized concrete area. It uses an electrolytic solvent and electricity to cause the contamination ions in the concrete to migrate to the surface. Electromigration is a slow process, but inexpensive. If either the solvent or contaminant is very conductive then, because electrokinetic techniques work best in high fields, the process is slowed down (Bundy 1993).

2.5 Bulk Decontamination

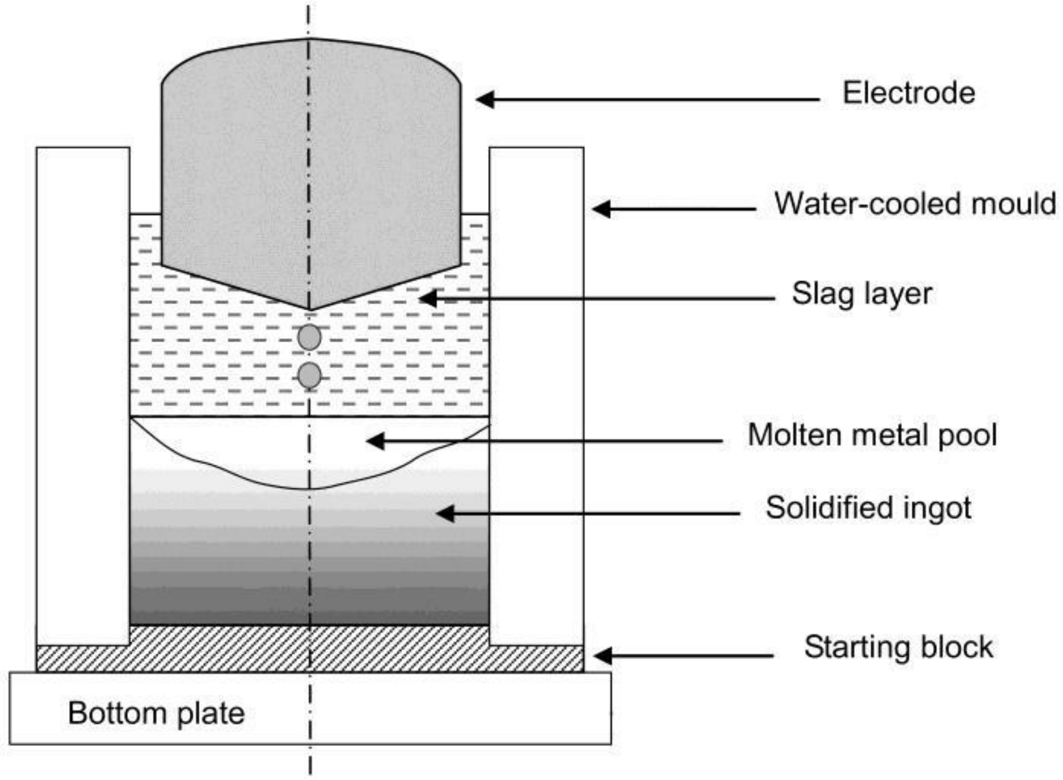
Contamination resulting from neutron activation of elements or impurities present in the materials themselves is called bulk contamination. One of the primary sources of bulk contamination is material containing activation products (cobalt, iron, nickel, zinc) from reactor facilities. Surface decontamination technologies will not be effective on bulk contaminated materials. Thus, methods must be developed that allow for access to the contamination in the interior of the material. Two such methods are thermal refining and catalytic extraction.

2.5.1 Thermal/Melt Refining

Thermal processes are used throughout the metals industry for processing ores and metal reprocessing. A number of different furnace technologies have been used but induction and resistance furnace technologies are the most applicable to processing of radioactively contaminated metals due mainly to the increased ability for maintaining contamination control and proper atmospheric-processing environments.

Key parameters in melt refining include type of metal, types and concentrations of radioactive contaminants, the partitioning of the radionuclides between the slag and ingot, the compatibility of slags and refractory materials, melting techniques and flux chemistries. The flux, typically an oxide or alkali material, allows a higher solubility of the contaminant than the metal. The slag (and flux) is less dense than the metal and physically separate from the molten metal by a difference in density. Melt refining does not remove radionuclides (such as cobalt, iron, nickel and carbon) that are part of the initial metal-alloying elements. Most uranium and transuranic isotopes and their daughter products partition into the slag/flux and can be removed, with the exception of technetium and strontium. To increase separation efficiencies, various types of fluxes and slag compositions can be used (Heshmatpour and Copeland 1981). One such metal refining technique is the Electro-Slag refining process shown in Figure 12.

Figure 12. Electro-Slag Metal Melt Refining Diagram (Basu and Kumar 2014)



The Center for Nuclear Studies at Saclay, France, reported that they achieved a separation of cobalt from the other elemental constituents of a mild steel, type C 1023. Melting-process operations were carried out with liquid/liquid, liquid/solid, and solid/solid systems. The best results were obtained in the solid/solid phase at 1000°C in an oxidizing atmosphere using a slag containing barium, which resulted in approximately 84% of the contained cobalt being separated. The purpose of this program was twofold: to reduce the volume of waste for burial and to permit recycled use of the metal in either controlled or uncontrolled applications (NEA Group of Experts 1981).

2.5.2 Catalytic Extraction Process (CEP)

The catalytic extraction process uses an induction or electric-arc furnace to form a molten-metal bath. The high temperature bath (operating at about 2000K) causes metal to be liquefied and dissociated into its constituents. The addition of certain catalytic reactants (such as alkali salts or silica) causes the partitioning of contaminants into different phases of the molten bath (often a vitreous phase or a off-gas phase). The catalytic extraction process uses the molten bath, not only as a means for metal purification, but also as a high-temperature, high-energy-density medium for more effectively reducing hazardous-waste materials, such as PCBs, hydrocarbons, and cyanide, to nonhazardous material. The molten metal provides much more effective contact with the material in a smaller volume than is possible with hot gases in a conventional incinerator.

CEP was developed by a commercial vendor to use standard off-the-shelf steel-industry equipment. It is unique in using a molten-metal bath to more effectively disassociate hazardous materials with potential recovery of valuable of usable constituents. If oxygen is needed by the waste being processed, it is added as pure oxygen rather than air. Off-gases are 1/5–1/50 of the volume created in an incinerator for the same amount of material processed. Capital costs are estimated at one-half that of an incinerator, and operational costs are estimated at 1/3 those of an incinerator. It is estimated that ~22.7 kg of slag would be generated for every 1000 kg of scrap metal processed by smelt purification. However, unless a suitable fluxing agent can be demonstrated to remove radionuclides, the process may find little use in decontamination work. If the problem of removing radionuclides is corrected, then the recovery of nickel alone could possibly pay for the process (Meservey, et al. 1994).

These previous sections have reviewed traditional (and in some cases advanced, state-of-the-art techniques) decontamination methodologies for removing contaminants from metal and nuclear facility structures. A less developed subset of decontamination methods are the vitally important ones suitable for cleaning up the urban environment after a contamination event. Those will be examined in the next section.

2.6 Special Methods for Urban Decontamination

Remediation and decontamination of urban, city environments may require special techniques not typically used with contaminated nuclear equipment and facilities. An urban environment may become contaminated with radiological material by intentional (terrorist) or unintentional (accidental) events. One major difference between urban and nuclear facility environments is that urban areas, while having significant concrete infrastructure, also have a lot of “green” areas; residential lawns, trees and shrubbery as well as parks, school yards and other public vegetated areas. Decontamination of vegetation and other urban materials requires special techniques not previously introduced in this section on decontamination methods. Another urban decontamination consideration is that, unlike most nuclear facilities, cities do not have the capability to manage large quantities of radioactive waste. This is a particularly sensitive issue when considering the use of large volumes of wash water that will itself become contaminated during cleanup. In many nuclear facilities, water is a convenient decontamination method because radioactive water management has been engineered into the facility system. However, municipal sewage treatment systems are not designed with the necessary radioactive waste management processes.

This often leads cleanup project managers to the conclusion that modern, efficient decontamination technologies are not appropriate to urban task because they are not designed for urban application. As a generalization, this remains somewhat true; wholesale demolition of buildings and removal of vegetation are certainly the "tried and true" approach that continues to solve the problem for most applications. However, there are also some new approaches that lend themselves to effective decontamination while minimizing the resultant waste presented by demolition or by wholesale washing.

2.6.1 Demolition and Removal

In many cases, the best way to minimize the hazard left within an environment is to obliterate the existing structures and remove any vegetation. This approach is virtually 100% effective as a solution to the public perception of leaving residual radioactivity within that urban environment. However, this method has its own particular difficulties:

1) It obliterates the individual's sense of neighborhood, recovery of property and well-being

2) It is inefficient, removing large quantities of "potentially" radioactive debris (most of which is uncontaminated) to resolve a purely surface problem

3) It is not protective of public infrastructure, and may be forbidden for many buildings of cultural or societal significance.

Thus, the principle difficulty is to balance the value of demolition against decontamination, remediation and recovery.

Large scale demolition typically involves the use of the large scale earth moving and construction equipment. Specialized destruction equipment, such as the shear equipped excavator shown in Figure 13, has been successfully employed even on very contaminated facilities. If airborne contamination is suspected, then dust abatement and fixative methods (such as latex paint coatings or strippable coatings) are employed. Wholesale removal of vegetation and soil is usually undertaken with large graders and scrapers. These can remove up to several meters of soil, as opposed to localized efforts with only centimeter depth removal.

Figure 13. Nuclear facility demolition at the DOE Hanford Site (Nuclear Street 2012).

If large scale demolition and earth removal are deployed, highly expensive and wasteful disposal issues may be created. It is estimated that thousands of huge trucks, with millions of highway miles (likely that available disposal space is at least one thousand miles from event site (western U.S. disposal, eastern event)), would be required to remediate even a small portion of a major city given such methods. However, there are technological options available that can be applied to reduce this landfill load. Options such as automated segregation and soil washing will be discussed later. Disposal could be accomplished at a localized site outside of the main city cleanup project area minimizing the anticipated cost and risk of million-mile transportation tasks.

2.6.2 Plowing and Triple-digging

Plowing fields up to 50 cm deep in contaminated soil is an effective method of reducing the dose. This method differs from removing the soil because it does not move the contaminated soil to a different location for disposition. In this option the contaminants are moved to a lower section of the soil profile, thus shielding it from the surface, and the contaminant concentration is reduced from being mixed with cleaner soil (IAEA 1999). While this method reduces radiation significantly, any deeply plowed soils may be less fertile, produce poor crops and cause radioactive uptake in the plants.

Figure 14. Plowing and triple digging (EPA /600/R-13/124 2013).

Triple-digging soil is a technique that involves removing the very top layer of soil (about 5-10 cm), removing the next portion (5-10 cm), then burying the first portion of top soil and replacing the top soil with the second portion (Witt 1990). This method was used in small garden areas after the Chernobyl Disaster. This accomplishes the same basic task as plowing, but mostly from shielding not dilution. While much slower than plowing, the likelihood is that the resulting soil is more fertile because the depth is not as great (Witt 1990).

2.6.3 Limited Vegetation Removal

Partial vegetation removal may be effective decontamination when certain, more efficient methodologies are applied. In some cases, certain species of plants absorb radioactive contamination more strongly than other species; removal of the selected species can effect a major dose reduction. It was found that lichen in the Fukushima area concentrate radioactive contamination. Pressure washing trees removes the moss and lichens, reducing the radiation dose (Cardarelli 2012). In many cases, debris around forests, needle piles and leaves, were found to be the highest contamination areas and that simply removing this debris was a key to radiation reduction (Ito 2012).

In the urban landscape, it is always expected that a large quantity of grass from lawns will be contaminated. Simply mowing the lawn isn't adequate because a high portion of the contaminant will simply be shaken loose from the grass clippings prior to their being recovered. Adding a powerful vacuum system with high efficiency particulate absorption (HEPA) filtration (to protect the operator from high dose of airborne particulate) improves the effectiveness of this technique. Customizing the system to reduce the "mulch", (reducing both the amount of grass left behind and any previously existing debris) will greatly increase the overall efficiency of the decontamination.

Figure 15. Sod cutter used in residential setting (Evergreen 2015).

Radioactive materials are sometimes deposited beneath the surface layer of the grass and mulch. To remove the material that is held below this layer, a sod cutter (Figure 15) can be used to loosen and separate the top (5-15 cm) layer of grass, root mat and soil (Evergreen 2015). The thickness of the cut and removal can be set based on surveys of the soil and thus minimize the volume of waste collected. Removing 5 cm of soil and grass (sod) has been found to reduce the radioactive contamination level by 94% (James and Menzel 1973); which is a very high reduction when compared to most urban decontamination technologies.

A final method of localized vegetation/decontamination is simply the directed removal of leaves and foliage from trees, shrubs and other plants (Figure 16) (EPA/600/R-13/124 2013). The majority of the surface area of these plants is the foliage. Since removing the foliage and yet preserving the function of the original plant requires some skill, this techniques would require huge amounts of hand labor.

Figure 16. Hand labor removal of vegetation (EPA/600/R-13/124 2013).

2.6.4 Street Sweeping

Cleaning the pavement of a city to return transportation and other infrastructure is a vital part of remediating after a radiological event. The streets are vital to recovery because they become the arteries that workers use traveling into the contaminated zones; they are also the conduit by which contamination can be tracked back out of those zones. Using a common street sweeper, or one customized to reduce aerosolization of contaminants (and even to allow reuse of water) can be a practical and effective method of reducing contamination levels on streets (Brown, Haywood and Roed 1991). Attention must be paid to reducing dust and limiting disturbance of dry radioactive particles unnecessarily. A well designed system should have vacuuming and washing simultaneously. Such a system should include some provisions (like a filtered, pressurized cabin) for reducing the potential hazard to the operator.

2.6.5 High-pressure Washing

A very practical and inexpensive method to urban decontamination is high-pressure washing. A longer discourse on high-pressure water washing is given in section 2.1.7. Nonetheless, it would be an omission to not at least summarize it here, mainly because it is so well used throughout so many radiological events; it has become perhaps the 2nd most popular method of urban dose reduction (behind hand wiping) However, in recent tests, the effectiveness of high-pressure washing (with vacuum assist removal) was only a modest 36% removal (Demmer 2012). Using this technique on soluble contamination can cause the contamination to spread and become even more "fixed" than it was before washing. However, if the contaminant is insoluble and loose, this technique has been shown to be highly effective.

2.6.6 Soil Washing

One of the problems with removing soil by way of large scale demolition methods is that substantial quantities of soil pile up quickly. One method of reducing this mounting waste stream is to decontaminate the contaminated soil itself. Some soil washing methods use mechanical and chemical methods to remove contaminants from the soil particles. One process uses gravity separation methods to separate silt and clay particles from coarser sand and gravel; with the contaminants typically adhering to the clay and silt (Van Deuren 2002). With another process, chemical technologies (such as cation substitution or chemical dissolution) are used to dissolve, bind and remove the contaminant. Soil washing has been shown to reduce the volume of contaminated soil by 90%. An unfortunate consequence is that the remaining soil may be sterile and require further treatment prior to reuse as topsoil.

2.6.7 Segmented Gate System

A segmented gate system (SGS) consists of a series of conveyer belts that pass soil beneath a set of radiation detectors. If radiation is detected, the computerized system positions a gate to direct the contaminated soil (which has moved upstream of the detector) into a section where it can be secured for further management. The SGS can also be used for extruded (rubbilized) well divided asphalt or concrete. This type of system has been shown to have an average soil waste reduction of up to 97% (Patteson 2000).

2.6.8 Wash-Aid

A new technology that enhances the ability of water to remove contaminants has been developed by researchers at the Argonne National Laboratory. This system is composed of salt brine that serves as a "counter-ion" for cesium and other cationic contaminants. This brine is designed to be deployed by firefighters (or other first responders) over structures and equipment to reduce radiation doses (by simple flushing) during the first stages of the recovery (Kaminski, Mertz and Kivendas 2014). While ordinary water flushing may simply spread the contamination and cause it to be mobilized and imbibed by concrete, the brine solution protects from imbibition with the high concentration of counter ion. A clay based treatment system sequesters and removes the contaminant from the brine solution and return it for reuse (EPA/600/R-13/232 2013). This process has shown some significant results, achieving up to 90% cesium reduction from concrete and asphalt (EPA/600/R-13/159 2013).

2.6.9 Wiping, Brushing and Vacuuming

As discussed earlier in section 2.1 (Mechanical Methods) wiping, brushing and vacuuming have been successfully employed in contaminated environments for spot cleaning for decades. These tried and true methods continue to be valuable and well established during any contamination event. The most recent evidence using these hand labor methods has been provided in the environs near the Fukushima Nuclear Reactors; very good results have been achieved in the reduction of cesium contamination (Kihara 2012).

2.7 Urban RDD Cleanup Examples

A historical look at large scale decontamination efforts provides valuable insight into general specific examples of decontamination applications. There have been several accidents that have contaminated urban environments with radiological materials. Unfortunately, prior to Chernobyl, recovery was seldom the subject of intense scientific data gathering and some of the obvious lessons were not published nor even widely shared. Such is the case for any decontamination efforts that might have occurred in Hiroshima and Nagasaki; no literature was discovered detailing decontamination efforts in those cities. Other large-scale contamination events, like those involving incidents at nuclear waste repositories, military sites or processing plants during the Cold War were not extensively documented, primarily due to secrecy and security issues. However, three more recent events, the Chernobyl Reactor Explosion (Ukraine, 1986) and the Goiania Sealed Source Breakage (Brazil, 1987) and the Fukushima Reactors Explosions (Japan, 2011), give significant opportunity to study large-scale urban decontamination methods. Brief descriptions of these events will be given and the highlights of decontamination will be summarized.

2.7.1 Chernobyl, Ukraine 1986

On April 26, 1986, the Chernobyl Reactor #4 exploded and caught fire in the early morning at a location in Eastern Europe just north of Kiev, Ukraine. A large amount of radioactive material (about 10 X 10^{18} Bq) was distributed into the atmosphere both during the initial explosion and over the next few days because of the fire. The contamination was wide spread, including areas ranging hundreds of miles to the east, north and west of the reactor site. Hundreds lost their lives containing the fire and during cleanup immediately following the disaster. Hundreds of thousands were evacuated from their homes and many were never able to re-occupy those areas. The scale of the disaster is unprecedented and there is no way to truly comprehend the misery of people affected by this event (Nesterenko 2009).

Decontamination efforts began soon after the event. One obvious, but not always considered factor, is characterizing the amount and location of the contamination in terms of radiation dose for residents. Because of the airborne nature of the contaminant, and the changing atmospheric conditions the contamination encountered as it swept across Europe, this was not always consistent. The location of contamination radiation dose was generally found to be in this order: soil (high), trees (moderate), roofs (moderate), walls (lower) and roads (lower) (Andersson 1996). Because of this information, efforts were focused on removing soil and vegetation contamination along with cleaning roofs. While these decontamination efforts were examples of the usefulness of available technologies, the actual volume of contaminated material that was successfully decontaminated is small (relative to the total). This is a clear example of how a planning effort dealing with what will and will not be cleaned up after a RDD would aid in recovery.

Several different kinds of decontamination techniques were chosen to decrease the radiation dose from Chernobyl contamination. These included flushing (hosing) contaminants from building and paving materials, digging up and removing heavily contaminated soil, plowing contaminated soil, chemically treating building materials and using absorbents to extract contaminants. One report by Hewitt, et. al. found that the flushing of roads was moderately successful for cleaning roads (45%-50% removal) and that dry-sweeping with a rotary brush was less effective (27%-30%) (Hewitt 1993). Using water flushing has a disadvantage of creating secondary liquid waste that must be managed. Another report (Brown 1996) showed that soil removal, while varying with depth removed, was up to 90% effective at removing overall dose rate; plowing (simply turning the soil over) was not as effective. Other reports indicate that the use of acids and ammonium nitrate was more effective than simply flushing with water, removing up to 90% of the cesium contamination (Witt 1990, Thornton 1988). These results were compared in different situations, such as dry deposition and contamination during rainy conditions, showing that environmental factors (i.e. rain) create a complex need for different decontamination methodologies (Brown, Haywood and Roed 1991). The use of clay absorbents was also found to be somewhat effective, with removal up to 80% (Movchan 1996). The efficacy of many of the different techniques employed were collated and compared and are collected as shown in Table 3 below (Brown, Haywood and Roed 1991).

2.7.2 Goiania, Brazil 1987

The Goiania contamination was much smaller and more localized than the Chernobyl contamination, requiring a limited response more closely approximating that of a RDD. In late September of 1987, an old ^{137}Cs medical source (5.1 X 10^{13} Bq) was removed from an abandoned hospital site and its packaging broken open. It was subsequently handled by many people with a total of 249 people being contaminated. Of these, four died and 28 suffered radiation burns, many requiring skin grafts (Bandiera De Carvala 1994). An urban area of about 1 km^2 was contaminated by the opening and handling of the source, the handlers spreading the contamination along

Table 3. Comparison of decontamination effectiveness for common urban decontamination techniques.

Technique	**Effectiveness (% removed)**	**Age of contamination**
Low Impact		
Grass Cutting	32 (wet deposition)	recent
Firehosing of buildings	0 (walls), 30 (roofs)	recent
Firehosing of buildings	0 (walls), 25 (roofs)	old
Firehosing of roads	0	old
Sweeping roads	20	recent
Ammonium nitrate treatment of buildings	15 (walls), 20 (roofs)	recent and old
Medium Impact		
Sandblasting buildings	40	
Firehosing of roads	45 (wet deposition)	
Grass cutting	65 (dry deposition)	
Vacuum-sweeping roads	50	
High Impact		
Washing vacuuming indoor surfaces	80	
Soil removal to 10 cm	80	
Road planning	100	
Firehosing of roads	95 (dry deposition)	
Sandblasting buildings	100	
Roof replacement	100	
Plowing soil to 30 cm	Altered activity profile	up to 1 year
	0 - 1 cm = 0.5%	
	1 - 5 cm = 2%	
	5 - 15 cm = 25%	
	15 - 30 cm = 72.5%	

with the movements of their families (Pires Do Rio and Amaral 1994). Subsequent surveys of the neighborhoods near the end of October, 1987, found 45 homes and 45 points on public roads contaminated. Eight of the homes were demolished (not decontaminated) and removed as radioactive waste (Ferreria 1994).

Both the Brazilian government and the International Atomic Energy Agency (IAEA) conducted a detailed investigation of the event. An IAEA report summarized the decontamination measures performed on those buildings not destroyed and removed (IAEA 1988). Major decontamination work began in mid November of 1987. Residences furthest from the highest contamination areas were the first to be decontaminated. The belongings in the houses were placed outside on plastic, surveyed for contamination, and cleaned if practical. Items with complicated or absorbent surfaces with no inherent value were disposed of. Vacuum cleaners with high-efficiency particulate filters were used to clean all interior surfaces. Painted surfaces were stripped and floors were cleaned with an acid/Prussian Blue mixture; which preferentially chelates and removes cesium contamination. Roofs were washed with pressurized water jets, but with only about 20% reduction in radiation dose. Trees were pruned and fruit was destroyed (along with many pets and livestock). New soil replaced contaminated topsoil.

2.7.3 Fukushima, Japan 2011

On March 11, 2011 the eastern coast of Japan was struck by a magnitude 9 earthquake and tsunami, severely damaging the cooling capability of the Fukushima Daiichi boiling water nuclear reactors. During the next few days the status of the three operational reactors (1, 2 and 3) went from bad to worse as the cores overheated, melted down, emitted hydrogen and the containment buildings were racked with explosions. An estimated 1 X 10^{17} Bq of radioactivity was released to the Central Japanese Coastal Area (UNSCEAR 2013). Some 7000 m^2 was contaminated by the Fukushima effluent and nearly 100,000 people were evacuated (NNSA 2011).

Since the reactor explosions there has been significant work on deploying decontamination methods. For the most part, this effort has been organized to apply existing, commercially available methods. As discussed in section 2.3, there are a number of very basic decontamination technologies that have wide application to urban decontamination. Nearly all of those traditional methods have been applied to the Fukushima Cleanup. The principle methods being utilized are (MOE 2013):

- Wipe down and vacuuming of "hard" surfaces (for decontamination of roofs and pavement)
- High pressure water blasting (pavement, drain pipes)
- Top soil, sod and foliage removal

The primary application of novel decontamination methods have been focused on reducing the quantity of liquid waste generated. To this end, methods like the DeconGel (1101) strippable coating (see section 2.1.18) have clearly shown benefits (MOE 2013). Additional effective efforts have been made in recovering and recycling the large amount of contaminated water that is being generated both during cleanup and in closure of the damaged reactors. Another advance is the use of robotic and automated equipment. Fukushima (primarily the highly contaminated reactor site) is pushing the forefront of remotely operated equipment. The Fukushima Operating Contractor, Tokyo Electric Power Company (TEPCO) has set up development programs to provide the best tools to cleanup after the disaster.

This chapter has considered a wide range of decontamination methods and, in Chapter 1, a series of methodologies for evaluating these different methods. New methods are also being developed and tested each year; often spurred by the kinds of events discussed briefly in the case studies provided above. No true international standards for decontamination effectiveness exist at this time. Most decontamination criteria apply health physics guidelines to protect the individual from excessive radiation exposure. The development of appropriate protocols for decontamination testing will be an important part of moving this process forward accurately. The development of the methods described in this thesis, both SIMCON, Urban RDD and others, are examples of reliable testing decontamination protocols. These will be the subject of the next chapter.

3 Understanding Methods of Contamination Simulation

(Originally delivered at the Waste Management Symposia, WM'12, February 26-March 1, 2012, Phoenix, AZ, USA – revised and updated for presentation here)

3.1 Background

3.1.1 The Need to Simulate Contamination

Testing decontamination effectiveness for mechanical and chemical decontamination methods has been documented for over 70 years. In most cases, this is typically an "applications based", empirical approach where an item, process system or facility is tested with different decontamination regimes to determine which method works the best. In the decontamination community, this is colloquially referred to as a "Beauty Contest" method of determining a result; for a particular process, under a certain set of conditions, an acceptable result is usually found. This approach is appropriate for a given test to derive an answer based on the criteria driving the test. Where the beauty contest approach begins to fail is when correlation to other, even similar, contamination/decontamination problems is made. The continuity from one particular case to another is very difficult to apply, and there is a lack of overall "big picture" view.

Figure 17. ORNL DeconGel test of painted floor (Kirk 2009).

A case in point is the recently published effectiveness results of DeconGel, a product of the CBI Company of Honolulu, Hawaii. This particular product, DeconGel 1101, known in the industry as “Blue Goo”, has been shown to be tremendously effective at removing some kinds of radioactive contamination. However, when reviewed carefully, the majority of data leads to misunderstanding the real value of this method. Tests on "Blue Goo" at Oak Ridge National Laboratory (ORNL) in 2009 showed between 37% to 90% removal of multiple radionuclides for a 6.1 m × 9.1 m painted concrete floor (Figure 17) (Kirk 2009). Lawrence Livermore National Laboratory (LLNL) also reported between 37% and >99% removal of plutonium from different, non-porous surfaces of the same glovebox (Sutton and Campbell 2011 and Sutton et al. 2008).

A Sandia National Laboratory (SNL) study, performed shortly after the release of the product in 2007, found that the removal of contamination from non-porous materials (Plexiglas, steel) achieved a high 99.6% removal, reduced to 15.6% for removal on concrete (Holt 2007). A Colorado State University (CSU) study of three strippable coatings (ALARA 1146, DeconGel 1101 and Bartlette TLC), demonstrated the high performance of DeconGel at 97% from vinyl tile for ^{99m}Tc, ^{201}Tl and ^{131}I and 99% for stainless steel (Draine 2009). While these are superb laboratory efforts, in terms of the internal quality of the data, they may not provide a good basis for recommending this technique for any other decontamination problems. They are fairly limited to those conditions and criteria placed upon the test at the point in time it was generated and fail to provide a "level playing field".

The level-playing-field approach is a concept pioneered by researchers at the Idaho National Laboratory (INL) (Demmer 2014). This approach is provided by multiple tests, using different techniques that can be repeated many times. This produces a depth of data that can be viewed in context and allows the sorting of decontamination techniques with reference to overall efficiency. In context of this concept, the DeconGel tests described above fail to provide the elements of decontamination testing referred to as the three "Rs": operational relevancy, reproducibility, and range. The applied, empirical tests (at ORNL and LLNL), by their very nature, are limited because the contamination quantity/availability, age, and mechanism of contamination (the character and conditions of the mechanism by which the contamination was applied many years before) are not available to other researchers. They were one time only tests and cannot be reproduced. While they present valuable information, it is not possible to realistically replicate nor compare those results in a meaningful way. The CSU laboratory data compare three strippable coating methods, which gives some perspective for comparison within that limited data set. But the other tests (ORNL, LLNL and SNL) have no “relative” method comparison. Even the comparison against other coatings does not truly provide relevance with respect to other methods; their data does not place them in a field relative to other methods. Lastly, in most cases, the decontamination values place most of these tests at the extremely high end of the efficacy scale. This clustering of values at the high end of the decontamination scale also gives no process by which more effective methods to be judged. These test methodologies would be unable to discern methods that are more effective at removing contamination (like sand blasting) than strippable coatings. Placing a strippable coating method at 97% (or greater) only begs the question of whether this was really a tenacious contamination in the first place. For example, when CBI released their new product, DeconGel 1108, it was found by Drake et al. to be a superior product that is almost twice as effective at removing contamination (Drake et al. 2011). The tests described above would be unable to determine that increase as they are at near maximum removal at the current level. These kinds of tests cannot provide an adequate dynamic range or a level playing field for multiple methods. This chapter describes a range of contamination simulation methods developed by the author, either singly or in collaboration with colleagues at INL. Use of these simulation methods in evaluating a range of decontamination is given in Chapter 4.

3.1.2 Simulation Methods Proven Over Many Years

There are many different methods to simulate contamination so that screening of decontamination methodologies can be assessed. In choosing or designing a simulation method, thought must be given to the mechanisms by which the target contaminant is held; e.g. as loose solids, trapped in a metal oxide layer, or deposited in a porous material like concrete. It is important that thought be given to the criteria for the decontamination, including operational relevance, reliability and the appropriate range of simulation methods. In choosing from existing, or more recently in designing new, contamination simulation methods, the author found that many different non-intuitively obvious factors that can affect the ability of the contamination to be removed; for instance, the duration that the contamination remains on the surface reduces the effectiveness of the overall decontamination A wide variety of contamination simulant methods have been developed by researchers to reproducibly test radiological decontamination methods, some having a notable pedigree and thus may be more meaningful for comparison.

While it is important to recognize the value of many different decontamination testing methods (including applied tests on real contaminated systems) having reliable, well-developed methods of simulating contamination can provide a better overall comparison. Having the ability to compare decontamination methods on preferably non-radioactive surrogates, outside of actual contaminated facilities, gives us the ability to screen those methods for value prior to doing an actual application again, preferably under conditions of low radiological risk. To this end, a few common methods of applying radionuclides (or non-radioactive surrogates) have been developed for simulant fabrication and then applied to a large number of decontamination methods over the last several decades. Several national laboratories or other government institutions have adopted similar, common practices. The most common means of applying a surrogate to substrate is via pipetting. Known quantities of radioactive salts (or non-radioactive surrogates) are pipetted onto the surface of different coupons (representative samples) of chosen substrate. This technique, often referred to as "stippling", is a well-established method sometimes used to prepare radioisotope standards for assay counting. Another common means of applying a liquid surrogate to surfaces is a spray application, either with a simple atomizing pump or a more sophisticated air atomizing system (MTOP 2013).

But by far the most common method of applying contamination is using a pipette to deposit small drops (approximately 0.05 ml each) of a known concentration of contaminate solution uniformly over the surface of a substrate. This stippling method has been practiced for many years by a large number of researchers and practitioners. Defense Research Development, Canada, the radiological decontamination research arm of the Canadian military, has performed decontamination simulation testing at their Ottawa, Quebec facilities using a pipetting methodology (MTOP 2013), as have laboratories in the United Kingdom that do radiological testing (MTOP 2013). Similar simulants were used in some of the example DeconGel tests given above (Holt 2007, Draine 2009). This type of commonly used and long established stippling methodology became the basis for SIMCON 1 and 2 coupons developed by this author.

3.2 SIMCON Nuclear Process and Facility Contamination Simulant

3.2.1 SIMCON Background

SIMCON contamination methods were developed at the INL by this author to simulate the contamination found on stainless steel; they were termed SIMCON 1 and SIMCON 2 (Demmer 1994a). SIMCON 1 was designed to model loose contamination on stainless steel. Discussions with engineers and operators that process solutions at the Idaho Chemical Processing Plant (ICPP) on the INL site indicated that the primary contamination problems that they encountered were loose, dried solids (like salts) produced by leakage from equipment, and tenacious, fixed contaminants, acid-etched into the surface of the processing equipment. Those discussions revealed that in some instances, contamination may dry on the inside top of a pipe, but flushing usually only reaches the bottom and sides of the pipe. Therefore, the pipe appears to have fixed contamination while it may be more or less removable if accessible.

A review of the literature uncovered a number of methods that replicated dried contaminants on steel surfaces. A simulated radioactive dried matrix was tested by Westinghouse Savannah River Laboratories during their evaluation of CO_2-pellet blasting (Cobb, et al. 1991). Sample coupons of stainless steel were dip-coated with a cesium, cerium, and zirconium-nitrate salt solution (each salt at 2 M concentration in the mixture) then dried and subsequently cleaned with CO_2-pellet blasting. Samples were also coated with a cesium/cerium/zirconium/grease matrix to determine the effectiveness of the method against this type of matrix. DuPont Savannah River Laboratories used a different dried matrix for test evaluations of a decontamination method for their vitrification plant (Cobb, et al. 1991). This type of contamination was produced by drying one drop of a plutonium-nitrate solution on the surface of 304L stainless steel specimens at 600°C for sixteen hours. This method produces a plutonium-oxide film similar to that formed during vitrification.

3.2.2 SIMCON Contaminant Selection

The chemistry and concentration of the contaminants used on SIMCON coupons differed from the previous examples because it models the waste solutions produced during decontamination campaigns at the ICPP. During the 1980s, a large number of samples were taken during decontamination of first-cycle process equipment at the ICPP. The data resulting from these samples were collected and reported by Zohner (Zohner 1996) and are presented in Table 4. These were used by this author for the purpose of designing an ICPP-systems contamination simulant. Though each individual spent-fuel campaign has a different distribution of radionuclides, this author created a nominal contaminant type for ICPP contamination by statistically averaging these data. The average distribution (relative quantities) was normalized to a 10 mSv/h dose at 30 cm (along with the percentage of radiation from each constituent) and interpreted to represent a surface-contamination concentration also shown in Table 4.

Table 4. Nominal radionuclide distribution for ICPP contamination.

Isotope (Gamma)	OverallDistribution (Sv/hr)	% Distribution	Amount (mg) of Element required (for10 mSv/hr)
Sb-125	2.56	3.9	0.047
Ce-144	0.11	0.17	0.006
Cs-137	19.99	30.7	0.924
Ru-106	3.64	5.6	0.029
Zr-95	38.78	59.6	0.005

3.2.3 SIMCON 1 Method Development

The ICPP radionuclide distribution data were employed to develop a contaminant doping and detection methods for comparing decontamination techniques. For all of the contaminants of interest, X-ray fluorescence (XRF) is a technique that yields rapid surface composition analysis. The typical range of the XRF instrumentation allowed an upper limit of 1000 μg and gives a lower limit of about 1 μg (Wade 1993). This is an adequate range, allowing determination of a single-pass percent removal of 99.9% for a given contaminant. Preliminary laboratory work concluded that a two-element system could be managed with minimal interferences. Since 90% of the radioactive species from Table 4 are cesium and zirconium these were initially used as the target analytes. One milligram (1000 μg) quantities of non-radioactive cesium and zirconium salts were chosen as the target value for initial (or before decontamination) quantities. One advantage of this choice of contaminants is that zirconium forms a highly insoluble oxide deposit whilst cesium exhibits a high aqueous stability – this allows for the study of the decontamination of both tenacious and non-tenacious contaminants in one sample.

These SIMCON target values diverge from the ICPP average concentrations in that the quantity of zirconium is increased in order to give an amount that can be easily quantified via X-ray fluorescence. One milligram was in the general range (for cesium, though not for zirconium) described by Zohner and, also, was at the top end of the detection requirements of the XRF analysis. These concentrations of non-radioactive cesium and zirconium salts are also not considered a hazardous shipment, which led to ease of transport and shipping of the coupons. The two-component system turns out to be valuable because it may distinguish the effectiveness of a method in removing either chemical species versus the other or in being more versatile (by removing both).

SIMCON coupons had to be robust, standing up to a variety of mechanical and chemical decontamination techniques, be easy to manipulate and secure in position, and be reasonable in size to ship over great distances. Punching out a 1-in. coupon of ¼-in.-thick steel proved a cost effective method of preparing 304L stainless steel—that is, the primary material of construction at the ICPP, though other metals were employed in later tests—coupons. Because coupons could be cut, prepared and analyzed for about $4.00 each, this was also an inexpensive method of evaluation.

Creating a reproducible simple chemical simulant combination for these coupons required some laboratory development. A solution of 1 mg/1 ml of the chemical surrogates was applied to the surface of the coupon using a 1 ml pipette. This resulted in some of the solution overflowing the surface of the coupon. A 0.200 ml aliquot of solution was applied, but solution overflow was sometimes still encountered. Solids buildup on the surface could also be excessive; often crystals grew very large as the solution dried. This problem was overcome by using 0.100 ml, delivered in 0.025 ml aliquots of solution containing 10 mg/1 ml surrogate solution. An electronic pipette, using the titration mode, provided the proper solution. Thus SIMCON 1 was produced as a versatile, salt-coated, stainless steel pellet.

3.2.4 Development of SIMCON 2

The limitations of SIMCON 1 were apparent even as it was fielded. Virtually all of the decontamination testing results obtained using SIMCON 1 were very high (water alone could wash off nearly 100% of the contaminant), and there was very little differentiation between the poor and effective methods (Demmer 1994). A more tenacious type of contamination was required to truly differentiate between methods and to simulate ICPP's more difficult problems. Several fixation mechanisms were examined to determine whether any would be applicable for this method. Acid-etching was known to cause erosion of the grain boundaries in metal. This etching allows the contaminants to be carried more deeply into the metal surface. The depth of this contamination prevents decontamination solutions from being effective in removing the contaminants. Interaction with acids also forms an oxide-passivation layer on stainless steels. Contaminants become trapped in the oxide layer of steels. This oxide layer mechanism is commonly acknowledged as a significant factor in the contamination of reactor cooling-loop systems (though from heat, not acid etching) (Ocken and Wood, 1991). The oxide type and the acid-etched type are closely associated and are both likely contributors to ICPP contamination mechanisms.

Other mechanisms that may support the fixation of the radionuclides to the process equipment at the ICPP facilities were considered as well. Silicate layering and the exchange of cesium on the active silicon sites has been suggested, since silicate fouling of ICPP evaporators is common. However, no mention of this was discovered in the literature, though entrapment of readily exchangeable contaminants, e.g. cesium, in this manner would be feasible (this kind of entrapment is common in the literature concerning cesium interaction with clays for example). Also, a weak interaction of contaminant and substrate, similar to Van Der Waals forces, could be at work. Another mechanism could involve diffusion of the contaminant into the metal, either physically into the metal pores and cracks or chemically by substitution (becoming a spinel) with non-radioactive metal components.

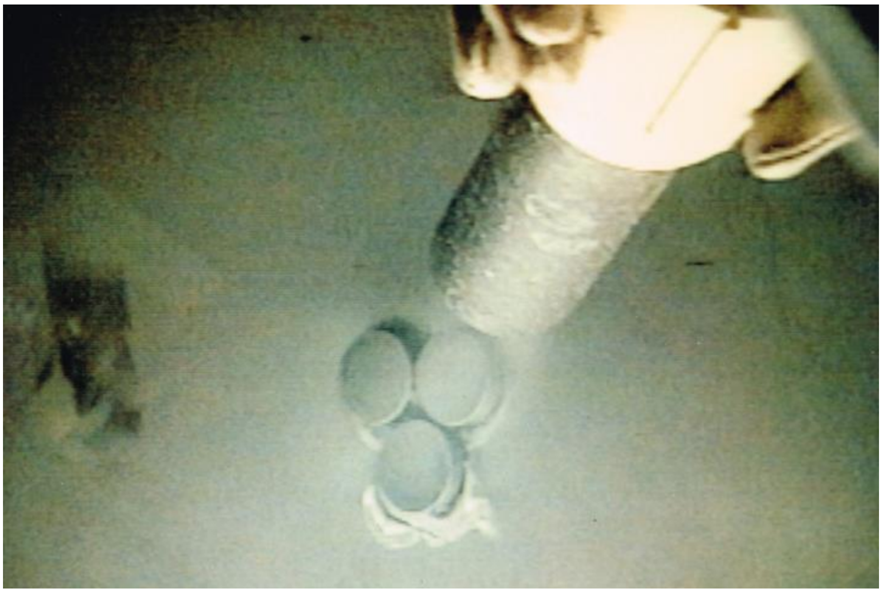
The contamination mechanism with the greatest ubiquity, and certainly the one favored by the commercial nuclear industry, is the oxide layer growth model discussed previously in Chapter 1 (Ocken and Wood, 1991). With this in mind, a first (failed) attempt at SIMCON 2 was to sensitize coupons (prior to contamination) by heating them to 660°C for 24 h., then boiling them in nitric acid, to cause intergranular degradation, so providing an oxide layer and crevice-rich surface for trapping surrogate contaminants. SIMCON 1-type contamination was then applied to these sensitized coupons. The coupons were then cleaned in an ultrasonic water bath. XRF measurements conducted before and after decontamination revealed no real improvement in the retention of the contaminants above SIMCON 1 levels was provided with this method.

The next attempt placed the SIMCON contaminants on the coupon surface prior to oxidation. Basically, this approach heated SIMCON 1 pellets at 400°C for 24 hours. XRF measurement revealed that this increased the retained surrogate materials above the previous attempts. This method was optimized for time and temperature, results being shown in Table 5. For SIMCON 2 coupon development, a temperature of 700°C for 24 hours was selected; this was chosen as an upper limit due to the high volatility of cesium above this temperature.

Table 5. SIMCON 2 development conditions (μg/coupon).

Conditions Used	Cesium (μg)	Zirconium (μg)
Etched then SIMCON 1 app.	<1	4
SIMCON 1, 400 °C , 8 h	11.32	111.2
SIMCON 1, 400 °C , 24 h	10.57	321.8
SIMCON 1, 400 °C , 48 h	6.45	43.32
SIMCON 1, 400 °C , 72 h	2.42	30.42
SIMCON 1, 400 °C , 96 h	3.37	59.01
SIMCON 1, 500 °C , 24 h	7.65	209.7
SIMCON 1, 600 °C , 24 h	10.51	181.7
SIMCON 1, 700 °C , 24 h	18.50	228.5

Figure 18. SIMCON 2 coupons being cleaned with an abrasive blaster.



The development of SIMCON 2 coupons resulted in a tenacious, “fixed” type of simulated contaminant that was very difficult to remove. A solution of cesium salt, containing 5 mg Cs/100 μl, was substituted for the lower (1 mg/100 μl) concentration of that salt. Coupons were removed from the oven, cooled, rinsed, and brushed with a soft nylon bristle brush to remove a "scab-like" precipitate of iron oxide and residual (loose) salts. Subsequent XRF analysis revealed that SIMCON 2 prepared in this manner retained zirconium and cesium in the 100–200 μg/coupon range, yielding a tenacious residue of oxide and salts. A portion of this residue remained on the coupon through most chemical and mechanical decontamination methods. This is thought to be representative of a “real-world” worst case, tenacious contaminant.

A wide variation was found in the quantity of salts that remained adhered to the surface of the coupons during the SIMCON 2 preparation. The X-ray fluorescence results showed that the initial quantity could be as much as 20% different in the amount of cesium or zirconium that remained adhered. This was attributed mostly to the vigorous hand scrubbing that the coupons undergo to remove loose contaminants after baking. Because of this, the coupons required analysis both before and after decontamination analysis, and could not be simply used immediately after preparation and only analyzed after decontamination treatment. These issues notwithstanding, SIMCON 2 preparation was regarded as a success and such coupons have been used at INL to determine the effectiveness of many types of decontamination techniques (laser ablation, CO_2-pellet blasting, alternative chemicals, abrasives, strippable coatings, etc.) prior to using the techniques in radioactive environments.

After coupons were treated (i.e. decontaminated), they were removed from the array plate and analyzed using X-ray fluorescence to determine traces of simulants remaining on the surface. From this information, an estimate of the cleaning efficacy and decontamination factor may be derived. Over 500 coupons have been prepared and tested on the various methods evaluated.

In summary, the development of SIMCON 1 and 2 allowed many different decontamination methods to be evaluated for nuclear fuel reprocessing plant decontamination. A relative distribution of radionulcides was derived and developed into a chemical simulants formulation which was quantified using the convenient and quick method of X-ray fluorescence. While SIMCON 1 was useful for evaluating simple, loose contamination, it had a limited range, and did not simulate more fixed (tenacious) contamination types. SIMCON 2 gave us a range that allows much better discrimination between different decontamination methods and gave us a better method of evaluating techniques to be used on those tenacious contamination types. Those effectiveness results of many different decontamination results for both SIMCON 1 and 2 are discussed in detail later in the results section (Section 4.1, Discussion of SIMCON Decontamination Results).

3.3 Urban Contamination Simulant

3.3.1 Introduction

SIMCON1 and SIMCON2 simulate loosely held and fixed radioactive contamination that might be encountered in a variety of civil nuclear plants including reprocessing and waste treatment facilities and reactor cooling circuits. However, other non-civil decontamination needs to be envisaged. Of particular concern to national governments and their defense agencies is decontamination of urban areas after detonation of a radiological dispersal device (RDD) or so-called “dirty bomb”. Thus, working with and supported by the US Defense Advanced Research Projects Agency (DARPA) and the US Environmental Protection Agency – National Homeland Security Research Center (EPA, NHSRC), this author has developed newer simulants and methodologies to compare the efficacy of different decontamination technologies against RDD-type contamination. The development of these simulants and technologies, and their use in assessing a range of methods for urban decontamination, are the subject of this section.

There are many different scenarios for how RDD contamination may be spread, but the most commonly used approach to simulating RDD contamination in the work described here involves the application of an aqueous solution containing ^{137}Cs (or other radionuclides) to selected surfaces commonly encountered in the urban environment (Drake 2011). This sprayed-on contaminant-application method was chosen at an early stage of this work and was used throughout most of the decontamination trials described below. It produces a tenacious fixed contamination from which, as a result of its characterization and subsequent use in the many hundreds of contaminated coupon decontamination tests described later in this thesis (see Chapter 4.4), much has been learned about the interaction of radionuclide contamination with building materials, particularly concrete.

The relationships of the contaminant and substrate were never well understood during the DARPA supported tests as originally conducted – evaluations were restricted to simply reporting percentage decontamination and semi-quantitative comparison of decontamination efficacy on that basis. However, the more recent results of the NHRSC supported tests and reappraisal of the DARPA funded test results, (both described later in this thesis in Chapters 4.2 - 4.5), show that definite trends are seen in the deposition and adhesion of this type of contamination. Detailed interpretation of these results underscore that it is not just the character of the contaminant alone or the character of the substrate alone that affect the decontaminability of the system – the character of both affect contamination penetration and adhesion. In terms of removal, the interaction of both the contaminant and substrate with the particular decontamination technology employed also have an effect on decontaminability. Based on the conclusions drawn from results of the extensive testing described below, some of these effects can be quantified and perhaps even related to specific characteristics. In particular, the porosity and permeability of the material have been found to be factors in determining contaminant tenacity.

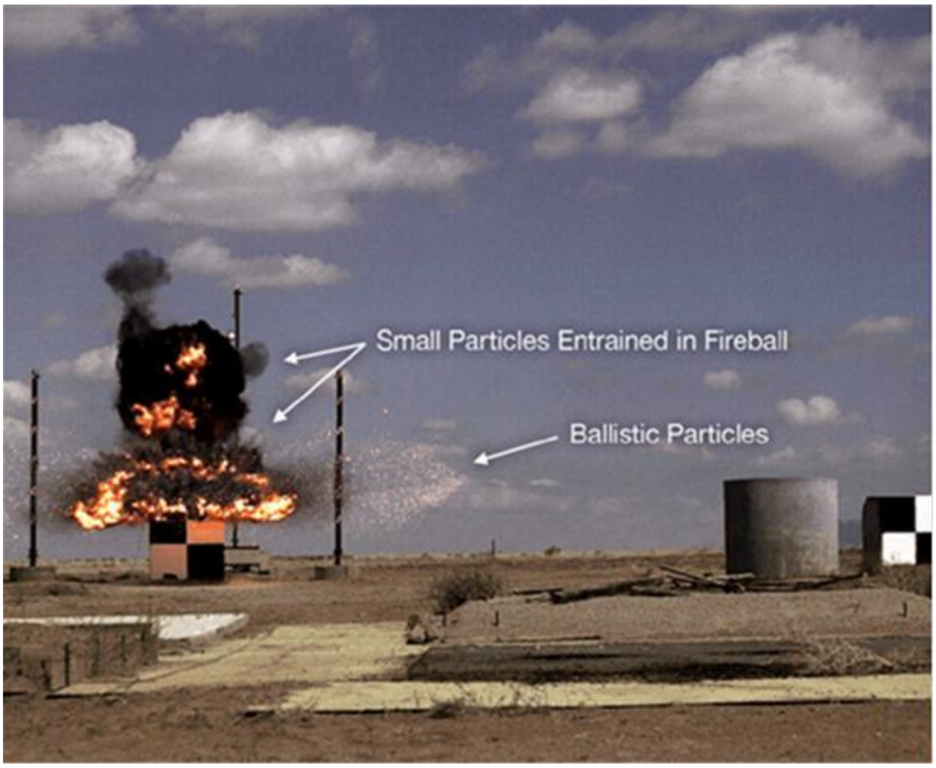
3.3.2 The Origin and Nature of RDD Contamination

While we refer to an RDD as a dirty bomb, that is actually an over simplification. There are many different terrorist RDDs that might be constructed (e.g. see Figure 19). A conceptual dirty bomb is a conventional explosive with radiological material packed around it such that the explosion liberates the radiological material in a large cloud. The easiest way to envision this is as several pounds of plastic explosive, typically C-4, packed in a container and surrounded by a dry, powdered radiological material such as CsCl. In real terms, this type of explosion would directly spread a loose contamination over a very small area, but could create a cloud of radioactive particulates several miles long.

Initially, the dry cesium-chloride powder would not interact strongly with building materials, but would likely remain on the surface as particulate. Because the pressure wave of the blast travels at a very high speed, it is unable to carry particulate (less dense, non-missile type material) great distances (Gould 1981). Thus, in an explosion of this type, the majority of the contamination would likely be spread only in a small area, perhaps 30 m from the blast. While this is not a very effective contamination-spreading device, the effect would be much, much larger as smaller particles are entrained in the fireball and carried hundreds of meters in the air. The fireball effects heat the air and cause the material to be carried high up (Figure 20), where wind currents, often substantial through cities, can carry the particulate significant distances. This material is likely to be only loosely attached to the building-material substrate (Kaminski 2014).

Figure 19. Chechen rebel dirty bomb in Moscow City Park (Krock & Deusser 2003).

Figure 20. Example of dirty bomb test explosion effects (Musolino, S.V., et al, 2013).



Decontamination becomes much more difficult within hours of deposition largely because of the presence of high humidity. In many U.S. cities, such as New Orleans, Louisiana, during much of the year, a rain shower is often only a few hours away; for most other cities, a rain shower is only a few days away at most. Mobilizing to remove the contamination is unlikely to occur within that small window when the contamination remains loose. This lends credence to the conclusion that removing loose dirty bomb (dry) contamination is not a particularly useful test. An added aspect for soluble contamination is that early dose-reduction and firefighting efforts may have been accomplished by spraying substantial quantities of water upon the contaminants, with the net effect of fixing the contamination even more tightly to the substrate.

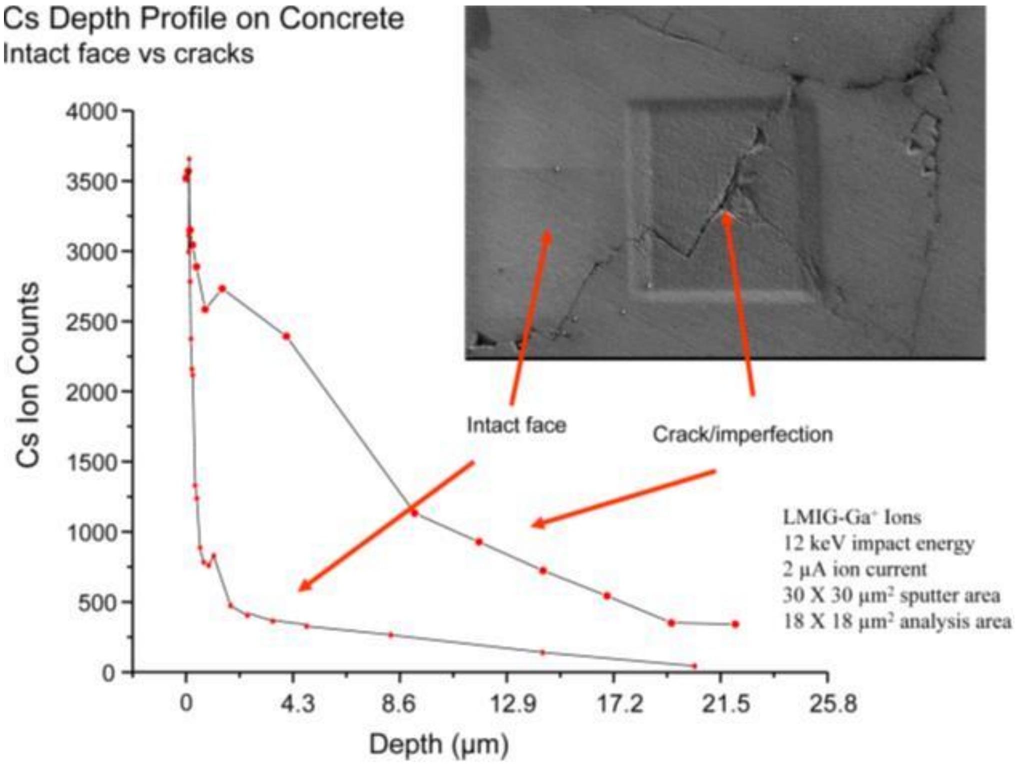
Another scenario is that an RDD will not resemble the conventional dirty bomb, but will resemble one of the more inventive RDDs (Barnett 2006). An attack that could potentially do more damage to items of societal importance would include spreading a soluble contaminant via a garden sprayer or similar distribution device. In this scenario a contaminant, typically a cesium-chloride solution, is loaded into a sprayer device and then sprayed onto a building surface. This leaves a very tenacious contamination that this author has found provides a wide range of percentage decontamination values (see Section 4.5.4 of Chapter 4), and thus discrimination between different methods, during decontamination testing (Demmer 2014).

3.3.3 RDD Contamination Simulant – Development

As described above, researchers previously developed a method of creating a radiological contamination that replicates the effect of a radiological terrorist device (Fox 2007). This provides the basis for a new, tenacious type of urban RDD-contamination simulation employed in the tests described here. Using a spray-based deployment of CsCl solutions, Fox's contamination methodology replicates the Cs contamination described immediately above, forming a more tenacious contamination than particulates loosely adhered to building surfaces. Cesium contamination deployed in accordance with the method of Fox penetrates into the pores of the surface and begins to bind and become fixed within the surface. As described above, physico-chemical characterization of the nature of this contamination stimulant, as well as the herein-described decontamination tests conducted using this methodology, have yielded significant information about the character of the substrate, the contaminant and their interactions.

Using, *inter alia*, secondary-ion mass-spectrometry analysis techniques, Fox found that contamination remained primarily in the upper portions of the surface layer of the building substrate. In Figure 21, Fox demonstrates that the penetration of the contaminant affected only in the upper 20 μm of concrete (Fox 2007). In this experiment, 2.5 ml of a solution containing 20 μCi/ml of ^{137}Cs (as CsCl) was sprayed/airbrushed over a 225 cm^2 sample of ASTM Type 1 Portland Cement (as concrete). As might be expected, penetration can be seen to be deeper for cracked surfaces than intact surfaces. Fox's view of Cs deposition being primarily confined to the surface or near surface is one that is neither entirely intuitive nor universally accepted. Other researchers have shown that penetration of the surface may occur beyond that found by Fox (Wellman, et al 2007, Rohold, et al. 2012).

Figure 21. Cesium depth penetration in concrete (Fox 2007).



However, as well as surface morphology as indicated by Figure 21, the penetration of the contaminant is also partly a function of the amount of contaminant solution applied to the surface. Given high humidity and sufficient duration (typically 4 weeks or less) the CsCl contained in the solution will travel deeply into the surface (Maslova 2013).

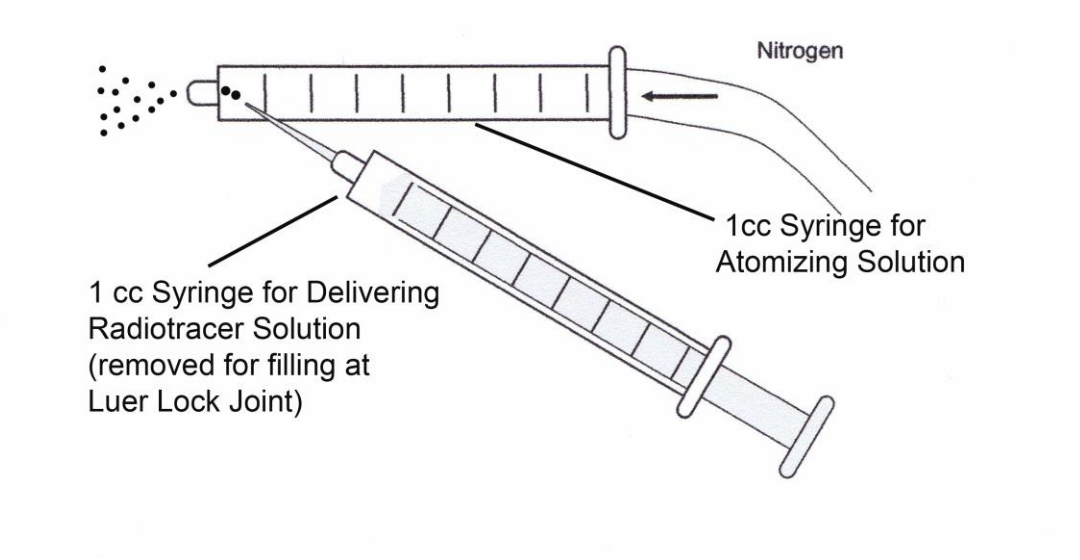
3.3.4 RDD Contamination Simulant – Deployment

3.3.4.1 Radionuclide Deposition

Initial tests used a contamination level of 50 µCi/ coupon. Later experiments used a much lower level (1 µCi/coupon), which was more appropriate for larger-scale tests. For large-scale tests, involving many coupons over a larger area and using abrasive methods (which may generate airborne contamination) it was determined that health and safety concerns dictated lower levels, and a new analysis of the contamination scenario agreed that a 1 µCi/coupon (1 µCi/225 cm^2) was valid for urban contamination.

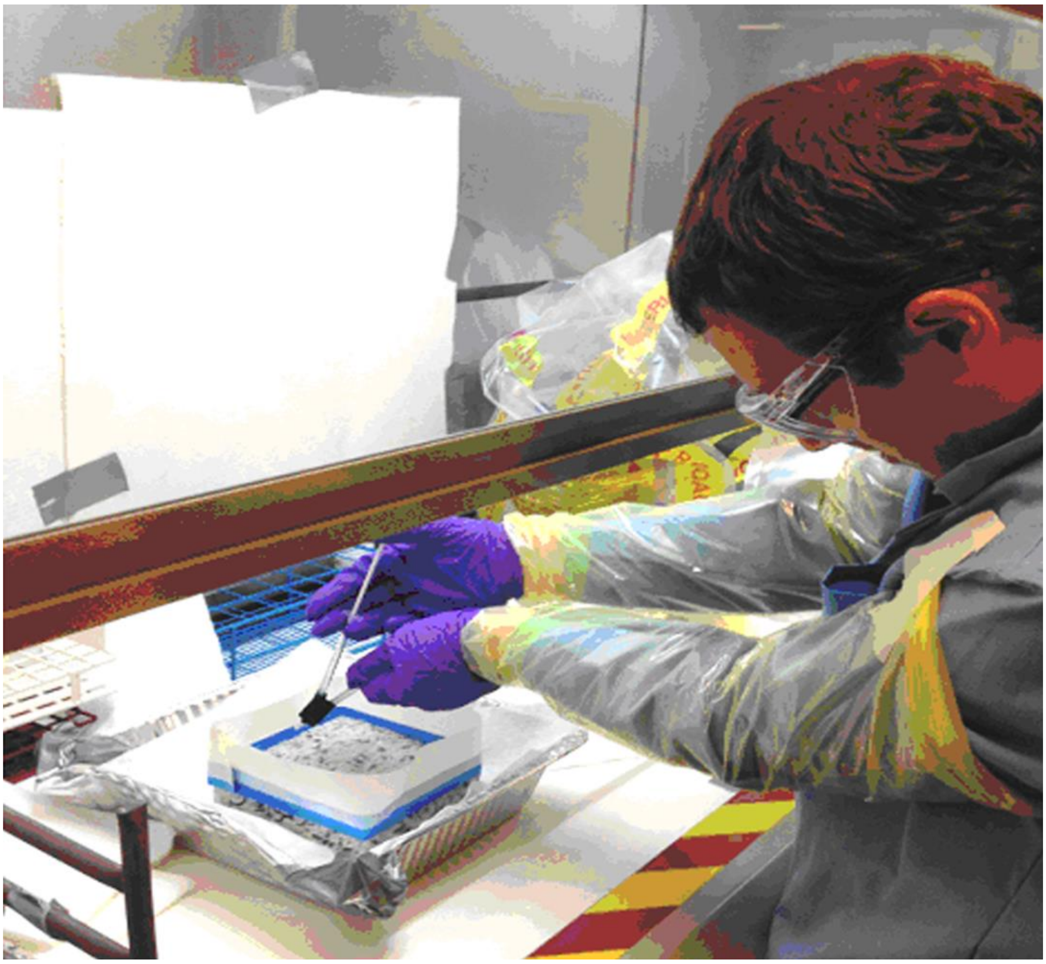
Based on the Fox methodology, the contamination simulant implemented used a simple nebulizer process and an air-brush type device to deposit a single radionuclide in an aqueous solution for RDD testing. Each coupon selected for contamination was spiked with 2.5 milliliters of an unbuffered, slightly acidic aqueous solution containing an appropriate amount of aqueous cesium chloride solution (e.g. 0.4 µCi/ml ^{137}Cs) for the 1 µCi per coupon tests. The liquid spike was delivered to each coupon using an aerosolization technique. The aerosol delivery device was constructed of two syringes, see Figure 22.

Figure 22. Syringe Device



The first syringe had the plunger removed and a pressurized nitrogen line attached to the rear of the syringe. The second syringe contained the aqueous contaminant solution and was equipped with a 27-gauge needle that penetrated through the plastic housing near the tip of the first syringe. The needle is not removed during refilling, but the solution syringe is disconnected at the Luer Lock. Air was supplied at a flow rate of approximately 1–2 liters/minute creating a turbulent flow through the first syringe. The liquid spike in the second syringe was introduced and became nebulized by the turbulent gas flow. The result was a very-fine aerosol ejected from the tip of the first syringe, creating a controlled and uniform spray of fine liquid droplets deposited over the entire coupon working surface. The operator panned the nebulized fluid and resulting fine droplets over the surface of a 225 cm^2 square coupon (brick or tile) of concrete, marble, granite and limestone, see Figure 23. The coupon sides were masked so that the solution was directed onto the surface only. The masking was removed after the solution was deposited, and the coupons were allowed to air-dry in the hood for 24 hours. They were then bagged in 0.1 mm thick plastic bags, tagged, surveyed, removed from the hood, and analyzed using a Canberra, Model BE 2025S (12.1% relative efficiency) high purity germanium (HPGe) gamma spectrometer. Since the first applications of this simulation method for cesium contamination, it has been used nearly 500 times (see Section 4.5.4 of Chapter 4). In addition to ^{137}Cs, ^{60}Co, ^{85}Sr and ^{243}Am gamma emitter radionuclides have been tested (Drake et al. 2011). So-produced coupons are typically used within a short time frame: at least 7 days, but not more than 21 days after contamination. This time period was chosen to standardize the process and because the uptake for cesium had been shown previously to be stable during this period.

Figure 23. Laboratory preparation of RDD coupons.



3.3.4.2 The Substrate

The earliest tests reported in this thesis were conducted so as to evaluate the performance of commercial off-the-shelf radiological-decontamination technologies such as those originally developed for the nuclear-power industry and the DOE complex using the protocols developed under the DARPA program. These tests initially focused on the decontamination of concrete contaminated with ^{137}Cs (Drake, James, and Demmer 2011). This type of testing, with coupons placed vertically in a stainless steel wall, is shown in Figure 24. Latterly, three types of building materials were chosen as substrates along with initially two common radionuclides as contaminants. The building materials were concrete, marble and granite. The two radionuclides studied initially were ^{137}Cs and ^{60}Co. A fourth building material, limestone, and two additional radionuclides (^{241}Am and ^{85}Sr) were added subsequently.

Figure 24. Decontamination Testing conducted by this Author

Concrete coupons used in the above tests were typically made from a single batch of concrete based on Type II Portland cement. The concrete was poured into 0.9-m^2 plywood forms, and the surface was “floated” to bring the smaller aggregate and cement paste to the top. Coupons were then cured for 21 days. Following curing, square coupons were cut to the desired size with a laser-guided saw. For this evaluation, the floated surface was used as the working surface to minimize the possibility of chemical interferences due to mold-release agents. The coupons were approximately 225 cm^2 square and 4 cm thick, with a surface finish that was consistent across all the coupons and that was representative of concrete structures typically found in an urban environment. The edges of the coupons were sealed with polyester resin and masked with tape to ensure that the contaminant would be applied only to the working surface of the coupon. These coupons were used for both the contaminated samples as well as the clean, uncontaminated, control samples.

3.3.5 RDD Contamination Simulant – Decontamination Testing

Ideally, decontamination technologies must not only be effective in removing threat contaminants from typical building materials, but must do so without being destructive to building surfaces. Due to the large areas likely to be affected by such an event, both the time required to perform decontamination and deployment cost are significant issues. An emphasis on low-technology methodologies led to the selection of simple, low-cost, easy-to-use technologies which can be transported and deployed quickly, requiring only minimal support services or infrastructure.

For illustrative purposes, Table 6 summarizes the results of decontamination tests conducted using a range of representative technologies chosen on the basis of the criteria given above. A detailed evaluation of each decontamination technology—by performance, operability, costs, etc.—is available in Chapter 2. A more detailed overview of all 500 tests conducted as part of this work is provided in Chapter 4.

Table 6. Chemical and non-chemical removal of cesium contamination from concrete.

Method	% Removal	Std. Dev.
EAI Rad-Release II	85	± 2
Argonne SuperGel	73	± 5
EAI Rad-Release I	71	± 13
Decon Gel 1108	67	± 9
QDS Liquid	53	± 7
INTEK ND-600	52	± 12
QDS Foam	51	± 8
Decon Gel 1101	49	± 7
INTEK ND-75	47	± 6
Empire Blast Grit Blaster	96	± 3
Dust Director Diamond Flap Wheel	89	± 8
CS Unitech Sander	54	± 10
Dust Director Wire Brush	38	± 7
River Technology Rotating Water-jet	36	± 4

All tests were conducted using coupons contaminated with radionuclide solutions where the level of gamma radiation emanating from the surface of the concrete coupons was measured both before and after application of the decontamination technologies to evaluate their decontamination efficacy. These measurements were made using an intrinsic high-purity-germanium detector (see Section 3.3.4.1 above for details) that was regularly calibrated over the course of testing using standard instrument-calibration procedures.

The majority of the decontamination methods tested throughout the studies presented here are chemical methods. These various chemical methods were chosen because they are commercially available, are less likely to produce airborne contamination and have a proven track record that places them above average in efficiency. The remainder of the methods are: grit blasting, diamond flap abrasive stripping wheel, an orbital sander, a rotary wire brush stripping system, and a rotating water blaster system. These mechanical methods, introduced in Chapter 2, are all specialized tools that include shrouds attached to vacuum sources that withdraw contaminated materials and keep the dust removed from the cleaning area.

The results of Table 6 give an idea of the degree of difficulty for removal of contamination resulting from a cesium-containing RDD. For this contamination scenario it is interesting to note that the chemical techniques were not as effective as brute force removal of the surface (as in grit blasting). But the trade-off is more damage to the surface and more potential for transfer of contamination, i.e. imparting energy into the radioactive particles via pneumatic or rotary force and potentially generating airborne contamination. While no contamination was noted on the blanks, one air-radioactivity monitor showed a slight elevation of contamination during mechanical tests, but not during chemical tests. As mentioned above, this is a very tenacious type of contamination and that by contaminating an item (as an intentional act), researchers created a very difficult problem to solve.

Complementing the decontamination techniques based overview of Table 6, Table 7 shows the results of a series of tests that was conducted to determine the effectiveness of common household cleaners on a range of cesium-contaminated indoor surfaces. These tests involved the use of the widely available Simple Green detergent side-by-side with water. Simple Green is a proprietary blend of fairly simple organic and inorganic cleaning and degreasing agents which is available throughout the United States, at Walmart for example. Simple Green is also approved by the U.S. EPA for cleanup of oil spill residue. It is comprised of an aqueous blend of 5% 2-butoxy ethanol, 5% ethoxylated ethanol, 5% potassium pyrophosphate and 5% sodium citrate.

The test results in Table 7 show that the Simple Green removal efficacy was not significantly different from that of the water (Drake, James and Demmer 2010). Additionally, the porosity of the material being decontaminated had a large effect on the overall ability for both Simple Green and water to remove the contamination. In the case of granite, it is likely that the mineralogy of the granite causes the cesium to become fixed, reducing the ability of both the detergent solution (Simple Green) and water to remove the contaminant (though with a significant difference between these two). This role of the substrate in determining decontamination efficiency has been heavily trialled above and will be discussed in more detail in Chapter 4.

Table 7. Comparison of the percent removals for Simple Green and water on typical interior surfaces.

Material	%R (Simple Green)	%R (water)
Plastic laminate	97.6	93.4
Vinyl flooring	96.7	96
Granite	31.4	7.7
Poly coated wood	67.2	68.1
Painted wallboard	9.5	7.3
Stainless steel	97.5	94.8

From Tables 6 and 7, it can be seen that the RDD contamination simulant system described in sections 3.3.3 to 3.3.4 provides both the level playing field and the wide dynamic range of percentage decontamination values required for the testing of a broad range of decontamination technologies on a truly comparative basis. As well, the variations in both substrate and radionuclide that may be both easily and systematically introduced into the simulant system afford the possibility of test results providing fundamental insights into both the interaction of the contaminant with the substrate and the key mechanistic features of an efficient decontamination method. These matters will be discussed in detail in Chapter 4.

3.4 Improvised Nuclear-device Fallout Simulant

3.4.1 Introduction

Perhaps one of the greatest fears people have world wide is that a nuclear weapon will be detonated in their home country. The devastation that would ensue from the detonation of a nuclear weapon extends well beyond the initial high loss of life; the environmental effects could reach beyond the borders of any country in which it occurs. Thus the cleanup of resultant radioactive contamination might be an international activity.

Modern nuclear weapons are sophisticated instruments that have taken decades to develop. These sophisticated weapons are really only within the reach of major national governments. With the close of the "Cold War" in 1989, two of the great nuclear powers were no longer in an arms race. But the threat of the use of nuclear weapons was not eliminated because there were still thousands of modern nuclear weapons outside of the control of major powers. While control has essentially been regained over the vast majority of these munitions, the threat of use of a nuclear weapon (particularly by Iran and North Korea) is still a worldwide concern.

This relatively new aspect of the nuclear threat comes from the desire of extremists to obtain and detonate a nuclear weapon. While there may be some rogue modern nuclear weapons available on the world market, the likelihood is that terrorists would not be able to obtain a sophisticated weapon. The more likely scenario (apart from the dirty bomb threat discussed before) is the construction and use of a less sophisticated, low yield weapon known as a "improvised nuclear device" (IND) (Barnett 2006). Though the effect would be much smaller, the destruction caused by even a small nuclear device would be horrific, including substantial loss of life and substantial fallout cleanup needs.

3.4.2 Development of a Fallout Simulant

Previous efforts to characterize and simulate nuclear fallout have been for the purposes of detection and identifying transfer, assimilation and transmission biological pathways, but little has been done in terms of simulating fallout for the purpose of decontamination research. Fallout particle composition is primarily made up of the local soil with radionuclides precipitated and condensed on the surface of the particles. Most city soils contain both sand and clay. The intense heat of a nuclear explosion vaporizes the soil, which becomes radioactive through inclusion of fission products like ^{137}Cs. As those particles condense they form vitrified material (Rynders 1996). These particles agglomerate with other particles of dirt that were swept into the nuclear fireball.

During the development of a spherical, particulate, cesium-retaining fallout contamination simulants, several absorbent materials were evaluated. Research shows that contaminants do not readily leach from the particles because of their spheroid, vitreous nature (Rynders 1966). Various cesium-retaining, sequestering materials have been tested in the laboratory by this author. These were:

- Amberlite IRC-748 iminodiacetic acid chelating cation-exchange resin
- Diversified Industries cesium-specific aluminosilicate/zeolite DT-30
- kaolinite clay
- montmorillonite clay

Two grams of each material was spiked with 2 mL of 0.4 µCi/ml of ^{137}Cs (yielding 0.8 µCi of ^{137}Cs on each of the materials), brought to a mixture volume of 15 ml, equilibrated in a test tube and allowed to separate for two hours. The supernate was decanted, an additional 15 ml of deionized water added, the tube shaken, and the slurry allowed to separate for two hours. This process was repeated again and an aliquot of each rinsate was counted via liquid scintillation. After the first rinse, the DT-30 zeolite and kaolinite clay each achieved very high rates of retention (measured by loss to the rinsate) of about 98%. These two materials were then used to create the solid, particulate non-leaching cesium-fallout simulant.

The target particle-size distribution of typical nuclear fallout has been estimated to be between 44 and 1000 µm (Lane and Lee 1968), with the majority less than 700 µm (Lee and Borella 1960). The kaolinite clay was already of a particle size that allowed adequate yield to pass through a number 25, 300 µm sieve. The DT-30 was crushed with a mortar and pestle and passed through a similar sieve, yielding particles less than 710 µm. After the appropriate particle sizes were obtained, various proportions of DT-30 to clay were prepared. A 75/25% mixture of DT-30/clay produced a powder that was easy to manipulate and free flowing, and gave an adequate representation of a two-component soil/clay matrix used as the fallout simulant.

A 40 gram batch of contaminated, simulated IND fallout was prepared by combining the appropriate amounts of DT-30 and kaolinite clay particles (sized as described above) to obtain the 75/25% ratio. The two components were poured into a plastic bottle and mixed well by inverting repeatedly for approximately one minute. A 50 mL aliquot of aqueous ^{137}Cs radiotracer with a total activity of 100 µCi was added to the bottle containing the simulated IND fallout. The bottle was sealed and shaken for approximately 30 seconds and then poured into a plastic dish to dry overnight in a fume hood. The water evaporated leaving the ^{137}Cs adhered to the particles at a concentration of approximately 1 µCi/g of simulated IND fallout material. The uniformity of the simulant was tested by removing an aliquot of both the DT-30 and clay particles (gravimetrically separated) and analyzing separately after the overnight drying. Those aliquots showed that the cesium had uniformly distributed through both materials.

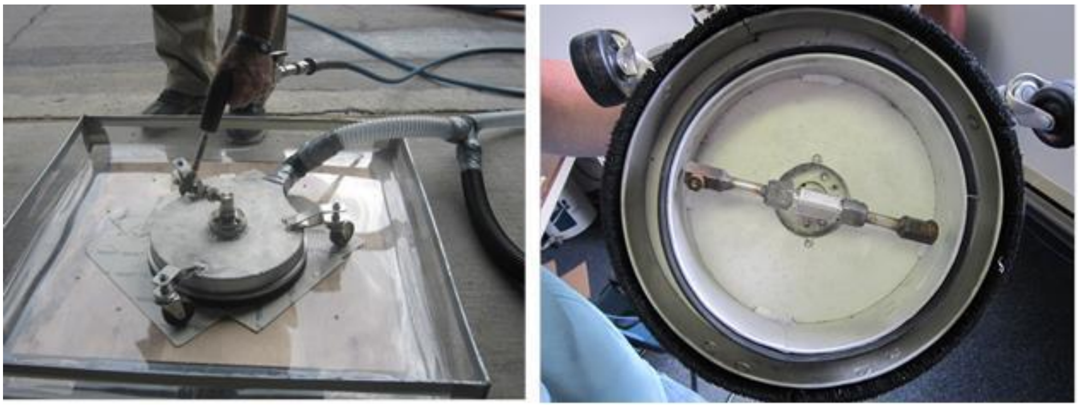
To allow for even distribution of the particles during application to a substrate surface, the solid simulant was placed in a mesh-covered bottle and covered with a number 50 sieve, which passes particles less than 710 µm for application onto the concrete coupons. The mass of the fallout simulant applied was determined by weighing an aliquot into each bottle. The target applied mass was 1.5–2.0 g across the surface of the concrete coupons. Mockup testing using non-radioactive simulant provided an indication of how thickly to apply the particles to attain the target mass. A picture of a concrete coupon contaminated with DT-30, a component of the fallout simulant, on a concrete coupon is shown in Figure 25.

Figure 25. Concrete coupon contaminated with the DT-30 component.

3.4.3 Fallout Simulant Decontamination Tests

Decontamination tests were conducted using a sophisticated, high-pressure rotary water-jet system (RWJS) to remove this simulated fallout from the concrete coupons. The RWJS is manufactured by River Technologies for the purpose of surface cleaning at nuclear power plants. It is composed of a rotating double-ended spray wand inside of a housing, along with a concentric outer housing that draws a very high vacuum. This unit is shown in Figure 26.

Figure 26. River Technologies rotating water-jet.



The results of the tests are shown in Table 8, (Snyder, James, and Demmer 2011). They demonstrate that this simulant performed its function quite well, with virtually all of the simulant removed by the water-jet. Even the vacuum system without the water jet was shown to be quite effective at removing this type of contamination; not unexpected with a truely loose contaminant.

Table 8. Results of decontamination using RWJS.

Method	Average %R	Std. Dev.
Dry Vacuum Only	95.4	1.6
Ambient Water (25 C) RWJ	97.5	0.7
Hot Water (82 C) RWJ	97.3	0.7

3.4.4 Fallout Decontamination Test Result Discussion

The results of the RWJS decontamination tests on coupons of the type shown in Figure 25 show high removal efficiency and indicate that little residual contamination remains on the surface of the concrete after water jetting. The likelihood is that, within the error of the instrumentation, all of the contamination was removed from the coupons. Data obtained using this device for the removal of cesium from concrete, in earlier tests (Table 6), indicates a removal of 36%, i.e. more tenacious cesium contamination is not effectively removed from the surface of concrete using water jetting. This confirms that the application of the cesium to the absorbent material from the fallout simulant was entirely different to that of the Urban RDD Simulant; that the cesium was retained on the absorbent and not released to contaminate the concrete. Thus the replication of the desired criteria, of a loose (removable) contaminant that was not significantly retained on the concrete, was achieved.

Thankfully there have been few opportunities to put these wide scale decontamination practices to the test in a real-world sense. During this study use was made of data collected in the Chernobyl and Goiannia incidents and evaluation is ongoing using data from urban decontamination in Japan. It also provided an opportunity to use the decontamination testing and assessment protocols described above with respect to SIMCON, RDD and IND type contamination to develop an effective decontamination strategy for a real contamination scenario.

3.5 Case Study: Waste Repository Accident Decontamination Evaluation

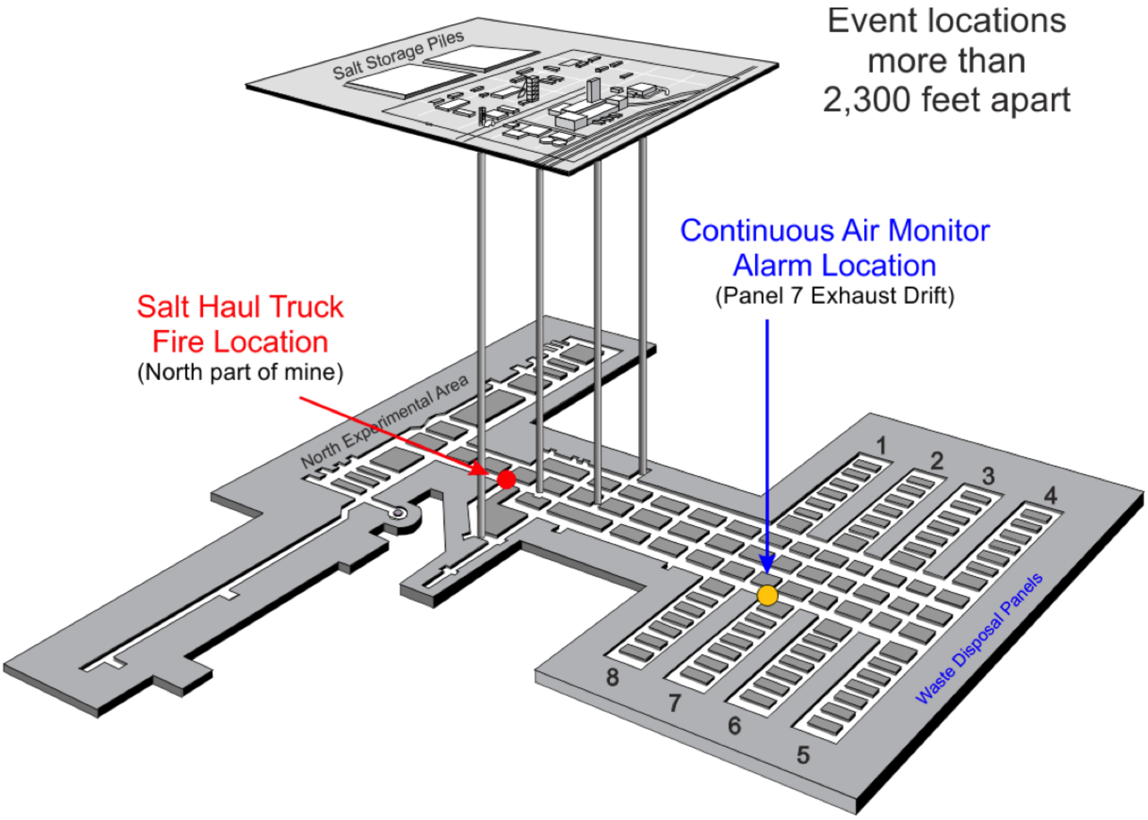
3.5.1 Introduction

One instance where real world deployment of decontamination techniques have been assessed and validated as efficient using the above described simulants is the recent contamination incident at the U.S. Waste Isolation Pilot Plant (WIPP). This provided a real opportunity to deploy a range of decontamination techniques previously studied using simulants, yielding a significant quantity of data for comparison with those simulant results.

Because of the nature of the decontamination testing, particularly on problems such as dirty bombs or nuclear devices (which are best left theoretical) the usefulness of urban decontamination test data is seldom realized. This author employed simulation of a wide variety of decontamination scenarios (i.e. SIMCON, Urban RDD and IND types), requiring significant laboratory development to produce the best simulant possible. In the case of the Waste Isolation Pilot Plant (WIPP) contamination, significant laboratory development was not permitted because of emergency nature of the contamination (and subsequent cleanup) event; instead of allowing months to develop a simulant, the entire project was only allowed 2 months to complete the evaluation. In this case, a background with previous types of contamination simulation made this quick project possible. The evaluation of simple decontamination methods for use on the WIPP contaminated waste repository is an example of using this information on contamination simulation methods to resolve a real world problem.

On February 14, 2014, a release of contamination occurred within the Department of Energy's (DOE) WIPP underground transuranic (TRU) waste repository near Carlsbad, New Mexico. The release of contamination, noted by a constant air monitor alarm, was preceded on February 5, 2014 by a fire in a salt haul truck (see Figure 27). The WIPP is a deep geologic repository carved out of a salt bed. Rooms interconnected by drifts (i.e., corridors) are mined out of the salt. Containerized TRU waste is stored in the rooms. It has been determined that one or more of the waste containers breached and released americium and plutonium, contaminating the mine, the ventilation system, and 21 site personnel (WIPP 2015) .

Figure 27. WIPP Facility with Locations of Events.



3.5.2 WIPP Type Contamination Method of Application

The contamination in the WIPP mine is best described as loosely attached to surfaces and thus in some ways analogous to INL/fallout type contamination. Fixed, tenacious contamination usually arises from species that are liquid and corrosive in nature, penetrating the surface of a material. Dry (dusty contaminants are generally less tenacious and thus loose.

Prior to active trials, non-radioactive tests were conducted first using an insoluble powder called “Glo Germ”. Glo Germ is a good simulant for dry powder contamination and is comprised of a melamine (1,3,5-triazine, 2,4,6-triamine resin). Glo Germ is visible when irradiated with ultraviolet (UV) light. The brightness of the surface pre and post decontamination treatment can be quantified and used to calculate decontamination effectiveness results. A radioactive tracer solution containing americium (^{241}Am) subsequently used to replicate real contamination in radioactive tests. Applied via a stippling technique (see section 3.1.2) the slightly acidic (^{241}Am) radiotracer solution penetrates the salt surface more than a loose particulate contaminant would, but it provided a convenient method (via stippling) to distribute a homogeneous layer of contamination on the samples.

3.5.3 WIPP Substrate Surface Simulants

To simulate the surface conditions in the WIPP mine drifts, solid chunks of rock salt (halite) were used as an analog for the wall and ceiling surfaces in the mine. The halite was cut from a WIPP mine core taken well before the contamination event. Readily available WIPP loose salt rubble was employed to simulate the floor surfaces in the mine. The rubble was pressed into a salt rubble bed ~ 30 cm square and ~4 cm thick. The rock salt core was cut into squares approximately 10 cm on a side and 3 cm thick using a water jet. However, the core was cylindrical, so there were a number of irregular, pie shaped pieces leftover from around the edges after the 10 cm × 10 cm coupons were cut out. Those irregular scraps were used primarily for Glo Germ surrogate contamination tests. The square cut coupons were used for the radioactive tests. While the mine surface is quite irregular, it was decided that the best data (in terms of consistency between coupons) would be gathered with relatively smooth, water jet cut coupons.

The coupons, contaminated with Glo Germ were subjected to a number of different decontamination methods: brushing, vacuuming, mechanical grinding, water washing, and strippable coatings. UV sensitive Glo Germ powder was selected as the surrogate contaminant because it is safe, non-toxic, and easy to detect. Three coupons were used for each test. The coupons used in these tests are the irregular scraps, with approximately 100 cm^2. Because every coupon is analyzed individually, the data stays consistent and reproducible to that coupon. Of primary importance was determining how effective each of these methods is at removing (or fixing it to) contamination from a halite surface. More qualitative aspects of the methods were also evaluated: ease of use, potential for contaminant re-suspension, volume and type of secondary waste, and (relative) rate of application/removal.

3.5.4 Glo Germ Decontamination Tests

The preliminary, non-radioactive Glo Germ coupons were contaminated by applying 100 mg of powder to each coupon. The measured quantity of powder was distributed on the surface using a small bottle with six holes in the top (similar to a salt shaker). Using a manually adjusted digital camera, pictures were taken before and after decontamination. The images were processed through Adobe Photoshop to determine the amount of white light and thus the quantity of Glo Germ powder. The coupon shown in the left pane of Figure 28 is illuminated under ultraviolet (UV) light. A purple/blue (long wave UV) haze can be seen. The bright spots are the Glo Germ surrogate contaminant. The coupon area in the image is selected (cut), then changed to a black and white image (2nd pane of Figure 28) and then the area of the white peak of the histogram (insets in Figure 28) is quantified. The two black-and-white images are before and after renderings of the ultraviolet images. The center image shows the before water rinse cleaning image, with a large “white light” peak in the histogram (below the image). While the far right image shows the after water rinse cleaning with a tiny “white” peak in the histogram. This method does not give high precision results; however, the amount of light is proportional to the mass of fluorescing powder. Therefore, the histogram discriminates (via peak intensity in that wavelength) between large piles and small smudges of powder.

Figure 28. Halite coupons dusted with Glo Germ Powder, B&W images show before and after decontamination and histogram quantification.

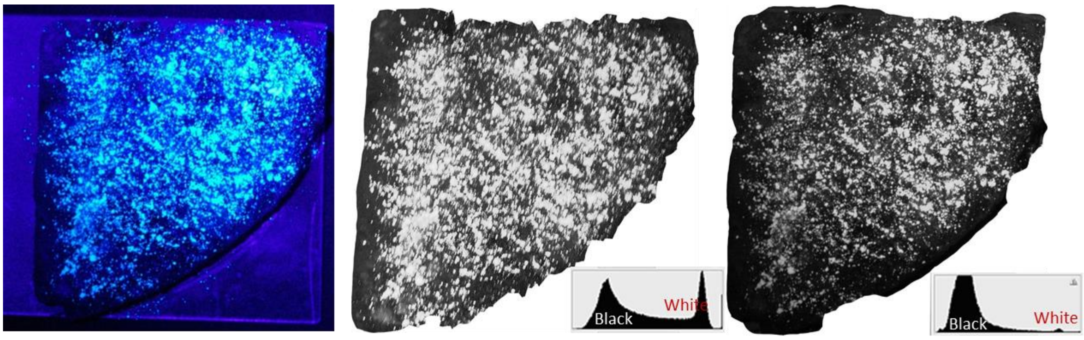


Table 9. Relative Decontamination Levels for Surrogate Contaminant Tests

Method	**% Removal**	**Std. Dev.**
Dry Brush	21.7	12.2
Water Wash	98.0	2.0
DeconGel Strippable	91.3	6.0
Vacuuming	23.5	7.8
Stripcoat Strippable	25.0	8.9

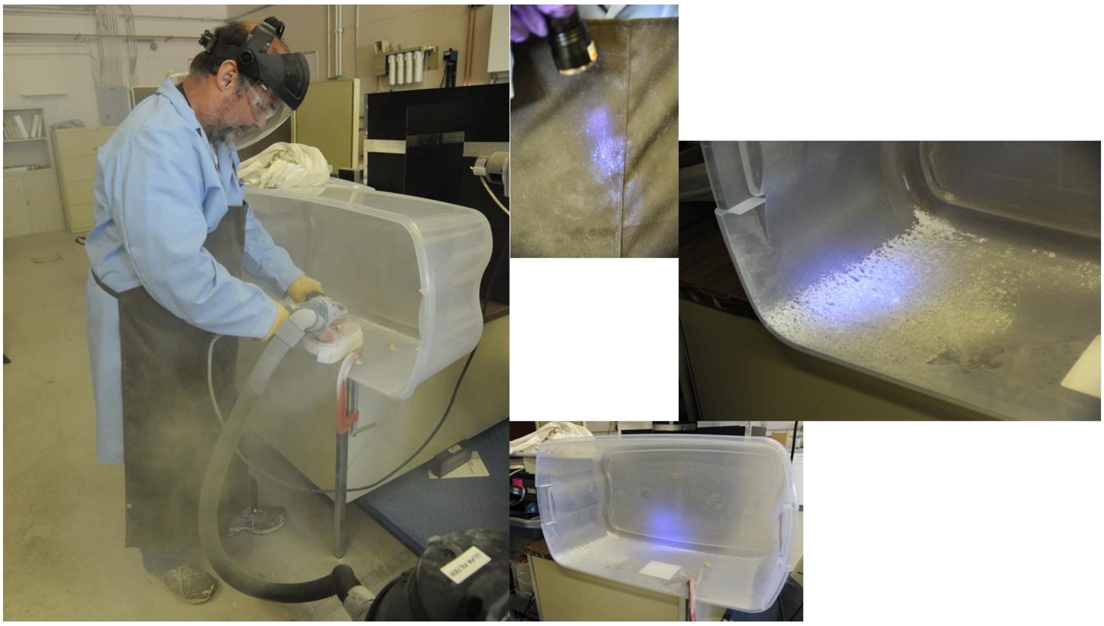
The results from the five decontamination tests (excluding grinding based methods) performed on these WIPP salt coupons are shown in Table 8. As can be seen in Table 9, two of the methods, water washing and DeconGel 1108, were highly successful at decontaminating the powder from the salt surface. There was obviously some residual material in the “after” photo (Figure 29), however, the residual is so slight that it is difficult to resolve from the noise in the histogram. Based on removal efficacy, both water washing and DeconGel are good candidates for use on the salt. However, removing the DeconGel strippable coating took a significant amount of time compared with the other methods, rendering it quite inefficient. In the case of the Stripcoat material, removal of the coating from the ~100 cm^2 coupon took over 15 minutes – an extremely long time period for a strippable coating. The salt of the halite surface seems to interact with the coatings, increasing their adherence to the surface. Based on the results given in Table 8, brushing, vacuuming, and Stripcoat have minimal effectiveness.

Figure 29. Image (after Photoshop processing) of a water washed coupon after decontamination.

Separately, surface grinding was also evaluated for use as a simple method. Three coupons were each dusted with 100 mg of Glo Germ fluorescent powder in the same manner as the previous removal tests. The sample surfaces were then ground down with a Makita side arm grinder at 1200 r/min with a wire cutter head and a vacuum dust collection system. The dust collection cowling was connected to a Minuteman HEPA vacuum.

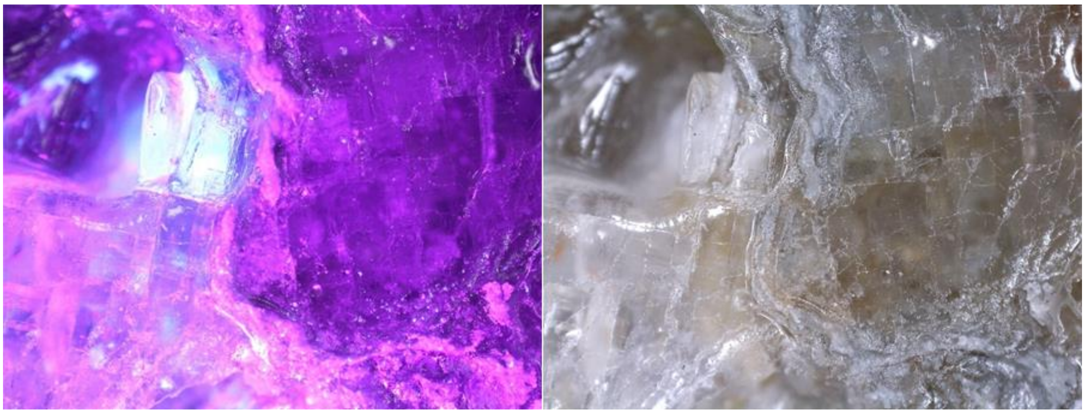
Grinding efficiently removes the surrogate contaminant, as well as a layer of the salt/halite surface; however, some contaminant is retained in the pores and grain boundaries of the sample. Unfortunately, as can be seen in Figure 30, the removed contaminant and salt is widely dispersed in the working area, despite the grinder head employing a dust collection system. While some contaminant is captured in the vacuum during removal, this method would disperse contamination that is settled and adhered to a surface. Under UV illumination, significant contamination could be seen on the operator and on the surrounding surfaces (See Figure 30). It seems that this method would make the situation worse, not better, especially in an actively ventilated mine drift. Based on these results, it was not considered worthwhile to quantify the grinding removal efficiency using the white light histogram method.

Figure 30. Salt and Glo Germ dispersed during grinding decontamination.



The water washed Glo Germ coupons were submitted to microscopic evaluation to determine the location of any residual contamination within the salt coupon. Figure 31 shows side-by-side comparisons of two microscope photographs taken at a site on the salt coupon that brightly fluoresces white/green after application of the water wash decontamination technique. The purple/blue photo on the left is obtained under a UV light source. The photo on the right shows the same site under visible (i.e., white) light, showing the natural look of the salt surface. In the right hand photo, it is clear that the source of blue fluorescence in the left hand photograph is a contaminant particle in an inclusion within the salt. These tiny surface irregularities, visible under magnification, can act as contaminant traps, and are equally, if not more, important to proper decontamination as the more obvious cracks, crevices, and general surface irregularities visible to the naked eye. This observation yields additional, microscopic evidence that high porosity and permeability of the substrate inhibit decontamination, an observation that will be revisited in detail in Chapter 4.

Figure 31. Microphotograph of Contaminant inclusion in salt pore (UV and visible, 20X magnification).

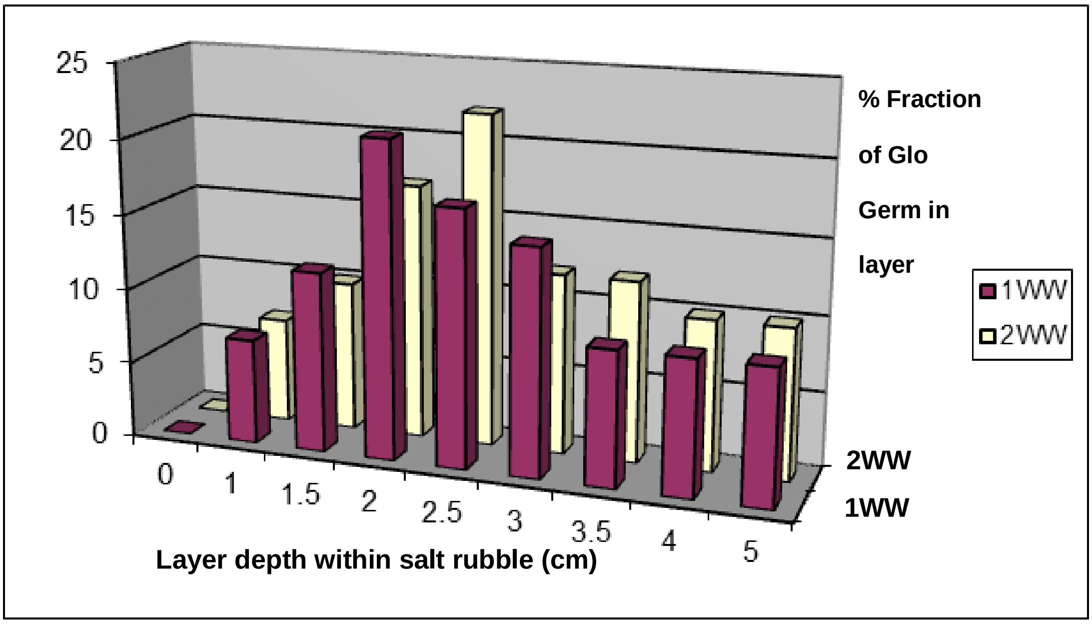


3.5.5 Operational Considerations for Tested Methods

If simple water washing were to be pursued as a decontamination method for the WIPP halite surfaces, there are some considerations that should be understood. The first priority is typically to select vacuum-based decontamination; the second to wash down-based methods. Upon the application of water or upon a significant increase in humidity, the salt surface may become “sticky”. With this in mind, vacuum cleaning was predicted to be a more effective decontamination method than was found in testing, showing as it does only 23.5% efficiency in Glo Germ removal. The high humidity present in the laboratory during the Glo Germ tests (due to rain that week) may have caused the powder adhere more strongly to the surface. This could become a factor as large amounts of water are applied in the mine drifts; as the humidity rises, the surface may hold contaminants more tenaciously. A second consideration may be that contaminants successfully removed from the wall during wash down may re-suspend into the air after drying out. Thus, contaminants remaining on a humid wall or ceiling surface and those entrained in wet floor rubble may be prone to aerosolization once moisture levels return to salt cavern norms.

As a follow-on to testing the wash down efficacy, a test was conducted to determine if surrogate contamination is transported significantly into a bed of WIPP salt rubble upon wash down. The floor surface in the WIPP mine consists of 10-20 cm of salt rubble that exists as residue from mining activities to open up the drifts and rooms of the mine. The test showed that rinsing of the surface did transport contamination into the rubble bed, the distribution peaking around 2 cm depth. In the test, a 100 cm^2 salt rubble surface contaminated with a deposited layer of 100 mg of Glo Germ powder was washed with a common hand pump sprayer that delivered about 20 ml of water over 15 seconds. Figure 32 shows the depth distribution of the powder within the rubble (red/maroon bars) for the two tests a first water wash (1ww) and a second water wash (2ww). Salt rubble was surgically excavated in a ~5 cm diameter circle (~20 cm^2) and each layer was examined. After the first water wash, Glo Germ powder was found throughout the 5 cm column, but the majority was in the 1.5 – 3 cm range. That distribution may be adequate to remove the threat of re-suspension, but it is still relatively close to the surface. Further irrigation via the second water wash pushed the contamination lower (yellow/cream bars); however, the figure shows that some fraction of the contamination is likely to remain in the upper portion of the salt rubble bed, within 1 cm of the surface.

Figure 32. Vertical distribution of contaminant in rubble bed.



3.5.6 Radioactive Tracer Decontamination Tests

Simulant tests using Glo Germ determined that water washing and DeconGel 1108 strippable coating were effective methods for removing surrogate contamination from the surface of the salt, while other methods were decidedly less capable. Radioactive tracer tests were conducted with these two most effective methods. An americium tracer solution (^{241}Am) at a concentration of approximately 8 nCi/cm^{3}was applied to salt coupons and steel plates in a stippling fashion. Stippling consists of pipetting 40 small drops, in this case 0.025 cm^3 each, of contaminant onto the surface of the target material. This level of tracer yielded alpha contamination levels of approximately 21,000 disintegrations per minute (dpm) for the steel plates (Figure 33, used as a standard/baseline) and about 2,700 dpm for the salt coupons, indicating significant imbibition by the latter. As explained in Section 3.1.2, stippling is an established technique for preparing standards to determine matrix effects with radiometric instruments. The stippling was confined to an area the size of the radiometric detector probe being used for these tests.

Figure 33. Americium stippled stainless steel “standard” plate.

The americium tracer was applied to two steel plates and six salt coupons. The salt coupons used were the most regular of the twelve, ~100 cm^2, 3 cm thick coupons sectioned from the original, uncontaminated halite coupons, see Section 3.5.3 above. As the tracer was applied to the surface of the salt, it was observed that it did not bead, as seen on the steel surface of Figure 33, rather it wicked into the surface pores, cracks, and imperfections. The structure of the salt appears to have ~1 cm grains, which allows solution to imbibe into the intergranular areas. This explanation for the observed behavior is supported by the results of pre-decontamination measurements: The same amount of tracer returned ~13% of the radiometric counts that were found on the steel plates. The tracer had likely penetrated into the salt matrix, attenuating/shielding its detectable activity even before decontamination had taken place.

Pre and post-decontamination treatment radiometric counting was conducted using a Ludlum 2224 "scaler" handheld meter, using a 60 second count. This meter has a 20% efficiency for alpha and beta/gamma activity. Analysis showed typically 2500 – 3000 dpm/100 cm^2 alpha before decontamination and 70 – 195 dpm/100 cm^2 alpha, post decontamination, using either water washing or DeconGel decontamination method. See Table 10. The alpha activity data shows that removal efficiency averaged 96% and was consistently ≥ 93%.

Table 10. Alpha Contamination Quantification for Americium Tracer Tests

Decon Method	Sample #	Pre-decontamination Treatment Alpha Count		Post-decontamination Treatment Alpha Count		Alpha Removal [%]
		[cpm]	corrected [dpm]	[cpm]	corrected [dpm]	
Water wash	W103	579	2895	29	145	94.99
Water wash	W101	526	2630	22	110	95.82
Water wash	W102	658	3290	14	70	97.87
None	Steel coupon	4322	21610			
Strippable	W105	713	3565	20	100	97.19
Strippable	W106	561	2805	39	195	93.05
Strippable	W104	475	2375	23	115	95.16
None	Steel coupon	4188	20940			
Water wash	WB201 blank*	0	0	3	15	
Strippable	WB202 blank*	0	0	11	55	

* Alpha background determined to be ~27.5 dpm.

Two different quantification methods were proposed for the use of gamma radiation monitoring assess decontamination efficiency. Unfortunately, neither could provide a sensitive method for quantifying the decontamination results. A portable, high purity germanium gamma scan unit, the ORTEC Detective, found insufficient radiation signature from the ^{241}Am (59.6 keV) spike levels to permit good quantification, although it did provide ready identification of the spike material as ^{241}Am. The Ludlum 2224 unit used for alpha detection was also employed, this time in beta/gamma mode. It did not provide acceptable results. The Ludlum beta/gamma readings averaged 746 dpm before decontamination and 674 dpm after, with a background of ~640 dpm (general background activity in the radioactive fume hood). Gamma and beta/gamma based detection methods to access decontamination efficiency were discarded in favor of the alpha based method of Table 10.

While the difference in removal efficiency between the two methods tested in Table 10 was minor, water washing was by far the easiest method of decontaminating these coupons and was also highly effective at ^{241}Am contamination removal. The process used was the same as that previously established during the non-radioactive testing: a 15 second water rinse using a spray bottle delivering 20ml of water in total to the surface. A photograph of this method is shown in the left pane of Figure 34. The rinsate was collected and found to be approximately 20 ml from each coupon, which is essentially complete recovery of the solution (as measured in earlier experiments). Scaled to practical use, the volume used for water washing is ~2 L/m^2 of decontaminated surface. One ml of each 20 ml volume was counted using liquid scintillation to determine the amount of radioactivity recovered. The average measured activity at the halite and steel surfaces prior to decontamination, as measured with a Ludlum meter, was 21,275 dpm alpha per coupon. Average measured activity recovered by the water wash of the halite surface was 6,533 dpm alpha per coupon. This result indicates that washing removed virtually everything from the surface and, in fact, removed a significant portion of contamination from within the halite material bulk. However, it only removed ~31% of the total applied versus the steel control plates registered ~21,000 dpm. The remaining contamination is likely to have permeated into the halite coupon.

Figure 34. Water wash and strippable coating americium decontamination tests.

While the DeconGel strippable coating was also highly effective at removing contamination, it was time consuming and difficult to remove - as it was during the non-active Glo Germ tests. It took, on average, 15 minutes to remove approximately 95% of the coating. Complete removal was not possible, with the last 5% being held tenaciously. As in the non-radioactive tests, the strippable coatings became partially incorporated into the salt surface and were strongly adhered and very difficult to remove – much more difficult to remove from the salt surface than from stainless steel or even concrete. A photograph of this portion of the test is seen in the right pane of Figure 34. The surface of the coating was scored with a plastic knife to give a place to begin peeling the coating. The coating materials were found to work better as fixatives (immobilizing the contaminant) than as strippable coatings.

3.5.7 Validation of Simulation Tests at WIPP

Actual decontamination of the americium contaminated salt in the WIPP caverns using water and a small agricultural sprayer (Figure 35) began in early 2015 (Clark 2015). Water was sprayed to about 1 meter high along the walls and over the floor. Extensive surveys before decontamination confirmed that contamination was affixed to the walls at approximately 1 m height and below. Follow-up contamination surveys showed that the americium was completely decontaminated by the use of the water rinse. This was a satisfactory validation of the non-active, simulant-based decontamination testing results prepared for the WIPP. The simulant test results showed the effectiveness of this simple, quick, non-hazardous and cheap decontamination method and allowed for WIPP to move ahead quickly with decontamination. It demonstrates the value of such simulated surface testing which ultimately leads to a science-based solution option that, in this case, was ultimately implemented with great success.

Figure 35. WIPP Agricultural Water Spray Vehicle

3.6 Conclusions

These studies of the simulation of radiological contamination allow for several conclusions to be drawn:

- A large variety of contamination scenarios exist, which leads to many ways to simulate contamination.
- Some contamination will usually remain on or near the surface for a short duration. This contamination will often be termed loose or removable because it can be washed, vacuumed, or brushed off. Loose contamination can also become fixed if it is allowed to remain on the surface for long periods of time or to experience an event (such as rainfall) that mobilizes it further into the substrate. Therefore, removing contamination quickly and with a low-impact

method (strippable coatings, vacuum cleaning, etc) can often be cost-effective.

- The best way to simulate contamination is to understand how it is held on the surface and to research how to replicate those conditions. In the case of SIMCON 2, that was to create a tenacious oxide layer on the surface that could incorporate the contaminants. For Urban RDD contamination that was to allow the contaminant to penetrate the surface. In the case of IND, research showed that the contamination was not tenaciously attached to the surface, but was attached to a particle; which created a very "loose" contamination in comparison.
- There is a tremendous difference between contamination that is simply deposited on the surface and contamination that is purposely and tenaciously fixed into the surface. Solid particles deposited onto the surface, particularly if they are loose (e.g. the IND case), are the easiest contamination to remove.
- Surface removal, though more destructive (e.g. abrasive blasting) can be far more effective at removing contamination than more-sophisticated methods that chemically draw it away from the surface. However, there are many removal situations in which non-destructive techniques can be more cost effective; particularly if a high-value item (or structure) is sensitive to damage caused by mechanical techniques. There is no single method that satisfies every decontamination criteria.

- Researching and simulating contamination before a genuine contamination event (i.e. WIPP) can provide insight into the molecular interaction between the contamination and the surface, thus informing the choice of the most cost effective choice of decontamination technology for ultimate deployment.

4 Discussion of Decontamination Testing Results

4.1 Introduction

The contamination simulation methods described in Chapter 3 were developed to test the efficacy of a wide variety of different decontamination methods. The simulation methods had to replicate the different substrate and contaminants found in the nuclear industry. Four principle methods were highlighted in Chapter 3 for reproducing contamination concerns:

- fission products on stainless steel;
- fission products, activation products and actinides on urban substrate;
- nuclear weapon fallout on concrete; and
- actinides on halite rock.

Correlating the results of the tests with the characteristics of contaminant and substrate, may lead to unique, fundamental insights into the nature and mechanisms of radiological contamination.

While the original reason for the execution of these simulated contamination tests was simply to determine the effectiveness of individual decontamination methods on an empirical basis, the fundamental understanding of radiological contamination mechanisms was nonetheless advanced during this testing. In addition to the efficacy evaluations, extensive data analysis was performed to determine whether other, fundamental information and insights could be generated by these tests. A data-mining effort, initiated during the course of this dissertation, was performed on this data with many additional features being discovered.

It is now an increasingly widespread activity to “mine” previously gathered data to determine whether fresh analysis can bring new information to light. Commercial businesses are at the forefront of this effort, examining sales data to determine which products sell best in different areas of the country in different seasons. The overall 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 database and data-management, data pre-processing, model and inference consideration, interesting metrics, complexity considerations, post-processing of discovered structures, visualization, and online updating (Ponelis 2009). In the case of the decontamination data considered here, many of the secondary conclusions about the simulated decontamination tests are somewhat qualitative or intuitive, (such as: different contamination-fixation mechanisms produce very different results.) However, when quantified as they are in this data set, they take on greater significance. Essentially, these data quantify some relationships that have been thought to exist, but may have only been previously established by anecdote.

Part of the analysis exercise for this set is to apply simple, spreadsheet-type statistical methods and charts. 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:

- The decontamination methods
- The different radionuclides; and
- The different substrates.

Data-mining terminology refers to this as clustering (i.e. discovering groups of data that are similar) and association-rule learning (searching for relationships among the data). Essentially, this effort identifies and quantifies some important aspects of the resultant data that were not the intention of the test, are sometimes hidden, and are more of an additional premium.

Some of the data presented in this analysis (most especially during analysis of the Urban RDD data) will be presented in a box-and-whisker format and analyzed using Tableau software (Tableau, Seattle, WA 98103). Box-and-whisker diagrams show the median and 50% of the data (the middle two quartiles) graphically within the box, while the remainder of the data is within the “whiskers” of lines that extend beyond the box. It is not, strictly speaking, a statistical plot, but is based on the number of data points, and where the quartiles (lower 25% and upper 75%) of how many data points are plotted. In simplest form, for a set of fifteen data points (of ordered data, low to high), the median will be placed at data point seven, the box will extend from point four to point eleven. Of course, this visual depiction of the data will be valuable to display the “tightness” of the data and how far it overlaps. The smaller the box and whiskers become, the better discrimination between different individual kinds of data based on the data ordering criteria selected.

In the first instance, two specific groups of test data, the SIMCON and Urban RDD types, were analyzed for underlying relationships. These two groups were chosen because of the wide variety of methods and the larger volume of data available.

4.2 SIMCON Decontamination Test Results

The first data to be discussed and data mined is the SIMCON Data used to determine the effectiveness of stainless steel decontamination. As discussed in Chapter 3, SIMCON 1 was not ideal, in terms of strength of contaminant fixation, resulting in a narrow dynamic range for decontamination efficiency. However, if this had not been the case, SIMCON 2 would not have been needed and, facilitated by its wider dynamic range, new insight into the relative tenacity of contamination types would not have been developed.

4.2.1 Importance of range and discrimination

The difference in relative response between loose (SIMCON 1) and fixed (SIMCON 2) cesium and zirconium contamination types, prepared as discussed in Chapter 3 and decontaminated using a representative range of common methods, is shown on Table 11. From this data it can be seen that the cesium contamination in the form of SIMCON 1 is much easier to remove than cesium contamination in the form of SIMCON 2; giving much higher decontamination results for all methods studied here. As shown in Table 11, a T-test value was performed for these two sets of data with the result being a p value of 1.2×10^{-4} well below the accepted p limit of 0.05 and indicating that the means of the two data sets differ significantly. This in turn indicates the two sets of data, for identical decontamination methods are significantly different. For the zirconium SIMCON 1 & 2 sets, the T-test value is 0.066, indicating

Table 11. Selected results of SIMCON 1 and 2 tests.

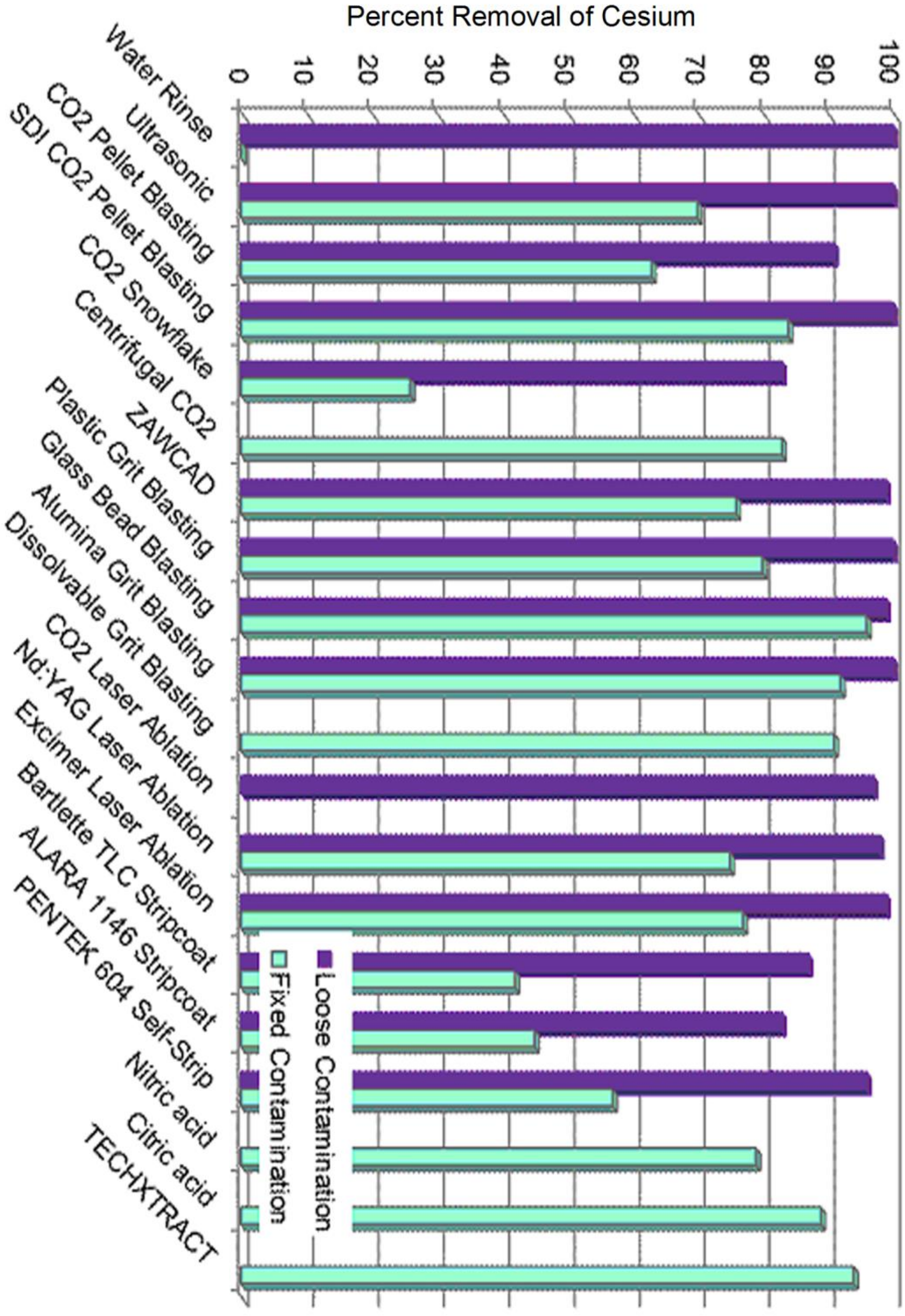
Technology	**SIMCON 1 Cs(% removal)**	**SIMCON 1 Zr(% removal)**	**SIMCON 2 Cs(% removal)**	**SIMCON 2 Zr(% removal)**
Water Rinse	100	99	0	0
Ultrasonic	100	100	70	88
CO_2 Pellet Blasting	91	92	63	78
SDI CO_2 Pellet Blasting	100	99	84	100
CO_2 Snowflake	83	94	26	78
Centrifugal CO_2			83	98
ZAWCAD	99	99	76	95
Plastic Grit Blasting	100	100	80	93
Glass Bead Blasting	99	100	96	100
Alumina Grit Blasting	100	100	92	100
Dissolvable Grit Blasting			91	97
CO_2 Laser Ablation	97	86		
Nd:YAG Laser Ablation	98	99	75	99
Excimer Laser Ablation	99	98	77	99
Bartlette TLC Stripcoat	87	66	42	73
ALARA 1146 Stripcoat	83	76	45	76
PENTEK 604 Self-Strip	96	90	57	75
Nitric acid			79	23
Citric acid			89	23
TECHXTRACT			94	83
Mean % Removal	95.4	93.7	67.4	75.5
Standard Deviation	6.5	10.3	26.1	30.7
T-test for SIMCON 1 vs SIMCON 2 (Cs)	1.2×10^{-4}			
T-test for SIMCON 1 vs SIMCON 2 (Zr)		0.066		

that the data could possibly be considered of the same family of data. Yet, the difference in standard deviation shows the narrow and wide range of these different SIMCON methods; the standard deviation for SIMCON 1 (many different methods) is very small compared to that for SIMCON 2, indicating that the SIMCON 1 data (from vastly different decontamination methods) are all very similar.

The results of SIMCON-coupon decontamination testing highlight the importance of understanding the decontamination-simulation method. Even though these SIMCON methods have a common root, specifically the contamination found at nuclear-fuel-reprocessing plants, they vary greatly in their ability to represent the tenacity of contamination and, thus, the comparative ability of a decontamination technique to be of value in cleanup. Though these coupons have the same substrate and contaminants, they employ very different mechanisms of fixation. However, both are valuable for discussions about various levels of decontamination effectiveness in terms of simulated contamination types. They underline an intuitive, though often unappreciated, aspect of contamination simulation: making a simple change - in this case forming an oxide layer using heat - changes the entire nature of the test. The 200-odd SIMCON results underpinning the data of Table 11 prove valuable in this discussion as they lay the groundwork for more detailed discussions about 400 contaminant/substrate tests and interactions that are presented in the Urban RDD portion of this chapter.

The inability of SIMCON 1, a good and interesting loose contamination simulant, to discriminate the real effectiveness of different decontamination methods is the first key point for SIMCON discussion. Our task was to create a contamination-simulation process that represented certain real-world reprocessing plant conditions. However, we found that overall reprocessing plant type contamination was not replicated by a loose contamination system. This was understood only after the SIMCON 1 based approach to contamination simulation was recognized as not being

Figure 36. SIMCON 1 (loose) & 2 (fixed) Comparison By Method.

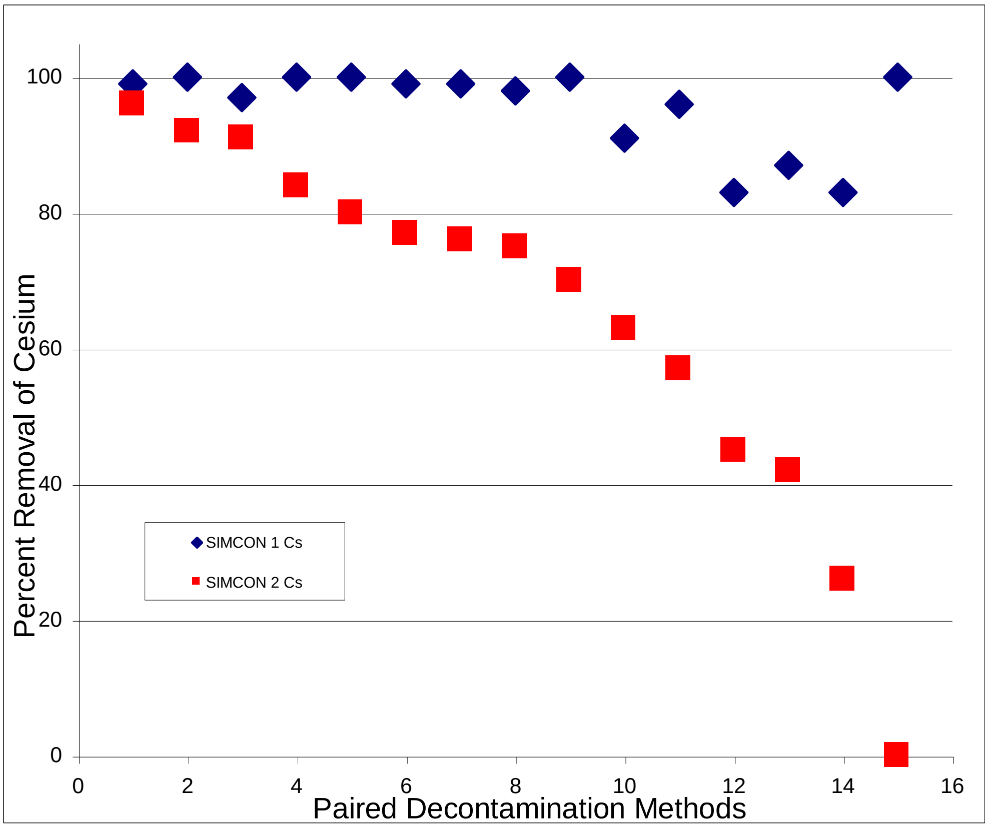


representative of worst-case scenarios. Figure 36 shows a comparison of cesium contamination percent removals for both SIMCON 1 ("loose contamination") and the more tenacious SIMCON 2 ("fixed contamination") when subjected to the range of both chemical and mechanical decontamination techniques presented in Table 11.

As can be seen, the loose contamination-based SIMCON 1 offers much less discrimination than the fixed contamination-based SIMCON 2 system; SIMCON 1 cesium percent removal values ranged from 81% up to 100%, while SIMCON 2 cesium percent removal values provide substantially greater discrimination between decontamination techniques, with a dynamic range of percent removal of between 0% to 95%.

Figure 37 again summarizes the cesium decontamination data of Table 11, this time pairing SIMCON 1 and SIMCON 2 data points where both types of contamination simulation were used in the testing of a particular decontamination method. In all, 15 decontamination methods were assessed for Cs removal using both SIMCON 1 and SIMCON 2

Figure 37. Comparison of cesium SIMCON 1 & 2 results.



In Figure 37, each set of data points (upper, blue dataset for SIMCON 1 and lower, red, dataset for SIMCON 2) represent data from the same method. Data have been arranged in decreasing Cs percent removal for SIMCON 2 results.

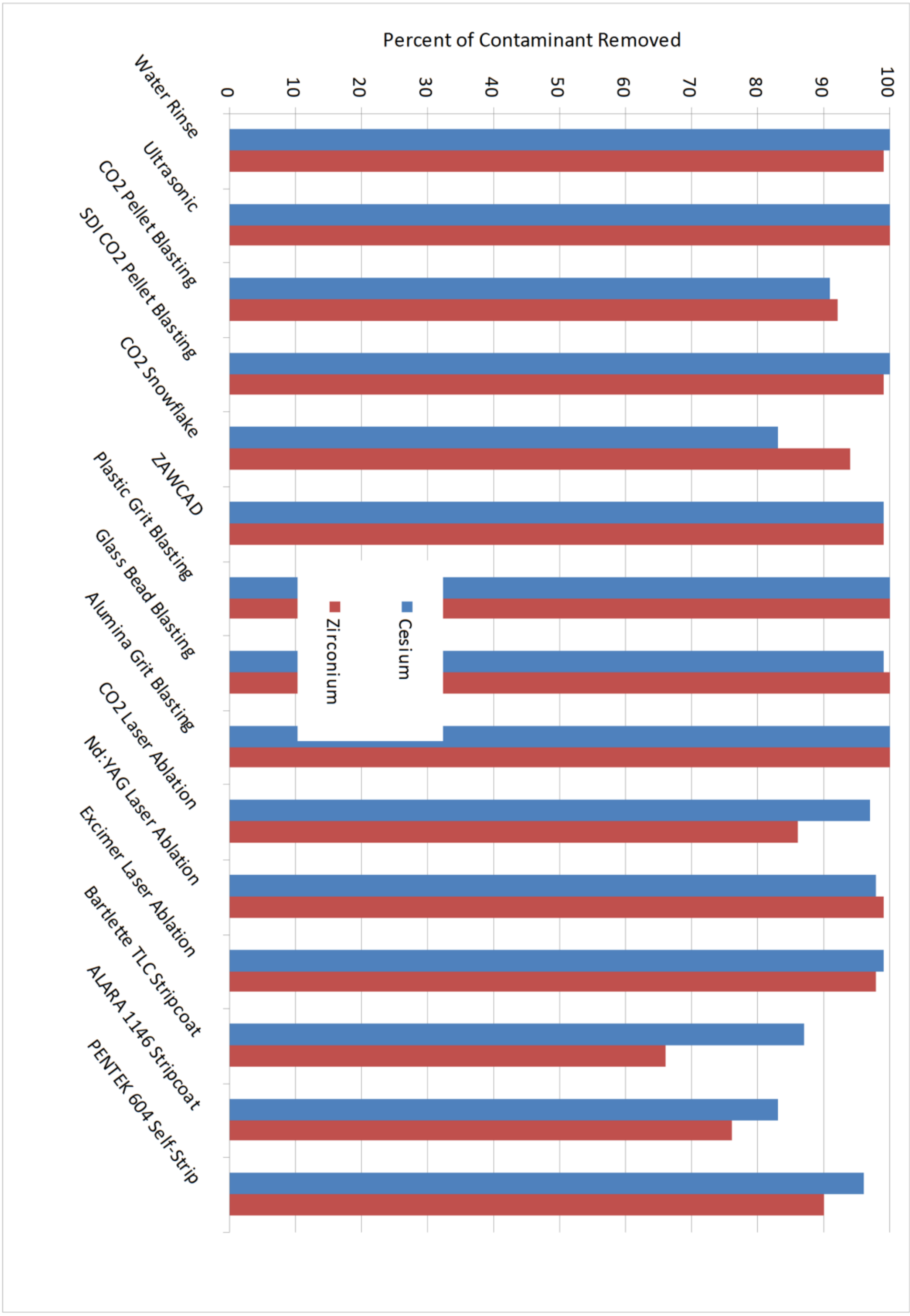
As can be readily seen from Figure 37, most of the decontamination results for cesium SIMCON 1 are in the upper 10% (90% or greater removal). The difference between the most effective methods and the least is very small and allows for minimal quantitative assessment as to decontamination methods are most effective. This issue is resolved in the fixed contamination case (SIMCON 2) where a great deal of differentiation between decontamination methods can be made. These are visually two different sets of data - a qualitative observation in agreement with the quantitative findings of the T-tests presented in Table 11.

4.2.2 Importance of tenacity of contaminant in selecting technologies

Knowing the relative strength of the contamination-fixation mechanism (i.e. fixed or loose) saves time and money during decontamination campaigns. More aggressive decontamination methods, like abrasive blasting, laser ablation and CO_2-pellet blasting are costly and may not be necessary for less tenacious contamination. Less tenacious contamination is typically removed using water or strippable coatings which, typically, are less costly. Understanding how the contamination is held can help reduce wastes and costs.

Simply: understanding the chemical behavior of a particular contamination aids in selecting the decontamination method. When the SIMCON 1 percent removal data for Cs and Zr is plotted alone as in Figure 38 below, it becomes obvious that zirconium was nearly always more tenacious (percent removal is lower) than cesium. The only decontamination method for which cesium was significantly more tenacious than zirconium was the CO_2 snowflake method. This leads to the conclusion that, for simple salts of the cations cesium and zirconium, cesium is typically easier to remove than zirconium. For these simple salt simulants, the difference is likely due simply to the aqueous solubility of the species (cesium salts being more soluble than zirconium salts). Tellingly, the CO_2 snowflake method is a water free method i.e., it is dry (and the snowflakes evaporate) in the same manner as CO_2 pellet blasting.

Figure 38. SIMCON 1 Cesium and Zirconium Results



Grouping the SIMCON data by method families provides further insight into the relative efficacy of different kinds of decontamination methods for different contaminants. Figure 39 shows percent contamination removal data for Cs and Zr, applied via SIMCON 2, grouped by decontamination method family. These families are described by similar decontamination methodologies and have been grouped as follows:

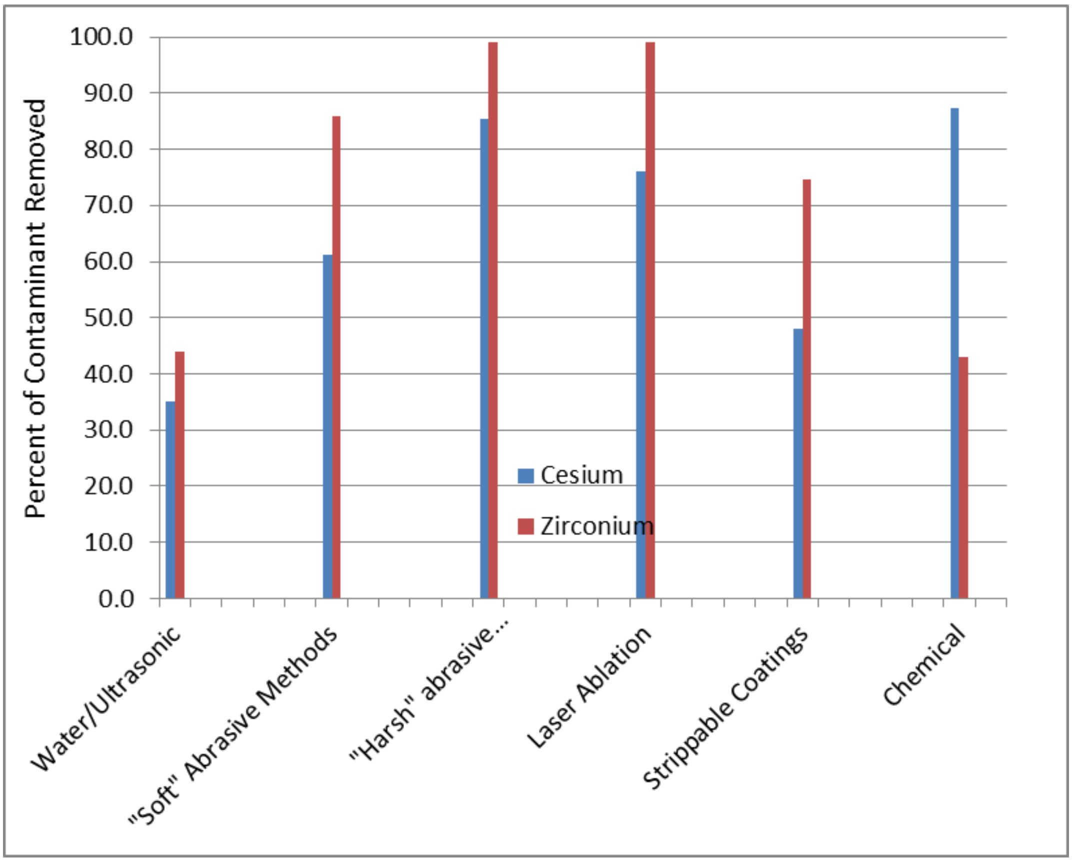
- Application of ultrasonics and water
- "Soft" abrasive methods (CO_2 Pellet Blasting, ZAWCAD (liquid nitrogen blasting), CO_2 Snowflake, Plastic Grit Blasting)
- "Harsh" abrasive methods (Centrifugal CO_2 Blasting, Shaved Dry Ice (SDI) Blasting, Glass Bead Blasting, Alumina Grit Blasting, Dissolvable Grit Blasting)
- Laser ablation (CO_2 Laser, Nd:YAG Laser, Excimer Laser)
- Strippable coatings (e.g. proprietary coatings ALARA 1146, Bartlette TLC, PENTEK 604)

Though the resultant aggregated family group levels of decontamination are not specifically indicative of individual decontamination methods, they can be taken as being representative of the collection of methods described within that family. Being able to group the decontamination methods into a family thus gives a convenient way to describe them in terms of their ***general*** effectiveness and the ***general*** nature of contaminant removal; establishing this relationship gives a simplified means of categorizing decontamination methods akin to the biological-family nomenclature.

Family-to-family differentiation is most obvious for the SIMCON 2 data, where the contamination is more tenacious and the percent removal/decontamination data has a larger dynamic range. The narrower dynamic range notwithstanding, broadly speaking, the same percent removal/decontamination family trends are seen for SIMCON 1 as SIMCON 2.

Specifically, in nearly all cases the zirconium contamination in SIMCON 2 is shown to be much less tenacious than the cesium contaminant. The exceptions to this observation are the simple chemical decontamination methods, for which the fixed Cs appears to be less tenacious than fixed Zr. For all other family groups, the reverse is true; i.e. Zr is less tenacious than Cs. Particularly the results for harsh abrasive methods and those for laser ablation are very similar. These two, principally mechanical decontamination methods, show that mechanical methods are more versatile and less discriminating with respect to chemical nature than chemical methods. Overall these results, for the fixed simulated contamination of SIMCON 2, are in contrast to the general trends observed for the loose simulated contamination of SIMCON 1, wherein Cs was found to be at least as easily removed as Zr for all decontamination methods tested save for the CO_2 snowflake method (see Figure 38). This is discussed in the next section.

Figure 39. SIMCON 2 Method Family Grouping Results

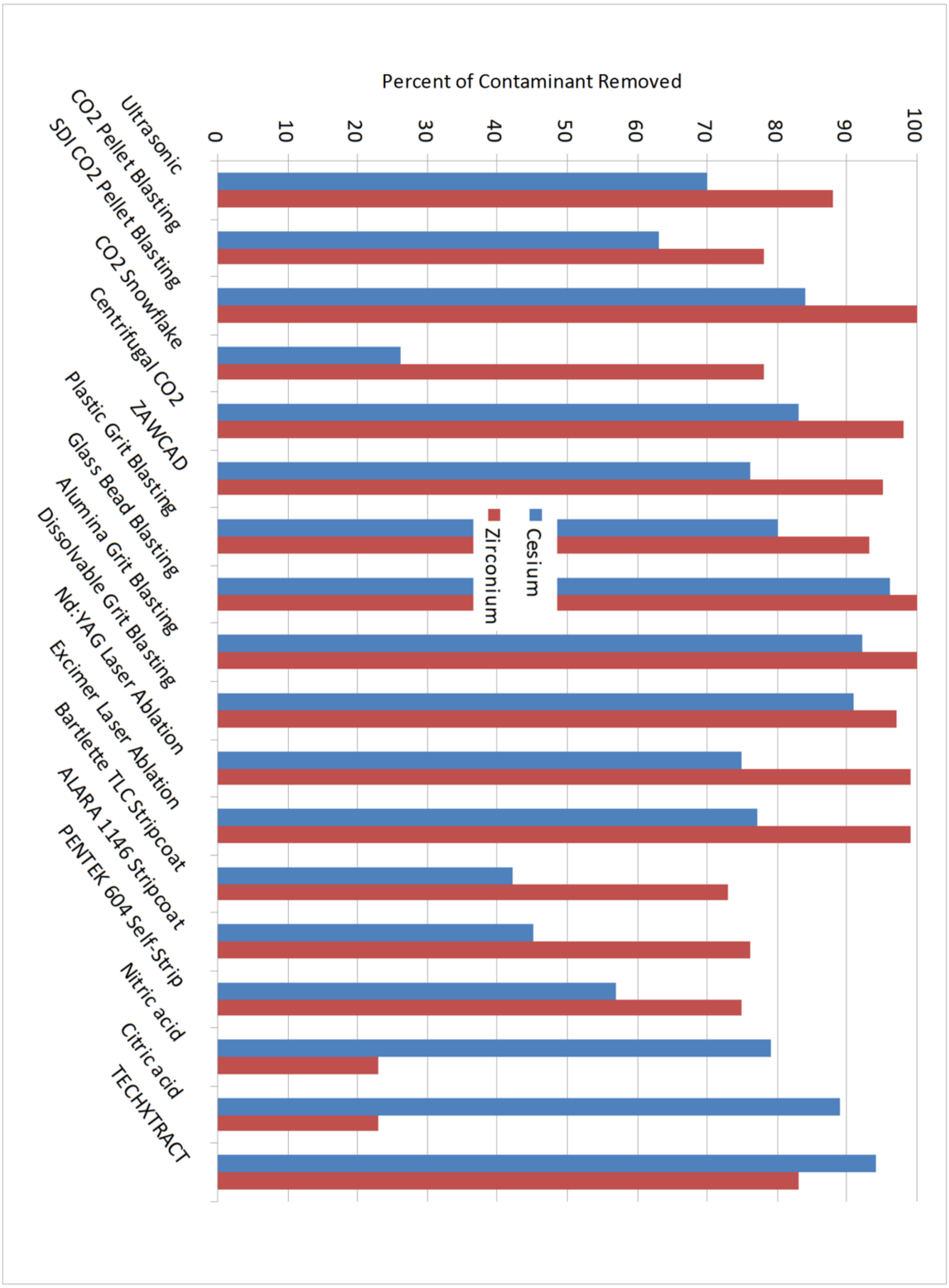


4.2.3 The effects of different contaminants

Again taken from the data of Table 11, Figure 40 shows a graph of percent removal of cesium and zirconium simulant contamination applied using the SIMCON 2 methodology, as a function of decontamination method. This provides some interesting points for discussion, especially when compared to the analogous dataset for SIMCON 1 shown in Figure 38. For the simulated fixed contamination of SIMCON 2 contamination removal results, zirconium is typically easier to remove than cesium. As discussed at the end of the last section, this is in contrast to the general trend shown in Figure 38 for SIMCON 1. In terms of the removal of cesium and zirconium by physical methods (abrasives, ablation, strippable coatings…), this difference can almost certainly be accounted for by the difference in the respective capacities for cesium and zirconium to be incorporated into the passivation oxide layer formed on steel surfaces. The results are consistent with observations of SiO_2 passivation where Cs is incorporated *into* the passivation layer (Grauvogl 1996), whilst Zr forms an insoluble, refractory layer of zirconium oxide/oxyhydroxide *over* the passivation layer surface. Indeed. Zr oxides layers may be applied to stainless steel surfaces during metal finishing processes to provide an additional level of corrosion protection (Bikic 2014). In terms of the physical decontamination methods, such a surface layer of zirconium oxide will be easier to remove than the cesium that has percolated/been incorporated into the underlying steel passivation layer – hence the results shown in Figure 40.

This difference in respective percent removal values for Cs and Zr reverses when non-attritive chemical methods are employed, with the values for cesium typically being twice those of zirconium. Chemical decontamination technologies are significantly less able to remove zirconium from the surface than the cesium. Zirconium oxides have a refractory (ceramic type) nature (hence their use as corrosion protection layers, *vide supra*) and are very difficult to dissolve relative to the highly soluble, alkali metal cesium from the steel surface oxide. The solubility of the cesium oxide (formed at the higher temperature) and the zirconium oxide will be vastly different. The zirconium resides on the surface, while the cesium is distributed throughout the passivation layer. Mechanical methods preferentially remove that

Figure 40. SIMCON 2 Cesium and Zirconium Results



surface coating while chemical methods are less able to dissolve the refractory, surface zirconium. The fact that chemical methods appear to be able to dissolve Cs out of the passivation layer whilst leaving a significant fraction of the upper zirconium oxide film intact suggests that the latter is highly porous – a conclusion that is consistent with the passivation model presented in Section 1.3 (Figure 1).

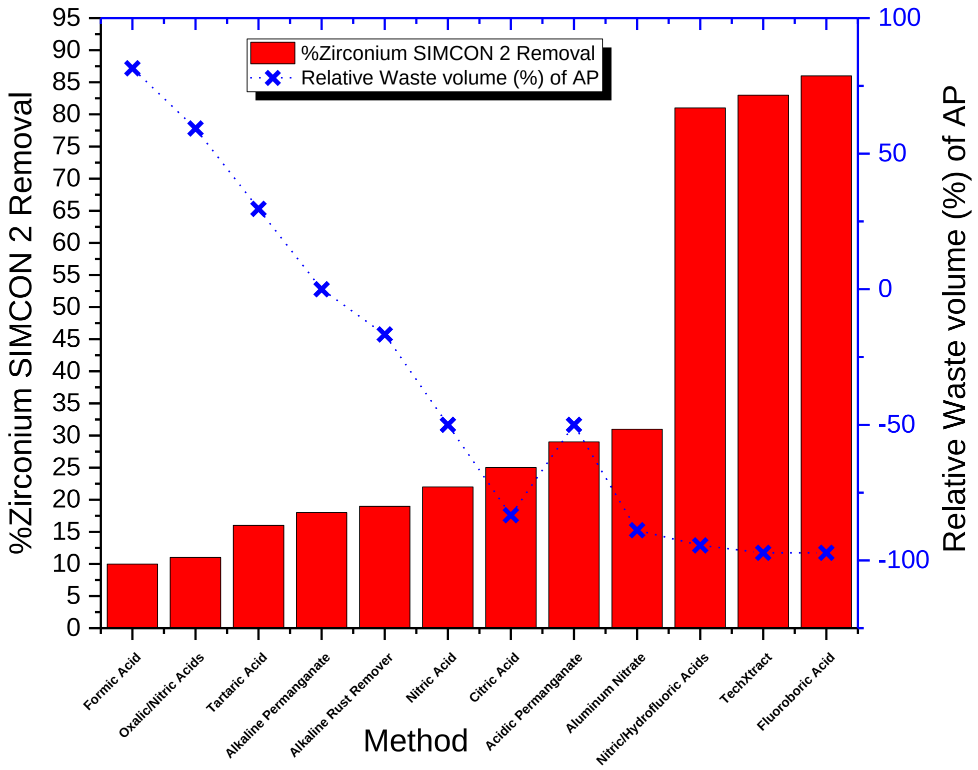
4.2.4 Systematic, integrated approach to decontamination

As well as providing insights into the nature and locus of contamination adherence within loose and fixed contamination simulants, yet another benefit from examining the SIMCON data is that they enable the evaluation of decontamination-methodology effectiveness as part of a systems approach. For example, as discussed above, SIMCON 2 testing for chemical-decontamination methods provides a wealth of data related to percent removal effectiveness; however, additional criteria, such as waste volume produced during decontamination technique deployment, can also be shown alongside these effectiveness values.

One means by which the waste volumes for these chemical methods may be determined without recourse to expensive and radiological hazardous active tests is by using a chemical process modelling program (AspenTech, Bedford, Mass., 01730 USA) that evaluates each solution compatibility with the nuclear-fuel-reprocessing plant (e.g. the bespoke equipment at the ICPP). The volume calculated depends on the chemistry of the solution and the admixtures required for waste processing in that facility; i.e. sodium and potassium salts require an additional 3 volumes of aluminum nitrate to be added prior to calcination (thus changing the waste volume significantly). Since calcination is very expensive, as is all high-level radioactive waste treatment, reducing the volume of waste also results in significant cost savings.

When these two criteria of the SIMCON 2 decontamination techniques (when employed in a nuclear fuel reprocessing facility) are displayed, as shown on Figure 41, it illustrates how decontamination effectiveness, in SIMCON 2 relative terms, can be compared, against a key criteria and how those criteria may be related to each other. In the specific case of Figure 41, the relationship between percent removal and waste volumes arising may be interrogated.

Figure 41. Decontamination effectiveness versus relative waste volumes.



This allows us to conclude not only which method is most effective (highest percent removal), but also which has waste characteristics that will be most beneficial (lowest waste volumes generated). For example, Figure 41 shows that current practices employed in the decontamination of the Idaho Chemical Processing Plant (ICPP) - specifically low effectiveness acidic permanganate and alkaline rust remover - are comparatively high waste generator decontamination methods that should be discontinued. Figure 41 is a visual representation of the trend (moving from the left to the right) towards higher efficiency and lower waste to be achieved with better decontamination techniques. As mentioned, this results in significant cost savings because of the reduction of waste volumes.

Other criteria may also be tested in this kind of systematic analysis. In a 1994 systematic decontamination method analysis at the ICPP, the following criteria were evaluated: costs, ease of safety and environmental compliance, technical performance, operator radiation dose and waste considerations (Demmer 1998). Those primary categories broke into additional levels, with waste considerations subdividing to: recycling potential, waste volume generated and waste compatibility (with existing processing equipment). Each of these criteria was weighted and evaluated for the scenario and method proposed. Figure 41 is just one example of how that could be used in selecting the best option. The systematic approach allows trade-offs to be examined when these key criteria are identified and quantified.

4.2.5 Summary of SIMCON results

The development of the SIMCON 1 & 2 contamination simulant systems and their use in the testing of a range of physical and chemical decontamination techniques allows for the following conclusions to be made:

- The availability of a deliberately designed contamination simulant system allows for the comparative assessment of a wide range of decontamination methods in a common frame of reference on a “level playing field”.

- It is important to have a simulated contamination that has an adequate dynamic range of percent decontamination such that the data allows one to differentiate between different decontamination methods.

- Though somewhat intuitively obvious, the SIMCON methods evaluation unambiguously demonstrated that chemically different contaminants may behave quite differently during a decontamination action. The exact nature of this behavior depends upon the nature of application (loose or fixed) and the decontamination method itself. This characteristic of the fixed nature of the contaminant may be dependent on the substrate, for example, to the degree that the substrate forms a "barrier" layer (i.e. tenacious oxide layer) where contaminants may become lodged at the surface.

- If a wide range of decontamination methods are deployed on a well-designed contamination simulant, comparison of the results of the decontamination tests may provide insight into the mechanism of contamination e.g. how it is held (loose, fixed etc.), where it is held (on the surface, in a protective oxide layer etc.) and so forth. The same insights might be expected to be obtained from real contamination samples if a similarly wide range of decontamination methods are trialed on those samples.

- During the process of decontamination method selection grouping of methods by family type can save time in technique evaluation. Selecting one method from each family group may greatly reduce the evaluation effort.

- Having a "systems approach" which includes important criteria (like secondary waste generation) can improve the evaluation/selection of decontamination methods. In the case of the waste volume vs effectiveness graph, a case can also be made that reduced waste volume also reduces costs; in the case of ICPP high-level radioactive wastes, those reduced waste volumes relate to significant cost savings. This systems approach may be different for each substrate/contaminant and waste processing system, thus the evaluation is going to be specific to that system. While the example was for decontaminating ICPP chemical processes, which preferred the use of chemical flushing, use of non-chemical decontamination methods must also be evaluated for criteria, including possible primary and secondary wastes.

SIMCON is an example of a specific kind of contamination simulation, one that shows the benefits of using multiple metal contaminants in any one simulant, be that a simulant for loose (SIMCON 1) or fixed (SIMCON 2) contamination. It demonstrated the benefits that can be obtained from the well designed contamination simulant as a “level playing field” in the objective and comparative evaluations of the respective efficiencies of a range of decontamination techniques for contaminated metal (steel) surfaces. The Urban RDD system in the next section of the chapter allows us to do similar studies for the decontamination of common mineralogical based construction materials as well as allowing for the development of a new understanding of the chemistry and physical characteristics of contamination of such materials.

4.3 Urban RDD Contamination Simulant Background

Efforts to mitigate the threat of a modern radiological dispersal device (RDD) were initiated by the U.S. Defense Advanced Research Projects Agency (DARPA) in 2003. These efforts were spurred by terrorist's efforts to obtain, not just weapons of mass destruction, but RDDs, weapons of mass disruption. The U.S. Congress responded to the terrorist efforts to employ RDDs by calling for cleanup alternatives. In an effort that paralleled the SIMCON evaluation program, DARPA took up the challenge to identify cleanup alternatives. This effort required a new, robust simulation method to test the effectiveness of emerging decontamination methods for contamination arising from RDD events. DARPA sought a contamination simulant not for process equipment, but for items of high value in highly populated urban environments. The targets were specifically facilities or items of cultural, historical, or social value, such as national monuments or similar structures. Given their ubiquity of use in such urban structures/structures of societal significance, DARPA chose to use marble, granite and concrete as the substrate for these tests.

Dealing with items of cultural/societal importance allows new freedom and opportunities, and provides the resource to develop new and sophisticated decontamination methods. The access to resource is especially important as the development of such novel and advanced methods may be expensive and time consuming – especially if such methods are, ultimately, to be deployed safely in population dense urban environments.

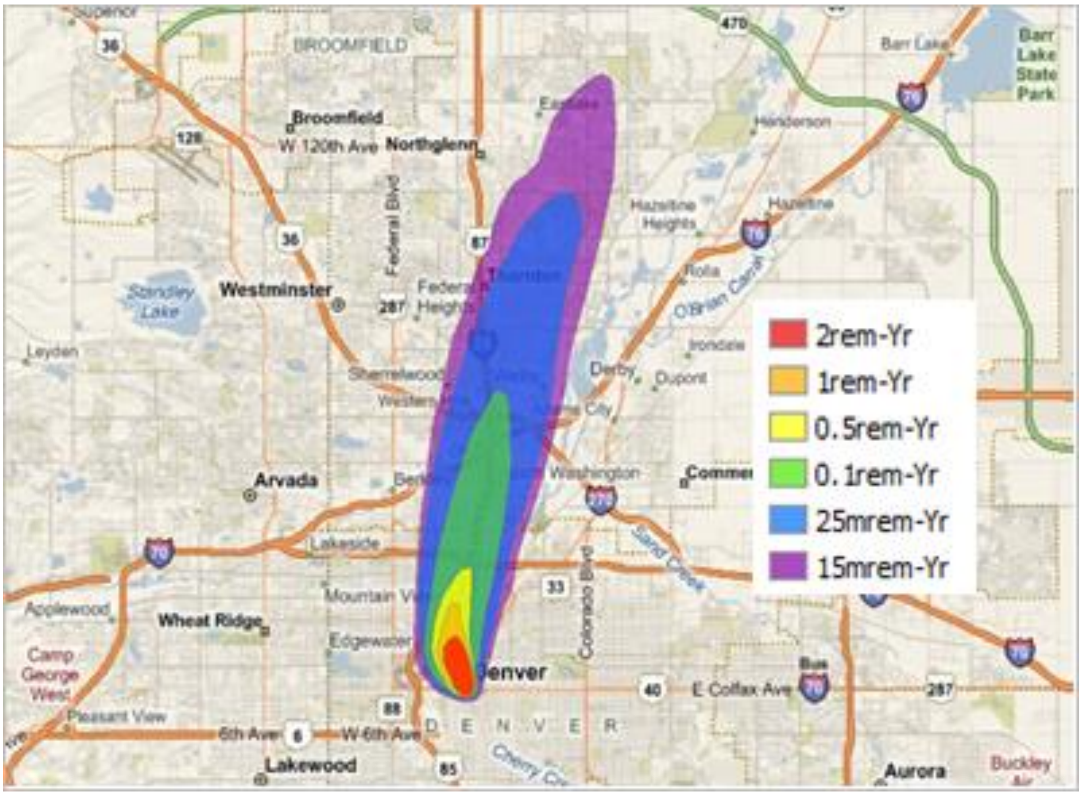
Normally, a decision is made to decontaminate items based on their construction or replacement. If the cost of decontamination approaches the value of a building, then typically a decision is not to decontaminate, but to destroy the building and rebuild. In most instances, the decision is biased towards destroying the building and not attempting decontamination. Again, this can be partially based on the common fear of radiological contamination discussed above; who would really want to risk returning to a building after it was contaminated?

However, with items of societal importance, that financial equation tips strongly in favor of decontamination and return to public use. It is simply not practical, nor prudent to destroy and rebuild historically or culturally important icons. Within the United States, the focus of this study includes items such as the Washington Monument, the Lincoln Memorial (Figure 42), and Constitution Hall. Most of these are clustered in Washington, D.C., New York City, and Philadelphia, but there are buildings of societal importance throughout the United States.

Figure 42. Lincoln Memorial in Washington D.C., USA (Highsmith 2010).

In addition to financial and societal considerations, an important consideration is the disposal of waste. During the Denver, Colorado, Wide Area Response and Recovery Program (WARRP) Workshops in 2012, a strong point was made by U.S. Environmental Protection Agency (EPA) researchers that recovery of the city of Denver by tearing it down and rebuilding could create some 1 million cubic meters of waste accompanied by huge radioactive landfill problems (EPA 600/R-13/124 2013). Visually it is a plume of contamination about 2 km wide and 25 km long (see Figure 43) (EPA 600/R-13/124 2013). The magnitude of this waste is envisioned that, packaged and loaded, it would require a line of dump trucks 6000 km long (stretching from London to Washington D.C., a very difficult drive) to transport this quantity to a landfill (WARRP 2012).

Figure 43. WARRP Denver radiological dose by a dirty bomb example.



Since radioactive waste is not considered a common landfill item in the United States it requires special considerations and the siting of radiological disposal facilities is difficult and fraught with public concern. Using the Denver location of the WARRP workshops as a case study, the following governance questions can be asked, illustrating the political difficulties associated with the disposal of large amounts of such potentially radioactive waste:

- Will that waste be allowed to remain in the State of Colorado, where there is currently no available radioactive-materials disposal facility?
- If that waste is not allowed to remain in Colorado, will it be allowed to travel to the nearest radioactive waste site in Utah, even though Colorado does not belong to the Utah Waste Compact?

This is to say nothing regarding the technical and logistical difficulties associated with large scale contaminated structure demolition, radiological containment and waste packaging. Thus, even tearing down buildings, digging up sidewalks and car parks, and packaging trees, grass, and shrubs has significant consequences.

Decontamination can make a significant contribution to the positive side of that waste-disposal equation. In some cases, only small areas of contamination are found in buildings. Even in the worst contamination cases, only the uppermost layer (typically about 50 μm depth) of surface is contaminated. Most of this layer, and any hot spots, can be removed. Thus, even the decision to destroy or decontaminate buildings that are not of high societal value should be viewed in terms of the impact to a well-understood balance of criteria. If the cost of disposing of large quantities of waste and rebuilding are weighed against the cost of decontaminating and living with an extremely low risk radiological hazard—as most city dwellers already live with small hazards such as air and noise pollution— the balance could easily shift towards decontaminating and managing the hazards.

4.4 Urban RDD Variations in Contaminant Effects

One of the primary objectives of the (first DARPA then US EPA, sponsored) Urban RDD decontamination evaluation program was to determine the behavior of different radionuclide contaminants during decontamination and the effect the chemical nature of those contaminants has on decontamination efficiency. As noted previously during SIMCON evaluations, different contaminants behave differently during decontamination even when applied to the same substrate and treated with the same decontamination technology. This difference in behavior is an age-old concept; it has long been qualitatively understood by decontamination practitioners that the chemical nature of a contaminant has a significant impact on its ability to be removed. For instance, it has been recognized for many years that soluble aqueous contaminants (like mud) are much easier to remove by water based cleaning techniques than organic materials (like pine tar). From a fundamental, less heuristic perspective this may be attributed to the polar/non-polar nature of the contamination, inspiring the prescriptive “Like dissolves like”.

The variety of contaminants used in the U.S. EPA’s Urban RDD tests conducted by this author and reported below, provides a large database for the quantitative comparison of the effect of contaminant chemical properties on decontamination efficiency observed from a range of (i) substrates and (ii) decontamination techniques.

Four different radionuclides, with differing chemical natures, were applied over the course of these tests, the basis for the selection of which is given in the next subsection 4.4.1. While the principle target substrate for these different contaminants is concrete, several other substrates, principally marble, granite and limestone, were also used, each exhibiting a different surface chemistry and/or mineralogy.

The Urban RDD decontamination test procedure is described in section 3.4 and the data is summarized in Tables 12 and 15 (Table 15 is presented later in the text). This data has been analyzed using the data mining techniques described in section 4.1 in order to identify and quantify relationships between the chemical nature of the contaminant, the physical characteristics of the substrate and the decontamination technologies employed in contaminant removal. This data has also been analyzed using the Tableau data-mining visualization software, also described in section 4.1. Figures 44 and 45 below show examples of how the data of Tables 12 and 15 may be displayed in the data-mining dashboard format. Figure 44 shows a “screen shot” of the box-and-whisker data mining “dashboard” diagram for the entire data set whilst Figure 45 shows a similar diagram but restricted to data obtained from decontamination experiments conducted on a single substrate i.e. concrete. Detailed interpretation of these figures, as well as the source data of Tables 12 and 15 will form the basis of sub-sections 4.4.2 - 4.4.4. The next subsection is concerned with the basis for section of the contaminants studies, as well as summarizing some of their key radiological and chemical properties.

Table 12. Urban RDD Data Organized by Contaminant.

Contaminant	Method Used	Substrate	Year Performed	Average % Removal
Cesium-137	CS Unitech Sander	Concrete	2009	53.7
Cesium-137	River Tech Water Jet	Concrete	2009	36.4
Cesium-137	Empire Blast Abrasive	Concrete	2009	96.7
Cesium-137	Diamond Wheel Grinder	Concrete	2009	91.6
Cesium-137	Wire Wheel Grinder	Concrete	2009	37.6
Cesium-137	DeconGel 1101	Concrete	2010	45.3
Cesium-137	DeconGel 1108	Concrete	2010	66.6
Cesium-137	RAD-Release II	Concrete	2010	85.4
Cesium-137	Rad-Release I	Concrete	2010	71.0
Cesium-137	RDS Liquid	Concrete	2010	52.5
Cesium-137	Argonne Super Gel	Concrete	2010	71.4
Cesium-137	INTEK ND-75	Concrete	2010	44.1
Cesium-137	INTEK ND-600	Concrete	2010	57.3
Cesium-137	MSDF	Aluminum	2011	92.2
Cesium-137	SDF	Aluminum	2011	90.5
Cesium-137	Water	Aluminum	2011	59.3
Cesium-137	SDF	Concrete	2012	51.4
Cesium-137	MSDF	Concrete	2012	61.8
Cesium-137	Water	Concrete	2012	6.1
Cesium-137	Argonne Super Gel	Concrete	2012	75.2

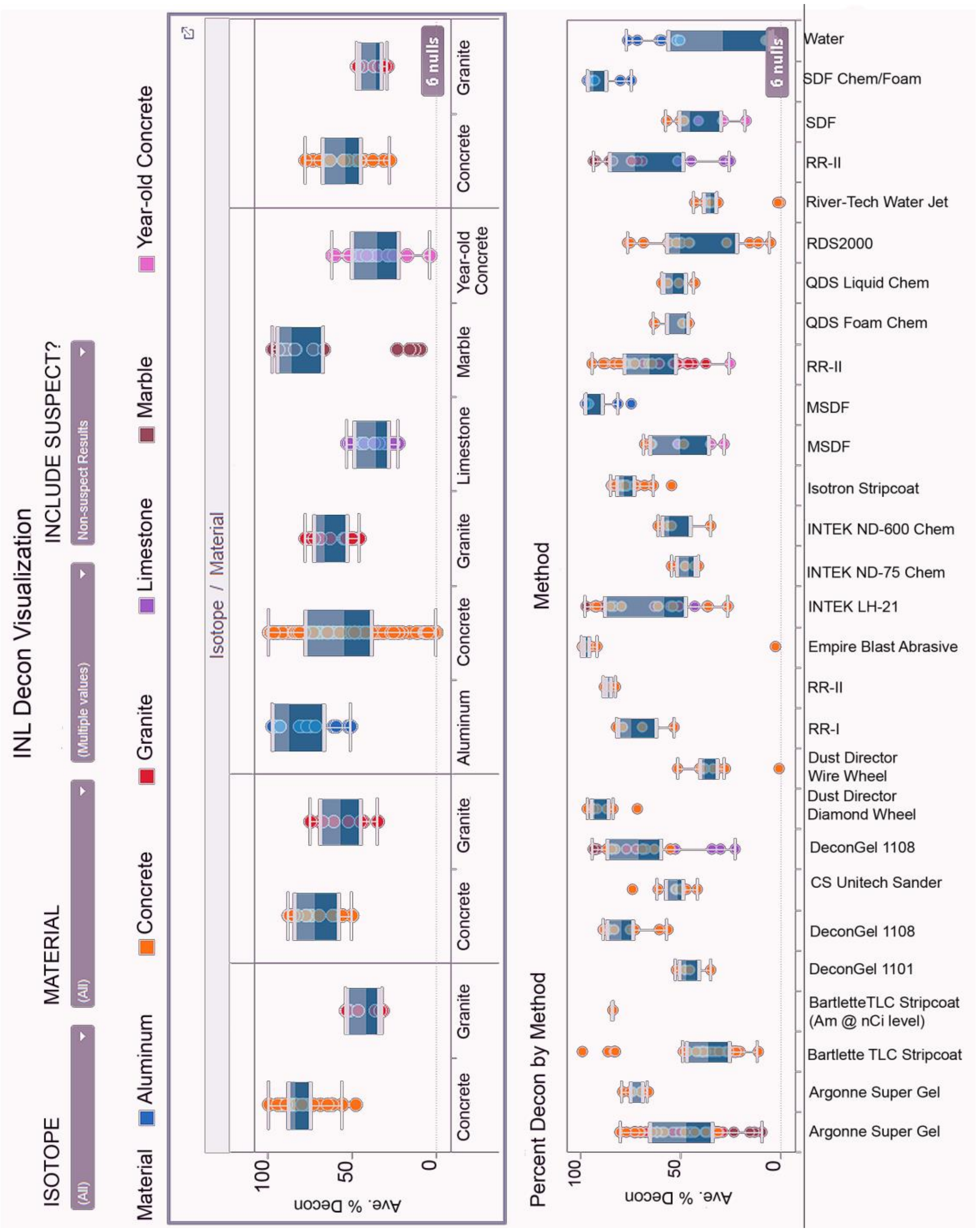
Contaminant	Method Used	Substrate	Year Performed	Average % Removal
Cesium-137	RAD-Release II	Concrete	2012	74.2
Cesium-137	SDF	Year Old Concrete	2012	29.2
Cesium-137	MSDF	Year Old Concrete	2012	37.5
Cesium-137	Water	Year Old Concrete	2012	4.0
Cesium-137	Argonne Super Gel	Year Old Concrete	2012	45.6
Cesium-137	RAD-Release II	Year Old Concrete	2012	49.6
Cesium-137	DeconGel 1108	Marble	2013	93.1
Cesium-137	DeconGel 1108	Granite	2013	72.0
Cesium-137	DeconGel 1108	Limestone	2013	35.1
Cesium-137	RAD-Release II	Marble	2013	89.0
Cesium-137	RAD-Release II	Granite	2013	72.4
Cesium-137	RAD-Release II	Limestone	2013	37.6
Cesium-137	Argonne Super Gel	Marble	2013	71.0
Cesium-137	Argonne Super Gel	Granite	2013	49.9
Cesium-137	Argonne Super Gel	Limestone	2013	35.1
Cesium-137	INTEK LH-21	Marble	2013	90.6
Cesium-137	INTEK LH-21	Granite	2013	55.8
Cesium-137	INTEK LH-21	Limestone	2013	39.4
Cesium-137	INTEK LH-21	Concrete	2013	44.7
Cesium-137	RDS-2000	Concrete	2013	10.8
Amercium-243	RAD-Release II	Concrete	2012	83.6
Amercium-243	RAD-Release II	Granite	2012	51.2
Amercium-243	Argonne Super Gel	Concrete	2012	62.8
Amercium-243	Argonne Super Gel	Granite	2012	33.7
Americium-243	Bartlette TLC Stripcoat	Concrete	2011	87.2
Americium-243	DeconGel 1108	Concrete	2011	86.3
Americium-243	INTEK LH-21	Concrete	2013	87.4
Americium-243	RDS-2000	Concrete	2013	69.1
Cobalt-60	RAD-Release II	Concrete	2012	79.2
Cobalt-60	RAD-Release II	Granite	2012	64.2
Cobalt-60	Argonne Super Gel	Concrete	2012	62.4
Cobalt-60	Argonne Super Gel	Granite	2012	55.1
Cobalt-60	DeconGel 1108	Concrete	2013	84.9
Cobalt-60	RDS-2000	Concrete	2013	51.6
Strontium-85	RAD-Release II	Concrete	2012	70.3
Strontium-85	RAD-Release II	Granite	2012	43.6
Strontium-85	Argonne Super Gel	Concrete	2012	39.9
Strontium-85	Argonne Super Gel	Granite	2012	33.7
Strontium-85	DeconGel 1108	Concrete	2013	63.9

Contaminant	Method Used	Substrate	Year Performed	Average % Removal
Strontium-85	RDS-2000	Concrete	2013	42.7

4.4.1 Urban RDD Contaminant Selection

The most common contaminant utilized in the decontamination evaluations shown in Table 12 is ^{137}Cs. A principle byproduct of the nuclear industry, its persistence owes to its long half-life (30.17 years) and ease of detection as an emitter of gamma radiation with a mean energy of 662 keV (from its daughter ^{137m}Ba). Other fission products are also present after nuclear reactions, but, after 25 years, the typical lifetime of a nuclear-facility, one of the most dominant radioisotopes is ^{137}Cs. Radioactive cesium has also found a place in the commercial industry; it is utilized primarily because of its strong, relatively long-lived gamma energy as an irradiator for food and equipment sterilization, well logging, thickness gauges, and cancer treatment, (both in teleradiation and bracheotherepy). The likelihood that ^{137}Cs may be potential cleanup target, either by accident or by terrorist intention, is high because of its widespread use in diverse fields of application and thus its relative availability. One source estimates that there are over 50 million curies of ^{137}Cs in prepared sources at US DOE sites alone (Okumura 2003).

Figure 44, INL decontamination data mining dashboard


INL Decon Visualization

ISOTOPE (All)

MATERIAL (All)

(Multiple values)

INCLUDE SUSPECT? Non-suspect Results

Another characteristic of cesium that leads us to expect it to be a major decontamination environmental clean-up problem is its high chemical mobility; cesium compounds are highly soluble in aqueous solutions and thus are not easily restrained within water flows/water courses. Because of these characteristics, they may travel significant distances from their original contamination point (via water borne seepage for instance). Further, because of its aqueous mobility, cesium can penetrate easily into porous surfaces typical of urban substrates – potentially becoming fixed by ion exchange at sites within those substrates. Its intractability and ubiquitous presence in the nuclear industry thus make it a perfect tenacious radionuclide to be used in an RDD. Table 13 lists, in no particular order, other suspected radionuclides identified for RDD purposes (Peterson 2007). Four species on this list, namely ^{137}Cs, ^{60}Co, ^{90}Sr and ^{241}Am, have been included in the RDD tests described in this thesis, results given in Table 12 above.

Table 13. Likely radionuclides used in RDDs.

Radionuclide	Isotope Half-life (years)	Specific Activity (Ci/g)	Decay Mode	Radiation Energy (MeV)		
				Alpha	Beta	Gamma
Americium-241	430	3.5	α	5.5	0.052	0.033
Californium-252	2.6	540	α (SF, EC)	5.9	0.0056	0.0012
Cesium-137	30	88	β, IT	-	0.19, 0.065	0.6
Cobalt-60	5.3	1,100	β	-	0.097	2.5
Iridium-192	0.2 (74 d)	9,200	β, EC	-	0.22	0.82
Plutonium-238	88	17	α	5.5	0.011	0.0018
Polonium-210	0.4 (140 d)	4,500	α	5.3	-	-
Radium-226	1,600	1	α	4.8	0.0036	0.0067
Strontium-90	29	140	β	-	0.20, 0.94	-

SF = spontaneous fission; IT = isomeric transition; EC = electron capture. A hyphen means not applicable. The radiation energies for cesium-137 include the contributions of barium-137 metastable(Ba-137m), and those for strontium-90 include the contributions of yttrium-90. (data reproduced from Peterson 2007).

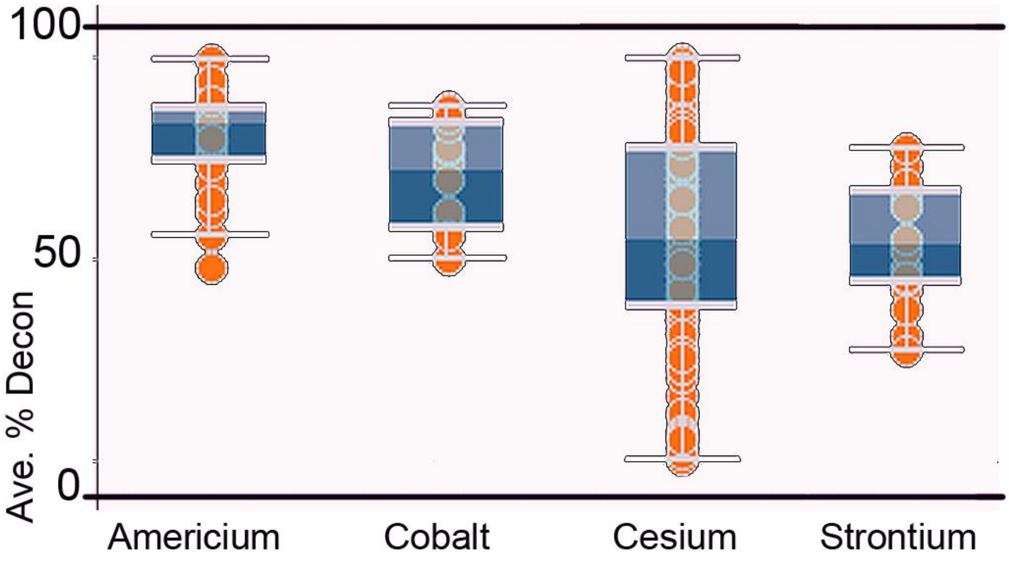
For the ^{137}Cs tests, a salt solution (CsCl) is prepared in a slightly acidic (very dilute nitric acid, ~pH 1.5) matrix. The preparation and application technique used is described in Section 3.3. In use, the contaminant solution rapidly becomes neutralized upon application to an urban substrate surface, mostly concrete with a high matrix pH (pH 10.7). In some cases, the neutralization of the cesium solution is accompanied by foaming and heat due to the liberation of carbon dioxide during neutralization of the carbonate by the slightly acidic contaminant. The cesium ion has an alkali character and is highly soluble across the pH range and thus it can readily penetrate into the surface of the porous substrates typical of urban structures. Due to its positive charge and associated cationic character, this penetration continues until the Cs^+ ions become strongly adhered to cation-exchange sites. This mechanism of penetration and adherence is representative of how the substrate may interact with the contaminant, making Cs^+ a good choice to study in a simulant system.

The tests reported in Table 12 and summarized in box-and-whisker notation in Figure 44 use radionuclides that give a strong gamma signature. This is due to the ease of detecting gamma-energy radionuclides. Beta- and alpha-energy radionuclides are more difficult to quantify and are more easily shielded by thin sections of the surface, dirt or substrate oxide material that might be loose on the surface which may give rise to less-accurate decontamination results. While abundant ^{137}Cs and ^{60}Co are strong gamma emitters, the most abundant strontium and americium radionuclides, ^{90}Sr and ^{241}Am, do not have strong gamma-energy emissions. Thus, in the tests reported here, the ^{90}Sr and ^{241}Am were replaced with ^{85}Sr and ^{243}Am, which are chemically identical but have strong gamma lines and are thus easier to detect and quantify.

4.4.2 Contaminant Removal Relationships

A box-and-whisker diagram summarizing and comparing the decontamination efficiencies for the removal of the radionuclide species studied from concrete is shown in Figure 45. It shows the relative relationship between americium, cobalt, cesium and strontium over some 64 different tests, using three different chemical decontamination methodologies - Rad Release 2, Argonne Super Gel, and DeconGel. The main observation is that the data are well grouped for each radionuclide and they exhibit a trend in median % removal, from high to low, from americium to cobalt to cesium to strontium. These data begin to paint a picture of the tenacity of these different chemical species relative to each other. It suggests a difference in the chemical nature of the radionuclide itself as a major factor in decontamination results.

Figure 45. Tableau analysis of decontamination results from concrete vs radioactive species.



4.4.3 Contaminant Behavior on Alkaline Surfaces

A range of physico-chemical characteristics influence whether a particular radiochemical contaminant is more tenacious (less able to be removed) than others. Two of the contaminants studied in Figure 45, Cs^+, Sr^{2+}, are fairly mobile, cationic species and thus may penetrate significant distances into the porous materials typical of urban structures. However, amphoteric species, such as americium, may become less soluble in basic media. Because of the abundance of calcium hydroxide and calcium carbonate in concrete, the pH of the surface of concrete is very alkaline (i.e. has high pH) (Wellman 2007). Thus, while the Am(III) contaminant simulant may be applied as a 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 the surface concrete. In order to better illustrate the difference in behavior on alkaline concrete, Figure 46, shows a comparison between the E_h–pH speciation, or Pourbaix diagrams for the cesium-H_2O and americium- H_2O systems.

A clear observation from these Pourbaix diagrams is the dependence of americium speciation on pH. The vertical (*y*) axis of the 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, labeled "a", the H_2O of the aqueous solution is reduced, leading to hydrogen evolution via reduction of the water. Above the upper dashed line, labeled "b", the H_2O of the aqueous system is oxidized, leading to oxygen evolution, due to the oxidation of water. Within the two dashed lines (a and b) lie the solution condition for an aqueous system which are of relevance to the RDD simulant decontamination test results shown in Table 12.

From low to high pH, the cesium (left pane) and americium (right pane) systems shown in Figure 45 exhibit vastly different chemistries. The cesium ion remains unchanged in its character throughout that 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, the americium cation, Am^{3+}, either hydrolyzes to form $Am(OH)_3$ or hydrolyzes and oxidizes to form $Am(OH)_4$ at higher pH 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; i.e. as pH increases the solubility of americium is greatly decreased.

The two other principle chemical species included in the tests described in Table 12 have similar character to the two just reviewed. Figure 47 shows the Pourbaix diagrams for cobalt (left pane) and strontium (right pane). Examining these two diagrams reveals that cobalt undergoes analogous chemical speciation changes to the americium; at high pH it forms insoluble $Co(OH)_2$ or $Co(OH)_3$ species, again, depending on the redox conditions of the system. However, in contrast to americium, at very high pH>13, the soluble anion $HCoO_2^-$ may be formed; i..e., cobalt solubility with pH decreases with increasing pH, goes through a minimum, then increases again from pH 7-13. In contrast, strontium (like cesium) has virtually no change in its speciation, maintaining as a double positive charge cation Sr^{2+} up to pH 14, so retaining soluble alkali-earth character to a very high pH.

Figure 46. Comparison of Pourbaix diagrams for cesium and americium (Pourbaix 1974).

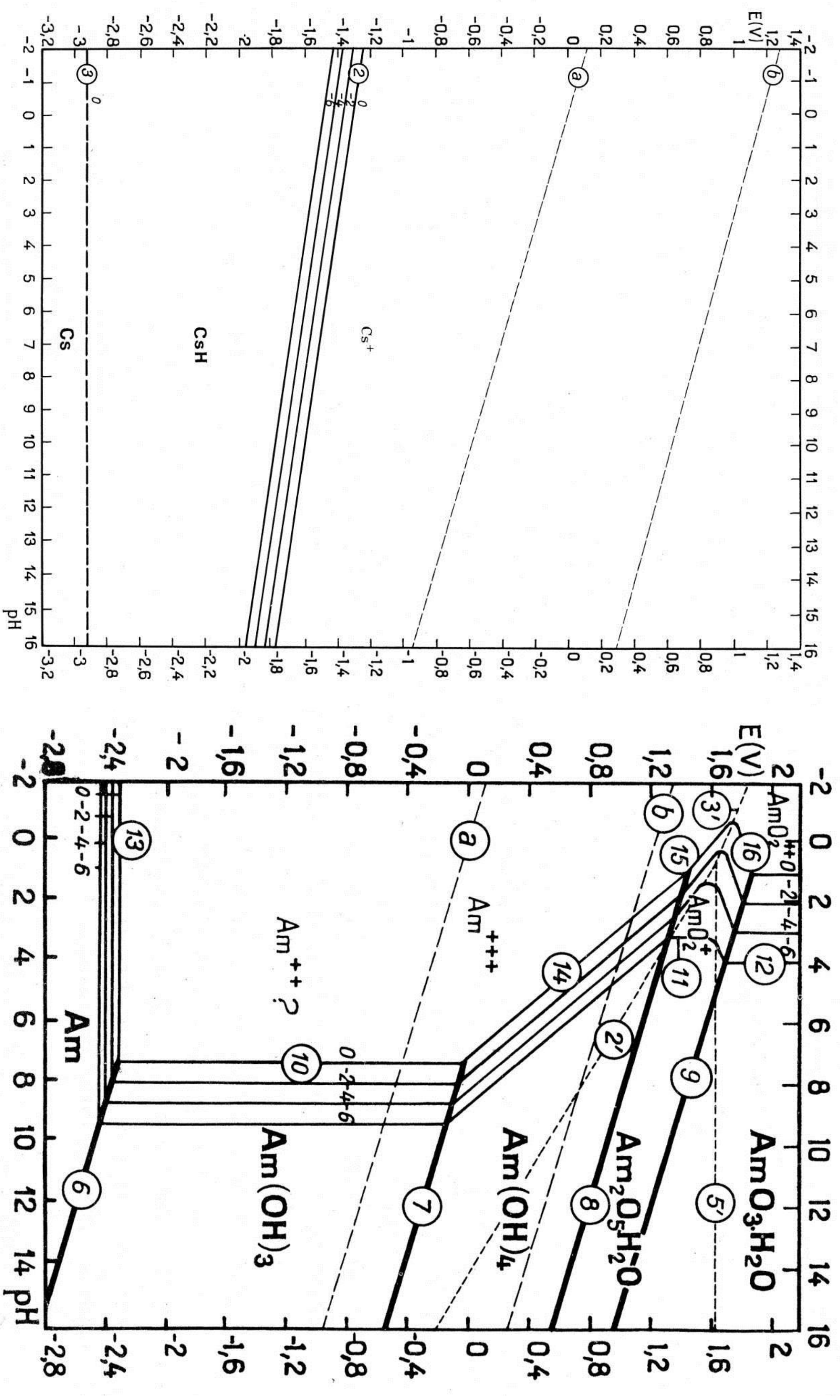
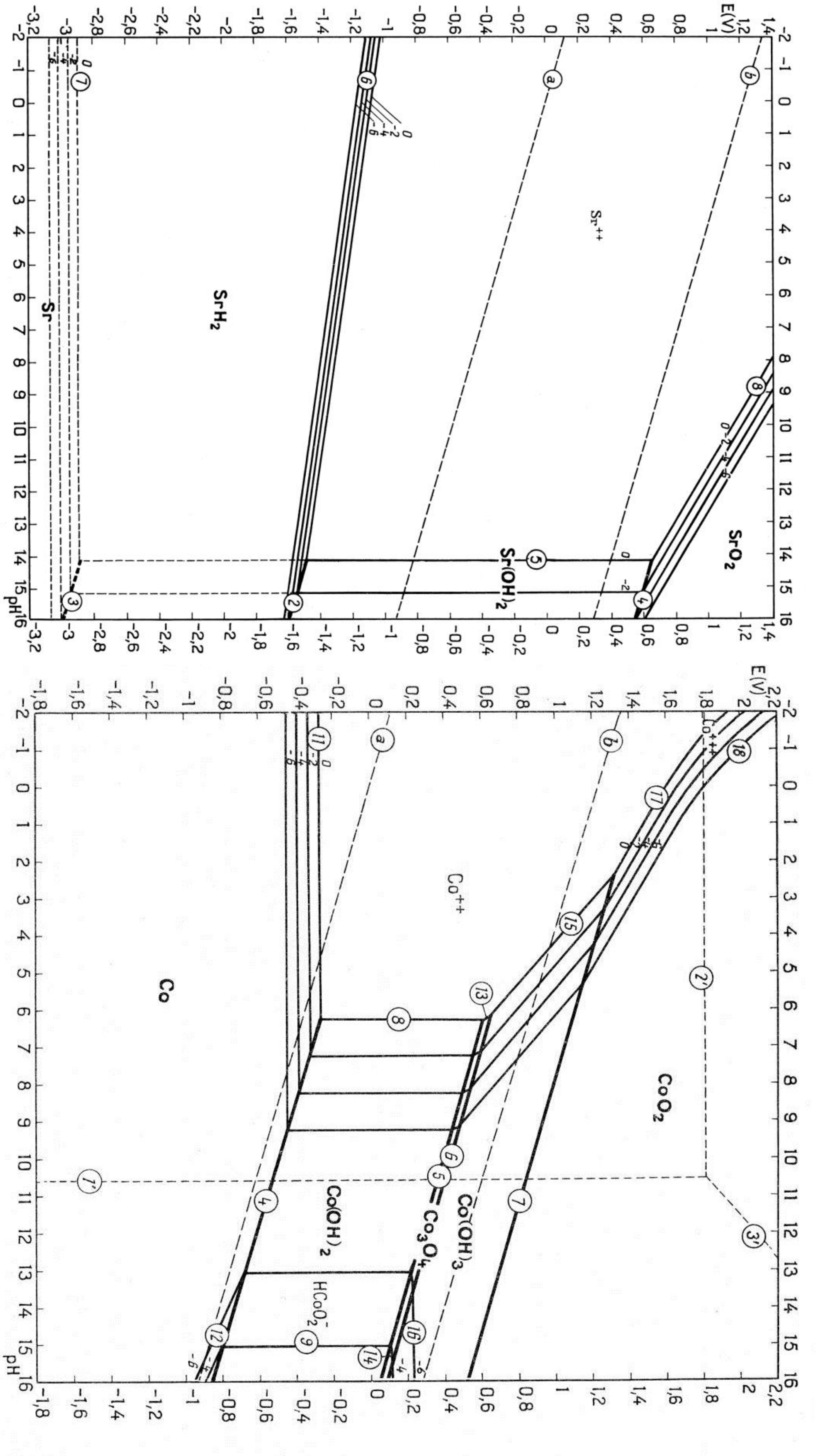


Figure 47. Cobalt and strontium Pourbaix diagrams (Pourbaix 1974).



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 diagram figures. The two alkali/alkali earth metals, cesium and strontium, have high solubility across the pH range whereas cobalt and americium have hydroxide species and oxy-hydroxides forming at even moderate pH levels, in some cases down to pH 4. The solubility of these hydroxy species under alkaline conditions is low, as described by the solubility-product data shown in Table 14 below. 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, but precipitate upon contact with the basic surface of the substrate.

This characteristic of surface pH will be discussed in more detail in the context of the characteristics of the substrate later in this chapter. However, it is clear that chemical solubility of a specific radionuclide strongly influences its tenacity as it relates to the percent of contaminant removal; tenacious contaminants exhibit low percentage removals. That the more soluble radionuclides exhibit greater tenacity during the application of surface decontamination techniques is indicative of the role played by into-the-substrate penetration in determining ease of contaminant removal.

To be clear, it appears from Figure 45 that the low solubility of Am and Co at basic pH causes these metals to precipitate at the alkaline surface of the concrete, allowing for their highly efficient removal by a range of chemical decontamination techniques. In contrast, the high solubility of Cs and Sr across the pH range renders these metal ions mobile on concrete – especially with respect to diffusion into the substrate bulk, most likely via interconnected pores. That these nuclides have penetrated the concrete renders them more difficult to remove by any surface-based decontamination technique. Once again, this conclusion is consistent with the observations of Figures 46 and 47.

4.4.4 Other Physical/Chemical Characteristics Effecting Decontamination

The dependence of decontamination technique efficacy described above indicates that individual radionuclide tenacity must be viewed in terms of its interactions with a given substrate. Historically, the characteristics given in Table 14 below have been related to cation / substrate interaction and it is instructive to consider these relationships in more detail. The decontamination results listed in Table 14, are the average (the simple mean) of results of just three comparable chemical decontamination methods: DeconGel 1108, Rad Release II and Argon Super Gel. Some of the properties listed in Table 14 – specifically ion radius, solubility product and ionic potential - will exert a stronger influence than others on ion-substrate interactions and thus tenacity; correlating the properties described in Table 14 with the decontamination data of Table 12 and Figure 44 will allow for those properties most relevant to contaminant tenacity to be identified.

Table 14. Comparison of radionuclides decontamination from concrete versus some physical characteristics of those radionuclide.

Radionuclide	Decon Result	Ionic Radius[1]	Solubility Product (k_{sp})(~pH 8)	Ionic Potential/nm^{-1}
Americium	75%	180 X 10^{-10} cm	[2] 3.2×10^{-18} mol^4 dm^{-12} (as $Am(OH)_3$)	16.7
Cobalt	70%	126 X 10^{-10} cm	[3] 5.9×10^{-15} mol^3 dm^{-9} (as $Co(OH)_2$)	15.9
Cesium	73%	244 X 10^{-10} cm	[4] 1.2×10^2 mol^2 dm^{-6} (as CsOH)	4.1
Strontium	54%	195 X 10^{-10} cm	[5] 6.4×10^{-3} Mol^3 dm^{-9} (as $Sr(OH)_2$)	10.3

[1] Cordero, et al. 2008, [2] Rai, Strickert, Moore and Ryan 1983, [3] Generalic 2015, [4] Etacude 2015, [5] Krishnan 2007

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 so-called constant partition coefficient K_d (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), and resistance to contaminant removal, particularly for Cs and Sr, when in contact with natural mineral substrates and urban surfaces such as concrete (Bayulken, et al, 2011, Real et al. 2001). The parameter K_d is in fact a convolution of two more fundamental properties of any given cation-substrate system – the strength of adsorption, most usually expressed in the form of an equilibrium constant such as that used in the Langmuir adsorption isotherm equation, and the number/concentration of sites available for adsorption, most usually expressed in the form of a cation exchange capacity, CEC.

A more detailed consideration of mechanisms of adsorption, and particularly their associated strengths is informative here. Adsorption onto mineral substrates such as those from which concrete is constituted can take place via 3 mechanisms:

- **By inner sphere complex formation**: an inner-sphere surface complex is one in which the adsorbing metal is in direct contact with the adsorbent surface and lies within the Stern Layer, i.e. the metal ion has become dehydrated either immediately before or during the sorption event. The tendency for a cation to form an inner-sphere complex has been seen to increase with increasing cation charge (valence) and can be related to its ionic potential – defined as ion charge divided by its ionic radius (Sposito, 1984).

- **By outer sphere complex formation**: an outer-sphere surface complex is one in which the adsorbing metal ion has at least 1 water molecule between the cation and the adsorbent surface/charged surface functional group i.e. the cation has not been fully dehydrated during binding, retaining its innermost hydration sphere.

- **Within the diffuse ion swarm**: If a solvated ion does not form a complex with a charged surface functional group but instead neutralizes surface charge only in a delocalized sense, the ion is said to be adsorbed in the diffusion swarm, and these ions lie in a region of the electrical double layer called the diffuse layer.

The diffuse-ion swarm and the outer-sphere surface adsorption mechanisms involve exclusively ionic bonding, whereas inner-sphere complex mechanisms are likely to involve ionic, as well as covalent, bonding.

Generally, the relative affinity of a contaminant to sorb onto a mineral surface, and thus its strength of adsorption, will increase with its tendency to form inner-sphere surface complexes. As described above, the tendency to form inner sphere complexes is related to a cation's ionic potential. This is defined as the cation's charge to radius ratio and is essentially a measure of charge density. Cations with low ionic potentials/charge densities are not strongly hydrated and can easily shed their waters of hydration to participate in inner-sphere surface complexation and thus strong adsorption. Cations with high ionic potentials are strongly hydrated and do not surrender their waters of hydration easily. They are therefore more likely to form outer-sphere surface complexes. Because inner-sphere complexes are more strongly held than outer-sphere complexes, we would expect cations with low ionic potentials (those more weakly hydrated) to sorb more strongly to surfaces than cations with high ionic potentials.

Based on these considerations and laboratory observations, the relative-adsorption affinity of metals has been described as follows (Sposito 1989, EPA/402/R-99/004A 1999):

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

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

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

$Fe^{3+} > Fe^{2+} > Fe^{+}$

In experiments designed to investigate the removal/extraction of adsorbed cations from clay minerals, the same researchers found that the pH of the extraction was important in determining efficacy of cation desorption. Typically, extractions conducted under acid conditions were found to be most effective in the removal of alkali metal cations – most likely facilitated by proton / cation exchange at individual inner sphere / outer sphere sorption sites during the cation extraction process.

However, we are not studying sorption onto clay minerals: we are studying sorption onto concrete substrates – and whilst 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 12 and Figure 45. Table 14 shows the ionic potential values for the radionuclides used in these tests, the order of potential being:

$Am^{3+} > Co^{2+} > Sr^{2+} > Cs^{+}$

The removal percentages (decontamination efficiencies) from concrete for the contaminants listed in Table 14 follow the following order:

$Am^{3+} > Co^{2+} > Cs^{+} > Sr^{2+}$

This shows a different order than might be expected on the basis of the contaminants ionic potentials – especially with respect to the position of Cs in the rank order - and indicates that other factors, in particular chemical solubility and precipitation at higher pH discussed in the immediately preceding section, exert a stronger influence than ionic potential in controlling in the removal of these radionuclides.

Due to their solubility behavior at high pH, americium and cobalt are perhaps the worst examples to use to illustrate a relationship between high charge density/ionic potential and its retention in concrete substrates. Americium's preferred oxidation state in solution is +3; further, as previously shown in Figure 46, the oxidation state can vary greatly depending on the pH of the solution (or, in this case, the surface). In the tests summarized in Table 12, americium solution is applied to a surface as a slightly acidic contaminant in dilute nitric acid, thus assuring that the americium is initially presented as Am^{3+}. But, as shown in Figure 46 and discussed in detail in section 4.4.3, the Am^{3+} hydrolyzes at the alkaline concrete surface, precipitating as americium hydroxide. As indicated in Table 14, this has a low solubility product of 3.2×10^{-18} mol^4 dm^{-12} thus hindering significant ingress by Am(III) species into the concrete interior. Cobalt's behavior is broadly similar with any differences being accounted for by cobalt having a +2 charge rather than americium's +3 charge with a consequently higher solubility product of 5.9×10^{-15} mol^3 dm^{-9}. To elaborate: as for americium, this insoluble character tends toward precipitation of Co (II) on the surface of the alkaline concrete, again preventing its penetration into the bulk of the surface. Again as described above, such at- or near-surface precipitation would lead to an ease of removal for both the americium and cobalt contaminants because they do not travel into the bulk of the substrate, and precipitate on the surface. From Table 14, it can be seen that cobalt exhibits a lower % removal than americium; whilst this is consistent with the trend in ionic potentials, it is most likely due to its slightly higher solubility product at pH 8 (see Table 14) and its higher absolute solubility at $pH \geq 14$ where it can form soluble $HCoO_2^-$ anion, a state hitherto unreported for americium in that pH range. These solubility behavior differences (compared to Am) allow for greater permeation/penetration of the Co(II) cation into the concrete bulk before precipitation and thus result in a more tenacious contamination.

This consideration of the precipitation reactions available to Am(III) and Co(II) at the alkaline surface of concrete is consistent with the americium and cobalt decontamination testing results summarized in Tables 12 and 15 and Figure 44 where the decontamination levels for americium are unusually high given the expected cation-induced interaction with concrete. As well, this description of Am and Co hydrolytic chemistry at pH>8 illustrates the limitation of applying simple ionic potential-based analyses to material substrates that may induce chemical changes in the adsorbing species. In the case of the clay substrates studied by Sposito et al (see above and Sposito 1989, EPA/402/R-99/004A 1999) the cations interact with the clay by adsorption only and thus the strength of that interaction can be described effectively by using ionic potential arguments alone; in the case of the Am(III)/Co(II) adsorption onto concrete described here, the alkaline nature of the concrete substrate induces a chemical change in the sorbing species and thus the extent/strength of that sorption must be primarily described in the context of that chemical change.

Another relationship that has been suggested in the literature is absorption dependence with respect to the ionic size of the radionuclide beyond its influence on ionic potential. Interference in size between the contaminant and the pores of the material could potentially limit its penetration into the bulk of the material. Because the movement of the contaminant into the material is an important criterion for adherence/binding/adsorption to take place in the material substrate bulk, these mechanisms are dependent on contaminant mobility.

According to data summarized in Table 14, immobility due to size interference is unlikely to be a factor. There is barely a factor of two between the largest and smallest cationic species in these tests with no systematic relationship discernable between ionic radius and % removal. Thus, it is unlikely that ionic radii plays a substantial role in the mobility (and tenacity) of the contaminant.

Cation solubility, radius and ionic potential are important chemical and physical characteristics of the radionuclide. In the case of solubility, they help explain the behavior of these radionuclides during decontamination – especially with respect to the tenacity of the contaminant. In many aspects, no effect of commonly held beliefs, like ionic potential or ionic size exclusion, was observed. Thus, as indicated by the correlation between decontamination efficiency and cation solubility at the concrete substrate surface, % removal seems to be dependent on both the characteristics of the substrate as well as that of the radionuclide. Having considered the characteristics of the radionuclide above, material substrate characteristics will be examined in the next section.

4.5 The Effect of Different Substrates

Chemical, morphological and mineralogical effects attributed to the different material substrates are as important as chemical properties of the different radionuclides in determining the individual radionuclide’s tenacity. Americium, as noted previously, is particularly sensitive to pH for solubility - and the surface of the substrate will dictate that pH. In the case of cation sorption, the binding system of the material substrate will generally be anionic in character. A key question with respect to the material substrate is whether it has a high cation sorption capacity or cation exchange capacity (CEC) - i.e. what is the density of these anionic binding sites?

There are many physical and chemical properties of the contaminant system that are material substrate dependent. The tests described here were conducted on a diverse set of substrates, in terms of urban building materials, upon which to study these effects and interactions and develop a generic model of radionuclide/substrate interaction. The radionuclides-substrate data of Table 12 is organized on the basis of radionuclide first, then material substrate. For reader convenience and to assist analysis on the basis of substrate, Table 15 shows the same data set reorganized on the basis of substrate first and radionuclide section. As can be seen from Table 15 and Figure 44, the contaminant for which the largest range of substrates was studies was cesium. Hence the remainder of this section is focused on cesium/substrate systems with generic conclusions being drawn where scientifically defensible.

Table 15, Urban RDD Data Organized by Substrate.

Substrate	Method Used	Contaminant	Year Performed	Average % Removal
Concrete	CS Unitech Sander	Cesium-137	2009	53.7
Concrete	River Tech Water Jet	Cesium-137	2009	36.4
Concrete	Empire Blast Abrasive	Cesium-137	2009	96.7
Concrete	Diamond Wheel Grinder	Cesium-137	2009	91.6
Concrete	Wire Wheel Grinder	Cesium-137	2009	37.6
Concrete	DeconGel 1101	Cesium-137	2010	45.3
Concrete	DeconGel 1108	Cesium-137	2010	66.6
Concrete	RAD-Release II	Cesium-137	2010	85.4
Concrete	Rad-Release I	Cesium-137	2010	71
Concrete	RDS Liquid	Cesium-137	2010	52.5
Concrete	Argonne Super Gel	Cesium-137	2010	71.4
Concrete	INTEK ND-75	Cesium-137	2010	44.1
Concrete	INTEK ND-600	Cesium-137	2010	57.3

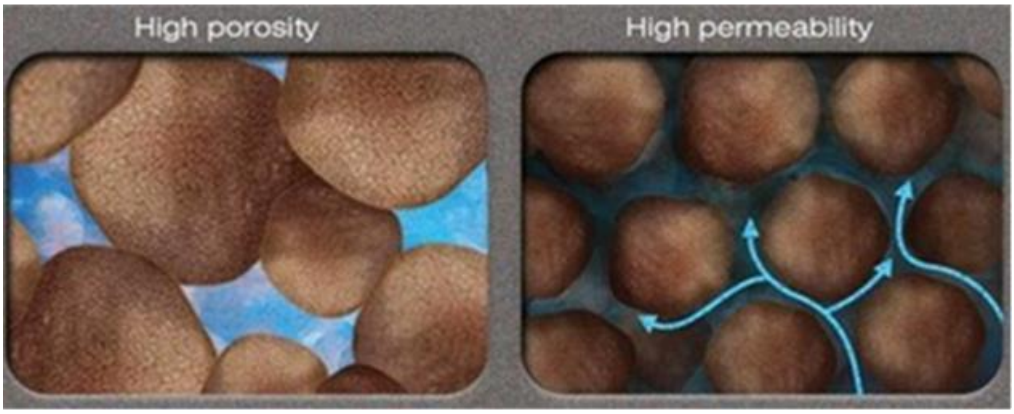
Concrete	SDF	Cesium-137	2012	51.4
Concrete	MSDF	Cesium-137	2012	61.8
Concrete	Water	Cesium-137	2012	6.1
Concrete	Argonne Super Gel	Cesium-137	2012	75.2
Concrete	RAD-Release II	Cesium-137	2012	74.2
Concrete	INTEK LH-21	Cesium-137	2013	44.7
Concrete	RDS-2000	Cesium-137	2013	10.8
Concrete	RAD-Release II	Amercium-243	2012	83.6
Concrete	Argonne Super Gel	Amercium-243	2012	62.8
Concrete	Bartlette TLC Stripcoat	Americium-243	2011	87.2
Concrete	DeconGel 1108	Americium-243	2011	86.3
Concrete	INTEK LH-21	Americium-243	2013	87.4
Concrete	RDS-2000	Americium-243	2013	69.1
Concrete	RAD-Release II	Cobalt-60	2012	79.2
Concrete	Argonne Super Gel	Cobalt-60	2012	62.4
Concrete	DeconGel 1108	Cobalt-60	2013	84.9
Concrete	RDS-2000	Cobalt-60	2013	51.6
Concrete	RAD-Release II	Strontium-85	2012	70.3
Concrete	Argonne Super Gel	Strontium-85	2012	39.9
Concrete	DeconGel 1108	Strontium-85	2013	63.9
Concrete	RDS-2000	Strontium-85	2013	42.7
Granite	DeconGel 1108	Cesium-137	2013	72
Granite	RAD-Release II	Cesium-137	2013	72.4
Granite	Argonne Super Gel	Cesium-137	2013	49.9
Granite	INTEK LH-21	Cesium-137	2013	55.8
Granite	RAD-Release II	Amercium-243	2012	51.2
Granite	Argonne Super Gel	Amercium-243	2012	33.7
Granite	RAD-Release II	Cobalt-60	2012	64.2
Granite	Argonne Super Gel	Cobalt-60	2012	55.1
Granite	RAD-Release II	Strontium-85	2012	43.6
Granite	Argonne Super Gel	Strontium-85	2012	33.7
Limestone	DeconGel 1108	Cesium-137	2013	35.1
Limestone	RAD-Release II	Cesium-137	2013	37.6
Limestone	Argonne Super Gel	Cesium-137	2013	35.1
Limestone	INTEK LH-21	Cesium-137	2013	39.4
Marble	DeconGel 1108	Cesium-137	2013	93.1
Marble	RAD-Release II	Cesium-137	2013	89
Marble	Argonne Super Gel	Cesium-137	2013	71
Marble	INTEK LH-21	Cesium-137	2013	90.6
Year Old Concrete	SDF	Cesium-137	2012	29.2
Year Old Concrete	MSDF	Cesium-137	2012	37.5

Year Old Concrete	Water	Cesium-137	2012	4
Year Old Concrete	Argonne Super Gel	Cesium-137	2012	45.6
Year Old Concrete	RAD-Release II	Cesium-137	2012	49.6
Aluminum	MSDF	Cesium-137	2011	92.2
Aluminum	SDF	Cesium-137	2011	90.5
Aluminum	Water	Cesium-137	2011	59.3

4.5.1 Effect of Permeability and Porosity of Substrate

The first characteristic of the substrate to explore is that of permeability. This characteristic is known by a wide range of other names: porosity, hydraulic conductivity, etc. Permeability is essentially the same as hydraulic conductivity; it defines the relationship that allows liquid to move through the material via the pores and channels. It is not exactly the same as porosity because porosity is a measure of the pore volume relative to the total volume. Porosity does not measure the connectivity of the pores. Thus, a porous material may transfer very little liquid

Figure 48. Illustration of high porosity versus high permeability materials (NYSM 2014).



through its bulk if it has no connectivity or permeability. Figure 48 shows an example of porosity versus permeability.

Table 16 provides porosity and permeability, as well as surface pH and CEC data for the four urban material substrates used in the tests summarized in Tables 12 and 15 – specifically concrete (made with ASTM Type I Portland Cement), Granite, Marble (99% calcite) and Limestone (92% calcite). Table 17 reports average % removals for Cs from these four material substrates, calculated from the decontamination test data of Tables 12 and 15.

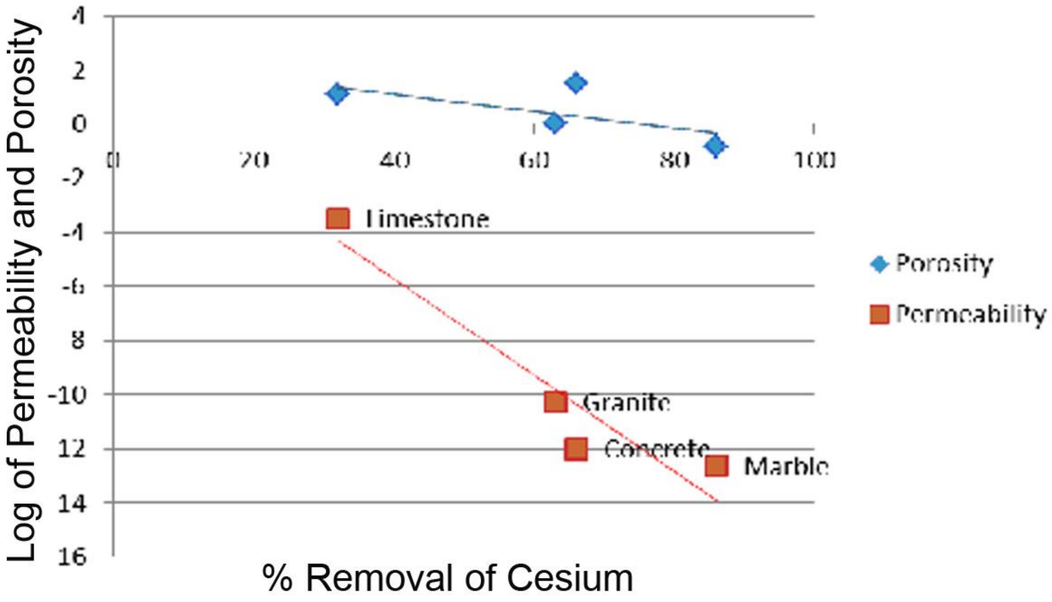
Correlation of the results of the average % removal decontamination data of Table 16 with and the substrate data indicates a dependence of % removal on the permeability of the substrate. Figure 49 shows plots of log (material substrate permeability) and log (material substrate porosity) versus average % removal for cesium on the four urban substrates tested

Table 16. Materials characteristics of substrate employed in Table 14 and Figure 48.

Substrate Test Material (and composition)	Average % Removal of Cesium	Porosity	Isoelectric point (IEP)	Surface pH	Permeability	CEC
Concrete (ASTM Type 1 Portland Cement)	66%	30% [3]	5.5	10.7	1 X 10^{-12} m/s [5]	0.242 cmoles/kg
Granite (Plagioclase (albite) 20%, Quartz 40%, Microline 38 %, Biotite 1%, Muscovite 1, Garnet 1%)	63%	~1% [4]	2.3	7.3	5.35 X10^{-11} m/s [5]	0.088 cmoles/kg
Marble (Calcite 99%, Plagioclase 1%)	86%	0.15% [7]	6.5	8.3	2.39 X10^{-13} m/s [5]	<0.02 cmoles/kg
Limestone (Calcite 92%, dolomite 2%, quartz 4%)	32%	13% [2]	9.3	8	3.3 X10^{-4} m/s [6]	<0.02 cmoles/kg [9]

[2] Freire-Gormaly 2013, ([4] Dale 1908), ([5] Mehta and Monteiro 2006), ([6] Selvadurai 2010), ([7] McGee 1999), ([8] Kakade 2014), ([9] Vilks, Miller and Felushko 2011)

Figure 49. Correlation between cesium average decontamination efficiency and material substrate permeability and porosity.



Particularly, Figure 49 shows that there is a near linear relationship between % removal and log (permeability) showing a "near" first-order dependency of contaminant tenacity with permeability. A similar relationship can be shown for porosity as well, though that relationship is not nearly linear, as shown in Figure 49; the order of porosity values being concrete > limestone > granite > marble. In terms of % removal the order is limestone < granite < concrete < marble, out of order in attempted correlation of substrate porosity with decontamination results. Essentially there is no correlation between porosity and % cesium removal for this set of substrate.

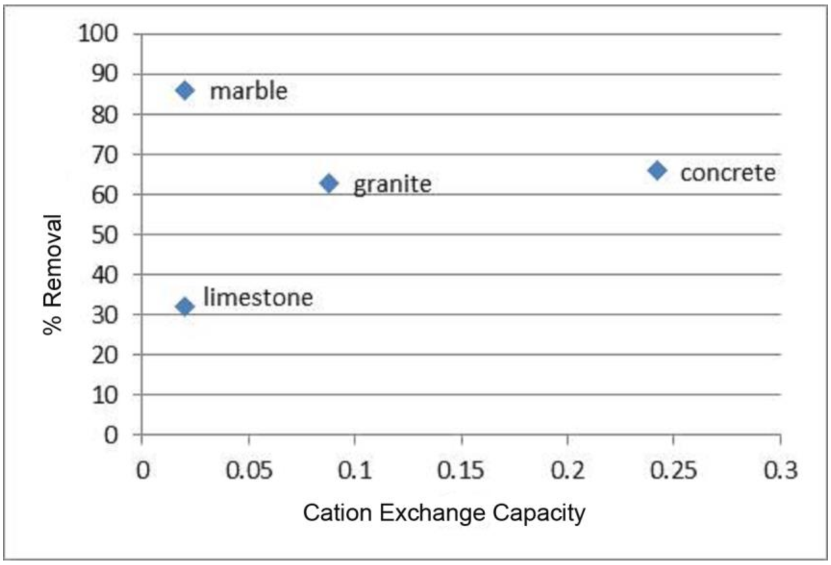
This shows that materials with larger permeability typically retain cesium contamination more tenaciously, most likely as a result of the ease with which the contamination can penetrate and diffuse into the surface of the substrate. Material substrates with a high permeability demonstrate connectedness of the pores in the structure of the substrate. Thus a soluble contamination such as cesium has the opportunity to move into the substrate wherein it may be influenced by other substrate characteristics such as CEC.

4.5.2 Other Physical/Chemical Characteristics of Substrate

Other material properties that may affect the tenacity of cesium contamination on the substrate include the material CEC, isoelectric point (IEP) and surface pH – values for all of which are given in Table 16 for the four urban substrates under study here. The CEC was briefly discussed above from the perspective of several radionuclides deposited on concrete alone. While concrete has a high CEC, it was determined that CEC alone did not adequately describe the observed order of the average removal percentages (decontamination efficiencies) from concrete for the radionuclides studied. In particular, Am^{3+} showed a very high % removal due primarily to surface pH effect and the tendency of Am^{3+}, and to a lesser extent Co^{2+}, to precipitate as metal oxyhydroxides at the high surface pHs typical of concrete – the pH is typically 10.7, see Table 16.

In contrast to americium and cobalt, cesium exists as the Cs+ ion at all of the surface pHs of the urban material substrates given in Table 16 and so provides a means by which to interrogate the role of other material properties such as CEC on decontamination efficiency. Accordingly, Figure 50 shows a plot of % removal vs material substrate CEC for the data of Table 16, from which it can be seen that no real correlation may be determined. This is perhaps unsurprising given the dominant effect of material substrate on % removal elucidated above.

Figure 50. Correlation between cesium average decontamination efficiency and material substrate CEC.



Whilst Cs+ may be considered a non-reactive cation over the pH range studied here, surface pH may also play a role in its retention at the material substrate surface. As discussed above, the total CEC of a material substrate may be considered to be derived from three main sources: inner sphere complex formation; outer sphere complex formation; and coulombic localization in the diffuse ion swarm/diffuse layer of the electrical double layer.

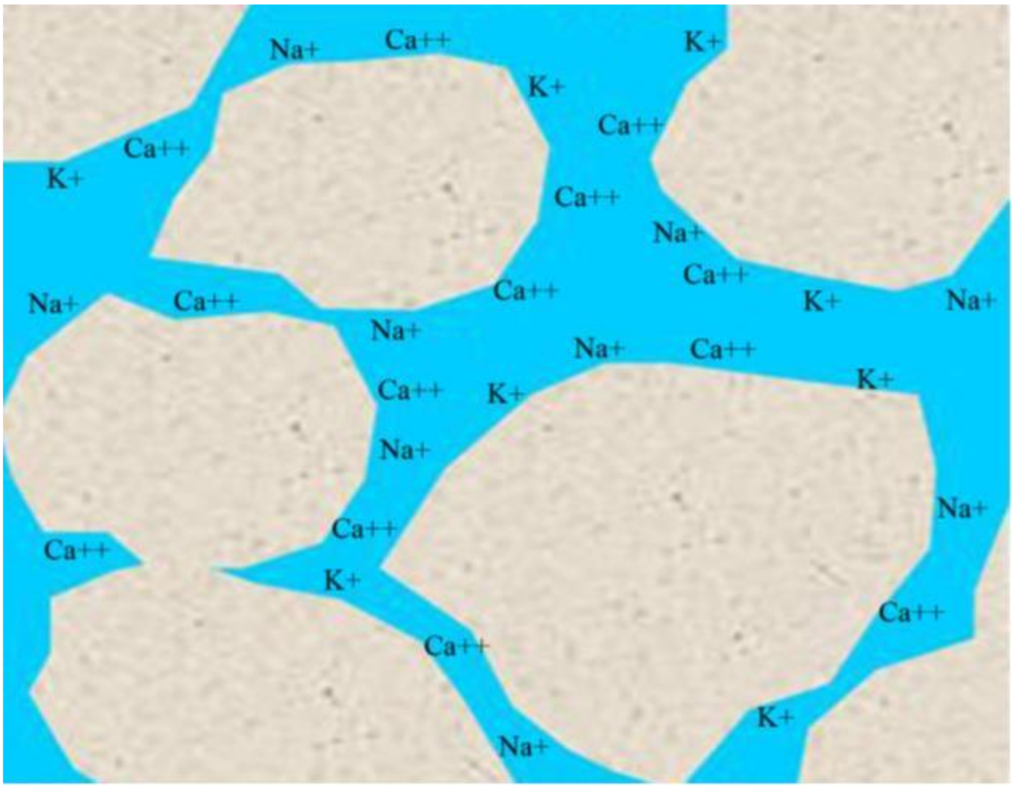
The coulombic attraction between cationic contaminants and the substrate occurs principally when positively charged species are attracted to a negatively charged substrate surface - so providing a reservoir of acid exchangeable metal ions and thus a contribution to the CEC, as shown pictorially in Figure 51. This tendency towards the charging of a substrate surface typically stems from the protonation or deprotonation of metal-OH groups present at the surface of all metal oxides - including those that comprise the principle components of the urban material substrates under study here e.g. aluminum oxide, calcium oxide or silicon oxide. Reactions of this type are shown in the following equations:

$$\text{M-OH} + H_2O \rightarrow \text{M-O}^- + H_3O^+$$

$$\text{M-OH} + H_3O^+ \rightarrow \text{M-OH}_2^+ + H_2O$$

The former results in the generation of a negative charge site on the substrate surface, the latter a positive site. If the former were to predominate over the latter, then the net excess of anionic M-O$^-$ sites would increase the adsorption of cations on the minerals and thus increase the CEC.

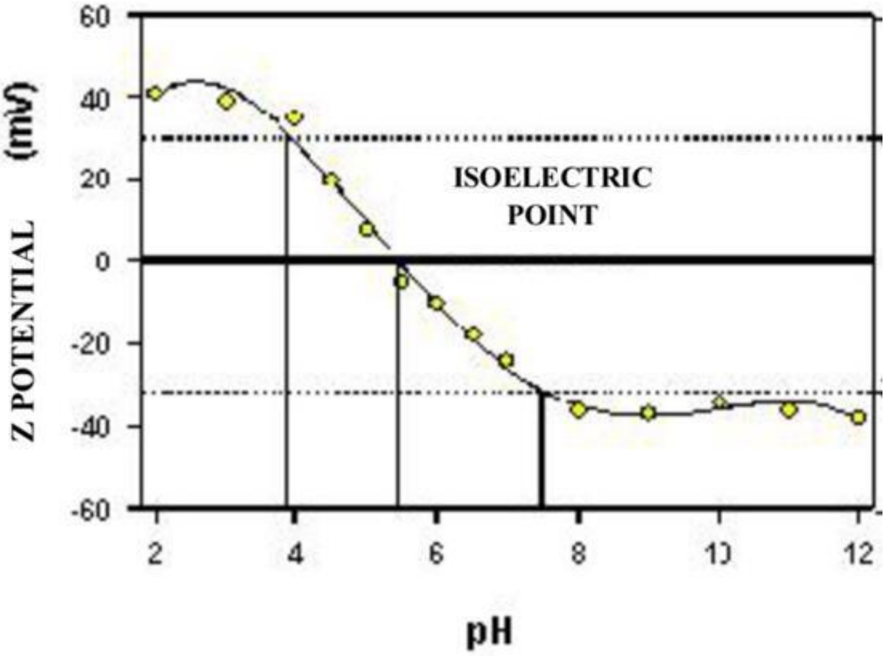
Figure 51. Illustration of the contribution of coulombic attraction to Cation-Exchange Capacity.



The extent to which the two metal oxide surface protonation/deprotonation reactions described above occur on a material substrate surface is determined by the pH of the environment in which the substrate is immersed. At high pH, the hydroxide ions present in solution will favor the former, deprotonation process at the surface. At low pH the excess of H^+ ions will favor the latter, protonation process at the surface. Thus, this coulombically derived contribution to the CEC can be seen to be pH dependent - the larger the pH induced negative charge on the substrate surface, the larger the "coulombic CEC".

However, the electrical charge on a particular substrate surface is not just determined by the solution pH. It is also a property of the pK_a values for the protonation and deprotonation reactions given above i.e. the inherent acid-base properties of the material surface. An important measure of these properties is the iso-electric potential (IEP). The IEP value is the result of an acid-titration curve where the inflection, recorded in pH units, shows the point at which the negative and positive charges are balanced within the material (which is the neutral, iso-electric point, also often called the zero (zeta) potential). This tendency is shown graphically in Figure 52. Importantly, the more acidic the IEP (the lower it is below 7 for instance) the wider the pH range that the material surface has a negative charge. As well, for any one given pH, materials with lower IEPs tend to have larger net negative charges at that pH. Thus, the lower the IEP, the stronger and more pronounced the general cation-exchange capacity exists.

Figure 52. Zeta potential (isoelectric point) curve for fresh concrete (Talero, Pedrajas and Rahhal 2013).

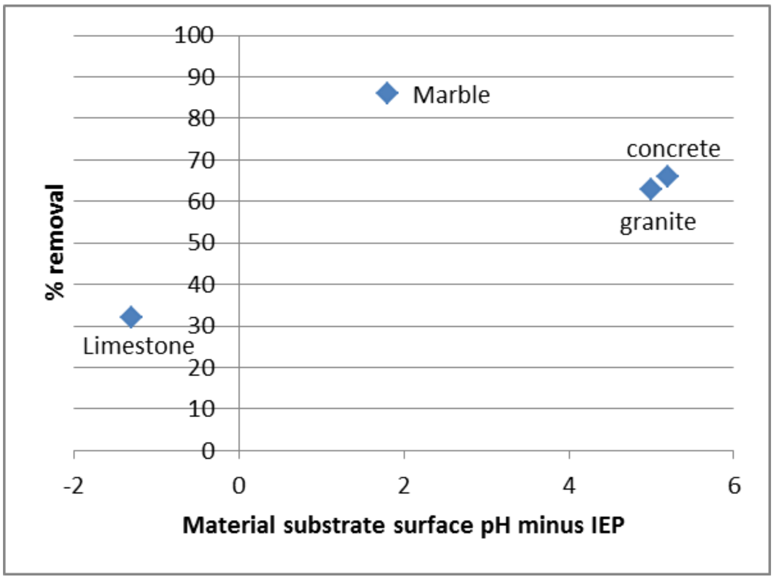


Thus, it would seem reasonable to conclude that materials with the lowest IEPs should retain their cationic contamination more strongly. However, plotting the Table 16 data for the % removal of cesium on concrete, granite, marble and limestone as a function of the IEPs of those material gives a similar result as plotting % removal vs CEC as in Figure 50 above - i.e. no correlation between the two parameters may be discerned.

This result initially seems counter intuitive, but may be understood in light of the material substrate property that was so important in determining the % removal of americium - specifically the surface pH of the material. According to Figure 53, substrates with a surface pH close to their IEPs may be expected to have a small surface charge. In contrast, those material substrates with surface pHs significantly higher than their IEPs will have a high net negative charge - whilst those with surface pHs significantly lower than their IEPs will have a high net positive charges. The former would be expected to lead to strong cation uptake and retention during decontamination, whilst the latter would be expected to lead to the opposite. Accordingly a relationship between % removal and the difference between surface pH and IEP (i.e. surface pH minus IEP) might be expected.

Figure 53 shows a plot of % removal vs (surface pH minus IEP). For marble, granite and concrete is found that surface pH > IEP and thus a net negative charge would be expected on the substrate surface. Further, those materials for which the surface pH-IEP difference is largest - i.e. those for which the net surface negative charges would be expected to be the greatest - evidence the lowest % removal for cationic Cs^+, as might be expected, based on coulombic grounds.

Figure 53. Correlation between cesium average decontamination efficiency and difference between material substrate surface pH and IEP (i.e. surface pH minus IEP)



Two other observations may be made from Figure 53. The first is that concrete and granite both exhibit similar differences between surface pH and IEP and similar % removal values for Cs+. The former suggests that coulombic forces of similar magnitude are in operation on both materials, the similarity in the latter values in light of this suggests that the primary locus of retained Cs^+ in these materials is within the diffuse ion swarm, i.e. cesium is primarily retained by non-specific coulombic adsorption rather than site specific outer-sphere/inner-sphere complexation.

The second observation concerns the behaviour of limestone. Alone amongst the substrates studied it possesses a surface pH *less* than its IEP, i.e. a net positive surface charge would be expected. This suggests that coulombically based sorption of Cs^+ would be weak with consequent high % removal efficiencies. However, the opposite is found, with Cs^+ % removal from limestone being the lowest from the four urban material substrates studied. This is to be expected, though, given that, as evidenced by Table 17 and Figure 49, limestone is at least six orders of magnitude more permeable than granite, marble or concrete. It is thus more capable of imbibing cesium contamination into its bulk, resulting in greater difficulty in its removal using the decontamination techniques employed in Tables 12 and 15.

Thus, from the above study of % removal of Cs^+ from urban substrartes, the following general conclusions can be drawn:

1. For cationic radionuclides such as Cs^+ that do not exhibit any nuclide/material surface specific chemistry (e.g. the surface pH promoted precipitation of americium) the prinicpal material property controlling the tenacity of that nuclide during decontamination from urban material substrates is the permeability of that substrate.

2. For substrates of similar permeability, net surface negative charge on the material substrate plays a major role in determining the tenacity of non-reactive cations such as cesium; the larger the net negative charge on the substrate surface, the more tenacious the contamination.

The above conclusions have been drawn using mean % removal values calculated on both a per nuclide and per substrate basis from a wide range of decontamination techniques. However, in some instances, the spread around those mean values can be non-insignificant, see e.g. Figure 45. Thus, further insight may be obtained by considering the decontamination of specific substrates or the use of specific decontamination techniques in detail. This is the subject of the next sections.

4.5.3 Detailed Explanation of Urban RDD Substrate

The results of the Urban RDD decontamination tests have been evaluated against the general characteristics of the materials substrates studied. The following section describes the background and commercial uses of the substrate as well as certain specific characteristic (e.g. surface microstructure) with a view to providing further insights into the main determining factors of contamination tenacity.

4.5.3.1 Milford Pink Granite

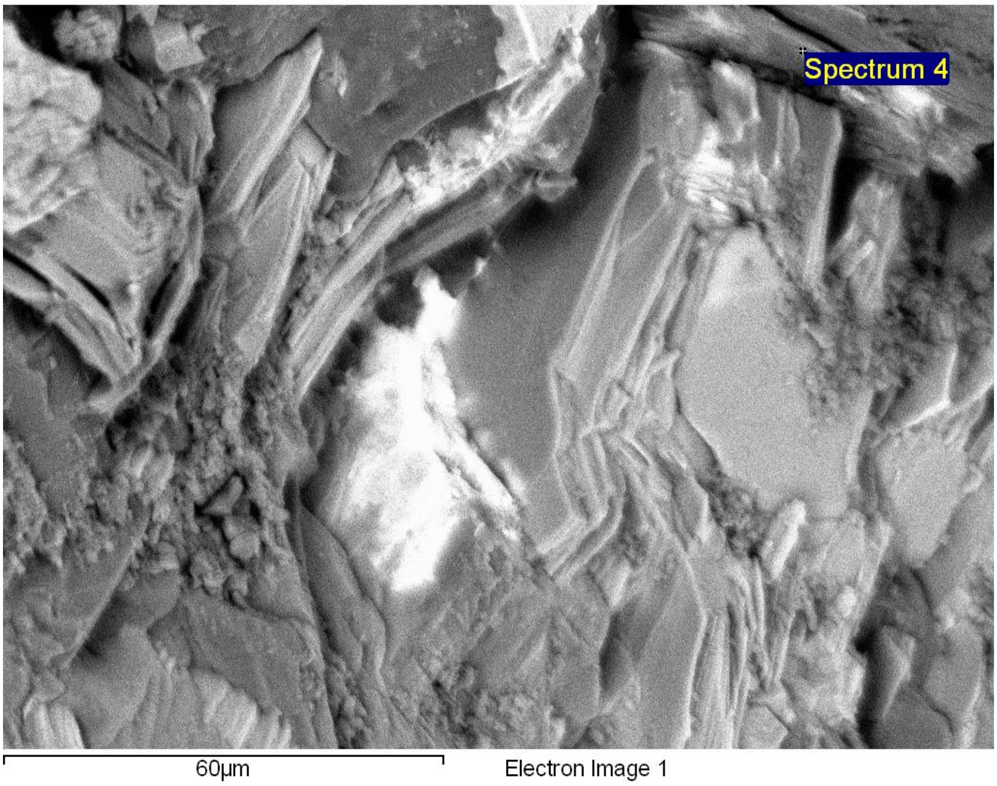
Milford Pink Granite obtained from the Fletcher Granite Company at a Quarry near Milford, Massachusetts, USA was used in all the testing described above. Granite is an igneous rock, having formed from solidified lava. Milford Pink Granite has a general light/white/yellow appearance, with light pink tone spots and many small black flecks on the surface. Granite is a material of choice for memorials, monuments and archival structures in the USA because of its hardness, strength and ability to resist weathering (estimated at 2 mm of surface deterioration in 1000 years). It was chosen for the decontamination tests described here specifically because it has been used in several important government buildings such as the Boston Chamber of Commerce in Boston, Massachusetts, Main Post Office, New York City, New York and the National Archives in Washington D.C.

Granite should theoretically be a highly contaminant resistant material, while in practice it doesn’t perform as well as expected. It has little or no reactive mineral structure, being composed primarily of quartz and feldspars; essentially unreactive silicate and aluminosilicate minerals respectively. But granite fairs little better than the far more porous concrete with respect to % removal of contaminating Cs^+ in the tests described above. Part of the reason for this can be divined from the discussion of permeability explained earlier in this chapter; from Table 16 it can be seen that granite is an order of magnitude more permeable than concrete.

However, there seems to be two factors in granite that mitigate towards the higher adsorption of cesium: the permeability of the microstructure of the granite and the preferential substitution of the cesium in the plagioclase minerals. The role of the former is reinforced by Figure 54, which shows a scanning electron microscope (SEM) photograph of the typical surface conformation of the granite used in these tests. The granite surface shows a layered, random, fractured profile with significant cleavage of the structure. The layered surface presents ample opportunity for contamination to become trapped within the structure. The surface is not homogeneous in its mineral structure; the very identity of the granite, its multicolored appearance and indeed its beauty, stem from this non-homogenous surface nature.

Unfortunately that structure also makes it much more difficult to decontaminate. In this case those surface minerals are not easily dissolved in acid based decontamination techniques (as with concrete and the calcite based minerals) and thus provide that surface a stable, inert trap for contamination to be adsorbed out of the reach of contamination solutions.

Figure 54. Scanning electron micrograph of Milford Pink Granite layered mineralogy.



The second factor is the ability of the minerals themselves to adsorb the contamination. Minerals like the plagioclase are made up substantially of alkali species, predominantly potassium (Rafferty 2012). As these minerals swell with the application of moisture, through rain events or the application of a wet contaminant, the plagioclase swells and may exchange alkali metal cations, thus incorporating the cesium (and strontium) into their structure. Some of the minerals (biotite for instance) are clay like micas. These layered minerals readily trap contamination within their layers or "sheets" of material, so contributing to the "coulombically derived CEC" discussed with reference to Figure 53 above.

4.5.3.2 Concrete

The most common urban building material remains concrete. While most buildings are typically not constructed entirely of concrete (though there are some notable exceptions like the Roman Coliseum and the Baha'i Temple in Wilmette, Illinois), substantial portions of most buildings are concrete. Many an industrial structure and much of the infrastructure (dams, canals, pavement and bridges) are constructed of concrete. Modern concrete (like the test specimens employed in this study) is a complex composite of different materials. Ordinary Portland Cement consists of a mixture of kiln dried limestone, clay and gypsum (calcium sulfate). When fully hydrated this mixture becomes calcium silicate hydrates and forms a strong, adhesive "polymer". When mixed with aggregate (sand and rock) and reinforced with steel it becomes high strength concrete.

Concrete is fairly non-reactive (inert) on the surface, especially with solutions above neutral pH. However, with decreasing pH and increasing salt solution composition, the concrete surface degrades more rapidly. Concrete however is porous, (though not highly permeable, hence its low permeability in comparison to limestone, see Table 16), its microstructure includes surface cracks and channels. During the tests of Tables 12 and 15 some minor cracks and pinholes were noted in the material used; hence care was exercised to select coupons without significant surface imperfections.

4.5.3.3 Colorado Yule Marble

The Colorado Yule Marble used in the decontamination tests has a less complicated surface structure than either concrete or granite. Colorado Yule Marble is only obtained in the north central mountains of Colorado (the Yule Valley). It is a true marble, having undergone extreme heat and compression (contact metamorphosis) within the earth to recrystallize from sedimentary limestone into a complete metamorphic stone. This metamorphosis forms a homogeneous, consolidated structure with fine grains, tightly packed and with very narrow, irregular boundaries (Figure 55), so explaining its extremely low permeability compared to that of concrete, granite and especially its mineralogical precursor, limestone, presented in

Figure 55. Scanning electron micrograph of Colorado Yule Marble (McGee 1999)

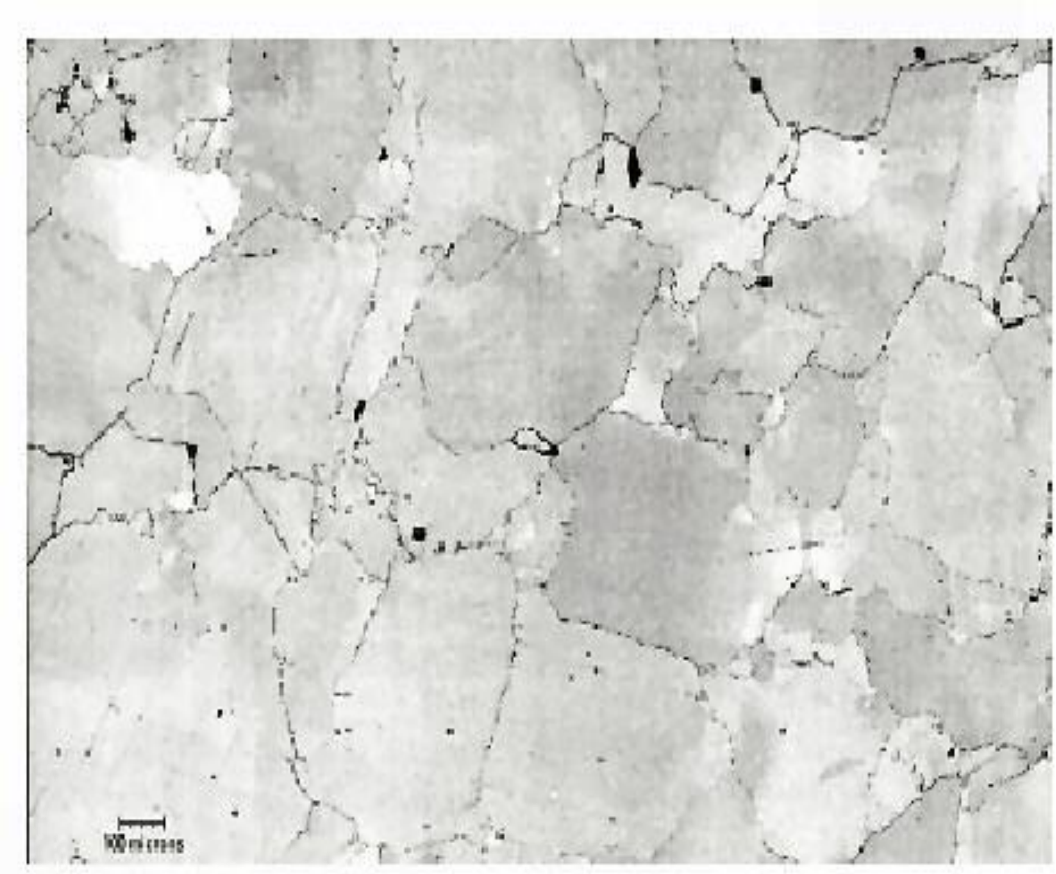


Table 15. Colorado Yule Marble is another commonly used monument building material used in the United States; notably in the Tomb of the Unknown Soldier and the Lincoln Memorial.

Colorado Yule Marble produces a flat, consolidated and dense surface. The calcite material, calcium carbonate ($CaCO_3$), is no longer a loose, highly porous material like limestone. This dense surface is very alkaline, with a high pH (unsurprisingly close to that of limestone, see Table 16) and is readily dissolved in acidic solutions (as employed in several of the decontamination methods reported in Tables 12 and 15). However, marble's low native permeability combined with its low difference between surface pH and IEP undoubtedly contributes to the comparatively high % removal values reported for Cs^+ in Table 16.

4.5.3.4 Indiana Gray Limestone

Limestone has a similar chemistry to the marble, essentially calcite albeit with some additional, minority components. Unlike the more consolidated, metamorphic marble, the Indiana Gray Limestone used in the tests reported here is an "open" porous, sedimentary material. Limestone has found use in numerous famous buildings in the U.S., such as the Empire State Building in New York City, New York and the White House in Washington D.C. As discussed above, it is the "open" highly permeable nature of limestone (as reported in Table 16) that dominates its decontamination behavior with respect to non-reactive cations such as cesium.

Detailed consideration of the nature of each material substrate employed in the urban RDD simulant testing reported here only reinforces conclusions made on the basis of their general nature. In contrast, the next section explores the insights that may be derived from detailed consideration of the most common chemical decontamination techniques used in the compilation of the % removal data reported in Tables 12 and 15.

4.6 The Effect of Different Chemical Decontamination Solutions

The properties of the decontamination agents have a significant effect on the removal efficiency of the contaminants. Complex, commercially available decontamination methods (primarily chemical solutions) were employed in the side-by-side tests used for most of the comparisons reported in Tables 12 and 15 and in the compilation of the derived figures/box and whisker diagrams. The characteristics and chemical properties of the five decontamination agents most frequently used in the tests of Tables 12 and 15 are given in Table 17.

Table 17. Active ingredients in common INL decontamination testing methodologies.

Decontamination System	Components or Steps	Use	Chemical Constituents	Overall Chemistry Description	pH
RDS 2000 (pH in use is approximately 3)	Component 1	Components 1 and 2 are mixed at a ratio of 2:1	Fatty alcohol glycoside 10-25%, citric acid 10-25%, fatty alcohol polyglucoside 10-25%, alkyl polyglucoside 2.5-5% (remainder water)	Slightly acidic with reducing agents and organic chelants	2.1
	Component 2		2-hydroxy-1,2,3-propane tricarboxylic acid 25-49%, Reducing salt 0.5-5% (remainder water)	Slightly basic with wetting agents	8.2
Rad Release 2	Step 1	Use step 1, then rinse, then step 2, then rinse	Phosphoric acid 1%, Ammonium bifluoride <1%, Citric acid 1-3%, Nitric acid 1-5%, surfactants, buffers, water.	Acidic with chelants	2.5
	Step 2		Ethylene glycol monobutyl ether 5-15%, Isopropanol 0-2%, Sodium hydroxide 1-5%	Basic with wetting agents	12.5
	Rinse		Nitric acid 10%	Acidic	<1

Decontamination System	Components or Steps	Use	Chemical Constituents	Overall Chemistry Description	pH
LH-21	(one component)	Spray on, wash off with water	Lactic acid 20-30%	Organic acids and wetting agents	1
DeconGel 1108	(one component)	Strippable coating	Sodium hydroxide 0.1-1%, proprietary binder (paintlike)	Physical action of encapsulating and removing the contaminant from the surface, basic chemistry	5-7.5
Argonne Super Gel	(one component)	Absorptive gel, apply by spray or trowel and vacuum or rinse off	Sodium polyacrylate super absorbent gel, linked polyacrylamide, ammonium chloride, potassium carbonate, 1-Hydroxyethylidene-1, 1-Diphosphonic acid.	Slightly acidic, chelant, common ion flush and absorbent.	4 (estimated)

These agents produce significantly different results with respect to the removal of the contaminants. The methods described in Table 17 are both the most common methods used in the tests of Tables 12 and 15 and are typical of the variety of chemical methods available for use in the decontamination industry; ranging from strongly acidic to basic solutions and including the use of counter-ions, chelants and organic acids (which have both low pH and can act as reductants and chelants). They also produce a large dynamic range of decontamination % removal results as evidenced by Figures 56 and 57. Figure 56 compares % removal of Cs^+ from four different urban material substrates (concrete, granite, marble and limestone) using four different radionuclides (Cs^+, Sr^{2+}, Co^{2+} and Am^{3+}), again using four of the methods of Table 17.

Figure 56. Comparison of cesium % removal results for four different decontamination methods on four different urban material substrates.

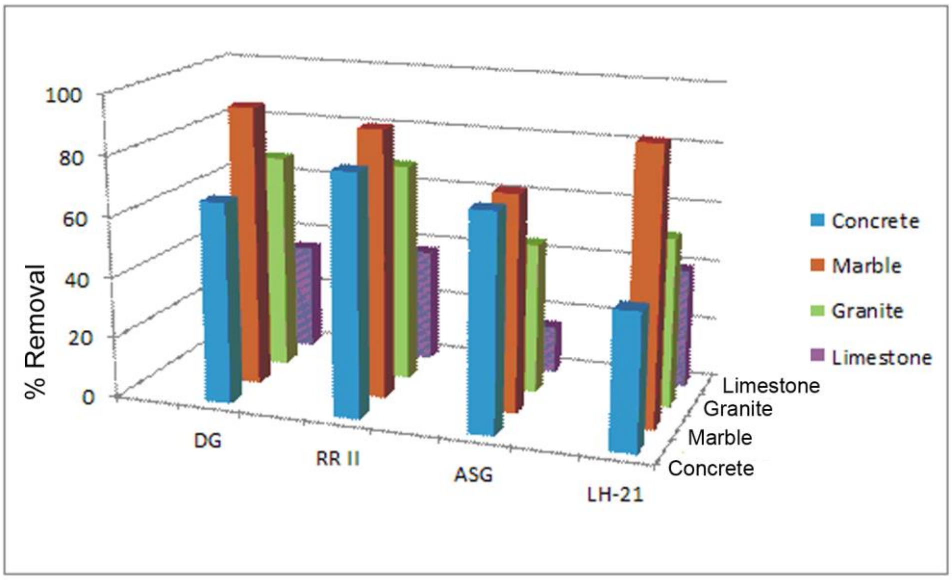
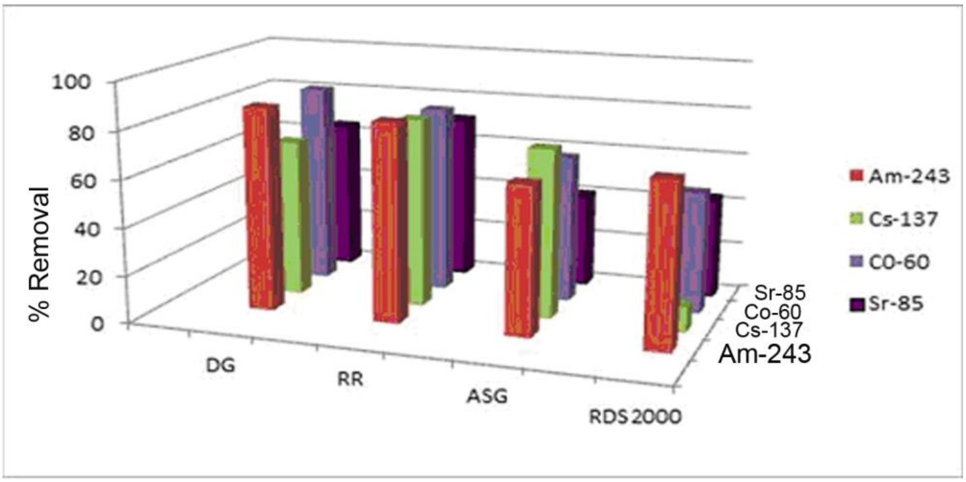


Figure 57. Relative decontamination results of different radionuclides on concrete.



If strong enough, acidic solutions dissolve the oxide or carbonate constituents of the surface, effectively dissolving some of the surface itself and so suspending and redissolving the contaminant. Contaminants which precipitate at higher pH, like cobalt (which precipitates at pH just less than 3), therefore return to solution upon treatment with low pH decontamination agents and thus should become easier to remove from the surface. This is especially true of strongly acidic solutions such as Rad-Release 2 (RR-II), Argonne Super Gel (ASG) (when used with hydroxylethylidene-1,1 diphosphonic acid) and lactic acid (LH-21). As can be seen from Figures 56 and 57, the highest overall decontamination results were obtained with the acidic Rad-Release 2 treatment; a method that accesses pHs less than 1 during its rinse stage, thus it readily dissolves the alkaline surfaces of marble, concrete and limestone, freeing contamination trapped in the upper surface, see Figure 52. However, as evidenced by Figure 57, it also solubilizes contaminants such as Am(III) and Co(II) – both of which, as well as Sr (II) and Cs(I), are all highly soluble at pH <5 (see Figures 44 and 45).

A surprising revelation from the tests was the efficiency of the near neutral (or basic) solutions, like the DeconGel (DG), at removing contaminants. In most cases the DG was nearly as effective at removing contamination as RR-II (which itself has a basic component in “Step 2”), and more effective than most of the other decontamination methods. Using the overall, combined results from four decon agents (RR-II, DG, ASG and LH-21) the DG is second only to RR-II (3 % less overall) and significantly higher than the others (some 7% higher) - suggesting the presence of strong chelating and/or adsorbing agents in DeconGel's proprietary formulation.

Chelants and adsorbent additives are chemical components that “bind” the contaminant and are very effective in decontamination solutions. The chelant’s job is to help dissolve the contaminant, typically making it more soluble in less aggressive chemical solutions and to bind the contaminant in the decontamination solution so the surface becomes less saturated with contaminant and the removal equilibrium is driven towards pushing more contaminant into the decontamination solution. Most organic acids, such as oxalic and citric for instance, are reasonably good chelants. The most commonly used decontamination chelant is ethylenediaminetetraacetic acid (EDTA). A low pH chelant, HEDPA, is used in the ASG. ASG also makes use the gelatin-like absorbtive properties of its acrylic polymer gel. This polymer sets up a contaminant binding mechanism similar to a chelant and helps accelerate the removal equilibrium. The DeconGel also makes use of this kind of an absorbtive mechanism within its strippable, paint-like polymer formulation.

Some of the chemical methods utilize a non-radioactive counter-ion to force the contaminant away from the surface and into solution, replacing it with an overwhelming quantity of the counter ion. The best results are obtained when the counter-ion has been formulated directly to substitute or compete with a specific contaminant; if possible, the substrate should prefer the counter-ion, thus preferentially releasing the contaminant. Most often this counter-ion is an alkali cation, usually sodium, potassium or ammonium. These are used to counter cesium typically, but are also likely to exchange with other cations in cation-exchange sites. Rad Release II utilizes a high ammonium salt loaded solution at low pH 2.5 during its first treatment. Given RR-II's high % removal efficiency for almost all of the contamination simulant systems studied in Figures 56 and 57, it can be concluded that RR-II combines these modes of decontamination action (acid pH and counter-ion-driven contaminant displacement) to good effect.

Surfactants, oxidizers and reductants are employed in many of these solutions to improve their performance. Surfactants increase the ability of a solution to deliver the decontamination agents into pores and crevices by reducing the surface tension of the solutions. From Table 18 and Figures 56 and 57, it would once again appear that RR-II uses these within its formulation to great decontaminative effect. Particularly, RR-II gives one of the best % removal efficiencies for the decontamination of highly mobile Cs^+ from highly permeable limestone - consistent with the role played by surfactants in assisting the delivery of decontamination agents into high tortuosity pore networks via the wetting of pore walls.

One observation from Figure 56 is that the efficiency of the different decontamination solutions varies greatly depending upon the material upon which they were being used. All of these tests used the same Cs-137 spike material, which has a good penetration into surfaces in general and whose chemistry is fairly independent of the surface pH of the substrate (i.e. it does not precipitate at the substrate surface). A good example of the wide variation of the decontamination efficiency is the LH-21 treatment. It has one of the highest efficiencies for marble, but one of the lowest on concrete. Likewise, the Argonne Super Gel has the second highest efficiency on concrete, but a very poor level for limestone. This probably relates to the effectiveness of a more acidic solution, like LH-21, on calcite containing (easily dissolvable) marble and limestone. ASG depends more on its polymer gel that binds cesium and withdraws it from concrete, while the porosity and permeability of limestone tend to allow the contaminant to penetrate further into the surface. In short, the mean % removals reported in Tables 12 and 15 may have an associated spread in actual % removal data around that mean that can be non-significant, see e.g. Figure 45. This is undoubtedly a result of the wide range of chemistries in the decontamination methods themselves (see e.g. the five methods summarized in Table 18) and the specific manner in which those chemistries interact with the target contaminant and the material substrate.

Figure 58 shows the effectiveness of different decontamination solutions on different contaminants. The substrate used in these tests was concrete. Some of the earlier discussion related to the mean % removal efficiencies of Am(III), Co(II), Sr(II) and Cs(I) from concrete is relevant here - particularly (i) the role played by Am(III) and Co(II) precipitation at alkaline concrete surfaces resulting in high % removal efficiencies and (ii) the non-specific adsorption of Cs^+ in the diffuse ion swarm resulting in its mobility within the pore network of the concrete bulk and thus ultimate ease of removal. Note that the Rad-Release II (an acidic solution) has a fairly consistent decontamination efficiency over the range of radionulcides. It appears to be quite versatile with respect to contaminant chemistry. RDS 2000, on the other hand, is effective on Am-243, but significantly less effective on Cs-137. This is likely because the RDS 2000 has more of a “soap-like” nature than strongly chelating agents. It seems to lack a mechanism to adsorb, chelate, bind and hold the (soluble) cesium within the decontamination solution but is highly effective at loosening the already precipitated americium (and, to a lesser extent, cobalt). This seems to indicate that the response of the decontamination solutions is somewhat species dependent and not universal.

This section reviewed the characteristics of different, mainly chemical, decontamination agents. In all tests, overall, the highest % contamination removal results were achieved with abrasive blasting and grinding. However, these methods are also very destructive and the DARPA and US EPA customers were more interested in “softer” chemical decontamination agents. The methods used in this section were some of the best chemical decontamination agents tested, and a number of observations were made concerning their results:

1. Harsh, high concentration chemical agents (e.g. RR-II) that utilize multiple decontamination processes (acids, bases and chelants) typically have an effectiveness advantage over more dilute, one component solutions.

2. Strongly acidic solutions (RR-II and ASG) achieved the highest overall % removal decontamination results. This is partly because they tend to dissolve small amounts of the substrate surface and liberate imbibed contaminants.

3. The neutral pH DeconGel material was surprisingly effective; likely because of its chelant/absorbtive character.

4. Some decontamination methods, i.e. LH-21 and ASG, have a wide variation in % contaminant removal results. This can be significant, and dictates that more care should be exercised when selecting these types of agents.

5 Conclusions

The results of the decontamination testing and research described and reported in this thesis demonstrate that relevant, reproducible contamination simulation exercises are achievable and have proven valuable. This is true both from their value as a means of determining the best decontamination methods and also from the insight they provide into the fundamental characteristics that drive the adsorption and removal of different contaminants.

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. It can be an effective, beneficial alternative for the cleanup of radiological contamination events. However, the costs and benefits of decontamination need to be balanced against the 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.

While selecting decontamination methods, careful consideration needs to be applied to understanding the relevant criteria and weighting of the methods. Not all highly effective decontamination methods are right for all tasks. A systematic approach should be taken to determine the proper method. The criteria for selecting the method should include: effectiveness, waste minimization, damage due to harsh (destructive) methods, waste characteristics, waste compatibility and cost.

Many decontamination simulation tests are flawed because they are not designed to adequately encompass a wide range of methods and provide quantitative values that differentiate between the methods. A meaningful simulated decontamination test must have an adequate range that allows discrimination between different methods. A "fixed" type of contamination simulant is usually required to provide the level of difficulty required to separate the decontamination methods. The tests detailed in this report addressed a range of simulated contamination systems:

- SIMCON 1 – loose (salt) contamination on stainless steel;
- SIMCON 2 – fixed contamination on oxide coated stainless steel;
- Urban RDD – radiological dispersal device (RDD) (dirty bomb) contaminants fixed to urban material surfaces.

The two SIMCON simulants were particularly effective at demonstrating that a “level playing field” was needed for the testing of various decontamination technologies. Developing these reproducible contamination simulants is a non-trivial, time intensive process. The SIMCON and Urban RDD simulants have been proven in over 400 tests.

Understanding the contaminant and substrate characteristics (especially how tenacious (how firmly fixed) the contamination) allows the rigorous selection of the correct method with lowest cost and least waste. Just as there are contaminant simulation methods which are easy to remove, there are some contamination types observed in the field that are not tenaciously attached. Great success has been found using simple methods such as vacuuming, wiping and simple water flushing for these types of contaminants. Vacuuming and wiping are typically very inexpensive methods and are perfectly adequate for loose types of contaminants.

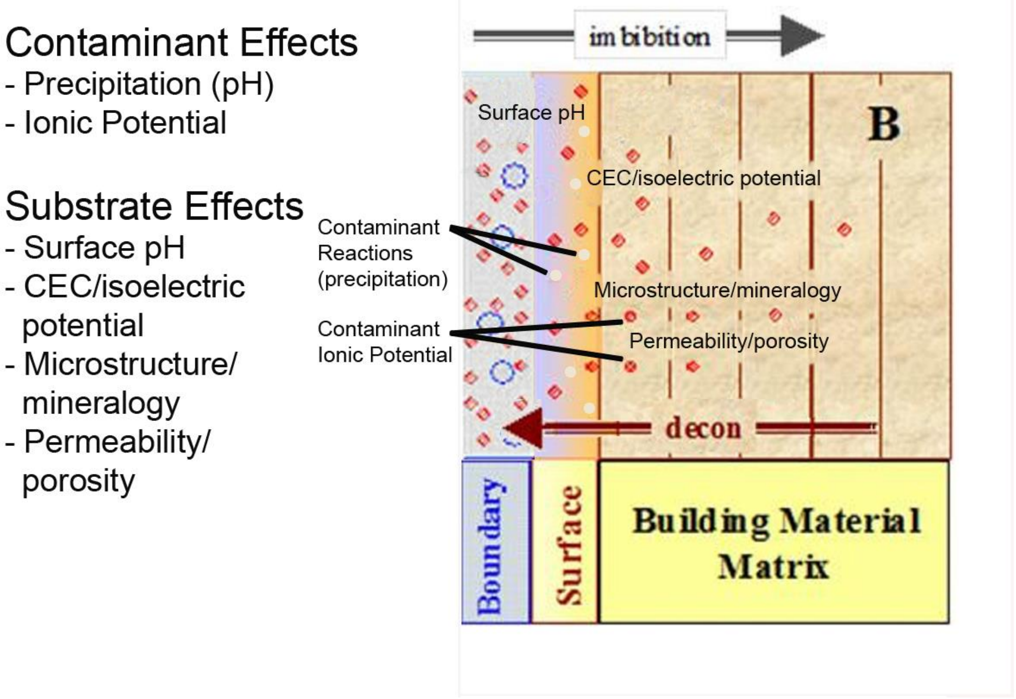
Different contaminants respond differently during decontamination. This was found to be true both with SIMCON and Urban RDD simulant tests. While intuitively obvious, SIMCON 2 demonstrated that chemically different contaminants respond differently to different decontamination methods: cesium appears to be less tenacious (more easily removed) using chemical methods than zirconium, which is the reverse of the relative removal with other, mechanical methods. These differences were underscored by 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.

In Urban RDD simulant testing, the characteristics of the substrate seemed to have a strong influence on the tenacity of the contaminant. The characteristics exhibiting the strongest influences on tenacity in these tests were found to be permeability and surface pH. However, these effects could only be evaluated when viewed from the perspective of whether a contaminant first precipitates at the surface. The % removal of cesium followed a near first order relationship with the log of permeability for the four substrates studied – concrete, marble, granite and limestone. This characteristic could be evaluated because cesium speciation is unaffected by pH over the range of surface pH studied. However, the effect of substrate permeability on americium retention, for instance, could not be studied because the pH of the surface (and subsequent precipitation) was the dominant factor in its tenacity. No relationship of this sort was noticed with the non-porous surfaces of stainless steel in the SIMCON studies.

Some characteristics of secondary importance noted during Urban RDD testing were: cation-exchange capacity, iso-electric potential and substrate microstructure. For cationic radionuclides that do not interact chemically with the substrate surface (i.e. pH promoted precipitation), and for substrate of similar permeability, the net surface negative charge (cation-exchange capacity (CEC) and iso-electric potential) of the material substrate plays a role in determining the tenacity of such radionuclides contaminant (along with the contaminant charge density). Special characteristics, for instance the microstructure of the granite, which has a layered claylike surface, seem to promote the sequestration of radionuclides within the substrate. However, the microstructure of marble is homogenous and it’s tighter fitting structure gives it far less of the "trapping" characteristic.

The relationships discovered during both the SIMCON and Urban RDD decontamination testing cause us to reassess our simplistic contamination model (Figure 2) presented at the start of this dissertation. No real impact was assessed in this model in neither the different chemistries of the contaminant nor the physical and chemical differences of the substrate. In this research we found that some of these characteristics are key to understanding the tenacity of contaminants with respect to different substrates. While the simple INL model incorporates the important mass transfer aspect of decontamination (which are dependent on permeability and porosity), it fails to identify key characteristics that we found during these tests and the evaluation of the data. A visual model more like that presented in Figure 58, describes the interaction of the contaminant and the substrate, particularly interactions at the surface (substrate surface pH for instance) is an important addition.

Figure 58, Updated INL Urban RDD Contaminant Model



There is no “one best” solution for every decontamination, many criteria must be examined before choosing the best method. Excellent results were found with abrasive blasting techniques for both SIMCON 2 and Urban RDD simulants. Harsh chemical methods were also effective on these types of contaminants. Typically acidic solutions seem to have better overall decontamination effectiveness for both types of contamination systems. But, some basic and neutral solutions with chelants and adsorptive binding mechanisms were also effective at removing Urban RDD contamination.

The Waste Isolation Pilot Plant (WIPP) decontamination simulation is an example of effective use of a simulation approach to develop an effective decontamination strategy. Several candidate methods were put to a non-radioactive trial (using actual halite rock) and two were found satisfactory to move to a radiotracer study. By performing this study radioactive exposure and wasted effort on inappropriate methods were both minimized; thus saving costs and reducing radiation dose. This approach (really, years of this approach) was validated as the WIPP decontamination campaign made successful use of the testing results.

Decontamination testing provides a fundamental understanding (via an applied methodology) of the chemical and physical properties that are important for successful contaminant removal. Such testing can identify specific characteristics that make the decontamination process easier and more effective. At a time when recovery and removal of contaminants is becoming more important, testing provides assurance that society can mitigate future radiological threats.

Suggestions for Further Study

During our studies, we discussed some characteristics about the radionuclides and chemical species that could be validated by further experimentation. In the SIMCON 2 work, we examined the decontamination properties of cesium and zirconium versus chemical and physical (mechanical) methods. In that case zirconium was more easily removed by chemical decontamination methods than was cesium and the order were reversed for mechanical methods. We theorized that this was caused by the nature of the diffusion of those chemical species into the surface oxide of stainless steel. The zirconium was not tightly incorporated into the oxide layer, thus it was less likely to be removed with the oxide, but more likely to be removed chemically. The penetration and position of the zirconium material could be verified by scanning electron microscopy (with electron probe analysis) or another sophisticated imaging/characterizing method.

A mathematical relationship might be developed that may direct the application of decontamination technologies for urban surfaces. The fundamental properties highlighted in this report could lead to such a model that predicts how different contaminants are adsorbed on different substrates. That predictive method could be used as a tool to suggest the best, cheapest and fastest methods to attack the contaminant. Currently, most on-scene management applies previous knowledge (and anecdotal evidence) to how to best cleanup contamination. As noted in the early chapters of this dissertation, that is very limited and seldom applies from one problem to the next. A model based on the principles of contaminant/substrate interaction may fill that void.

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