



Mitigation of Cesium and Cobalt Contamination on the Surfaces of RAM Packages

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Abstract

Techniques for mitigating the adsorption of ¹³⁷Cs and ⁶⁰Co on metal surfaces (e.g., RAM packages) exposed to contaminated water (e.g., spent-fuel pools) has been developed and experimentally verified. The techniques are also effective in removing some of the ⁶⁰Co and ¹³⁷Cs that may have been adsorbed on the surfaces after removal from the contaminated water. The principle for the ¹³⁷Cs mitigation technique is based upon ion-exchange processes. In contrast, ⁶⁰Co contamination primarily resides in minute particles of CRUD that become lodged on cask surfaces. CRUD is an insoluble Fe-Ni-Cr oxide that forms colloidal-sized particles as stainless steels corrode. Because of the similarity between Ni⁺² and Co⁺², CRUD is able to scavenge and retain traces of cobalt as it forms. A number of organic compounds have a great specificity for combining with nickel and cobalt. Ongoing research is investigating the effectiveness of chemical complexing agent, EDTA, with regard to its ability to dissolve the host phase (CRUD) thereby liberating the entrained ⁶⁰Co into a solution where it can be rinsed away.

1. Introduction

“Weeping” of a spent nuclear shipping cask occurs when a cask that swiped clean at the point of origin later releases radionuclides either during shipping or as it is stored at its final destination. Historical data suggest that up to 2% to 20% of packages in a given shipping campaign may exhibit weeping. The primary culprits involved in weeping incidents are ⁶⁰Co and ¹³⁷Cs. Methodologies for mitigating weeping would be of utility in the United States once centralized facilities for the long-term disposal of spent fuel are opened.

It was previously thought that radionuclides might be entrained in the passivating Fe-Ni-Cr oxide coatings developed on cask surfaces [1]. Radionuclides are then thought to be released by either chemical or mechanical means. Although reasonable for ⁶⁰Co, this mechanism is problematic for ¹³⁷Cs as cesium is not sorbed strongly onto oxide surfaces and its ionic radius is significantly larger than the metals that comprise the bulk of such oxide coatings. This paper suggests that the retention and release mechanisms for ¹³⁷Cs and ⁶⁰Co are likely to be quite different. In particular, it is likely that ⁶⁰Co contamination probably resides in the colloid-sized mixed Fe-Ni-Cr-oxide particles formed by corrosion in reactor cooling systems, “CRUD”. These are then transported to the spent-fuel pool on the surfaces of the fuel assemblies and ultimately find their way onto the surfaces of immersed shipping cask. On the other hand, ¹³⁷Cs is probably associated with small amounts of clay (or other aluminosilicate “soil components”) where it can readily substitute on sites normally occupied by potassium ions (compare [2] with [3]). Both types of particles are small enough to adhere tightly to the exterior of a shipping cask without being noticed. However, the chemical and mechanical processes likely to liberate the radionuclides to the environment will be significantly different. If this distinction is correct then two experimentally verifiable criteria should be met: 1) the presence of road grime (containing clays and other aluminosilicates) should enhance the uptake of Cs more than the retention of Co and 2) preloading the clay sites with non-radioactive Cs, or similarly sized ions (e.g., K⁺ or NH₄⁺) should diminish the later uptake of radioactive ¹³⁷Cs, but have minimal effect on ⁶⁰Co retention.

2. Experimental Studies

A number of tests were carried out to quantify different aspects of the processes thought to be responsible for the retention and release of ⁶⁰Co and ¹³⁷Cs. The first set of experiments assessed the uptake of ¹³⁷Cs and ⁶⁰Co onto variously treated steel surfaces. These same experiments were also used to assess if it was possible to pretreat the surfaces to block the uptake of radionuclides. These tests employed steel coupons that fit conveniently into the gamma-ray counter (6.3 cm by 0.75 cm by 0.25 cm) and were polished to have surface finishes representative of what might be found on a shipping cask (3.2 μm). Subsequent to machining, all of the coupons were washed with detergent to remove machine oils and air-dried. Half of the samples (“clean” vs. “soiled”) were submersed in suspension of road grime (from the undercarriage of the lead author’s 1966 Volvo) that dried on their surfaces over

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a weekend (~70 hours). The “soiled” coupons were then washed free of obvious contamination. They were then, variously, immersed in 0.1 M solutions of Cs₂SO₄, (NH₄)₂SO₄, or K₂SO₄ over a weekend, or given no treatment at all (designated “tap”). All coupons were then rinsed with deionized water and dried. These activities produced a 2x4 matrix of test coupons (soiled or unsoiled X four pretreatments). Each batch of four coupons was then placed together in 25 ml test tubes containing tap water spiked with 10 µCi/L ¹³⁷Cs and 25 µCi/L ⁶⁰Co and allowed to equilibrate for one day. Next, they were then removed, individually cleaned of adhering droplets test fluid by a quick rinse with deionized water, dried, and, finally, placed in a pre-calibrated gamma counter to quantify the amounts of ¹³⁷Cs and ⁶⁰Co retained (Table 1). It is evident that: (1) the presence of road grime had a large impact on Cs uptake – but not Co uptake, and (2) that the pretreatments, particularly with non-radioactive Cs, significantly diminished the later acquisition of radioactive ¹³⁷Cs but had little influence on ⁶⁰Co.

Table 1. Results of initial loading after different pretreatments: Average surface contamination and standard deviations on four unpainted coupons (10⁻³ µCi) for each pretreatment group.

Surface condition ⇒ Pre-Treatment ↓	Cs, clean	Cs, soiled	Co, clean	Co, soiled
Tap Water	2.44 ± 0.28	42.9 ± 5.6	1.77 ± 1.18	2.61 ± 0.41
0.2 M Cs ⁺	0.40 ± 0.46	4.24 ± 0.37	2.43 ± 0.35	2.78 ± 0.30
0.2 M K ⁺	3.21 ± 0.38	11.2 ± 1.7	2.16 ± 0.20	2.72 ± 0.16
0.2 M NH ₄ ⁺	2.99 ± 0.36	14.4 ± 2.8	2.01 ± 0.18	2.62 ± 0.14

The next phase of these tests was to assess whether a post-immersion washing might provide an effective treatment for removing ¹³⁷Cs and ⁶⁰Co. Toward this end, One previously contaminated coupon from each of the four retreatment groups was placed individually in each of the different radionuclide-free pretreatment fluids used initially to precondition the coupons. Samples were allowed to equilibrate with the fluid over the weekend and then removed, cleaned, dried, and counted in the manner described earlier. Tables 2 - 5 give residual surface loadings after this rinse process for, respectively: residual ¹³⁷Cs on unsoiled coupons, residual ¹³⁷Cs on soiled coupons, residual ⁶⁰Co on unsoiled coupons, and residual ⁶⁰Co on soiled coupons. Results are listed as follows: the residual activity prior to post-washing (upper left), the residual activity after post washing (upper right), and the percentage reduction resulting from the post-wash of that particular coupon is beneath these two figures.

For ¹³⁷Cs the notable results are that: (1) tap water and the K⁺-containing fluids generally worked somewhat better than the ammonium-containing rinse, and (2) a post-wash with a (non-radioactive) 0.2 molar Cs⁺ solution was clearly the least effective option. This probably reflects the fact that there would be little tendency for ion exchange processes to transport trace amounts of cesium off of a mineral surface when the surrounding solution already contains a significant amount of dissolved cesium. For ⁶⁰Co, the only observable trend was a slight apparent superiority for the 0.2 M K⁺ solution, but the distinction is too small to be useful as a decontamination strategy. Also, and none of the rinses removed ⁶⁰Co with the same efficiency that ¹³⁷Cs was removed.

Table 2. ¹³⁷Cs Retention and release by unpainted coupons that *were not exposed* to road grime: results are activity (10⁻³ µCi) remaining on the coupon surfaces.

Post-Treatment ⇒ Pre-Treatment ↓	Tap Water	0.2 M Cs ⁺	0.2 M K ⁺	0.2 M NH ₄ ⁺
Tap Water	2.4 to N.D., ~100% removed	2.6 to 1.7, 35% removed	2.1 to N.D., ~100% removed	2.7 to 1.1, 59% removed
0.2 M Cs ⁺	N.D.	0.72 to 0.20, 72% removed	N.D.	0.87 to N.D., ~ 100% removed
0.2 M K ⁺	2.8 to 0.30, 89% removed	3.7 to 2.4, 35% removed	3.2 to 1.1, 66% removed	3.3 to 1.5, 55% removed
0.2 M NH ₄ ⁺	2.8 to 0.39, 87% removed	2.8 to 2.0, 29% removed	2.8 to 1.3, 54% removed	3.5 to 1.5, 57% removed

Table 3. ^{137}Cs Retention and release by unpainted coupons that *were exposed* to road grime

Post-Treatment ⇒ Pre-Treatment ↓	Tap Water	0.2 M Cs^+	0.2 M K^+	0.2 M NH_4^+
Tap Water	47 to 17, 64% removal	39 to 32, 18% removal	37 to 18, 51% removal	49 to 25, 49% removal
0.2 M Cs^+	4.2 to 0.56, 87% removal	4.0 to 1.3, 68% removal	4.8 to 0.41, 91% removal	4.0 to 0.53, 87% removal
0.2 M K^+	12 to 3.2, 73% removal	13 to 8.3, 36% removal	8.9 to 1.9, 79% removal	10 to 5.3, 47% removal
0.2 M NH_4^+	13 to 3.6, 72% removal	12 to 6.5, 46% removal	16 to 4.8, 70% removal	18 to 2.3, 82% removal

Table 4. ^{60}Co Retention and release by unpainted coupons that *were not exposed* to road grime

Post-Treatment ⇒ Pre-Treatment ↓	Tap Water	0.2 M Cs^+	0.2 M K^+	0.2 M NH_4^+
Tap Water	2.4 to 1.7, 29% removal	2.5 to 1.5, 40% removal	2.2 to 1.1, 50% removal	N.D.
0.2 M Cs^+	2.9 to 1.8, 38% removal	2.1 to 1.3, 38% removal	2.5 to 1.5, 40% removal	2.3 to 1.5, 35% removal
0.2 M K^+	2.3 to 1.5, 35% removal	2.0 to 1.3, 35% removal	2.4 to 1.5, 38% removal	1.9 to 1.3, 32% removal
0.2 M NH_4^+	2.1 to 1.4, 33% removal	1.8 to 1.3, 28% removal	2.2 to 1.3, 41% removal	2.0 to 1.3, 35% removal

Table 5. ^{60}Co Retention and release by unpainted coupons that *were exposed* to road grime

Post-Treatment ⇒ Pre-Treatment ↓	Tap Water	0.2 M Cs^+	0.2 M K^+	0.2 M NH_4^+
Tap Water	2.9 to 1.7, 39% removal	2.8 to 1.4, 50% removal	2.9 to 1.2, 59% removal	2.0 to 1.1, 45% removal
0.2 M Cs^+	2.7 to 1.5, 44% removal	3.1 to 1.5, 52% removal	2.8 to 1.2, 57% removal	2.4 to 1.4, 42% removal
0.2 M K^+	2.7 to 1.7, 37% removal	3.0 to 1.6, 47% removal	2.7 to 1.1, 59% removal	2.5 to 1.2, 52% removal
0.2 M NH_4^+	2.6 to 1.6, 38% removal	2.5 to 1.2, 52% removal	2.6 to 1.0, 62% removal	2.8 to 1.4, 50% removal

ND = not detectable

3. Dissolution Of Aluminosilicates (Clays) Using Complexing Reagents

A second decontamination approach involved directly attacking the phases thought to be responsible for radionuclide retention; aluminosilicates in the case of ^{137}Cs and CRUD for ^{60}Co . In both cases the tactic taken involved selecting complexing agents with a known strong affinity (e.g., complexing ability) for the principal constituents making up the phase. For Cs releases, ammonium fluorosilicate $[(\text{NH}_4)_2\text{SiF}_6]$ and other strong complexing agents for aluminum were selected from a compilation by Nordstrom and May [4].

Artificially "contaminated" road grime was prepared by exposing 8 grams of material to a 10 parts per thousand [non-radioactive] Cs solution for 15 days, and then repeatedly washing the product with deionized water over the next six weeks. Next, a dilute slurry was prepared by suspending this material in 400 ml of deionized water and equilibrating the mix for six weeks. At the end of this period a sample of the filtered water (0.2 μm pore size) contained 20 ppm Cs, 0.02 ppm Al, and 6.5 ppm Si.

The relative effectiveness of the various Cs-release agents was assessed by mixing 1 ml of the various complexing agent stock solutions with 18 ml of the road grime-containing suspension. After seven days samples the fluids were passed through a 0.2- μ m filter and analyzed by ICP-MS for Al, Si and Cs. Several agents successfully scavenged Cs from the road grime: $(\text{NH}_4)_2\text{SiF}_6$ > oxalic acid > di-sodium chromotropic acid > glutamic acid > sodium salicylate. The two best performers also produced significantly elevated levels of dissolved Al, in addition to Cs concentrations significantly above the 20-ppm baseline level. This confirms that the phases sequestering the Cs had actually been attacked, rather than the Cs being released by an enhanced ion exchange process.

Table 6. Concentrations of complexing agents used in Cs release studies and concentrations of constituents leached from Cs-loaded road grime using these complexing agents.

Agent	Grams Water	Grams Agent	Al, ppm	Cs, ppm	Si, ppm
$(\text{NH}_4)_2\text{SiF}_6$	27	4.96	6.57	34.8	n/a
Sodium Salicylate	19.6	5.01	1.11	22.9	8.29
Salicylic Acid	saturated	saturated	0.017	20.71	6.25
Gallic Acid	saturated	saturated	0.052	21.6	10.3
Oxalic Acid	35.7	5.00	39.8	30.8	73.8
Catechol	35.8	5.03	1.79	21.2	12.5
8-Hydroxyquinoline	saturated	saturated	0.03	19.9	7.07
Di-Sodium EDTA	saturated	saturated	3.79	17.8	12.19
Di-Sodium Chromotropic Acid	17.9	1.22	1.74	25.9	9.41
Glutamic Acid	saturated	saturated	0.011	24.3	6.70
Sodium Isosaccharic Acid	17.9	1.00	0.266	20.8	7.20
Deionized Water Blank	N/A	N/A	0.019	20.0	6.48

4. Dissolution Of Crud Using Complexing Reagents

The literature contains numerous reports of strong complexing agents for the constituents making up CRUD (Fe, Cr, Ni, and Co). However, EDTA (ethylenediamine tetra acetic acid) is one of the strongest, as well as being readily available in bulk. The synthetic CRUD used in the leaching studies was prepared by adding an excess of sodium hydroxide to a solution of nitrate salts (Fe^{+3} , Ni^{+2}), sulfate salts (Fe^{+2}) and chloride salts (Co^{+2}). The slurry was then aged hydrothermally in a Teflon-lined PARR reactor at 150° C for 2.8 days, and, finally, washed free of soluble residues. X-ray diffraction verified that the resulting product was a moderately well crystalline spinel-phase material (matching “ferroan Trevorite”); X-ray fluorescence confirmed that the target molar ratios of Fe:Ni:Co (2.4 : 0.4 : 0.2) had been achieved.

EDTA performance was judged by placing about 0.1 g of synthetic CRUD in 25 ml of various test solutions. In all cases solids were clearly visible in the containers when experiments ended. Early tests employed the pure acid form of EDTA (strictly speaking “ H_5EDTA ”). This compound is only slightly soluble so only a limited amount of complexing agent went into solution. Only Ni exhibited any appreciable solubility in this solution (Table 7), Later experiments used the more soluble di-sodium salt (“ $\text{Na}_2\text{H}_3\text{EDTA}$ ”) but, again, only limited solubility was noted and as, with the H_5EDTA , the ratios of the dissolved metals differed from the bulk CRUD composition. This time, though, high levels of dissolved Co, rather than Ni, were observed.

Two additional sets of experiments were then set up to: (1) assess how increasing the $\text{Na}_2\text{H}_3\text{EDTA}$ concentration changed CRUD solubility, and (2) determine if adjusting the initial pH of the test solutions (to between 5 and 6) would enhance CRUD solubilities. However, after five days all of the solutions lacked significant color (indicating disappointingly low CRUD solubilities), so they were placed in an 80°C oven over the weekend. This imparted a dark brown color to the fluids, clearly indicating a significant improvement in CRUD solubility. ICP-MS analysis of the fluids not only confirmed this but also showed that now the ratios of the dissolved metals reflected the composition of the solid being dissolved (Co : Ni : Fe – 0.2 : **0.4** : 2.4). The first three 80°C experiments further demonstrate that a five-fold increase in EDTA concentration only about doubles CRUD solubility. The last three 80°C experiments show that initially adjusting the pH of a $\text{Na}_2\text{H}_3\text{EDTA}$ test solution upward decreased, rather than increased, CRUD solubility. Parenthetically, the increased pH generally seen during the CRUD dissolution experiments reflects the fact that as the metal is extracted from the oxide-phase the residual oxide hydrolyzes to hydroxide – raising the pH.

Table 7. CRUD Solubility in EDTA Solutions

Solution	Temp. - °C	pH - Initial	pH - Final	Co - ppm	Ni - ppm	Fe - ppm	Co : Ni : Fe (Ideally 0.20 : 0.40 : 2.4)
DI water	25	~6	5.6	0.008	ND	.02	0.91 : ? : 2.4
0.001 M H ₅ EDTA	25	2.6	2.2	2.9	45	9.3	0.71 : 11.1 : 2.4
0.134 M Na ₂ H ₃ EDTA	25	4.8	5.1	46	2.5	8.5	12.3 : 0.67 : 2.4
0.134 M Na ₂ H ₃ EDTA	25	7.0	7.5	21	1.6	4.4	10.8 : 0.83 : 2.4
0.026 M Na ₂ H ₃ EDTA	80	4.5	7.0	80	212	1070	0.17 : 0.45 : 2.4
0.067 M Na ₂ H ₃ EDTA	80	4.5	7.0	144	316	1850	0.18 : 0.39 : 2.4
0.134 M Na ₂ H ₃ EDTA	80	4.5	6.2	172	350	2130	0.18 : 0.38 : 2.4
0.067 M Na ₂ H ₃ EDTA	80	5.0	7.5	165	348	2090	0.18 : 0.38 : 2.4
0.067 M Na ₂ H ₃ EDTA	80	5.5	7.7	143	315	1860	0.17 : .039 : 2.4
0.067 M Na ₂ H ₃ EDTA	80	6.0	8.8	120	296	1670	0.16 : 0.40 : 2.4

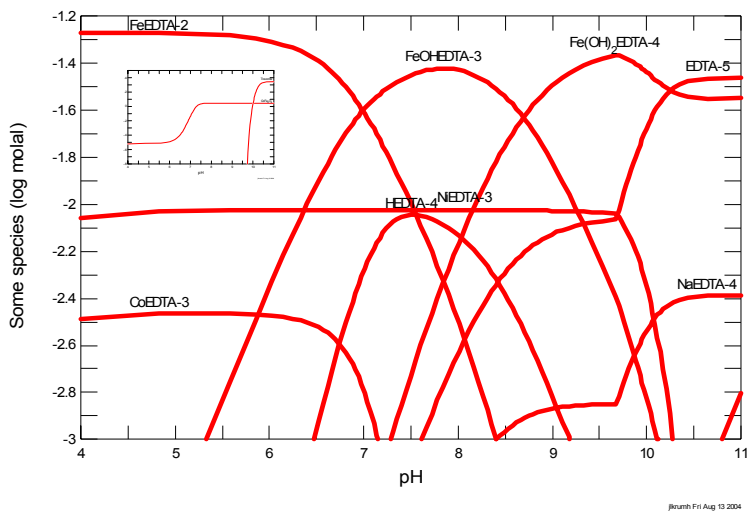


Fig. 1. Modeled solubility of Fe, Co and Ni in 0.067 M Na₂H₃EDTA as the pH is adjusted by adding NaOH. Curves illustrate how the ionic species causing CRUD dissolution change as a function of solution pH. Solid CoFe₂O₄ is present over the entire pH range, but the amount increases between pH 7 and pH 8. Trevorite (NiFe₂O₄) only appears above a pH of 9.7 (see insert, pH range is the same as main figure). Model input values: Fe⁺⁺⁺ = 0.0567 molal, Ni⁺⁺ = 0.00945 molal, and Co⁺⁺ = 0.00475 molal.

CRUD dissolution (Fig.1) was also modeled based on thermodynamic data for EDTA-metal complexes [5], and the solubility of two surrogate CRUD phases: CoFe₂O₄ and NiFe₂O₄, “trevorite”, using the Geochemists Workbench computational package [6]. The modeled results are complex and difficult to interpret at the pH where the experiments actually stabilized (pH ~7-8). By backing off to a pH 6.5, though, it can be seen that experimental and predicted solubilities for Co and Fe are in reasonable agreement for the heated 0.067 M Na₂H₃EDTA solutions. The model is limited by the fact that it does not predict trevorite precipitation below a pH of about 9. Thus, comparing experimental and modeled Ni concentrations is meaningless since predicted Ni value merely reflect how much Ni was added initially in building the model. In the 0.13 M Na₂H₃EDTA solution no solid phases are predicted until a pH of 8 (another disagreement with experiments, and also a condition that makes comparing solubility values meaningless).

Aside from providing a limited ability to predict CRUD solubility the model (Fig. 2) illustrates several useful points regarding the chemistry of such systems: (1) adding acid to keep the pH of a Na₂H₃EDTA solution below pH 6, rather than letting it to rise to pH ~7, should significantly enhance CRUD solubility, (2) Co-rich components are

more difficult to dissolve than Fe-Ni rich phases; (3) the enhanced solubility of CRUD does, in fact, arise because of the formation of metal-EDTA complexes and, (4) the overall solubility process is quite complex, which presents numerous possibilities for site-specific optimizations. The modeling also illustrates the superior strength of the Fe-EDTA complexes. Consequently, Co mobility may be diminished if a large excess of readily complexed iron is present and EDTA availability is limited.

Changes in the strength of the metal-EDTA complexes with temperature cannot explain the significant differences between the 25°C and 80°C experimental. This strongly suggests that CRUD solubility in the low temperature experiments was hindered by kinetic considerations rather than an inherently low solubility. This is consistent with the anomalous elemental ratios noted at 25°C as compared to the elemental ratios at 80°C, which reflect the composition of the material being dissolved. The dissolution rate was then quantified by mixing a (preheated) 0.134 molar Na₂H₃EDTA solution with an excess synthetic CRUD at 80°C, and then extracting splits of the solution at various times. The first sample, taken at 10 minutes, showed a slight yellowish coloration and had achieved about 8% of saturation. The last sample, after 24 hours, was about 75% saturated (as judged against the 7th entry from the top in Table 7).

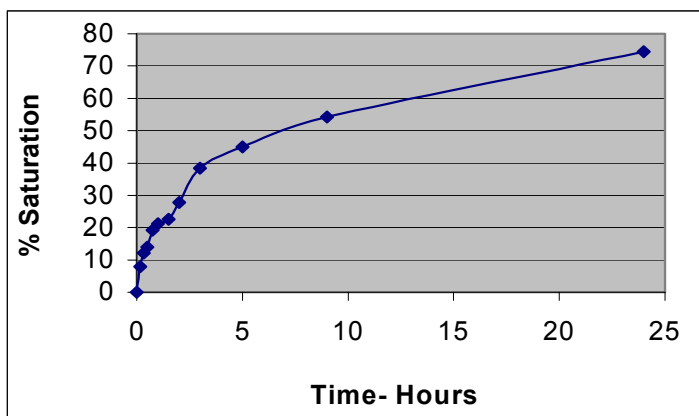


Fig. 2. Dissolution rate for CRUD at 80° C in 0.134 M Na₂H₃EDTA.

5. Discussion

Table 1 illustrates that road grime is a sink for Cs and that Co responds differently to both road grime and pretreatment options. The affinity of clays, particularly illite, for cesium has been known for some time [3] and X-ray diffraction studies on the road grime reveal the presence of minor amounts of illite, kaolinite and chlorite (no smectite) as well as larger proportions of quartz, calcite and various feldspars. The fact that the cobalt content of soiled coupons are only marginally greater than that of unsoiled coupons is consistent with the fact that the interlayer exchange sites on clays do not have a strong affinity for this element [7]. The behavior of Co on both soiled and unsoiled coupons is probably ascribable to the interactions with the metal oxide surfaces, as described in [1]. The relationship of this behavior to what might occur in the presence of CRUD lies in the fact that the oxide coatings on the stainless steel coupons may resemble the composition of CRUD, which in part is also derived from the corrosion of stainless steel. The minor loading of ¹³⁷Cs onto metal coupons that were not exposed to road grime may also be ascribed to such interactions, or to traces of dust present on allegedly “clean” coupons.

Secondly, it is noteworthy (Table 2) is that the uptake of radioactive ¹³⁷Cs can be effectively blocked by pretreating with non-radioactive Cs (or other similarly sized ions, but to a lesser degree). This is consistent with earlier reports [1] where using Ba⁺⁺ (a divalent ion almost the same size as K⁺) diminished the uptake of ¹³⁷Cs. Taken together, these findings confirm that at least some ¹³⁷Cs weeping incidents can be ascribed to an ion exchange mechanism, and that using a pre-washing technique might help prevent their occurrence.

Unfortunately, shipping casks may also acquire contaminated particulates from the spent-fuel pool water, which, of course, could not be mitigated by any pretreatment processes. In fact, CRUD, the presumed source for most of the ⁶⁰Co contamination, could only be acquired when a cask was immersed in a spent-fuel pool that had been also been used to store spent fuel assemblies. One might, also, reasonably suppose that dust (rich in clay) could fall into the pool, acquire ¹³⁷Cs, and then accumulate on the surface of a submerged shipping cask. The washing tests (Tables 2-4) suggest Cs-free wash solutions might remove some of this contamination but such treatments were found to be significantly less effective in removing Co.

To fully address the problems presented by particulate contamination acquired during immersion it may be necessary to chemically remove such particles once a shipping cask is again out of the water. Several options were explored for Cs, and two good candidates were identified: ammonium fluorosilicate and oxalic acid. The latter has been used in the nuclear industry to remove contaminated iron oxides during tank cleaning at Hanford and Savannah River and so may have some capacity for scavenging Co as well. Tabulations of relative complexing ability, however, argue for the use of much more potent Co-complexing agents such as EDTA. Screening studies with EDTA showed that: (1) the di-sodium salt is preferable to the pure acid because of its higher solubility; (2) the dissolution process is kinetically inhibited at room temperature; (3) at 80°C the CRUD can be qualitatively dissolved in reasonable amounts of time; and (4) Co solubilities of several hundred parts per million (100 ppm Co is equal to 1 g of cobalt in 10 liters of fluid) can be achieved, while the solubilities of Ni and Fe are even greater. These solubilities are high enough that only small volumes of rinse fluid would actually be needed to take care of the tiny amounts of particulate matter likely to become affixed to the surface of a shipping cask. All these leaching agents, both those for Cs and Co releases, are all hazardous to some extent - but none to the degree that precludes their use in the carefully controlled industrial settings such as normally exist at nuclear facilities.

6. Conclusions

To summarize, it is likely that ^{137}Cs and ^{60}Co are retained on the surfaces of shipping casks by different mechanisms. This understanding has led to the development of several technologies with the potential for significantly mitigating the seriousness of cask weeping incidents.

For ^{137}Cs the principal findings were (see Fig. 3, below):

- The adsorption of ^{137}Cs onto metal surfaces exposed to surrogate spent-fuel pool water correlates with the presence of road grime. *An ion-exchange mechanism was demonstrated for Cs adsorption / removal.*
- *Pre-treatment of a metal surface with a non-radioactive Cs^+ solution mitigates the amount of Cs adsorbed when the coupon is exposed to surrogate pool water.*
- *Tap water, K^+ , and NH_4^+ post-wash solutions work well for Cs removal for all pre-treatment conditions. (In contrast to pre-treatment, post-washing with Cs is least effective due to a reduced driving force for ion exchange.)*
- *A factor of >100 reduction in absorbed/retained Cs is achievable: Optimal Cs mitigation was via a soluble Cs salt pre-wash followed with water or cation-solution (K^+) post-wash(es).*
- The clays responsible for retaining ^{137}Cs can be partially attacked using ammonium fluorosilicate, oxalic acid or a combination of the two. This may be an important option if contaminated clay is acquired from the spent-fuel pool rather than arising from a pre-existing surface condition that would be susceptible pretreatment.

For ^{60}Co the principal findings were:

- Cobalt uptake is not correlated with the presence of road grime and the various steps taken to manipulate ^{137}Cs retention had little impact on ^{60}Co distribution.
- Surface-sorbed ^{60}Co may be effectively removed using a room temperature $\text{Na}_2\text{H}_3\text{EDTA}$ solution.
- Most ^{60}Co is expected to be associated with oxides (derived from corrosion of cooling components in the reactor) that are rich in Fe, Ni and Cr, and generically referred to as CRUD. To release ^{60}Co entrained in these particles requires heating the $\text{Na}_2\text{H}_3\text{EDTA}$ leach solution to around 80°C.
- Small amounts of CRUD can be dissolved at 80°C in just a few minutes but several hours will be needed to remove the larger particles.

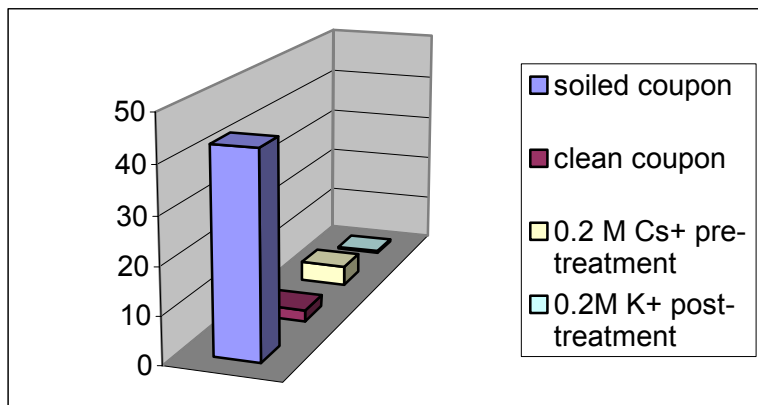


Fig. 3. Cs (in $10^{-3} \mu\text{Ci}$) retained by coupons receiving various treatments. Cesium levels were decreased by a factor of 105 when a 0.2M Cs⁺ pretreatment was followed by 0.2M K⁺ post-treatment.

These studies are of a preliminary, bench-scale nature. A patent application has been submitted for the cesium mitigation technology [8]. Much could be done to optimize and scale-up (“industrialize”) the technology for the treatment of spent-fuel transport casks to (presumably) mitigate weeping incidents.

7. References

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