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LEACH BEHAVIOR AND MECHANICAL-INTEGRITY STUDIES OF IRRADIATED EPICOR-II WASTE PRODUCTS*

R. E. BARLETTA, K. J SWYLER, S. F. CHAN, AND R. E. DAVIS

NUCLEAR WASTE MANAGEMENT DIVISION
BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

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ABSTRACT

The leachabilty of Cs and Sr from cement solidified ion exchange media claimed to be representative of the Epicor-II prefilters (D-mix) is presented. The Cs and Sr release is significantly lower than that typically observed for organic ion exchange resin/cement composites. The effect of radiation up to a total dose of 10^7 Gy upon the leachability and mechanical integrity (as measured by MCC-11) of D-mix/cement composites has been investigated. No deleterious effects were found.

INTRODUCTION

During the accident at Three Mile Island Unit 2, several hundred thousand gallons of contaminated water were released to the auxiliary and fuel handling building.(1) This water was decontaminated using a demineralization system, Epicor-II. Most of the acivity was localized on the first-stage liner (prefilter) of this system. Each 1.2-m-diameter x 1.2-m-high cylindrical prefilter contains typically 4.4×10^{13} to 4.8×10^{13} Bq of activity. This is not distributed uniformly through the prefilter. Rather, the majority of the activity in the liner is localized in a narrow band within the cylindrical liner. The exact width of this band is not known at present. Using an assumed thickness of this layer, Swyler et al.(2) have estimated that the total absorbed dose to portions of the prefilter media could reach 10^6 Gy in as little as 2 years. A dose of 10^7 Gy in this concentrated layer could be achieved in approximately 30 years.

Recent studies of radiation damage to organic ion exchange media(2,3,4) indicate that, for a total dose in the range of 10^6 to 10^7 Gy, a variety of effects occurs. These effects include gas generation, pH changes, agglomeration of ion exchange media, and accelerated corrosion of mild steel in contact with the ion exchange media. Although these studies were performed at high dose rates with ion exchangers which may or may not be representative of those in the first stage Epicor-II liners, these results raise serious questions regarding the short- and long-term behavior of the ion exchange media.

All of these studies, however, have considered the effects of radiation on unsolidified ion exchange resins. While the effects are pertinent to the short-term storage of spent, Epicor-II prefilters, they would not be relevant to the conditions of disposal of these liners in commercial shallow-land burial since solidification of the contents of the prefilters was mandated by the U.S. Nuclear Regulatory Commission.* One management option which was considered by General Public Utilities (GPU) for the prefilter wastes was cement solidification. A resin solidification test program was undertaken by Hittman Nuclear and Development Corporation under contract to GPU(5) in order to define the optimum formulation, or range of formulations necessary to solidify the prefilter material with cement. It was however beyond the scope of this program to determine the effects of radiation upon the solididification process. In particular, three questions were not addressed:

1. Was it possible to solidify in cement ion exchange material which had recieved a total dose in the range of 10^6 to 10^7 Gy using a formulation developed using unirradiated ion exchange media?

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

*Agreement to accept these wastes for treatment and/or disposal by the U.S. Department of Energy has recently rendered such requirements moot.

2. What was the effect of radiation upon the leachability of ion exchange media solidified using cement?

3. What was the effect of radiation upon the mechanical integrity of ion exchange media solidified using cement?

These questions cannot be addressed generically, however. Barletta et al.[6] have indicated that, based upon a survey of the literature, the properties of composite containing organic ion exchange resin solidified using cement depended quite strongly upon the particular resins being solidified. It was thus felt that the effects of radiation from resin/cement composites would also vary with resin type especially since the effects of radiation upon unsolidified ion exchange resin also show this dependence. We have, therefore, attempted to address these questions with respect to the solidification of a single mix of ion exchange media (D-mix) claimed by Epicor, Inc. to be representative of the Epicor-II prefilter experience. Further, since the results of our study were intended to compliment those of the resin solidification test program conducted by GPU, we selected a formulation for D-mix solidification recommended as a result of that program. The impact of irradiation upon solidification itself, in addition to the properties of irradiated D-mix, has been discussed elsewhere.[7] Only the effect of radiation upon the leachability and mechanical integrity of D-mix/cement composites will be discussed here.

EXPERIMENTAL

All ion exchange media used in this study were supplied by Epicor, Inc. Prior to solidification all material was chemically depleted to simulate average sodium and boron loadings of Epicor-II prefilters (3.2 kg of Na/m^3 and 9.6 kg of B/m^3). In addition, the D-mix was further depleted with nonradioactive CsCl and $SrCl_2$ to simulate a loading of 5×10^{13} Bq/m^3 (as ^{137}Cs) and 1×10^{12} Bq/m^3 (as ^{90}Sr). For D-mix used in leachability experiments, the ion exchange medium was also loaded with ^{137}Cs and ^{85}Sr to a level of 1.5×10^4 and 1.0×10^4 Bq/g of D-mix, respectively.

D-mix/cement composites were either prepared using irradiated ion exchange media or the composite was irradiated after fabrication. Two doses, 10^6 Gy and 10^7 Gy, were selected to bound short- and long-term conditions. All irradiations were carried out in BNL's ^{60}Co gamma pool at a dose rate of between 2.9×10^4 to 5.2×10^4 Gy/h. In addition to irradiated composites and unirradiated composites, containing irradiated D-mix, D-mix/cement composites were also fabricated from unirradiated D-mix and tested as such as controls.

All composites were fabricated using Portland Type I cement according to the formulation recommended by GPU. The composites contained D-mix, water, cement, and sodium metasilicate (Metso) in the weight ratio of 350:153:514:51. For D-mix which had been irradiated to 10^7 Gy, approximately 11% more water had to be added to obtain a solidified, monolithic product. Samples were fabricated in cylindrical containers to produce a composite with nominal dimensions of 4.6 cm diameter by 5.1 cm high. Prior to either leach testing or mechanical integrity testing, samples were cured for nine days followed by storage and/or irradiation for ten days.

Leach tests were conducted for a total of 30 days using a modified IAEA leach test[8]. The leachate used was deionized water at room temperature. Leachate was collected at 4 hours after the start of the test, after each successive 24-hour period during the first 2 weeks except for weekends and holidays, and twice per week for the following 2 weeks. The volume of the leachate was approximately 10 times the surface area of the composites (1160 mL). Each leach test was run using 3 replicate samples.

Mechanical integrity was tested by measuring the fracture tensile strength of the composite according to procedures set forth in MCC-11.[9] Samples for mechanical integrity tests were prepared by coring the solidified forms with an air-cooled diamond-edged coring drill, 12.3 mm I.D. This was followed by cutting the cores with an ISOMET Low-Speed Saw equipped with a 11-4244 diamond wafering blade to form disks with a nominal thickness of 6 mm. Each form was cored to give sufficient material to produce five samples per form. The fracture tensile strength, T,(MPa) for each sample was calculated from the maximum load, P,(N) by the following expression:

$$T = 2P/\pi dt$$

where d is the specimen diameter (mm) and t the specimen thickness (mm).

RESULTS AND DISCUSSION

The results of the leach tests are presented graphically in Figures 1 through 4. Further, the average cumulative fraction released normalized by the volume to surface area ratio (V/S) is given in Table 1. Unirradiated D-mix/cement composites indicate Cs and Sr release is as much as a factor of 30 times lower than that reported in the literature[10,11,12] for resin/cement composites. There are two possible explanations for this behavior. The first is the possible presence of zeolites in the D-mix. The D-mix is claimed by Epicor to be representative of the first-stage Epicor-II prefilters. If this is true, and since some of the prefilters are known to contain zeolites, one may speculate that zeolites are also present in the D-mix. Barletta et al.,[6] in a review of the literature in resin/ cement composites, have concluded that zeolites such as Zeolon Z-900 and Linde AW-500 may reduce the cesium leachability of resin-cement composites. Recent experiments[13] on the Cs and Sr leachability from IRN-77/cement composites, shown in Figures 5 and 6, tend to corroborate *this explanation. With respect to* the release of Sr, these experiments, however, indicate that the lowered Sr release cannot be explained by the possible presence of zeolites in the D-mix. A second explanation also offered in Reference 6 is the presence of silicates (Metso) in the composite. The data given in Figures 5 and 6 do not support this hypothesis.

The effect of irradiation upon the Cs and Sr release from D-mix/cement composites is much less profound than the lowered release observed for these elements in the unirradiated composites discussed above. Composites fabricated from D-mix which had been irradiated prior to fabrication showed only slight increases in the Cs and Sr releases. Composites irradiated after fabrication showed a slight decrease in the Cs release upon irradiation and a slight increase in Sr release.

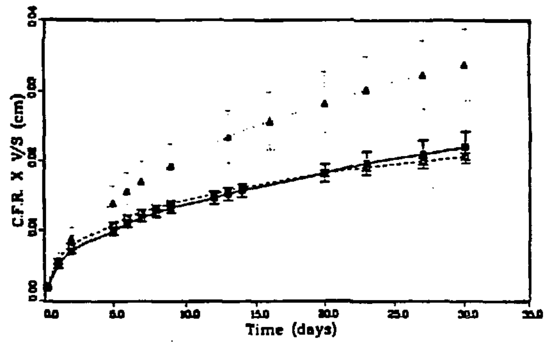

Figure 1 Average cumulative fraction release (C.F.R.) normalized by V/S for ^{137}Cs release in deionized water for D-mix/cement composites in which the D-mix was irradiated prior to solidification. □ - unirradiated D-mix; o - D-mix irradiated to a total dose of 10^6 Gy, Δ - D-mix irradiated to a total dose of 10^7 Gy.

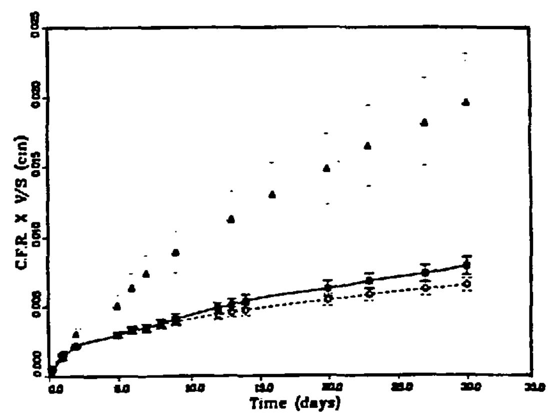

Figure 2 Average cumulative fraction release (C.F.R.) normalized by V/S for ^{85}Sr release in deionized water for D-mix/cement composites in which the D-mix was irradiated prior to solidification. □ - unirradiated D-mix; o - D-mix irradiated to a total dose of 10^6 Gy; Δ -D-mix irradiated to a total dose of 10^7 Gy.

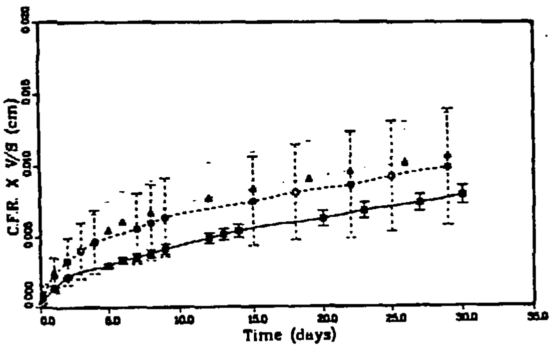

Figure 3 Average cumulative fraction release (C.F.R.) normalized by V/S for ^{85}Sr release in groundwater for D-mix/cement composites in which the D-mix was irradiated prior to solidification. □ - unirradiated D-mix; o - D-mix irradiated to a total dose of 10^6 Gy; Δ - D-mix irradiated to a total dose of 10^7 Gy.

Table 1

Results of Leach and Mechanical Integrity Tests on D-Mix/Cement Composites

Sample Preparation	Dose (Gy)	Ave. Cumulative Fraction Released[a] x V/S x 10^2 (cm) ^{137}Cs	^{85}Sr	$\bar{\sigma}$ (MPa)
Unirradiated	0	2.2 ± 0.2	0.79 ± 0.07	1.2 ± 0.3
D-mix irradiated prior to fabrication	10^6	2.1 ± 0.5	0.65 ± 0.05	1.2 ± 0.2
D-mix irradiated prior to fabrication	10^7	3.4 ± 0.5	1.9 ± 0.3	1.0 ± 0.3
Solid irradiated after fabrication	10^6	0.95 ± 0.11	0.98 ± 0.41	1.4 ± 0.3
Solid irradiated after fabrication	10^7	1.18 ± 0.03	1.71 ± 0.3	1.4 ± 0.3

[a]Deionized water leachate, 30 day leach test at room temperature.

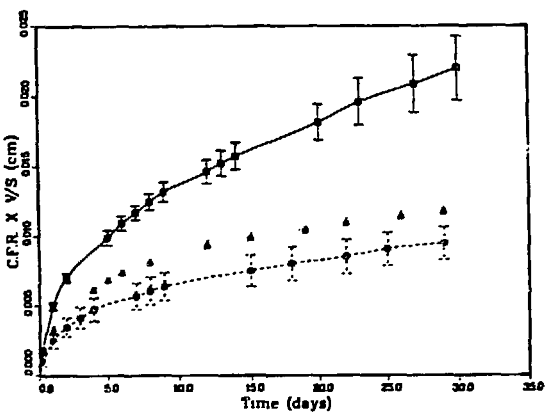

Figure 4 Average cumulative fraction ^{137}Cs release (C.F.R.) normalized by V/S for ^{137}Cs release in groundwater for D-mix/cement composites in which the D-mix was irradiated prior to solidification. □ - unirradiated D-mix; o-D-mix irradiated to a total dose of 10^6 Gy; Δ-D-mix irradiated to a total dose of 10^7 Gy.

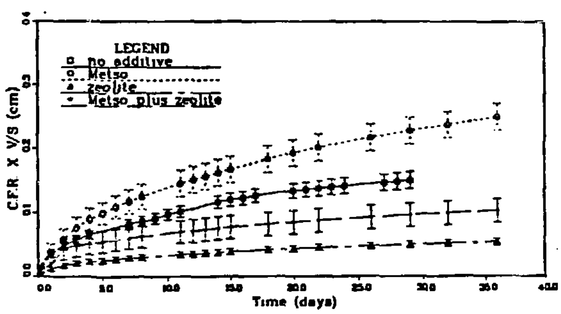

Figure 5 Average cumulative fraction release (C.F.R.) normalized by V/S for ^{137}Cs release from IRN-77/cement composites leached in deionized water at room temperature.

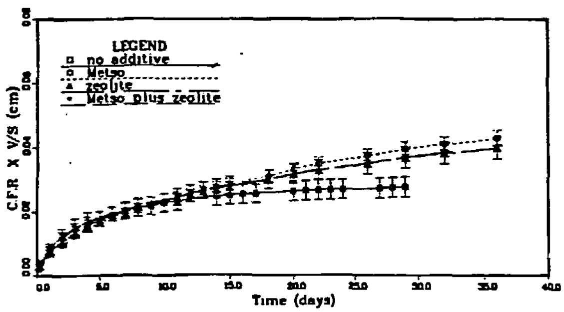

Figure 6 Average cumulative fraction release (C.F.R.) normalized by V/S for ^{85}Sr release from IRN-77/cement composites leached in deionized water at room temperature.

The mechanical integrity as measured by the average factor tensile strength (T) of these composites are also listed in Table 1. Within the variation of the measurement, no deleterious effects were observed in the mechanical integrity of D-mix/cement composites as a result of irradiation.

CONCLUSIONS

As a result of these experiments it can be concluded that radiation has no deleterious effects upon the Cs or Sr leachability or mechanical integrity of D-mix/cement composites. Further, the Cs and Sr leachability of unirradiated composites is significantly lower than that typically seen for resin/cement composites. This is apparently due to the components of the proprietary mix.

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