LA-UR-17-28647
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Author(s): Hyer, Holden Christopher
Duque, Juan
Smith, Paul Herrick
Stroud, Mary Ann

Intended for: Report

Issued: 2017-09-22

Effects of Laser Etching on the Corrosion Susceptibility of SAVY 4000 and Hagan Containers

Holden Hyer, Juan Duque, Paul Smith, and Mary Ann Stroud

Introduction

1. SAVY 4000 and Hagan Containers

Since the late 1990's, the Hagan container was used as the primary container for packaging of plutonium-bearing materials. The Hagan design consisted of a threaded closure, a Viton® O-Ring, a carbon-carbon filter, and a 304L stainless steel (SS) body. Over the years, Hagans have shown vulnerability in their design [1]. In 2008, The Department of Energy (DOE) issued DOE M 441.1-1, Nuclear Material Packaging Manual, which detailed an approach to obtain high-confidence in containers by including specific design requirements, material contents and an approach to determine life span from said contents, and surveillance techniques [2]. In response to both the vulnerability issues with the Hagan and DOE M 441.1-1, the SAVY 4000 container with its twist style closure, Viton® O-Ring, Fiberfrax-Gortex filter, and annealed 316L SS body, was designed as the replacement for Hagan containers, but only for a short term lifespan of 5 years [1]. However, both the Hagan and SAVY 4000 are being pushed to maintain a lifespan of 40 years. Therefore, proper confidence must be placed on each component of each container to last a minimum of 40 years.

So far, the biggest concern found during surveillance of these containers is corrosion and the potential for failure by corrosion. One concern is that the containers fail due to stress corrosion cracking (SCC), especially around the weld between the collar and the body as welds leave residual stresses. One advantage the SAVY 4000 has is that the body is annealed, but its weld is still susceptible as it was welded after annealing [3, 4]. Moreover, 316L SS is known to have a higher pitting resistance (pits are a precursor to SCC and can also lead to extensive failure of the material), than 304L SS [4].

During recent surveillance activities, two SAVY 4000's containing Solution Assay Instrument (SAI) solutions were opened. The SAI SAVY 4000's contained plutonium (Pu) in 3M HCl solution in plastic volumetric flasks placed inside of polyethylene bags. Historically, a SAVY 4000 containing an SAI solution is packaged for 3 weeks, however, these particular containers were not reopened until 14 months later. When opened, brown-red corrosion product was found all over the inside of the container as shown in Figure 1.

Figure 1: SAI SAVY 4000 after 14 months exposed to HCl vapors. Red corrosion product was all over walls of container.

Besides the corrosion product, the most perplexing feature was that the laser etching on the outside of the container to mark the tracking number and QR code had shown through to the inside as shown in Figure 2. The laser etching cannot be seen on the inside of pristine SAVY 4000 container.

Figure 2: The NFT SAVY 4000 logo printed on the outside of the containers (left) and the same logo seen on the inside of the container after being exposed to HCl vapors for 14 months (right).

The image on the inside of the container is the heat affected zone (HAZ) that is produced from the heat of the laser when contacted with the container. The HCl may have chemically etched the interior removing all oxide layers and leaving the surface unprotected to chloride attack [4]. The etched area has never been thought to be a potential problem until this observation.

Laser marking is a simple process in which a finely focused laser (typically low power) is used to remove material on the outer surface of a part in order to “print” an image or writing. The SAI SAVY’s are etched with a tracking number and QR code to track and maintain surveillance on each individual container. Laser etching parameters can be adjusted for different results in the finished work. Laser etching involves a rastering (moving back and forth on an axis) laser head that pulses, creating tiny dots on the surface. As more and more of the dots are created, a seemingly cohesive image can be seen by the naked eye. Of the parameters that can be affected, power of the laser is typically the most important because it changes the laser's ability to cut into the material. Pulse frequency, which increases or decreases number of dots in a raster as the laser pulse timing is changed, and even the speed of the laser head rastering can also affect the finished print.

The laser etcher used on the SAVY 4000 and Hagan containers is a proprietary Ytterbium laser (similar to Nb:YAG) [5]. The containers were etched at 20 W (1 mJ, 2 J/mm^2) laser power, 20 kHz pulse frequency, and 150 mm/sec speed. As it is possible to change these parameters, it is curious to investigate if and how these parameters affect the corrosion potential of SS.

2. Literature on Laser Corrosion Potential

Limited literature is available on the effects of laser etching on SS corrosion potential. In a study by Valette et al. using low power 0.1 W (at 1 kHz, and 8 mm/sec) Nb:YAG pulse laser to etch 316 SS, pitting and corrosion potential (potential to corrode) of the material before and after etching was measured [6]. They found a 20% increase in pitting potential and over a 50% increase in corrosion potential [6]. A higher potential means a higher resistance. On the other hand, a study by Khalfallah et al. reported used a high power 2 kW Nb:YAG laser pulse , at low speed (15 mm/sec), reported carbide formation after etching the area, suggesting sensitization and decreased corrosion resistance [7].

These two studies are on either extreme of laser power as our laser falls in the middle at 20 W. Svanter et al. observed heat input and the amount of corrosion around an etched area of heat inputs on the range of the laser used on the containers [8]. After visually inspecting the etched area at 2 J/mm^2 (20 W), there was more than 60% "massive corrosion" as they described it [8]. However, as the heat input is stepped down, the amount of massive corrosion decreases severely. Moreover, they also looked at pulse frequency noticing that the larger frequencies around 400 kHz showed much less massive corrosion than lower frequencies between 150-200 kHz. But, our study on the SS containers is interested in much lower frequencies such as 1-100 kHz, which is the range at which the containers are etched with now.

No articles were found on the effects of the speed of laser head during etching on SS corrosion potential. However, Adams et al. studied oxide layer thickness before and after etching at different raster speeds at power ranges between 5.6 and 7.6 W [9]. The chromium oxide layer is important for corrosion resistance as it is the protection layer from chloride attack. Sensitization removes chromium from the grain boundaries to make chromium carbides, leaving the iron vulnerable. Adams et al. reported that faster speeds (200-300 mm/sec) cause a decrease in oxide layer thickness [9]. However, the oxide thickness layer was larger with more power. The laser speed used on the SAVY 4000 containers (150 mm/sec) falls in the right range as being slow enough to keep from removing too much of the oxide layer during etching. As well, the larger power used on the SAVY 4000 containers (20 W), even though out of the range of the study, may be allowing for a thicker oxide layer. Moreover, XRD revealed the formation of a more austenitic phase and the devolution of a ferritic-martensitic phase creating a duplex SS (two phased SS), which have been known to be more corrosion resistant [9]. The duplex SS is strongest at speeds of 100-150 mm/sec, right where the laser used on the containers already is [3, 4].

On a side note, lower speeds formed more ferritic-martenistic phases than austenitic. Ferrite is less closely packed than austenite and is more susceptible to being taken apart and formed into iron carbides [3, 4]. Martensite is a stronger phase, but more brittle [3, 4].

At one end of the spectrum at low power, low frequency, and low speed, the pitting potential (higher resistance) is greater at the etched area and lower at the heat affected zone (HAZ). However, higher power has shown an opposite effect as both the etched area and HAZ are less resistant to corrosion. From these studies, there is no real answer as to what affect the parameters the laser used on the SAVY 4000 containers does to the 316L SS or to the 304L SS for the Hagans.

Eto et al. reported a study on stress around the laser etching and HAZ [10]. The study focused one pulse at an area and measured residual stress via XRD. Stress in the etched area increased almost 400% when going from 0 to 30 mJ of input energy. Though, the laser used on the SAVY 4000 container only outputs 1 mJ (at 20W and 20 kHz), it is still possible to have stress concentrations [10]. Stress concentrations can lead to SCC, however, no cracking has been noticed in SCC tests in boiling $MgCl_2$ of the containers [4].

Even though literature was rather sparse, the laser etched area may be more of a concern than originally thought. It is possible that the chromium oxide layer is covering up of the HAZ on the inside of the container. Concentrated acids such as HCl have been known to degrade the oxide layer from the metal over time and it may be possible that this effect was seen on the SAI containers, which are exposed to HCl vapors. Therefore, it is pertinent to understand the effects of laser etching on the corrosion potential of the SS.

Experimental Procedure

1. Sectioning and Etching of Pieces

The bodies of a 5 qt. SAVY 4000 container and 1 qt. Hagan container walls were sectioned into rings. From the rings, undamaged areas were cut into 1” by 1” pieces. Pieces were also cut from the bottom of the container to determine if there were any differences in behavior between the side and bottom pieces. The laser marking area on the SAVY 4000 was carefully sectioned into six pieces for testing. All pieces were then cleaned with water.

The pieces were laser etched with a 50 W Epilog Fibermark Laser Marker. Three sets of SAVY 4000 pieces were etched varying the power, frequency, and speed of the laser. Each set had one varied parameter, while the other two parameters were held constant. The varying parameters can be found in Table 1.

Varying Power, Frequency = 20kHz, Speed = 150mm/sec					
Power (W)	5	10	20	50	
# Replicates	2	2	3	3	
Varying Frequency, Power = 20W, Speed = 150mm/sec					
Frequency (kHz)	1	10	20	50	100
# Replicates	2	2	2	2	2
Varying Speed, Power = 50W, Frequency = 20kHz					
Speed (mm/sec)	50	150	300		
# Replicates	1	1	1		

Table 1: Varied parameter sets for etching of SAVY 4000 pieces.

Once etched, the pieces were cleaned with ethanol in an ultrasonic bath for 5 minutes. After they dried, the weight and dimensions of each etched piece was measured and recorded. Pieces after cleaning can be seen in Figure 1.

Figure 3: SAVY 4000 samples before they were put in corrosion bath.

2. Corrosion Testing

Etched SAVY 4000 pieces were attached to small metallic binder clips. A 5-inch piece of 18-gauge wire were cut and used to attach the clips to a glass rod. The corrosion environment chosen was a 6% $FeCl_3$ aqueous solution, followed in accordance with *ASTM G48 - 11 Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution* [11]. A 100.3 g mass of $FeCl_3{\cdot}6H_2O$ was measured out and added to 900 mL of deionized water giving 1 L of liquid. The glass rod was then laid on top of the beaker, allowing for the SAVY 4000 pieces to be fully immersed in the $FeCl_3$ solution. The pieces were immersed for 72 hours. Temperature stayed between 22 and 23ºC. The pieces were then wiped with ethanol to remove corrosion products and weighed again. Dimension and weight measurements were also taken again to compare thickness measurements.

After 24 hours, the binder clips used to hold the samples disintegrated as can be seen in Figure 4.

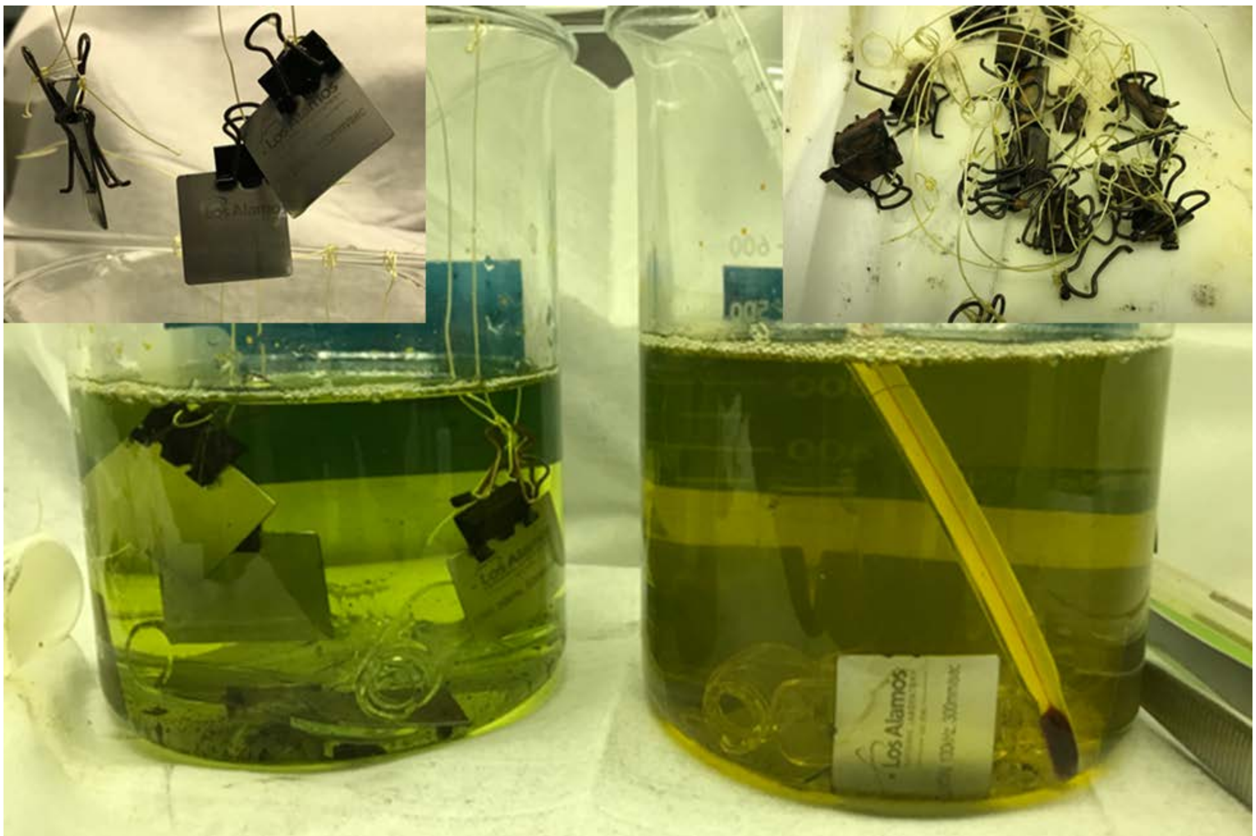


Figure 4: Corrosion baths after 24 hours. Upper left, shows original idea using binder clips and wire to suspend samples. Upper right, shows clips after 24 hours in $FeCl_3$ as heavily corroded and destroyed. Beakers show glass vials used to hold and separate samples in beaker to continue experiment.

Therefore, watch glasses and small sample vials (also seen in Figure 4) were used to separate and segregate the samples to maximize surface area and minimize crevice corrosion. The ASTM standard emphasizes having a minimum of 30 mL/in^2 of $FeCl_3$ solution per each samples' square inch. Reaction of the metal in the clips with the $FeCl_3$ would decrease the amount of $FeCl_3$ available to react with the SAVY 4000 pieces. Therefore, results from Set 1 were not in compliance with the ASTM standard.

A second test was completed on etched SAVY 4000 pieces without the use of clips. In the second experiment, a mass of 100.2 g of $FeCl_3 \cdot 6H_2O$ was dissolved in 900 mL of water. Set 2 pieces, described in Table 2, were placed against the side of the beakers as shown in Figure 3. A smaller beaker was placed in the center of the pieces to keep the pieces from falling flat on the bottom of the beaker. Set 2 was in solution for 96 hours. Temperature of the solution remained between 22 and 23°C for the duration of the experiment. After 96 hours, corroded samples were cleaned in ethanol in an ultrasonic bath for 10 minutes and then photographed. Dimensions and weight measurements were taken.

Set 1, All SAVY						
Varying Power (W)	50	20	10	5	50 Bottom	20 Bottom
Varying Frequency (kHz)	100	50	20	10	1	
Varying Speed (mm/sec)	50	150	300			
Extras	Oriignal SAVY Etched		50 W, 100 kHz, 300 mm/sec		20 W, 20 kHz, 150 mm/sec	
Set 2, SAVY						
Varying Power (W)	50	10	5			
Varying Frequency (kHz)	100	50	20	10		
Extras	Original Etched		Oriignal Unetched			
Set 2, Hagan						
Varying Power (W)	50	20	10	5		
Extras	Oringal Unetched					

Table 2: Samples placed into solution for set 1 and set 2.

3. Laser Confocal Microscope Imaging

Three SAVY 4000 pieces from the mid-side wall region of the SAVY 4000 container were selected for imaging using a VK-X Series Differential Interference Contrast Confocal Microscope (DIC-CM) from Keyence. The system provides a non-contact, nanometer-level 3D profile and high definition color images, which can be used to determine pit depth and density. The pieces included sections with original etching, etching done with repeated parameters (20 W, 20 kHz, and 150 mm/sec), and etching done with maximum potential of laser (50 W, 100 kHz, and 300 mm/sec). For each piece, a 2x10 image set (An array of 20 images taken 2 across and 10 down from the laser origin, which was considered the top of the SAVY 4000 piece) image was collected at 20x magnification on the interior side of the SAVY 4000 that included an etched area, the HAZ, and an unetched/unaffected area. After corrosion testing in $FeCl_3$ as described above, those same pieces were imaged with the DIC-CM in the same area for comparison with the baseline images.

Images were then analyzed with the DIC-CM software for average pit density, pit number, and other demonstrative defects in the SS. Moreover, these particular pieces had their dimensions checked before and after they were placed in a corrosive environment as a more qualitative way of measuring for defects.

Results

I. Mass Measurements

Two different sets of SAVY 4000 pieces cut 1” by 1” from a 5 quart SAVY 4000 container were corroded in an accelerated corrosion environment of $FeCl_3$ as per ASTM G48 that focuses on testing pitting resistance of SS. Weight measurements of the pieces were taken before and after being subjected to $FeCl_3$. Table 3 shows those weight measurements for set 1 pieces and Table 4 shows the weight measurements for set 2. Set 1 data shows little weight change for most of the samples. However, the two bottom pieces (50 W and 20 W) showed a more significant change. Moreover, the 50 W bottom piece showed a mass loss while the 20 W bottom piece shows a mass gain.

Besides the bottom pieces, the three pieces that had varied speed showed a larger mass change around ~7%, which is rather high for a parameter that was not suspected to be much of a concern.

Varied Power, 20 kHz, 150 mm/sec						
Power (W)	50 (bottom)	20 (bottom)	50	20	10	5
Weight Before (g)	2.947	2.8615	3.2578	3.8367	3.5406	3.6824
Weight After (g)	2.854	2.945	3.252	3.8358	3.5333	3.6754
% Mass Difference	3.16	-2.918	0.18	0.023	0.206	0.19
Varied Frequency, 20 W, 150 mm/sec						
Frequency (kHz)	100	50	20	10	1	
Weight Before (g)	3.7859	3.4067	3.8032	3.7082	3.3408	
Weight After (g)	3.7795	3.4024	3.7958	3.7081	3.34	
% Mass Difference	0.17	0.12	0.195	0.003	0.024	
Varied Speed, 20 W, 20 kHz						
Speed (mm/sec)	300	150	50			
Weight Before (g)	3.2069	3.6922	3.4345			
Weight After (g)	3.4288	3.6124	3.1858			
% Mass Difference	7.24	2.16	6.92			

Table 3: The weights (before and after corrosion) of the samples in set 1.

The set 1 samples were immersed with a system of binder clips and wire to hold the pieces from touching the bottom. The binder clips completely disintegrated after 24 hours causing the $FeCl_3$ to become unbalanced as much of it attacked the binder clips. Therefore, the data in Table 4 of set 2 may be more inherent. There was more mass loss, most likely due to crevice corrosion. However, the values are rather similar amongst each set: varying power (SAVY 4000), varying frequency (SAVY 4000), original SAVY 4000, varying power (Hagan).

SAVY - Varying Power, 20 kHz, 150 mm/sec				
Power (W)	50	10	5	
Weight Before (g)	3.4312	3.4591	3.4068	
Weight After (g)	3.0974	3.286	3.2312	
% Mass Difference	9.73	5	5.15	
SAVY - Varying Frequency, 20 W, 150 mm/sec				
Frequency (kHz)	100	50	20	10
Weight Before (g)	3.6636	3.4803	3.5184	3.7218
Weight After (g)	3.4391	3.2471	3.2887	3.5202
% Mass Difference	6.12	6.7	6.52	5.42
SAVY - Original				
	Unetched	Etched		
Weight Before (g)	3.3993	3.3636		
Weight After (g)	3.1473	3.1607		
% Mass Difference	7.41	6.03		
Hagan - Varying Power, 20 kHz, 150 mm/sec				
Power (W)	50	20	10	5
Weight Before (g)	3.2803	2.7511	3.2065	3.4362
Weight After (g)	3.0854	2.6146	3.0482	3.2744
% Mass Difference	5.94	4.96	4.94	4.71
Hagan - Original - Unetched				
Weight Before (g)	3.3246			
Weight After (g)	3.1365			
% Mass Difference	5.65			

Table 4: The weights (before and after corrosion) of the samples in set 2.

Figures 5 and 6 are photographs of the set 2 pieces after they were subjected to $FeCl_3$. There are many areas where the $FeCl_3$ ate away at SS. These areas are responsible for the larger amount of mass loss. Affected areas may not have been seen in set 1 as the $FeCl_3$ was disrupted by the disintegrated binder clips. Moreover, the binder clips were used to help reduce crevice corrosion. Crevice corrosion is a phenomneon in which a crevice is made (typically submicron to ~2 mm) with a corrosivley active material causing build ups of acidic ions such as H^+ and Cl^- [4]. The acidic ions then eat away casuing pits and corrosion products [4]. The eaten away areas of set 2 were more along the edges where the SS was in contact with the glass where a crevice may have been made casuing crevice corrosion.

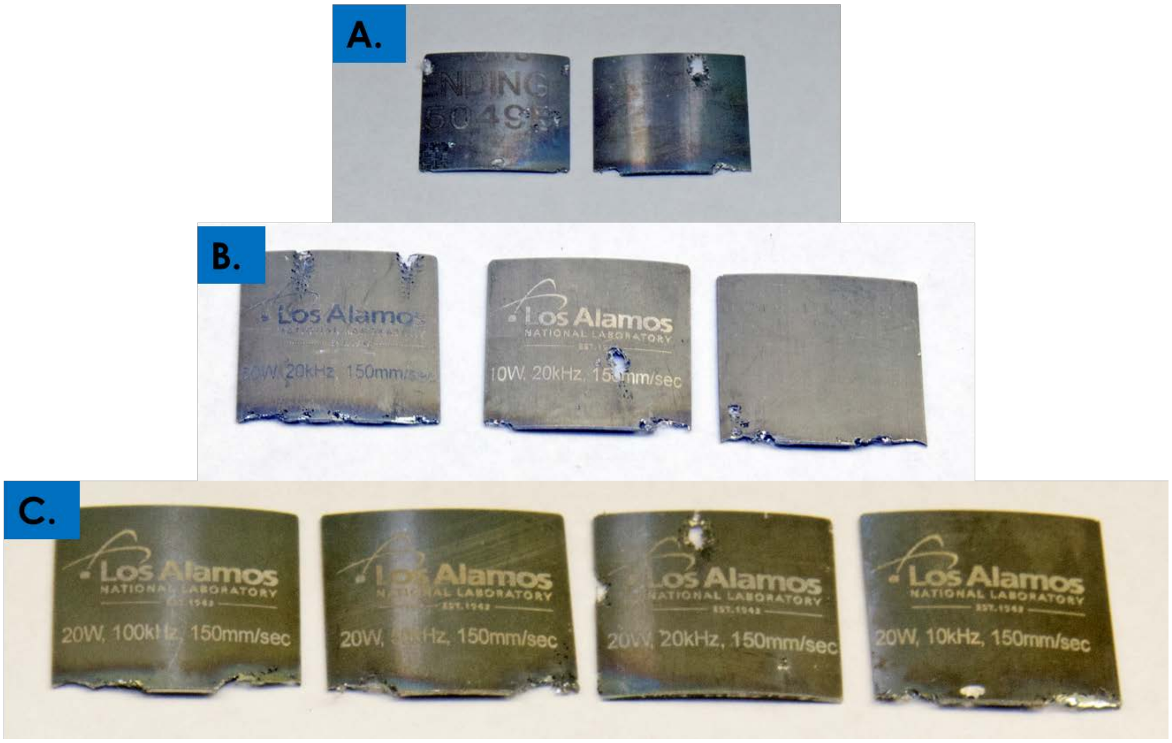
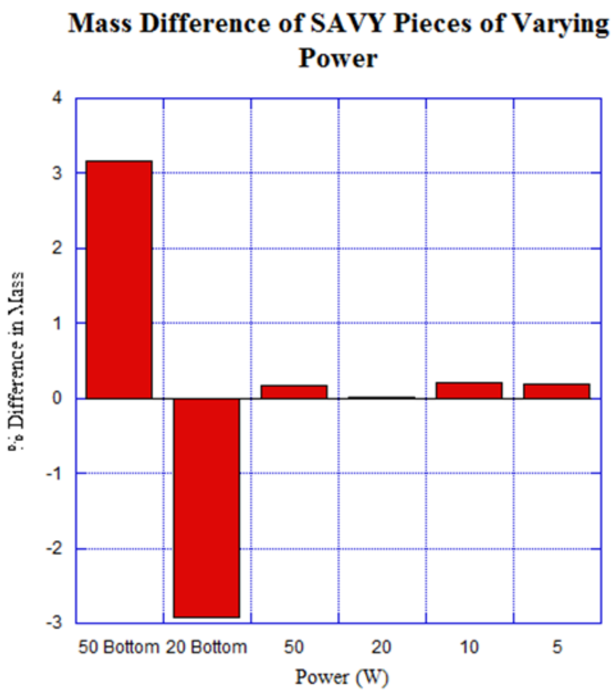


Figure 5: 2nd set of SAVY 4000 pieces after being in FeCl3 solution for four days. A. Original etched and unetched SAVY 4000. B. Varying power -- 50, 10, 5 W – 20 kHz, and 150 mm/sec. C. Varying Frequency – 100 kHz, 50 kHz, 20 kHz, 10 kHz – 20 W, and 150 mm/sec.

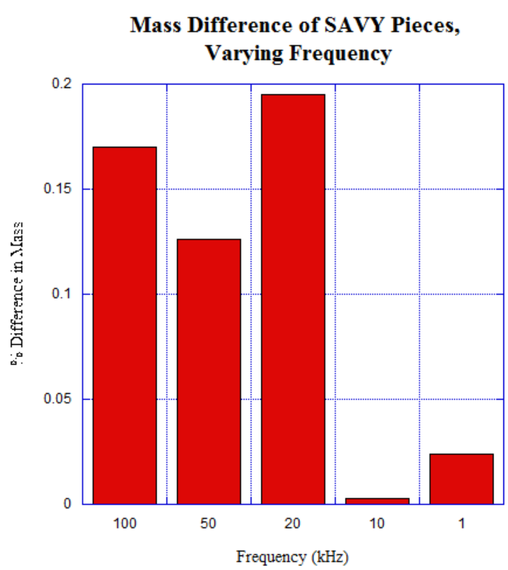
Figure 6: Hagan pieces after being in FeCl3 solution for four days. First four are replicated with varying power – 50, 20, 10, and 5 W -- 20 kHz and 150 mm/sec. Fifth piece is of the original unetched Hagan.

The following graphical figures below are plots based on mass change to look for any significant trend. Graphs 1-3 are for the SAVY 4000 pieces in set 1 and Graphs 4-8 are for set 2. In looking at Graph 1 for the varied power pieces, there was little mass loss among the four pieces. However, the two bottom pieces etched at 50 W and 20 W showed a larger mass difference. The bottom piece etched at 50 W lost ~3% mass while the bottom piece etched at 20 W gained ~3% mass.



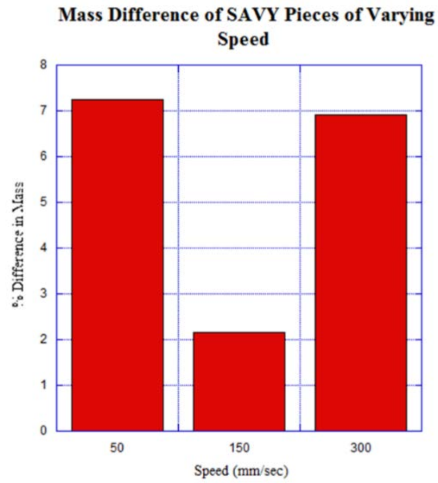
Graph 1: % Difference in mass of SAVY 4000 pieces etched with varying power – 50, 20, 10, and 5 W – 20 kHz, and 150 mm/sec. There are two bottom pieces etched at 50 W and 20 W.

Graph 2 shows mass loss for the varying frequency SAVY 4000 pieces. The bar graph may be misleading as the 1 and 10 kHz show no resemblance to the higher frequencies. However, the mass changes are below 0.2%, which is too nominal and not a significant enough change to count a trend.



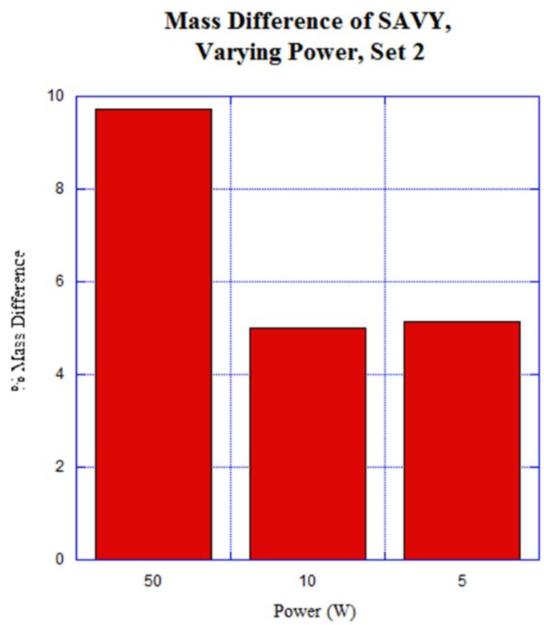
Graph 2: % Difference in mass of SAVY 4000 pieces etched with varying frequency – 100, 50, 20, 10, and 1 kHz – 20 W, and 150 mm/sec.

Of all three graphs, Graph 3 showing effect of speed to mass loss, there is a substantially higher % mass difference, close to ~7%. As odd as the % mass difference is, there is no underlying trend as to how differences in speed effect corrosion potential.



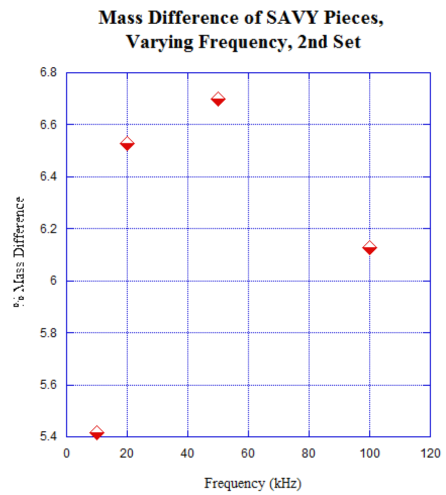
Graph 3: % Difference in mass of SAVY 4000 pieces etched with varying speed – 50, 150, and 300 mm/sec – 20 W, and 20 kHz.

Set 2 graphs show a higher % mass difference throughout all the samples as there was more material removed as can be seen back in Figures 5 and 6. In looking at Graph 4 for varied power, the sample etched at 50 W lost twice more mass than the 10 W or 5 W samples did suggesting a trend that higher power leads to more corrosion. However, due to the majority of the mass loss being attributed to the edges of the pieces and not to the center of the sample where the etching is, this trend cannot be attributed to laser etching power.

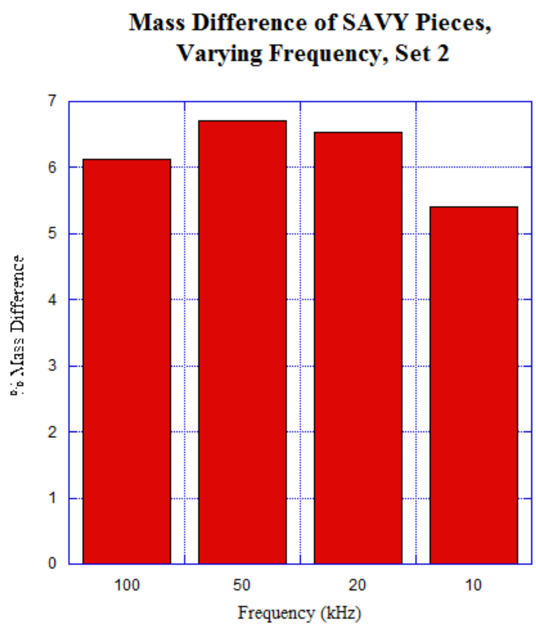


Graph 4: % mass difference of SAVY 4000 pieces etched with varying power – 50, 10, and 5 W – 20 kHz, and 150 mm/sec.

Graphs 5 and 6, showing SAVY 4000 pieces etched with varying frequencies, show a more reasonable trend as higher frequencies tend to show more mass loss. However, those changes are within ~1% and cannot be attributed to laser etching frequency.



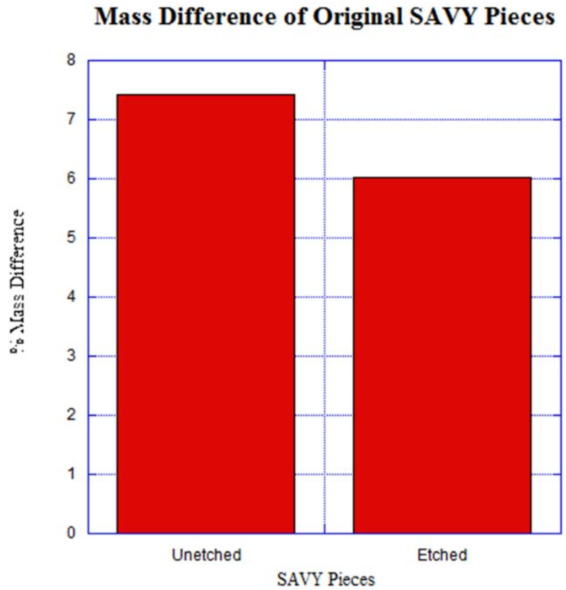
Graph 5: % mass difference of SAVY 4000 pieces etched with varying power – 50, 10, and 5 W – 20 kHz, and 150 mm/sec.



Graph 6: % Difference in mass of SAVY 4000 pieces etched with varying frequency – 100, 50, 20, and 10 kHz – 20 W, and 150 mm/sec.

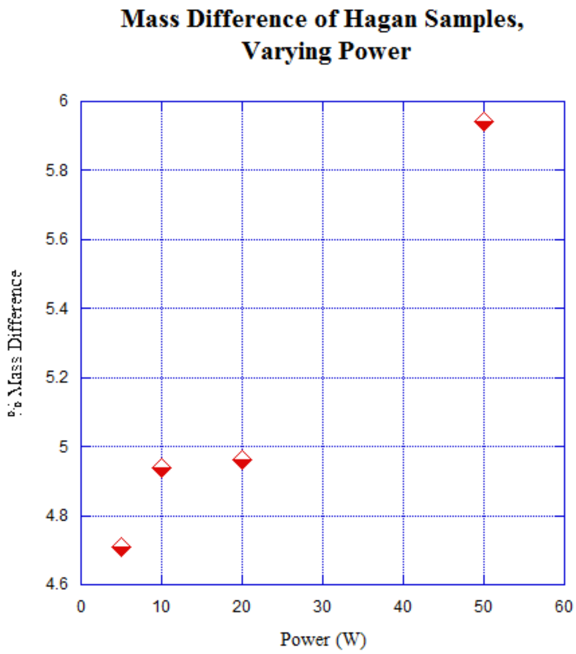
One of the more interesting finds in Graph 7 is the comparison between original SAVY 4000 etched and original SAVY 4000 unetched. The unetched showed a larger % mass difference than the etched sample suggesting that laser etching may help increase resistance to corrosion.

However, the differences between the two are in error bar and a second experiment may have to be ran to understand if there really is a trend present.



Graph 7: % mass difference for original SAVY 4000 pieces after corrosion: etched and unetched.

Finally, Graph 8 shows the Hagan pieces etched with varying power. There appears to be a specific trend that increasing power leads to a higher mass loss. However, there is only a range of ~2% between all the samples and the trend cannot be attributed to laser etching power without further evidence to support the trend.



Graph 8: % mass difference of Hagan samples etched with varying power – 5, 10, 20, 50 W – 20 kHz, and 150 mm/sec.

I. DIC-CM Images Analysis

DIC-CM analysis was performed on three select samples: original SAVY 4000 etched, repeated parameters (etched at 20 W, 20 kHz, and 150 mm/sec), and max capability of the laser (50 W, 100 kHz, and 300 mm/sec), a bottom piece of SAVY 4000 (etched at 50 W, 20 kHz, and 150 mm/sec). Images were collected on the back of the samples to look for and measure pit size and depth. Using this method, etched areas, unetched areas, and the HAZ were all viewed and analyzed.

Figure 7 shows three SAVY 4000 pieces that were imaged with the DIC-CM before being exposed to $FeCl_3$ for 72 hours. Table 5 shows dimensional and weight analysis of the pieces both before and after being exposed to $FeCl_3$. Dimensional analysis was only performed on the pieces being analyzed under the DIC-CM as calipers used were not sensitive enough to really reflect any changes in the dimensions. Weight changes were recorded and were minimal. These samples were corroded in the same solution as set 1.

Figure 7: Three samples imaged with the DIC-CM. Left to right: Max, original SAVY 4000, and replica of original SAVY 4000 parameters. Photos taken after 24 hours in $FeCl_3$.

Samples Viewed Under LCM			
Specimen	Original SAVY Etched	50 W, 100 kHz, 300 mm/sec	20 W, 20 kHz, 150 mm/sec
Weight Before (g)		3.5708	3.8367
Weight After (g)	2.8513	3.5621	3.8358
Height (mm)	2.505	2.502	2.502
After Corrosion	2.5654	2.362	2.5019
Width (mm)	2.445	2.507	2.507
After Corrosion	2.4333	2.85	2.6
Thickness (mm)	0.75	0.7	0.7
After Corrosion	0.07	0.07	0.07

Table 5: Weight and dimensions of the three samples viewed (before and after corrosion) with the LCM.

Figures 8b, 10, and 11 show the baseline DIC-CM images before the three samples were exposed to $FeCl_3$. Each sample was imaged starting from the origin taken as the top center. The dimensions of the image taken at 20x are about 1.5mm by 1mm. a 2x10 array of 20 images was taken down from the origin. This array included areas such as the unetched area, etched area, and HAZ. No scale bar for the depth differences in color was included as the dimensional difference was minimal.

In examining the backsides of the SAVY 4000 pieces after exposure to $FeCl_3$, the only poignant feature noticed was a large pit, as can be seen in Figures 8c and 9, on the original etched SAVY 4000 piece. Moreover, there were no other features seen whether on or near the etched area or on the unetched area.

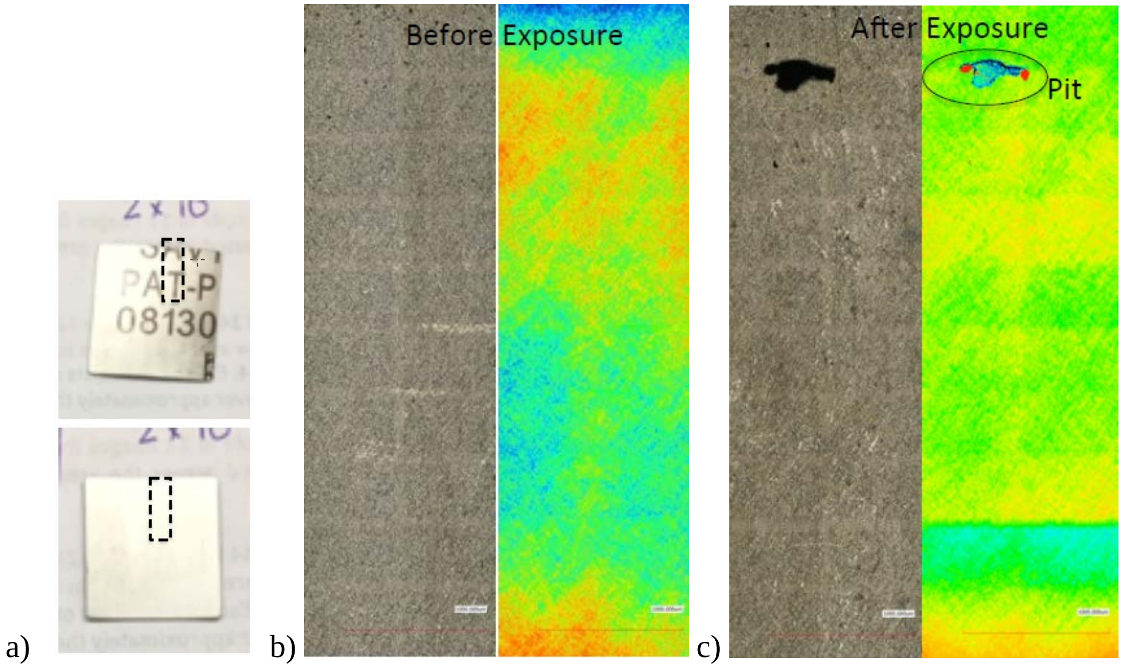


Figure 8: Photographs showing a) Original etched SAVY 4000 outer and inner surface contour. Dotted lines represent the approximate areas that were imaged, b) light micrograph and the DIC-LM image of the inner contour before exposure and c) light micrograph and the DIC-LM image of the inner contour after exposure.

Figure 9 shows a close up of the pit region.

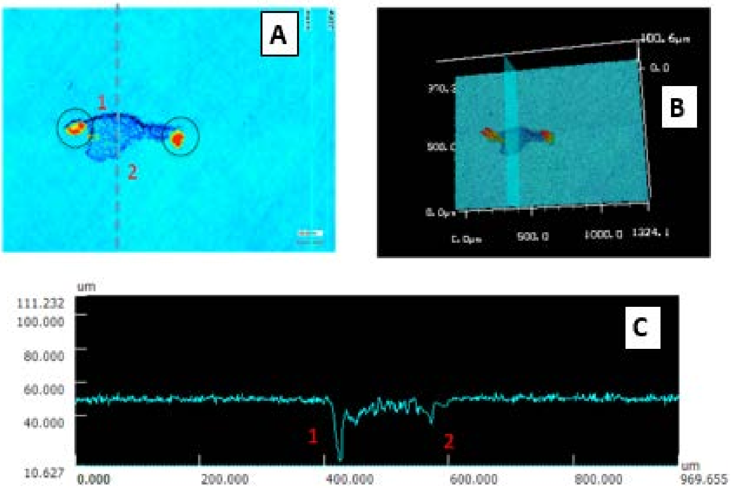


Figure 9: Surface profile of original etched SAVY 4000 after exposure to $FeCl_3$ taken with DIC-CM. Points 1 and 2 are endpoints showing length of the large pit found durng analysis. The pit was 460 µm long and 160 µm wide. The pit depth is non-uniform with depths changing between ~ 3 µm to 39 µm. Two masses ~ 40-55 in height were present above the surface with on either end of the pit. (Red features in Figure 9A and 9B).

Even though the large pit was the only feature it has a curious attribute, which is that the ends of the pit (looking horizontally) are the deepest part of the pit and cover relatively the length (~30µm). Through superposition, the pit covers part of the etched area as well as part of the unetched area around the A in SAVY as can be seen in Figure 8a.

Figure 10 shows the light micrograph and DIC-CM contour of the most extreme case (laser parameters used were 50 W, 100 kHz, and 300 mm/sec) before and after exposure to $FeCl_3$.

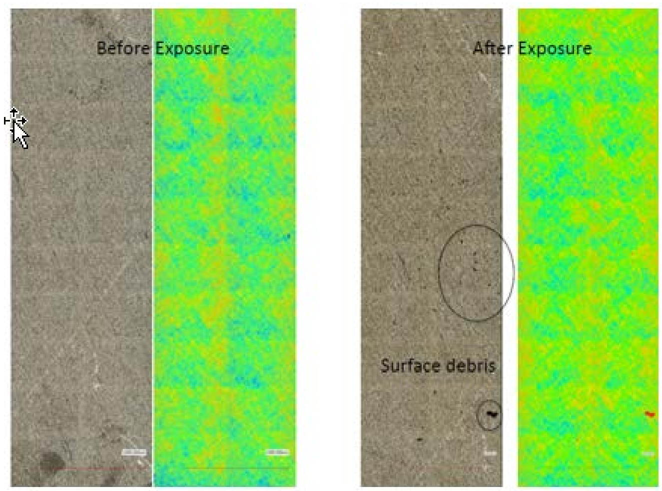


Figure 10: Light micrograph and DIC-CM contour of the most extreme case where the laser parameters used were 50 W, 100 kHz, and 300 mm/sec before and after exposure to $FeCl_3$.

There was no evident changes on the surface of the most extreme case after exposure, just surface debris.

The DIC-CM and light micrograph of the replica of the original SAVY 4000 paramters: 20 W, 20 kHz, and 150 mm/sec is shown in Figure 11.

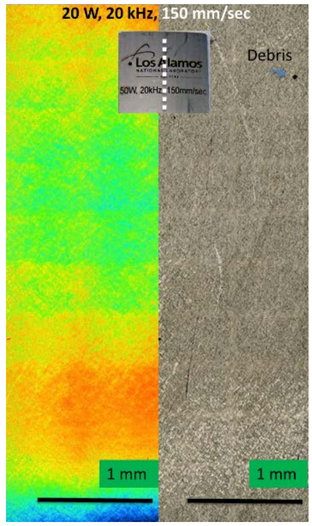


Figure 11: LCM contour and light micrograph of the a replica of the original SAVY 4000 paramters: 20 W, 20 kHz, and 150 mm/sec.

After looking at the original etched piece and the piece etched with maximum parameters (to produce a most extreme case), and not seeing a sign of significant corrosion, the replica of the original SAVY 4000 piece was not reimaged.

Instead, a bottom piece was imaged as the mass data suggested something more happening with the bottom of the canister. In addition, the bottom of the SAVY 4000 container is 0.6 mm thick while the walls of the container are 0.76 mm thick. Therefore, the thinner bottom may be of a larger concern. The image of the bottom piece after exposure to $FeCl_3$ is shown in Figure 12.

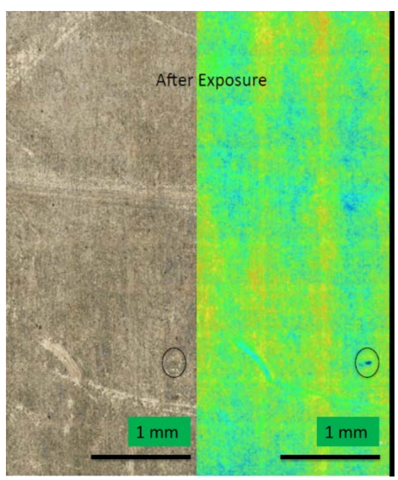


Figure 12: DIC-CM contour and light micrograph of the bottom of the original SAVY 4000 paramters: 20 W, 20 kHz, and 150 mm/sec.

The DIC-CM images revealed that there was no significant damage and only surface defects were observed.

Discussion

SS pieces cut from the SAVY 4000 and Hagan were corroded in $FeCl_3$ for 72 hours to compare the laser etched and unetched regions of the containers to detect whether the laser etching has any effect on the corrosion resistance of the container. Since the standard used was a pitting test, mass difference, were done on the samples to analyze any effect on the pieces. Moreover, DIC-CM analysis was also performed to visually inspect the pieces for pits and other defects before and after exposure to the $FeCl_3$.

Of the set 1 samples, the varied power in Graph 1 showed little mass loss over the 50, 20, 10, and 5 W samples. However, the 50 W etched on a piece cut from the bottom of the SAVY 4000 container showed a much larger mass loss. Moreover, the 20 W bottom piece showed a large reciprocal, mass gain. Besides the bottom pieces, the varied frequency pieces of set 1 shown in Graph 2 also show no real change in mass loss over the varied frequencies and similarly for the varied speed pieces in Graph 3, except for the one anomaly at 150 mm/sec. Even though the bottom pieces showed some results, the experiment did not show whether the etching had any significant effect on the corrosion resistance of the SS. It is curious though that the varied speed pieces showed a higher % mass loss than either the varied power or varied frequency, yet there are no signs as to what may have caused the higher mass loss with those pieces.

Moving on to set 2, there was a higher % mass difference in all the samples, most likely due to crevice corrosion around the corners of the samples and that the solution made fore set 2 was purer than set 1 as the binder clips disintegrated in solution. Graph 4 shows that the 50 W piece most more mass, but not significantly more so than the 10 W and 5 W samples. The varied frequency pieces in Graph 5 and 6 show a possible trend, but the % mass difference for each are too similar to confirm the trend. Graph 7 shows original etched and unetched pieces of the SAVY 4000 showing the unetched piece lost more mass than the etched, yet the differences are within error bar range and no discernable conclusion can be made other than the laser etching has no real affect to the SS pieces.

Finally, in Graph 8, the only Hagan pieces done had varied power, but showed some what of trend that higher power lead to a higher mass loss. However, the differences between each point are within 1% putting little confidence in that trend.

The DIC-CM imaging and contour analysis was expected to reveal better results. However, before and after exposure analysis revealed few defects except for one large poignant pit on the original SAVY 4000 etched piece after exposure. The pit is inclusive of etched and unetched areas and cannot necessarily be considered to have initiated near or on the etching without further analysis. The edges of the pit (looking horizontally) as in Figures 8 and 9 are the deepest part of the pit and may be spot on with the etching areas, but again, more analysis than superposition can be used to determine if those deeper areas are on the etching or HAZ.

Reproducibility in other SAVY 4000 containers

Unlike the SAI-SAVY 4000 exposed to HCl vapors, the laser etching was not visible on the inside of SAVY 4000 piece on any of the SAVY 4000 pieces exposed to the $FeCl_3$ solution. Laser etching was also not visible on the inside of the SAVY 4000 after exposure to boiling $MgCl_2$ at 155ºC for 47 hours. In addition, the inside area of a SAVY 4000 container opposite the etching was rubbed with cheesecloth soaked in 12M HCl for approximately one minute. Laser etching was again not visible on the inside of the SAVY 4000. The inability to reproduce the phenomena observed in the SAI-SAVY 4000 suggests that a unique gas phase mechanism may be responsible for the observation. These findings emphasize the importance of conducting surrogate studies under conditions as close as practical to in-service container storage conditions.

Future Studies

Even though the mass calculations were unable to support the data from the DIC-CM, there is one quick test that can be performed to help understand if there should be a concern with the laser etching. Potentiodynamic testing is form of testing that measures the corrosion potential and can also measure the pitting potential of a material. Even though 316L and 304L SS are well known and potentiodynamic curves exist for both, there is no data on an etched area vs. and unetched area.

Therefore, it would be a good piece of data to perform these tests on both the SAVY 4000 and Hagan container for both the etched and unetched area of the SS. Even if the tests show no real trend between etched on unetched, it would still provide data on our 316L and 304L specifically. Moreover, it can be used as an extra piece of evidence in confirming that the SAVY 4000 is superior to that of the Hagan in corrosion resistance.

Examining the etched sections of the SAI SAVY 4000 containers is also planned. Sections will be examined using the DIC-CM to determine if there are indications of increased corrosion in the etched area. Exposing a SAVY 4000 container to HCl vapors in an attempt to reproduce the observation of etching on the interior wall is also recommended.

Conclusion

On two SAVY 4000 containers exposed to 3M HCl gases for 14 months, laser etching on the outside of the container had shown through to the inside. This raised the concern that the reverse side of a laser etched SS may be more susceptible to corrosion than the unetched SS. Side wall pieces of SAVY 4000 and Hagan containers were laser etched varying the power, frequency and speed. The pieces were exposed to $FeCl_3$ solution as an aggressive corrosion environment for up to 72 hours to compare the amount of corrosion between the reverse side of the etched and unetched areas of the SS pieces. Mass and dimensional comparisons were made before and after exposure to the $FeCl_3$. The pieces showed little mass loss except for areas around the corners where the pieces touched the glass causing a possible site for crevice corrosion. In looking at the mass loss data, no trend could be distinguished suggesting any change in one parameter (power, frequency, or speed) of the laser used in etching or marking does not affect corrosion resistance. Furthermore, DIC-CM analysis was performed to look for pits and measure pit sizes. DIC-CM images showed a rough, but defect free surface of both the SAVY 4000 original etched and the replica using maximum settings of the laser for each parameter. After exposure, few defects were seen on the backsides of the pieces except for one large pit that appeared on the original etched SAVY 4000. However, that one pit cannot be suggested to have initiated or been helped to propagate from the etching or HAZ area without further information. In conclusion, no evidence was found that laser etching increased the susceptibility of the reverse side of Hagan or SAVY 4000 pieces when exposed to $FeCl_3$.

Acknowledgements

We would like to thank Tim Stone, Tristan Karnsand Kirk Reeves for their assistance and knowledge with SAVY 4000 and Hagan containers. We would also like to thank Timothy Schollenberger for assistance with laser etching.

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