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A STRIPPABLE COATING USED FOR THE TMI-2 REACTOR BUILDING DECONTAMINATION*

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ABSTRACT

Strippable coating material used in the TMI-2 reactor building decontamination has been tested for Sr, Cs, and Co leachability, for radiation stability, thermal stability, and for resistance to biodegradation. It was also immersion tested in water, a water solution saturated with toluene and xylene, toluene, xylene, and liquid scintillation counting (LSC) cocktail. Leach testing resulted in all of the Cs and Co activity and most of the Sr activity being released from the coating in just a few days. Immersion resulted in swelling of the coating³ in all of the liquids tested. Gamma irradiation and heating of the coating did not produce any apparent physical changes in the coating to 1×10^8 rad and 100°C, however, gas generation of H₂, CO, CO₂ was observed in both cases. Biodegradation of the coating occurred readily in soils as indicated by monitoring CO₂ produced from microbial respiration. These test results indicate that strippable coating radwaste would have to be stabilized to meet the requirements for Class B waste outlined in 10 CFR Part 61 and the NRC Draft Technical Position on Waste Form.

INTRODUCTION

The gross decontamination experiment (GDE)⁽¹⁾ and subsequent decontamination activities⁽²⁾ at TMI-2 have to date made use of over 400 gallons of strippable coating material.^{**} These are film forming liquids, usually containing chelating agents, which dry to a tough yet pliable coating. This coating was proven effective in the GDE in that it achieved decontamination factors (DFs) of 100 on epoxy painted surfaces after these surfaces had already been flushed with water to remove loose and readily soluble contamination.⁽¹⁾ Subsequently, it has been applied on decontaminated surfaces to prevent recontamination. The dried coatings have been stripped as sheets from the surfaces and manually compacted into steel drums for disposal. Average contact radiation readings of the drummed decontamination coating were less than 5 rem/h.⁽¹⁾

Activity readings measured by BNL on GDE samples received from TMI-2 showed a large variability in activity on the coatings. Activity readings from 3.5 to 250 mrem/h at 5 cm were measured on samples of approximately 6 grams each. This was due to the fact that activity was inhomogeneously deposited during the accident. Furthermore, as the surfaces were washed with a high pressure water spray preceding application of strippable coating, further redistribution of activity occurred. The average measured activities provided evidence that the strippable coating decontamination wastes would result in Class B waste as set forth in 10 CFR Part 61 and would require stabilization.

The properties of the coatings are of interest to predict long-term stability in the burial environment and with their container. As required by the Technical Position (TP) of the NRC,⁽³⁾ leachability of the coating in water, radiation and thermal stability, and resistance of the coating to biodegradation were tested. Immersion stability in water and organic liquids and leach behavior of chelates in the coating were

also examined. The material tested, ALARA 1146, produced by Imperial Professional Coatings,^{*} was the same as that used in the GDE at TMI-2. Results of laboratory tests were compared to actual GDE samples received from TMI-2.

Sample Preparation

Samples for testing were made from material purchased from Imperial. The as-received liquid was stirred to ensure uniformity, and a .018±.002-in. thick layer spread onto substrates of either Lucite or epoxy painted steel or cement^{**} using a grooved Teflon spreader. The coatings were cured in air at least 2 days before being stripped. The coatings used for the majority of the tests were prepared in two large batches. Cured coating not used immediately was stored in closed glass containers until needed. An 0.2-ml aqueous spike containing 20 µCi Cs-137, 40 µCi Sr-85, and 40 µCi Co-60 was also stirred into 40 ml of the coating prior to spreading samples for radioactive leach testing.

Leach Testing

Half-inch squares of spiked coating were leached in triplicate in 32-ml deionized water; the leachant was changed in a batch method after 1, 2, 3, 4, 8, 9, 11, 15, and 18 days. A GeLi detector was used to measure gamma radiation in the coating sample itself. After each leach interval, samples were counted, counts were integrated over 5 or 10 minutes, decay corrections applied, and the remaining activity compared to the initial activity. Leaching behavior of the coating is shown in Figure 1.

*Imperial Professional Coatings, Inc., P.O. Box 2977, New Orleans, LA 70189.

**Keeler and Long, Inc., Watertown, CT. Specimen forms furnished included 2x4x1/4-inch carbon steel coupons primed and painted with 6548/7107 epoxy primer and E-1-7475 epoxy enamel and 2x4x2-inch concrete blocks finished with 4129 epoxy curing compound, 6548S epoxy surfacer, and E-1-7475 epoxy enamel.

*Work carried out under the auspices of the U.S. Nuclear Regulatory Commission.

**Personal communication between J. Adams (BNL) and D. Giefer (Bechtel), February, 1984.

Figure 1 shows that Cs and Co leached readily in water (>90% in less than 1 day). The Sr activity leached more slowly, however a major portion (>60%) of the Sr activity was removed in two weeks. The radionuclide leaching of the coating measures the combined result of at least two effects: (i) the effect of the chelating agents in the coating and, (ii) the properties of the coating material itself. Chelating agents tend to solubilize metal ions and would be expected to enhance leachability, whereas radionuclides more strongly bound to the coating material might leach less readily. One may then speculate that Co is in a chelated form in the set coating whereas Sr may be bound preferentially to the coating material. Cs may or may not be complexed by the chelate since it is very soluble in water in virtually all of its chemical compounds. Standard analyses for chelates in nonradioactive aqueous leachates were performed. Results were less than 0.1% by weight allowable under 10 CFR Section 20.311b.

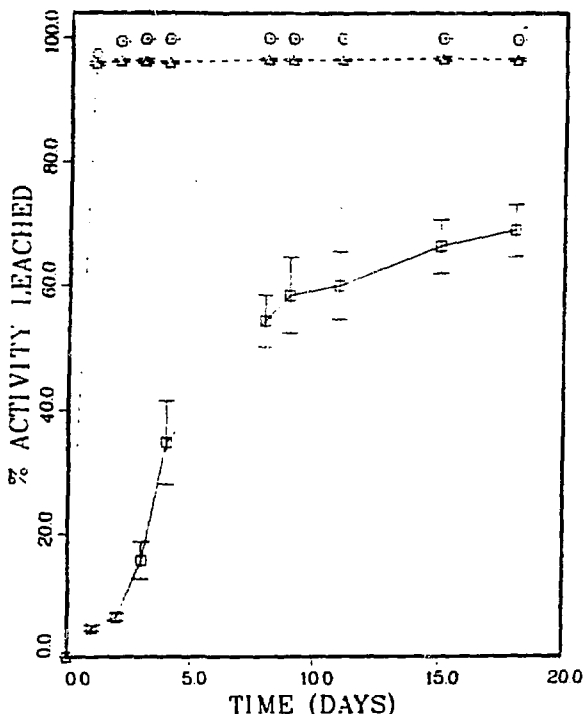


Fig. 1. Percent activity loss vs time for Imperial 1146 strippable coating leached in deionized water. Δ - Co-60; \square - Sr-85; and \circ - Cs-137.

Immersion Testing

One-inch square samples were suspended in five liquids which might be found in a shallow land burial environment: liquid scintillation cocktail (LSC), deionized water (DIW), xylene, toluene, and DIW saturated with xylene and toluene. Average percent weight gains of four samples were calculated after 1, 2, 6, 8, 9, 13, 17, and 34 days of immersion. Samples were removed from the liquid and lightly blotted before weighing. After 34 days, the samples were allowed to dry in air. Percent weight losses at 1, 2, 3, 4, and 7 days after removal from the liquid were determined. Sample dimensions were measured following the immersion phase and

again following the drying phase. The immersion liquids were also evaporated and the residues weighed. Data for immersion testing are shown in Table I.

Table I
Immersion and Drying Data for
ALARA 1146 Strippable Coating

Liquid	Immersion Phase ^a		Drying Phase ^b	
	Weight Gain (%)	Volume Gain (%)	Weight Loss (%)	Residue Weight ^c (%)
Water	23	53	6.2	4.9
Water Saturated with toluene and xylene	37	71	15	5.7
Toluene	72	146	19	29
Xylene	56	113	19	29
LSC Cocktail	530	---	---	---

^aAfter 34 days immersion.

^bAfter 7 days drying in air.

^cThe leach liquids of each type were combined and evaporated so the value listed is the average for the four samples in each liquid (expressed as % of initial sample weight).

Each liquid tested caused the coating material to swell and absorb liquid. A dry residue remaining from the DIW and organic saturated DIW immersion liquids suggested dissolution of part of the coating. The residue from toluene and xylene was a viscous oil. This oily residue weighed more than could be accounted for by the weight loss from the coating. This may suggest a possible reaction with some part of the coating. Samples immersed in LSC swelled to approximately twice their initial size, and weight gains were difficult to measure. This swelling resulted in such a loss of mechanical strength that samples dropped off their suspending wires when removed from the liquid.

Radiation Testing

Pyrex breakseal tubes, containing either 0.5 or 5.0 grams of coating material, were sealed both in ambient atmosphere and under vacuum. Samples were irradiated to total gamma doses of up to 1×10^9 rad in the Co-60 irradiation facility at BNLL. A plot of gas pressure generated versus irradiation dose is shown in Figure 2. At total doses less than 10^8 rad, oxygen depletion by reaction with the coating caused the slope of the line to be negative. At doses above 10^8 , radiolytic gas generation became dominant. A G value of 1.3 was calculated from the data from 0.5-g samples. Hydrogen was the primary radiolysis product, along with smaller amounts of CO_2 , CO and traces of hydrocarbons including methane, ethane, propane, butane, plus others. Higher exposures caused the material to become stiff and tough, and blistering of the surface was observed in some cases.

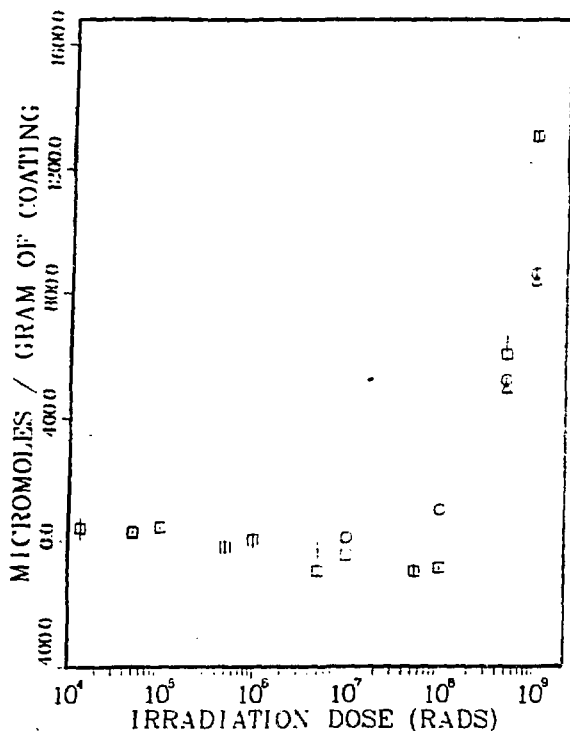


Fig. 2. Plot of gas generation vs Co-60 gamma dose for ALARA 1146 strippable coating. Three sample configurations were used in 20 cm³ sealed tubes: □- 0.5-g coating in air; △- 5.0-g coating in air; and ○- 5.0-g coating in vacuum.

Thermal Testing

The effect of heat on the coating was tested by subjecting 1 inch squares (0.5 g) to temperatures of 100 and 200°C for 24 h. The coating pieces were sealed in Pyrex breakseal tubes in air atmosphere. Another set of samples was heated in open test tubes. Coating material heated in open tubes darkened with increasing temperature. Very little discoloration was evident in samples heated in sealed tubes. Mass spectroscopic analyses of the atmospheres in the sealed tubes after heating are shown in Table II. Oxygen was depleted from the air over these samples and CO₂, H₂, and CO were generated. Analyses of control specimens also showed that the coating apparently scavenged oxygen and liberated CO₂, CO and a small amount of H₂ spontaneously at room temperature. Pyrolysis at higher temperatures produced various additional decomposition products. Flame spread behavior, tested according to ASTM E84-77 (Surface Burning Characteristics of Building Materials), has been determined to document compliance of Alara 1146 to NRC Draft Regulatory Guide 1.120.(4)

Table II

Gas Analysis From the Thermal Testing of ALARA 1146 Strippable Coating

Temp. (°C)	Gas (% by Volume)							
	N ₂	O ₂	CO ₂	H ₂ O	H ₂	CO	CH ₄	Total
24 ^b	72.5	11.8	10.8	----	0.2	3.7	---	100.0
100	37.3	1.4	21.7	36.6	0.9	-	2.0	99.9
200	11.3	0.5	74.5	-	6.9	4.3	2.8	100.3

^aThe hydrocarbons detected included methane plus higher alkanes and benzene. Alcohols were also detected.

^bRoom temperature control. This specimen had been in a breakseal tube for seven weeks prior to analysis.

Biodegradation Testing

Two methods were used to determine biodegradability of the 1146 coating. First, in keeping with the TP on Waste Form,⁽³⁾ ASTM G21 (Determining Resistance of Synthetic Polymer Materials to Fungi) and G22 (Determining Resistance of Plastics to Bacteria) were performed. In these tests, an ideal environment of moisture, temperature, and nutrient minerals is provided to evaluate the ability of microbes to utilize the coating as a food source. The tests were run on 1-inch square samples of the coating. G21 showed no growth for fungi, whereas G22 was positive for bacterial growth on the samples.

A biodegradation test which measured CO₂ production from microbial respiration was also performed. Approximately 12 grams of coating were buried in 100 g of moist soil (the moisture content was adjusted to make the soil wet but still porous and not muddy) from either the Barnwell or Hanford shallow land burial site. Two samples in each soil were tested, as were controls of 100-g moist Barnwell and Hanford soil with no coating, and 12-g coating plus 15-ml water with no soil. Special flasks and the procedure described by Bartha and Pramer⁽⁵⁾ were used to determine total CO₂ present in the soil/coating mix. The net CO₂ produced (subtracting CO₂ generated in soil only controls) was indicative of biodegradation.

Biodegradative CO₂ gas evolution results for 220 days are shown in Table III. The rates of CO₂ generation from all four samples are essentially equal from about days 60-220 except Sample B1, which tailed off after 120 days. Biodegradation was consistently greater in Hanford soil than either of the Barnwell samples. Relative differences in CO₂ evolution may have been caused by differences in the way the coating samples were mixed with the soils, i.e., overlapping coating pieces. The coating samples were removed from the soils on day 220. Net CO₂ production decreased significantly but did not immediately return to background. This was thought to be due to a small amount of adhered or solubilized coating remaining in the soil.

Table III

Scoping Test Results on the Biodegradation of ALARA 1146 Strippable Coating in Soils From the Barnwell, SC, and Hanford, WA, Shallow Land Burial Sites

Sample	Initial Weight W ₀ (g)	Biogenically Generated CO ₂ (mg)	Carbon Loss (%) ^a	Weight Loss (%) ^b
B1 ^d	12.11	875.5	3.77	4.87
B2 ^d	11.97	961.0	4.19	7.69
H1 ^e	11.24	1094.5	5.08	8.27
H2 ^e	11.24	1189.5	5.52	6.76
Control	11.74	nil	----	-3.75 ^c

^aFrom the biogenically generated CO₂ data and the measured 52.3% C content of the coating used in these tests.

^bPercent biodegradation from the initial and final weight following 220 days of biodegradation in soil at 20-24°C.

^cThe sample did not detectably biodegrade in the absence of soil. The weight increase should not be due to retained water since all samples were dried both before and after the tests in the same environment.

^dBarnwell soil.

^eHanford soil.

Testing of the Strippable Coating from TMI-2

The Alara 1146 samples sent to BNL from the GDE at TMI consisted of five pieces individually packaged in numbered plastic bags. A summary of data on the coating pieces is listed in Table IV.

Table IV

Strippable Coating Samples From the TMI-2 Reactor Building Gross Decontamination Testing (The bag numbers were on the plastic bags containing the individual coating samples as received)

Bag No.	Sample Weight (g)	Sample Width (cm)	Sample Length (cm)	Activity at 5 cm (mrem/h)
50	7.77	9.0	17.5	3.5
51	6.95	9.0	19.0	230
52	4.50	9.8	15.2	150
162	5.94	8.5	16.5	250
163	4.13	8.5	11.5	4.0
Total	29.29			

A TMI coating sample from bag 162 was leached in DIW for 43 days and then the leachate and leached coating residue were sent to EAL Corp., a commercial analysis laboratory, for analysis for Sr and Pu content. Leachates (70 mL) were changed daily, except for weekends, for three weeks, then weekly for three more weeks. Each leachate volume was counted for activity in a gamma spectrometer. No gamma emitters other than Cs-134, 137 and the Ba-137m daughter were unambiguously detected in the leachate. No Cs or other gamma emitters remained in the leached coating samples after the

^aEAL Corporation, Richmond, CA.

6-week period. Table V lists the data on the activities of Cs-134, 137, Sr-90, and Pu-239, 240 from the leachate and residue of the TMI coating sample from bag 162.

Table V

Activity Distribution^a Between Leachate and Coating for a Sample Coating^b From the TMI-2 Gross Decontamination Experiment

Radio-nuclide	Activity in Leachate	Activity Remaining in Leached Coating	Specific Activity in Sample ^c (μCi/g)	Volumetric Activity in Sample (μCi/cm ³)
Cs-134	4.3	nil	0.73	0.91
Cs-137	52.0	nil	8.7	10.8
Sr-90	1.23	1.05	0.38	0.47
Pu-239, Pu-240	0.006 ^e	0.02 ^e	0.004 ^f	0.0059

^aThe Cs-134, 137 activities were determined by gamma spectroscopy at BNL. The Sr and Pu activities were determined by EAL Corp. Richmond, CA.

^bThe sample came from bag 162 as listed in Table 4.5. The coating is ALARA 1146 Decon, product of Imperial Professional Coatings Corp., New Orleans, LA.

^cTotal activity divided by the sample weight of 5.94 g.

^dSpecific activity in units of μCi/g multiplied by the density of the set coating in g/cm³. The density used is 1.24 g/cm³.

^eActivity for Pu-239, 240 expressed in nCi.

^fSpecific activity for Pu-239, 240 expressed in nCi/g.

^gVolumetric activity for Pu-239, 240 expressed in nCi/cm³.

Bartha-Pramer biodegradation of TMI strippable coating samples in Hanford and Barnwell backfill soils was conducted. The sample size in these tests was reduced to 10 cm² (approximately 0.4 grams) in 100 grams of soil. This was done to assure uniform contact of soil with the sample surfaces in each flask. As in the previously described test, controls of soil only and coating only were simultaneously monitored for CO₂ generation. Table VI summarizes the data for the biodegradation experiment, including weight losses that occurred during the 208 days of the test. Biodegradation measured by weight loss falls in the range of expected biodegradation based on CO₂ measurements.

Table VI

Biodegradation Test Results for Strippable Coating Samples From the TMI-2 Reactor Building Gross Decontamination Experiment

Sample	Initial Weight (g)	Biogenically Generated		Carbon Loss (%) ^a	Weight Loss (%) ^b
		CO ₂ (mg)	CO ₂ (mg)		
B	0.544	48.62	4.65	3.31	
H	0.554	94.86	8.92	8.84	
Control	0.554	None	0	1.44	

^aFrom the biogenically generated CO₂ data and the measured 52.3% C content of the coating.

^bPercent biodegradation from the initial and final weights following 208 days of biodegradation in soil at 20-24°C.

Summary

Samples received at BNL from the TMI-2 GDE indicate that strippable coating decontamination waste would probably be classified as Class B under NRC regulation 10 CFR Part 61. As such, stabilization of the waste form or disposal in a high integrity container would be required.

Leach tests performed on both BNL-prepared 1146 coatings and GDE samples indicated that Cs leached readily and completely from the coating, Co leached readily except for a small amount apparently retained by the coating and Sr and Pu leached from the coating more slowly. Chelating agents in the coating leached in deionized water. However, the amount leached accounted for less than 0.1% of the coating by weight. Immersion in water and several organic liquids showed the 1146 coating absorbs liquid, and part of the coating dissolves. Tests done at BNL on the coating showed the material was not significantly changed by gamma radiation to a total dose of 1×10^8 rad. It was, except for slight darkening of the coating, resistant to temperatures to 100°C. No significant gases were generated at these doses or temperatures. Biodegradation tests showed that the coating biodegrades readily in soil. It appeared to biodegrade slightly faster in Hanford soil than in Barnwell soil. The biodegradation is probably caused by bacteria and not fungi. This susceptibility to microbe attack dictates that coating radwaste classed as B or C under 10 CFR Part 61 would require stabilization.

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