Prediction of Dissolver Lifetimes Through Non-Destructive Evaluation and Laboratory Testing

J. I. Mickalonis
Savannah River National Laboratory
Materials Science and Technology
Aiken, SC 29808

W. R. Hinz
Savannah River National Laboratory
Materials Science and Technology
Aiken SC 29808

T. D. Woodsmall
Savannah River Nuclear Solutions
NNSA Programs
Aiken, SC 29808

T. Edwards
Savannah River National Laboratory
Computational and Engineering Sciences
Aiken, SC 29808

Abstract

Non-destructive evaluation was used as the primary method of monitoring the corrosion degradation of nuclear material dissolvers and assessing the remaining lifetimes. Materials were typically processed in nitric acid based (4-14M) solutions containing fluoride concentrations less than 0.2 M. The primary corrosion issue for the stainless steel dissolvers is the occurrence of localized corrosion near the tank bottom and the heat affected zones of the welds. Laboratory data for a range of operational conditions, including solution chemistry and temperature, was used to assess the impact of processing changes on the dissolver corrosion rate. Experimental and NDE-based general corrosion rates were found to be in reasonable agreement for standard dissolution chemistries consisting of nitric acid with fluorides and at temperatures less than 95 °C. Greater differences were observed when chloride was present as an impurity and temperatures exceeded 100 °C.

Keywords: Stainless steel, nitric acid, corrosion rate prediction

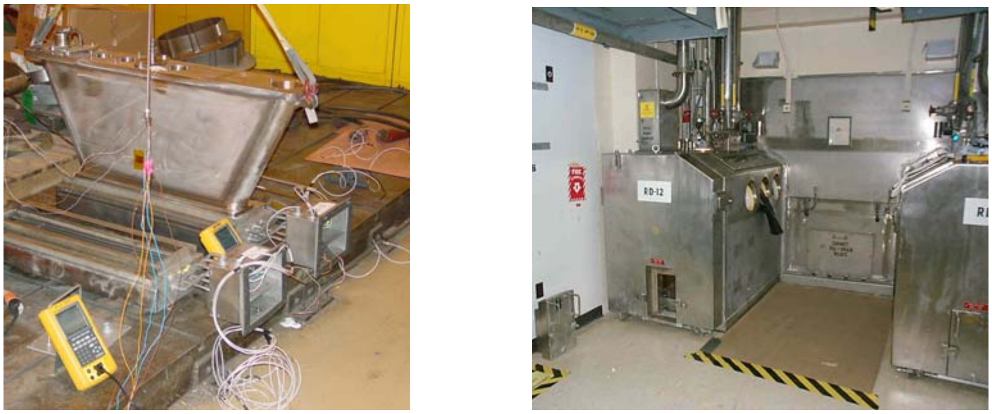
Introduction

For over fifty years at the Savannah River Site, processing of nuclear material has taken place in stainless steel vessels with nitric acid based flow sheets of variable strength depending on the material being processed. One facility was installed in the early 1980s to support the production of plutonium-238 (Pu-238) as a power source for deep space exploration and to recover legacy nuclear materials stored at the site. The facility adopted a "run to failure" approach to dissolver vessels and processed successfully with manageable failures until recent years when the dissolver vessels started failing at significant rates when processing difficult material requiring extremely aggressive flow sheets. Failures led to unplanned outages which negatively impacted the production schedule and required hazardous work to replace the vessels. A three-prong approach was used to understand the failures and to estimate future lifetimes so outages could be planned to support production schedule.

Since the cause of failure was assumed to be corrosion, although the exact mechanism was not known, non-destructive evaluation (NDE) techniques were used to asses the dissolvers and estimate lifetimes through measurements of wall thickness. Laboratory corrosion testing was also initiated to support future flow sheets and estimate the damage impact on the dissolver vessels as well as the off-gas system and other supporting equipment. Additionally, statistical analysis was used with laboratory and literature data to determine equations for estimating corrosion loss as compared to NDE measurements. This paper describes the outcome of this approach in estimating dissolver lifetimes.

Dissolver Description

The dissolver is a narrow trapezoidal-shaped vessel of nominally 30 liters and constructed of 304L stainless steel (304L). The facility was originally equipped with four dissolvers in two identical lines, but only one line (two dissolvers) have been in service since the mid 1980's. Figure 1 shows a dissolver during mock up and the active glove boxes where the dissolvers are located during processing. The dissolver is placed on a heater block in the glovebox and heat transfer is largely achieved with a combination of conduction and radiation. Single plane heating drives a distinct temperature profile vertically through the vessels.



(A) (B)

Figure 1 Pictures of A) a dissolver during mock up and B) gloveboxes where dissolvers are located during service.

A vessel is constructed from several pieces. The bottom is made of either a heavy plate or forging, which is machined out to have a cylindrical shape with hemispherical ends. The centerline of the bottom has a nominal thickness of 0.5 in at the thinnest point. The side or shell walls are constructed from plates with nominal thickness of 0.375 in. The wall ends are made of annealed pipe halves. All sections are joined by welding with 308L weld filler metal. All cut edges of plate and exposed ends of pipes are overlaid with weld metal to minimize end grain exposure. The interior vessel dimensions are approximately 3 in wide, 20 in deep, 29 in long at the bottom and 44 in long at the top. Non-idealities in the design were necessitated by safety considerations to mitigate potential nuclear criticality events. Additionally, the interior width had to be maintained below a maximum value to avoid such events.

The dissolver has several pieces of equipment and instrumentation that are exposed to the solution and inserted through openings in the top. Material to be dissolved is charged into the vessel through a charging funnel at the penetration labeled F in Figure 2. An agitator is labeled J and is used for solution mixing during dissolution. Opening N contains the 0.5-in tubing for solution transfer. Opening E is the connection to the off gas system. Other openings are for the high level probe, thermowell, and level instrumentation dip leg (these instruments not shown).

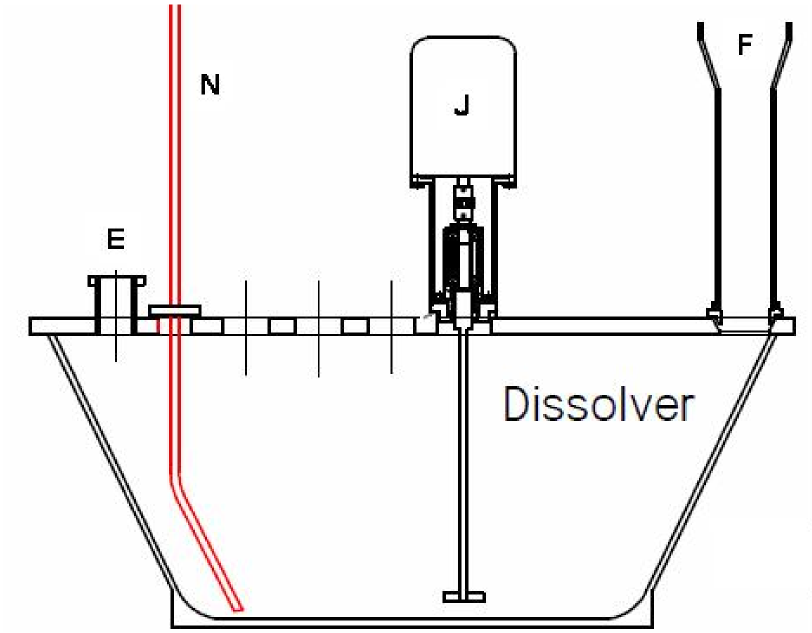


Figure 2 Dissolver schematic showing location of components.

During dissolution, glove box air is drawn into the dissolvers and exits, along with hot gases generated by the dissolution process, into the stainless steel off gas system. Condensers return acid to the vessels that are evaporated (or boiled) during the heating cycle. Chlorides present in the dissolver feed are also volatilized and may become deposited in the piping system above the dissolvers. Since the temperature is much less in the off gas system piping, significant corrosion has not been observed.

After dissolution, the contents of the dissolvers are allowed to cool and are then transferred via suction into one of two stainless steel product hold tanks. While these tanks experience acid concentrations similar to those in the dissolvers, the low temperature provides a much less corrosive environment and no leaks have occurred. In addition, a significant portion of the fluorides used as catalysts in the dissolution process are consumed before they reach the product hold tanks and this helps to preserve these vessels as well. To date, the dissolvers and associated equipment are the only parts of the system that have required replacement due to corrosion.

Dissolver solutions are typically nitric acid and generally contain fluorides to aid in catalytic dissolution as shown in Table 1. Over the last five years, acid concentrations have ranged from 4 to 14M and fluoride concentrations have generally been about 0.1 M. Potassium fluoride has been the source of fluorides. Temperatures have ranged from 90 °C to boiling. The most recent feed materials have been very difficult to dissolve (condition #7 in Table 1) and the flow sheets have been correspondingly aggressive. This is contributory to the accelerated corrosion and recent failures.

Table 1. Dissolver Operating Conditions

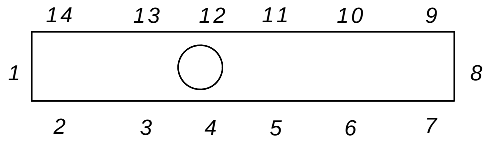
Condition	Acid (M)	KF (M)	Temp (C)	Time (hr)	Chloride (ppm)
1	0.5	0	Boiling	4	0
2	3-4	0	90-100	4	0
3	12-14	0	100	4	0
4	14	0.06	115	4	0
5	14	0.1	Boiling	4-6	0
6	14	0.1	60/80	2/2	0
7	12	0.2	110	12	10-3000

Non-Destructive Evaluation Techniques

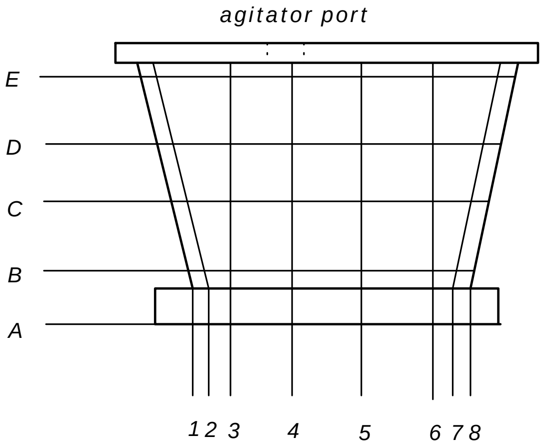
The NDE techniques that were used to inspect the dissolver and to assess dissolver integrity were ultrasonic testing (UT) and video examination. Both techniques were performed remotely. For the video inspection an assortment of cameras were used with different levels of resolution. Dissolver videos were difficult to interpret at times because of misleading shadows produced by the location of the light on the same arm as the camera.

The UT measurements were made to measure wall thickness. After the initial failure, UT wall thickness measurements were obtained on vessels prior to putting into service (preservice or baseline) so more precise data than nominal thickness values were available for assessing the interior width and corrosion of the dissolver walls. On the new vessels, UT measurements were made on the exterior of the dissolver at numerous locations across the sidewall and along the center line of the bottom plate. Measurements were made only on the centerline because of the curvature of the bottom plate. Figure 3 shows the initial measurement locations. For the first two failed vessels, UT measurements were also made on the exterior with no measurement being made on the bottom plate since the dissolver vessels were located in the glove box.

In order to measure and monitor the bottom thickness and lower shell walls in-situ , UT measurements needed to be performed from inside the tank, preferably with a non-contact technique. The method involved filling the tank to approximately 3/4 full with process water (0.5 M nitric acid) and using one or more ports of entry at the tank top for installation of the manipulator tool and probe. The bottom was also cleared of sludge by flushing of the dissolver with process water.



TOP VIEW



SIDE VIEW

Figure 3 Schematic drawing of dissolver showing locations for exterior UT measurements [10,11].

Figure 4 shows a drawing of the tool. The water acted as a reliable couplant for the UT probe. The probe was manipulated with the custom tooling to measure continuously along the shell wall to the shell/bottom weld. The probe was swiveled 90 degrees to take a measurement at the tank bottom center line. The probe was returned to the initial position and rotated 180 degrees to allow measurements up the opposite side shell wall. The probe could be moved to another port opening in the top plate to measure at different locations along the wall.

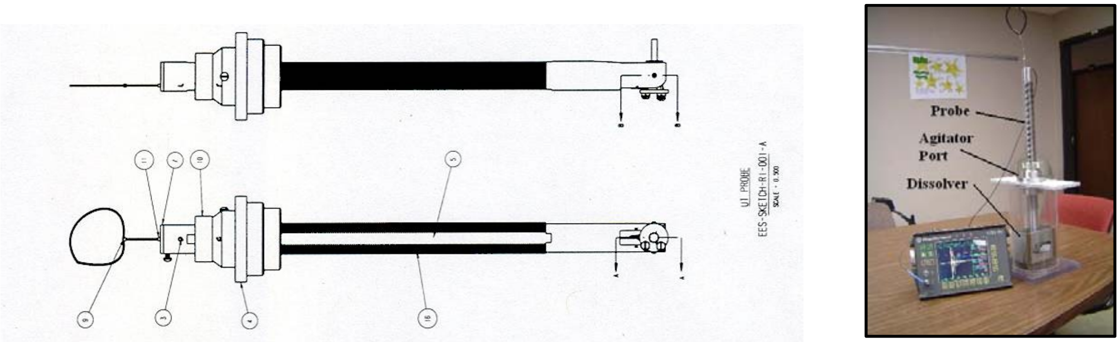


Figure 4 Drawing of Manipulator Tool and UT Probe and Mock Set Up

Compared to contact examination from the exterior, this method allowed use of a higher sensitivity spherically focused probe. The interior method also was easier than exterior measurements from the end panel of the glovebox and eliminated the need to open up the cabinet and to construct containment huts. This probe provided an improved signal to noise ratio by eliminating near field effects, permitted more consistent coupling and most importantly, provided a bottom thickness measurement of the tank. The interior UT measurement has a resolution of approximately 0.1% of thickness.

This approach provided excellent repeatability for trending degradation over time as measurements are compared from the exact same locations. Thickness data were continuous down the entire tank height for a complete wall thickness profile. The measurement locations ranged from approximately 11 in from the bottom (7 in from the top) of the dissolver tank to 2.5 in from the bottom (16 in from the top). As the inner surface begins to curve, forming the bottom of the dissolver, the inner and outer walls are no longer parallel, and the UT probe can no longer accurately measure wall thickness. The vertical interval of the measurements was every 0.25 inches.

Laboratory Testing

The corrosion testing was performed to estimate corrosion rates for conditions where literature or previous data did not exist. The testing was conducted following the ASTM standard G31, “Standard Practice for Laboratory Immersion Corrosion Testing of Metals.” The test parameters and values were temperature (80, 95, and 110 °C) and concentrations of nitric acid (6, 8, 12, and 14 M), fluoride (0.01, 0.1 and 0.2 M) and chloride (100, 350, 1000, and 2000 ppm). The values were chosen to establish a statistical test matrix that bracketed a target dissolver condition of 12 M nitric acid, 1000 ppm chloride, 0.1 M fluoride, and 95 °C. Test periods were generally six hours to simulate the dissolution process. The test samples were 304L stainless steel rectangular coupons with and without a weld, which was either an autogenous or butt weld. The complete description of the corrosion experiments was given previously.[1] The generated results were analyzed to model the corrosion in the identified parameter space.

Statistical Analysis

Prior to using UT data for estimating corrosion degradation and remaining life, statistical models for predicting corrosion rates were composed based on the available SRS laboratory data as well as literature corrosion rates. As input to the model, a corrosion analysis first considered the operable corrosion mechanism, documented corrosion rates, and known histories of exposure. The models estimated the corrosion impact and was validated with follow up inspections of the dissolvers.

The operations department provided the known histories after an evaluation of the dissolver operation records. These data are summarized in Table 1. Historically, dissolver vessels were exposed to nitric acid solutions with or without potassium fluoride additions and for a range of temperatures. The processing conditions were dependent on the type of material to be dissolved.

More recently the dissolvers were used for processing more impure materials, so chlorides from the material became significant components (100-3000 ppm) of the solutions.

At first a model was developed for dissolutions that were chloride free (conditions 1-6 in Table 1). The available literature and laboratory data are shown in Figure 5, which shows a large spread in the measured corrosion rates (CR). To develop this model, JMP's stepwise regression platform was used to select the important terms from the set of candidate terms provided by a response surface model in the 3 factors (i.e., Acid, KF, and T).[2]

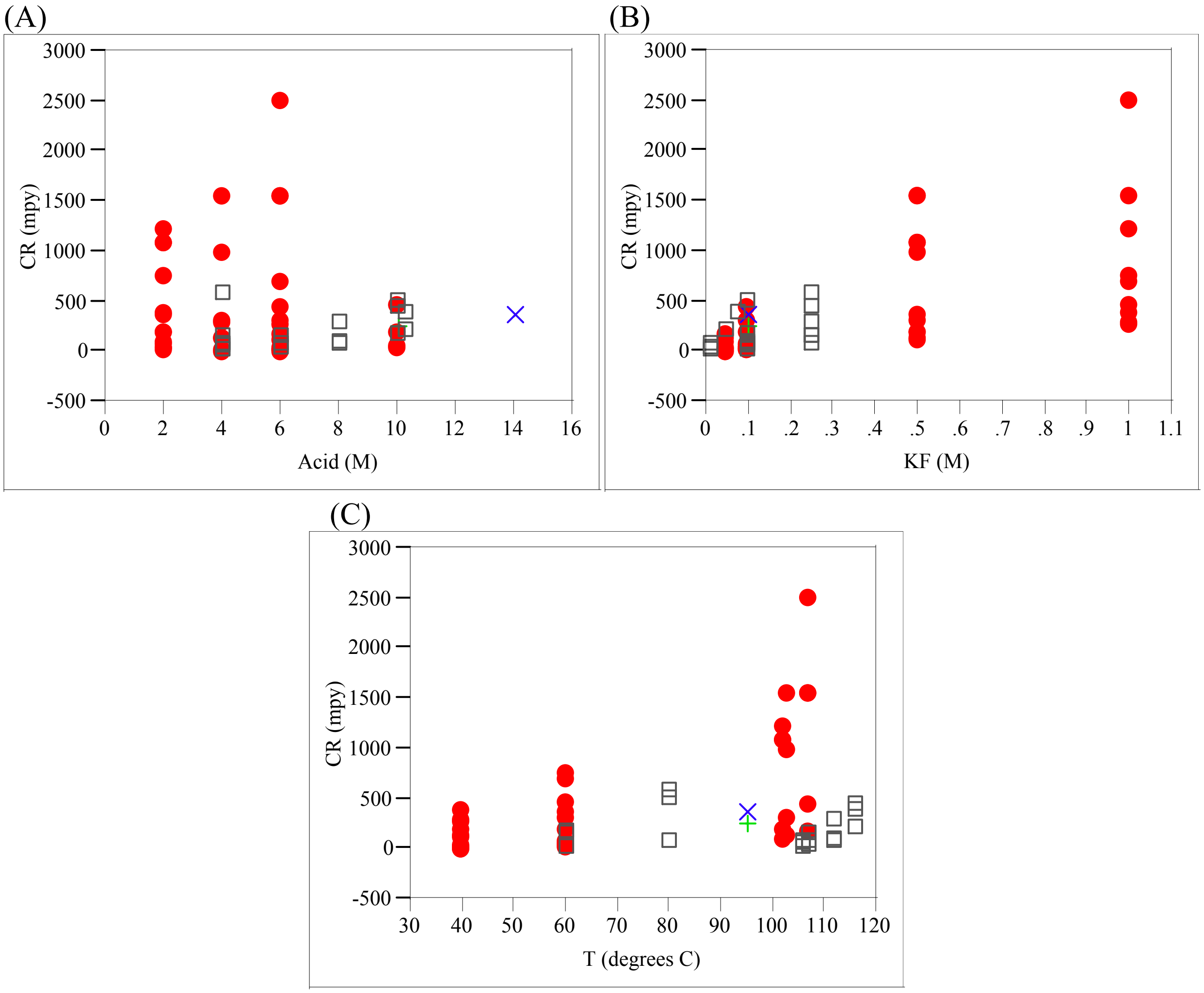


Figure 5 Plots of Corrosion Rate Data Used In Statistical Analysis: (A) Nitric Acid Concentration; (B) Potassium Fluoride Concentration; and (C) Temperature.

A response surface model is a model that includes terms for an intercept, for each of the factors, for each possible two-way interaction between pairs of factors, and for each factor squared (a total of 10 candidate terms). The natural logarithm of the CR value was used as the response variable since the resulting models were an improvement over the models developed using the CR values. The model was given by Equation (1).

$$\ln(CR) = \beta_0 + \beta_1(\text{Acid}) + \beta_2(\text{KF}) + \beta_3(\text{T}) + \beta_4(\text{Acid-KF}) + \beta_5(\text{Acid-T}) + \beta_6(\text{KF-T}) + \beta_7(\text{Acid})^2\ \beta_8(\text{KF})^2 + \beta_9(\text{T})^2 + \varepsilon \qquad \{\text{Equation 1}\}$$

where the β's represent the unknown coefficients and ε represents the error term of the model.

The regression routine was used to down select from this set of candidates to a smaller number of statistically significant terms. For the complete data set, an R^2 value was approximately 85%. When the data set was reduced to those literature sources providing complete experimental conditions, such that no assumptions were necessary about one of the factors (Acid, KF, temperature), the R^2 value increased to 97%.

The second model was based solely on SRS laboratory data for chloride bearing dissolution solutions that were target around the expected operational conditions for the chloride bearing material, which initially were 12 M nitric acid, 1000 ppm chloride, 0.1 M fluoride, and 95 °C . The actual operational conditions shifted to a higher fluoride concentration (0.2 M) and higher temperature (100-110 °C). The testing was executed per a 2^3 factorial design with one center point to provide data for a regression model. Two additional points at 8 and 12M nitric acid with 350 ppm chloride were added during testing. The regression analysis was similar to that of the first model.

The significant variables affecting the corrosion rate were evaluated including temperature and the concentrations of fluoride, chloride and nitric acid as well as any interactions between these variables. The temperature was the most important variable. Some interactions were also significant. For the liquid exposure, the acid/fluoride and chloride/fluoride interactions were important, whereas for the vapor only the chloride/fluoride interaction was significant. With all the data analyzed together, temperature and fluoride concentration were the significant primary variables. Acid and chloride concentrations were not significant although the interactions of these variables with fluoride were important. The models differed slightly for the liquid and vapor exposure. The liquid model predicted 90 % of the data and the vapor model approximately 80%. The model for the liquid exposure was given by Equation 2.

$$CR = \text{Exp}(-1.0726 + 10.4696\ F + 0.0516\ T - 0.9106\ (A-10.1176)(F-0.1259) + 0.0037\ (C-958.824)(F-0.1259)), \qquad \{\text{Equation 2}\}$$

Model/Measurement Comparison – Nitric Acid- Fluoride Chemistry

The baseline corrosion rate of the dissolver is established by the solution, which is typically high molar nitric acid containing fluoride. For 304L, corrosion rates increase with rising nitric acid and fluoride concentrations.[3] The dissolver corrosion rates were also affected by the operating temperature. Rates above 60 °C became detrimental to the dissolver at the necessary operating times to perform dissolutions. Corrosion studies performed at SRS around 1960 showed that corrosion rates of 304L nearly doubled with 20 °C increases in temperature. Data for a solution consisting of 8M nitric acid with 0.2 M fluoride are given in Table 2. Using Equation 1 for chloride-free dissolution. the model predicted a general corrosion rate range for the same chemistry and an operating temperature of 95 °C of 261 to 531 mils per year (mpy). All corrosion rates were measured without heat transfer and service conditions.

Table 2
Corrosion Rates of 304L Stainless Steel in 8M NO_3^- with 0.2 M F^-

Temperature (C)	Corrosion Rate (mpy)
24	<10
40	25-50
60	50-100
122	>500

Heat transfer across the bottom surface and service conditions further complicate determining the corrosion rate or mechanism without actual measurements. Localized corrosion mechanisms were particularly of concern, including pitting, intergranular attack (IGA) or crevice corrosion because these forms of corrosion are currently unpredictable and may accelerate rapidly. Literature and laboratory data were not available to aid in determining these effects. Heat transfer will cause changes in the local chemistry by altering the diffusion characteristics and solubility of solution constituents.[4] These effects differ if heat transfer occurs during boiling. Fabrication and service parameters, such as welding procedure and incomplete solution transfer alter both material and environmental conditions.

General corrosion rates based on actual thickness measurements of the shell wall yielded similar rates to Equation 1 results. The UT measurements of a dissolver in service for approximately five years are shown in Table 3. The measurement locations are shown in the schematic in Figure 3. The measurements were made at the bottom (A, 2000 only, as-received), at different heights along the shell wall (B-E), and around the perimeter of the dissolver (1-14). Fewer measurements were made in 2005 because of the difficulty of making measurements in the glovebox. The initial shell wall measurements were close to the nominal value of 0.375 in. The bottom center line measurements were found to about 0.1 in greater than the nominal value of 0.5 in. The centerline is the only position on the bottom measured with UT because at all other locations the inner and outer walls are not parallel due to the cylindrical shape of the bottom.

Table 3
Initial and Final Thickness Measurements of a Dissolver Vessel*

Position	1	2	3	4	5	6	7	12	13	14
A (2000)		0.58	0.58	0.581	0.577	0.58	0.567			
B (2000)	0.387	0.383	0.378	0.375	0.376	0.376	0.374	0.374	0.374	0.376
C (2000)	0.389	0.375	0.375	0.374	0.374	0.374	0.376	0.38	0.38	0.376
D (2000)	0.389	0.38	0.38	0.38	0.38	0.38	0.38	0.378	0.376	0.377
E (2000)	0.389	0.379	0.376	0.376	0.374	0.374	0.374	0.376	0.376	0.383
A (2005)										
B (2005)	0.274	0.296	0.291	0.284	0.291	0.284	0.278	0.288		0.304
C (2005)	0.311	0.283			0.298	0.31			0.282	0.314
D (2005)	0.319	0.293	0.283				0.296			
E (2005)	0.312									

* Measurements for positions 8-11 are not shown since no measurements were made in 2005.

For the five years of operation, the dissolver had approximately 1648 hours of operation. Based on this value and the average UT measurements for B and D locations, the estimated general corrosion rates are 245 and 197 mpy, respectively. These rates are near the lower end of the range calculated from the model. The shell wall corrosion is reasonably approximated by laboratory data for general corrosion. The general corrosion rate, however, does not provide any information as to the extent of localized corrosion occurring in the dissolver at locations not accessible by exterior UT measurements. These locations include the tank wall shell-to-bottom weld and the entire tank bottom section. Localized corrosion phenomenon, such as pitting and IGA, may be leading to faster penetration than general corrosion since failures were occurring near seam welds.

Model/Measurement Comparison – Nitric Acid- Fluoride-Chloride Chemistry

At the start of processing chloride-bearing nuclear material, corrosion rates for the solution chemistries were unknown so UT measurements were set up as a monitoring tool for the dissolver vessels. A total of four different vessels were used during this processing with two vessels running simultaneously. For the first two vessels that failed during the processing of this material, UT measurements were made prior to the start of processing and once the vessels failed. For the two replacement vessels, the UT measurements were performed more frequently and usually associated with process or chloride concentration changes. The measurements for one vessel over three interval inspections is shown in Figure 6.

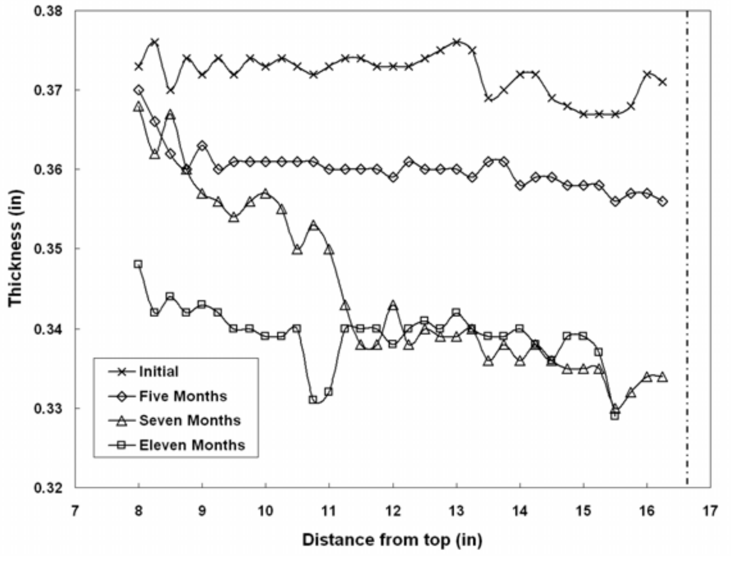


Figure 6 Wall thickness measurements of a dissolver vessel wall after various time periods.

The wall thickness measurements were used to estimate the corrosion rate in the solution and predict the remaining lifetime. For each time interval the actual hours of operation differed which impacted the actual wall loss. As can be seen in the figure, the wall loss was generally variable down the wall with greater losses being closer to the seam weld between the wall and tank bottom. The dotted line in the figure is the approximate location of the weld. For the eleven-month inspection, thickness measurements could not be made near the weld which was believed to be associated with increased scatter of the signal from a greater amount of intergranular attack. This hypothesis could not be confirmed by visual examination because of the limited resolution of the camera.

The corrosion rates varied with both the wall location and the time of exposure. In Table 4, the corrosion rates are shown for the thickness measurements presented in Figure 6 at several locations down the wall as measured from the dissolver top. As can be seen in Figure 6, the thickness measurements for the seven and eleven months inspections were similar at locations between 11 and 15 inches from the top. This similarity lead to minimal or negative corrosion rates. The corrosion rates increase with distance from the top or at distances closer to the bottom where the temperatures are higher. The corrosion rates were also higher with time of exposure, but as can seen by the data in the table this was not consistent at each location. This inconsistency in the data is attributed to the variability in both the thickness measurement as well as the precision of relocating the UT probe for each inspection.

Table 4
Calculated Corrosion Rates of a Dissolver Vessel Based on UT Wall Thickness Measurements

Distance from Top (in)	Corrosion Rates (ipy)		
	5 Months	7 Months	11 Months
8.5	0.3	-0.3	1.5
10	0.4	0.2	1.2
11.5	0.5	1.0	0.3
13	0.6	1.3	-0.2
14.5	0.4	1.4	0
16	0.5	1.4	ND

When applying Equation 2 to predict the corrosion rate for the dissolver when chlorides are present, some estimate was needed for the chloride concentration because the exact chloride concentration of the material charged to the dissolver was not know and chemical analysis of the solution were not made for chloride concentration. The material charged to the dissolver was generally part of a lot for which some measure of chloride concentration was known. Initially, a chloride limit of 100 ppm was set for dissolutions. For the dissolutions between the seven and eleven month inspection, the chloride limit had been raised to 2000 ppm.

In using Equation 2, the limits were taken as chloride concentration to produce the most conservative estimate. The estimated corrosion rate was 0.6 ipy and 1.0 ipy for 100 and 2000 ppm chloride, respectively, with 12 M nitric acid, 0.2 M fluoride and an approximate temperature of 100 °C used for the other parameters. The equation produces a reasonable estimate for the five-month inspection and the eleven-month inspection results. The data from which equation 2 was modeled were from coupons after only one exposure period so limits application to subsequent exposures. Not having a a specific temperature profile for the wall temperature also limits the model estimates.

Conclusions

The statistical models for predicting the general corrosion rates were in reasonable agreement with the values calculated from UT measurements of wall thickness made during operation of nuclear material dissolver. The UT measurements gave a real snapshot of the variations in the thickness of the dissolver walls and the width of the dissolver, which was important for nuclear criticality issues. Both the model and the UT measurements, however, were not utilized to estimate or measure the localized corrosion rate, i.e. IGA, which was the hypothesized failure mode.

Acknowledgements

The authors wish to acknowledge the support of the Department of Energy through contract number DE-AC09-08SR22470.

References

1. J. I. Mickalonis, “Testing of 304L Stainless Steel in Nitric Acid Environments With Fluorides and Chlorides,” CORROSION/2011, paper no. 19237 (Houston, TX: NACE International), 2011.

2. SAS Institute, Inc., JMP™ Version 5 Statistics and Graphics Guide, SAS Institute, Inc., Cary NC, 2002.

3. P. M. Kranzlein et al, "Corrosion of Stainless Steel In HNO3-HF Solutions," DP-486, 1960.

4. T. K. Ross, “Corrosion and Heat Transfer – A Review,” British Corrosion Journal, Vol. 2, 1967.