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

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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.

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 issued. Analysis of the data currently available 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.

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(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

1. 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 $\geq$ 5 and conductivities < 50 umhos.

(2) Solutions with pH $\geq$ 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.

2. 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.

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	Metal 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° - 90° 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.

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

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 ($pH \geq 5$) 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

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.

Recommendations (continued)

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.

ATTACHMENT 1

Evaluation of Internal Environment
Epicor Liners for Storage of
Spent Resins

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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 stored 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:

1. 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 conductivity 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:

	Category			
Parameter	1	2	3	4
pH	5.0	7.0	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			
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

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_2O_3 should be the predominant species. As the oxygen in the liner is depleted, formation of Fe_3O_4 would be favored. In actuality, 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.

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	O_2 g(lb)	Fe,g(lb)(Fe_2O_3 formation)	Fe,g(lb)(Fe_3O_4 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.

TABLE ONE

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

ID	Final pH	Final Cond, umho	Final Na, ppm	B, ppm	Category
PF-26	4.96	13.1	1.23	757	1
PF-27	4.82	6.31	<1	779	1
PF-28	7.19	440	35	1514	2
PF-29	5.55	18	4	757	1
PF-30	5.0	6.68	<1	763	1
PF-31	5.12	4.6	<1	965	1
PF-32	5.19	4.12	<1	963	1
PF-33	5.66	1.86	<1	595	1
PF-34	4.70	9.25	<1	920	1
PF-35	5.34	3.40	<1	693	1
PF-36	5.43	3.15	1.5	985	1
PF-37	5.08	4.6	2.1	963	1
PF-38	5.13	4.0	<1	1039	1
PF-39	5.53	8.5	<1	909	1
PF-40	4.0	41.5	<1	930	3
PF-41	3.8	55	<1	985	3
PF-42	4.7	9.65	<1	952	3
PF-43	3.67	69.0	<1	1017	3
PF-44	7.6	370	100	433	2
PF-45	6.89	230	88	757	2
PF-46	6.05	140	38	822	2

TABLE TWO

DEMINERALIZER #1 (DF) SUMMARY

ID	Final pH	Final Cond, umho	Final Na, ppm	B, ppm	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

ID	Final pH	Final Cond, umho	Final Na, ppm	B, ppm	Category
DS-1	5.58	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

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.

2. 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 Fe_3O_4 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.

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POOR ORIGINAL

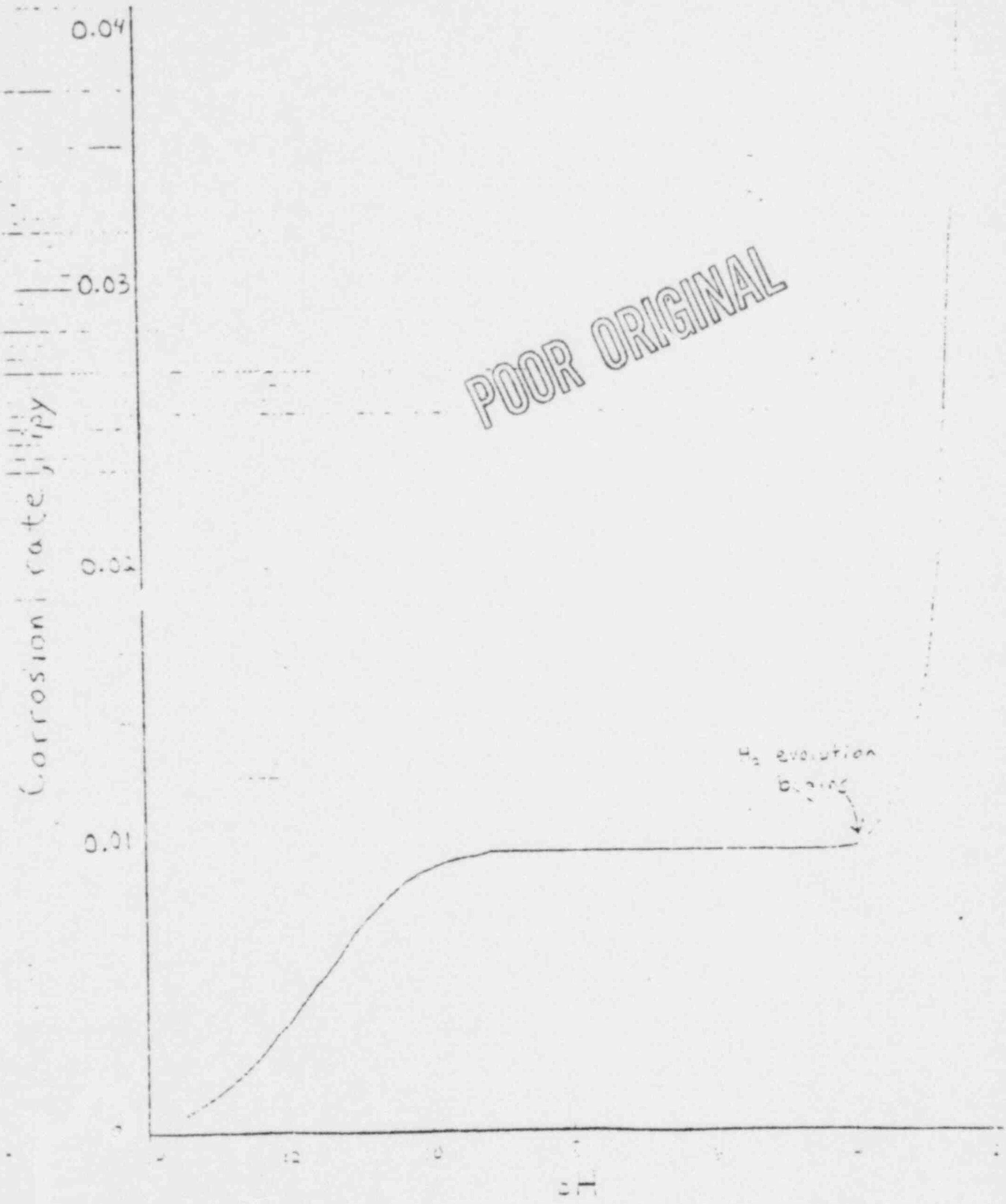

Fig. 1 Effect of pH on corrosion of iron in aerated soft water, room temperature (Whitman, Russell, and Altieri).