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Writer's Direct Dial Number

December 4, 1980 TLL 634

TMI Program Office Attn: Mr. John T. Collins, Deputy Director U. S. Nuclear Regulatory Commission c/o Three Mile Island Nuclear Station Middletown, Pennsylvania 17057

Dear Sir:

8012100451

Three Mile Island Nuclear Station, Unit 2 (TMI-2) Operating License No. DPR-73 Docket No. 50-320 EPICOR II Liner Evaluation Status

Forwarded herewith is the initial evaluation of the possibility of corrosion of EPICOR II liners, which corrosion might result in loss of full integrity of the liners with resultant leakage. Also, included below is other information related to this subject.

It must be remembered that leakage of the liners would have only very minimal consequences. This is because of the cumulative effect of several factors, such as:

- The free water content of each liner can be expected (based on extensive testing of the dewatering procedure) to be less than 1.5 gallons--possibly approaching zero.
- Radioactivity of residual water, based on experience with the EPICOR I and II systems, is expected to be minimal.
- At worst, based on the attached evaluation, the loss of integrity, should it occur, would be only in the nature of pin-hole leaks, not a failure that might alter the structural integrity of the liner.
- o The liners are stored in a high-integrity, massive structure with internal drains and a sump, that would confine any credible leakage, conducting liquid to the sump from which it could be removed for appropriate handling and treatment.

Perusal of the attached evaluation report will, we believe, make it apparent that, for the parameters which might contribute to the possibility of corrosion, the worst credible situation has been assumed. Even so, with this assumption of the worst aggressive possible combination of variables, it is concluded that only eight (8) of the sixtyfive (65) liners studied might fail sconer than twenty-five (25) years. Under the assumed conditions, these eight liners might be perforated in some fifteen (15) to nineteen (19) months.

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However, it is very likely that the parameter that is the principal contributor to corrosion, the pH of water in the liner, is not at all likely to be as low in these eight liners as was assumed. The material in the liners was selected and located with the intent of assuring that the residual water would be over 5 pH. Sampling of eight EPICOR I liners, in storage for up to one (1) year, showed that while the final effluent from the liner was as low as 3.3 pH, in all liners, the pH of the later sample was over 5. It, therefore, seems that there is assurance that the low pH values in the EPICOR II liners' effluent have not persisted, the pH has risen, and that corrosion rates are less than those used in the study.

Every effort has been and continues to be made to gain information that would allow a more precise assessment of conditions existing in these liners. Several programs such as: (1) Sampling EPICOR II Liners, (2) More Exact Integrated Dose Calculation, (3) Exchange of Information with Epicor, Inc., and (4) Testing Results from Various Resin Degradation Studies, all pose as providing information that may improve the generalized assumptions made in these evaluations.

In addition to discussing and transmitting the evaluation report, this letter also discusses, below:

- o Resin integrated dose calculations
- o Liner Sampling Program
- o EPICOR II Liner Contingency Plans
- o Liner Staging "odule

METALLURGICAL EVALUATION REPORT

A. LINER INTERNAL ENVIRONMENT ASSESSMENT

The internal environment of an EPICOR resin liner is based upon such variables as chemical, thermal, and radiation reactions. All variables must be accounted for when determining the environment existing within a liner at any specified time. Various assumptions have been made in characterizing these reactions. A continuing effort is being made toward verifying these assumptions. It is expected the liner sampling program, completion of the integrated dose calculation, and the exchange of information with Epicor, Inc., and the availability of Penn State, Georgia Institute of Technology, and Brookhaven National Laboratory (BNL) testing results will assist in this effort.

B. LINER METALLURGICAL EVALUATION

Following the categorization of the internal environment of the liners, a metallurgical evaluation was performed. This analysis included several assumptions while attempting to determine when a liner might first be perforated. Since the assumptions are subject to change in the near future, the conclusions are also subject to change. The Attachment to this letter is the study from which these conclusions were reached.

As the internal environment of a liner is more accurately characterized, this metallurgical evaluation will be updated to present an <u>actual</u> vs. a worst case condition.

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RESIN INTEGRATED DOSE

Very general calculations of Integrated Dose have been made and reported to the NRC and Brookhaven National Laboratory (BNL) personnel. These calculations were based on methods employed by Georgia Institute of Technology.¹ As has been reported, these were considered preliminary until a more exact analysis had been completed.

A method employing a computer code has now been developed and bench marked to actual liner radiation surveys. A discussion of this method will now be forwarded to the NRC by December 18, 1980.

EPICOR LINER SAMPLING PROGRAM

One effort in progress that will significantly aid in more precisely defining the internal environment of an Epicor liner is the liner sampling program. Two recent meetings with NRC representatives have been held discussing the details of this program; therefore, the details are not provided herein. An updated summary is discussed:

A. TMI SAMPLING PROGRAM

The TMI Sampling Program is proceeding with a liquid and gas sample from prefilter expected to be taken the latter part of December, 1980. The prefilter and its storage location were inspected on November 21, 1980. A video tape of this inspection was made. This inspection found the liner in excellent condition with nothing unusual observed. A test of the liquid and gas sampling procedure is expected during the week of December 1, 1980, in the EPICOR II Chemical Cleaning Building. This test will verify the adequacy of the procedure. Some of the items which MetEd/GPU are hoping to gain from this task are:

- o Water Sample and Analysis
- o Gas Sample and Analysis
- o Liner Gas Pressure
- o Internal and External Radiation Profile
- o Thorough External Liner Inspection with Video Tape

Assuming no problems are experienced with prefilter 16, prefilter 3 will undergo the same sampling program at a later date. A contingency plan has been developed should a water sample not be withdrawn. This plan involves adding an organic material to the liner which would liberate resin water of hydration. In this manner, this liberated water can then be removed from the liner by the underdrain system. This method allows water sampling, with the added benefit of inerting a portion of the resin bed.

¹R. C, McFarland, "The Effect of Gamma Radiation on Ion Exchange Resins and Activated Charcoal", Appendices A & B to Section 3 of TMI-II-RR-6, TMI Unit 2 Recovery Quarterly Progress Report to NRC for the Period Ending March 31, 1980, Metropolitan Edison Company, Middletown, PA, pp. 3-18 to 3-40, 1980.

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B. DOE SAMPLING PROGRAM

The DOE Liner Sampling Program has just recently gained full endorsement from the DOE and MetEd/GPU. This program should have significant progress in the near future, especially since the TMI Program should provide helpful information related to liner handling and inspection methods. The DOE program is more inclusive than the TMI effort and will aid in characterizing the internal environment of a liner and assessing the integrity of the liner. Since NRC representatives have recently received a presentation on this effort, details are not provided herein. However, it is requested the NRC reply to MetEd/GPU letter, TLL 413, dated September 4, 1980, regarding a waiver for shipment of non-solidified Epicor liners. Timely receipt of a waiver will remove an element of uncertainty from this program that currently exists.

EPICOR II LINER CONTINGENCY PLAN

As discussed previously, a leak of a liner, even though it should occur, will have little consequence. Even so, should it be decided that preventive or corrective actions are warranted, MetEd/GPU has been considering what action might be taken should a problem exist. Two (2) alternative actions have been identified as follows:

A. CHEMICAL ADJUSTMENT

An investigation has been made into how the corrosiveness of resins might be adjusted by chemical means. This work has included contacting various resin experts as well as performing tests at TMI. GPU laboratory, and contractor facilities. This work involves adding an organic material to a resin bed. The resins chemically bind this material preferentially to the water of hydration, thereby liberating the water of hydration. In this manner, the medium within the liner which allows for the transfer of ions during corrosive reactions would be replaced with a material that would fail to act as a transferring medium. This action would make the bed essentially inert by retarding corrosive attack. Liberated water would be removed by dewatering methods. A major concern with this procedure is the possibility of releasing the bound radioisotopes. A test was performed on a resin column previously used for verification of the Epicor resin mixes for processing the 'B' Reactor Coolant Bleed Tank (RCBT). The column used for the test was scaled and loaded with resins similarly to a prefilter. 250 ml of 'B' RCBT water was passed through this column dewatered by draining. The organic material visibly dried the resins. The liberated water contained only very low concentrations of radioisotopes indicating the radioisotope to resin bond was not altered significantly.

The details of this option and exact material selection have not been made, however, this option offers significant advantages.

B. ADDITIONAL LINER BARRIER PROGRAM

A second contingency plan involves placing the carbon steel liner into a container made of more corrosion resistant material. This container will provide an additional protective barrier to liquid loss around the sides and bottom of the liner. An engineering package will be developed for this option.

John T. Collins

LINER STAGING MODULE

EPICOR liners have been stored since removal from service. Two (2) items of interest are discussed below:

A. MOVEMENT OF LINERS

Liners in the Interim Liner Staging Area have been moved to the A and/or B Liner Staging Module at the rate of two (2) per week. This rate has been constant over the past few weeks and should remain constant bearing adverse weather conditions. It is of note that some of the oldest EPICOR II liners have already been moved. For example, prefilters 1, 2, 3, 4, and 5 have been successfully moved. No irregularities or unusual conditions were noted or experienced during these evolutions.

B. STAGING MODULE SUMP WATER

The 'A' and 'B' Liner Staging Modules share a common sump. This sump collects liquids entering individual module cells or leakage directly into the sump. Design of the modules was intended to preclude rain water introduction, however, it has been observed the sump level increases slightly during rain. The sump water has been recently analyzed by both TMI and offsite laboratories. This analysis has shown the presence of Tritium at a concentration of 3×10^{-5} µc/ml and Cesium 137 at 2×10^{-8} µc/ml. For comparison, the NRC limits (10 CFR Part 20) for these isotopes in water discharge to restricted areas are, for Tritium, 3×10^{-3} µc/ml and Cesium, 2×10^{-5} µc/ml, many times higher than found in the sump. Four (4) possible scenarios have been identified which could explain how these isotopes entered the sump.

- One or more liners may well have been externally contaminated when in service. While in storage, changing humidity and temperature conditions could cause condensation resulting in the washing of this contamination to the sump.
- One or more liners may have been perforated releasing free standing water existing in the liner. This liquid would have been collected in the sump.
- 3. The heat generated by the deposited curies could cause a vaporization of the water of hydration of the resins. This vaporization could carry radioisotopes with it. Knowing the liners release gases at approximately 2 PSI these radio-isotopes could be released from the liner, then condensed in the storage cell. This condensation would be collected in the sump. (While liners do not leak with up to 18 psig water pressure, they have been found to leak air through the threaded connections at 2 psig).
- 4. As resins break down due to chemical and radiation interraction gases are liberated. Although the gases themselves may not necessarily be radioactive, they could carry radioisotopes with them. These radioisotopes could be released from the liner and collected in the sump, similarly to method 3.

The precise mechanism has not been identified nor has any credible method been excluded.

However, as the Interim Liner Staging Area is emptied, the storage cells are being studied with respect to contamination of the cells. To date, no contamination has been detected in the cells once containing resin liners.

There is not, at present, any reason to believe a liner is leaking. To the contrary, both the above-described and attached metallurgical evaluation and the studies of the Interim Liner Staging Area lead to the conclusion that the source of the comtamination in the sump is other than a perforated liner.

Action is in progress to minimize further the introduction of rain water into the sump. The sump will be pumped dry and any additional liquid introduction will be closely monitored.

It is premature to draw any conclusions concerning the low levels of contamination in the Staging Module Sump Water. MetEd/GPU recognizes the importance of identifying the source of this contamination at the earliest possible date. The NRC will be kept advised of our activities in this regard.

The above up-dates the NRC on current activities at TMI-2 related to EPICOR II liner integrity. We will continue to keep you informed.

Sincerely,

Vice-President and Director, TMI-2

GKH:RIN:dad

Enclosure

cc: Bernard J. Snyder

EVALUATION OF THE LINER INTEGRITY OF THE TMI UNIT 2 EPICOR II RADWASTE SYSTEMS

> F. S. Giacobbe K. H. Fredericks

Rev. 1, December 2, 1980

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The contents of this study are based upon available data at the time of issuance. Data which may have a direct bearing upon the conclusions is expected in the immediate future. This data will include, but not be limited to, the Epicor Proprietary Disclosures, data from liquid samples to be taken from selected prefilters and the results of various resin degradation studies which are currently in progress. The right to alter any portion is reserved.

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Introduction

The integrity of the Epicor II Spent Resin Liners as affected by various internal environments which are believed to exist at this time was evaluated. Effluent data was provided by TMI for the sixty-five liners which contained spent resin as of August, 1980. This data was reviewed by the GPUN System Laboratory Chemistry Section in order to provide a basis for determining the nature of the environment which would be present during storage. When additional liners are processed or when additional data regarding the internal environment is developed, this data will be evaluated and a revised report available issued. Analysis of the data currently/led to a classification of the internal environment into four categories. These categories grouped the various environments according to the corrosiveness to the ASTM: A36 carbon steel liner base material. A complete analysis of the environments are contained in Attachment I. The most aggressive environment (category 4) postulated is a dilute, air saturated, hydrochloric and boric acid solution with a pH of approximately 2.5 and very low solids/salt concentration. Based on the dewatering technique utilized (1), it has been demonstrated that a maximum of 1.5 gallons of this solution can be expected to be on the floor of the liners.

Although corrosion resistant coatings had been applied to the liner internals no nondestructive examinations were performed on the coatings after application. Subsequent examination of liner coatings onsite with a holiday detector found them to contain numerous defects, the analysis of the liner integrity, therefore, was carried out assuming that the 1.5 gallons of solution were in direct contact with a pinhole in the coating and that the carbon steel substrate is currently being acted upon by the internal environment. This case would produce the earliest liner penetration as opposed to a liner with no coating, with a large patch of coating removed or a defect free coating.

(1) TMI 2 Spent Resin Liner Dewatering Study, April 1980.

Introduction (continued)

Tests conducted onsite have also shown that the liners cannot be pressurized above 2 psig, thus eliminating concerns from overpressurizing the liners due to evolution of gases from the resins.

Another case which needs to be addressed but will not be discussed in this report is direct contact of the resin beads with the coating and/or the carbon steel when there is no free-standing water. This will be evaluated and will be reported on at a later date.

Conclusions

 Final effluent chemistry data for sixty-five liners have been reviewed and categorized in four groups representative of their inherent corrosiveness to the liners. These categories are:

- (1) Solutions with $pH \ge 5$ and conductivities < 50 umhos.
- (2) Solutions with pH > 5 and conductivities of 50-4000 umhos.
- (3) Solutions with pH 3.5-5.0 and conductivities < 70 umhos.
- (4) Solutions with pH 2.5-3.5 and conductivities of 100-700 umhos.

 Category (4) is the most aggressive solution. Four liners fall into this category as follows:

Liner Designation	Size	Metal Thickness
• PF-16	4" x 4"	1/2" - 5/8"
• PF-17	4' x 4'	1/2" - 5/8"
• PF-18	4' x 4'	1/2" - 5/8"
• PF-19	4' x 4'	1/2" - 5/8"

Under the current worst case conditions postulated, small pinhole penetration of liners could be predicted at the earliest in 15 months for a 1/2" liner and 19 months for a 5/8" liner. This, however, is conservative considering the steady-state corrosion rate assumed is the initial high rate which would be expected to decrease to some lower value with time.

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Conclusion (continued)

3. Category (3), although the solution is slightly higher in pH than category (4), it is still sufficiently low that a slight drop in pH will probably occur within pits producing corrosion rates similar to category (4). Liners in category (3) are as follows:

Liner Designation	Size	Hetal Thickness
• PF-40	4' x 4'	1/2" - 5/8"
• PF-41	4' x 4'	1/2" - 5/8"
• PF-42	4' x 4'	1/2" - 5/8"
• PF-43	4' x 4'	1/2" - 5/8"

These liners under worst case conditions could also be perforated in the 15-19 month period.

4. For purpose of this analysis "worst case" has been defined as a .01% hydrochloric acid solution at $75^{\circ} - 90^{\circ}$ F in direct contact with the carbon steel substrate via a pinhole defect in the coating. The solution is air saturated, however, no intrusion of air into the container is predicted, therefore, with time the oxygen concentration will decrease as it is consumed in the corrosion process. The corrosive attack is expected to proceed in a pitting mode.

5. Categories (1) and (2), which encompass fifty-seven liners, have pH values in excess of 5. These liners are expected to have a life in excess of 25 years not counting any contribution to life by the coating and assuming that resin degradation will not lower the pH. Attachment II describes the corrosion of these liners in more detail.

6. For those liners where solutions are in contact only with the coating and no defects are assumed, life expectancy for the coating would be conservatively on the order of ten years. This being the typical life of a coating in contact with demineralized water with no coating maintenance.

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Conclusion (continued)

7. Long term resin degradation is expected to release borate anions plus amines which are predicted to establish a buffering action and possibly raise the pH of the solution. In this event the environment will become less aggressive to the carbon steel substrate (see Attachment I).

Discussion

The corrosion of the carbon steel substrate for the types of environments defined will be most significantly affected by the hydrogen ion concentration (pH) and oxygen concentration of the solution. The oxygen concentration for the internal environments defined, however, will be the overriding factor influencing both short term and long term corrosion rates. As the concentration of oxygen within the sealed liner is depleted the corrosion rate will be decreased accordingly. This factor will be most significant for liners in categories (1) and (2) where the corrosion rate is sufficiently slow that aggressive pitting is not anticipated but rather localized corrosion may occur initially with a gradual spreading out of the corrosion with time.

For category (4) liners, maximum corrosion rates for dilute aerated hydrochloric acid solutions would be on the order of 400 mils per year (mpy) as discussed in 'Corrosion and Corrosion Control', 2nd Ed. Knowing that the thickness at the bottom of the 4 X 4 liners is 500 mils (min), pinhole perforation could occur in as soon as 15 months assuming no competition for oxygen from other locations within the liner which could decrease the available oxygen thus slowing the corrosion rate and that the environment is able to maintain the initial high corrosion rate. Maintaining this high corrosion rate for long periods is unlikely but until the steady state rate can be adequately defined it is the most conservative approach.

In regard to category (3) liners, although the environment is somewhat less aggressive if one considers pitting as the primary mode of corrosion then

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Discussion (continued)

at pH 3.5, it would be necessary to assign a corrosion rate similar to that for category (4).

Liners in categories (1) and (2) with their assumed environments $(pH \ge 5)$ would be expected to experience corrosion rates on the order of 10 mpy. In this pH range, however, the formation of ferrous hydroxide is expected and this will both slow th diffusion of oxygen and act to produce an alkaline environment at the corroding surface. These factors will minimize both the pitting rate and general corrosion.

The potential for stress corrosion cracking to occur as well as hydrogen embrittlement were also considered. These corrosion mechanisms, however, were dismissed at this time as the current environmental, material and stress parameters did not indicate those mechanisms would occur. As additional data is available to further define the internal conditions, these mechanisms will be reconsidered as necessary.

In discussions with the coating manufacturers, it was learned that neither coating utilized is recommended for low pH environments; however, this recommendation, in general, is based on concentrated acid solutions and not dilute solutions. The fact is that few laboratory tests were conducted by the coating manufacturers in dilute acids and no test data exists for a 1% or less HCl solution. Tests in 1.5% oxalic acid at room temperature, however, showed no degradation in eight months on the Plasite 7155. Phenoline 368 tested in 1% citric acid at 130°F and 150°F showed both acceptable and unacceptable results in different tests. It is the opinion of the coating vendors, however, that the dilute acid at ambient temperature will not be significantly more agressive than demineralized water in terms of its effect on the coating but rather its effect on the carbon steel substrate due to exposure through coating defects or long term permeation will be critical. Initial results from on-going GPU Laboratory

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Discussion (continued)

tests on the effects of the proposed worst case environment on the liner coatings has shown no coating degradation in two months. It is our assessment that the coatings will be unaffected in the near term by the aqueous environment and can be expected to have a lifetime similar to that of coatings exposed to demineralized water (approx. 10 years). This assessment, however, may be altered based on the results of tests of resin beads in direct contact with the coating in a non-aqueous environment. Although initially the coating most likely will contribute to the overall liner integrity, in the long term its effectiveness in preventing corrosion will be nil.

Recommendations

1. Liners in categories (3) and (4) will require near term remedies to preclude leakage to the environment. Discussion should be commenced to identify a satisfactory method for restoring long term integrity. Potential solutions would include methods to modify the internal environment chemically by raising pH or scavenging oxygen.

2. Efforts should be made to sample the liquid remaining in liners in categories (3) and (4) initially followed by categories (1) and (2) to confirm or disprove the current hypothetical environments. This data would afford a more definitive analysis. If possible, gas samples should also be taken to determine if hydrogen is being produced or other gases which might indicate degradation of the resin beads.

3. Contingency plans need to be developed in the event leakage can result from corrosion to the liner. This might be best accomplished by designing a corrosion resistant container into which the current liners can be placed.

4. After the effluent sample has been analyzed as recommended in item 2, Electrochemical corrosion tests should be conducted to determine the actual corrosion rates which can be expected from the actual liner environment.

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Recommendations (continued)

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5. Once the resins have been identified which exist inside the liners, laboratory tests should be conducted exposing carbon steel coupons to resins of the same type and condition under the influence of a radiation source producing a dose rate equivalent to that inside the liners. The coupons should include stressed samples as well as welded samples.

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ATTACHMENT I

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Evaluation of Internal Environment

Epicor Liners for Storage of

Spent Resins

K. H. Frederick Rev. 1, December 2, 1980

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Two basic sets of conditions must be considered in order to make a complete evaluation of environmental conditions within the resin-liners which are employed for treatment of radioactive wastes at Three Mile Island. The first consideration is the chemistry of the free-standing liquids and gasses which remain in the cask when it is placed in storage. The second consideration is the changes which materials within the liner will undergo. These changes will consist largely of resin decomposition from normal aging or from radiation effects. Both of these processes represent long-range concerns.

Chemistry data from more than sixty liners has been evaluated and the results have been employed to characterize the conditions inside sto-ed liners. Experimental data indicates that following routine dewatering, a maximum of 1.5 gallons of liquid remain in the bottom of a liner. For purposes of evaluation, it is conservatively assumed that this liquid will have the same chemical composition as the last process liquid which was measured at the effluent of the liner during service.

Tables One, Two and Three contain tabulations of the final effluent data for the Epicor II liners used in the evaluations. Initial examination of the data suggests four general categories which are as follows.

 Liners in this category are characterized by low conductivity effluent and pH values in the range of 5 or greater. Conductivity values are generally less than 50 umho and range down to less than 1 umho. This range of pH and conductivity values suggests a solution of boric acid in demineralized water with minute quantities of neutral salts. Conductivity values toward the higher side of this range suggest the presence of slightly greater quantities of dissolved salts.

- 2. These liners contain primarily mixtures of salts. The pH value ranges from approx. 5 to 8 with the majority in the range of 7. Conductivities range from 50 to 4000 umho with the majority falling between 200 and 2000 umho.
- 3. Liners in this category contain very dilute mixtures of neutral salts and strong acids. pH values range from 3.5 to 5.0 and conductivities are less than 70 umho.
- 4. This category also contains liners with mixtures of neutral salts and strong acids but is somewhat less dilute than those described in Category 3. pH values range from 2.5 - 3.5 and conductivities from 100 - 700 umho.

For purposes of evaluating actual concentrations of the various constituents of solutions, the predominant salt was assumed to be sodium chloride and the strong acid hydrochloric acid. Where the pH values were lower than could be attributed to boric acid concentrations corresponding to measured boron concentrations, hydrochloric acid was assumed to be present and a concentration was calculated from the pH values. A conduc-

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tivity value was assigned to the calculated acid concentration and the difference between this calculated conductivity and the measured conductivity was assumed to result from contribution by sodium chloride. When pH values were neutral, sodium chloride was assumed to be the sole contributor to conductivity. Equivalent conductances are from "CRC Handbook of Chemistry and Physics, 50th ed." and values from the 0.02 gram equivalents/ 1000 cubic cm column were used. Following is a listing of the conditions which were assumed in making the analysis of each category:

		Categor	y	
Parameter	1	2	3	4
рH	5.0	7.C	3.5	2.5
Conductivity, umho	50	2000	70	700
Boron, as ppm B	750	1500	950	1400
Sodium, ppm	1.0	200	1.0	2.0

Accordingly, the conditions in liners from each category should approximate the following:

		Category	and the second sec	
Parameter	_1	2	3	4
Boric Acid, w%	0.45	0.85	0.55	0.8
Hydrochloric Acid, w%	NP(1)	NP(1)	0.001	0.01
Sodium Chloride, w%	0.002	0.1	NP ⁽¹⁾	NP ⁽¹⁾
(1) Not present				

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Since there is evidence of strong acid presence in categories 3 and 4, a calculation was made to determine the mass of iron which could be displaced by the 1.5 gal. max. of the solution assumed to be present (from the GPU dewatering report) at the bottom of the liner. This quantity of iron would amount to approx. 0.1 g for liners in Category 3 and approx. 1 g for liners in Category 4, after which the acid would be spent.

A second consideration is the effect of oxygen remaining in the liner after it is sealed. Oxygen contained in free space at the top of the liner, that present in void spaces between dewatered resin beads and dissolved oxygen present in the water of hydration were considered. A free space of 18 inches at the top of each liner and a void volume of 40% were assumed. A dissolved oxygen content of 8 ppm was assumed for the water of hydration and water of hydration volumes of 125 and 450 gal. were assumed for the 4 x 4 and 6 x 6 liners. These assumptions would yield approximately 270 g (0.6 lb) of total oxygen in a 4 x 4 liner after closure and 800 g (1.86 lb) in a 6 x 6.

The oxygen present within liners would ultimately be expected to react with either materials within the liner or with exposed portions of the metal liner itself. The conservative assumption would be that all of the oxygen reacts with the liner. Although a series of intermediate reactions would be expected to take place, the final products should be iron oxides. Initially, Fe_20_3 should be the predominant species. As the oxygen in the liner is depleted, formation of Fe_30_4 would be favored. In actuality,

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Initial decrosslinkage of the cation resins would probably not result in any pH changes, since the functional groups would remain unaffected. More severe degradation would destroy the functional groups releasing sulfur compounds and the associated cation. Since sodium is the major cationic constituent, neutral compounds such as sodium sulfate would result with no depression of pH values.

Since it appears that radiation results in similar decomposition products to those produced by chemical agents, it is not anticipated that the environmental changes to the liner interiors would be significantly different than those which would result from normal resin decomposition due to aging. Radiation decomposition is believed to result from the effects of peroxides which are produced by irradiation of water associated with the resin and, perhaps, to a lesser extent from direct cleavage of molecule bonds by the radiation. According to Cohen ⁽¹⁾, the formation of peroxides occurs when reducing and oxidizing radicals are spatially separated and exist at high concentrations. This condition would exist only in the presence of very high beta-gamma exposure rates, neutron exposures or as the result of other reactions such as n, alpha which possess very high linear energy transfer values. At lower densities of energy absorption, the recombination reaction will be favored and peroxide levels should be minimal. This condition is expected to exist within the stored liners.

(1) Cohen, Paul, "Water Coolant Technology of Power Reactors", Gordon and Breach Science Publisher, New York, 1969.

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some combination of the two oxides would be expected.

Assuming no reaction with anion resin which is stored in a liner the oxygen could be expected to react with the quantities of iron described in the table below.

Liner	0 ₂ g(1b)	Fe,g(1b) (Fe ₂ 0 ₃ formation)	Fe,g(1b)(Fe ₃ 04 formation)
4 x 4	270(0.6)	628(1.38)	706(1.56)
6 x 6	800(1.76)	1788(3.94)	2093(4.61)

Competition from anion resin would be expected to reduce these quantities significantly, especially if the epoxy coating of the liner did not have an initial defect.

Long-term resin degradation will contribute to changes in the internal environment of the liners. Normal decomposition and radiation induced decomposition are potential contributors. It is assumed that both will result in similar products of decomposition. The anion resin appears most vulnerable with the breakdown mechanism being loss of functionality. The cation resin is significantly more resistant and is likely to suffer loss of cross linkage as its primary decomposition mechanism.

Loss of anion functionality would result in the release of the associated anion and various amines such as trimethylamine. Since the predominant anions are borates, which are buffers, and the amines are alkaline in nature, such decomposition would benefit the liner environment by buffering strong acids and/or raising the pH.

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TABLE ONE

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PREFILTER SUMMARY

ID	Final pH	Final Cond, umho	Final Na, ppm	B, ppm	- Category
PF-1	5.15	3.22	<1	672	· 1
PF-2	6.44	14.5	12	728 🖻	1
PF-3	7.33	202	19	1160	2
PF-4	8.0	942	10	822	2
PF-5	8.27	3980	<1	656	2
PF-6	7.57	1220	150	517	2
PF-7	7.09	365	3	1984	2
PF-8	7.36	235	24	1109	2
PF-9	7.58	342	27	1298	2
PF-10	7.92	24.6	1.8	76	1
PF-11	8.05	0.45	<1	<10	1
PF-12	7.87	1100	104	1568	2
PF-13	7.7	1220	180	1807	2
PF-14	8.08	1900	420	1460	2
PF-15	7.75	1300	115	1552	2
PF-16	2.79	700	<1	1392	4
PF-17	3.52	140	<1	1320	4
PF-18	3.39	180	6.6	1298	4
PF-19	3.13	300	<1	1353	4
PF-20	4.89	7.2	2	259	1
- PF-21	6.3	84.5	4.3	801	2
PF-22	5.28	3.15	<1	498	1
PF-23	7.56	2100	180	2770	2
PF-24	4.95	7.76	<1	801	1
PF-25	5.07	10.86	<1	686	1

Final pH	Final Cond, umho	Final Na, ppm	B, ppm	Category
4.96	13.1	1.23	757	1
4.82	6.31	<1	779	1
7.19	440	35	1514	. 2
5.55	18	. 4	757	1
5.0	6.68	<1	763	1
5.12	4.6	<1	965	. 1
5.19	4.12	<1	963	1
5.66	1.86	<1	595	1
4.70	9.25	<1	920	1
5.34	3.40	<1	693	1
5.43	3.15	1.5	985	1
5.08	4.6	2.1	963	1
5.13	4.0	<1	1039	1
5.53	8.5	<1	909	1
4.0	41.5	<1	930	3
3.8	55	<1	985	3
4.7	9.65	<1	952	3
3.67	69.0	<1	1017	3
7.6	370	100	433	2
6.89	230	88	757	2
6.05	140	38	822	2
	Final PH 4.96 4.82 7.19 5.55 5.0 5.12 5.19 5.66 4.70 5.34 5.08 5.13 5.08 5.13 5.66 4.70 5.43 5.08 5.13 5.08 5.13 5.66 4.70 5.66 4.70 5.66 6.05	Final PH Final Cond, umbo 4.96 13.1 4.82 6.31 7.19 440 5.55 18 5.0 6.68 5.12 4.6 5.19 4.12 5.66 1.86 4.70 9.25 5.34 3.40 5.43 3.15 5.08 4.6 5.13 4.0 5.53 8.5 4.0 41.3 3.8 55 4.7 9.65 3.67 69.0 7.6 370 6.89 230 6.05 140	Final PHFinal Cond, umboNa, ppm 4.96 13.1 1.23 4.82 6.31 <1 7.19 440 35 5.55 18 4 5.0 6.68 <1 5.12 4.6 <1 5.12 4.6 <1 5.12 4.6 <1 5.66 1.86 <1 4.70 9.25 <1 5.34 3.40 <1 5.43 3.15 1.5 5.08 4.6 2.1 5.53 8.5 <1 4.0 41.5 <1 3.8 55 <1 4.7 9.65 <1 3.67 69.0 <1 7.6 370 100 6.89 230 88 6.05 140 38	Final pHCond, umboNa, ppmB, ppm4.9613.11.237574.826.31 < 1 7797.194403515145.551847575.06.68 < 1 7635.124.6 < 1 9655.194.12 < 1 9635.661.86 < 1 5954.709.25 < 1 9205.343.40 < 1 6935.134.0 < 1 6935.538.5 < 1 9635.134.0 < 1 10395.538.5 < 1 9303.855 < 1 9303.855 < 1 9354.79.65 < 1 10177.63701004336.89230887576.0514038822

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TABLE TWO

DEMINERALIZER #1 (DF) SUMMARY

<u>ID</u>	Final pH	Final Cond, umho	Final <u>Na, ppm</u>	<u>B, ppm</u>	Category
DF-1	5.27	2.25	<1	600	1
DF-2	5.87	1.74	1.9	486	1
DF-3	5.56	55.7	<1	577	2
DF-4	8.62	58	9.8	75	2
DF-5	7.11	77	6.0	901	2
DF-6	6.37	0.7	<1	22	1
DF-7	7.21	0.405	<1	< 10	1
DF-8	7.56	935	120	2066	2
DF-9	7.66	1025	110	1926	2
DF-10	5.56	4.62	<1	1428	1
DF-11	6.93	730	75	3354	2
DF-12	5.24	3.15	<1	995	1
DF-13	5.53	3.0	<1	995	1

TABLE THREE

DEMINERALIZER #2 (DS) SUMMARY

<u>. ID</u>	Final PH	Final Cond, umho	Final Na, ppm	B, ppm	Category
DS-1	5.68	1.82	<1	420	1
DS-2	5.18	2.91	<1	893	1
DS-3	6.21	0.53	<1	15.1	1
DS-4	6.92	0.56	<1	11	1
DS-5	5.28	3.95	<1	1385	1
DS-6	5.34	3.10	< 1	736	1

ATTACHMENT II

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ATTACHMENT II

Corrosion of Carbon Steel Liners in Categories (1) and (2)

The effect of pH on the corrosion rate of carbon steel in aerated demineralized water is significant, as can be seen in Figure 1. It is readily apparent that between pH 4 to 10 where the pH is normally expected to be inside the liners, that the corrosion rate is relatively uniform and on the order of 10 mils per year.

For the purpose of defining the theoretical maximum amount of iron which can be corroded by a puddle of water on the tank floor under the above conditions the following assumptions were made:

1. The amount of oxygen which exists inside the liner is equal to 20% of the volume of air which would be present inside the liner assuming the resin already occupies 40% of the volume and that no in-leakage of air will occur once the liner is sealed.

 For solutions in categories (1) and (2) the total amount of corrosion will be dependent only on the amount of oxygen available.

Stoichiometric calculations indicate approximately 4.6 pounds of iron can be converted to Fe₃O₄ in a 6 X 6 liner at the time oxygen is depleted. With iron having a density of .28 lbs/cu. in. approximately 15 cubic inches of metal could be dissolved. This dissolution can occur over a variety of areas and will depend on the size of the corrosion initiation site and the progression of the corrosion laterally under the coating increasing the area of attack. Other factors affecting the corrosion rate would be the gradual depletion of oxygen in the system and the build up of corrosion products slowing the diffusion of oxygen to the corroding surface. Both these phenomena will tend to slow the corrosion reaction below the estimated 10 mpy.

Based on this assessment, perforation of the liners in categories (1) and (2) could occur in approximately 25 years. This is unlikely, however, as the corrosion rates will be decreasing with time as oxygen depletes. Also as Corrosion of Carbon Steel Liners in Categories (1) and (2) (continued) the corrosion spreads out to larger areas, there will not be sufficient oxygen to produce complete penetration. In addition, this analysis assumes no adverse changes in the environment with time. The liner bottom, however, may have been weakened in the corroded area depending on how long the solution has been in contact with the steel and precautions may have to be taken to prevent accidental perforation if the liner were ever lifted. However, at a 10 mil per year corrosion rate this is not a near term concern.

REFERENCES

1. W. C. Whitman and R. P. Bussel. The Acid Correction of Metals Industrial

2.	M. G. Fontana and N. D. Green. Corrosion Engineering, 2nd Ed., McGraw Hill
3.	H. H. Uhlig. Corrosion Handbook, John Wiley & Sons
4.	H. H. Uhlig. Corrosion and Corrosion Control, John Wiley & Sons
5.	G. W. Whitman, R. P. Russell and V. J. Altien. Effect of Hydrogen Ion
	Concentration in the Submerged Corrosion of Steel. Industrial and Engineerin

6. F. N. Speller. Corrosion, Causes and Prevention, McGraw Hill

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Fig. 1 Effect of pH on corresion of iron in derated soft water, room temperature (Whitman, Russell, and Altieri).