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Failure Prevention by Short Time Corrosion Tests

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Abstract

Short time corrosion testing of perforated sheets and wire meshes fabricated from Type 304L stainless steel, Alloy 600 and C276 showed that 304L stainless steel perforated sheet should perform well as the material of construction for dissolver baskets. The baskets will be exposed to hot nitric acid solutions and are limited life components. The corrosion rates of the other alloys and of wire meshes were too high for useful extended service. Test results also indicated that corrosion of the dissolver should drop quickly during the dissolutions due to the inhibiting effects of the corrosion products produced by the dissolution processes.

Introduction

The successful selection of materials and components for service in highly corrosive environments involves understanding the service requirements, assessing the costs and availability and testing to demonstrate anticipated behavior. In-service failures are prevented by qualification testing of potential material/component configurations and understanding the corrosion processes likely to cause materials degradation. This paper presents a test program used to qualify a material for service in a hot nitric acid environment.

Metal scraps will be processed through dissolvers as part of the ongoing stabilization efforts at the Savannah River Site in Aiken, South Carolina. The metal scraps, which include plutonium and uranium metal, alloys and compounds, will be put into the dissolver via a basket. The basket, which is referred to as a teabag, has to allow free flow of the dissolving solution and contain the material until dissolution is nearly complete. The basket thus assures that escaping metal pieces are too small to impact an agitator which stirs the solution and is required for subsequent processing of the solutions produced. Perforated metal sheet and wire meshes were considered as potential configurations for the basket side walls and candidate materials of construction included 304L stainless steel (304L), Teflon®, and high nickel alloys 600 and C276. Test results from several short-term coupon immersion tests in concentrated nitric acid solutions at 95 °C indicated that Type 304L perforated metal sheet had the best corrosion resistance and would be acceptable for this application.

Experimental Procedure

This scoping study used short-term coupon immersion tests to determine the corrosion rate and process for candidate materials of construction for dissolver baskets. The tests

were conducted according to ASTM G31, "Laboratory Immersion Corrosion Testing of Metals". The test solutions, which were based on those proposed for use with the FRM material, were primarily 4M and 14M nitric acid with 0.1 M KF. All testing was conducted at 95 °C. The test samples were cleaned and weighed prior to testing and after the tests were completed. Microscopic observations of the samples were made when the samples were weighed. Metallographic analysis of selected samples was performed to correlate corrosion rate and process with the microstructure and composition of the product form.

The testing included a series of four tests with different materials, product forms, test solutions and exposure times, which are summarized in Table 1.

Series 1 One-inch square mesh samples of Teflon® (TFE) and 304L were immersed individually in 40 ml of test solution contained in covered glass beakers. The test solutions were 4M nitric acid with 0.1 M KF and 14 M nitric acid without KF. Two different stainless steel meshes were used to investigate the effect of wire size and/or weave pattern (plain and diamond) on the corrosion resistance. Sample characteristics are given in Table 1 below. The test period was one week with five periodic weight measurements.

Series 2 304L perforated sheet, which had circular perforations, was exposed to either 4M or 14M nitric acid with 0.1 M KF at 95 °C. Two samples were exposed to 500 ml of the solutions and were approximately 1" by 4" by 0.03" inches. The tests were conducted for one week with no intermittent measurements.

Table 1. Series Test Conditions

Series	Material	Form	Opening (in)	Dimension* (in)	Test Solution**
1	304L	Plain Mesh	0.075	0.025	4M Nitric with 0.1 M KF
	304L	Diamond Weave Mesh	0.057	0.012	
	TFE	Diamond Weave Mesh	0.064×0.031	0.027	14 M Nitric without KF
2	304L	Perforated Sheet	0.0625	0.030	4M Nitric with 0.1 M KF
3	600	Plain Mesh	0.055 0.01	0.07 0.04	14 M Nitric with 0.1M KF
3	C276	Plain Mesh	0.07	0.055	
4	304L	Perforated Sheet	0.0625	0.030	

*Dimension: wire - diameter, sheet – thickness

** Test temperature of 95 °C

Series 3 Mesh samples of alloys 600 and C276 were tested and had variable dimensions, approximately 1" by 2". Table 1 presents the characteristics of these meshes. The mesh samples were exposed as a group so that a sample of each mesh type was exposed to the same 500 ml of either 4M or 14M nitric acid with 0.1 M KF test solutions. Test period was for one week with no intermittent weight measurements.

Series 4 tests exposed Type 304L perforated sheet at four-hour intervals for a total of twenty intervals. This series was set up to simulate the repeated exposure of the basket for the estimated dissolution time of 4 hours. Sample size was approximately 1" by 4" by 0.03". Three samples were tested in the 4 M and 14M nitric acid solutions with 0.1M KF. Two of the samples were identical; the third had the edges welded to minimize end grain attack. Two samples, welded and non-welded, were exposed together. The other non-welded sample was immersed separately to test the effect of surface area/volume ratio on the corrosion. Samples were hung in capped bottles containing 450 ml of test solution.

Each day two runs were performed. Samples were place into bottles and heated to temperature. After four hours, the samples were removed, rinsed, dried, weighed, and put back into test for another four-hour period. At the conclusion of each period, samples were weighed again. All the samples were stored in a dessicator over night to maintain surfaces.

Prior to the start of testing, vendors were contacted about the materials available as wire meshes and perforated metals. The selection of materials was limited and those readily available for testing were even more restricted. Several metals with nitric acid corrosion resistance better than alloys 600 and C276 are produced but were not available in mesh form. Also, the selection of metals as perforated sheet was more limited than those available as mesh. The nominal composition of the test samples are given in Table 2, which also shows the materials of construction, product forms, and thickness for sheet or diameter for wire mesh.

Table 2. Materials and Product Forms For HB-Line Dissolver Containers

Material	Form	Dimension** (in)	Composition		
			%Ni	%Cr	%Fe
304L	10 Mesh	0.025	8	18	72
	Exp. Mesh	0.012			
	Perf. Sheet	0.025			
I600	20 Mesh	0.016	72	15.5	8
	8 Mesh	0.028			
C276*	8 Mesh	0.028	57	15.5	5.5

*Other primary constituents are 16% Mo, 4% W, and 2.5% Co.

**Dimension: wire – diameter, sheet – thickness

All weights were made on equipment with M&TE calibration. Samples were examined with a stereomicroscope up to magnifications of 70X. Data was recorded in Laboratory Notebook, WSRC-NB-2004-00042.

Weight losses were used to calculate the corrosion rate (CR) using the following general formula [2]:

$$CR = \{(\text{Constant})(\text{Weight Loss})\} / \{(\text{Density})(\text{Surface Area})(\text{Time})\}. \text{ Equation (1)}$$

For perforated sheet, Equation 1 was used without further derivation. The constant in the equation, which is a unit conversion factor, is 3.45×10^6 mil-hr/cm-yr for units in mils per year (mpy). The nominal density of 304L was used (7.94 g/cm^3). Surface area calculations considered the reduction in surface area associated with the punched holes and the increased surface area associated with the exposure of the sidewall of a hole. There was a net increase in surface area because the radius of the holes was less than the thickness of the material.

For the wire meshes, surface area determinations were calculated from the initial sample weight, W, material density, ρ , and wire diameter, d and the total length of wire exposed, l, which was assumed to be $4W/\pi d^2 \rho$. The resulting surface area equation was πdl . The corrosion rate equation was then given by

$$CR = \{(\text{Weight Loss})(d/2)\} / 2\{(W)(\text{Time})\}. \quad \text{Equation (2)}$$

Corrosion of Mesh Materials

The wire meshes had variable results depending on the material and exposure conditions. The test results, which are summarized in Table 3, include total weight loss and corrosion rate. The corrosion rates in Series 1 tests were essentially constant over the test period and only the final rates are shown in the table. The 304L meshes although different in weave had similar corrosion rates. The corrosion rates for the higher alloyed metals in Series 3 were more variable. The post-test appearances of the samples are shown in Figures 1 and 2 for Series 1 and 3, respectively.

The results for the TFE wire mesh were as expected. In the table, only the initial weight changes are shown since the weights did not alter after that. No observable changes were noted in simplistic material evaluations, such as bending and twisting, or surface characteristics. The properties of Teflon® wire, however, would be impacted by radiation, which would significantly reduce the suitability of this material for corrosion.

Table 3. Corrosion Rates Of Wire Meshes In Simulated Dissolver Solutions

Series	Material	HNO ₃ (M)	KF (M)	Initial Weight (g)	Total Weight Loss (g)	Corrosion Rate (mpy)
1	304L Plain	4M	0.1	1.26068	0.39698	109
		14M	0.0	1.31131	0.00549	2
1	304L Diamond	4M	0.1	0.58189	0.38397	110
		14M	0.1	0.60861	0.00476	2
1	TFE	4M	0.1	0.59507	0.00221	NA
		14M	0.1	0.54829	0.00032	NA
3	600 – 8	4M	0.1	4.39272	1.5089	128
		14M	0.1	4.51456	--*	>370
3	600 – 20	4M	0.1	2.82113	0.35352	23
		14M	0.1	2.59591	--*	>1750
3	C276	4M	0.1	3.30282	0.85239	96
		14M	0.1	2.93651	--*	>370

* Sample either could not be measured or was completely dissolved.

The 304L wire meshes had similar corrosion rates (as shown in Table 3) but differed physically in their appearances (as shown in Figure 1). In the 4 M nitric acid solution with potassium fluoride, the corrosion was more severe than in the 14 M nitric acid solution without potassium fluoride. The higher acidity or oxidizing capability passivates the stainless steel surface. The greater corrosion was associated with the presence of fluoride ions. The 4 M solution was noted to have a blue/green coloring, whereas the 14 M solution without fluorides remained clear. The color change is typical for solutions enriched in Cr⁺³ [4], which would be associated with the corrosion products from the stainless steel.

For plain wire meshes in the 4 M solution, the most significant corrosion was at the wire ends as shown in Figure 3. Figure 3 shows photomicrographs of wire ends for the plain wire mesh exposed to both solutions. The corrosion occurred along grain boundaries and is referred to as end-grain corrosion, which can quite severe. End-grain attack was not observed in the 14 M solution. As can be seen in the photomicrographs, general corrosion was the principal mode of attack along the wire surfaces. The general corrosion was severe in the 4 M solution since the mesh lost its rigidity and resulted in a loosening of the wires.

The wires from the diamond mesh had extremely roughened surface, suggestive of intergranular attack (IGA), with deep furrows along edges and pits on the ends where grain dropping had occurred. Figure 4 shows a photomicrograph of the diamond mesh exposed to the 4 M solution. At locations along the surface, IGA was observed, unlike the plain mesh samples. The microstructure showed carbide precipitates dotted along the grain boundaries. Carbide precipitation can lead to a chromium depletion zone near the

grain boundary, making it more susceptible to corrosion. This mesh lost over 50% of its initial weight.

The lack of fluoride in the 14 M solution greatly reduced the corrosion rate in comparison to the 4M solution. The diamond mesh had only slightly roughened surfaces with some initial fabrication marks still observable. The plain weave mesh again retained a smooth surface. Both meshes had darkened oxides and showed highlighting of grain boundaries at the wire ends.

The mesh materials of alloys 600 and C276 both performed poorly as shown by the results in Table 3. In the 14 M solution which had fluoride ions, the alloy 600 meshes were nearly completely corroded. Only a few wire strands of one of the meshes remained at the bottom of the container. The C276 mesh performed better since it remained intact, although accurate weight measurements were difficult since the sample had lost a significant percentage of its initial weight. These materials would not be suitable for use as the dissolver basket material of construction.

The samples performed better in the 4 M solution as shown in Figure 2. The C276 and 600-8 samples had weight losses similar to those for 304L. The 600-20 mesh had significantly lower corrosion rates, which is quite different from the results for 304L where the two meshes had similar corrosion rates. This difference in rate for alloy 600 may be associated with wire fabrication, composition, or metallurgical condition. Both C276 and 600 suffered from IGA and end-grain attack similar to the 304L meshes. Figure 5 shows the IGA along the surface of the wire. The 600-20 mesh did not appear to have as corroded a surface as the other meshes. In areas where metal smearing had occurred at the ends, IGA and grain drop out were not observed.

Corrosion of 304L Perforated Metal Sheet

Two tests were performed for the 304L perforated sheet. In the first series, experimental difficulties occurred with the temperature controllers, so the test temperature dipped below 80 °C. Below 80 °C, the corrosion rate of 304L drops significantly [5]. The test results are summarized in Table 4 for Series 2 and include total weight loss and corrosion rate.

Table 4. Corrosion Rates of 304L Perforated Metal Sheets

Sample	Solution	Initial Weight (g)	Total Weight Loss (g)	Time (day)	Corrosion Rate (mpy)
A	4M	6.3822	1.2386	7	54
B		6.1056	1.1864	7	51
C	14M	6.1969	1.8634	3	188
D		5.7499	1.7185	3	174

In the second set of tests for the perforated sheet, the samples were exposed for twenty periods of four hours to simulate basket use in the dissolver. The samples from this test

are shown in Figure 6. The average corrosion rates for these samples are shown graphically in Figure 4. The final average corrosion rates for the two solutions ranged from 130 to 210 mpy for the 4M solution and 330 to 380 mpy for the 14M solution.

The samples showed a slowly decreasing trend in rate over the test period. The trend was associated with decreased effectiveness of fluoride due to iron complexing (which resulted from corrosion) and changes in the surface morphology. The two bumps or undulations can be seen in the curves at approximately 30 and 68 hour and occurred with solution replacement and are indicative of corrosion in new solutions. Test solutions were only replaced with fresh test solutions on the two occasions shown and the corrosion rates quickly returned to the lower values as the fluoride ions were complexed.

The data summarized in Figure 7 suggest that the paired samples had slightly lower corrosion rates than the samples exposed singularly. This difference was greater in the 4M nitric acid solution than in the 14 M nitric acid solution. The paired samples had a greater exposed surface area per liter of solution which probably led to more complexing of the fluoride by the iron corrosion products, thereby reducing the corrosivity of the test solution. Additionally, the corrosion rates in the two welded samples also had slightly lower corrosion rates probably because the weld metal buttered the outer edges of the samples and reduced the exposed end grain. The exposed end grain was approximately 38% of the exposed surface for the weld sample compared with 43% for the non-weld sample.

Overall, the perforated sheet experienced lower corrosion rates in the 4M nitric acid solution than in the 14 M solution. The presence of fluoride ions in the 4M HNO_3 test solution resulted in an increased chromium ion concentration in the solution as shown by the blue/green color of the test solution [4]. In the 14 M HNO_3 test solution, the solution became brown quickly, which was associated with aggressive dissolution of all steel constituents. Post-test solution analyses were not performed.

After testing the materials were examined under a stereomicroscope with magnifications up to 70X. Under low magnification, the samples had a granular rough appearance. End-grain attack was significant in the perforations as well as the edge of the sheet. These forms of attack caused grain dropping which was apparent along the exposed surface. Figure 8 shows the end grain attack within the perforated holes after exposure of the sheet to the 14 M nitric acid solution.

The attack was more prominent near one side of the sheet because the perforations are made by punching. Punching caused part of the perforated edge near the punched surface to be covered with smeared metal. The smeared metal prevented end grain attack in these areas and led to less corrosion on this side of the sheet. The prevention of end grain by metal smearing is similar to the effect of weld buttering which is commonly used to minimize such attack in rolled plate.

Discussion

The corrosion of Type 304L stainless steel and other alloys exposed in the test solutions of nitric acid and potassium fluoride was affected by the concentrations of the acid the presence of the fluoride anion and the metallurgical condition and composition of the material. The test results clearly showed that for all test materials the corrosion rates in the 14 M nitric solutions were greater than those in the 4 M solutions. The presence of fluoride greatly increased the corrosion rate of 304L as shown by a comparison of the rates from Series 1 tests to the rates obtained from the Series 2 and 4 tests.

Contributing factors to the corrosion of 304L were the concentrations of chromium ions and of species that complex fluorides. Chromium, as Cr^{+6} , acts as a cathodic depolarizer and accelerates the corrosion rate. The concentration of Cr^{+6} increases with nitric acid concentration since nitric acid is an oxidizing acid, thus chromium probably affected the tests in 14 M nitric acid more than the tests in 4 M nitric acid. Species from the corrosion products, such as iron anions, reduce the free fluoride concentration by complexing fluorides and decrease the solution corrosiveness. The complexing reactions were more prevalent in old solutions because of the presence of corrosion released iron anions; thus the corrosion rates in these tests decreased with time. Furthermore, the test results from Series 4 showed that the sample exposed singularly had greater corrosion rates than the two samples exposed together and that this difference in corrosion was greater for the 4 M nitric acid solution than for the 14 M solution.

The solution volume/surface area (SV/SA) ratios are a quantitative means to indirectly evaluate these factors. The SV/SA ratios were 7.7 ml/cm^2 for the single samples and 3.8 ml/cm^2 for the two samples. The two samples resulted in a greater concentration of corrosion products in the solution. These products include both chromium and iron ions, with iron composing a greater percentage of the products. The difference was greater for the 14 M solutions because 4 M nitric acid is not sufficiently oxidizing to transform the chromium from a state of +3 to +6.

A comparison of the corrosion rates from Series 2 and 4 shows the rates from Series 2 were significantly less than those in Series 4. The difference is associated with the experimental procedures. For Series 2, samples were exposed for the entire period with out intermittent weight loss measurements. Truman has shown that nitrogen peroxide, a reducing gas product, would be present and lead to lower corrosion losses [4]. With the frequent sample removal during Series 4, these gases could escape and result in higher corrosion rates.

The results of Series 4 showed that the corrosiveness of the solution decreases quickly. This effect is more clearly seen in the intermittent corrosion rate data which is shown graphically in Figure 9. The corrosion rates peaked during the period the samples were exposed to fresh solutions. During subsequent periods, the intermittent corrosion rate dropped to near average corrosion rates. The iron anions from stainless steel corrosion probably complexed free fluorides and reduced solution corrosiveness. Further testing, however, would be necessary to evaluate this effect.

The experimental change in corrosion rate may indicate that the corrosion of the dissolver may quickly decrease during the dissolution due to its own corrosion products. A surface area/volume ratio of 2.4 ml/cm^2 was calculated for a basket in the dissolver based on Drawing # PV180594, Revision 9, and a solution volume of 15L. The calculated ration is smaller than sample surface to solution volumes used during the test. Thus corrosion product in the dissolver should be more rapid than in the test solutions, improving the tendency for corrosion product inhibition of the reactions and slowing the corrosion rate.

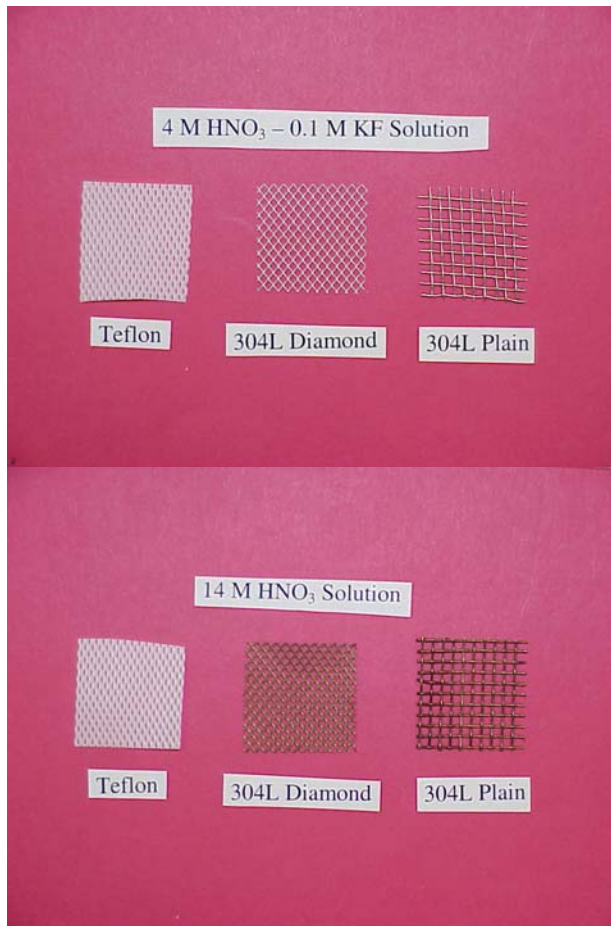
Dissolver baskets fabricated from 304L perforated sheet should perform favorably based on these test results. The corrosion rates will be high initially but should quickly decrease due to complexed fluorides. Other factors, such as the release of reducing gases, also act to lower the rate. After 20 exposures, the samples, although experiencing corrosion induced loss of material, still maintained stiffness and rigidity. The perforated sheet baskets would therefore be expected to be useful over an extended period.

Conclusion

Corrosion testing was performed on perforated sheets and wire meshes of alloys 304L, Alloy 600 and C276. The test results indicated that 304L stainless steel perforated sheet should perform well as the material of construction for dissolver baskets. The corrosion rates of wire meshes were too high for useful extended service as a dissolver basket. Test results also indicated that corrosion of the dissolver should drop quickly during the dissolutions due to the inhibiting effects of the corrosion products produced by the dissolution processes.

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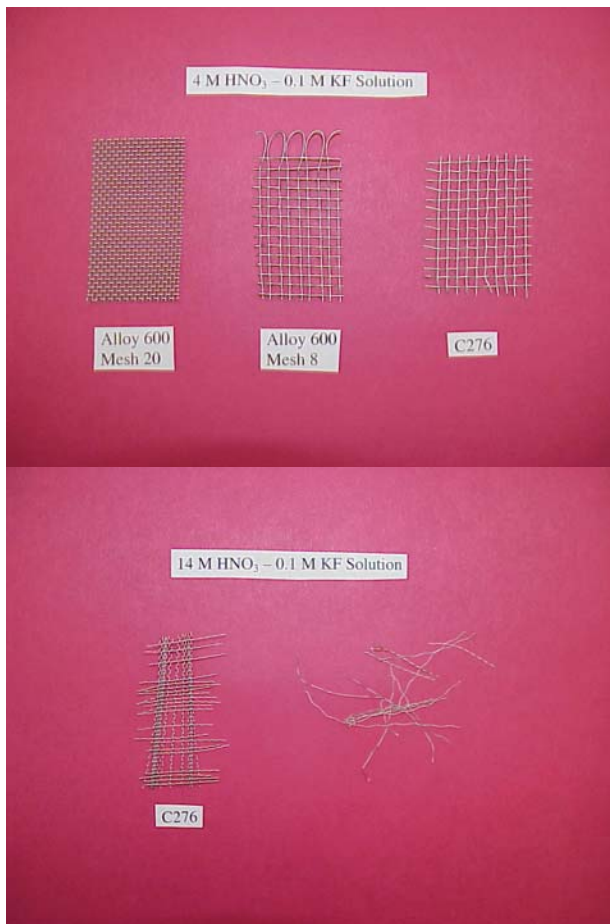
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(A)

(B)

Figure 1. Series 1 Mesh Samples After One-Week Exposure To 4 M (A) and 14 M (B) Nitric Acid Based Solutions (No KF was present in the 14 M solution)



(A)

(B)

Figure 2. Series 3 Mesh Samples After One-Week Exposure To 4 M (A) and 14 M (B) Nitric Acid Based Solutions (KF present in all solution)



(A)

(B)

Figure 3. 304L Stainless Steel Wire From Plain Mesh After Exposure At 95 °C: (A) 4 M Nitric Acid With 0.1 M Potassium Fluoride; (B) 14 M Nitric Acid Without Potassium Fluoride

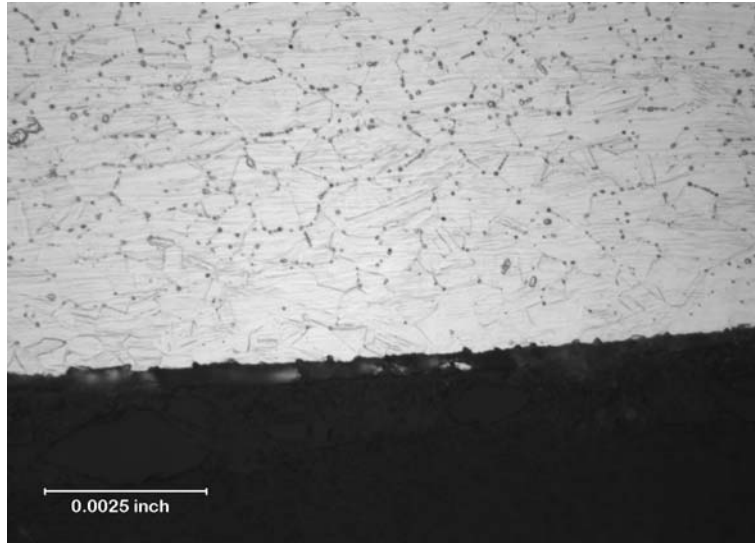


Figure 4. 304L Stainless Steel Wire From Diamond Mesh After Exposure In 4 M Nitric Acid Solution With Potassium Fluoride At 95 °C

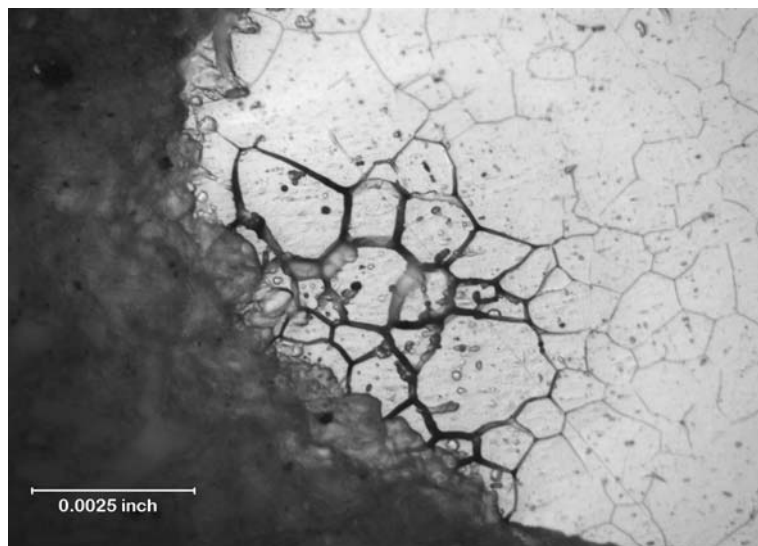


Figure 5. C276 Wire Mesh After Exposure In 4 M Nitric Acid Solution With Potassium Fluoride At 95 °C

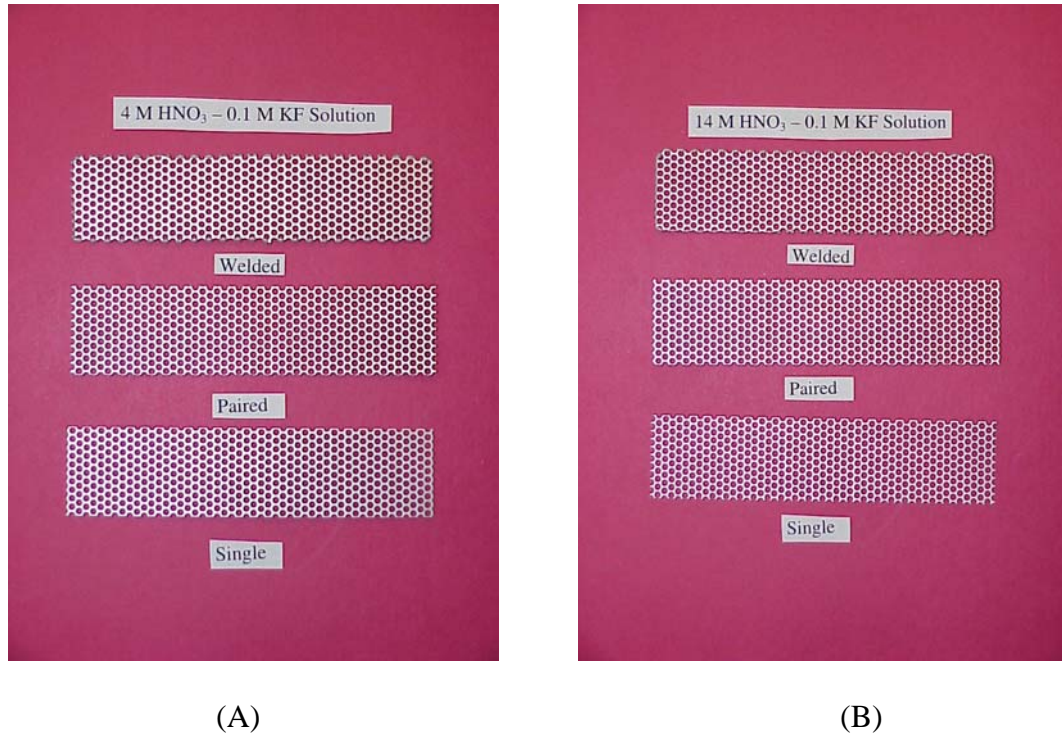


Figure 6. Series 4 Perforated 304L Stainless Steel Samples After Exposure to 4 M (A) and 14 M (B) Nitric Acid Based Solutions

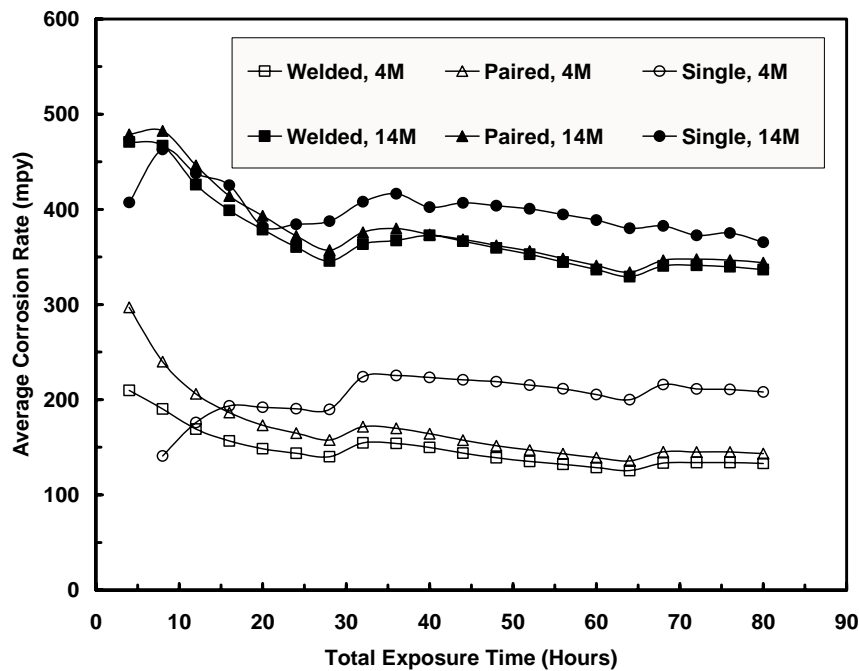


Figure 7. Average Corrosion Rate Of 304L Perforated Sheet In Simulated Dissolver Solutions At 95 °C

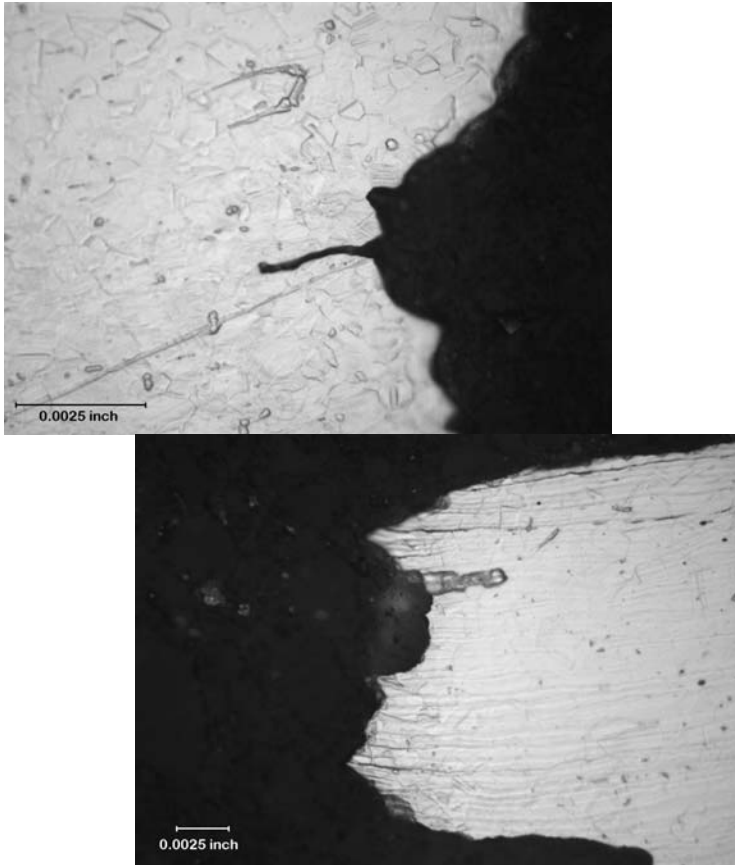


Figure 8. 304L Stainless Steel Perforated Sheet After Exposure In 14 M Nitric Acid Solution With Potassium Fluoride At 95 °C

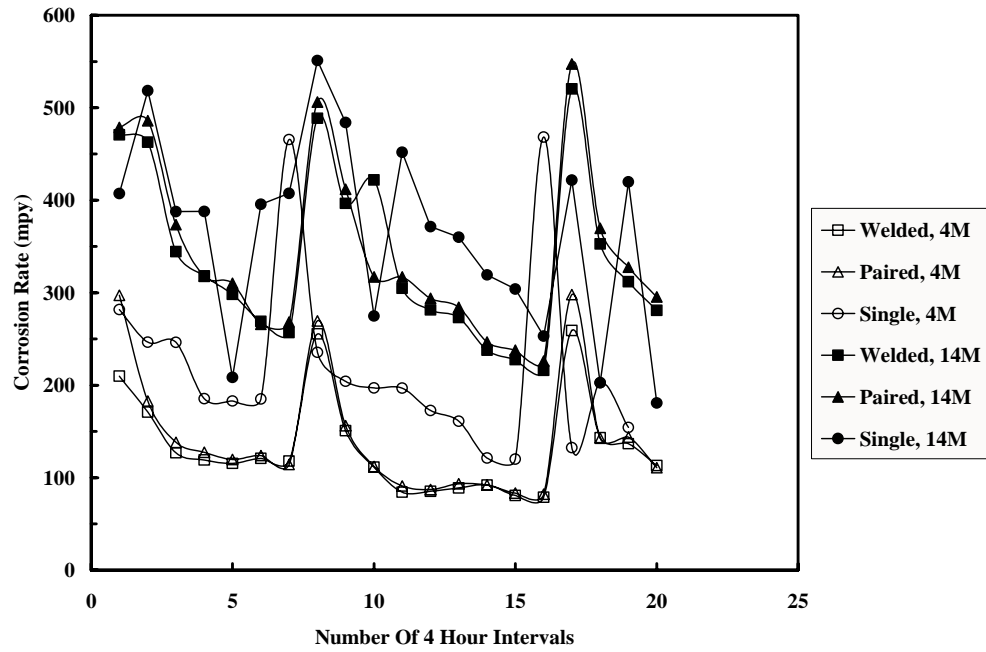


Figure 9. Intermittent Corrosion Rate Of 304L Perforated Sheet In Simulated Dissolver Solutions At 95 °C