

Results of Experiment to Determine Corrosion Rates for 304L in HB-Line Dissolver Vessel Ventilation System

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Summary

Radioactive material being processed as part of the DE3013 program for HB-Line will result in the presence of chlorides, and in some cases fluorides, in the dissolver. Material Science and Technology developed an experimental plan to evaluate the impact of chloride on corrosion of the dissolver vessel ventilation system. The plan set test variables from the proposed operating parameters, previous test results, and a desired maximum chloride concentration for processing. The test variables included concentrations of nitric acid, fluorides and chlorides, and the presence of a welded and stressed metal coupon.

Table 1 contains expected general corrosion rates in the HB-Line vessel vent system from dissolution of 3013 contents of varying nitric acid and chloride content. These general corrosion rates were measured upstream of the condenser in the experiment's offgas system near the entrance to the dissolver. However, they could apply elsewhere in the offgas system, depending on factors not simulated in the testing, including offgas system temperatures and airflow.

Table 1. Highest Observed General Corrosion Rates

| Test Number | Nitric Acid (M) | Chloride in Solution (ppm) | Fluoride (M) | Highest Expected General Corrosion Rate (mpy) |
|-------------|-----------------|----------------------------|--------------|---|
| 1 | 12 | 2000 | 0.1 | 334 |
| 2 | 12 | 10000 | 0.1 | >>1061 |
| 3 | 8 | 2000 | 0.1 | 55 |
| 4 | 12 | 0 | 0.1 | 18 |

Localized corrosion was significant in Tests One, Two, and Three. This corrosion is significant because it will probably be the first mode of penetration of the 304L steel in several places in the system. See Table 2.

Table 2. Highest Observed Localized Corrosion Penetration Depths

| Test | Positions with Significant Localized Corrosion | Deepest Penetration, mils | Position of Deepest Penetration | Hours of Operation |
|------|--|---------------------------|---------------------------------|--------------------|
| 1 | Pre-condenser | 29.6 mils | Entrance to offgas system | 180 |
| 2 | Pre- and post-condenser | <11 mils | Entrance to condenser | 180 |
| 3 | Pre- and post-condenser | 54 mils; full penetration | Entrance to offgas system | 186 |

For Tests One and Three, the penetration rate of localized corrosion was much higher than that for general corrosion. It was approximately four times higher in Test One and at least 45 times higher in Test Three, penetrating an entire coupon thickness of 54 mils in 186 hours or less.

There was no significant difference in corrosion between welded areas and un-welded areas on coupons. There was also no significant attack on stressed portions of coupons. It is probable that the lack of corrosion was because the stressed areas were facing downwards and offered no place for condensation or deposits to form. Had deposits formed, pitting may have occurred and led to stress corrosion cracking. The significant localized corrosion observed was usually associated with deposits.

General corrosion on the offgas coupons was extremely high for the test containing 10,000 ppm chloride in the dissolver solution. Localized corrosion caused deep penetration of coupon surfaces with a solution of 2000 ppm chloride, both at 12 M and 8 M nitric acid. We recommend that when processing chloride-containing solutions, the pre-condenser side of the vessel vent system be inspected at a frequency calculated from acceptable material losses and expected general corrosion rate. The presence of deposits and heavy condensation during inspection should be taken as indicators of possibly severe localized corrosion.

Introduction

As part of the DE3013 program for HB-Line, radioactive material removed from 3013 cans during the K-area interim surveillance inspection must be processed for disposal. These materials will contain variable quantities of chlorides and in some case fluorides. Both chloride and fluoride ions are known to impact the corrosion resistance of Type 304L stainless steel in nitric acid solutions. 304L stainless steel is the material of construction of most of the HB-Line process equipment.

A preliminary study found that average dissolver corrosion rates in nitric acid solutions (8-14 M) with fluorides (0.01-0.1 M) and chlorides (100-2000 ppm) were near the upper range of rates determined from UT measurements made on recent dissolver vessels. The study resulted in average dissolver corrosion rates of 52-280 mpy and the UT measurements resulted in corrosion rates up to 245 mpy [1]. In the study, pitting and intergranular attack (IGA) were noted mechanisms in the presence of chlorides. The corrosion rates were based on short-term tests. As the degradation of the dissolver vessel proceeds over time, the corrosion rate would be expected to increase until stabilizing at a high rate, as shown by long-term studies in nitric acid/fluoride environments [2, 3]. The increase would be due to intergranular attack leading to grain dropout. These higher rates would lead to a shorter operating life for the dissolver. The previous study concluded, however, that this decrease in dissolver operating life is expected to be manageable at chloride levels to 2000 ppm [1].

The effect of chlorides on the off-gas system of the dissolver became a concern when studies by Pierce showed that in high nitric acid solutions most of the chloride is removed as various gaseous chlorides and made available to the offgas system [4]. Pierce also reported that nitrates were found to be on the same surfaces as the chlorides. Nitrates generally act as inhibitor to chloride corrosion. During the preliminary study on dissolver corrosion in the presence of chlorides, corrosion rates in the head space region of the simulated dissolver vessel were found to be lower than those measured from the liquid region; 52-163 versus 65-280 mpy [1]. The entire off-gas system, however, was not tested.

Material Science and Technology developed an experimental plan to evaluate the impact of chloride on corrosion of the dissolver off-gas system. The plan set test variables from the proposed operating parameters, previous test results and a desired maximum chloride concentration for processing. The test variables included temperature, concentrations of nitric acid, fluorides and chlorides, and the presence of welded and stressed metal coupons.

Experimental Setup

Vapor space testing was conducted in a borosilicate glass reaction vessel which sat in a heating mantel. The complete apparatus is shown in Figure 1. The mantel was connected to a temperature controller which maintained the solution temperature at 105 °C (± 5 °C). The vessels had a domed glass cover with four ports for a thermocouple, the condenser sidearm, sampling, and a spare access port. The condenser was situated away from the heating mantel via the condenser sidearm. The off-gas of the condenser was connected to a scrubber through a polymeric tube. Coupons were placed in four positions, which are shown in Figure 1: in the vessel vapor space (A), at the bottom of the condenser (B), immediately after the condenser (C), and in the scrubber (D). During operation the top of the reaction vessel and Position A of the offgas system were wrapped with insulation to minimize cooling within the vessel vapor space. Cooling water at approximately 20 °C was run continuously through the condenser.

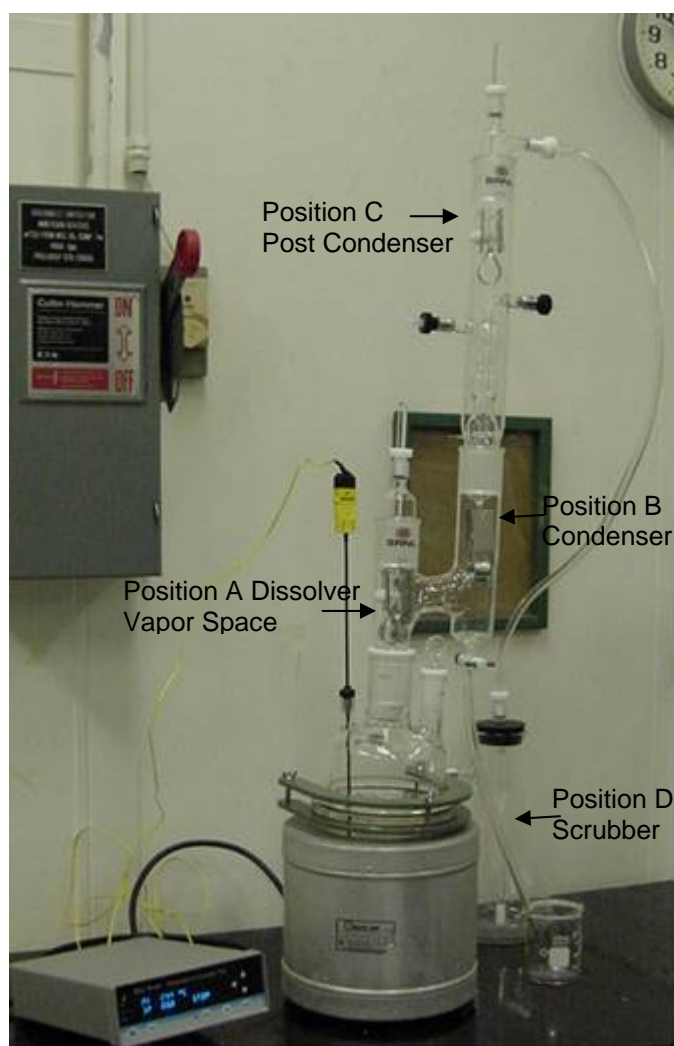


Figure 1. Apparatus for Corrosion Testing to simulate HB-Line Dissolver Off-Gas System.

The solution was brought to temperature and heated for six hours to simulate a processing cycle of the dissolver. After the solutions cooled, solution samples were taken to measure the acidity. The acidity was determined by titration using a 0.1 M NaOH solution with phenolphthalein as the indicator. The acidity was adjusted to the initial concentration by additions of concentrated nitric acid and water. Since the chloride is known to dissipate during a cycle, NaCl salts were added to the solutions to obtain desired chloride levels. Based on previous analysis [1, 4], 100 ppm Cl⁻ was assumed to remain in the solution. The solutions were replaced after about 10 cycles due to accumulation of salts in the bottom of the vessel. The condensate volume was also monitored during testing to evaluate mass balance.

The initial solution chemistries are shown in Table 3. Testing was performed in 12 M HNO₃ with 0.1 M F⁻ as a baseline for corrosion assessment since the probable flowsheet for the 3013 material will be at 12 M HNO₃. Two chloride levels were chosen which bracketed the desired operating range for processing the 3013 material and would include a majority of the material. A solution with 8 M HNO₃ was also tested as possible flowsheet chemistry. All chloride bearing solutions also contained 0.1 M F⁻.

Table 3. Solution Chemistries For HB-Line Simulants

| Number | Nitric Acid (M) | Chloride (ppm) | Fluoride (M) |
|--------|-----------------|----------------|--------------|
| 1 | 12 | 2000 | 0.1 |
| 2 | 12 | 10000 | 0.1 |
| 3 | 8 | 2000 | 0.1 |
| 4 | 12 | 0 | 0.1 |

The scrubbers contained a 1.0 M sodium hydroxide solution. This solution has been proposed for use in the scrubber for the HB-Line dissolver to capture chlorides and prevent their release into the surrounding environment [5].

Solution samples were taken for chemical analyses from batches of the initial and final solutions and the condensates. Solutions were analyzed for chloride, nitrate, chromium, iron, and nickel concentrations. Free acid measurements were also made.

Three types of test coupons were used to evaluate for SCC, crevice corrosion, general corrosion and pitting. All materials were made of 304L stainless steel, whose nominal composition in weight percent is C < 0.3%; Cr, 18-20%; Ni, 8-12%; Mn, 2.0% max; Si, 1.0 % max; and balance Fe. The coupons came from different lots, or heats, of 304L stainless steel. The initial coupons are shown in Figure 2. Teardrop coupons, which are used for testing susceptibility to SCC, were made of strips of material (0.75" × 4.75" × 0.054") bent around a 0.5"-radius mandrel and TIG fusion welded. The regular flat coupons had dimensions of 1" × 2" × 0.1" and the crevice coupons had dimensions of 1" × 2" × 0.12". The crevice coupons had a 0.25" hole in the center through which a crevice assembly was attached. The assembly consisted of a Teflon® washer with teeth and a stainless steel washer against opposite sides of the coupons. The washers were held in place with a Teflon® bolt and nut. All coupons had ground surfaces which were finished with a 600-grit paper. All coupons were weighed prior to testing.

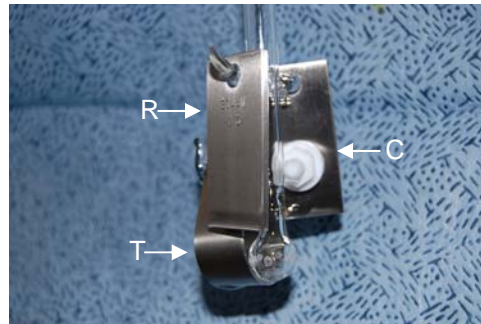


Figure 2. Test Coupons Hung on Sample Holder: T) teardrop; C) crevice; R) regular

At the conclusion of testing, coupons were removed from the test apparatus and photographed. Teardrops were rinsed immediately and dried, followed by examination for cracks. The regular and crevice coupons were allowed to dry with residual condensate. Select coupons were examined using scanning electron microscopy along with energy dispersive spectroscopy. Other coupons had corrosion products and salt deposits removed for x-ray diffraction analysis. Initial cleaning of the test coupons was in a solution made with Alconox™ soap. Additional cleaning, as needed, was in a 1.6 M nitric acid solution for short times at room temperature. Cleaning included a final rinse with water and then ethyl alcohol, followed by blowing dry.

After cleaning, coupons were weighed for determining a general corrosion rate. Corrosion rates were calculated from the weight loss based on the following equation:

$$CR = \frac{3.45 \times 10^6 \times W}{A \times T \times D} \quad \text{Equation 1}$$

where CR is corrosion rate (mils/year), W is the weight change (grams), A is surface area (cm²), T is time (hours) and D is density of 304L (7.94 g/cm³). The surface area was always taken as that of a new coupon.

Results and Discussion

General Results

The corrosion of 304L stainless steel was a function of several factors including the location in the off-gas system, the chemistry of the simulant, and the configuration of the coupon. Table 4 summarizes the measured general corrosion rates, a visual rating, and the occurrence of localized corrosion. The solution number corresponds to the chemistry given in Table 3 and the position corresponds to that shown in Figure 1. Appendix I has photographs of the coupons as they were removed from the test apparatus. Appendix II contains a more complete description of the corrosion for each position.

Table 4. Corrosion of 304L Stainless Steel in Nitric Acid-Based Solutions with Chloride

| Solution | Position | Corrosion Rate (mpy) | | | No. of Cycles | Overall Evaluation | Localized Corrosion* |
|----------|----------|----------------------|---------|---------|---------------|--------------------|----------------------|
| | | Teardrop | Regular | Crevice | | | |
| 1 | A | 333.6 | 123.4 | 222.2 | 30 | Poor | P |
| | B | 53.6 | 3.0 | 33.7 | 26 | Fair | P, CC |
| | C | 5.6 | 4.0 | 7.1 | 26 | Good | P |
| | D | 0.1 | 0.2 | 0.2 | 30 | Excellent | |
| 2 | A | ND | 714.7 | 1060.9 | 30 | Poor | P |
| | B | 51.4 | 8.7 | 15.7 | 30 | Fair | P, IGA |
| | C | 2.1 | 2.7 | 2.8 | 30 | Good | P, IGA |
| | D | 0.1 | 0.3 | 0.2 | 30 | Good | |
| 3 | A | 55.2 | 5.0 | 6.0 | 31 | Poor | CC |
| | B | 23.3 | 8.8 | 0.7 | 31 | Good | P, CC, IGA |
| | C | 6.8 | 9.9 | 5.9 | 31 | Good | P, CC |
| | D | 0.2 | 0.2 | 0.2 | 31 | Excellent | |
| 4 | A | 17.5 | 11.1 | 8.9 | 31 | Good | |
| | B | 1.1 | 1.4 | 1.3 | 31 | Good | |
| | C | 0.2 | 0.2 | 0.2 | 31 | Excellent | |

*P is pitting, CC is crevice corrosion, and IGA is intergranular attack.

In agreement with previous studies the corrosion rate of 304L increased with chloride and nitric acid concentrations, which are more aggressive conditions for stainless steel. Extremely high corrosion rates of > 1000 mpy were measured for Solution 2 (10000 ppm Cl⁻) in the dissolver vapor region (A). The corrosion generally decreased at positions farther from the dissolver which also corresponded to decreasing temperature. The corrosion in the scrubber was negligible, although the scrubber coupons for Solution 2 developed a copper/rust colored patina.

The teardrops had corrosion rates higher than the regular or crevice coupons for positions A and B where the temperatures were the highest. This difference occurred for several possible reasons. The teardrop was located in the lowest position on the sample holder and had a wide horizontal section. This exposed a large percentage of the surface area to the hottest gases flowing over the coupons. A difference in material lot may be a small factor since each coupon type came from a different lot of material.

Coupon thickness

Most of the coupons maintained close to their original thickness after testing. Coupons in Position A of Tests 1, and 2 were exceptions. There was significant, widespread thinning of the teardrop in Position A of Test 1 on the unstressed portion of the coupon, with the worst locations losing 24 mils (after 30 cycles). See Figure 3. A small area on the crevice coupon in that same position lost 29.6 mils just outside the crevice assembly.

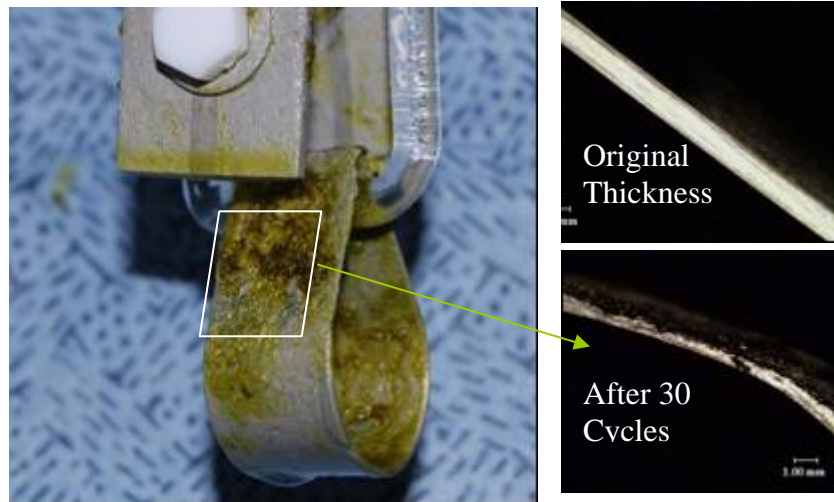


Figure 3. Thinning of Teardrop Coupon in Position A, Test 1

For Test 2, in Position A, the teardrop coupon was completely lost to corrosion. The regular coupon lost approximately 31 mils of thickness and the crevice coupon lost an average 45.3 mils of thickness outside the crevice area. See Figure 4.

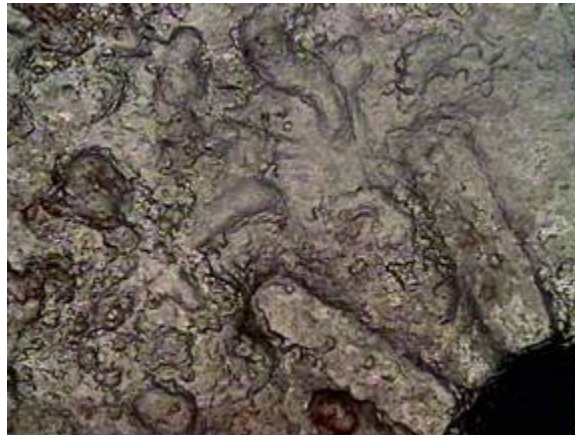


Figure 4. Loss of Material from Crevice Coupon in Position A, Test 2

Localized Corrosion

Localized corrosion occurred in all solutions containing chlorides. Pitting which occurred was either broad and shallow or small, deeper pits. The broad, shallow pits were generally associated with open, unoccluded areas, especially at the higher corrosion rates. The small, deeper pits tended to be associated with deposits on the coupon and along edges. Table 5 contains the average depths of the ten deepest pits on the regular and crevice assembly coupons in each position of Tests 1 and 3. Pits were not measured on the surfaces of the teardrop coupons because of the difficulty of measuring the angled surfaces. However, pitting was worse on them, probably due to the coupons having a somewhat greater horizontal surface (compared to the flat coupons) to collect condensation and deposits. Additionally, pits on coupons from Test 2 were

not measured because Test 2 experienced unacceptably high general corrosion rates. Therefore, the table represents pitting on vertical, unstressed surfaces in Tests 1 and 3.

Table 5. Pitting Depth on Regular and Crevice Coupons in Tests 1 and 3

| Solution | Position | Average Depth of largest 10 Pits (in mils) | | |
|----------|----------|--|------------------|------------------|
| | | Normal Surface | Under Crevice | On Weld |
| 1 | A | ND ¹ | ND ¹ | ND ¹ |
| | B | 2.5 | 3.0 ² | insignificant |
| | C | 1.3 | insignificant | |
| | D | insignificant | insignificant | |
| 3 | A | 0.5 | 2.43 | 0.8 |
| | B | 4.9 | insignificant | 5.4 ³ |
| | C | 8.7 | 2.6 | insignificant |
| | D | insignificant | insignificant | insignificant |

¹The general corrosion rate appears as rapid as the pitting rate. The largest ‘divot’ was measured from original surface to be 29.6 mils.

²There were no significant pits noted but there was one area of ditching along-side the weld that measured 3 mils deep.

³There were no significant pits noted, but there was one area of ditching along-side the weld that measured 5.4 mils deep.

Crevice corrosion under the crevice assembly occurred on several coupons. The corrosion under the deposits was also crevice corrosion and tended to exceed corrosion under the crevice assembly. This difference may be associated with the tightness of the crevice as well as the difference in solution chemistry within the crevice. Crevice corrosion thinned an unstressed area of the teardrop in position A of Test 1 by 24 mils. This corrosion also thinned an area outside the crevice assembly on the crevice coupon in Position A by 29.6 mils. For Test 3, in Position A, there was one thinned area approximately 0.25 inch-square inside of which was a hole penetrating the entire coupon thickness of approximately 54 mils (after 31 cycles). Corrosion may have started at the edge of the coupon and tunneled inwards at this point, but it is more likely that it was crevice corrosion under the deposits covering the surface. See Figure 5.

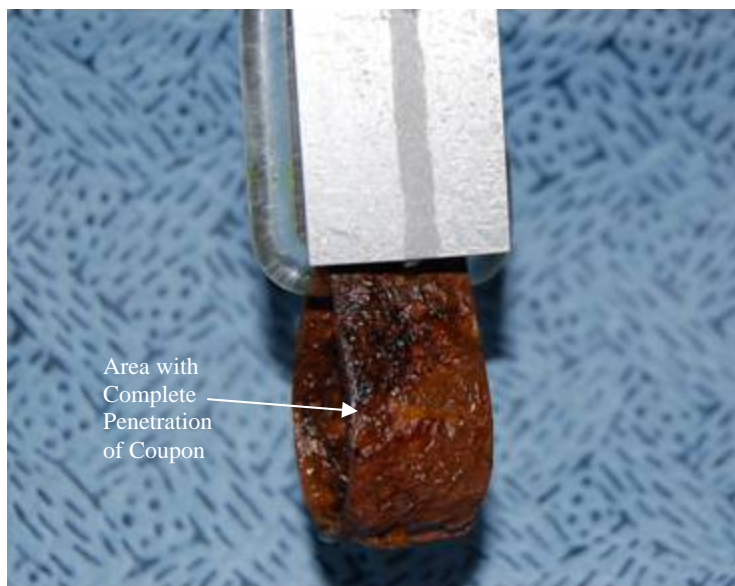


Figure 5. Area of Penetration of Teardrop Coupon in Position A, Test 3

Welds and Stressed Coupon

There was no significant difference between areas of the weld on the regular and crevice coupons and non-welded areas. Areas of shallow ditching right next to the weld were noted in Position B of both Tests 1 and 3. The ditching was contained to one spot each and was no deeper than 5.4 mils.

The stressed areas on the teardrop coupons were not cracked. The most highly tensile stressed portion of the coupons, the side facing out and bent to form the apex, were in better condition than the unstressed portions, in all instances. This is probably because the downward-facing surface did not offer a place for condensation or deposits to cling. Had deposits formed, it may be that pitting would have occurred and eventually led to stress corrosion cracking.

Deposits on Coupons

The coupons in all tests had some amount of salt or deposits form. Qualitatively, the most deposits formed in the apparatus containing Solution 4, which contained only nitric acid and fluoride. Solution 1 also had many deposits, with Solutions 2 and 3 having the fewest. Results from EDS, XRD and XRF analyses showed that these deposits contained an amorphous silicon dioxide. The ICPES results for the final solutions also showed a large amount of silicon in the solution. This silicon resulted from dissolution of the glassware by the nitric acid.

Chemical Analysis of Solutions

Chemical analyses were performed on initial and final solutions to verify chemical composition of the prepared solutions and to evaluate changes in solution composition during the heating process. The initial and final solutions were of the same batch. Condensates and the final

scrubber solution were also analyzed to investigate portioning of chlorides and fluorides. The variation of the data (one sigma) was usually 10-20%. The data are summarized in Table 6.

Table 6. Chemical Analyses of Initial and Final Solutions

| Solution | Nitrate (M) | Free Acid (M) | Chloride (ppm) | | Fluoride (ppm) |
|------------------|----------------|---------------------|-------------------|--------|-------------------|
| | | | ICA | NAA | |
| Initial #1 | 11.1 | 10.2 | 444 | ND | 3180 |
| Initial #2 | 12.8 | 11.2 | 2040 | ND | 1840 |
| Initial #3 | 7.8 | 7.03 | 1140 | ND | 1700 |
| Initial #4 | 12.3 | 10.8 | <20 | ND | 3880 |
| Final #1 | 12.2 | 9.88 | 5390 | 4637.5 | 1070 |
| Final #2 | 11.5 | 9.49 | 17100 | 16875 | 695 |
| Final #3 | 9.4 | 8.01 | 3540 | 3275 | 1790 |
| Final #4 | 12.5 | 11.0 | <20 | 46.25 | 843 |
| Condensate #1 | 2.1 | 2.27 | 11900 | 15500 | 13600 |
| Condensate #2 | 13.2 | 11.5 | 1860 | 1242.5 | 9020 |
| Condensate #3 | 0.3 | 0.33 | 1510 | 1787.5 | 2180 |
| Condensate #4 | 1.8 | 1.34 | <20 | ND | 23600 |

The data for the initial solutions showed that prepared solutions were close to target for the acid concentration, but both chloride and fluoride were variable. The chlorides were lower than target values which may be associated with the release of nitrosyl chloride during the waiting period prior to analysis or it may be that the sodium chloride salt did not entirely dissolve prior to taking the sample (sample taken prior to heatup of solution). In any case, the initial solutions were made fresh and almost certainly contained their target values of chloride (2,000 ppm for Tests 1 and 3, and 10,000 ppm for Test 2).

The fluorides exceeded target concentrations for Solutions #1 and #4 and may have contributed to higher corrosion rates. However, based on experience with these types of samples, accuracy of the analytical method used to quantify the fluoride has not been consistent.

The chemistry of the final solutions showed that there was a loss of both nitric acid and fluoride during the test, which was expected. The samples of the final solutions were taken after approximately eight experiments or 48 hours of runtime. The chloride was found to concentrate in the pot over time and was precipitating out as salts. Assuming the initial chloride concentrations were on target, 66–79% of the chloride passed into the ventilation system, while the rest remained in the simulated dissolver. In previous work, R. A. Pierce determined that 70-100% of chloride in the HB-Line dissolution process would make it past the condenser in the actual vessel vent system [4]. Therefore, the actual HB-Line process may be exposed to more chloride than was simulated in the experiment.

The condensate samples were taken after a single experiment (one six hour run). The measured concentrations had a large variability. Fluorides were highly concentrated in all but Solution #3 which had the lowest molar acid concentration. The condensates were generally of low acidity except for Solution #2 which also had the highest chloride concentration. Chlorides concentrations also had a large range of values with Solution #1 having a surprisingly high value. Condensate volumes varied also, generally decreasing over the course of testing; Solution #1, 120 to 50 ml; Solution #2, 60 to 90 ml; Solution #3, 80 to 20 ml; and Solution #4, 50 to 10 ml.

Differences in Experimental Setup as Compared to the HB-Line Offgas System

There were several differences in the setup of the experiment and the actual offgas system for the dissolver. Some the differences may have had an effect on the results. The differences included the lack of plutonium and gadolinium in the experimental dissolver solution, orientation of the coupon surfaces, the temperature profile across the system, air flow, and evolution rate of chloride from the solution. It should be noted, however, that regardless of the differences, the experiment successfully determined corrosion rates possible when running solutions of the tested chloride and nitrate concentrations.

A conservative difference was the lack of plutonium or gadolinium in solution during the testing. Either will complex with fluoride allowing less of it to be available to the offgas system. The availability of fluoride to the offgas system theoretically increases the corrosion rate [1]. A non-conservative difference between the setup and the actual offgas system was that in testing there were few non-vertical surfaces presented for deposits and condensation to form. The teardrop coupons were the exception with angled surfaces, and they did provide the highest corrosion rates.

Differences in temperature of the system may have had an effect as well. The experiment's dissolver was kept at 105 °C versus the HB-Line dissolver heating to 110 °C or more. This may have affected the evolution of chloride, with the testing being less conservative. The temperature profile across the offgas system was not controlled in the test and therefore the test system may have ran hotter or cooler than the actual HB-Line offgas system. The condenser in each test line was kept at approximately 20 °C, while the HB-Line condensers are kept at 0 °C. Although the warmer temperature in the test may have contributed to higher than expected corrosion rates at the condenser, the corrosion rates in this position and beyond were very low. The highest corrosion rates were found upstream of the condenser. Airflow was not introduced to the experimental offgas system and this too may have affected the corrosion rate in that airflow could provide a drier and therefore less corrosive atmosphere.

Lastly, the rate of chloride evolution may have been different for the experiment than for the HB-Line dissolver. 66-79% of the chloride added to the experimental system evolved from the dissolver solution. In previous work, R. A. Pierce determined that 70-100% of chloride in the HB-Line dissolution process would become available to the offgas system [4]. Because it did not evolve, the chloride in the experiment built up in solution over time and this may have affected the corrosion rate in the offgas.

Conclusions

Table 7 contains expected general corrosion rates in the HB-Line vessel vent system from dissolution of 3013 contents of varying nitric acid and chloride content. These general corrosion rates were measured upstream of the condenser in the experiment's offgas system near the entrance to the dissolver. However, they could apply elsewhere in the offgas system, depending on factors not simulated in the testing, including offgas system temperature and airflow. The rates all came from Position A of the tests, which was closest to the dissolver.

Table 7. Highest Observed General Corrosion Rates

| Test Number | Nitric Acid (M) | Chloride (ppm) | Fluoride (M) | Highest Expected General Corrosion Rate (mpy)* |
|-------------|-----------------|----------------|--------------|--|
| 1 | 12 | 2000 | 0.1 | 334 |
| 2 | 12 | 10000 | 0.1 | >>1061 |
| 3 | 8 | 2000 | 0.1 | 55 |
| 4 | 12 | 0 | 0.1 | 18 |

*The mils per year were calculated assuming continuous operation of the dissolver.

Localized corrosion was significant in Tests One, Two, and Three. It would likely be the first mode of penetration of the coupons in several positions. See Table 8. Test 2 had extremely high general corrosion rates in Position A which prevented pits or crevice corrosion from having an effect.

Table 8. Highest Observed Localized Corrosion Penetration Depths

| Test | Positions with Significant Localized Corrosion | Deepest Penetration, mils | Position of Deepest Penetration | Hours of Operation |
|------|--|---------------------------|---------------------------------|--------------------|
| 1 | Pre-condenser | 29.6 mils | Entrance to offgas system | 180 |
| 2 | Pre- and post-condenser | <11 mils | Entrance to condenser | 180 |
| 3 | Pre- and post-condenser | 54 mils; full penetration | Entrance to offgas system | 186 |

There was no significant difference in corrosion between weld areas and non-welded areas on coupons. There was also no significant attack on the stressed portions of the teardrop coupons used in the various portions of the experimental offgas system. It is probable, however, that this was because the tensile stressed areas were facing downwards and therefore offered no place for condensation or deposits to form. Had deposits formed on the stressed area, pitting may have occurred and led to stress corrosion cracking. The significant localized corrosion observed was always associated with deposition of materials from the offgas.

The tests represent conditions that could exist in the HB-line vessel vent system while processing 3013 contents with various concentrations of nitric acid and chloride. The four positions in which the coupons were placed were A) above the vessel vapor space, B) the inlet to the

condenser, C) downstream from the condenser, and D) in the scrubber solution. The names of these positions do not necessarily represent the same locations in the actual HB-Line vessel vent system, but instead represent conditions that can exist at various points inside the system, depending on a combination of similar distance, temperature, and airflow conditions. Because of this, it is recommended that the corrosion rates in Position A of the tests be considered as possible inside the vessel vent system itself, and not just in the dissolver vapor space.

General corrosion at 10,000 ppm chloride was shown to be extremely high. Localized corrosion caused deep penetration of the coupons when heating a solution of 2000 ppm chloride, both at 12 M and 8 M nitric acid. It is suggested that when running chloride-containing solutions, the pre-condenser side of the vessel vent system be inspected at a frequency dependent on acceptable material losses and expected general corrosion rate. The presence of deposits and heavy condensation during inspection should be taken as indicators of possibly severe localized corrosion in those areas.

It is possible that the rates as listed are too conservative and the conditions under which they are possible would not exist in the vessel vent system. The vessel vent system, for instance, may be cooler or drier than the experimental setup. It may also be that fluoride is not available to the vessel vent system in the same ratios due to its complexing with plutonium or gadolinium. The testing at SRNL did not simulate the actual temperature and airflow conditions that would be expected in the vessel vent system. It also did not simulate dimensional specifications that may influence the presence of heavy condensation in position A of the tests. If it is requested, SRNL could perform another test trying to simulate more precisely the conditions that exist in the vessel vent system, especially the point of concern that is closest to the dissolver. The temperature, airflow, and spatial ratios would be simulated or scaled in the test to match actual conditions as closely as possible. The availability of fluoride to the offgas would also be considered.

References

- 1) J. I. Mickalonis, "Steel Corrosion in Nitric Acid Solutions Containing Chlorides and Fluorides," WSRC-STI-2007-00075, February, 2007.
- 2) B. F. Dunnett, G. O. H. Whillock, "Intergranular Corrosion of Stainless Steels: A Method to Determine the Long-Term Corrosion Rate of Plate Surfaces from Short-Term Coupon Tests," Corrosion, Volume 59, pp. 274-283, National Association of Corrosion Engineering, Houston, Texas, March, 2003.
- 3) F. Balbaud, G. Sanchez, P. Fauvet, G. Santarini, G. Picard, "Mechanism of Corrosion of AISI 304L Stainless Steel in the Presence of Nitric Acid Condensates," Corrosion Science, Volume 42, pp. 1685-1707, Pergamon-Elsevier Science Ltd, Oxford, England, October 2000.
- 4) R. A. Pierce, "Chloride Distribution During Dissolution in Nitric Acid Solutions," WSRC-STI-2007-00273, May, 2007.
- 5) Private Communication (JIM) with D. P. Lemonds, September, 2007.

APPENDIX I
Solution 1: 12 M HNO_3 , 2000 ppm Cl^- , 0.1 M F

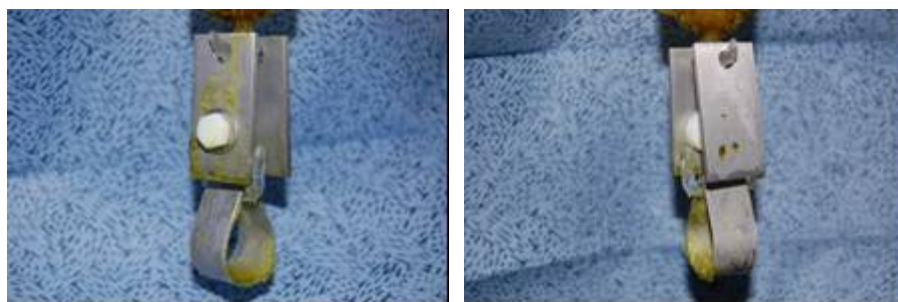


Figure 6. Test 1 Post Condenser

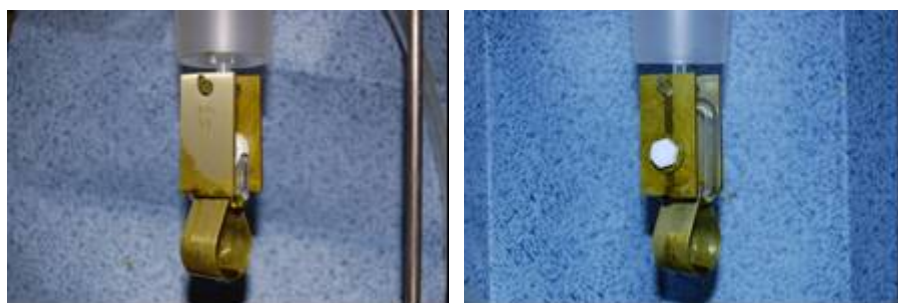


Figure 7. Test 1 Condenser

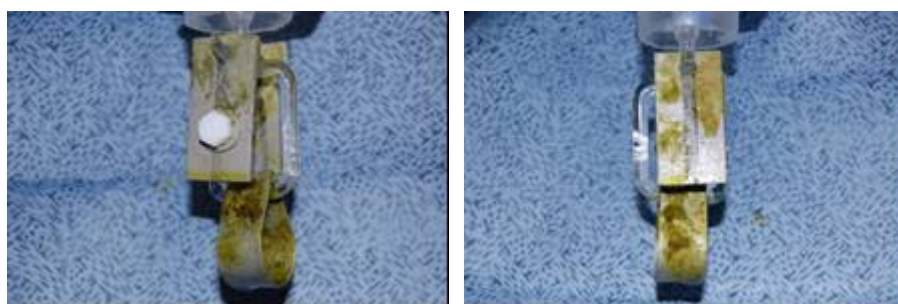


Figure 8. Test 1 Vessel Vapor



Figure 9. Test 1 Scrubber

Solution 2: 12 M HNO₃, 10000 ppm Cl⁻, 0.1 M F⁻

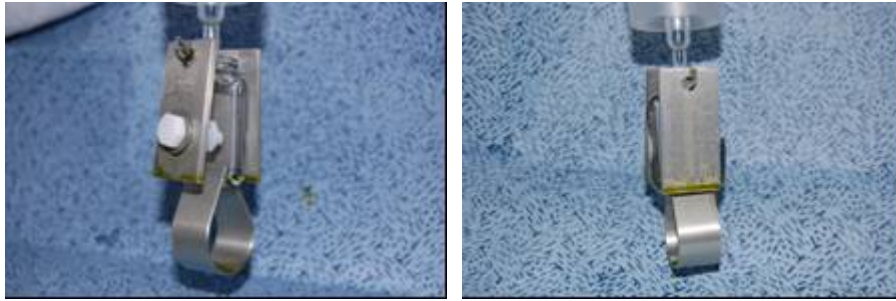


Figure 10. Test 2 Post Condenser

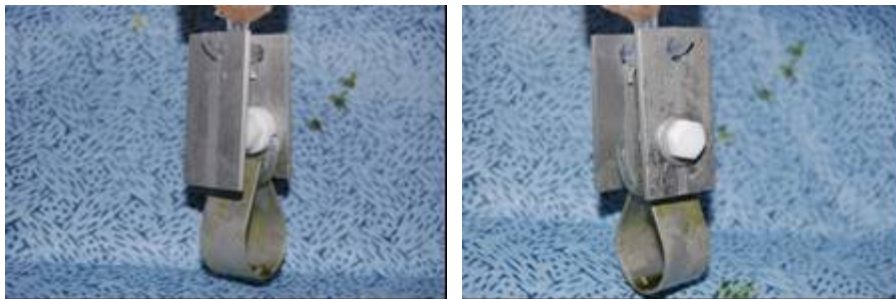


Figure 11. Test 2 Condenser

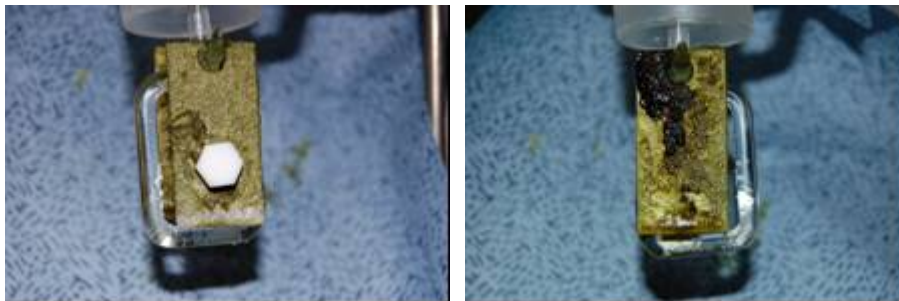


Figure 12. Test 2 Vessel Vapor

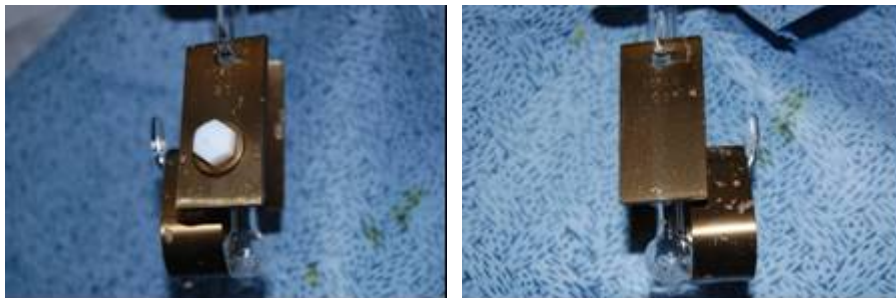


Figure 13. Test 2 Scrubber

Solution 3: 8 M HNO₃, 2000 ppm Cl⁻, 0.1 M F⁻



Figure 14. Test 3 Post Condenser



Figure 15. Test 3 Condenser

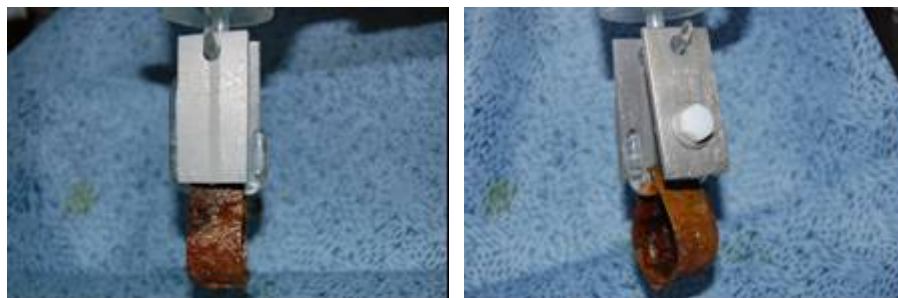


Figure 16. Test 3 Vessel Vapor

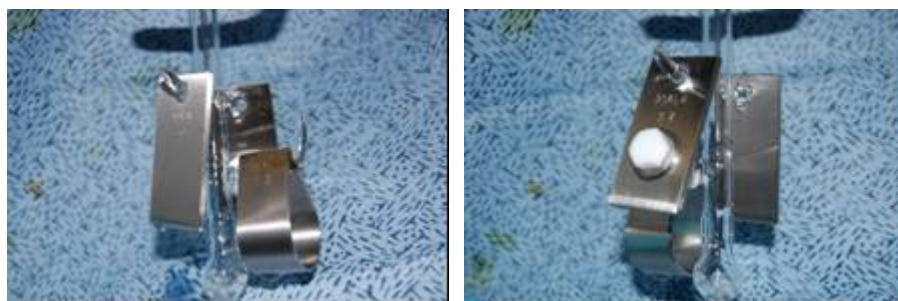


Figure 17. Test 3 Scrubber

Solution 4: 12 M HNO₃, 2000 ppm Cl⁻,



Figure 18. Test 4 Post Condenser



Figure 19. Test 4 Condenser

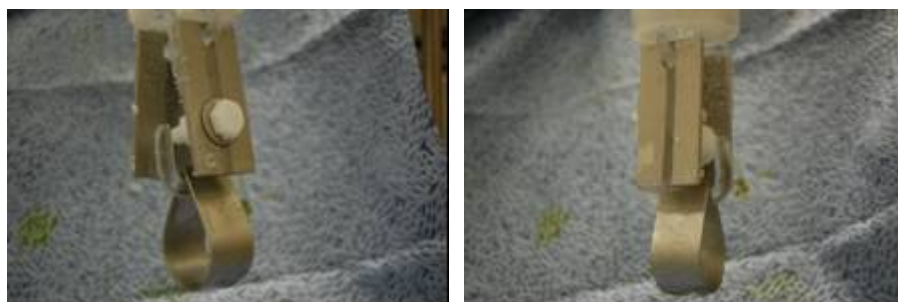


Figure 20. Test 4 Vessel Vapor

No scrubber samples

APPENDIX II

Table 9. General Description of Corrosion at Each Position for HB-Line Off-gas System

| Solution | Position | Description |
|-------------|--|--|
| 1 | A | Significant thinning in localized areas, pitting, less thinning under crevice ferrous corrosion products, rust staining along weld, possible IGA |
| | B | Pitting, especially under salt deposits, thinning, crevice corrosion |
| | C | Pitting in areas associated with salt deposits, no crevice corrosion, rust staining and some pitting along edges |
| | D | Shiny metallic finish, no pitting or crevice corrosion |
| 2 | A | Severe thinning, shallow pits, no crevice corrosion, weld greater corrosion |
| | B | Corrosion associated with deposits or pooled solution, pitting and IGA, Rust staining, no crevice corrosion |
| | C | Non uniform corrosion, pitting and IGA where solution collected, rust staining |
| | D | Covered with copper/rust colored patina, no localized corrosion |
| 3 | A | Mottled appearance, crevice corrosion, penetration of teardrop coupon |
| | B | Mottled appearance, broad shallow pits, possible IGA, some crevice corrosion Heavy corrosion along edge, pitting especially along edge and in weld, some crevice corrosion |
| | C | Shiny metallic finish, no pitting or crevice corrosion |
| | D | Shiny metallic finish, no pitting or crevice corrosion |
| 4 | A | Welds etched, some rust staining in weld, corrosion greater under deposits some corrosion along edge of crevice |
| | B | Slight mottled appearance, some rust staining along bottom edge |
| | C | Shiny metallic finish, no pitting or crevice corrosion |
| Solution 1 | 12 M HNO ₃ , 2000 ppm Cl ⁻ , 0.1 M F ⁻ | |
| Solution 2 | 12 M HNO ₃ , 10000 ppm Cl ⁻ , 0.1 M F ⁻ | |
| Solution 3 | 8 M HNO ₃ , 2000 ppm Cl ⁻ , 0.1 M F ⁻ | |
| Solutions 4 | 12 M HNO ₃ , 0.1 M F ⁻ | |
| Position A | Dissolver Vapor Space | |
| Position B | Condenser | |
| Position C | Post Condenser | |
| Position D | Scrubber | |