METALLOGRAPHIC EXAMINATION OF EPICOR-II LINERS FROM THREE MILE ISLAND[a]

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ABSTRACT

Materials from selected EPICOR-II prefilter liners were collected and examined as part of the EPICOR and Waste Research and Disposition Program sponsored by the Department of Energy at the Idaho National Engineering Laboratory (INEL). The intent of that examination was to define the internal condition of liners and ensure that liners could be stored at INEL for ten years. This paper discusses the liner-integrity examination and presents the results of these examinations.

Metallurgical examination of sections removed from the liners revealed no evidence of pitting or pitting-type corrosion. Measurements of wall thickness indicate that material was missing from the wall of PF-3 in an area where the protective coating had been removed to form a conductivity patch. If it is assumed that all thinning of the wall in that area is caused by corrosion, the liners will have a lifetime of approximately 50 years.

INTRODUCTION

The accident at TMI-2 on March 28, 1979 released approximately 600,000 gallons of contaminated water to the Auxiliary and Fuel Handling Buildings. That water was decontaminated using a demineralization system called EPICOR-II developed by Epicor, Inc. The contaminated water was cycled through three stages of organic and inorganic ion-exchange media. The first stage of the system was designated the prefilter, and the second and third stages were classified as demineralizers. After the filtration process, the ion-exchange media in a number of prefilters contained radionuclides in concentrations greater than those established for disposal of similar materials as low-level wastes. Fifty prefilters having high concentrations of radionuclides were transported to the Idaho National Engineering Laboratory (INEL) for interim storage prior to final disposal at the commercial disposal facility in the State of Washington.

During the interim storage period, research has been conducted on materials from those EPICOR-II prefilters as part of the EPICOR-II Research and Disposition Program[1,2] funded by the U.S. Department of Energy (DOE). Studies are presently being conducted on organic ion-exchange resin from selected EPICOR-II prefilters as part of the U.S. Nuclear Regulatory Commission's (NRC's) Low-Level Waste Data Base Development--EPICOR-II Resin Liner Investigation Project. That research is described in detail in Ref. 3. Two liners were examined to determine their integrity and determine if prefilters containing radionuclides can be stored for up to ten years at INEL without failure.[4] [Failure of a liner could result in spread of radioactive waste within the storage system.]

This report discusses the liner-integrity examination and presents results of metallographic examination of two liners. Because the construction and coating of EPICOR-II liners are typical of commercial nuclear storage and disposal systems, results of this study might be useful for other applications in the industry.

Liners PF-3 and -16 were characterized by Battelle Columbus Laboratories (BCL)[5,6] and also selected for metallographic examination to define their internal conditions. It is estimated that radiation doses to the walls and interior coatings of the liners at the time of metallographic sectioning approached 10^8 rad. That BCL work was a detailed study of the condition of the ion-exchange media contained within each liner, measurement of radiation dose rates outside and inside the prefilters, and a visual examination of both external and exposed internal metal surfaces of the liners.

MATERIALS AND METHODS

EPICOR-II liners are cylinders that are 49-in. in diameter by 54-ft in height. Their walls and tops are 1/4-in. thick and bottoms are 1/2 to 5/8-in. thick (Fig. 1). The liners are of welded construction using ASTM Type A-36 carbon steel. The internal and external surfaces are painted with Phenoline[b] 368 coating. A localized area of coating about 8 x 2 in. was removed from the interior surface of each liner. That bare area was used as the grounding point for a conductivity probe for measuring water level in the liner. Each liner contains about 30 ft^3 of ion-exchange media. Liner PF-16 contained both organic ion-exchange resin and inorganic zeolite. Liner PF-3 contained only organic resin. A perforated four-branch influent manifold distributed contaminated water over the exchanger bed, while the effluent was drawn off the liner bottom through a porous multibranched return manifold. Both manifolds are piped to a manifold plate on top of the liner. A vent port and adapters for liquid-level detectors also are located on the manifold plate. A manway is located beside the manifold plate on the liner top. Exchange media were loaded into the liner through

a. Work supported by the U.S. Department of Energy, Assistant Secretary for Nuclear Energy, Office of Coordination and Special Projects, under DOE Contract No. DE-AC07-76ID01570.

b. Trade name of the Carboline Company.

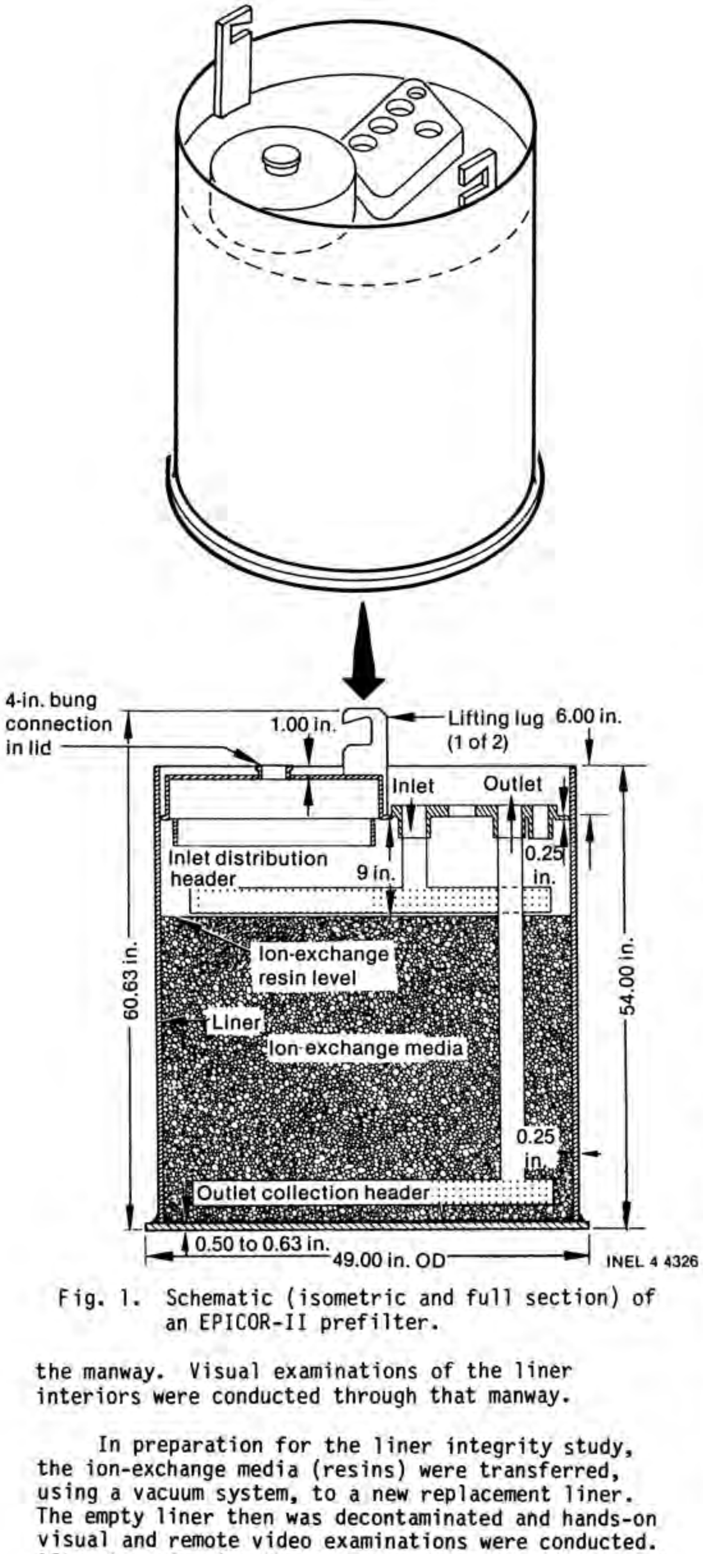

Fig. 1. Schematic (isometric and full section) of an EPICOR-II prefilter.

Fig. 2. Interior of liner PF-3 showing a dark area covered with rust and resin. The bottom of the liner contains residual resin. Streaks of rust from the manway area and numerous small coating blemishes are visible.

the manway. Visual examinations of the liner interiors were conducted through that manway.

In preparation for the liner integrity study, the ion-exchange media (resins) were transferred, using a vacuum system, to a new replacement liner. The empty liner then was decontaminated and hands-on visual and remote video examinations were conducted. After transferring the resins and removing the outlet headers, exterior and interior surfaces of the liners were examined visually and photographed (Fig. 2). Locations for metallurgical sectioning were marked on the exterior surfaces of the liners. Visual examination of the liners revealed that the exterior and interior base metal surfaces appeared sound as was previously reported by BCL in Ref. 5 and 6. It also was noted that the interior coatings were blistered, loose, and in some locations had spalled or chipped. There appeared to be more coating failures in liner PF-16 than -3 (see Fig. 2). The interior surface of liner PF-3 was coated with a thin, rust-colored film. Both liners had bands of rust on the interior walls at the level corresponding to the top surface of the resin. Detailed descriptions of visual examinations of liners PF-3 and -16 are given in Ref. 4, 5, and 6.

Locations selected for removal of metallurgical sections were marked on the exterior surface of the liner. Photographs were taken of the interior and exterior surfaces of the liner prior to sectioning. The marked locations coincided with specific areas of interest, such as the top surface of the exchange media, corroded areas on the sidewall, and the bottom to sidewall weld joint of the liner. Metallurgical sections were cut from the liner using hand-held power saws. The sections were washed in demineralized water and dried by gently wiping all surfaces, thereby preserving corrosion products. Surface radiation measurements were made to determine the radiation dose rate from each section. Those sections having radiation readings below 1 R/h β-γ at contact were transported to the metallography laboratory of the INEL Auxiliary Reactor Area (ARA), where specimens were prepared for detailed examination inside a ventilated hood. Those sections having radiation measurements above 1 R/h β-γ at contact were sent to the Hot Cells of INEL Test Reactor Area (TRA), where specimens were prepared for detailed remote examination inside a shielded hot cell.

Locations of metallographic sections (shown in Figs. 3 and 4 for liners PF-3 and -16, respectively) were selected from areas that exhibited discontinuities in the internal surface coatings. Three sections were cut from PF-3, and four sections were removed from PF-16. One section from liner PF-3 was removed from the bare area. Sections were obtained from the cylindrical walls of the liners using a 3-in. diameter metal-cutting hole saw. A section was removed from liner PF-16 at the junction of the cylindrical wall and bottom of the liner, using a portable reciprocating saw. Sections 2 and 3 from PF-3 and Section 2 from PF-16 were removed from the area corresponding to the top surface of the resin bed.

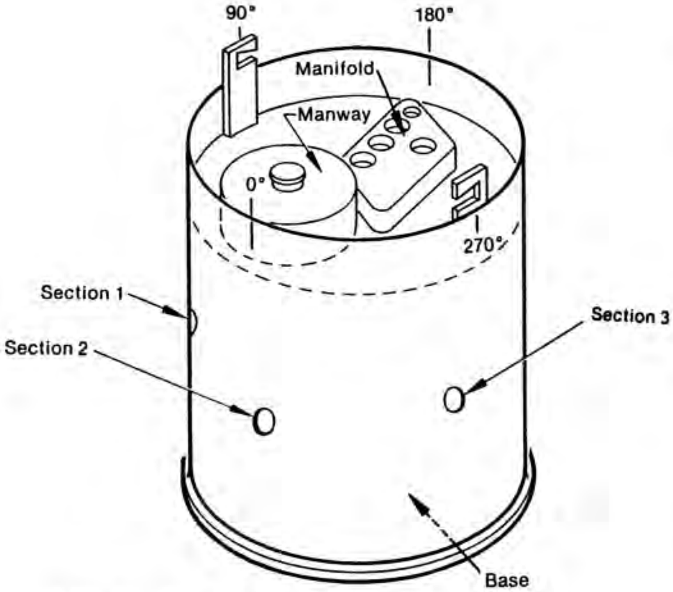

Fig. 3. View of liner PF-3 showing locations where metal sections were removed.

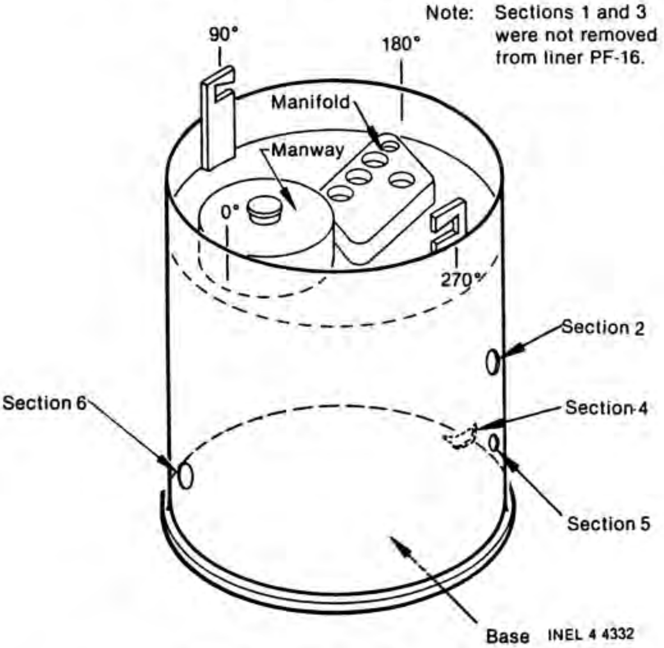

Fig. 4. View of liner PF-16 showing locations where metal sections were removed.

Liner PF-3

Section 1. Section 1 was removed from the center of the bare grounding area for the conductivity probe, about 30 in. from the bottom of liner PF-3, 45° clockwise from the manway (see Fig. 3). The internal coating had been removed mechanically from that area of the liner.[7] After decontamination by rinsing with mineralized water, contact readings of 35 R/h β-γ were measured. Visual examination of the interior surface of the section revealed a heavy deposit of corrosion products and residual resin (Fig. 5). The high radiation readings required remote examination of this section in the TRA Hot Cells.

Section 1, Specimen 1-B--Fig. 6 is a typical photomicrograph normal to the uniformly corroded interior surface observed for Specimen 1-B. No evidence of pitting or pitting-type corrosion was evident. No interior coating was evident on the specimen, but the exterior coating was determined to be about 0.010-in. thick. The corrosion products partially spalled off during remote preparation of the specimen; therefore, accurate thickness measurements of corrosion products could not be made.

Fig. 5. Photograph of the interior surface of Section 1 from liner PF-3 showing a heavy deposit of corrosion products and residual resin.

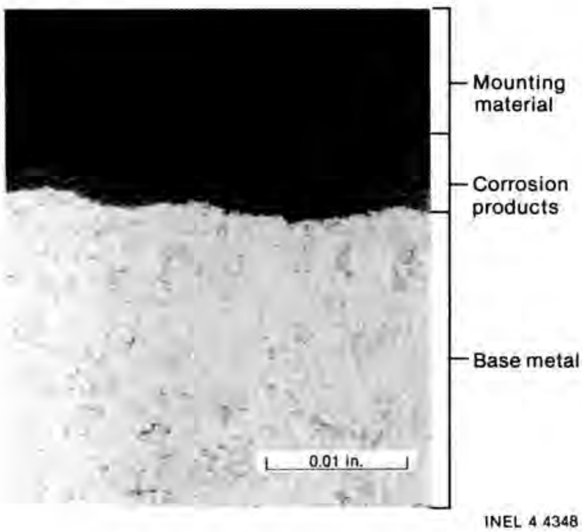

Fig. 6. Photomicrograph normal to the interior surface of Section 1 from liner PF-3 showing the uniformly corroded surface.

Section 3. Section 3 was removed from the sidewall of liner PF-3, 90° counterclockwise from the manway, about 30-in. above the bottom of the liner (see Fig. 3). That elevation corresponded to the top surface of the resin. Visual examination of the interior surface of Section 3 revealed numerous coating blisters and areas where coating was not adhering to the base metal and had spalled (Fig. 7). Light corrosion products under an adherent coating and heavily corroded areas under blisters were observed (Fig. 8). The adherent coating is about 0.005-in. thick.

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Fig. 7. Photograph of the interior surface of Section 3 from liner PF-3 showing coating blisters and areas where coating is missing.

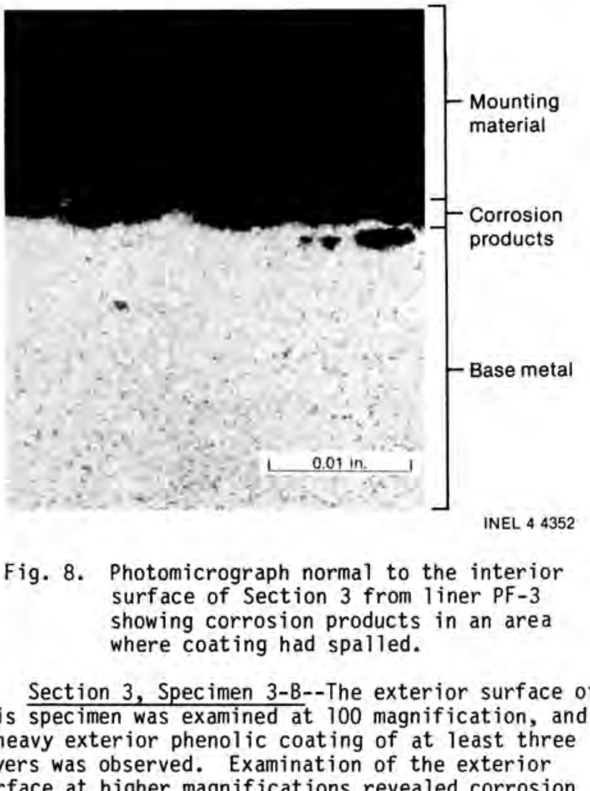

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Fig. 8. Photomicrograph normal to the interior surface of Section 3 from liner PF-3 showing corrosion products in an area where coating had spalled.

Section 3, Specimen 3-B--The exterior surface of this specimen was examined at 100 magnification, and a heavy exterior phenolic coating of at least three layers was observed. Examination of the exterior surface at higher magnifications revealed corrosion products (about 0.0005-in. thick) between the coating and base metal, with a total coating thickness of about 0.010-in. Evidence that the coating had been applied over previously present corrosion products is indicated by layers of coating between the base metal and corrosion products (Fig. 9).

Visual examination of interior surfaces of specimens prepared from Section 1 revealed a horizontal groove-like indentation on the surface of the grounding area for the conductivity probe. The indentation on Specimen 1-B can be seen in Fig. 10. The difference between the thickness of the base metal in the corroded and uncorroded areas can be attributed to (a) corrosion, and (b) removal of some base metal

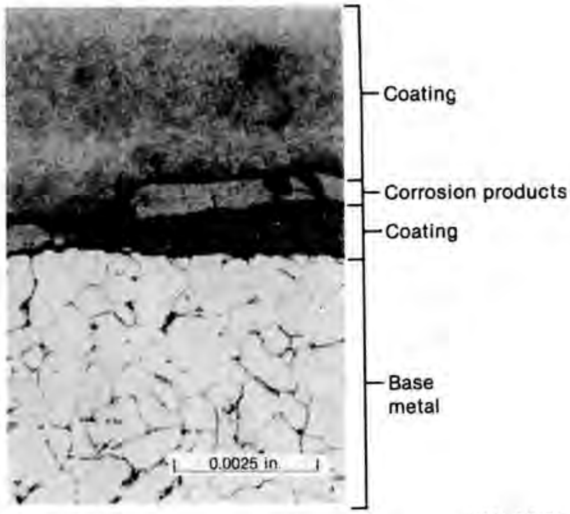

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Fig. 9. Photomicrograph normal to the exterior surface of Section 3 of liner PF-3 showing coating between the base metal and corrosion products.

while mechanically removing the coating for the conductivity probe.

Liner PF-16

Section 2. Section 2 was removed from the sidewall of liner PF-16, about 110° counterclockwise from the manway, about 30 inches above the bottom, at the level of the top of the resin (see Fig. 4). Visual examination of the interior surface of Section 2 revealed a nearly defect free surface with one large blister in the coating along one edge of the Section (Fig. 11).

Section 2, Specimen 1--Examination of Specimen 1 revealed some corrosion products (about 0.001 to 0.002-in. thick) between the coating and base metal (Fig. 12). Total coating thickness was measured at about 0.012 inch. The coating generally adheres to the corrosion products, indicating that corrosion occurred before painting of the liner.

Section 4. Section 4 was removed from the junction of the sidewall and bottom of liner PF-16, about 150° counterclockwise from the manway (see Fig. 4). Visual examination of the interior surface of Section 4 revealed numerous blisters in the coating on both the interior surface of the bottom plate and cylindrical wall of the liner. Metallographic specimens were prepared from this section which show the lack of adherence of the coating to both the internal wall of the liner and surfaces of the welds joining the sidewall to bottom plate. Those welds were made in single passes, joint preparations were not machined prior to welding, and there is a gap between the bottom plate and wall of the liner. Corrosion products are evident between the coating and base metal on both the interior and exterior coated surfaces of the liner.

RESULTS

Base metal thicknesses of corroded specimens prepared from Section 1 of liner PF-3 were compared with base metal thicknesses of uncorroded specimens taken from the coated area of Section 3. The adherent coating on the surface of specimens from Section 3 protected those specimens from corrosion. Ten thickness measurements were taken of the base metal of

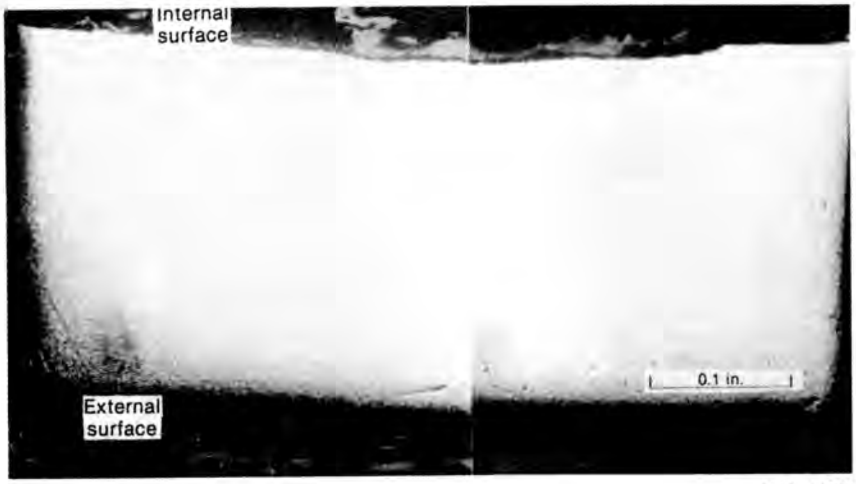

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Fig. 10. Photomicrograph of Section 1, Specimen 1B (a vertical section from liner PF-3 normal to the grounding area for the conductivity probe) showing the horizontal depression on the internal surface.

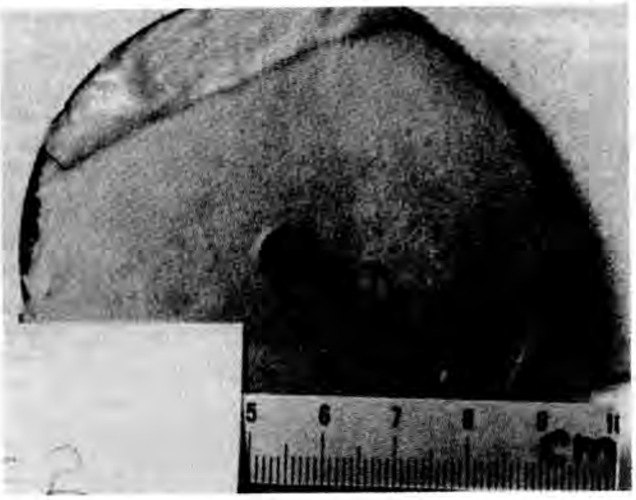

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Fig. 11. Photograph of the interior surface of Section 2 from liner PF-16 showing a nearly defect-free coating.

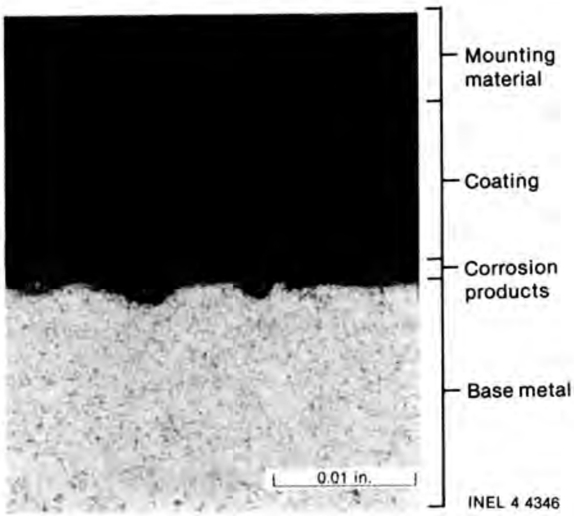

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Fig. 12. Photomicrograph normal to the interior surface of Section 2 from liner PF-16 showing corrosion products between the coating and base metal.

Specimen 3-B from Section 3. Those measurements ranged from 0.2493 to 0.2506 in., with an average calculated thickness of 0.2501 in. Those measurements are compared with thickness measurements of a corroded specimen taken from Section 1. Measurements of Specimen 1-B ranged from 0.2346 to 0.2507 in., with an average calculated thickness of 0.2440 in. Thickness measurements of the base metal were obtained for a second coated, uncorroded specimen from Section 3. Those measurements ranged from 0.2451 to 0.2509 in., with an average base metal thickness of 0.2488 in. A second corroded specimen taken from Section 1 had base metal thickness measurements ranging from 0.2397 to 0.2496 in., with an average thickness of 0.2456 in. A nominal uncorroded wall thickness of 0.250 in. was calculated from the data.

The thickness of coatings on the internal and external surfaces of both liners varied considerably. The thickness of the exterior coating on specimens from liner PF-3 ranges from 0.009 to 0.012 in., and the interior coating from 0.005 to 0.009 in. The thickness of the exterior coating on specimens from liner PF-16 ranges from 0.005 to 0.010 in., and the interior coating from 0.010 to 0.020 in. Coating failures are located primarily on interior surfaces of both liners, with the exception of those noted on the specimens from the bottom-to-sidewall weld area on the exterior surface of liner PF-16. The coating on liner PF-3 was in better condition than that on PF-16. Coating thickness measurements show little difference between PF-3 and -16. Failures of coatings (and especially the coating of PF-16) occurred in the area of the ion-exchanger bed. The more extensive coating damage observed in liner PF-16 can be attributed to the acidity of the water processed through that prefilter. The pH of the water processed through prefilter PF-16 was about 3, compared with a pH of about 7 for water processed through prefilter PF-3. The thickness of the coating adjacent to the blisters and spalled areas was about the same as that of adherent coating. The thicknesses of the coatings on test plates provided by Epicor, Inc., were determined to be 0.011 to 0.012 in. No correlation can be made between coating thickness and extent of damage observed in the coating and base metal.

Corrosion products were found between the coatings and the base metal on both the interior and exterior surfaces of both liners. In general, the corrosion products and coatings adhered to the base metal. Areas were observed where corrosion products were surrounded by coating, which suggests that corrosion products were formed before the coating was applied to the liner.

Some coating failures observed on the interiors of both liners PF-3 and -16 are attributed to improper base metal surface preparation before coating. Radiation also was examined as a possible cause of failure. Radiation doses to the coatings on the internal surfaces of both liners were estimated at less than 10^8 rad. Tests performed on Phenoline coatings by Oak Ridge National Laboratory established limiting radiation resistance dose ratings.[8] Those limiting doses ranged from 2.1×10^9 to 8.3×10^9 rad for Phenoline 368 coating systems in demineralized water. Since the estimated doses for liners PF-3 and -16 are less than the limiting dose ratings, it can be stated that radiation damage was not the cause of the coating failures. It also should be noted that the total estimated dose for the highest loaded liner after 13 years storage is about 4×10^8 rad, which is below the limiting dose rating.

DISCUSSION AND CONCLUSIONS

An area on the interior surface of each liner is bare. That area was used as a ground for a conductivity probe liquid level detector. The bare area on liner PF-3 exhibited the minimum wall thickness for either liner. The metallurgical section removed from that area of PF-3 had a heavy buildup of corrosion products mixed with ion-exchange media on the surface. Although it is known that some base metal was removed mechanically during removal of the coating from the grounding area, that loss of metal could not be identified separately from the amount of metal lost by corrosion. In calculating the minimum lifetime of an EPICOR-II liner, it was assumed that all metal was lost by corrosion. It also was assumed that the corrosion rate was, and will continue to be, linear because the prefilter was a flowing system. That was a conservative assumption because, although the prefilter was a flowing system during use, approximately three years of storage provided stagnant conditions. Also, the bare area is small compared with the total interior area of the liner in contact with resin (about 3%); that resulted in a maximum amount of base metal removal through corrosion by concentrating the total corrosion capability of the liner contents on that small area. The minimum thickness of corroded base metal from Section 1 of liner PF-3 is subtracted from the maximum thickness of uncorroded base metal from Section 3 of liner PF-3. Mathematically, the lifetime of each prefilter is estimated at 50 years, based on the following calculations:

From thickness measurements:

Maximum thickness of Section 3, $x_3 = 0.2509$ in.
minimum thickness of Section 1, $x_1 = 0.2346$ in.

gives

wall thickness loss, $x = 0.0163$ in.

Then,

length of time between use and examination, $t = 3.3$ yr.
(31 October 1979 to 24 March 1983)

and

$$\text{corrosion rate, } R = \frac{x}{t} = \frac{0.0163 \text{ in.}}{3.3 \text{ yr}} = 0.005 \text{ in./yr}$$

gives

$$\text{minimum liner lifetime} = \frac{\text{nominal thickness}}{R}$$

$$= \frac{0.250 \text{ in.}}{0.005 \text{ in./yr}} = 50 \text{ yr.}$$

The area of maximum corrosion on liner PF-3 was determined to be the bare area on the inside surface where coating was intentionally removed. Corrosion in that area was uniform with no evidence of pitting or pitting-type corrosion. Comparing the minimum measured wall thickness in that corroded area with the measured uncorroded base metal thickness resulted in a calculated minimum lifetime for liner PF-3 of 50 years. That exceeds the required liner interim storage life of 13 years at INEL. The grounding area for the conductivity probe was not examined on liner PF-16, but it is assumed that corrosion in that area would be similar to the amount and type of the corrosion observed in liner PF-3.

Visual and metallographic examination of sections removed from the liners of EPICOR-II prefilters PF-3 and -16 revealed that the coatings had been breached and some areas of the carbon steel liners were uniformly corroded. No pitting or pitting-type corrosion was found in those areas. The coatings in many areas had been applied over corrosion products, which indicates that the base metal had not been properly prepared before application of the coatings. Through a literature study it was determined that coating failure was not attributable to radiation damage.[4]

It is recommended that waste containers of this type be procured to specifications defining engineering requirements for all materials and processes used in fabricaton.

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