Journal of Environmental Chemical Engineering 4 (2016) 1514–1522

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Sorption of radionuclides to building materials and its removal using simple wash solutions

Michael Kaminski*, Carol Mertz, Luis Ortega, Nadia Kivenas

Nuclear Engineering Division, Argonne National Laboratory, United States

ARTICLE INFO

Article history:
Received 2 November 2015
Received in revised form 20 January 2016
Accepted 2 February 2016
Available online 3 February 2016

Keywords:
Decontamination
Remediation
Radioactive contamination
Ammonium
Cesium-137
Concrete

ABSTRACT

Decontamination after a nuclear or radiological release requires a detailed understanding of the materials hosting the contamination, the chemistry of the radionuclide, and the chemical properties of the decontamination agent. Urban contamination via a number of radiological release scenarios may require simple decontamination methods that can be deployed for wide-area decontamination. This paper investigates a number of factors of importance for developing such decontamination methods, focusing on cesium. These factors include the influence on decontamination approaches from the cesium deposition conditions, the urban building material composition and, when washing with an ionic solution that is utilized for decontamination, the composition of the wash solutions. In summary, the sorption chemistry of cesium onto urban building materials and roadways has been studied to develop simple decontamination methods that can be deployed for wide-area decontamination efforts.

To improve the understanding of the sorption of cesium onto common urban building materials and roadways the desorption of cesium deposited from solution and as a dry powder was tested. Using ammonium (NH_4^+) salt solutions, we tested the desorption of ionic cesium bound to individual components of concrete and coupons of several common building materials. While the tests on concrete aggregate suggest that a concentration >10 mM NH_4^+ does not improve the desorption of cesium, tests on concrete, asphalt, marble, limestone and granite monoliths showed improved decontamination factors when the NH_4^+ concentration increased from 0.1 to 0.5 M. We also found that cesium as dry particulate material could be removed quite effectively although the contamination became tenacious upon wetting the surface.

1. Introduction

An airborne release of radioactive material may occur primarily from three sources—a nuclear weapon detonation, a nuclear reactor core accident, or a radionuclide dispersal device (RDD). Each source can contaminate large areas of urban and rural land. Depending on the mechanism for release of the radioactive material and the environmental conditions, the method for remediating affected areas contaminated with the radioactive fallout material may differ drastically. For example, actinide elements tend to condense quickly, forming large agglomerated particles that travel relatively short distances from the detonation site [1], while important radionuclides such as cesium-134 and cesium-137 are much more volatile than the actinides, highly soluble in water, can form compounds/complexes with many other substances, are known to condense onto the fine dust in the fallout from an explosive discharge [1] or a reactor core accident [2], and can travel long distances in the plume [3]. The prevalence of highly soluble salt forms of concentrated cesium-137 used in industry and government suggests that potential RDD sources may produce similarly condensed soluble forms of cesium.

Radiological decontamination is a well-established field in the nuclear industry, practiced during routine operations [4] or in decommissioning of a nuclear facility [5]. However, remediating an urban or rural environment for unrestricted use is not common practice because of the cost and scale of the remediation effort. The Chernobyl nuclear reactor accident in 1986 proved that we are not prepared to remediate an urban or rural environment for unrestricted use even though Nordic researchers had begun to investigate wide-area decontamination [6,7]. The Exclusion Zone surrounding the Chernobyl reactor persists and, most recently, the reactor accidents at Fukushima showed we are still ill-prepared for such large scale remediation efforts.

Because of the density of inhabitants and of economic activity the remediation of the urban environment and, particularly, the

* Corresponding author. Fax: +1 630 972 4499.
E-mail address: Kaminski@anl.gov (M. Kaminski).

http://dx.doi.org/10.1016/j.jece.2016.02.004
2213-3437/

hard external surfaces of buildings and roadways is an area of pressing concern. The recommended practice for decontaminating these surfaces relies primarily on methods for small-particle removal (vacuuming, sweeping, washing/rinsing with water). Ideally, the decontamination technique should treat large areas quickly. For cesium sorbed to loose particulate or debris, the first step is to remove this loose material. However, rain or even humidity can render cesium into solution as cations that can bond to copious negative sorption sites present on building materials such as clays, rock minerals, and cement. Once bound to the surface, the surface needs to be physically removed or chemically treated to promote the desorption of cesium cations. Moreover, any cesium that had become irreversibly bound into the network of transition metal oxides or carbonates would be essentially unavailable for removal except by methods that chemically or physically scoured the surfaces. In a wide-area remediation effort conducted outdoors, such techniques using aggressive chemicals to etch the surface or scabbling tools might be too laborious or time consuming to complete. Instead, simpler methods are sought. For example, a fire hose can distribute water to wash down building roofs, facades, and paved areas rapidly. However, washing cesium with water from a fire hose is generally ineffective, as studies have demonstrated [7,8]. There were simply insufficient ions present to desorb the solubilized cesium that was bound strongly to ion exchange sites on the building materials.

To improve decontamination of cesium, researchers tested solutions containing cations similar to cesium in ion exchange properties since ion exchange is believed to be an important mechanism in the immobilization of solubilized cesium onto common building materials, especially immediately after deposition. Sandalls [9] first reported the use of an ammonium nitrate wash to remove cesium from building materials, employing the ion exchange properties of ammonium nitrate that are very similar to cesium (cationic charge density and resultant hydrated radii). Ahn et al. [10] employed ammonium-loaded clay suspensions to decontaminate cesium deposited on brick and slate but found that the ammonium provided only marginal improvement in decontamination factors compared to the clay suspension alone. DeWitt et al. [11] found that ammonium concentrations above 0.2 M generally improved decontamination factors only marginally for concrete, asphalt and clay tiles. Real et al. [12] reported dramatic improvement in the removal of cesium deposited on clay tile and concrete as an aerosol using aqueous ammonium solutions. Drake [13] recently discussed several approaches for decontamination technologies and tools for use after radionuclides, including cesium, are released from a radiological dispersal device. Demmer et al. summarized methods used to date at Chernobyl and Goiania [14], including the advent of benchmark testing methods [15]. Most recently, the EPA has reported results from testing ionic formulations on concrete, granite, marble, limestone and asphalt [16], and Kaminski et al. [17] reported the development of a system for washing buildings and roadways with potassium or ammonium salt solution, containing the produced waters, and treating remaining cesium on-site, thereby enabling reuse of water during decontamination operations.

Table 1
ICP-MS and gamma* analysis results of Cs-137 stock solution.

Element	Concentration (μg/L)	Estimated accuracy
Lithium	<7.2	±13%
Boron	<25.5	±18%
Sodium	120	±11%
Magnesium	<3.1	±10%
Aluminum	<28.8	±10%
Silicon	<7.4	±10%
Potassium	133	±12%
Calcium	248	±10%
Iron	66.7	±10%
Rubidium	0.14	±10%
*Cs-137	17.8	±2%

To improve the understanding of the sorption of cesium onto common urban building materials and roadways, the desorption of cesium deposited from solution and as a dry powder was tested. Using aqueous NH_4^+ salt solutions, we tested the desorption of ionic cesium bound to individual components of concrete and coupons of several common building materials. While the tests on concrete aggregate suggest that a concentration >10 mM NH_4^+ does not improve desorption of cesium, tests on concrete, asphalt, marble, limestone and granite monoliths showed improved decontamination factors when the NH_4^+ concentration increased from 0.1 to 0.5 M. Cesium as dry particulate material could be removed quite effectively, although the contamination became tenacious upon wetting the surface.

2. Methods

All chemicals used were reagent grade or better, and all solutions used deionized water (~18 MΩ×cm resistivity at 25 °C). The ammonium chloride solutions were prepared by adding the salt to tap water. The cesium-137 stock solution was obtained from in-house stores and was analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) for potential contaminants after acidifying with Optima nitric acid (ELAN DRC II, PerkinElmer/SCIEX, calibrated with standards prepared from NIST-traceable solutions procured from Ultra Scientific, North Kingstown RI. Reported data were calculated from the ICP-MS concentration data and the dilution factors of the samples. Samples were acidified to 1% HNO3 prior to analysis.). The results verified the purity of the stock solution (Table 1).

Table 2
Coupon material descriptions and sources.

Material	Description	Name	Locality	Source
Red brick	Red, fine-grained	Paving brick	Made from red Triassic clay	Triangle Brick Company, Durham, NC
Limestone	Light-grey, coarse-grained, ~75% skeletal grains, remainder calcite cement and trace (1%) quartz, dolomite, pyrite, clay	Indiana	South central IN	Cathedral Stone Products, Hanover Park, MD
Granite	Pink with dark banding, medium-coarse texture, biotite	Milford Pink	Milford, MA	Fletcher Granite Company 534 Groton Road Westford, MA
Concrete	Cement with sand aggregate	Quikrete® concrete mix	N/A	Local supply store, Raleigh-Durham, NC area
Asphalt	Laboratory-pressed asphalt	N/A	N/A	North Carolina Department of Transportation