UNITED STATES NUCLEAR REGULATORY COMMISSION WASHINGTON, D. C. 20555

MAY, 1-5-1980 NRC/TMI-80-087

80-189/SDC MAY 1 6 1980

E. Suller /R. M. You

will be assigned the responsibility and

of taking the action required by this letter. He will receive an

Action Item Notification Including

details in the near future.

Docket No.: >50-320

Mr. R. C. Arnold Senior Vice President 100 Interpace Parkway Parsippany, NJ 07054

Dear Mr. Arnold:

Due Date:

MAY 3 0 1980

Subject: Evaluation of EPICOR-2 Wastes Under Projected Handling,

Storage, Transportation and Disposal Conditions

As you know, there are a number of alternative methods for handling, storage, transportation and disposal of the EPICOR-2 wastes. The Commission's Memorandum and Order dated October 16, 1979, directed Metropolitan-Edison to expeditiously construct a facility for solidification of these wastes. Metropolitan-Edison is presently investigating use of cement solidification. Regardless of the means ultimately proposed by Metropolitan-Edison, it is essential that the near term and long term performance of the resin liners and the ion exchange resins under the conditions projected to be encountered be analyzed and well understood. A recent letter status report from Brookhaven National Laboratory (BNL) on the leachability, structural integrity and radiation stability of organic ion exchange resins (copy enclosed) notes a number of concerns following preliminary analysis by BNL.

To assist us in understanding the performance capabilities of EPICOR-2 liners, it is important that the NRC staff have detailed drawings and specifications covering the fabrication, assembly and coating of the liners. The data shall include, but not limited to, the shop drawings used for manufacturing the parts, fabrication and assembly instructions, welding specifications, liner structural and process material specifications, coating material specifications, surface preparation and coating application procedures, quality control and testing procedures. The only documents available to the NRC staff to date have been essentially engineering sketches that do not indicate any liner internals nor do they cover many of the liner aspects that could be important determinants of performance for both short and long term periods.

With regard to the resin material, a phone conversation of May 7, 1980, between R. McGoey (GPU) and H. Lowenberg (NRC) indicates that an approximate analysis of resin performance under radiation conditions was carried out by your vendor, EPICOR, last year. We understand that no documentation of that work was or is now available, but that your staff is at this time undertaking such studies.

It has been indicated that the analyses are to include evaluation of the resins from the aspects of agglomeration, off gassing and ion retention capability. We request that you expedite these assessments and include in your report consideration of the concerns expressed in the BNL status report. We further request that this assess must be provided to the NRC as soon as they are concluded.

In order for the NRC staff to independently review the aspects of the EPICOR-2 liner/resin system overall performance, it is essential that the staff be provided with the detailed resin content of each liner used or projected to be used. It is important that the information provided for each liner include, but not be limited to:

the quantity of each media

the composition of each media

the precise form of each media (including any pretreatment, etc.)

the precise method of media introduction and placement (mixed or in discrete layers, etc.)

an estimate of media loading with radionuclides, and

any other aspects that can affect either short or long term media performance.

We recognize that some of this information may be of a proprietary nature. If this is the case, the information can be submitted under the provisions of 10CFR Part 2.709.

We would appreciate receiving the requested information by May 30, 1980, so that the NRC staff can carry out its activities in a timely manner and that resolution of the matter of liner/resin treatment and disposal can be planned and finalized. We are prepared to meet with you and your staff to discuss the requested information in more detail, if you believe it would be helpful in responding to this request.

Sincerely,

John T. Collins

Deputy Program Director

John T. Collins

TMI Program Office

Enclosure: Status Report from BNL

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UNITED STATES NUCLEAR REGULATORY COMMISSION WASHINGTON, D. C. 20555

MAY 3 1980

MEMORANDUM FOR: Those on Attached List

FROM:

Robert E. Browning, Deputy Director

Division of Waste Management

SUBJECT:

TRANSMITTAL OF BNL LETTER REPORT

Attached is a letter report from Brookhaven National Laboratory identifying concerns related to disposal of the first stage EPICOR-II organic resin wastes from TMI-2. Although the letter report focuses on TMI-2 waste, it could also be applicable to some of the higher activity organic resin wastes from other operating plants. Thus, in parallel with pursuing these concerns with respect to TMI-2 wastes, I believe we should also be taking action to alert other reactor operators to these concerns with respect to efforts they may have underway to develop resin solidification capabilities. As a possible means to cut through these concerns with respect to $^{TMI-2}$ waste, we are pursuing the possibility of eluting the Cs 137 and Sr from the organic resins onto inorganic resins. The resulting inorganic resins with higher concentrations of Cs 137 and Sr 90 would be handled along with the first stage inorganic resins from the submerged demineralizer system as if they were high-level waste and the eluted organic resins would be handled as low-level waste. This would essentially eliminate the need to resolve all the concerns expressed in the attached BNL letter for TMI-2 waste but would still leave open questions regarding waste from other operating plants. I would appreciate receiving your comments as quickly as possible.

Robert E. Browning, Deputy Director Division of Waste Management

Enclosure: as stated

ADDRESSEES FOR MEMORANDUM DATED

MAY.

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 R. Weller, TMI Program Office (w/encl)
 R. Bangart, DSE (w/encl)
 L. Barrett, EEB (w/encl)

 - H. Lowenberg, FCOT (w/encl)
 - B. Snyder, TMI Program Office (w/encl)
 - R. D. Smith, WM (w/o encl)
 - F. Arsenault, SAFER (w/o encl)
 - J. B. Martin, WM (w/o encl)
 T. Johnson, WM (w/encl)

BROOKHAVEN NATIONAL LABORATORY

ASSOCIATED UNIVERSITIES, INC.

Upton, New York 11973

Department of Nuclear Energy

(516) 345-

May 5, 1980

Mr. Robert E. Browning
High Level Waste Technical
Development Branch
Division of Waste Management
Mail Stop SS-965
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555

Dear Mr. Browning,

Enclosed is a letter report titled, "Status Report on Leachability, Structural Integrity, and Radiation Stability of Organic Ion Exchange Resins Solidified in Cement and Cement With Additives."

Sincerely,

Donald G. Schweitzer, Head

Nuclear Waste Management Division

DGS/nms Enclosure

cc: F. Arsenault

R. E. Browning

J. Davis

T. Johnson

J. C. Malaro

J. B. Martin

R. D. Smith

STATUS REPORT ON LEACHABILITY, STRUCTURAL INTEGRITY, AND RADIATION STABILITY OF ORGANIC ION EXCHANGE RESINS SOLIDIFIED IN CEMENT AND CEMENT WITH ADDITIVES May 1980

R. E. Barletta, R. E. Davis, T. E. Gangwer, N. Morcos, D. G. Schweitzer and A. J. Weiss

The first stage Epicor-II resins from TMI-2 will have Cs-137 activities (approximately 40 Ci/ft³) that are about 10³ times greater than the concentration guides (.02 to .04 Ci/ft³) for shallow land burial sites proposed in 10 CFR Part 61 and NUREG/CR-1005. The composition of waste from the TMI-2 auxiliary building cleanup differs in radionuclide content from the waste normally collected on spent reactor resins and is considerably more concentrated in isotopes of cesium. The total inventory is about fifteen times the normal allocation for three months operation of TMI-2 and is equivalent to about 20 years production of waste by a PWR and about five years of nuclear waste production by a BWR.

The waste considered in this report is considerably higher in inventory and specific activity than any spent reactor resins previously placed in shallow land burial sites. Therefore, we have assumed that if this material is going to be considered for shallow land burial in a form solidified with cement, leachability properties of this type of matrix should be understood, predictable, and of a sufficiently low value so that the radionuclide release rate and total release over the burial lifetime should be comparable to other materials put into the shallow land burial sites. Once transportation and shipping requirements have been met and the waste forms have been buried, we believe that a measure of the adequacy of immobilization of the radionuclides is directly related to the leachability from the waste form and container.

Summary of Conclusions

The preliminary conclusions that were arrived at in the course of assembling this report are summarized below.

- 1. We were not able to find any study or set of studies which was systematic enough and extensive enough to answer or address the questions we believe are pertinent to shallow land burial for waste of the specific activity and quantity of the first stage TMI-2 resins.
- 2. We were not able to infer from published material that specialists in the field are aware that cesium and perhaps other radionuclides appear to be rapidly removed from the ion exchange resin during the initial stages of mixing with cement and water. The cesium displaced from the resin appears to distribute itself approximately equally between the water and the cement.
- 3. We were not able to find leaching data on samples larger than about a liter. (The two types of TMI-2 containers are about 1400 liters and 4800 liters.)
- 4. We do not believe adequate evidence exists that justifies predicting leach rates of large samples from data on small samples.
- 5. Along with known differences between anion and cation resins, we believe the swelling of the organic resins with frequent concomitant cracking of the resin-cement matrix in laboratory experiments may be associated with (a) improper resin-cement-water ratios, (b) improper curing conditions for the matrix and (c) inadequate saturation of the resins with H₂0. If so, this problem may be avoided.
- 6. We do not believe that there is a unique stability or integrity region for relative compositions of resin, cement, and $\rm H_2O$. Existing evidence shows that for similar conditions the structural integrity may depend on the type of

resin rather than its weight fraction. Since most of the available data deal with mixes that tend to maximize resin proportions, this problem may be avoided in mixes with greater cement and/or H₂O proportions.

- 7. The literature on vermiculite and zeolite additions to cement-organic resin mixes and cement-liquid waste mixes is promising but sparse. Ball milled vermiculite gives improved leach resistance in both cement-resin mixtures and cement-liquid waste forms. European studies indicate no adverse mechanical effects on cement-resin additive mixtures. Studies on cement-liquid wastes at Savannah River Laboratory showed the resulting concrete was weak.
- 8. The fundamental processes causing radiation damage in resins are not understood. However, resins loaded at 40 Ci/ft³ will undergo significant decomposition. The extent of decomposition is specific to resin type. Preliminary calculations indicate a moderate level of gas generation as a result of radiolysis.
- 9. Since data on small samples indicate that large fractions of the cesium can be leached in hundreds of days and since there do not appear to be sufficient studies on impregnation of these systems with asphalt or polymers, the first stage TMI-2 organic resin waste may not be adequately immobilized by simply mixing with cement and solidifying. We believe this type of waste should be treated by thoroughly understood more stringent waste management procedures.

1. Mechanical Properties of Organic Ion Exchange Resin/Cement Waste Forms

The available literature was reviewed to determine whether there were any correlations between the preparation characteristics (i.e., water, cement ratios, resin loading, and curing procedure) and the mechanical integrity of resin/cement composites. These composites have been known to exhibit poor mechanical strength during both preparation(1,2) and upon subsequent immersion of a seemingly good composite in water(1,3) as evidenced by swelling, cracking, and in extreme cases, complete desintegration of the composite. The papers reviewed cover a range of 11 anion, cation, and mixed bed granular resins (see Table 1). The results of these experiments, as well as the resin loadings and water content for experiments involving granular ion exchange resin/cement composites are shown in Table 2. Given the state of the art, it is possible to draw several conclusions from these data.

- 1. The lack of mechanical integrity is not a problem generic to either all ion exchange resins or to any particular resin type. Acceptable composites have been produced using anion exchange resins, (2) cation exchange resins, and mixed bed resins. (3) Conversely, composites made from all three types of resins have been known to exhibit poor mechanical properties. (1)
- 2. Resin loading <u>per se</u> is not a particularly sensitive variable for loadings less than 50 wt.% (17 wt.% dry resin).(3)
- 3. Fast setting cements may be somewhat superior matrix materials for granulated resins than ordinary cement. (3) In other experiments using powdered resins, (3) it was concluded that low heat quality cement was more suitable.

Table 1

Resin Types Used for Preparation of Resin/Cement Composites

- 1. Amberlite IRN-150 (Mixture of IRN-77 and IRN-78).
- 2. Amberlite IRN-77. Strong acid cation exchange resin loaded with Na⁺ and containing 55 wt.% water.
- 3. Amberlite IRN-78. Strong base anion exchange resin loaded with C1- and containing 60 wt.% water.
- 4. Dowex 1 x 8. Strong base anion exchange resin.
- 5. Dowex SAR. Strong base anion exchange resin, CIT form. Resin was dewatered and contains approximately 45 wt.% water.
- 6. Amberlite-200. Strong acid cation exchange resin, Na⁺ form resins was dewatered and contains approximately 45 wt.% water.
- 7. Dowex 50. Cation exchange resin, H⁺ form, saturated with water.
- 8. Dowex 21K. Anion exchange resin, OH- form, saturated with water.
- 9. Dowex 50 W-21K. Mixed bed ion exchange resin, $\mathrm{H}^+\text{-OH}^-$ form, saturated with water.
- 10. Dowex 50 W-21K. Mixed bed ion exchange resin, Na⁺-OH⁻ form saturated with water.
- 11. Diaion SKIB. Cation exchange resin, H⁺ form.

Table 2 Mechanical Properties, Resin Loadings, and Water Content of Resin-Cement Composites

| 1. | Veight Ra | tio | | Resin | | Good | |
|--|-----------|-------|------------------|--------------------|---------------|------------------------|-----------------------|
| | : Resin | Added | | Loading | Resin Type | Mechanical | Ref. |
| | | Water | w/c ^b | (wt.%) | (see Table 1) | Integrity ^C | No. |
| 1a | 0.9 | 0.9 | 0.9(1.4) | 31 | 1 | no | 2 |
| 1ª | 0.9 | 0.9 | 0.9(1.4) | 31 | 2 | no | |
| 1ª | 0.9 | 0.9 | 0.9(1.4) | 31 | 3 | yes | 2 |
| 1 ^a | u | u | ù | 14.3 | 4 | ud | 1 |
| 1ª . | u | u | u. | 23.5 | 4 | ud | ī |
| 1a | 0.25 | 0.4 | 0.4 | 14 | 4 | ud . | 1 |
| 1ª | 1 | 0.28 | 0.28 | 44 | 4 | ud | 1 |
| 1^{a} | . 2 | 1.2 | 1.2(2.1) | 48 | 5 | no | 1 |
| 1ª | 2 2 | 0.85 | 0.85(1.8) | 52 | 5 | no | . 1 |
| 1 ^a 1 ^f 1 ^f 1 ^f | 2 | 1 | 1(1.9) | 50 | 6 | no | 1 |
| 1 ^f | u | u | (0.65) | 14 ^e | 7 | yes | 3 |
| 1 ^f | u | u | (0.65) | 14 ^e | 8 | no | 3 |
| 11 | , u | u | (0.55) | 14e | 9 | no | 3 |
| | u. | ้น | (0.65) | 14-17 ^e | 10 | no | 3 |
| 19 | u | u | (0.56) | 4.3e | 10 | yes | 3 |
| 19 | u | u | (0.45) | 4.3 ^e | 10 | yes | |
| 19 | u | u | (0.62) | 5.8e | 10 | no | 3 |
| 19 | u | u | (0.51) | 5.8 ^e | 10 | yes | . 3 |
| 19 | u | u | (0.64) | 7.3 ^e | 10 | no | 3 |
| 19 | u | u | (0.52) | 7.3 ^e | 10 | yes | 3 3 3 3 3 |
| 19 | u . | u | (0.67) | 8.6e | 10 | no | 3 |
| 19 . | u | u | (0.60) | 8.6 ^e | 10 | no | 3 |
| 19 | u | u | (0.70) | 10 ^e | 10 | no | 3 3 |
| 19 | u | u | (0.62) | 10 ^e . | 10 | no | 3 |
| 19 | u | u | (0.65) | 16e | 10 | no | 3 |
| 19 1h | u | u · | (0.52) | 10 ^e | 10 | yes | 3 4 |
| 1 ^h | 0.7 | 0.4 | 0.4 | 17.6 | 11 | ud | 4 |

aportland Type II.

bWater/cement wt. ratio, value in parentheses is ratio with total water. CNo cracking or swelling during incorporation curing or subsequent water immer-

dused in leach tests, condition of specimen not given.

eDry resin.

fPortland Type 300 (NS 3050). SPortland RHC (rapid hardening).

hportland blast furnace slag.

Uunspecified.

- 4. For a particular resin (or resin mix) there exists a window of water cement ratios within which an acceptable composite may be produced. Water content either greater or less than this range produces composites exhibiting poor mechanical properties. This window is not the same for all resins or for all resins of a given type. For the granular resins which they studied, Bonnevie-Svendsen, et al.(3) indicate that the region of the water/cement ratio within which an acceptable product is produced is small. The window was somewhat larger for the powdered resins tested. Thus, in order for valid conclusions to be drawn concerning the mechanical properties of a given resin/cement composite, scoping experiments must be performed using resin or resin mix identical to that of interest.
- 5. Since, in a water deficient environment, one might expect a competition for available water between ion exchange resins and cement, curing conditions and most particularly those relating to water availability (i.e., humidity, amount of free standing water during curing, etc.) might be expected to affect the mechanical integrity of the product. Indeed, improved strength has been noted for cement products when curing is done in the presence of a large excess of water. In the papers reviewed however, no systematic study of this variable has been undertaken, and it appears that, at best, composites were allowed to cure in water-saturated air. (3) Thus, the effect of curing conditions upon the mechanical strength and integrity of ion exchange resin/cement composities is unknown.

2. Leaching of Organic Ion Exchange Resin/Cement Waste Form

Historically, the reasons for solidification of low level wastes arose from consideration of interim storage and transportation concerns. Furthermore, under existing low level waste regulations, ion exchange resin wastes are normally acceptable for disposal if shipped in a dewatered form. (5) For these reasons, we believe there has been limited interest in detailed characterization of the leaching of solidified resin wastes. No systematic studies of resin/cement waste forms have been identified. While the present review has identified several studies of resin/cement waste form, they are of limited scope, often focused on a single resin or cement type or a very limited subset thereof. There are approximately 20 generic types of synthetic organic ion exchange resins, and literally hundreds of specifics brands, exhibiting property variation by manufacture and even production batch. (12) Leach behavior of a resin/cement waste form is not a generic property. Leaching varies with the resin and cement types. The leach behavior of cesium is stressed since cesium represents the most mobile fission product of immediate concern.

As a baseline for comparison of resin/cement waste forms, the results of experiments to determine the leach behavior of unbound ion exchange resins are shown in Figures 1, 2, 3, and 4.(6) Figures 1 and 3 indicate that ion exchange resins exhibit some retention of 137 Cs and 85 Sr when leached with distilled water. When ion exchange resins are leached with saltwater, the total activity of Cs and Sr are leached within five days. The leaching of resins in groundwater (figures unavailable) is intermediate to that in distilled water and saltwater.(6) However, the Cs release was essentially complete after ten days.

Recent scoping experiments were performed at BNL to determine if ionic species present in unset cement could elute activity from an ion exchange resin. Rohm and Haas IRN-77, a strong acid cation resin, was loaded with approximately 1 mCi/ft 3 of 137 Cs (substantially less than the 40 Ci/ft 3 expected for the first stage Epicor-II resins). Resin, water, and cement mixtures, having waste to cement wt. ratio of 1.8 and water to cement wt. ratio of 0.8, were prepared with two cement types. For Portland type II cement, resin/cement samples were contacted for 5 and 60 minutes, then seperated into a resin fraction and a cement/water fraction. Similarily for Lumnite cement, contact times were 5 and 45 minutes. Ion exchange resins were counted for $^{137}\mathrm{Cs}$ activity before and after cement contact. After 5 minute contact, for both Portland II and Lumnite cements, approximately 10% Cs activity was eluted. While, for Portland II cement and 60 minutes contact, approximately 30% Cs was released. For Lumnite cement and 45 minutes contact, approximately 35% of the initial Cs was released. The maximum extent to which Cs could be replaced by the ionic species present in cement/water mixture was not determined. However, these preliminary experiments indicate a substantial amount of Cs was liberated from the ion exchange resin upon mixing with cement and water. Since both the average ion exchange resin site binding energy and the kinetics of elution would be more unfavorable at the loading expected for first stage Epicor-II resins, these results should be viewed as conservative.

Earlier studies⁽⁶⁾ on Portland II cement waste form had been performed to measure the decontamination factors for cesium, strontium, and cobalt. Cement samples were prepared with a water to cement wt. ratio of 1 to insure intentional free standing water above cement samples. No resins were incorporated in

these experiments. After a 3-day curing, samples of the free standing water were analyzed for the radioisotopes of interest. Decontamination factors (DF) were calculated as the ratio of radionuclide in the initial waste (mCi/mL) to the radionuclide concentration in the free standing water (mCi/mL). The values reported were 137 Cs, DF = 1, 85 Sr, DF = 11; and 60 Co, DF = 200. These results indicate scant incorporation (interaction) of the Cs with the cement matrix in contrast to Sr and Co. It was concluded that a mixture of resins in cement liberates a substantial fraction of cesium with an uncertain degree of incorporation within the cement matrix. The use of additives to enhance radionuclide retention is discussed in the following section.

The earliest examination of leaching of ion exchange resin/cement wasteform was reported by Holcomb.(7) This work predates IAEA leach testing and reporting conventions. Samples were prepared with 50% Portland cement, 25% mixed resins, and 25% water by volume. The total volume, surface to volume ratio, and concentration of radionuclides in the sample were not reported. Static leach tests in 3 liter of seawater were performed. The fraction of 137Cs activity leached was approximately 3-4% in one year. Another leaching study, which also predates IAEA recommendation, on powder resin/ cement waste form has been reported by the Hanford Engineering Development Laboratory.(1) Samples, having volumes of 131 cm³ and volume-to-surface ratio of 0.85 cm, were leached in 250 mL of deionized water with mechanical agitation. After 14 days, the cumulative fractions of released reported were 0.8cm for cesium and 0.1 cm for strontium.

More recently, several studies on ion exchange resins/cement composite have been reported. (3,4,8) Results representative of studies are shown in Figures 5, 6, and 7. Leaching experiments carried out in these studies conform to the

IAEA recommendation. (9) From these studies of small samples, generally indicate that 30 to 100 percent of the initial Cs is leached within 100 days. Variations can be attributed to many parameters; type of resin, type of cement, resin to cement and water to cement ratios, length of curing period before leaching was initiated, and possibly the surface to volume ratio of the sample.

The mechanisms of leaching are not well understood, and hence an unambiguous interpretation of leach test results is not currently possible. However, the following diffusion model has been proposed. In the model, the fraction, f, release at time, t, is given by

$$f = \frac{2S}{V} \sqrt{\frac{Dt}{\pi}}$$
 (1)

where D is the diffusion coefficient, and S and V are the geometric surface and volume of the sample. If the model was applicable, then a plot of f versus $t^{1/2}$ would yield a line passing through the origin. However, see Figure 6 for example, the model generally is not followed. During an initial period of approximately 25 days, the leaching is significantly more rapid than the latter period, which is linear. Beyond the initial period, the leach process has been described by the following equation,

$$f = \frac{2S}{V} \sqrt{\frac{Dt}{\pi}} + \alpha = m\sqrt{t} + 2 \tag{2}$$

where α is simply the f axis intercept. The rationale often given for this expression is that after the initial period of rapid leaching dominated by a not well understood mechanism, the leaching is diffusion controlled.

A primary goal of leach testing is to characterize what is to be expected after disposal of a candidate waste form. Of interest here is the extension of

data obtained on small laboratory samples to predict the behavior of realistically sized waste forms. To date, no study of a resin cement composite has been reported which explores the functionality of fraction release and the surface to volume ratio expressed in Eqs. 1 and 2. Matsuzuru(10) has reported a study on the effect of sample dimension on the leaching of sodium sulfate waste/ cement composites. Samples having surface to volume ratios over the range 2.47 to 0.587 cm⁻¹ were leached in accordance with IAEA recommendations. sults could be represented by Eq. 2. Linear dependances on S/V were observed for both the m and b; see Figure 8. Extrapolation of this data can provide an estimate of the release from a realistic sized waste form. Estimates for a 200 L drum were given in reference 10 and are reproduced here in Table 3. While these results are not directly applicable to resin/cement composites, specimen number 8 is spectulated to be most applicable. Clearly, significant gains in cesium retention are predicted for large monoliths. The largest sample tested in the study was 10 cm (3.9 in.) diameter and 12 cm (4.7 in.) high. Given the empirical nature of interpretion of leach results, it would seem important that this type of measurement be extended to larger if not actual sized resin/cement waste form.

Table 3
Estimated fraction leached from a cement composite of 2001 drum size

| Specimen No. | Leaching p | arameters | Leaching fraction | | | | | |
|----------------------|---|---|---|--|---|---|---|--|
| | m (day -1 2) | α | 1 yr | 10 yr . | 50 yr | 100 yr | 200 yr | |
| 11:Cs | | | | | | | | |
| 121341561-8 | 1. 3 × 10 ⁻⁴ 7. 4 × 10 ⁻⁴ 1. 4 × 10 ⁻⁴ 1. 1 × 10 ⁻³ 2. 4 × 10 ⁻⁵ 8. 6 × 10 ⁻⁶ 4. 2 × 10 ⁻⁶ 1. 9 × 10 ⁻² | 4.7×10 ⁻³ 8.1×10 ⁻³ 4.7×10 ⁻³ 1.3×10 ⁻³ 5.7×10 ⁻³ 1.1×10 ⁻³ | 7. 2 × 10 ⁻³ 2. 2 × 10 ⁻² 7. 4 × 10 ⁻³ 3. 4 × 10 ⁻³ 4. 6 × 10 ⁻⁴ 1. 6 × 10 ⁻³ 1. 4 × 10 ⁻² 4. 7 × 10 ⁻² | 1. 3 × 10 ⁻² 5. 2 × 10 ⁻² 1. 3 × 10 ⁻² 7. 9 × 10 ⁻² 1. 4 × 10 ⁻² 5. 2 × 10 ⁻³ 3. 1 × 10 ⁻² 1. 3 × 10 ⁻² | 2. 2 × 10 ⁻¹ 1. 1 × 10 ⁻¹ 2. 4 × 10 ⁻¹ 1. 6 × 10 ⁻¹ 3. 2 × 10 ⁻¹ 1. 2 × 10 ⁻² 6. 2 × 10 ⁻¹ 2. 6 × 10 ⁻¹ | 3. 0 × 10 ⁻⁷ 1. 5 × 10 ⁻¹ 3. 1 × 10 ⁻² 2. 2 × 10 ⁻¹ 4. 6 × 10 ⁻² 1. 6 × 10 ⁻² 8. 6 × 10 ⁻² 3. 7 × 10 ⁻¹ | 4. 0 × 10 ⁻² 2. 1 × 10 ⁻¹ 4. 3 × 10 ⁻² 3. 1 × 10 ⁻³ 6. 5 × 10 ⁻³ 2. 3 × 10 ⁻² 1. 2 × 10 ⁻¹ | |
| "Sr | | | | 1.3 × 10 | 2.0 × 10 | 3.7 × 10 · | 5.2×10^{-1} | |
| 13 11 17 15 | 2. 5×10^{-3} 3. 5×10^{-5} 3. 5×10^{-5} 5. 5×10^{-5} | 9. 1×10 ⁻⁸ 2. 3×10 ⁻⁴ 1. 3×10 ⁻⁴ 3. 1×10 ⁻⁴ | 5.7×10 ⁻⁴ 9.0×10 ⁻⁴ S.6×10 ⁻⁴ 1.4×10 ⁻² | 1. 6 × 10 ⁻³ 2. 3 × 10 ⁻³ 2. 4 × 10 ⁻³ 3. 6 × 10 ⁻³ | 3.4×10^{-3} 5.0×10^{-3} 5.3×10^{-3} 7.7×10^{-3} | 4.8×10 ⁻² 6.9×10 ⁻² 7.4×10 ⁻² 1.1×10 ⁻² | 6.8×10 ⁻³ 9.7×10 ⁻³ 1.0×10 ⁻² 1.5×10 ⁻² | |
| (:Co | • | | | | | | | |
| 21 22 25 26 | 1.1×10 ⁻⁴ 1.6×10 ⁻⁷ 3.4×10 ⁻⁴ 5.5×10 ⁻⁷ | 5. 1×10 ⁻⁴ 1. 2×10 ⁻⁴ 1. 2×10 ⁻³ 1. 5×10 ⁻⁴ | 2.9×10 ⁻³ 4.7×10 ⁻⁴ 7.7×10 ⁻⁴ 1.2×10 ⁻⁴ | 7.5×10 ⁻⁵ 1.1×10 ⁻⁵ 2.2×10 ⁻⁶ 3.5×10 ⁻⁵ | 1. C × 10 ⁻⁴ 2. 3 × 10 ⁻⁴ 4. 7 × 10 ⁻⁴ 7. 4 × 10 ⁻³ | 2.2×10 ⁻⁴ 3.2×10 ⁻³ 6.6×10 ⁻⁴ 1.1×10 ⁻⁴ | 3.0×10 ⁻⁴ 4.4×10 ⁻⁴ 9.3×10 ⁻⁴ 1.5×10 ⁻⁴ | |

Inherent in scaling to a realistically sized waste form, is the assumption that the sample is a structurally sound monolith (a waste form, absent of any cracking which would increase the effective surface to volume ratio). In the case of resin/cement composites, large monoliths have not been demonstrated.

- 1. The leach behavior of resin and cement waste forms depends upon resin type, cement type, loading (waste to cement ratio), curing, type of leachant, and temperature.
- 2. Preliminary experimental evidence suggests substantial liberation of cesium from resin immediately after mixture with cement and probably little incorporation within the cement matrix.
- 3. Recent leach testing of small samples indicates little retention of cesium: 30-100% loss within 100 days.
- 4. Some experimental evidence exists to suggest substantial improvement of radionuclide retention with increased size of waste form. However, this has not been verified for resin/cement waste forms of realistic size.

 Reduced leachability may be realized if the waste form exhibits good mechanical integrity.

3. Effect of Additives Incorporated In Concrete Waste Forms

In Summary

A variety of additives have been used in the solidification of radioactive wastes in cement to alter properties of the resultant waste form, such as set time, strength, swelling, and leachability. Spent ion-exchange resins constitute a major fraction of radioactive waste from nuclear reactors. Cement waste forms containing ion-exchange resins often swell, crack, and tend to disintegrate in water. Addition of vermiculite to the resin/cement mixture is reported to reduce this tendency of the waste form to swell and crack, however, there is

a paucity of information available in the literature on the effects of additives incorporated in ion exchange resin/cement waste forms.

Bonnevie-Svendsen, et al.,(3) discusses the leachability of cesium from ion exchange resin/cement products and the effects of additives, including vermiculite, on the quality of the resin/cement products. High leaching of cesium is a main objection against incorporation of fission product wastes in cement, and the leaching of cesium from resin/cement products is sometimes higher than from pure cement. With 2.5% by wt. vermiculite (particle size 30-70 mesh) cesium leach coefficients in cement were reduced 2 to 3 orders of magnitude without impairing the mechanical properties. No resins were incorporated in these waste forms. Similar effects were achieved for cement products with approximately 18% (dry wt.%) new granular resins (H+-SO₃-2), 10% new powdered resin (H+-OH-), and 9% spent powdered resin. The reduction of cesium leach rates with increasing vermiculite content from 2.5% to 10% cement weight is shown in Figures 9, 10, and 11. Since vermiculite is known to have cationic adsorptive properties, it is reasonable to expect that vermiculite will aid in recapturing the cesium that is released from the ion exchange resins.

A Savannah River Laboratory study⁽¹¹⁾ tested a series of sorbents for cesium sorption kinetics, compressive strength of concrete containing the sorbent, and leachability. The best cesium sorbents, in terms of sorption kinetics, were Linde AW-500 and Zeolon Z-900 out of the following materials: Z-200, Z-500, Z-900, Linde 13-X, Linde AW-300, Linde SK-40, Linde AW-500, clinoptilolite, and vermiculite. The effect of the sorbents on the compressive strength of concretes was measured with and without simulated sludge waste. In the absence of sludge, AW-500 and Z-900 had little effect on the strength of concrete, whereas Z-200, AW-300, and vermiculite severely weakened the concrete.

In the presence of sludge, Z-900 and AW-500 actually strengthened the concrete while vermucilite weakened it badly. No data are available for resin/cement waste forms. Comparative leachability of cesium from two concretes containing 2 wt.% of the sorbents are shown in Table 4.

Table 4(11)Leaching of Concretes

| % Cesium Leached After 28 day | | | | | | |
|-------------------------------|------|--------------|--------|-------------------|--|--|
| Sorbent | High | Aluminum | Cement | Pozzolanic Cement | | |
| AW-500 Z-900 | | 5.7 6.0 | | 4.6 3.9 | | |
| Vermiculite | | 6.3 6.5 | | 3.8 | | |
| Z-500 Z-200 | | 9.1 | | 4.5 6.5 | | |
| Clinoptiloli AW-300 | te | 13.1 17.9 | | 9.2 9.3 | | |
| M4-200 | | 11.47 | • | 3.3 | | |

On the basis of leachability, AW-500, Z-900, and vermiculite were the best sorbents for cesium. It has been shown that addition of silicates to cements reduces free calcium in the final product. It was postulated that free calcium in concrete might displace cesium from ion exchange sites in the solidified material. However, addition of silica gel to cement containing sorbents had no additional effect on cesium leachability.

Conclusion

These data suggest that if ion exchange resins are solidified in cement, additives may reduce the potential for swelling and cracking and at the same time decrease the cesium leachability resulting from its desorption by free cations in the cement.

4. Radiation Stability of Organic Ion Exchange Resin Systems

A loading of the organic ion exchange resins to the 40 Ci/ft³ level will result in total dose exposure of 10⁹ rads. Based on the literature⁽¹²⁾ such a dose level will result in significant decomposition of the resins. The loss of the ability to retain radionuclides and generation of organic products, which would be free to migrate away from the resin sites, will occur in these systems. Resin degradation processes may continue even after the majority of the radiation has decayed due to long lived reactive species formed by various chemical reactions. For example, radiation induced oxidation can generate peroxides which will subsequently decompose and react with the resin. Production of such strong oxidizing species could also result in conditions favoring exothermic chemical reactions.

For more than three decades there have been extensive applications of ion exchange materials in the nuclear process industry. Process related problems of a serious nature caused by radiation chemical changes in the ion exchange medium have been mentioned occasionally in the open literature as well as in safety evaluation studies of radioactive material processing. The present literature survey(12) identified a number of reports on experimental studies relevant to evaluating the process related properties of organic ion exchangers. Still, there are numerous problems associated with the radiation chemical changes of ion exchange materials due to radiation damage which are not properly understood. Thus, in spite of the apparent abundance of experimental studies, there is no reliable information to allow one to predict the chemical effects on long term storage of ion exchange materials with loading comparable to the first stage TIM-2 materials.

Understanding the effects of radiation on ion exchange materials may be important in deciding how disposal of spent resins should be carried out. From the present survey of current knowledge on the radiation effects on both organic resin and inorganic zeolite ion exchange materials, it can be-concluded that:

- The fundamental processes involved in radiation damages to ion exchange materials are not understood.
- 2. Structural and chemical constituent modifications can significantly change the radiation resistance of ion exchange materials.
- 3. There have not been systematic investigations to develop standards for use of and loadings of ion exchange resins.
- 4. There is a need to extend the radiation effect studies to investigations of secondary reactions of the radiolysis products with the materials to be used in waste disposal.

Gas Evolution as a Result of Irradiation

Irradiation of ion exchange resins results in evolution of gaseous products. There are only a few reported experimental studies which have attempted to study the nature of gas evolution and make some quantitative estimates of the gaseous product formation during the radiolysis of ion exchange resins(12). The main gaseous products formed during the irradiation of ion exchange resins are hydrogen and carbon dioxide. Other gases such as carbon monoxide, oxygen, methane, nitrogen, and oxides of nitrogen and sulfur have been identified. The radiation chemical yields (G values) for the gaseous products, taken from Table VII of reference 12, are reproduced here in Table 5.

In cation exchange resins, the evolution of hydrogen is a linear function of absorbed dose. Hydrogen evolution is also shown to increase with the water content (swelling) of the resin. Sulfur dioxide is formed by the direct action

of ionizing radiation on dry forms of sulfonic acid resins. In the presence of water, the SO_2 undergoes secondary reactions to form acidic solutions and for this reason, SO_2 is not identified during the irradiation of moist and wet resins. Carbon dioxide and carbon monoxide are products of irradiated resins. Like hydrogen, the evolution of CO_2 and CO is quite linear with absorbed dose. In general, the radiation chemical yield of carbon monoxide is significantly less than that of carbon dioxide.

Based on the G values in Table 5, which range for the various gases from 0.001 to 3.0, the yield of gas from an organic resin subject to 10^9 rad will correspondingly range from .02 to 70 cm³ of gas per gram of resin. An estimate of the corresponding gas yield from cement is 1.3 cm³ per gram of cement. (6) If one assumes a G = 0.01 for gas evolution from resins subjected to 10^9 rad, then pressures in the range of 1.5 to 15 atmospheres would be produced in a sealed 4800 L (4 ft. dia. by 4 ft. high) cylindrical canister containing solidified waste with 60 volume % resin and a void volume of from 1 to 10%. If the gas were CO_2 , for example, the container would be subjected to the pressure. If on the other hand, the gas were SO_2 and the void volume was filled with water, then the 9.2 moles of SO_2 produced would result in an acidic solution whose strength would be in the range of 0.07 to 0.7 M.

These preliminary calculations serve to illustrate that the quantities of gases which could be generated are not trivial, and therefore, gas generation warrants further consideration.

Organic Ion Exchange Failures

Ion exchange resin failures have been reported for systems involving nitric acid. Critical ignition temperatures as low as 135°C have been reported

for resins in the nitrate form with the potential of this going below 100°C for radiation damaged resin systems. Self ignition temperatures for anion resins depend on resin form, heating rate, resin brand, cross linkage, loading, resin bed volume, aging and pretreatment. Of particular concern to the TMI resin systems is the resin bed volume. Increasing the geometrical dimensions of the resin bed was reported to lower the ignition temperature. As pointed out in the Miles report(13) although only nitric acid/resin system have been observed to be unstable to date, one cannot assume any resin system is safe: "Therefore, experimental work to establish safe limits in these areas before using a given ion exchange system should be considered mandatory." As a first step, the precautionary measures such as those listed in Table 3 of Miles' paper should be verified for the specific resin systems under consideration.

Conclusion

We do not know if every one of the many uncertainties discussed in this report is directly or indirectly related to safety aspects of shallow land burial. However, we believe that the uncertainties do warrant that more stringent waste management procedures be applied to the TIM-2 first stage Epicor II resins.

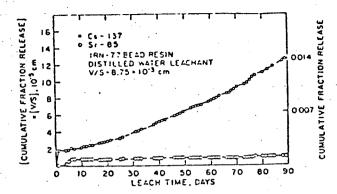


Figure 1. 137Cs and 85Sr release from IRN-77 bead resin for static leaching in distilled water. (6)

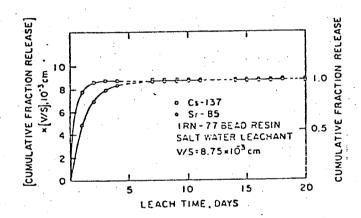


Figure 2. 137Cs and 85Sr release from IRN-77 bead resin for static leaching in saltwater.(6)

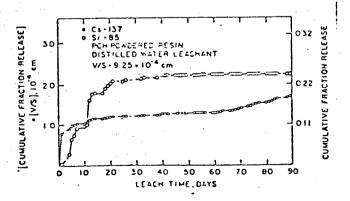


Figure 3. 137 Cs and 85 Sr release from PHC powdered resin for static leaching in distilled water.(6)

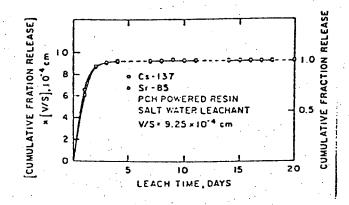


Figure 4. 137_{Cs} and 85_{Sr} release from PCH powdered resin for static leaching in saltwater.(6)

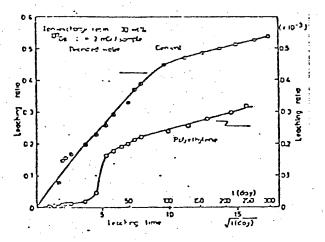


Figure 5. Leaching of 137Cs from ion exchange resin incorporated in polyethylene or cement.(8)

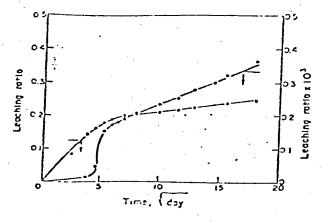


Figure 6. Plots of f vs t for leaching of ¹³⁷Cs from ion-exchange resin incorporated in polyethylene or cement, o polyethylene, o cement. (4)

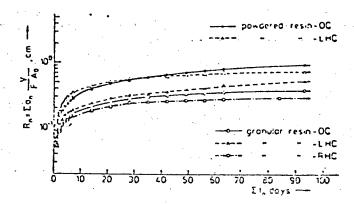


Figure 7. Effect of cement qualities on the cesium leach rate of resin/cement products. OC- Portland cement, Type 300; LHC-Portland cement, rapid hardening.(3)

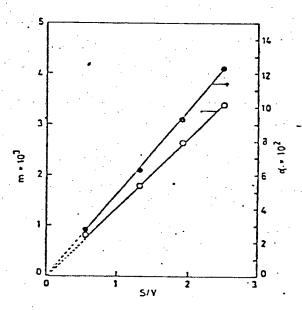


Figure 8. Typical plots of m and $\alpha(10)$ vs S/V (Specimen No. 1)

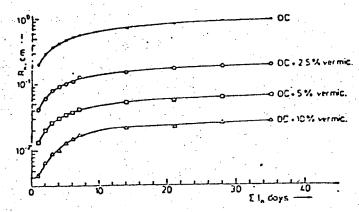


Figure 9. Accumulated Cs leach rates $\binom{R_n = \Sigma a_n \cdot \frac{V}{F \cdot A_0}}{\text{for powdered resin}}$ cement vermiculite products. OC- Portland cement, type 300.(3)

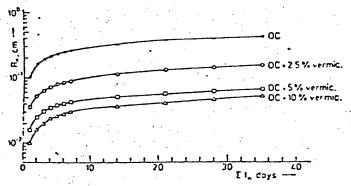


Figure 10. Accumulated Cs leach rates $\begin{pmatrix} R_n = \Sigma a_n \cdot \frac{V}{F \cdot A_o} \end{pmatrix}$ for granular resin cement vermiculite products. OC- Portland cement, Type 300.(3)

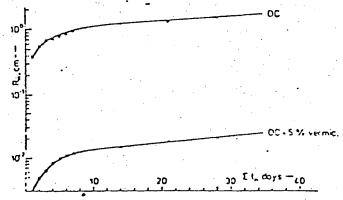


Figure 11. Accumulated Cs leach rates $\binom{R_n = \Sigma a_n \cdot \frac{V}{F \cdot A_0}}{F \cdot A_0}$ for Oscarshamn spent resin-cement vermiculite products. (Cs tracer added). OC- Portland cement, Type 300.(3)

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