

## **Understanding Mechanisms of Radiological Contamination - 14054**

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### **ABSTRACT**

Over the last 50 years, the study of radiological contamination and decontamination has expanded significantly. This paper 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. About twenty years ago the Idaho Nuclear Technology Engineering Center (INTEC) at the US Department of Energy (DOE) Idaho National Laboratory (INL) began a search for decontamination processes which could minimize secondary waste. In order to test the effectiveness of these decontamination technologies, a new simulated contamination, termed SIMCON, was developed. SIMCON was designed to replicate the types of contamination found on stainless steel, spent fuel processing equipment. Ten years later, the INL began research into methods for simulating urban contamination resulting from a radiological dispersal device (RDD). The initial work was sponsored by the Defense Advanced Research Projects Agency (DARPA) and included the development an aqueous application of contaminant to substrate. Since 2007, research sponsored by the US Environmental Protection Agency (EPA) has advanced that effort and led to the development of a contamination method that simulates particulate fallout from an improvised nuclear device (IND). The IND method diverges from previous efforts to create tenacious contamination by simulating a reproducible “loose” contamination. Examining these different types of contamination (and subsequent decontamination processes), which have included several different radionuclides and substrates, sheds light on contamination and decontamination processes that occur throughout the nuclear industry and in the urban environment.

### **INTRODUCTION**

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 between filth and overcrowding in populated areas and the rise of disease in those areas, and began advocating better sanitation.<sup>1</sup> Less than 200 years later a new health threat began with the rise of nuclear energy. Even as the

first nuclear materials were being processed at the Hanford Site in the desert of Eastern Washington State in 1944, radioactive waste material was being generated and collected, some of which still contaminates that site today. Operation and maintenance of the process equipment at that site began to require special remotely operated equipment, methods and decontamination techniques developed specifically for those processes.<sup>2</sup>

Radiological contamination has been described as radioactive material (substances that spontaneously emit radiation because of instability within their atoms) lodged in places where it is unwanted. Removal of the contaminated residue resulting from the operation of nuclear infrastructure is called “decontamination”. In reality, radiological contamination is not more difficult to control, nor more pernicious than other types of surface dirt or grime. One fundamental difference with radiological contamination is its ability to be detected by specialized instrumentation, and not by human senses, even at very low levels. “Clean”, with regard to presence of dirt on a surface, may simply be the result of removal of 95% or more of the contaminant. High levels of clean, as one might expect in a “clean room”, are typically achieved such that the air within the room contains only 1 part in 10,000 parts (100 parts-per-million or ppm) of unwanted contaminants. But radiological contamination, which cannot be seen or smelled, can be easily detected even at a quantity of less than  $1 \times 10^{-13}$  grams (typically parts-per-trillion).

In addition, radiological contamination carries with it a public perception that results in justifiably high levels of diligence in control and removal. Radiological contamination is a public health hazard that causes tremendous fear in the general population. Even scientists who may comfortably work with human pathogens may be more concerned with minor amounts of radiological contamination, though it may be far less lethal than most diseases<sup>3</sup>. This sets the stage for one of the real challenges of radiological decontamination: removing very small quantities of material (far smaller than may be required for other hazardous or “dirty” contaminants) so that radiological contamination is maintained below levels of concern.

### **Mechanisms of Radiological Contamination**

While much time and attention has been given to understanding different decontamination techniques, not as much attention has been given to understanding the underlying fundamentals of contamination mechanisms. Understanding these fundamentals is a difficult task as there are many different kinds of contamination and many different mechanisms that could be envisioned.

Contamination of materials occurs because of the physical or chemical transfer of radioactive materials onto surfaces where it is unwanted. Some contamination may be strongly adhered (difficult to remove) to the surface, which is called “fixed” contamination, and some is relatively easy to remove, referred to as “loose” contamination. Generally loose contamination is simply

deposited on the surface such as by an aerosol and it has little interaction with the surface. The removal of loose contamination requires little skill, usually a simple wipe with a damp cloth.

Examples of loose contamination can be found in some of the US Department of Energy (DOE) nuclear facilities such as fuel-fabrication plants. 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. While this surface contamination is usually loose, although adherence can be increased by oily films, grease, grime, or chemical vapors that are found on the inside of ducts. Since ventilation systems usually operate at negative pressures, they tend to draw in dust and aerosols that may contain radioactive 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.

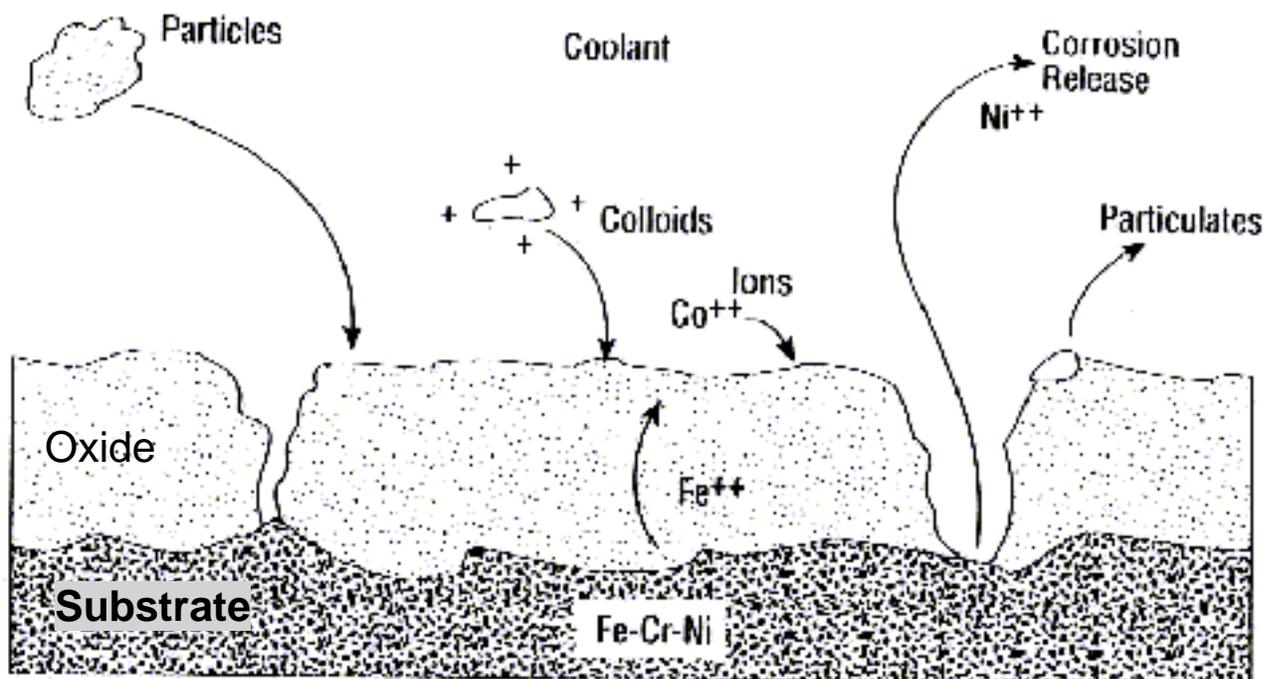
The primary mechanisms by which contamination is deposited include: (1) as solid particles deposited on the surface, as in the loose contamination case, (2) deposited in a barrier layer in the near surface or (3) materials deposited via transport (like capillary action or crevice corrosion) into the bulk of the substrate. In some cases of loose contamination a positive/negative charge interaction may exist between the contaminant and the substrate, but this is usually a very weak, covalent, interaction. Where contamination becomes lodged in the 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 more tenacious contamination problems that exists across the DOE complex involves huge quantities of contaminated metal processing equipment in uranium enrichment facilities. Most of this contamination consists of an overwhelming amount of low-level contamination from the processing of uranium (which has a relatively low radiotoxicity) or recycled contaminants in the feed materials. In these facilities the uranium was dissolved in hydrofluoric acid, to produce uranium hexafluoride ( $UF_6$ ) and these acidic vapors created contamination that was etched into that surface barrier layer of the metal and the metal oxide. As the metal etches and corrodes, it tends to “passivate”, adding additional oxide layers that trap the contaminants.

Nuclear reactors, on the other hand, present a different mechanism of contamination from the enrichment facilities, but share some similarity 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 from the fission products but rather from corrosion products that are released from the cooling loop walls (as a component in the steel alloys) and from the hard faced valves. This corrosion product passes through the reactor core and becomes 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 is shown in Figure 1.<sup>4</sup> This figure shows the accumulation of contamination within and on the oxide layer, technically called the “crud” layer. Decontamination of this type of contamination, 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 the metal is non-porous.

**Figure 1. Crud Layer Contamination Model<sup>4</sup>**



DOE fuel reprocessing chemical processes, not unlike enrichment facilities, tend to generate a tenacious scale and oxide layer on piping and equipment. This type of contamination is removable with an aggressive oxide removal treatment. Acid etching also may cause erosion/corrosion at the metal grain boundaries, which in turn trap contaminants. Contamination in crevices may prevent decontamination solutions from being effective in removing the contaminants. The use of organics in fuel extraction processes leads to the generation of occasional heavy, pasty, organic deposits in pipes and tanks.

Building surfaces experience a somewhat similar contamination process, but with less emphasis on surface barrier layer phenomena and greater emphasis on transport. Studies show that the majority (up to 66%) of construction and demolition debris is concrete.<sup>5</sup> Contaminated concrete associated with these buildings provides a convenient case study, as it comprises the majority of existing structural material found throughout DOE facilities. Contamination is transferred to

concrete by similar mechanisms to those at play in the metal examples, but typically under less aggressive conditions. Another plausible scenario might be contamination of an urban environment from deposition of aerosolized particles, as in the case of a dirty bomb or an accidental release of industrial radiological materials.

The barrier layer associated with a concrete surface is not composed of an oxide layer as described earlier (i.e., nuclear reactor “crud”) but instead composed of a degradation layer of calcium hydroxide, along with typical urban grime such as carbonation, dust, dirt and soot.<sup>6</sup> Also, while traditional process equipment surfaces may be somewhat uniformly coated (as in the case of metal equipment such as tanks or pipes), urban surfaces that have complex geometries, non-metal surfaces, and great deviations in orientation to contamination fallout” (dry deposition) or “rainout” (wet deposition, e.g., due to precipitation). The most challenging contamination mechanism for concrete is transport (or imbibition) into deeper layers of the material. This is primarily because of the high porosity of concrete.

Another interesting consideration in the case of urban contamination is the method by which the contamination was deposited. Urban contamination would be likely to have been airborne when it was transported to the surface of the concrete, such as contamination from an RDD contamination event. In addition, contamination deposited during a precipitation event (rainout) becomes much more difficult to remove as compared to a dry deposition.

Other urban materials have similar considerations with respect to surface/boundary layers and porosity, but may also have additional interesting characteristics. As in the case of metals, surface finish (i.e., roughness) can dramatically affect successful decontamination. 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. Heterogeneity of the surface may increase surface contaminant retention, as in the case of granite where the colored veins are composed of amphiboles and micas that trap cesium or other contaminants within the inner layers of the mineral and “fix” it in place.

### **Examples of Simulating Contamination**

Testing decontamination effectiveness for various mechanical and chemical processes has been conducted and documented for over 70 years. In most cases, these tests have been typically empirical, where an item of equipment, a process system, or a facility has been decontaminated using several different decontamination processes or products to determine which method works best for that situation. This approach may be appropriate for a particular decontamination scenario to determine an operational course of action. However, this approach would not be appropriate if the results are intended to be used as a basis for decontamination decisions

regarding other, even similar, contamination/decontamination scenarios. Successful results from one particular application do not necessarily translate to another even slightly different case.

A case in point involves some recently published test results of the strippable coating DeconGel™ (Cellular Bioengineering Inc, Honolulu, HI). One particular formulation of the product, DeconGel™ 1101, was shown to be very effective at removing certain kinds of contamination. Tests at the Oak Ridge National Laboratory (ORNL) in 2009 showed between 37% to 90% removal of several radionuclides from a 6.2 m X 9.2 m painted concrete floor.<sup>7</sup> Lawrence Livermore National Laboratory (LLNL) reported between 37% and >99% removal of plutonium from a stainless steel glovebox.<sup>8, 9</sup> 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 99.6% removal, but only 15.6% removal from bare (unpainted/unsealed) concrete.<sup>10</sup> A Colorado State University (CSU) study of three strippable coatings (ALARA 1146™, DeconGel™ 1101 and Bartlett TLC™), demonstrated removal of Tc-99m, Tl-201 and I-131 by DeconGel™ of 97% from vinyl tile and 99% from stainless steel.<sup>11</sup> While these were, for the most part, more rigorous laboratory efforts, in terms of the quality of the data, the results were limited to those test conditions and criteria and do not provide sufficient basis for recommending this technology for any other decontamination scenarios.

A more universally applicable approach to evaluating product performance has been taken by both INL and the US Environmental Protection Agency (EPA) which includes the principles of operational relevancy, reproducibility, and range. The empirical tests conducted by ORNL and LLNL by their very nature are limited because of the limited information available concerning the contamination quantity, age, and mechanism of contamination. The character and conditions surrounding the contamination which occurred many years before are not documented, nor available to other researchers. While the data do provide some valuable information, these results cannot be realistically replicated, nor can they be compared to other results in a meaningful way. The CSU laboratory data compares three strippable coating methods, which gives some degree of perspective. However the other tests (ORNL, LLNL and SNL) have no “relative” method to allow comparison.

These high values also give no range to allow comparison with potentially more effective methods. In other words, these test methodologies would be unable to discern methods that might be more effective at removing contamination (like sand blasting) than strippable coatings. Demonstrating a strippable coating removal efficacy of 97% (or greater) only begs the question of whether this was really a tenacious contamination. For example, when CBI released their new product, DeconGel™ 1108, it was shown to be almost twice as effective as DeconGel™ 1101 (based on third party evaluations<sup>12</sup>) for removing contamination. The ORNL, LLNL, and SNL

test methods would be inappropriate to replicate that result. Tests such as these cannot provide an adequate range for evaluation against competing methods and provide a “level playing field”.

### **Simulation Methods Proven Over Many Years**

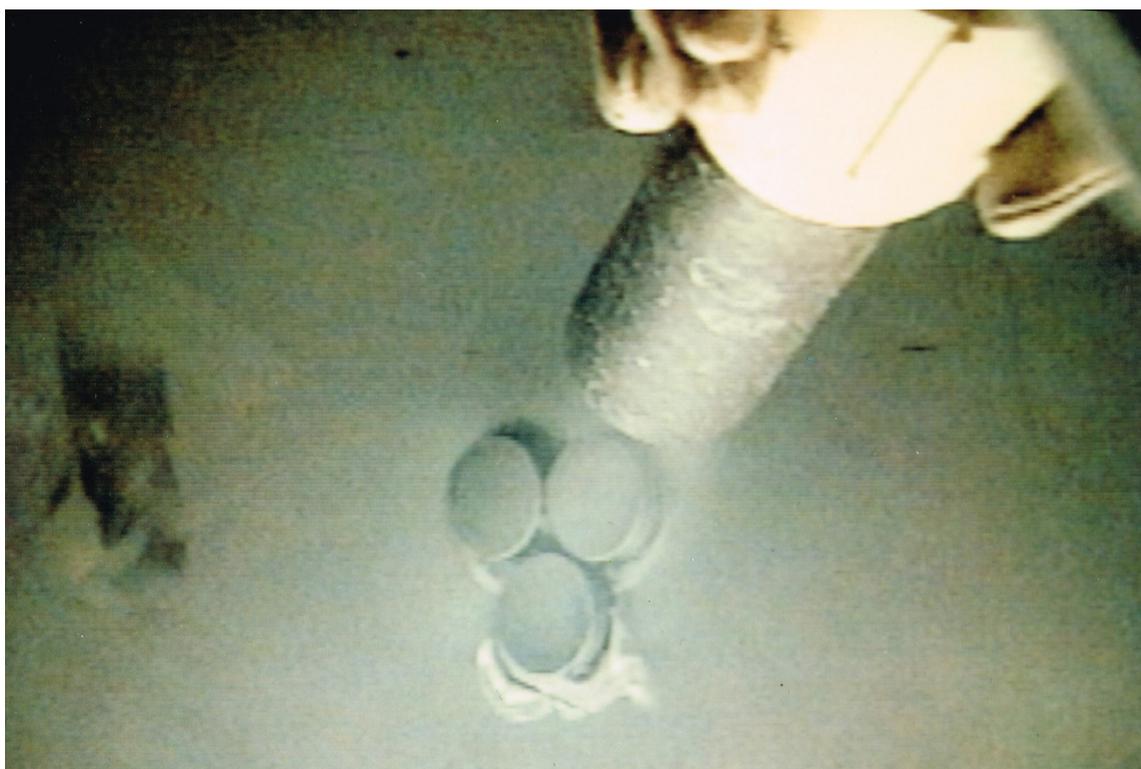
While it is important to recognize the value of the different decontamination tests referred to above, including applied tests on “real” contaminated systems and having reliable, well-developed methods of simulating contamination can provide a better overall comparison. Having the ability to compare decontamination methods in a controlled and repeatable fashion gives researchers the ability to screen those methods for value prior to application at an actual clean-up site. To this end, a few common methods of applying radionuclides (or non-radioactive surrogates) have been developed and applied to a large number of decontamination methods over the last several decades. Several national laboratory or other government institutions have adopted some more or less common practices. The most common means of applying a contaminant or surrogate to a substrate is via a pipetting method. Known quantities of radioactive salts (or non-radioactive surrogates), are dissolved in aqueous solution, are pipetted onto the surface of coupons of a chosen substrate, and typically air dried. Another common means of applying a liquid contaminant to surfaces is by spray application, either with a simple atomizing pump or a more sophisticated air atomizing system.<sup>13</sup>

By far the most popular of these methods is the pipette method which has been practiced at many different institutions. The Defense Research Development Canada, the radiological decontamination research arm of the Canadian military, has performed decontamination simulation testing at their Ottawa, ON facilities using a pipetting methodology, as have similar laboratories in the United Kingdom. This methodology was used in some of the DeconGel™ examples given above.<sup>10, 11</sup>

The INL used this method for the SIMCON 1 and SIMCON 2 methodologies to replicate contamination on stainless steel in the 1990s. All constituents of SIMCON test simulants are non-radioactive. SIMCON 1 Coupons were prepared using 1 milligram (mg) of cesium (cesium nitrate) and 1 mg of zirconium (zirconium nitrate). This simulates actual levels of cesium-137 and zirconium-95 contamination typically found on surfaces in reprocessing facilities. These particular simulants are not considered hazardous materials; thus it is far easier to distribute these coupons to potential decontamination technology vendors. The SIMCON 1 simulants are dried on the surface of a 304 stainless steel coupon of approximately 2.5 cm diameter, 0.6 cm thickness to give a fairly uniform stain or crust. SIMCON 1 coupons exhibited a less tenacious “loose” contamination that could mostly be removed by rinsing the coupons with water. The method was valuable for testing loose decontamination methodologies (like strippable coatings), but was not applicable to some of the more aggressive methods, such as abrasive blasting. SIMCON 2 was developed to create a “fixed” type of contamination.<sup>14</sup>

SIMCON 2 coupons were produced by pipetting 5 mg of cesium and 1 mg of zirconium salts onto the metal coupon surface and baking the coupon at 700°C for 24 hrs. The excess salts were removed from the surface by brushing and rinsing the coupons (leaving about 0.2 mg of cesium and zirconium). This resulted in a "fixed" type of simulated contaminant embedded in the passivated oxide layer that was very difficult to remove. 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 the surrogate salts. SIMCON 2 prepared in this manner retained zirconium and cesium in the 100 to 200 ug/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. Figure 2 shows two SIMCON 2 Coupons being decontaminated with an abrasive blaster.

**Figure 2. SIMCON 2 Coupons Being Cleaned with an Abrasive Blaster**



These coupons have been used at the INL to determine the effectiveness of many types of decontamination techniques (e.g., laser ablation, CO<sub>2</sub> pellet blasting, alternative chemicals, abrasives, strippable coatings, etc.) prior to using the techniques in radioactive environments. After coupons were decontaminated, they were removed from the array plate and analyzed using X-ray fluorescence to determine traces of simulants remaining on the surface. Analysis of the coupons before and after treatment gave an estimate of the cleaning efficacy and decontamination factor was derived. Over 1000 coupons have been prepared and tested using

various methods evaluated by the INL. A selected group of results from SIMCON 1 & 2 decontamination testing is seen in Table 1.

**Table 1. Selected Results of SIMCON 1 & 2 Tests.**

<b>Technology</b>	<b>SIMCON 1 removal Cs (%)</b>	<b>SIMCON 1 removal Zr (%)</b>	<b>SIMCON 2 removal Cs (%)</b>	<b>SIMCON 2 removal Zr (%)</b>
Water Rinse	100	99	0	0
Ultrasonic	100	100	70	88
CO2 Pellet Blasting	91	92	63	78
SDI CO2 Pellet Blasting	100	99	84	100
CO2 Snowflake	83	94	26	78
Centrifugal CO2			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
CO2 Laser Ablation	97	86		
Nd:YAG Laser Ablation	98	99	75	99
Excimer Laser Ablation	99	98	77	99
Bartlett 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

A new contamination simulation process was developed at the INL for urban materials that might become contaminated by a terrorist act (e.g. RDD). A simple nebulizer process and an air-brush type device were used to deposit a single radionuclide in an aqueous solution onto coupons of various materials. Nitrogen was introduced to an open ended syringe body, while a radionuclide solution was slowly introduced via a fine capillary tip. The liquid spike deposited on each coupon was typically 2.5 ml of an aqueous cesium chloride solution (<sup>137</sup>Cs). The operator panned the syringe of nebulized fluid across the coupon surface resulting fine droplets

evenly distributed over the surface of a 15 cm square coupon of concrete, marble, granite, or limestone. The coupon sides were masked so that the solution was applied onto the working surface only. The masking was removed after the solution was deposited and the coupons were allowed to air dry in a fume hood for 24 hrs. They were then were bagged in 4 mil plastic bags, tagged, surveyed, removed from the hood, and analyzed using high purity germanium (HPGe) gamma spectrometry. Since the first applications of this simulation method for cesium contamination, it has been used nearly 500 times and with additional radionuclides including Co-60, Sr-85 and Am-243 (all gamma emitters).<sup>15</sup> A sampling of results for decontamination efficacy, expressed in terms of percent removal, of cesium from concrete are shown in Table 2.

**Table 2. Urban Decontamination Results for Cesium on Concrete**

<b>Technology</b>	<b>Removal (%) Cs-137 from concrete</b>
Empire Blast Grit Blaster	96
Dust Director Diamond Flap Wheel	89
EAI Rad-Release II (Chemical)	85
ISOTRON (Stripcoat)	78
Argonne SuperGel (Chemical)	73
EAI Rad-Release I (Chemical)	71
Decon Gel 1108 (Stripcoat)	67
CS Unitec Sander	54
QDS Liquid (Chemical)	53
INTEK ND-600 (Chemical)	52
RDS 2000 (Chemical)	52
Decon Gel 1101 (Stripcoat)	49
INTEK ND-75 (chemical)	47
INTEK LH-21	44
Dust Director Wire Brush	38
River Technology Rotating Water-jet	36
Bartlett TLC (Stripcoat)	30

## CONCLUSIONS

There are many different methods to simulate contamination so that screening of decontamination methodologies can be assessed. Thought must be given to the mechanisms by which the target contaminant is held; for instance as loose solids, particles trapped in a metal oxide layer, or deposited into pores of a porous material like concrete. It is important that thought be given to the success criteria for the decontamination, including operational relevance, reliability, and the appropriate range of the simulation methods. Some contamination simulation

methods have a notable “pedigree” and may be more meaningful for comparison. There are many different factors that can affect the ability of the contamination to be removed. For instance, the duration that the contamination remains on the surface has been shown to reduce the effectiveness of the decontamination. Even for simple tests many factors must be taken into account such as the chemistry of the substrate surface (such as the pH), the geology (mineral or clay phases) of the material, porosity, and the material’s cation exchange capacity. It is important to use a reproducible contamination simulation methodology that has undergone a large number of tests so that the individual characteristics of the substrate and the contaminant can be minimized and the effect of the decontamination technology can truly be evaluated.

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