Hawaii National Marine Renewable Energy Center (HINMREC)

U.S. Department of Energy Award Number: DE-FG36-08GO18180

Task 6: Supporting Studies

OTEC Heat Exchanger Program: 2016 Ultrasonic Scanning for Corrosion Monitoring Progress Reports

Prepared by:
Makai Ocean Engineering

Prepared for:
Hawaii Natural Energy Institute, University of Hawaii

2015 - 2016

HNEI
Hawai'i Natural Energy Institute
University of Hawai'i at Mānoa

OTEC HEAT EXCHANGER PROGRAM

ULTRASONIC SCANNING FOR CORROSION MONITORING

RACK CONSTRUCTION AND STATUS

SUBAWARD MA150017

Prepared For

HAWAII NATIONAL MARINE RENEWABLE ENERGY CENTER

LUIS VEGA

1680 East West Road, POST 112A

Honolulu, HI, 96822

USA

Prepared By

MAKAI OCEAN ENGINEERING

PO Box 1206, Kailua, Hawaii 96734

April 2015

1. INTRODUCTION

Aluminum alloys have been proposed for use in Ocean Thermal Energy Conversion (OTEC) heat exchangers for their high thermal conductivity, comparatively low cost, and overall good general corrosion resistance (due to formation of a protective oxide layer) in seawater environments. Although uniform corrosion rates for aluminum alloys are low, aluminum alloys are susceptible to surface pitting and crevice corrosion at gasket interfaces which can initiate when local galvanic cells develop between alloying elements and deposit corrosion product on the surface of the metal. Corrosion product can encase the immediate area and change the local environment which acts to accelerate the corrosion process. It is important to quantify this phenomenon because, in time, pits or crevice corrosion can penetrate the wall of the heat exchanger and cause refrigerant to leak into the seawater. For heat exchangers, this is considered a catastrophic failure and must be avoided.

Makai Ocean Engineering has been studying and quantifying the development of corrosion on aluminum alloys being considered for OTEC heat exchangers. Makai has developed a setup in which pit growth can be observed in-situ by optical imaging and ultrasonic scanning. Pitting sites are identified and corrosion product accumulation on the metal surface is observed using imagery. However, once corrosion product encapsulates a pit, no accurate measurements of pit size or depth can be made with imaging alone. With the addition of ultrasonic thickness scanning, the surface underneath the corrosion product can be observed and the 3-dimensional structure of the pit can be measured. Pit development can now be monitored over time without removal or destruction of samples.

In the last year, Makai used these techniques to study corrosion in aluminum alloys Al 2024, Al 6061-T651 and Al 5086-H116. Pitting occurred quickly on the Al 6061 and Al 2024 samples, reaching depths of 1 mm in 9 months. The Al 5086 samples have performed well and only show some crevice corrosion at the gasket. Testing has expanded to include 18 new samples. For these new samples, we will test three alloys (Al 1100-H112, Al 3003-F and Al 5086-H116) and three corrosion mitigation techniques (warm seawater pre-treatment, hypo-chlorination and exposure to a diluted sulfamic acid) in flowing (1 m/s) and near stagnant cold seawater; an additional 5 samples will be tested as control samples. The expansion rack construction is complete and warm seawater pre-treatment on selected new samples has begun.

2. STATUS

2.1. EXPANSION RACK CONSTRUCTION

The construction of the expansion rack has been completed (Figure 1). Corrosion samples have been relocated from the current cold seawater (CSW) Multi Column Imaging Rack (MCIR) to the expansion rack.

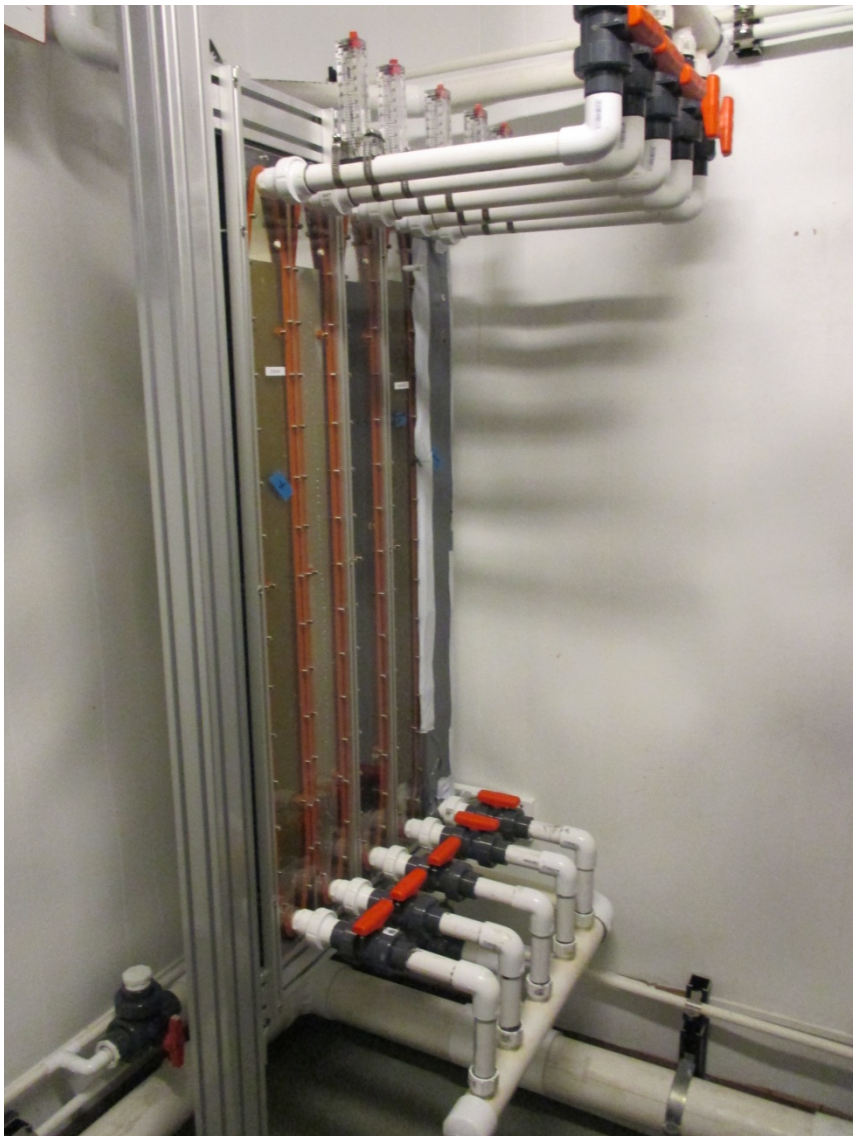


Figure 1: Expansion Rack

New ultrasonic testing samples will be mounted using the same fixtures and in the same manner as the current ultrasonic testing samples (3 samples per column) with the new alloys arranged in order from top to bottom: Al 5086, Al 3003, and Al 1100. The CSW MCIR will have a total of 8 ultrasonic testing columns (24 samples total).

2.2. SYSTEM MODIFICATIONS FOR PROVIDING TREATMENTS

2.2.1. Warm seawater pre-treatment

Warm seawater pre-treatment samples were installed on April 22, 2015 and will be exposed to warm seawater for 40 days before being moved to CSW MCIR for testing in June 2015. No modification to the existing systems was required.

2.2.2. Hypo-chlorination treatment

The hypo-chlorination system incorporates real-time monitoring of oxidation reduction potential (ORP), computer controlled pump rate, and the ability to treat samples in cold seawater via solenoid valves. A custom program on the multi-column computer performs both the control and recording functions for the hypochlorite system. A Cole-Parmer Series 1 Piston Metering Pump (single piston pump, controlled via a 4-20 mA signal) has replaced the Chemtech metering pump. The pump delivers diluted bleach from a storage tank to the samples slated to receive hypo-chlorination treatment through designated solenoid valves controlled by the control program using a National Instruments Digital Output module. A level sensor on the storage tank is used to calculate the delivered concentration and provide warning to replenish the tank with dilute bleach. A reverse osmosis / de-ionized water system was installed to produce clean water used to dilute bleach. Samples will receive 100 ppb hypochlorite treatment for one hour each day.

2.2.3. Sulfamic acid treatment

Piping modifications for treating the samples with acid have been completed. Acid treatments will be performed manually.

2.3. ONGOING TESTING

Six samples of three different aluminum alloys (Al 2024, Al 5086, and Al 6061) have been exposed to both flowing (1 m/s) and near-stagnant cold seawater. Three samples have been exposed for just over one year and the other three for just over seven months (Table 1). Imaging, ultrasonic thickness measurements and electro-chemical monitoring have been performed on a regular basis.

The corroded surface area continues to increase on the Al 2024 and Al 6061 samples (Figure 2). There is good correlation between areas covered in corrosion product and the corrosion location detected ultrasonically (Figures 3-4, and 8). The Al 5086 in near-stagnant seawater has developed corrosion product at two of the gasket edges, while the Al 5086 samples in flowing seawater have no corrosion detected (Figures 5-7). As reported previously, the ultrasonic scanner's beam width (~4 mm) makes the pits appear wider in the scans relative to the images but corrosion depths agree with profilometer measured depths within 0.03 mm.

Table 1: Summary of on-going testing.

Alloy	Serial #	Source	Exposure Date	Removal Date
5086	ut 5-1	Flowing	4/16/14	
	ut 5-2	Stagnant	4/16/14	9/8/14
	ut 5-4		9/8/14	
6063	ut 6-3	Flowing	4/16/14	
	ut 6-2	Stagnant	4/16/14	9/8/14
	ut 6-4		9/8/14	
2024	ut 2-1	Flowing	4/16/14	9/8/14
	ut 2-3		9/8/14	
	ut 2-2	Stagnant	4/16/14	9/8/14
	ut 2-4		9/8/14	

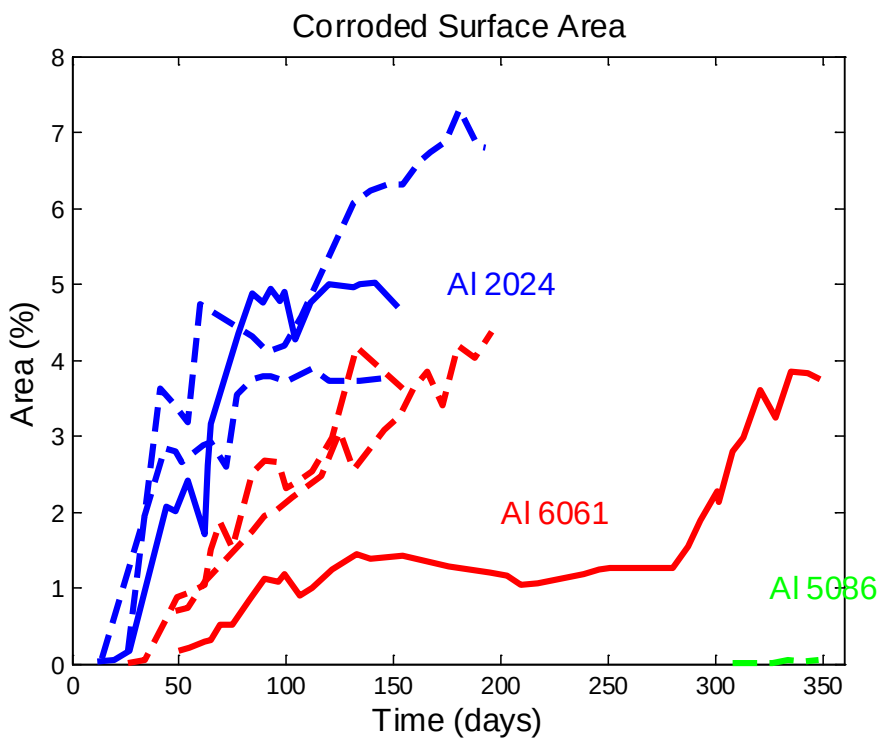


Figure 2: Corroded surface area measured ultrasonically. Dashed lines are samples in near-stagnant seawater and solid lines are in 1 m/s flowing seawater.

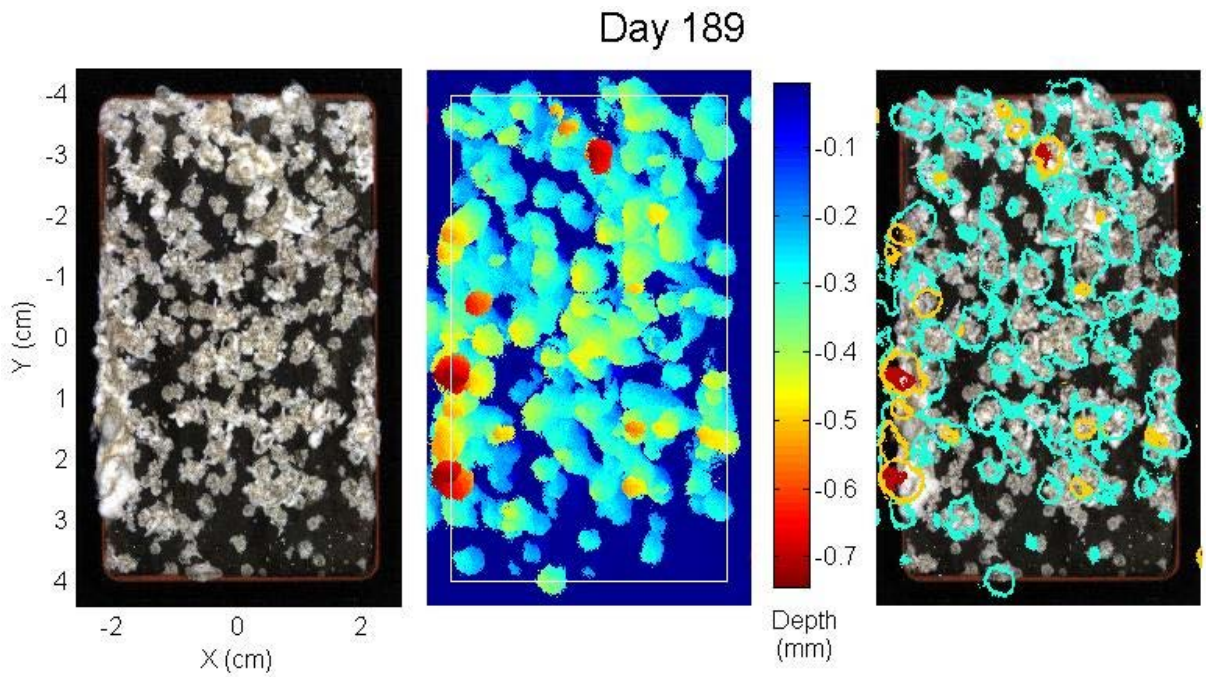


Figure 3: Al 2024 sample in near-stagnant cold seawater at 189 days. Left – imaging, center – ultrasonically determined depth, right – overlay of the two images

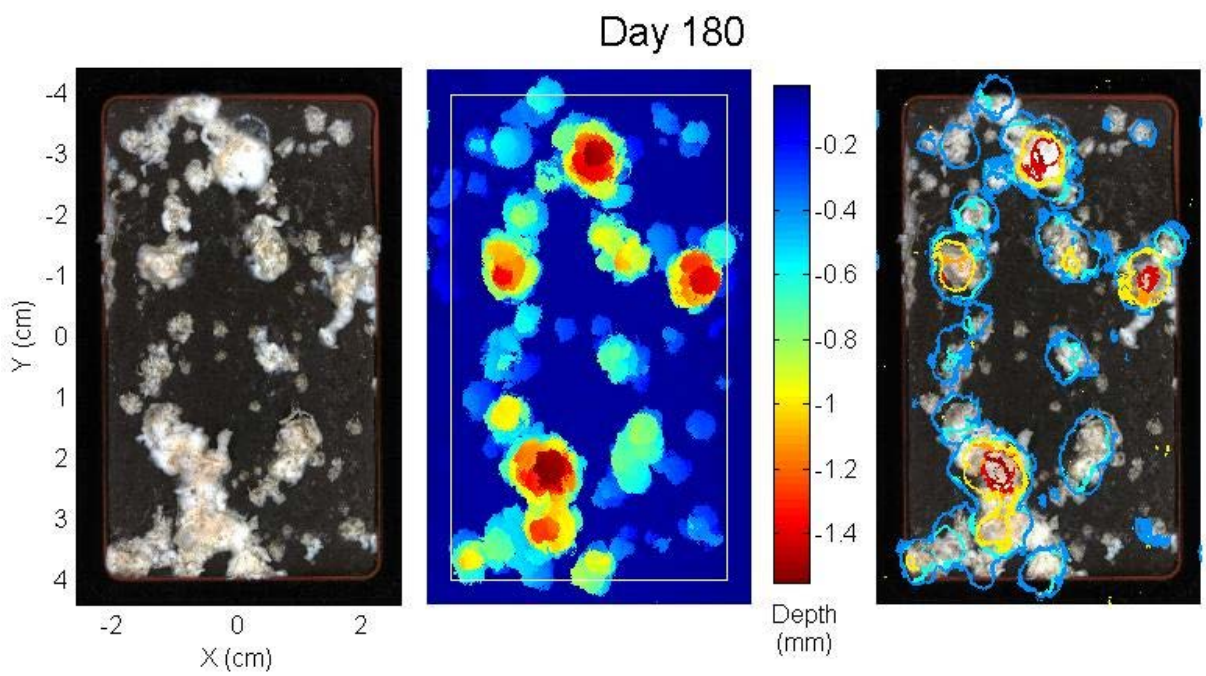


Figure 4: Al 6061 sample in near-stagnant cold seawater at 180 days. Left – imaging, center – ultrasonically determined depth, right – overlay of the two images

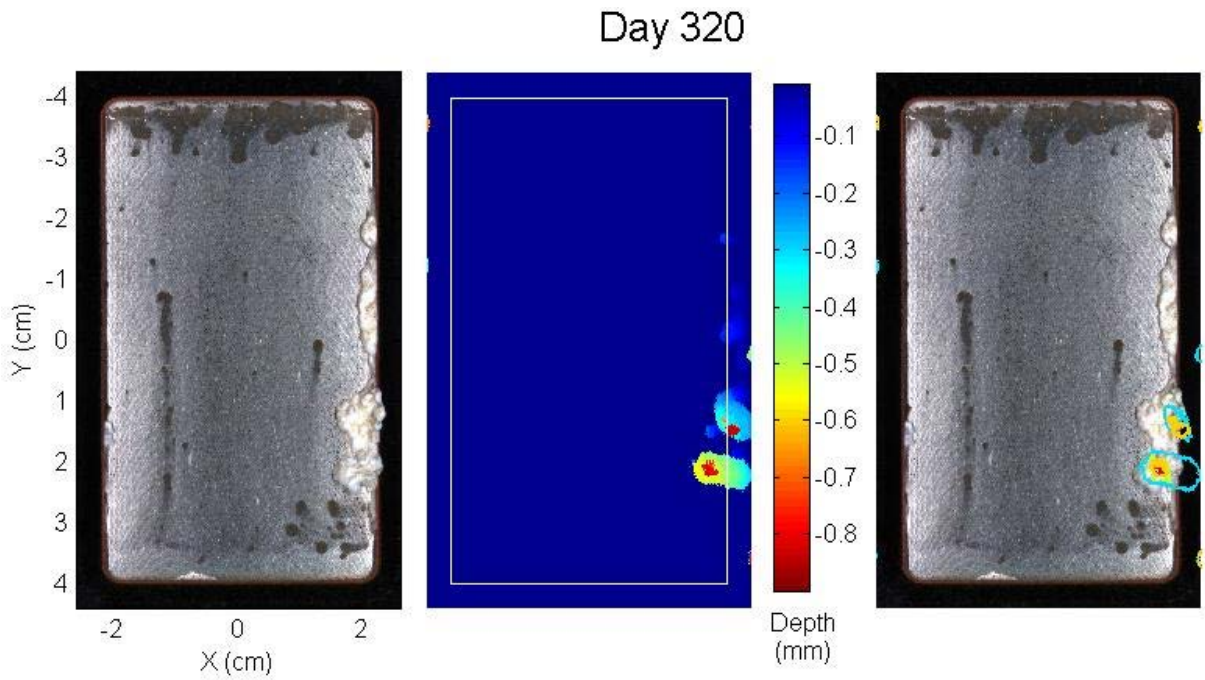


Figure 5: Al 5086 sample in near-stagnant cold seawater at 320 days. Left – imaging, center – ultrasonically determined depth, right – overlay of the two images

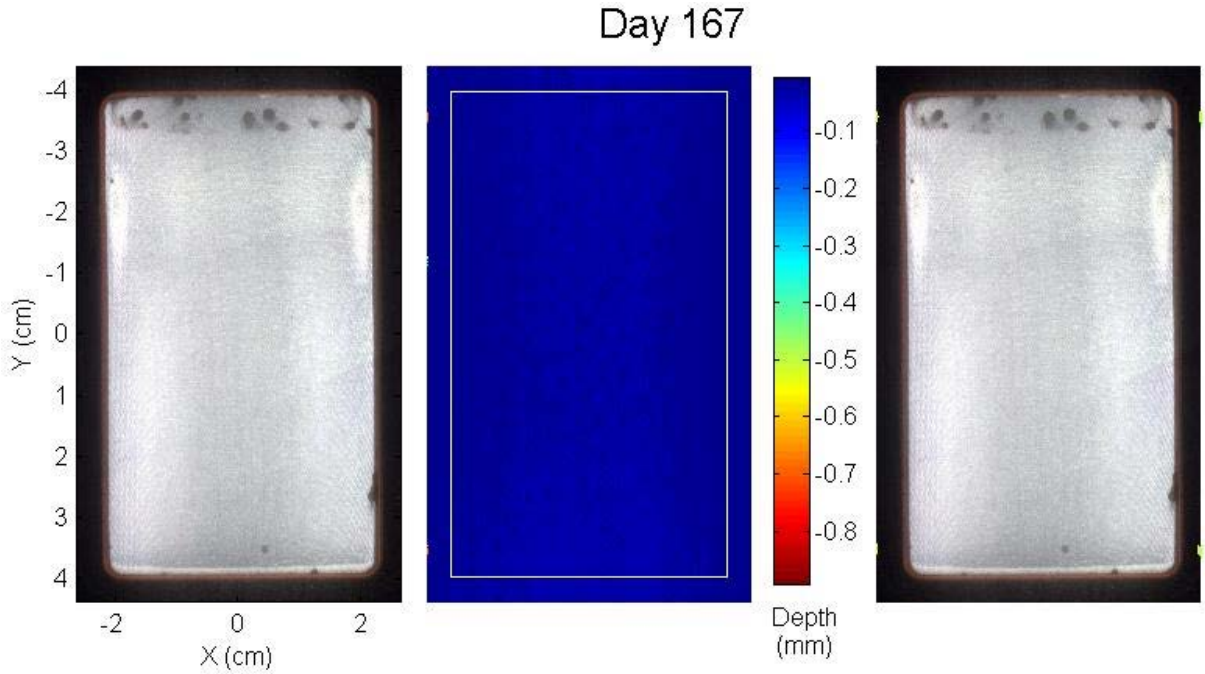


Figure 6: Al 5086 sample in 1 m/s cold seawater at 167 days. Left – imaging, center – ultrasonically determined depth, right – overlay of the two images

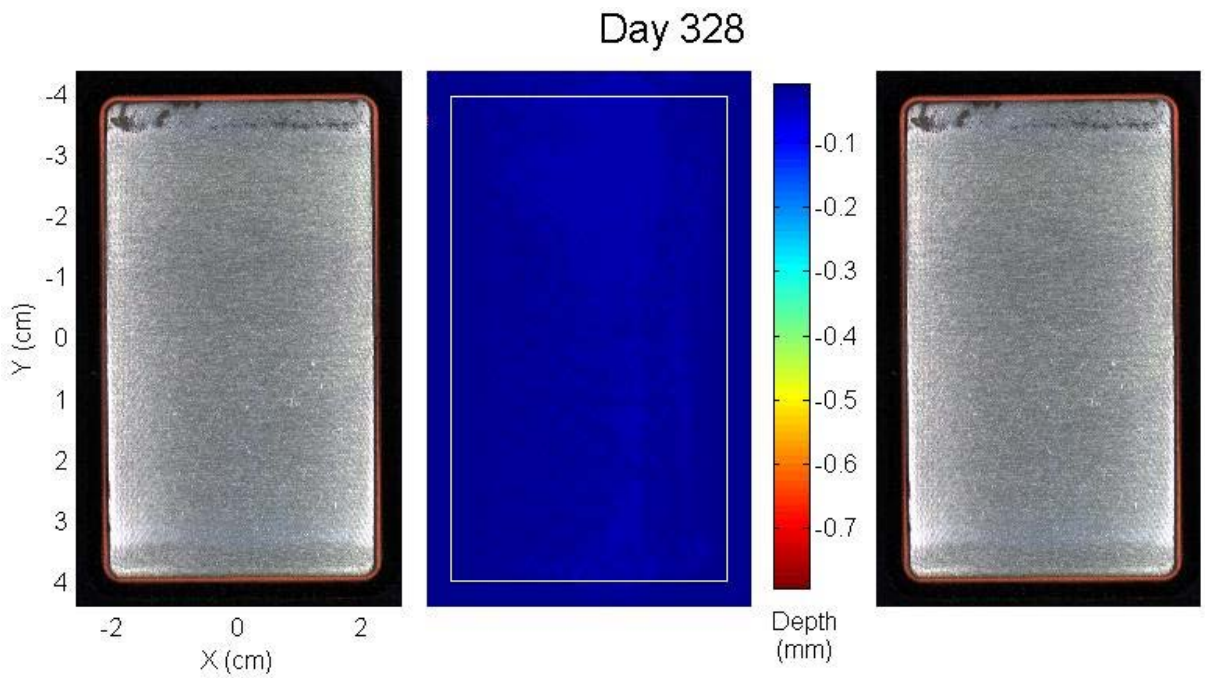


Figure 7: Al 5086 sample in 1 m/s cold seawater at 328 days. Left – imaging, center – ultrasonically determined depth, right – overlay of the two images

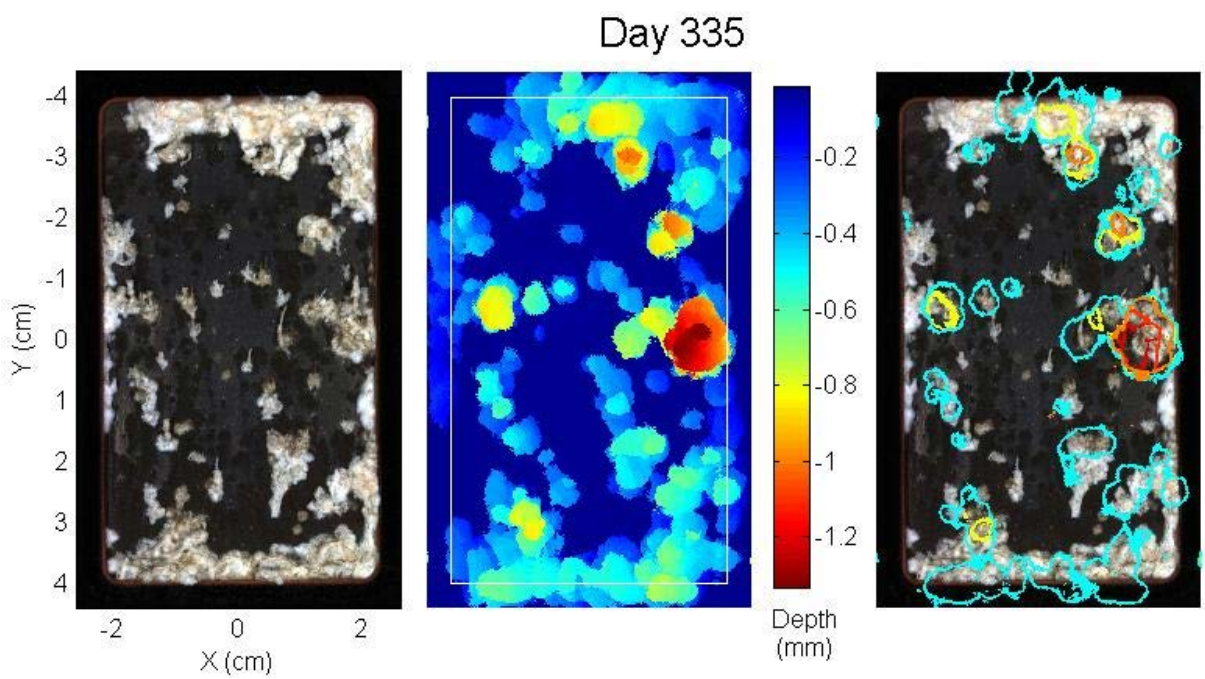


Figure 8: Al 6061 sample in 1 m/s cold seawater at 335 days. Left – imaging, center – ultrasonically determined depth, right – overlay of the two images

Figure 9 shows maximum pit depth over time. On all Al 2024 samples, pits deepened rapidly in the first few weeks. The pit deepening rate then slowed and pit depths have remained

~0.75 mm. For Al 6061 in flowing seawater, pits deepened rapidly for the first few months, then the rate of deepening slowed. In contrast, in near-stagnant seawater, the Al 6061 samples showed a nearly uniform rate of pit deepening. Pit depths reached ~1 mm within a few months; at these rates, a shell-and-tube heat exchanger made from either Al 2024 or Al 6061 would quickly fail. Al 5086 in stagnant seawater has had corrosion at the gasket interface and little to no corrosion elsewhere. Gasket corrosion has reached a depth of 0.9 mm. No corrosion has been detected on Al 5086 in flowing seawater.

The total volume of material removed (Figure 10) is estimated by calculating the mean corrosion depth over the corroded surface area. Due to overestimation of pit area associated with the ultrasonic transducer's beam width, these measurements had to be normalized based on post-processing profilometer data of the three removed samples. The relative trends are informative and were similar to the corroded surface area and maximum pit depth trends.

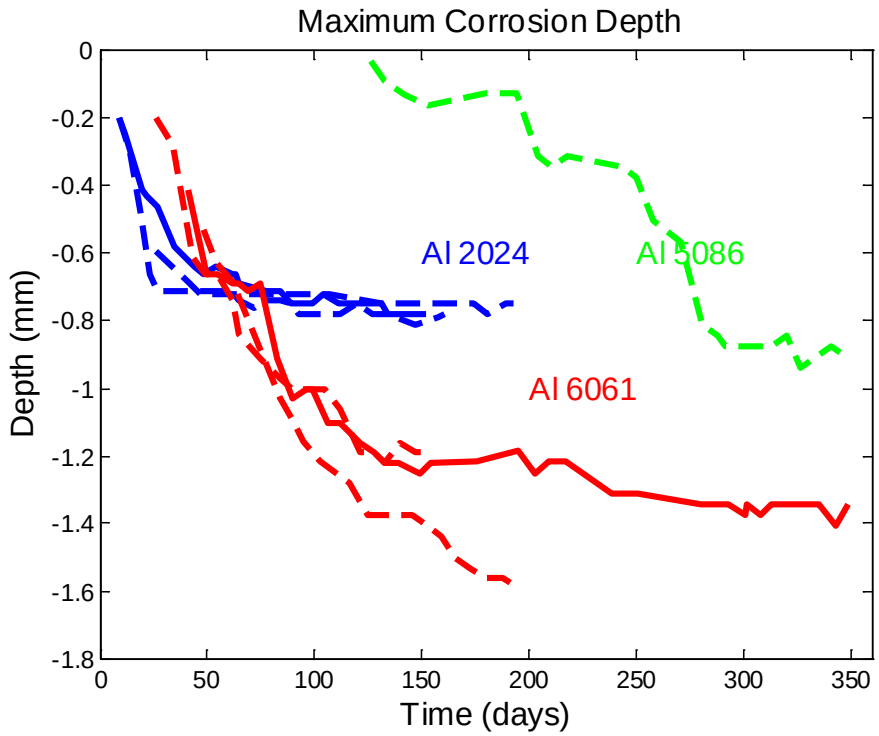


Figure 9: Maximum corrosion depths measured ultrasonically. Dashed lines are samples in near-stagnant seawater and solid lines are in 1 m/s flowing seawater.

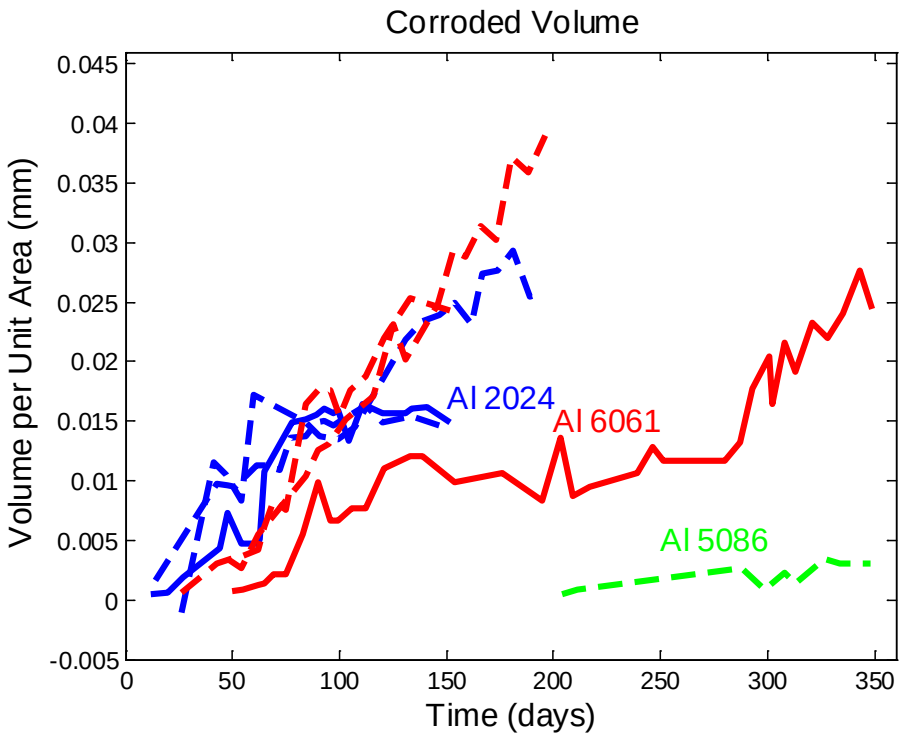


Figure 10: Corroded volume measured ultrasonically. Dashed lines are samples in near-stagnant seawater and solid lines are in 1 m/s flowing seawater.

Figures 11-14 show the progression of corrosion for the currently exposed samples with observable corrosion product.

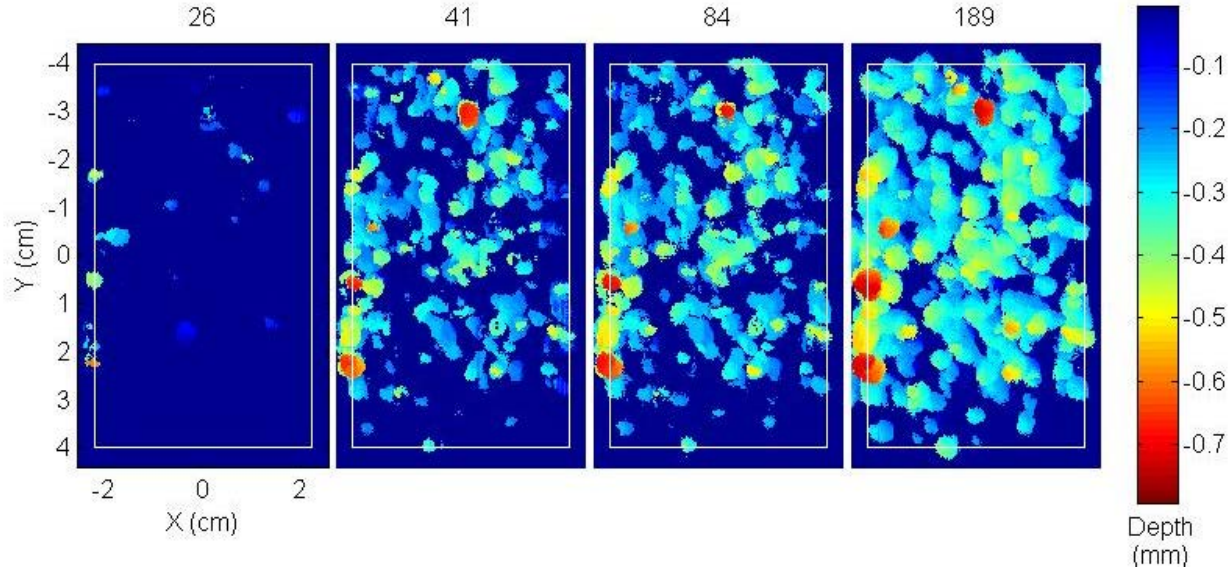


Figure 11: Development over time of the Al 2024 sample in near-stagnant cold seawater.

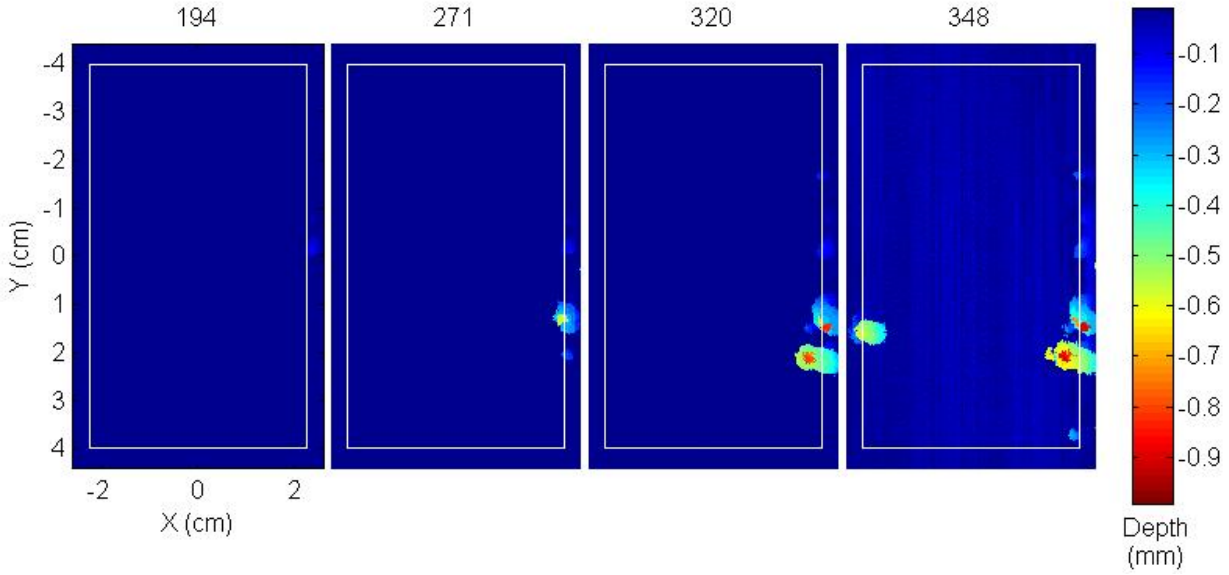


Figure 12: Development over time of the Al 5086 sample in near-stagnant cold seawater.

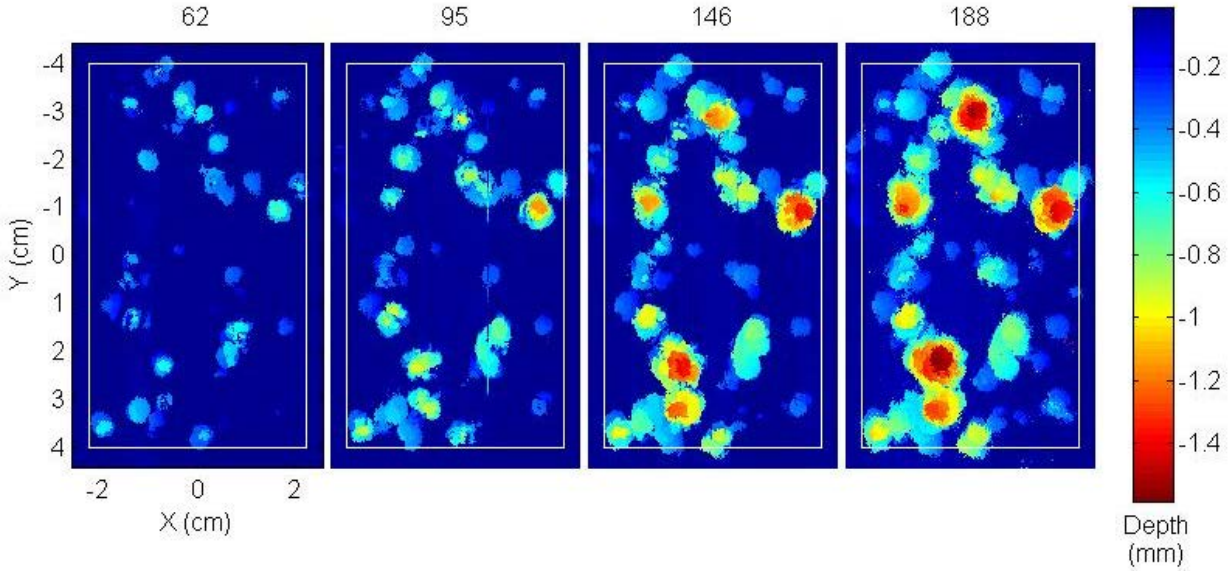


Figure 13: Development over time of the Al 6061 sample in near-stagnant cold seawater.

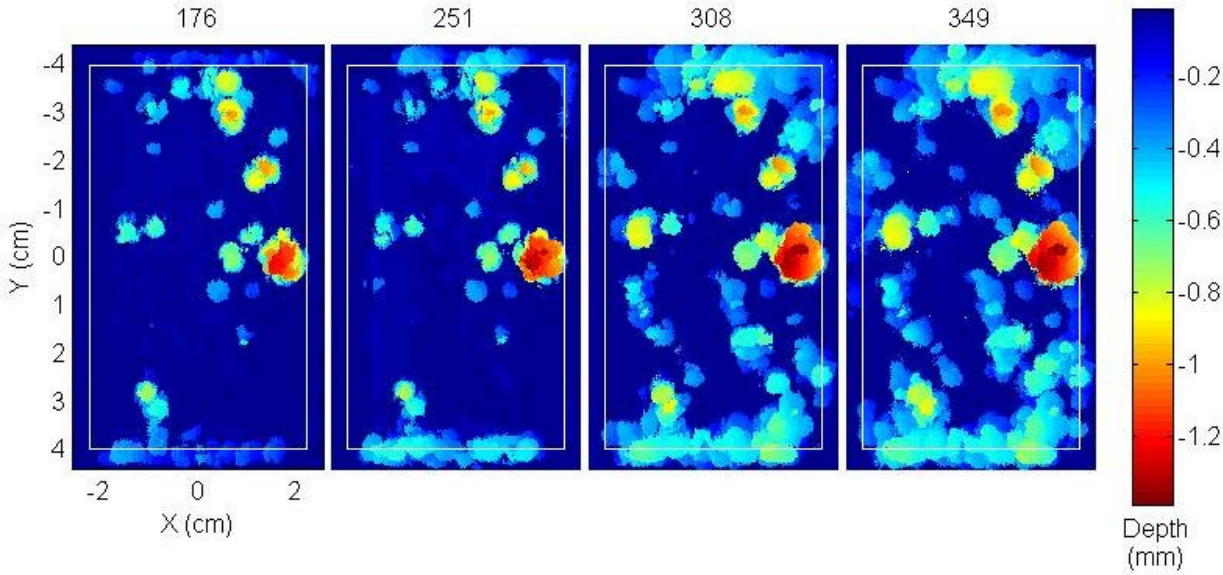


Figure 14: Development over time of the Al 6061 sample in 1m/s flowing cold seawater.

The ultrasonic scanner is capable of detecting corrosion penetration underneath the sample gaskets (Table 2). Although leaks were not observed in any of the samples, the Al 2024 and Al 6061 samples in near-stagnant water developed corrosion outside the gasket, indicating seawater had penetrated under the gasket to the non-exposed side.

Table 2: Gasket corrosion penetration as determined by ultrasonic scans. Lateral penetration is the distance from the inner edge of the gasket to the furthest extent of detected corrosion

Source	Sample	Lateral Penetration from Interior Gasket Edge (mm)	Maximum Corrosion Depth Underneath Gasket (mm)
Near-stagnant Seawater	Al 2024	11.5	0.7
	Al 5086	7.4	0.9
	Al 6061	2.7	0.8
1 m/s Flowing Seawater	Al 5086	-	-
	Al 5086	-	-
	Al 6061	4	0.9

Open-circuit potential (OCP) relative to an Ag/AgCl reference electrode was monitored for all samples (Figure 15). Al 6061 samples show a dramatic change in OCP when corrosion product is first observed, rising abruptly from approximately -1050 mV to approximately -700 mV. OCPs of the Al 2024 samples did not undergo an abrupt change coinciding with the appearance of corrosion, but continue to change over time. The OCP of the two Al 5086 samples in 1 m/s flowing seawater are currently different by about 50 mV while the Al 5086 sample in near-stagnant seawater remains around -700 mV.

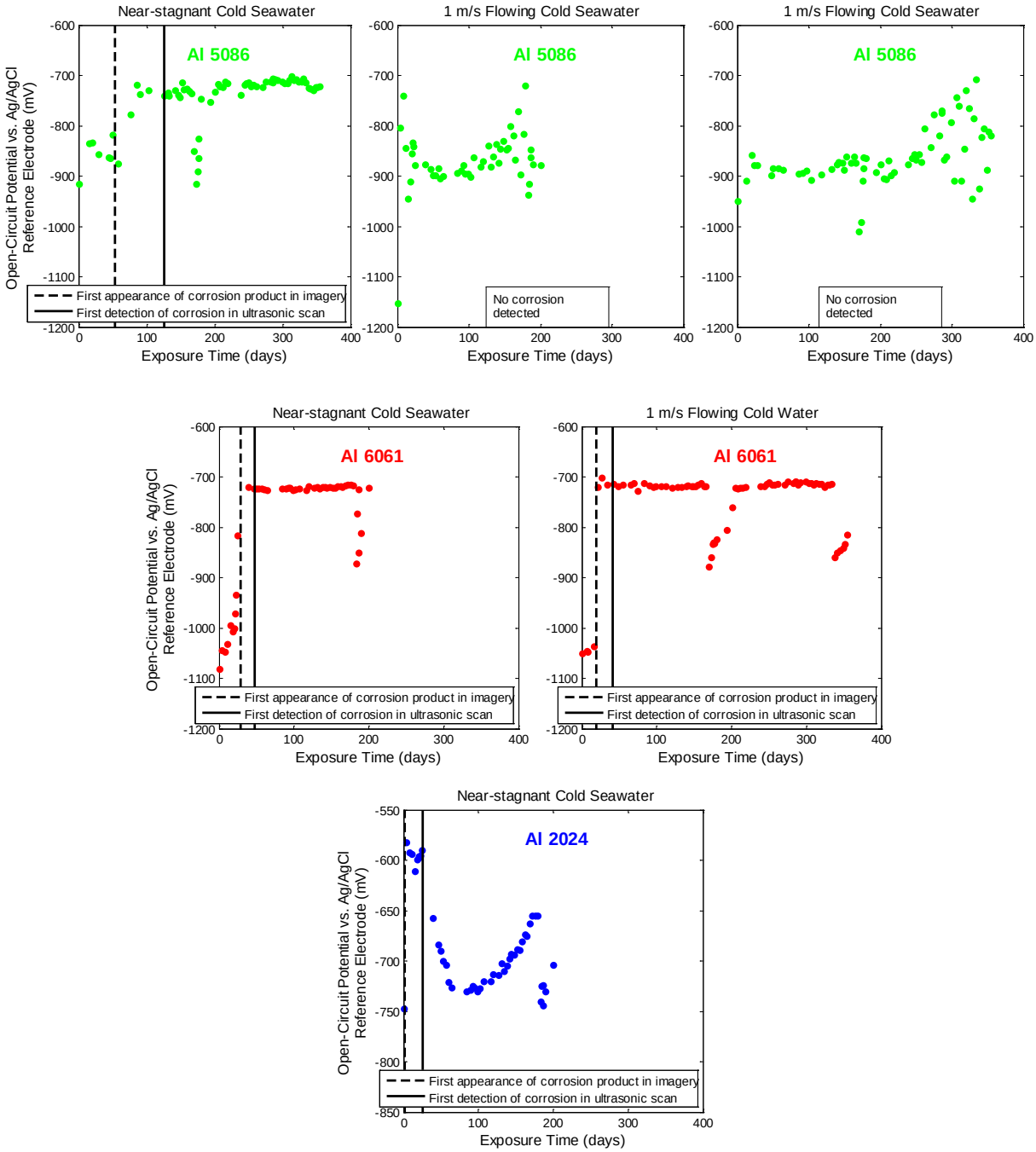


Figure 15: Open-circuit potentials vs Ag/AgCl reference electrode

2.4. FUTURE WORK

All existing samples except Al 5086 in flowing cold seawater will be removed in May 2015. Control samples of Al 1100, Al 3003, and Al 5086 will replace the removed samples. New samples will be placed in the CSW MCIR and testing will start in May 2015. Warm seawater pre-treatment samples will be moved to cold seawater after 40 days, in June 2015.

OTEC HEAT EXCHANGER PROGRAM

ULTRASONIC SCANNING FOR CORROSION MONITORING

SHAKEDOWN TEST

(revised, version 2)

SUBAWARD MA150017

Prepared For

HAWAII NATIONAL MARINE RENEWABLE ENERGY CENTER

LUIS VEGA

1680 East West Road, POST 112A

Honolulu, HI, 96822

USA

Prepared By

MAKAI OCEAN ENGINEERING

PO Box 1206, Kailua, Hawaii 96734

November 2015

1. INTRODUCTION

Aluminum alloys have been proposed for use in Ocean Thermal Energy Conversion (OTEC) heat exchangers for their high thermal conductivity, comparatively low cost, and overall good general corrosion resistance (due to formation of a protective oxide layer) in seawater environments. Although uniform corrosion rates for aluminum alloys are low, aluminum alloys are susceptible to surface pitting and crevice corrosion at gasket interfaces which can initiate when local galvanic cells develop between alloying elements and deposit corrosion product on the surface of the metal. Corrosion product can encase the immediate area and change the local environment which acts to accelerate the corrosion process. It is important to quantify this phenomenon because, in time, pits or crevice corrosion can penetrate the wall of the heat exchanger and cause refrigerant to leak into the seawater. For heat exchangers, this is considered a catastrophic failure and must be avoided.

Makai Ocean Engineering has been studying and quantifying the development of corrosion on aluminum alloys being considered for OTEC heat exchangers. Makai has developed a setup in which pit growth can be observed in-situ by optical imaging and ultrasonic scanning. Pitting sites are identified and corrosion product accumulation on the metal surface is observed using imagery. However, once corrosion product encapsulates a pit, no accurate measurements of pit size or depth can be made with imaging alone. With the addition of ultrasonic thickness scanning, the surface underneath the corrosion product can be observed and the 3-dimensional structure of the pit can be measured. Pit development can now be monitored over time without removal or destruction of samples.

Makai is currently testing three alloys (Al 1100-H112, Al 3003-F and Al 5086-H116) and three corrosion mitigation techniques (warm seawater pre-treatment, hypo-chlorination and exposure to a diluted sulfamic acid) in flowing (1 m/s) and near stagnant cold seawater for a total of 18 samples. Six control samples, one of each alloy in flowing and near stagnant cold seawater, are also being tested.

2. STATUS

All parts for the experiment have been procured and installed into our multicolumn imaging rack. The ultrasonic scanner has been mounted on the backside of the rack and plumbed to provide freshwater to ultrasonically couple the transducer to the sample. In each column, samples are subjected to one of three treatments: warm seawater pre-treatment, hypochlorination, or acid treatment; in either flowing (1 m/s) or near stagnant cold seawater (Table 1). Alloys in each column are arranged in the same order from top to bottom: Al 5086, Al 3003, and Al 1100. Laser profilometer scans of the test surfaces were conducted prior to exposure for each sample. All corrosion samples were degreased, cleaned with simple green, and rinsed with ethanol before installation to remove surface contaminants.

Table 1. Current test samples.

Column	Sample IDs	Water Flow	Treatment
9	ut5-18, ut3-18, ut1-18	Near Stagnant	Control
10	ut5-1*, ut3-17, ut1-17	Flowing	Control
4	ut5-11, ut3-11, ut1-11	Flowing	Warm seawater pre-treatment
5	ut5-12, ut3-12, ut1-12	Near Stagnant	Warm seawater pre-treatment
6	ut5-16, ut3-16, ut1-16	Near Stagnant	Hypochlorination
7	ut5-15, ut3-15, ut1-15	Flowing	Hypochlorination
14	ut5-14, ut3-14, ut1-14	Near Stagnant	Acid Treatment
15	ut5-13, ut3-13, ut1-13	Flowing	Acid Treatment

* Original sample, continued from previous round of testing.

Treatments are expected to minimize pit depths (and/or presence). The warm seawater pre-treatment protocol was developed on the hypothesis that corrosion resistance in cold seawater would improve if samples exposed in cold seawater had the same protective oxide layer as samples in warm seawater. Initially exposing samples in warm seawater allows the oxide layer to develop and, when performed carefully, the developed oxide layer remains when samples are relocated to cold seawater. Previous testing established 40 days in warm seawater is the sufficient time to build the oxide layer.

The hypochlorination treatment protocol is currently used in warm seawater to control biofouling. Bacterial colonies have been observed on samples exposed to cold seawater; while the exact mechanism for pit initiation is unknown, any difference in the local surface environment can accelerate corrosion. Thus, bacterial colonies on a sample's surface may act as pit initiation sites. Samples are exposed to 100 ppb chlorine for 1 hour daily to control the growth of bacterial colonies.

The acid treatment protocol was developed based on observations of open circuit potential (OCP) and corresponding corrosion activity. Samples have shown a marked change in OCP once pitting begins. Treatment of a sample with a mild acid will strip the oxide layer and possibly remove local environments that may have developed, essentially 'resetting' the surface to the condition it was in when first exposed to seawater. In previous tests, application of 5% sulfamic acid for 5 minutes lowers OCP to the passive region for Al 6063.

Several issues arose in the procurement and installation of the new samples. The original samples were received with a sanded surface finish which was unacceptable for testing. Samples were returned for re-surfacing and received with tool marks on the surface. Although not ideal, we decided the finish was acceptable for testing. Samples also did not have countersunk holes as specified in the drawing. Countersinking was performed on-site by Makai, with care taken to ensure the exposed surface would not come into contact with metal or other contaminants. Finally, perhaps due to the re-surfacing, the non-exposed side (the side scanned by the ultrasonic scanner) of some samples did not lie flush with the mounting plate. A smooth transition is needed for the transducer to maintain adequate contact and not "catch" on edges. With the samples screwed into place, a sander was used to remove excess material from the mounting plate and create a smooth, even transition for the transducer. Some material may have also been removed from the back of the sample in the process.

Warm seawater pre-treatment samples were exposed to warm seawater on 4/22/15 and moved to cold seawater on 6/15/15. Control, hypo-chlorination, and acid treatment samples were exposed to cold seawater on 5/21/15.

The imaging system automatically images the front face of each sample daily. The samples are scanned ultrasonically at least once a month. The frequency of ultrasonic scanning will be adjusted based on corrosion development. We continue to encounter frequent corrupted data files despite two repair attempts by the manufacturer. They determined it is a problem with all their scanners so they are working on a firmware fix which we still do not have. We have developed a work around where we can re-assemble the corrupted data and we will do so until the manufacturer can provide resolution.

PREVIOUS SAMPLES RESULTS

All previously tested samples except Al 5086 in flowing seawater were removed in May 2015 (Table 2). The Al 5086 sample in flowing seawater continues to be tested and will be used as the control.

Table 2. Previous test samples.

Alloy	Serial #	Source	Exposure Date	Removal Date
5086	ut 5-1	Flowing	4/16/14	ongoing
	ut 5-2	Stagnant	4/16/14	9/8/14
	ut 5-4		9/8/14	5/21/15
6061	ut 6-3	Flowing	4/16/14	5/21/15
	ut 6-2	Stagnant	4/16/14	9/8/14
	ut 6-4		9/8/14	5/21/15
2024	ut 2-1	Flowing	4/16/14	9/8/14
	ut 2-3		9/8/14	5/21/15
	ut 2-2	Stagnant	4/16/14	9/8/14
	ut 2-4		9/8/14	5/21/15

Al 2024 and 6061 samples were severely corroded; maximum pit depths measured by ultrasonic scans prior to removal were ~ 0.78 mm and ~ 1.8 mm, respectively (Figure 1). As previously observed, pit depths in Al 2024 for both flowing and near stagnant seawater were comparable and reached maximum depths around 150 days and have not deepened significantly. Pits in Al 6061 continued to deepen, with the near stagnant sample having deeper pits than the flowing sample. The corroded surface area has continued to increase for samples of both alloys in both flowing and near-stagnant seawater. Pits were identified on the near stagnant Al 5086 sample after 180 days. The corroded surface area has not changed significantly but the maximum pit depth has increased, reaching -0.9 mm after one year. Pits on the Al 5086 sample in flowing seawater were detected in images after 477 days and by ultrasonic scan after 499 days. Crevice corrosion was observed on all samples.

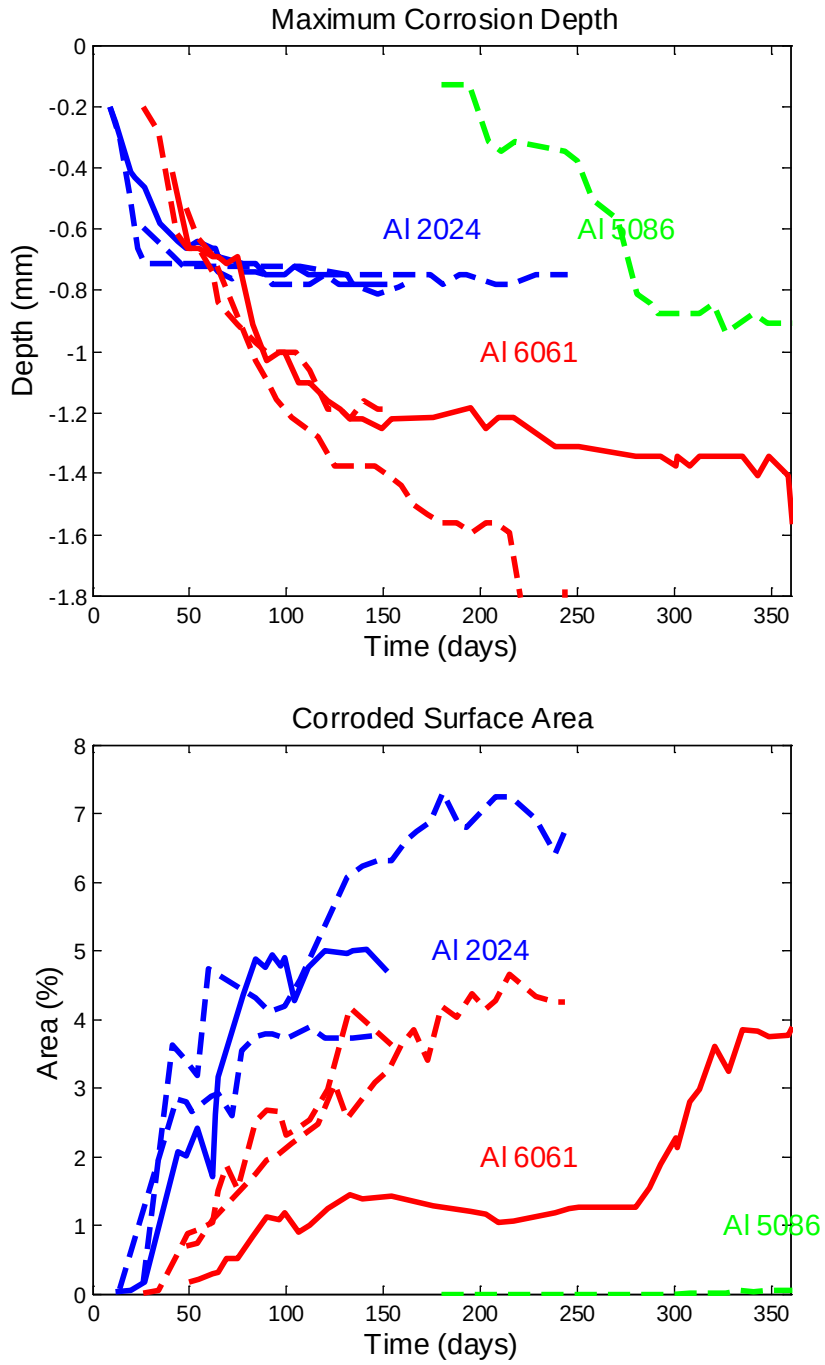


Figure 1. (top) Maximum pit depths and (bottom) corroded surface area of removed samples. Solid lines represent samples in flowing cold seawater, dashed lines represent samples in near stagnant cold seawater.

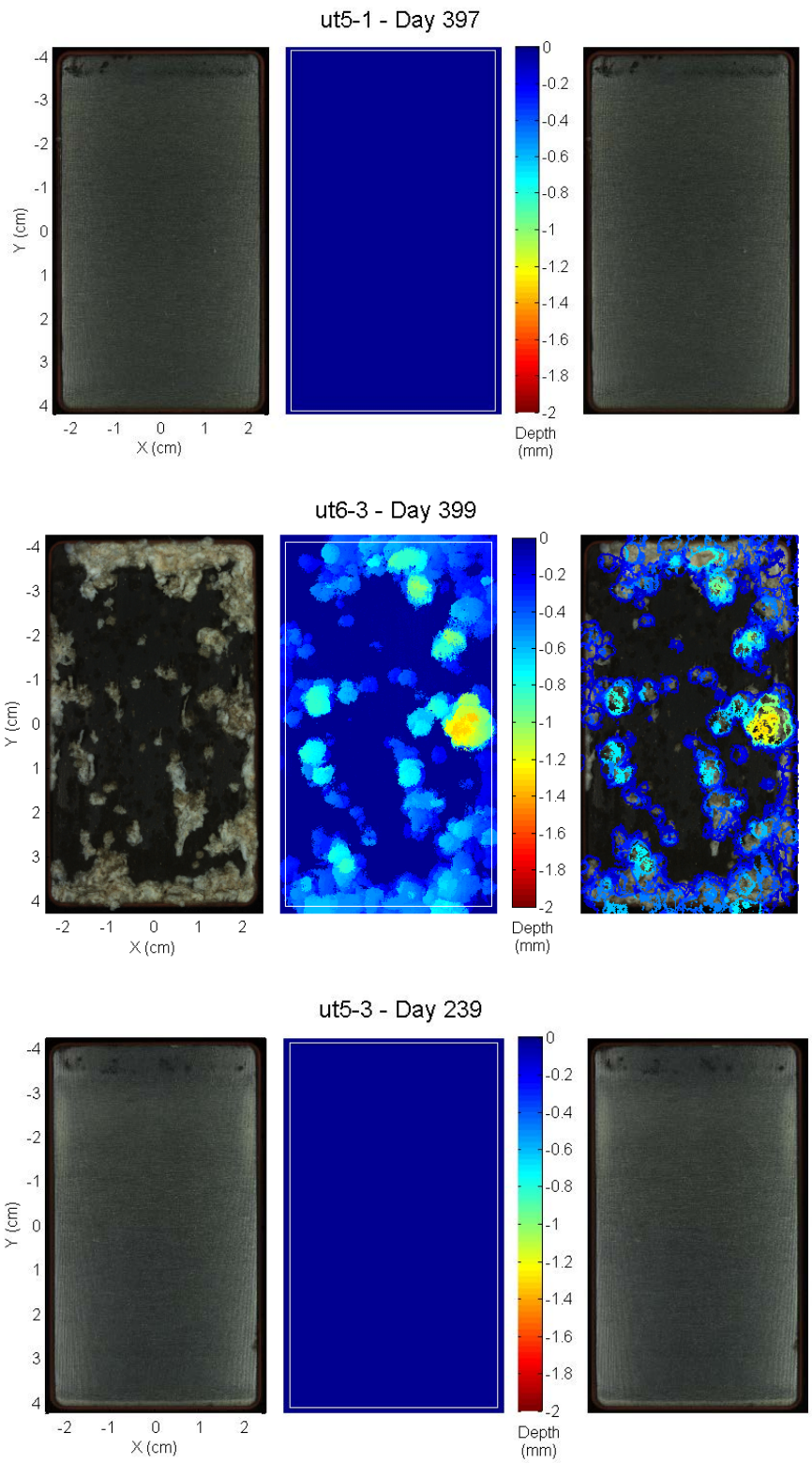


Figure 2. Samples from previous test in flowing seawater just prior to removal on 5/21/15. Only ut5-1 is still being tested. Panels from left to right: imaging, ultrasonic scan, image overlain with depth contour lines from the ultrasonic scan.

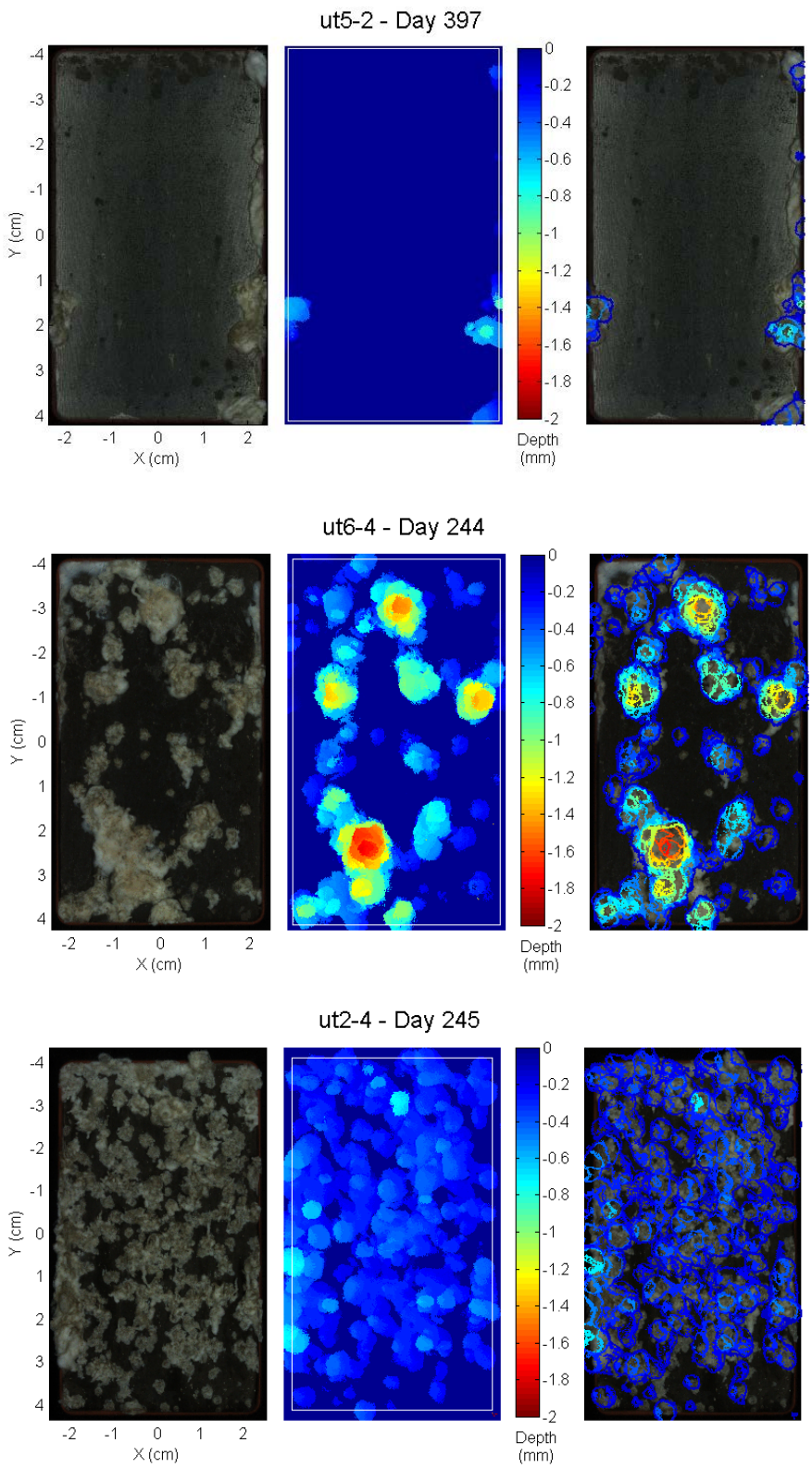


Figure 3. Samples from previous test in near stagnant seawater just prior to removal on 5/21/15. Panels from left to right: imaging, ultrasonic scan, image overlain with depth contour lines from the ultrasonic scan.

Table 3. Crevice corrosion at the gasket interface at time of removal. Lateral penetration is the distance from the inner edge of the gasket to the furthest extent of corrosion. The maximum corrosion depth underneath gasket is not necessarily in the same location as the maximum lateral penetration.

Source	Sample	Lateral Penetration (mm)	Maximum Corrosion Depth Underneath Gasket (mm)
Near-stagnant Seawater	Al 2024	2	-0.5
	Al 6061	4	-0.7
	Al 5086	4	-0.9
1 m/s Flowing Seawater	Al 2024	4	-0.7
	Al 6061	3.7	-0.7
	Al 5086*	-	-

* Sample is still being tested. No crevice corrosion observed on sample at time of removal of other samples.

CURRENT SAMPLES DATA COLLECTION

This report contains data collected up to the end of August 2015. As of September 1, 2015, the warm seawater pre-treatment samples have been exposed for a total of 131 days and the control, hypochlorination, and acid treatment samples have been exposed for 103 days.

2.1.1. Pitting corrosion

No pits have been observed on any of the new samples. Only an 1.5” x 2.75” area at the center of each sample is analyzed for pitting to minimize the influence of crevice corrosion. Small pits were observed on the Al 5086 control sample in flowing seawater (ut5-1) after 477 days via imaging and after 499 days via ultrasonic scans.

2.1.2. Crevice corrosion

Crevice corrosion is present on most samples. Most samples with crevice corrosion identified in the images also have crevice corrosion identified in the ultrasonic scans. Of the samples that received warm seawater pre-treatment, only Al 1100 in near stagnant seawater has crevice corrosion. Of the samples receiving daily hypochlorination treatment, only the Al 1100 samples in flowing and near stagnant seawater have crevice corrosion. All samples receiving acid treatment have crevice corrosion. All control samples have crevice corrosion, although, crevice corrosion did not occur on the Al 5086 until 477 days of total exposure. The Al 1100 and Al 3003 control samples in flowing seawater developed crevice corrosion before the Al 5086 sample.

Table 4. Crevice corrosion at the gasket interface. Lateral penetration is the distance from the inner edge of the gasket to the furthest extent of corrosion. The maximum corrosion depth underneath gasket is not necessarily in the same location as the maximum lateral penetration.

Water Flow	Treatment	Sample	Present on image?	Lateral Penetration [mm]	Maximum Depth under Gasket [mm]
Near Stagnant	Control	ut5-18	Yes	n.d.	n.d.
		ut3-18	Yes	3.2	0.75
		ut1-18	Yes	2.9	0.4
Flowing	Control	ut5-1	No*	-	-
		ut3-17	Yes	3.1	0.1
		ut1-17	Yes	1.6	0.1
Near Stagnant	Hypochlorination	ut5-16	No	-	-
		ut3-16	No	-	-
		ut1-16	Yes	n.d.	n.d.
Flowing	Hypochlorination	ut5-15	No	-	-
		ut3-15	No	-	-
		ut1-15	Yes	n.d.	n.d.
Near Stagnant	Acid treatment	ut5-14	Yes	2.7	0.2
		ut3-14	Yes	3.2	0.7
		ut1-14	Yes	2.9	0.3
Flowing	Acid treatment	ut5-13	Yes	n.d.	n.d.
		ut3-13	Yes	2.5	0.4
		ut1-13	Yes	0.8	0.03
Near Stagnant	Warm seawater pre-treatment	ut5-12	No	-	-
		ut3-12	No	-	-
		ut1-12	Yes	n.d.	n.d.
Flowing	Warm seawater pre-treatment	ut5-11	No	-	-
		ut3-11	No	-	-
		ut1-11	No	-	-

n.d. = not detected on ultrasonic scans.

* For the same exposure time, no crevice corrosion or pits were detected on the Al 5086 control sample in flowing seawater. Crevice corrosion was detected on images after 477 days.

Images of samples with crevice corrosion are shown in Figures 4-7. Samples without corrosion features are not shown at this time.

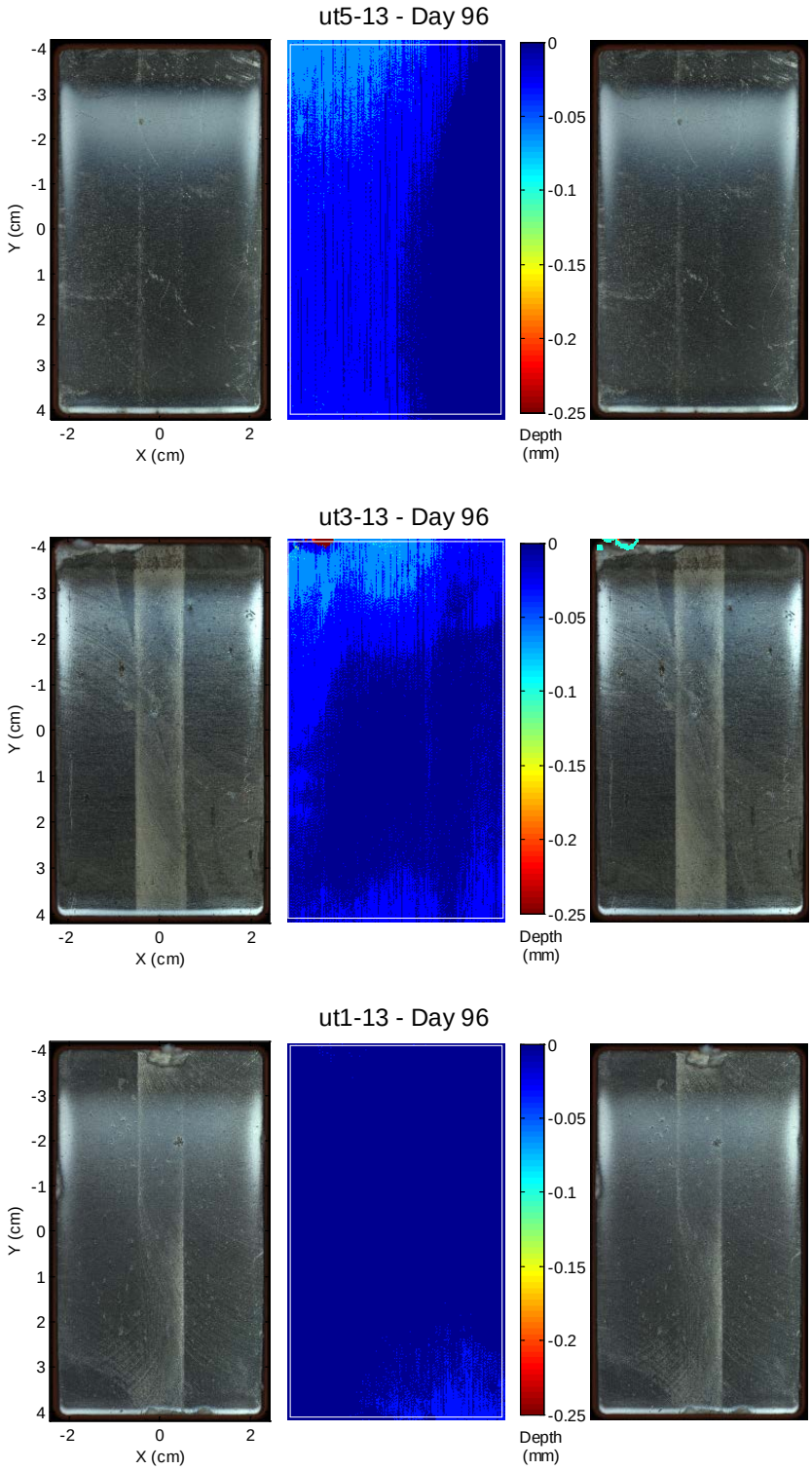


Figure 4. Acid treatment samples in flowing seawater. Crevice corrosion is visible in all images but barely detectable in ultrasonic scans for Al 1100 and Al 5086. Crevice corrosion is most severe on Al 3003. Panels from left to right: imaging, ultrasonic scan, image overlain with depth contour lines from the ultrasonic scan.

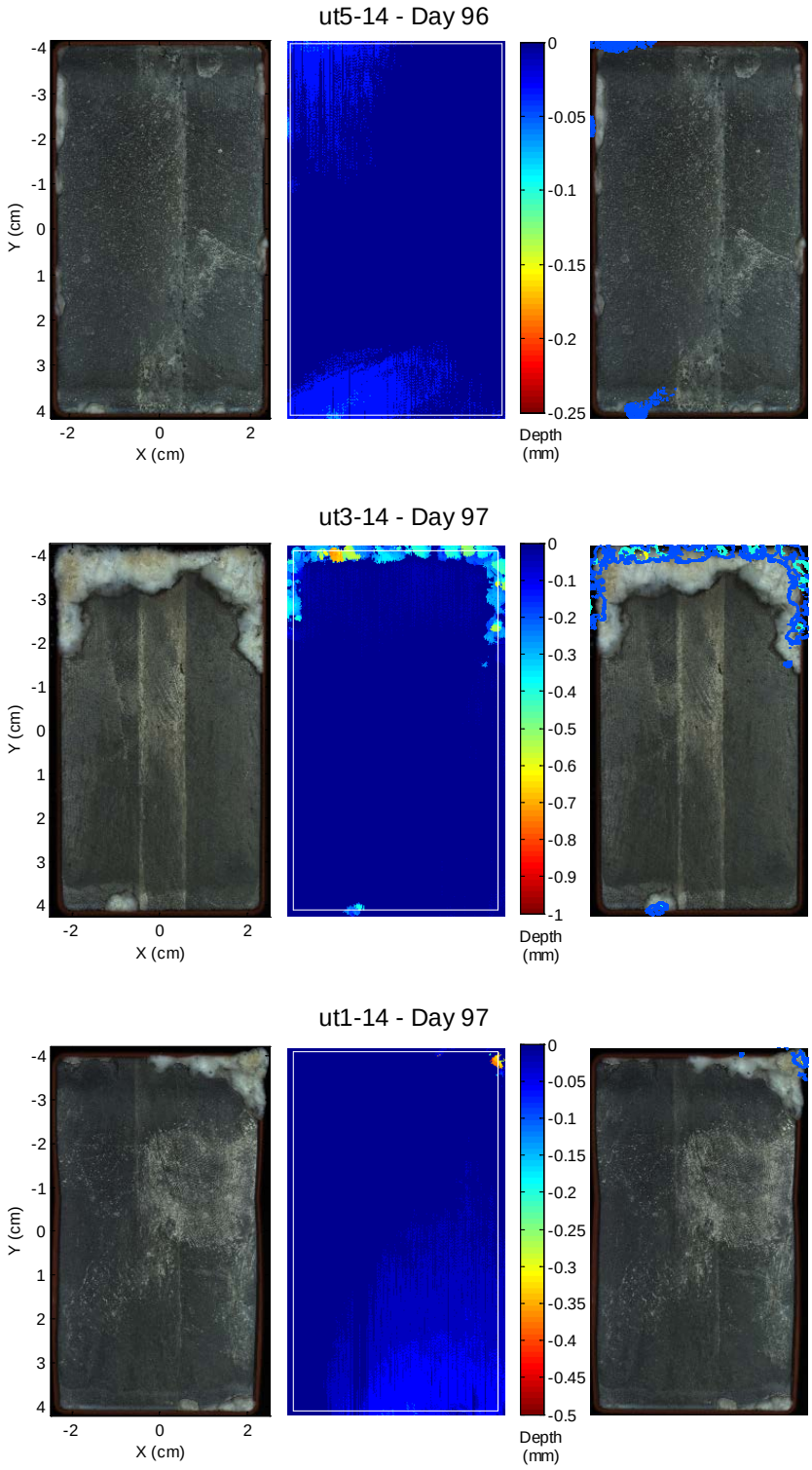


Figure 5. Acid treatment samples in near stagnant seawater. Crevice corrosion is visible in all images but barely detectable in ultrasonic scans for Al 5086. Crevice corrosion is most severe on Al 3003. Panels from left to right: imaging, ultrasonic scan, image overlain with depth contour lines from the ultrasonic scan.

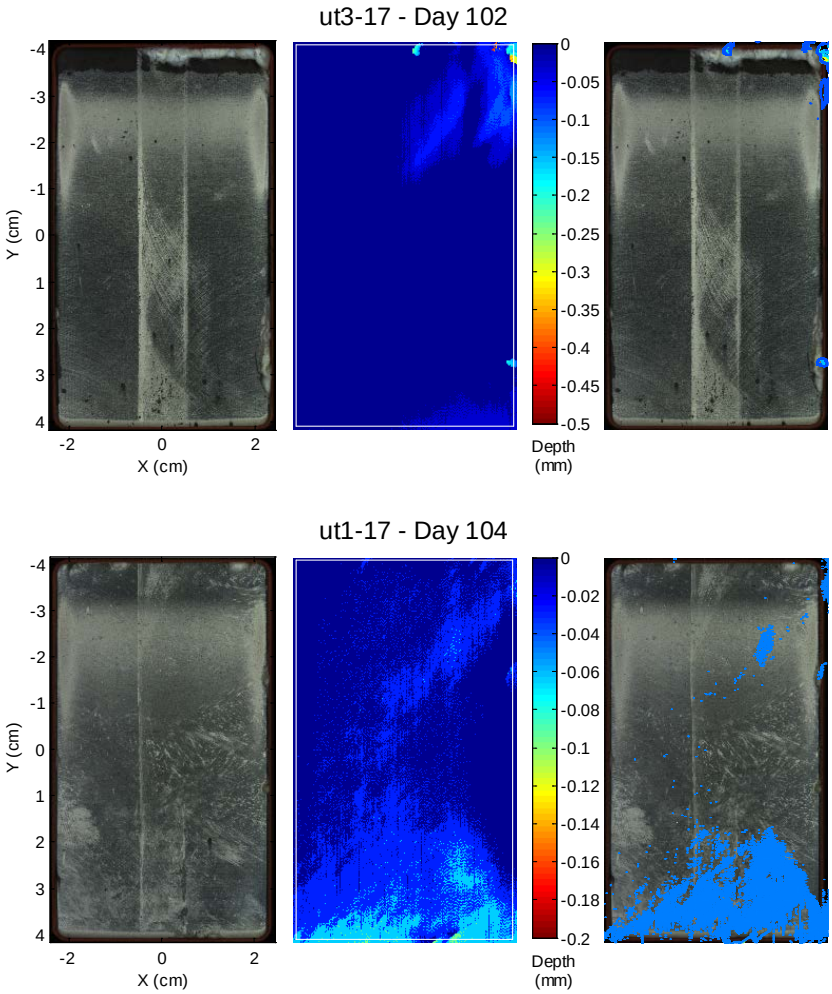


Figure 6. Al 3003 and Al 1100 control samples in flowing seawater. The start of crevice corrosion is detected on ut1-17. ut1-17 has uneven thickness, the variability makes shallow crevice corrosion difficult to distinguish. Panels from left to right: imaging, ultrasonic scan, image overlain with depth contour lines from the ultrasonic scan.

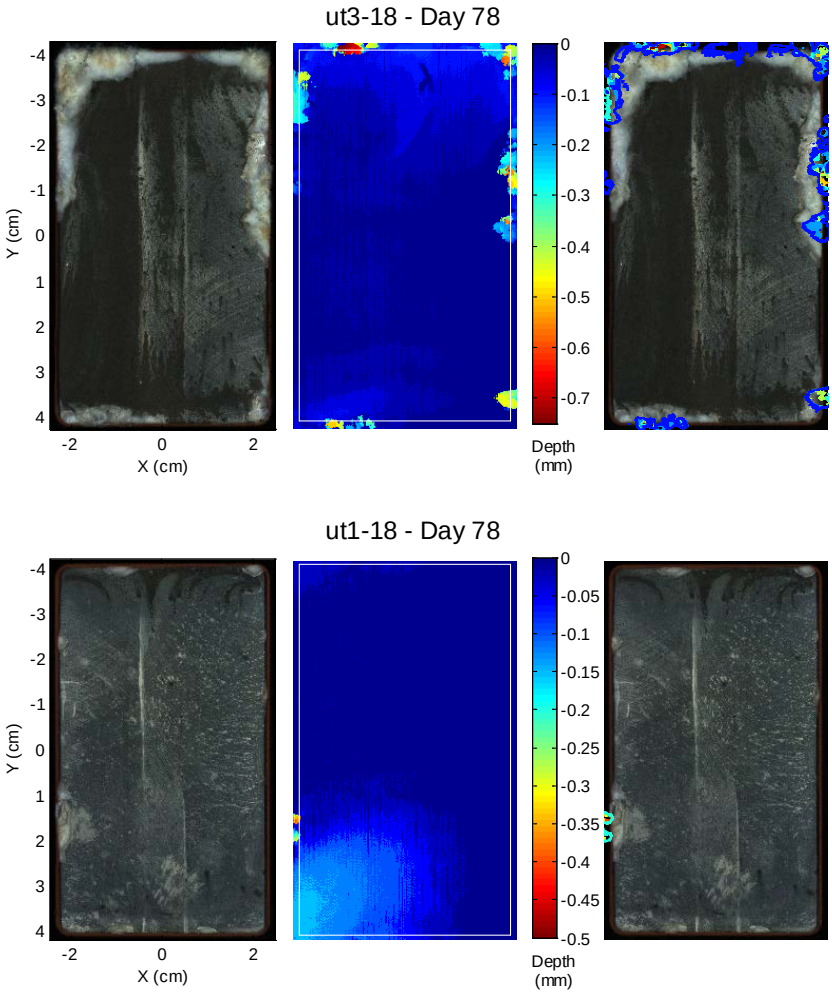


Figure 7. Al 3003 and Al 1100 control samples in flow near stagnant seawater. Uneven thickness on ut1-18 accounts for the lower left corner of the sample. Panels from left to right: imaging, ultrasonic scan, image overlain with depth contour lines from the ultrasonic scan.

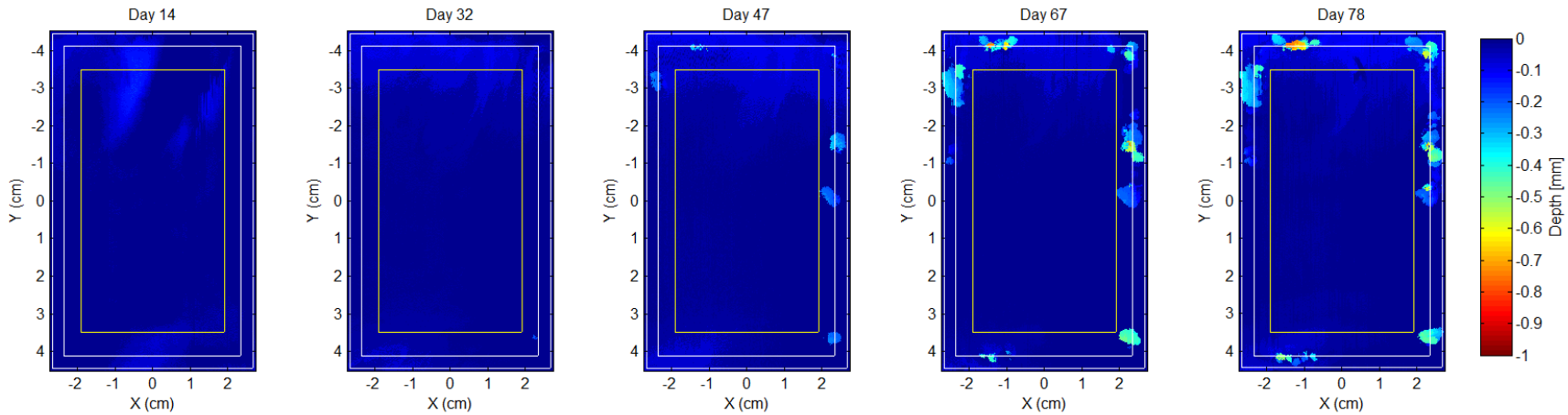


Figure 8. Gasket corrosion development on Al 3003 control sample in near stagnant seawater. Inner yellow rectangle is the area analyzed for pitting. The white rectangles are the inner and outer edges of the gasket.

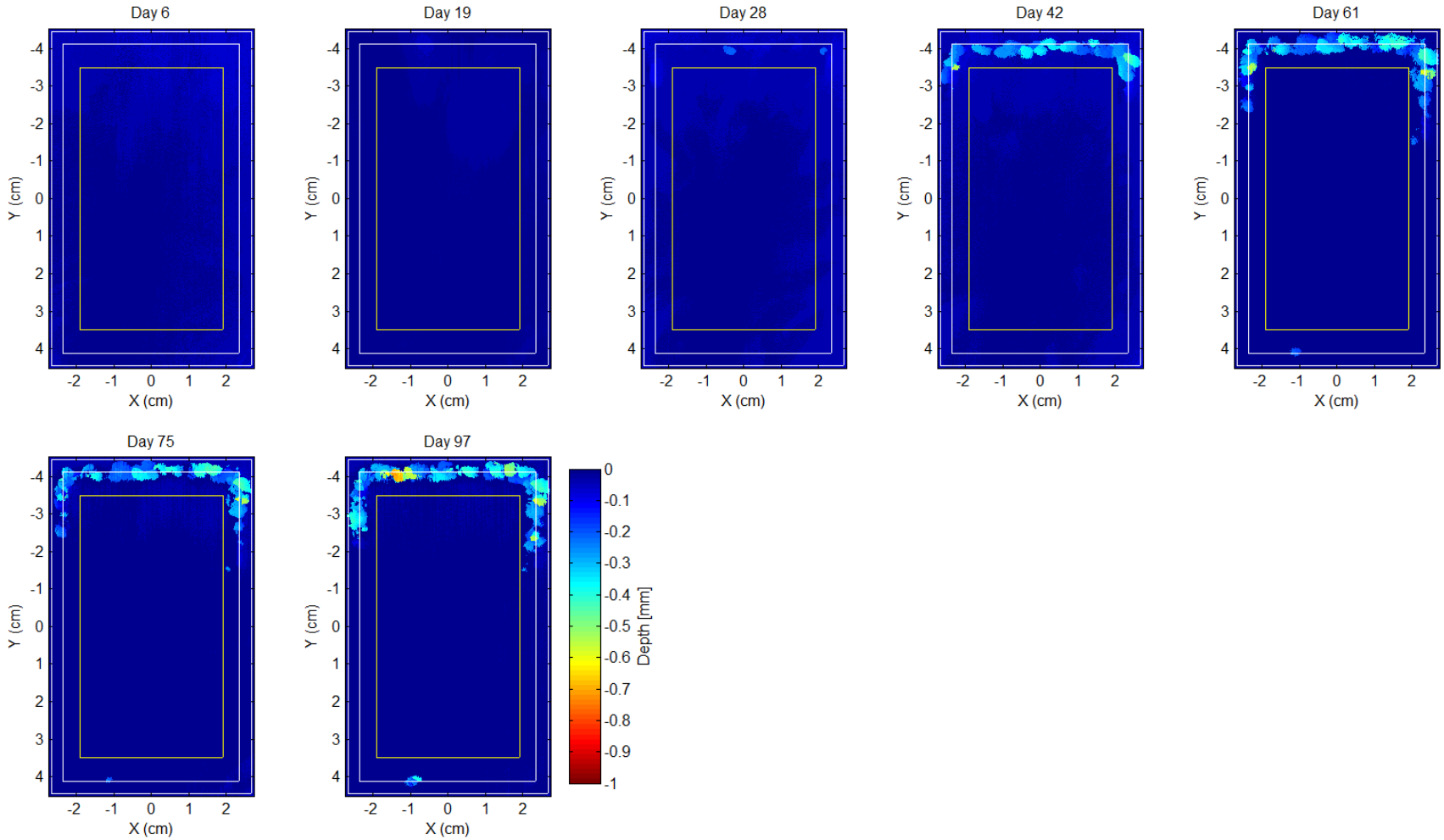


Figure 9. Crevice corrosion development on acid treated Al 3003 sample in near stagnant seawater. Inner yellow rectangle is the area analyzed for pitting. The white rectangles are the inner and outer edges of the gasket.

2.1.3. Open Circuit Potential (OCP)

For Al 1100 samples, there is little difference in OCP between the different treatments in either flowing or near stagnant seawater. No change in OCP was observed after an acid treatment. All OCPs are comparable, yet only the warm seawater pre-treatment sample in flowing seawater is free from crevice corrosion. OCP is not a strong indicator of corrosion for Al 1100.

For Al 3003 samples, the warm seawater pre-treatment, acid treatment, and control samples have comparable OCPs in flowing and near stagnant seawater, whereas hypochlorination samples have lower OCPs. Acid treatments lowered OCP immediately after treatment but OCPs returned to higher values within 20 days post treatment. Crevice corrosion was detected on the acid treatment and control samples in flowing and near stagnant seawater. The OCPs of those samples is in the expected pitting range. However, the warm seawater pre-treatment samples' OCP is also in the pitting range, yet no pitting or crevice corrosion has been detected. It is possible the warm seawater pre-treatment alters the OCP response of the sample and OCP may still be a good indicator of localized corrosion for Al 3003.

For Al 5086 samples, warm seawater pre-treatment samples in flowing and near stagnant seawater have comparable OCPs. The acid treatment samples have lower OCP in flowing seawater than in near stagnant seawater. In flowing seawater, OCP lowers after an acid treatment, whereas in near stagnant seawater, there is little change in OCP after an acid treatment. The acid treatment and warm seawater pre-treatment samples in near stagnant seawater have comparable OCPs. The hypochlorination and control samples have comparable OCPs in the same water source with slightly lower OCPs in flowing seawater than in near stagnant seawater. OCP value and the appearance of crevice corrosion do not appear correlated for Al 5086.

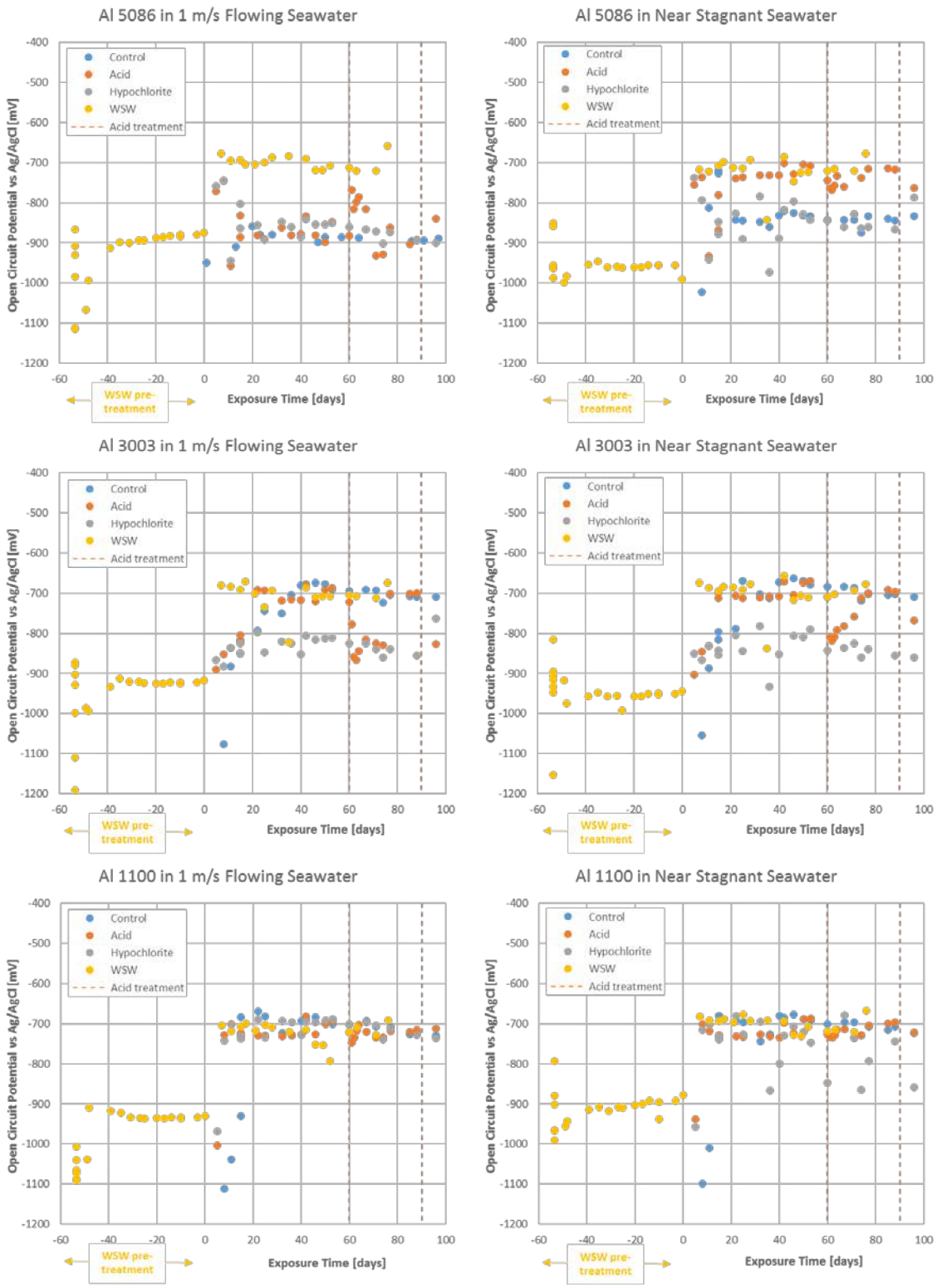


Figure 10. Comparison of treatment effects on open circuit potentials of three aluminum alloys.

DISCUSSION

Some samples had thickness variations around 0.05 mm, usually around the corners and edges, which makes crevice corrosion identification more difficult. Variations in thickness may have resulted from sanding the mounting plate with the sample mounted in place to attain a smooth transition for the transducer. Subtracting the first ultrasonic scan from subsequent scans did not eliminate the biases; noise in the original scan would propagate and made analysis more difficult.

Crevice corrosion is more severe in near stagnant samples than in flowing seawater samples. Acid treated samples were also more susceptible to crevice corrosion than samples receiving hypochlorination or warm seawater pre-treatment. Warm seawater pre-treatment samples have performed the best; only the Al 1100 warm seawater pre-treatment sample in near stagnant seawater shows crevice corrosion.

OCP did not appear strongly correlated to the onset of crevice corrosion for Al 1100 or Al 5086. For Al 3003, OCP may not be a good indicator of localized corrosion for warm seawater pre-treatment samples. The Al 3003 hypochlorination treatment samples have not showed crevice corrosion yet; we continue to monitor for a change in OCP when/if the samples develop localized corrosion.

Cumulative findings of Makai's ongoing corrosion testing program are summarized in Table 5 (draft only, not for publication). Box coupon testing data was also used in the analysis presented in Table 5. One major limitation is that box coupon data collection is discrete and destructive. It is not possible to determine if observed pits were established and continued to deepen over time (as observed for Al 6061) or levelled off and remained at a stable depth (as for Al 2024) or if the observed pits or crevice corrosion could be traced back to a singular disturbance. Continuous, in situ monitoring, as in ultrasonic scanning and imaging, has been advantageous in studying corrosion development.

FUTURE WORK

Daily imaging and as-needed ultrasonic scanning will continue on the samples. Daily hypochlorination treatments will continue. Acid treatments will continue to be performed every two months.

Table 5. Cumulative findings corrosion suitability of bare aluminum alloys for use in OTEC heat exchangers.[1]

Alloy	Evaporator	Cumulative Test Exposure	Expected Life Cycle[2]	ANL 1980's Test Results	Condenser	Cumulative Test Exposure	Expected Life Cycle[2]	ANL 1980's 5-years Test Results
3003	Yes[3]	ongoing, ~6 years	at least 6 years	Yes	TBD[4]	ongoing, ~6 years	at least 6 years	Yes with caution
3003 (treated[6])	Not Tested	Not Tested	Not Tested	-	TBD[5]	ongoing, ~6 years	at least 6 years	-
5052	Yes[3]	ongoing, ~6 years	at least 6 years	Yes	TBD[4]	ongoing, ~6 years	at least 6 years	Yes
5052 (treated[6])	Not Tested	Not Tested	Not Tested	-	TBD[5]	ongoing, ~6 years	at least 6 years	-
6063-T5	Yes	ongoing, ~6 years	at least 6 years	Yes	No (pitting)	ongoing, ~6 years	Not suitable	Yes
6063 (treated[6])	Not Tested	Not Tested	Not Tested	-	No (pitting)	ongoing, ~6 years	Not suitable	-
6061	Not Tested	Not Tested	Not Tested	Not Tested	No	~1 year	Not suitable	Not Tested
5086	Not Tested	Not Tested	Not Tested	Not Tested	TBD	ongoing, ~1.5 years	TBD	Not Tested
5086 (treated[6])	Not Tested	Not Tested	Not Tested	Not Tested	TBD	ongoing, ~1.5 years	TBD	Not Tested
1100	Yes	ongoing, ~6 years	at least 6 years	Not Tested	No (pitting)	ongoing, ~6 years	Not suitable	Not Tested

1. These alloys are solely evaluated based on their corrosion and pitting characteristics as determined at Makai Ocean Engineering's Marine Corrosion Lab when coupons are exposed to flowing seawater (~ 1 m/s) ranging from 24 to 28 °C for evaporator uses and 6 to 7 °C (CSW from 674-m) for condenser uses. Alclad alloys are not acceptable for OTEC HXs.
2. Over 30-year life expect losses of TBD micrometers (Makai) in the evaporator and 200 micrometers (ANL) in the condenser.
3. Some pitting has been observed. Pits initially observed after 3 years, pit depths have not significantly increased in samples removed at 5 years. Maximum pit depth observed is ~ 0.75 mm (0.030").
4. Some pitting has been observed. Pits initially observed after 1.5 years, pit depths have not significantly increased in samples removed at 5 years. Maximum pit depth observed is ~ 0.125 mm (0.005").
5. Some pitting has been observed. Pits initially observed after 1 year, pit depths have not significantly increased in samples removed at 5 years. Maximum pit depth observed is ~ 0.2 mm (0.008").
6. Warm seawater pre-treatment is tested on Alloys 3003, 5052, 6063, and 5086. Acid treatment is tested on Al 5086 and Al 6063. Hypochlorination is tested on Al 5086.

Caveats:

1. To avoid pitting of braze joints in evaporators, silicon must be removed from surface by, for example, machining off the top layer.
2. Braze joints fabricated using commercial fluxes <u>are not acceptable in the condenser.</u>
3. Avoid stagnant water especially near gaskets.
4. Care must be taken during manufacturing to avoid defects such as extrusion lines or concentrated areas of cold work, e.g., during roller expansion.

OTEC HEAT EXCHANGER PROGRAM

ULTRASONIC SCANNING FOR CORROSION MONITORING

STATUS REPORT #1

SUBAWARD MA150017

Prepared For

HAWAII NATIONAL MARINE RENEWABLE ENERGY CENTER

LUIS VEGA

1680 East West Road, POST 112A

Honolulu, HI, 96822

USA

Prepared By

MAKAI OCEAN ENGINEERING

PO Box 1206, Kailua, Hawaii 96734

January 2016

1. INTRODUCTION

Aluminum alloys have been proposed for use in Ocean Thermal Energy Conversion (OTEC) heat exchangers for their high thermal conductivity, comparatively low cost, and overall good general corrosion resistance (due to formation of a protective oxide layer) in seawater environments. Although uniform corrosion rates for aluminum alloys are low, aluminum alloys are susceptible to surface pitting and crevice corrosion at gasket interfaces which can initiate when local galvanic cells develop between alloying elements and deposit corrosion product on the surface of the metal. Corrosion product can encase the immediate area and change the local environment which acts to accelerate the corrosion process. It is important to quantify this phenomenon because, in time, pits or crevice corrosion can penetrate the wall of the heat exchanger and cause refrigerant to leak into the seawater. For heat exchangers, this is considered a catastrophic failure and must be avoided.

Makai Ocean Engineering has been studying and quantifying the development of corrosion on aluminum alloys being considered for OTEC heat exchangers. Makai has developed a setup in which pit growth can be observed in-situ by optical imaging and ultrasonic scanning. Pitting sites are identified and corrosion product accumulation on the metal surface is observed using imagery. However, once corrosion product encapsulates a pit, no accurate measurements of pit size or depth can be made with imaging alone. With the addition of ultrasonic thickness scanning, the surface underneath the corrosion product can be observed and the 3-dimensional structure of the pit can be measured. Pit development can now be monitored over time without removal or destruction of samples.

Makai is currently testing three alloys (Al 1100-H112, Al 3003-F and Al 5086-H116) and three corrosion mitigation techniques (warm seawater pre-treatment, hypo-chlorination and exposure to a diluted sulfamic acid) in flowing (1 m/s) and near stagnant cold seawater for a total of 18 samples. Six control samples, one of each alloy in flowing and near stagnant cold seawater, are also being tested.

2. STATUS

Warm seawater pre-treatment samples have been exposed for 8 months. Control, acid treatment, and hypo-chlorination samples have been exposed for 7 months. Except for the control samples, samples are subjected to one of three treatments: warm seawater pre-treatment, hypo-chlorination, or acid treatment; in either flowing (1 m/s) or near stagnant cold seawater (Table 1). Alloys in each column are arranged in the same order from top to bottom: Al 5086, Al 3003, and Al 1100. Laser profilometer scans of the test surfaces were conducted prior to exposure for each sample. All corrosion samples were degreased, cleaned with simple green, and rinsed with ethanol before installation to remove surface contaminants.

Warm seawater pre-treatment samples were exposed to warm seawater on 4/22/15 and moved to cold seawater on 6/15/15. Control, hypo-chlorination, and acid treatment samples were exposed to cold seawater on 5/21/15.

Table 1. Current test samples.

Column	Sample IDs	Water Flow	Treatment
9	ut5-18, ut3-18, ut1-18	Near Stagnant	Control
10	ut5-1*, ut3-17, ut1-17	Flowing	Control
4	ut5-11, ut3-11, ut1-11	Flowing	Warm seawater pre-treatment
5	ut5-12, ut3-12, ut1-12	Near Stagnant	Warm seawater pre-treatment
6	ut5-16, ut3-16, ut1-16	Near Stagnant	Hypo-chlorination
7	ut5-15, ut3-15, ut1-15	Flowing	Hypo-chlorination
14	ut5-14, ut3-14, ut1-14	Near Stagnant	Acid Treatment
15	ut5-13, ut3-13, ut1-13	Flowing	Acid Treatment

* Original sample, continued from previous round of testing.

Treatments are expected to minimize pit depths (and/or presence). The warm seawater pre-treatment protocol was developed on the hypothesis that corrosion resistance in cold seawater would improve if samples exposed in cold seawater had the same protective oxide layer as samples in warm seawater. Initially exposing samples in warm seawater allows the oxide layer to develop and, when performed carefully, the developed oxide layer remains when samples are relocated to cold seawater. Previous testing established 40 days in warm seawater is the sufficient time to build the oxide layer.

The hypo-chlorination treatment protocol is currently used in warm seawater to control biofouling. Bacterial colonies have been observed on samples exposed to cold seawater; while the exact mechanism for pit initiation is unknown, any difference in the local surface environment can accelerate corrosion. Thus, bacterial colonies on a sample's surface may act as pit initiation sites. Samples are exposed to 100 ppb chlorine for 1 hour daily to control the growth of bacterial colonies.

The acid treatment protocol was developed based on observations of open circuit potential (OCP) and corresponding corrosion activity. Samples have shown a marked change in OCP once pitting begins. Treatment of a sample with a mild acid will strip the oxide layer and possibly remove local environments that may have developed, essentially 'resetting' the surface to the condition it was in when first exposed to seawater. In previous tests, application of 5% sulfamic acid for 5 minutes lowers OCP to the passive region for Al 6063.

The imaging system automatically images the front face of each sample daily. The samples are scanned ultrasonically at least once a month. The frequency of ultrasonic scanning will be adjusted based on corrosion development. We continue to encounter frequent corrupted data files despite two repair attempts by the manufacturer. They determined it is a problem with all their scanners so they are working on a firmware fix which we still do not have. We have developed a work around where we can re-assemble the corrupted data and we will do so until the manufacturer can provide resolution.

PREVIOUS SAMPLES RESULTS

All previously tested samples except Al 5086 in flowing seawater were removed in May 2015. Results were reported in the November 2015 Shakedown Report. The Al 5086 sample in flowing seawater continues to be tested as the control.

CURRENT SAMPLES DATA COLLECTION

This report contains data collected up to December 15, 2015. As of December 15, 2015, the warm seawater pre-treatment samples have been exposed for a total of 237 days and the control, hypo-chlorination, and acid treatment samples have been exposed for 208 days.

2.1.1. Pitting corrosion

No pits have been observed on any of the new samples. Only a 1.5” x 2.75” rectangle at the center of each sample is analyzed for pitting to minimize the influence of crevice corrosion. Small pits were observed on the Al 5086 control sample in flowing seawater (ut5-1) after 477 days via imaging. Pits were initially reported on the ultrasonic scan at 499 days but subsequent scans do not show pits and the original observation may have been due to noise in the scan. Pits are still visible on images.

2.1.2. Crevice corrosion

Crevice corrosion is present on most samples. Most samples with crevice corrosion identified in the images also have crevice corrosion identified in the ultrasonic scans. Of the samples that received warm seawater pre-treatment, only Al 1100 in near stagnant seawater has crevice corrosion. Of the samples receiving daily hypochlorination treatment, only the Al 1100 samples in flowing and near stagnant seawater have crevice corrosion. All samples receiving acid treatment have crevice corrosion. All control samples have crevice corrosion, although, crevice corrosion did not occur on the Al 5086 until 477 days of total exposure. The Al 1100 and Al 3003 control samples in flowing seawater developed crevice corrosion before the Al 5086 sample.

Table 2. Crevice corrosion at the gasket interface. Lateral penetration is the distance from the inner edge of the gasket to the furthest extent of corrosion. The maximum corrosion depth underneath gasket is not necessarily in the same location as the maximum lateral penetration.

Water Flow	Treatment	Sample	Present on image?	Lateral Penetration [mm]	Maximum Depth under Gasket [mm]
Near Stagnant	Control	ut5-18	Yes	3.9	0.3
		ut3-18	Yes	3.9	1.0
		ut1-18	Yes	3.9	0.7
Flowing	Control	ut5-1	No*	-	-
		ut3-17	Yes	3.9	1.0
		ut1-17	Yes	n.d.	n.d.
Near Stagnant	Hypochlorination	ut5-16	No	-	-
		ut3-16	No	-	-
		ut1-16	Yes	n.d.	n.d.
Flowing	Hypochlorination	ut5-15	No	-	-
		ut3-15	No	-	-
		ut1-15	Yes	0.1	0.1
Near Stagnant	Acid treatment	ut5-14	Yes	3.9	0.4
		ut3-14	Yes	3.9	1.2
		ut1-14	Yes	2.1	0.9
Flowing	Acid treatment	ut5-13	Yes	n.d.	n.d.
		ut3-13	Yes	2.0	0.8
		ut1-13	Yes	3.3	0.8
Near Stagnant	Warm seawater pre-treatment	ut5-12	No	-	-
		ut3-12	No	-	-
		ut1-12	Yes	3.9	0.5
Flowing	Warm seawater pre-treatment	ut5-11	No	-	-
		ut3-11	No	-	-
		ut1-11	No	-	-

n.d. = not detected on ultrasonic scans.

* For the same exposure time, no crevice corrosion or pits were detected on the Al 5086 control sample in flowing seawater. Crevice corrosion was detected on images after 477 days.

The latest ultrasonic scan (middle panel) and associated image (left panel) for each sample are shown in Figures 2-1 through 2-8. The third panel in each figure is the image overlain with 0.1 mm contours from the ultrasonic scan.

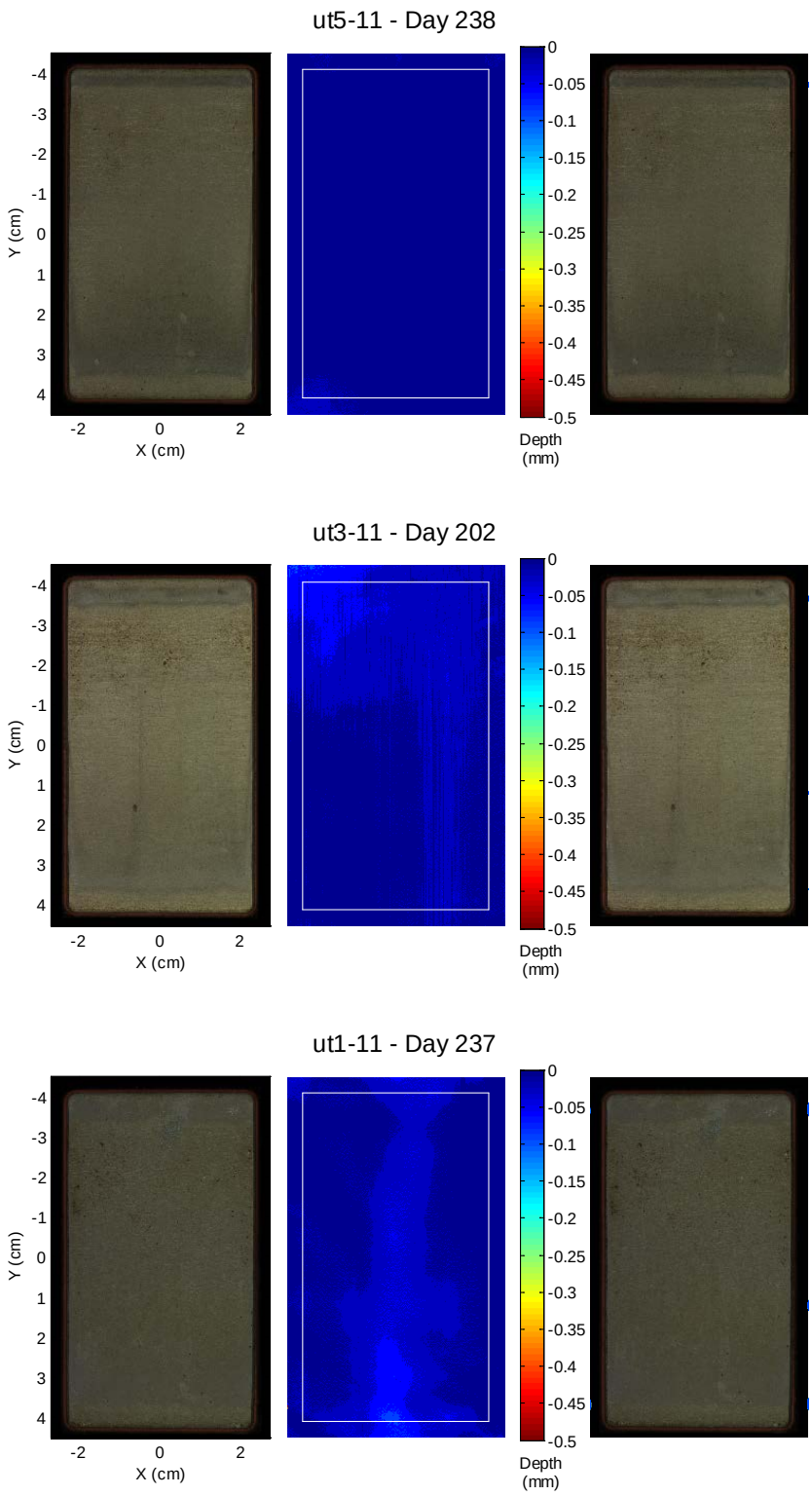


Figure 2-1. Warm seawater pre-treatment samples in flowing seawater. No corrosion features have been observed.

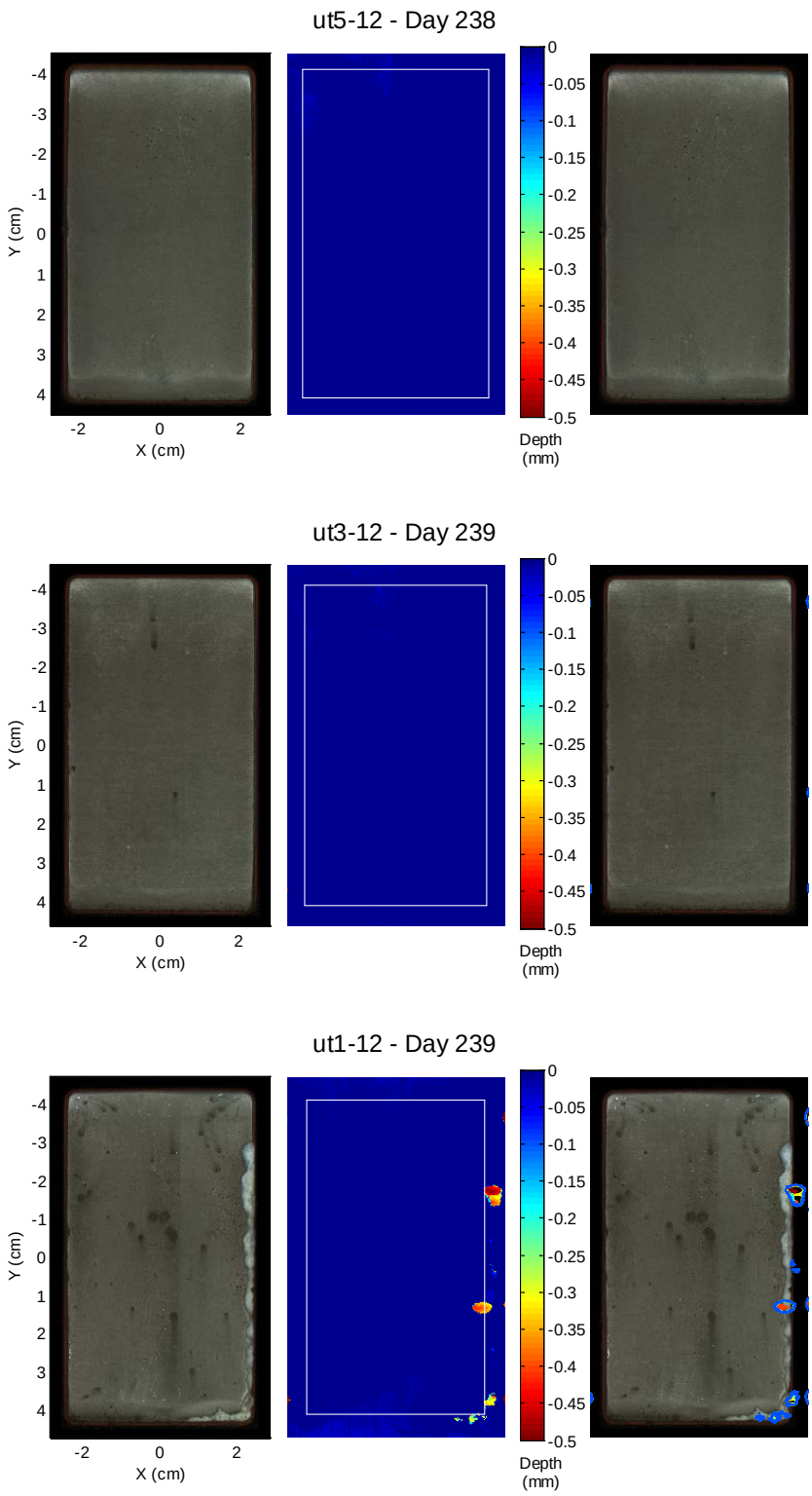


Figure 2-2. Warm seawater pre-treatment samples in near stagnant seawater. Crevice corrosion observed in images and ultrasonic scans on Al 1100.

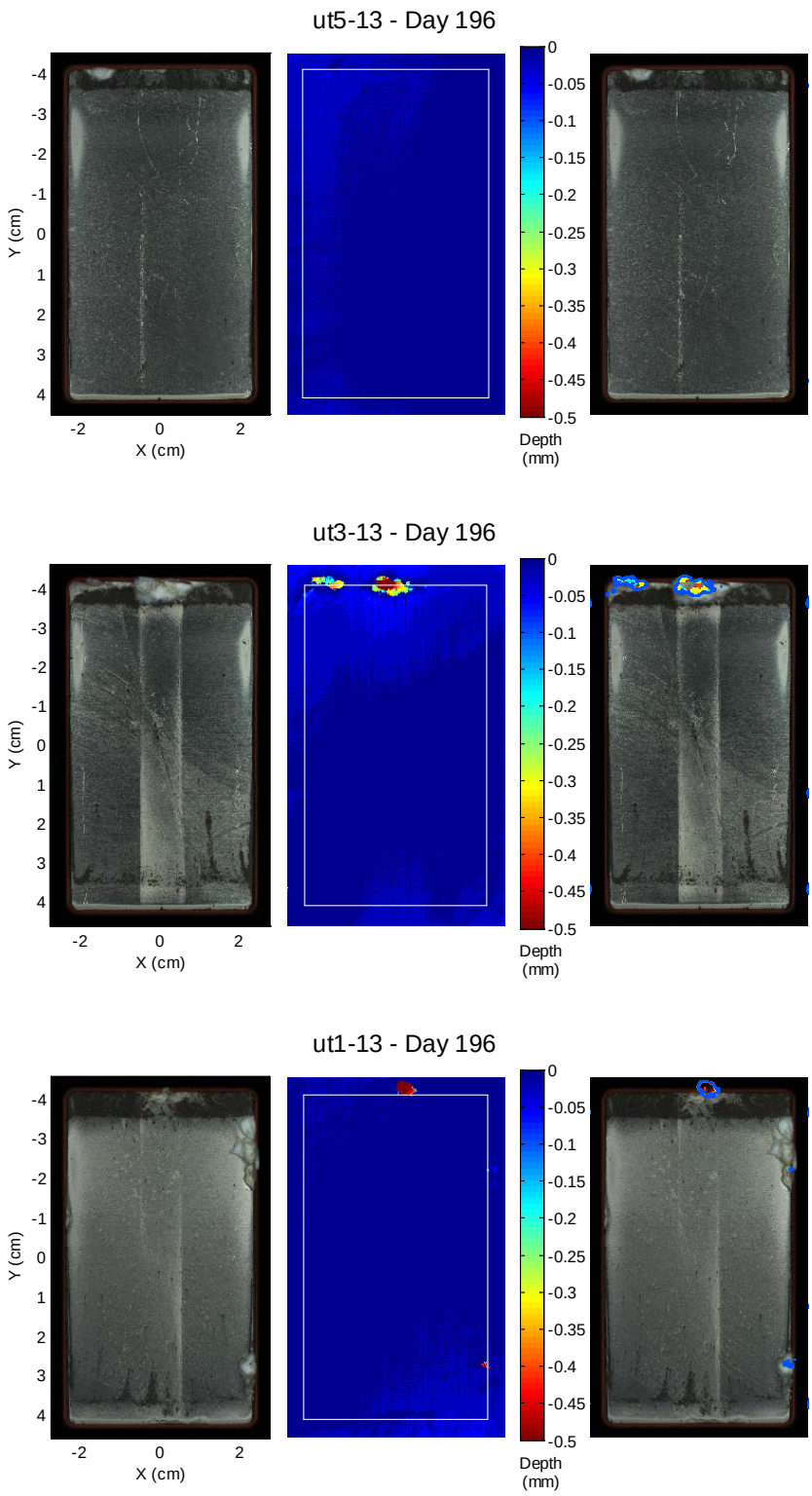


Figure 2-3. Acid treatment samples in flowing seawater. Crevice corrosion is visible in images for all samples but not detectable in ultrasonic scans for Al 5086.

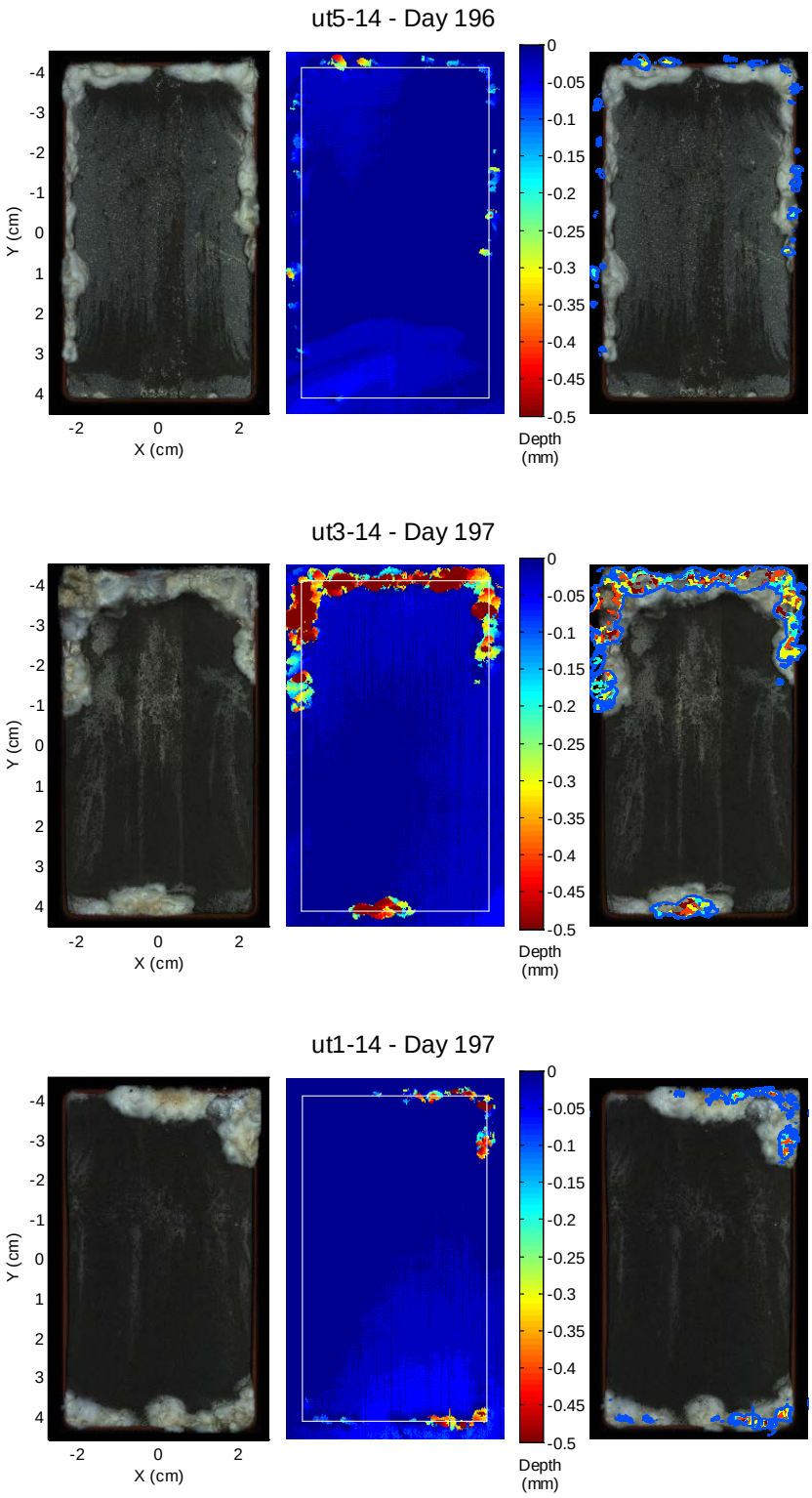


Figure 2-4. Acid treatment samples in near stagnant seawater. Crevice corrosion is visible in imaging and ultrasonic scans for all samples. Crevice corrosion is most severe in Al 3003.

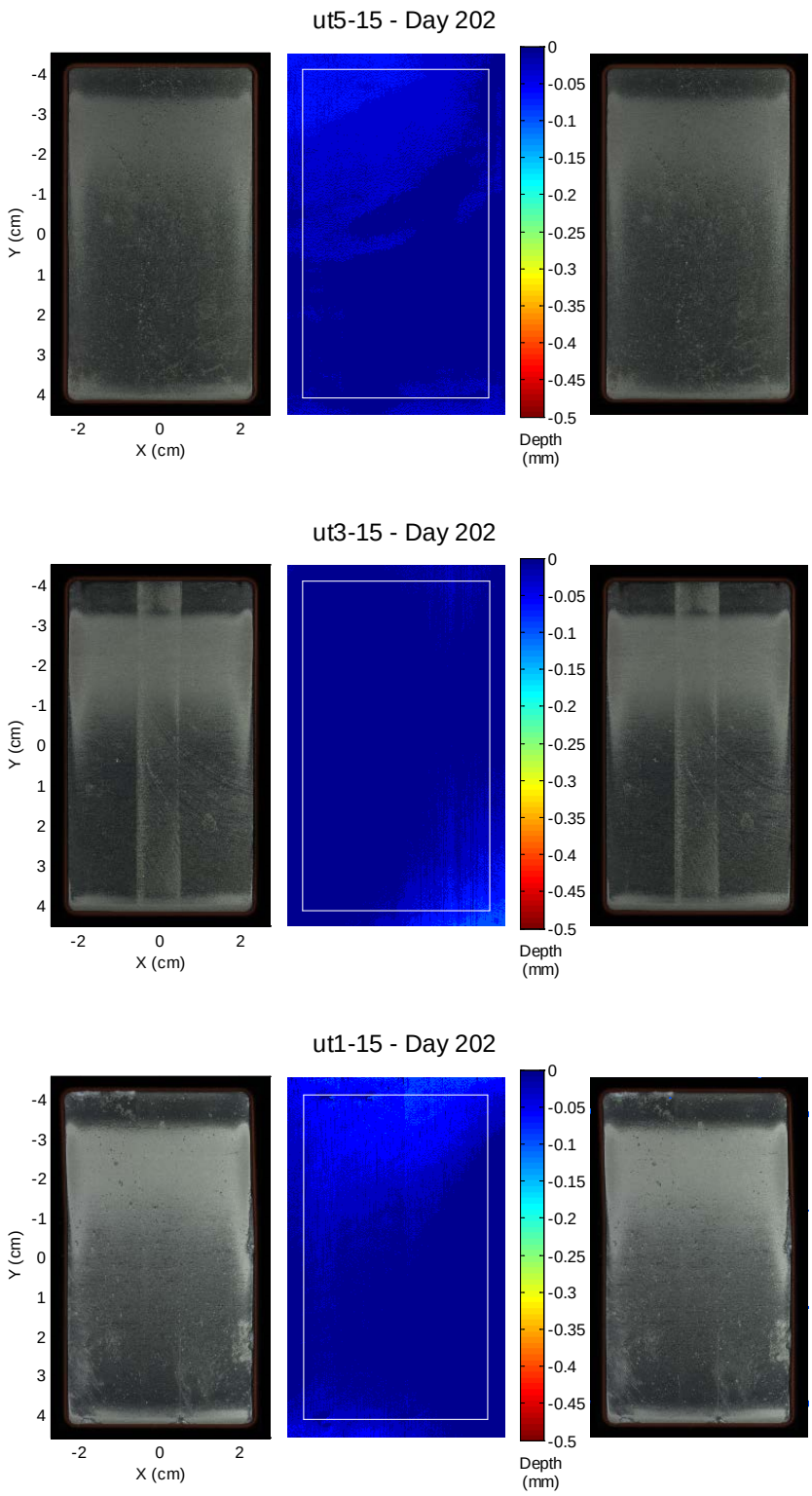


Figure 2-5. Hypo-chlorination treatment in flowing seawater. The beginning of crevice corrosion is visible in images on Al 1100 but not detected on the ultrasonic scan. Al 3003 and Al 5086 do not have observable corrosion features.

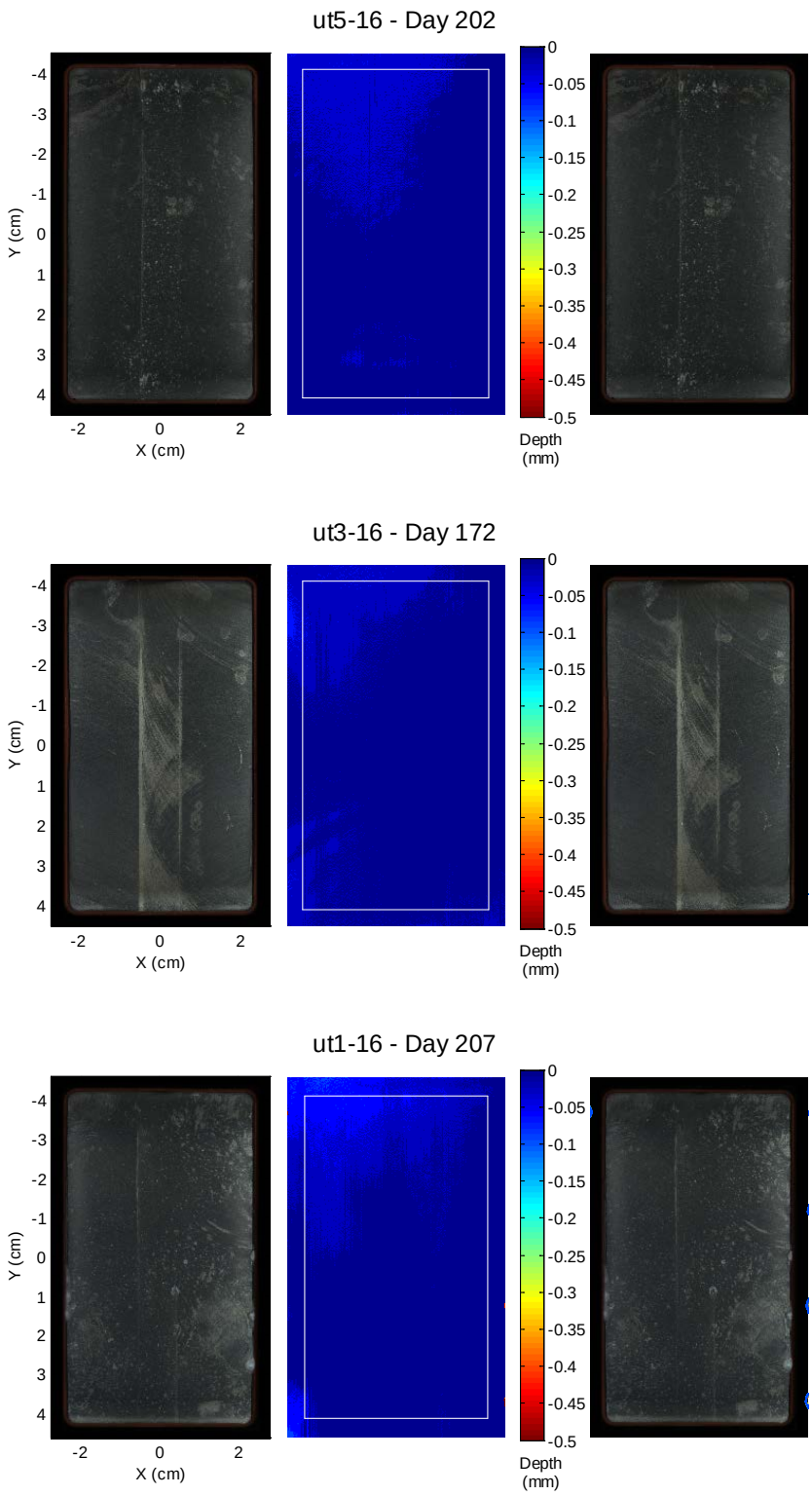


Figure 2-6. Hypo-chlorination samples in near stagnant seawater. The beginning of crevice corrosion is visible in images on Al 1100 but not detected on the ultrasonic scan. Al 3003 and Al 5086 do not have observable corrosion features.

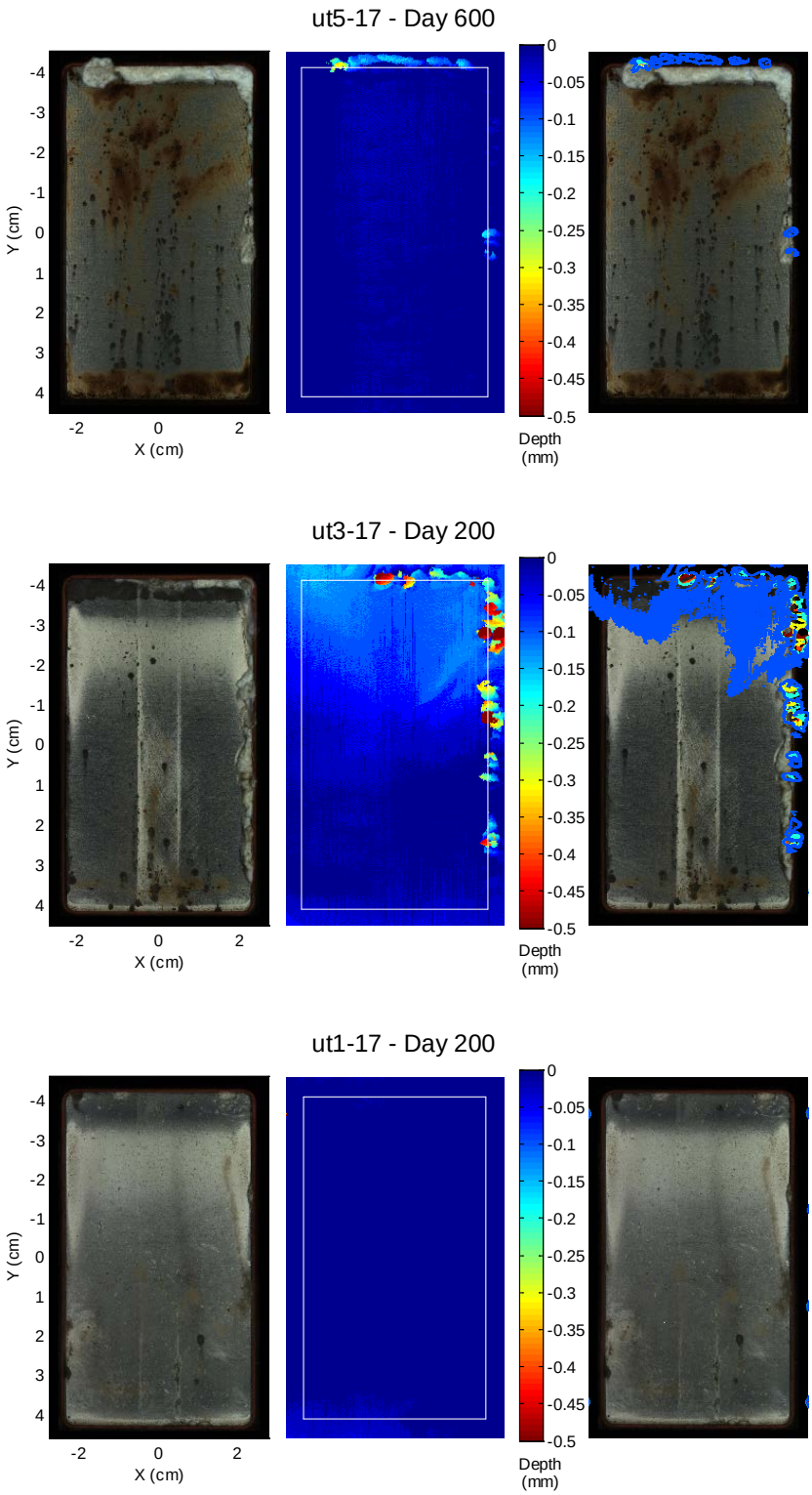


Figure 2-7. Control samples in flowing seawater. ut5-17 is continued from the previous testing. Biofouling on the surface has worsened. Crevice corrosion and biofouling is more severe on Al 3003 than Al 1100. Contour on top edge of ut3-17 is due to uneven thickness. Corrosion has not been detected on Al 1100 via ultrasonic scans.

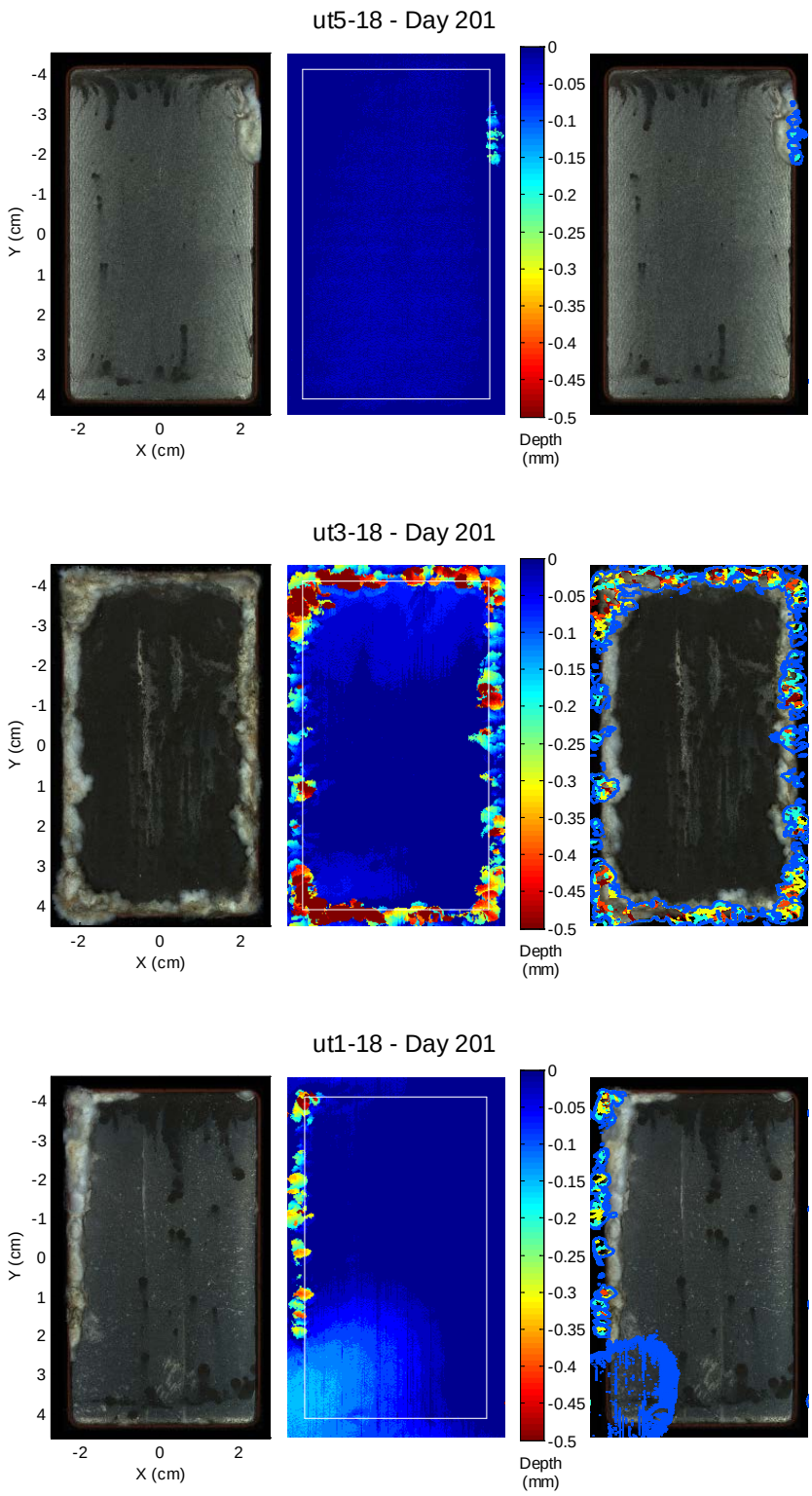


Figure 2-8. Control samples in flow near stagnant seawater. Crevice corrosion is observed on images and ultrasonic scans of all samples; corrosion (and biofouling) is most severe on ut3-18. Contour on the lower left corner of ut1-18 is due to uneven thickness.

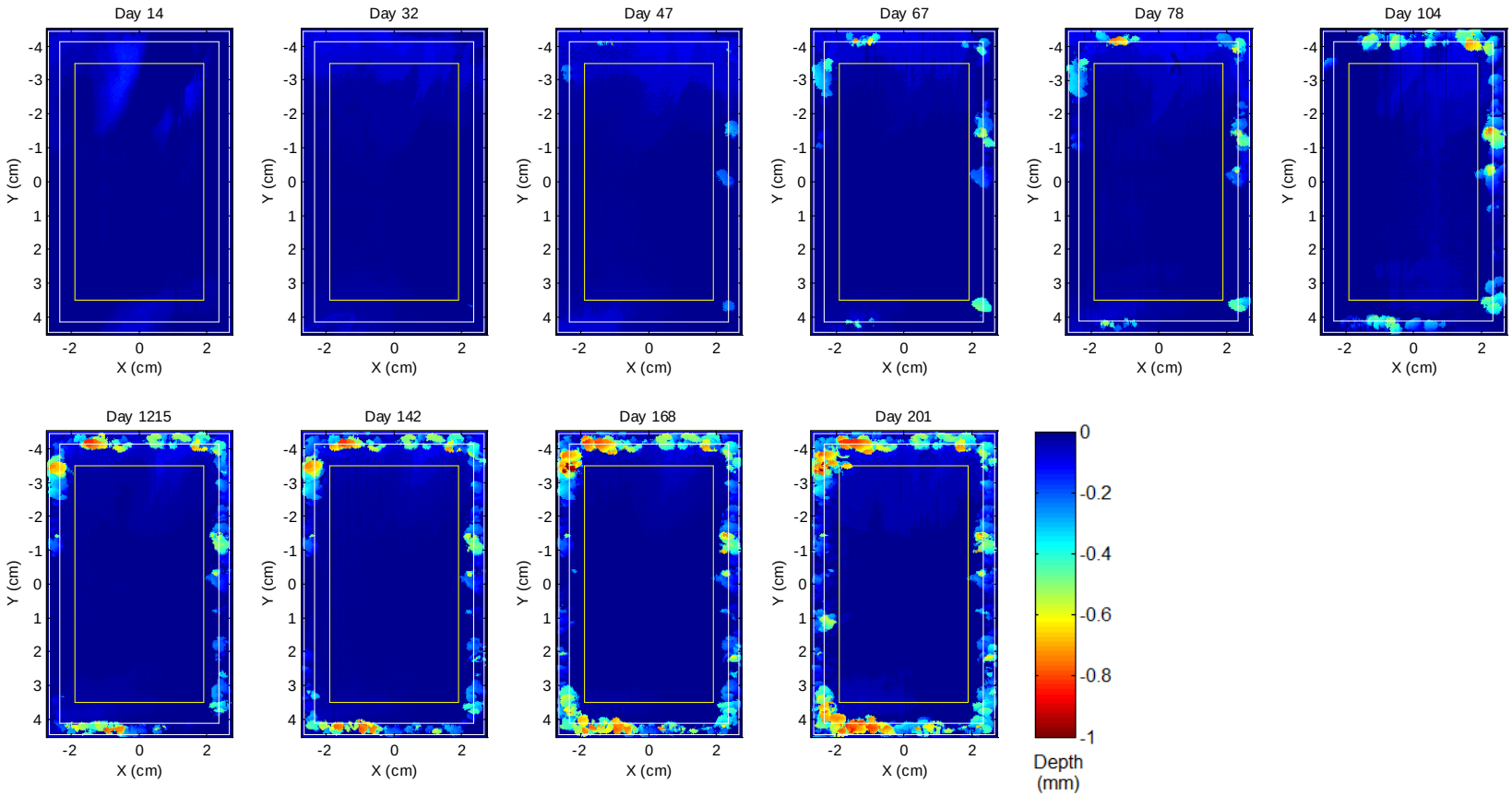


Figure 2-9. Gasket corrosion development on ut3-18 (Al 3003 control sample in near stagnant seawater). The white rectangles are the inner and outer edges of the gasket. Inner yellow rectangle is the area analyzed for pitting. In the upper left corner, crevice corrosion is encroaching on the pitting analysis area.

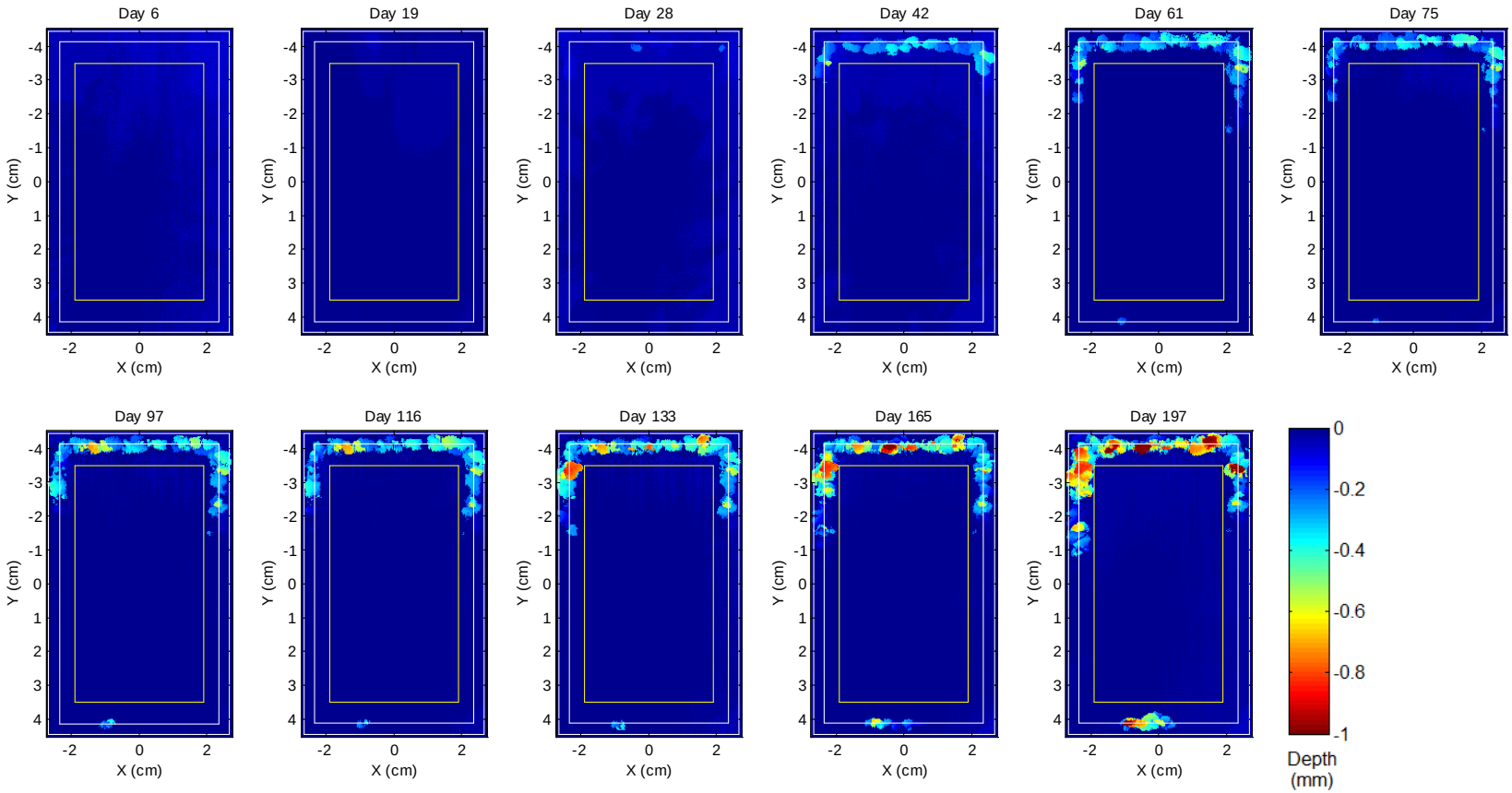


Figure 2-10. Crevice corrosion development on ut3-14 (acid treated Al 3003 sample in near stagnant seawater). Inner yellow rectangle is the area analyzed for pitting. The white rectangles are the inner and outer edges of the gasket.

2.1.3. Open Circuit Potential (OCP)

For Al 1100 samples, there is little difference in OCP between the different treatments in either flowing or near stagnant seawater except for the warm seawater pre-treatment sample in flowing seawater (which is free from crevice corrosion). All other samples have some crevice corrosion. No change in OCP was observed after an acid treatment. OCP is not a strong indicator of corrosion for Al 1100.

For Al 3003 samples in flowing seawater, warm seawater pre-treatment, acid treatment, and control samples have comparable OCPs, whereas the hypo-chlorination sample has lower OCP. In near stagnant seawater, control and acid treatment samples have comparable OCPs and the hypo-chlorination sample has lower OCP. The warm seawater pre-treatment sample OCP was initially around -700mV, decreased to -800 mV after 100 days in cold seawater, and began in increase towards -700 mV at 150 days. OCP for the warm seawater pre-treatment sample in flowing seawater looks to be lowering towards -800 mV after 180 days. In both flowing and near stagnant seawater, acid treatments lowered OCP immediately after treatment but OCPs returned to higher values within 20 days post treatment. Crevice corrosion has been detected on all acid treatment and control samples. OCPs of the acid treatment and control samples are in the expected pitting region (around -700 mV) and entered into the pitting region around the same time crevice corrosion was detected via imaging. OCP may be a good indicator of localized corrosion for Al 3003.

For Al 5086, acid treatment samples in flowing and near stagnant seawater and the control sample in near stagnant seawater have OCPs in the pitting region and crevice corrosion has been observed on images and ultrasonic scans. OCP entered the pitting region prior to the appearance of crevice corrosion on images. Crevice corrosion has not been observed on the five other samples. Hypo-chlorination and control samples have comparable OCPs in the same water source with slightly lower OCPs in flowing seawater than in near stagnant seawater. OCP for the warm seawater pre-treatment sample in near stagnant seawater was initially around -700 mV and began to lower to -800 mV after 70 days in cold seawater. In flowing seawater, OCP for the warm seawater pre-treatment sample has remained at -700 mV. As with Al 3003, warm seawater pre-treatment appears to alter OCP behavior. OCP may still be predictive of localized corrosion for Al 5086.

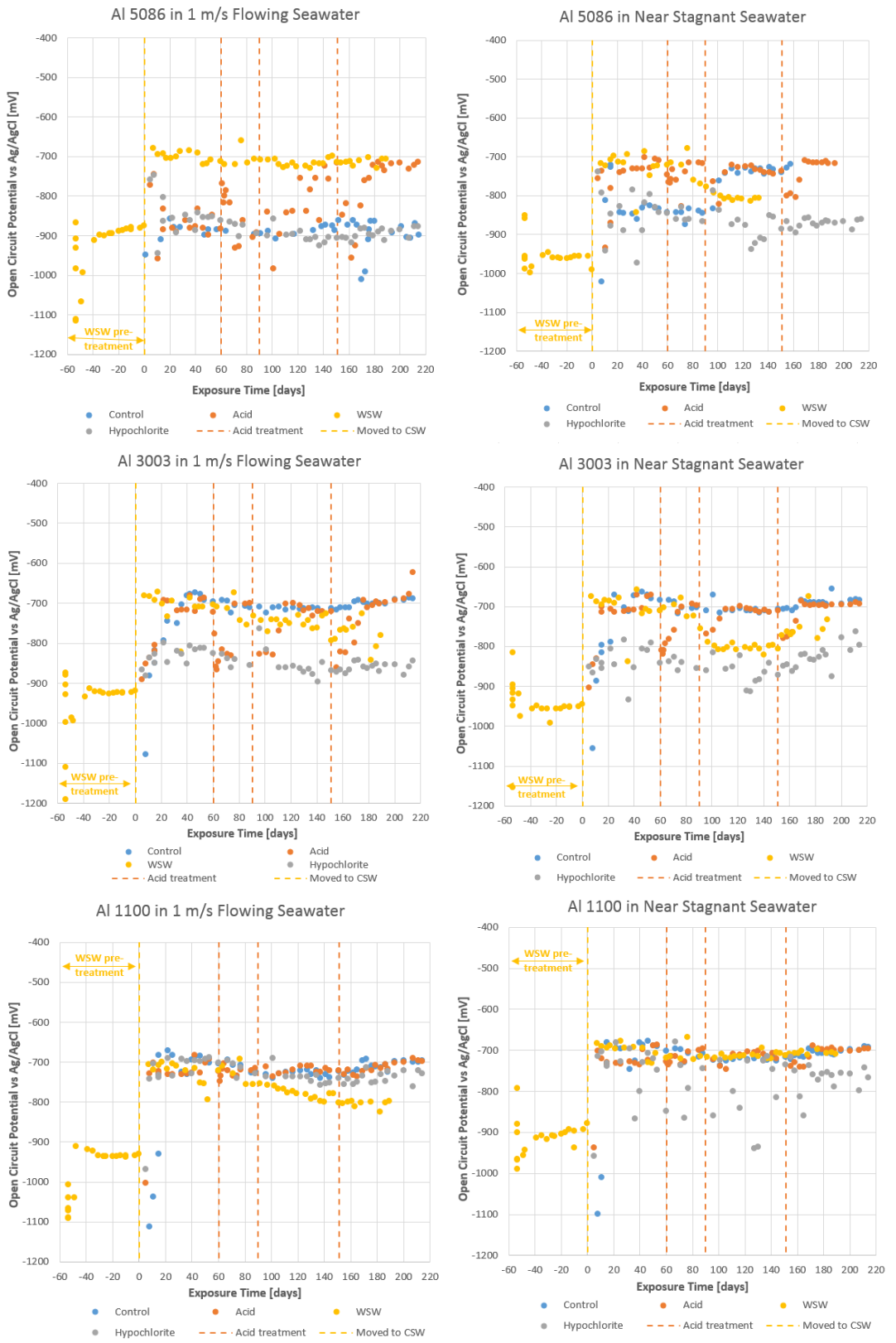


Figure 2-11. Comparison of treatment effects on open circuit potentials of three aluminum alloys.

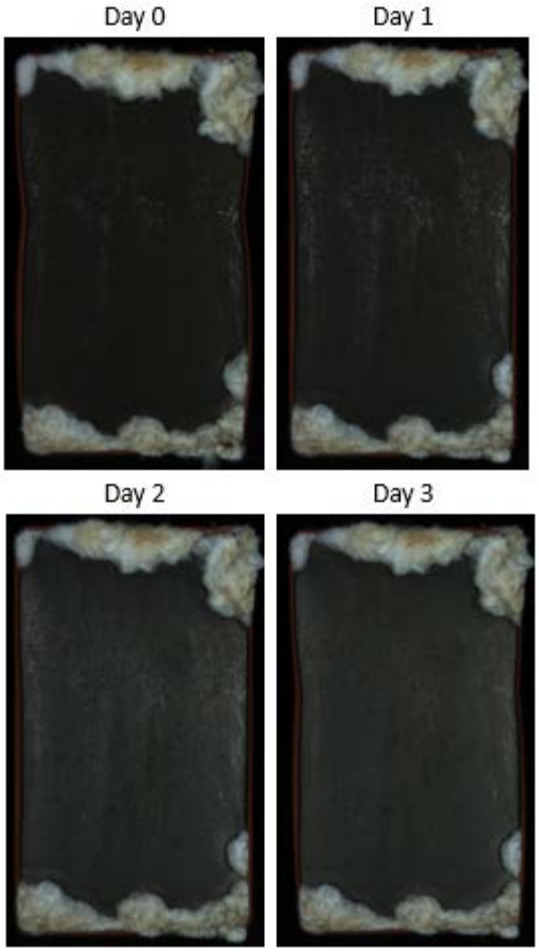


Figure 2-12. Acid treatment removes surface biofouling on ut1-14. Same effect was observed on other acid treated samples. Images were taken before treatment, 1 day, 2 days, and 3 days after treatment.

DISCUSSION

Crevice corrosion continues to expand and deepen. Crevice corrosion continues to be more severe in near stagnant samples than in flowing seawater samples. Acid treated samples were also more susceptible to crevice corrosion than samples receiving hypo-chlorination or warm seawater pre-treatment. Warm seawater pre-treatment samples have performed the best; only the Al 1100 warm seawater pre-treatment sample in near stagnant seawater shows crevice corrosion. Hypo-chlorination appears effective for Al 3003 and Al 5086, neither flowing nor near-stagnant samples have corrosion and the sample surfaces look new.

Pitting has not been observed on images or on ultrasonic scans of new samples, only the Al 5086 control that has been continued from previous testing.

Biofouling on several sample surfaces has been severe, covering nearly the entire surface. Acid treatment and control samples in near stagnant seawater have the most coverage. Acid treatment removes the visible fouling but biofouling re-establishes coverage before the next treatment (Figure 2-12). Biofouling on the Al 5086 control sample in flowing seawater has developed a rust colored patches (Figure 2-7), unlike the black spots and patches typically observed. The Al 3003 and Al 1100 control samples in flowing seawater have also begun to develop the rust colored patches. Except for the hypo-chlorination samples, which appear free from biofouling, biofouling is worse on near stagnant samples compared to flowing seawater samples.

OCP appears correlated to the onset of crevice corrosion for Al 3003 but not for Al 1100 or Al 5086. Warm seawater pre-treatment appears to alter OCP behavior in Al 3003 and Al 5086. OCP starts high (~ -700 mV) upon exposure to cold seawater and begins to lower after a certain exposure time (varies with alloy and water source).

Cumulative findings of Makai's ongoing corrosion testing program are summarized in Table 3 (draft only, not for publication). Box coupon testing data was also used in the analysis presented in Table 3. One major limitation is that box coupon data collection is discrete and destructive. It is not possible to determine if observed pits were established and continued to deepen over time (as observed for Al 6061) or levelled off and remained at a stable depth (as for Al 2024) or if the observed pits or crevice corrosion could be traced back to a singular disturbance. Continuous, in situ monitoring, as in ultrasonic scanning and imaging, has been advantageous in studying corrosion development.

FUTURE WORK

Daily imaging and as-needed ultrasonic scanning will continue on the samples. Daily hypo-chlorination treatments will continue. Acid treatments will continue to be performed every two months.

Table 3. Cumulative findings corrosion suitability of bare aluminum alloys for use in OTEC heat exchangers.[1]

Alloy	Evaporator	Cumulative Test Exposure	Expected Life Cycle[2]	ANL 1980's Test Results	Condenser	Cumulative Test Exposure	Expected Life Cycle[2]	ANL 1980's 5-years Test Results
3003	Yes[3]	ongoing, ~6 years	at least 6 years	Yes	TBD[4]	ongoing, ~6 years	at least 6 years	Yes with caution
3003 (treated[6])	Not Tested	Not Tested	Not Tested	-	TBD[5]	ongoing, ~6 years	at least 6 years	-
5052	Yes[3]	ongoing, ~6 years	at least 6 years	Yes	TBD[4]	ongoing, ~6 years	at least 6 years	Yes
5052 (treated[6])	Not Tested	Not Tested	Not Tested	-	TBD[5]	ongoing, ~6 years	at least 6 years	-
6063-T5	Yes	ongoing, ~6 years	at least 6 years	Yes	No (pitting)	ongoing, ~6 years	Not suitable	Yes
6063 (treated[6])	Not Tested	Not Tested	Not Tested	-	No (pitting)	ongoing, ~6 years	Not suitable	-
6061	Not Tested	Not Tested	Not Tested	Not Tested	No	~1 year	Not suitable	Not Tested
5086	Not Tested	Not Tested	Not Tested	Not Tested	TBD	ongoing, ~1.5 years	TBD	Not Tested
5086 (treated[6])	Not Tested	Not Tested	Not Tested	Not Tested	TBD	ongoing, ~1.5 years	TBD	Not Tested
1100	Yes	ongoing, ~6 years	at least 6 years	Not Tested	No (pitting)	ongoing, ~6 years	Not suitable	Not Tested

1. These alloys are solely evaluated based on their corrosion and pitting characteristics as determined at Makai Ocean Engineering's Marine Corrosion Lab when coupons are exposed to flowing seawater (~ 1 m/s) ranging from 24 to 28 °C for evaporator uses and 6 to 7 °C (CSW from 674-m) for condenser uses. Alclad alloys are not acceptable for OTEC HXs.
2. Over 30-year life expect losses of TBD micrometers (Makai) in the evaporator and 200 micrometers (ANL) in the condenser.
3. Some pitting has been observed. Pits initially observed after 3 years, pit depths have not significantly increased in samples removed at 5 years. Maximum pit depth observed is ~ 0.75 mm (0.030").
4. Some pitting has been observed. Pits initially observed after 1.5 years, pit depths have not significantly increased in samples removed at 5 years. Maximum pit depth observed is ~ 0.125 mm (0.005").
5. Some pitting has been observed. Pits initially observed after 1 year, pit depths have not significantly increased in samples removed at 5 years. Maximum pit depth observed is ~ 0.2 mm (0.008").
6. Warm seawater pre-treatment is tested on Alloys 3003, 5052, 6063, and 5086. Acid treatment is tested on Al 5086 and Al 6063. Hypo-chlorination is tested on Al 5086.

Caveats:

1. To avoid pitting of braze joints in evaporators, silicon must be removed from surface by, for example, machining off the top layer.
2. Braze joints fabricated using commercial fluxes <u>are not acceptable in the condenser.</u>
3. Avoid stagnant water especially near gaskets.
4. Care must be taken during manufacturing to avoid defects such as extrusion lines or concentrated areas of cold work, e.g., during roller expansion.

OTEC HEAT EXCHANGER PROGRAM

ULTRASONIC SCANNING FOR CORROSION MONITORING

STATUS REPORT #2

SUBAWARD MA150017

Prepared For

HAWAII NATIONAL MARINE RENEWABLE ENERGY CENTER

LUIS VEGA

1680 East West Road, POST 112A

Honolulu, HI, 96822

USA

Prepared By

MAKAI OCEAN ENGINEERING

PO Box 1206, Kailua, Hawaii 96734

March 2016

1. INTRODUCTION

Aluminum alloys have been proposed for use in Ocean Thermal Energy Conversion (OTEC) heat exchangers for their high thermal conductivity, comparatively low cost, and overall good general corrosion resistance (due to formation of a protective oxide layer) in seawater environments. Although uniform corrosion rates for aluminum alloys are low, aluminum alloys are susceptible to surface pitting and crevice corrosion at gasket interfaces which can initiate when local galvanic cells develop between alloying elements and deposit corrosion product on the surface of the metal. Corrosion product can encase the immediate area and change the local environment which acts to accelerate the corrosion process. It is important to quantify this phenomenon because, in time, pits or crevice corrosion can penetrate the wall of the heat exchanger and cause refrigerant to leak into the seawater. For heat exchangers, this is considered a catastrophic failure and must be avoided.

Makai Ocean Engineering has been studying and quantifying the development of corrosion on aluminum alloys being considered for OTEC heat exchangers. Makai has developed a setup in which pit growth can be observed in-situ by optical imaging and ultrasonic scanning. Pitting sites are identified and corrosion product accumulation on the metal surface is observed using imagery. However, once corrosion product encapsulates a pit, no accurate measurements of pit size or depth can be made with imaging alone. With the addition of ultrasonic thickness scanning, the surface underneath the corrosion product can be observed and the 3-dimensional structure of the pit can be measured. Pit development can now be monitored over time without removal or destruction of samples.

Makai is currently testing three alloys (Al 1100-H112, Al 3003-F and Al 5086-H116) and three corrosion mitigation techniques (warm seawater pre-treatment, hypo-chlorination and exposure to a diluted sulfamic acid) in flowing (1 m/s) and near stagnant cold seawater for a total of 18 samples. Six control samples, one of each alloy in flowing and near stagnant cold seawater, are also being tested.

2. STATUS

Warm seawater pre-treatment samples have been exposed for 10 months. Control, acid treatment, and hypo-chlorination samples have been exposed for 9 months. Except for the control samples, samples are subjected to one of three treatments: warm seawater pre-treatment, hypo-chlorination, or acid treatment; in either flowing (1 m/s) or near stagnant cold seawater (Table 1). Alloys in each column are arranged in the same order from top to bottom: Al 5086, Al 3003, and Al 1100. Laser profilometer scans of the test surfaces were conducted prior to exposure for each sample. All corrosion samples were degreased, cleaned with simple green, and rinsed with ethanol before installation to remove surface contaminants.

Warm seawater pre-treatment samples were exposed to warm seawater on 4/22/15 and moved to cold seawater on 6/15/15. Control, hypo-chlorination, and acid treatment samples were exposed to cold seawater on 5/21/15.

Table 1. Current test samples.

Column	Sample IDs	Water Flow	Treatment
9	ut5-18, ut3-18, ut1-18	Near Stagnant	Control
10	ut5-1*, ut3-17, ut1-17	Flowing	Control
4	ut5-11, ut3-11, ut1-11	Flowing	Warm seawater pre-treatment
5	ut5-12, ut3-12, ut1-12	Near Stagnant	Warm seawater pre-treatment
6	ut5-16, ut3-16, ut1-16	Near Stagnant	Hypo-chlorination
7	ut5-15, ut3-15, ut1-15	Flowing	Hypo-chlorination
14	ut5-14, ut3-14, ut1-14	Near Stagnant	Acid Treatment
15	ut5-13, ut3-13, ut1-13	Flowing	Acid Treatment

* Original sample, continued from previous round of testing.

Treatments are expected to minimize pit depths (and/or presence). The warm seawater pre-treatment protocol was developed on the hypothesis that corrosion resistance in cold seawater would improve if samples exposed in cold seawater had the same protective oxide layer as samples in warm seawater. Initially exposing samples in warm seawater allows the oxide layer to develop and, when performed carefully, the developed oxide layer remains when samples are relocated to cold seawater. Previous testing established 40 days in warm seawater is the sufficient time to build the oxide layer.

The hypo-chlorination treatment protocol is currently used in warm seawater to control biofouling. Bacterial colonies have been observed on samples exposed to cold seawater; while the exact mechanism for pit initiation is unknown, any difference in the local surface environment can accelerate corrosion. Thus, bacterial colonies on a sample's surface may act as pit initiation sites. Samples are exposed to 100 ppb chlorine for 1 hour daily to control the growth of bacterial colonies.

The hypo-chlorination system uses a metering pump that pumps a pre-calculated amount of bleach from a bleach reservoir/tank into the designated seawater header. The amount of bleach to be pumped is based on the desired concentration and the flow rate. We recently discovered the amount of bleach the pump is delivering to seawater headers is affected by the tank level, leading to variability in the chlorine concentration. In general, concentration levels were lower than intended because ORP values were lower than expected. In response, the pumping volume was manually increased to deliver enough bleach that would lower ORP values into the sterilization range. This defect is now corrected programmatically; the pumping volume will take into account the tank level and we will continue to monitor ORP levels as a system check.

The acid treatment protocol was developed based on observations of open circuit potential (OCP) and corresponding corrosion activity. Samples have shown a marked change in OCP once pitting begins. Treatment of a sample with a mild acid will strip the oxide layer and possibly remove local environments that may have developed, essentially 'resetting' the surface to the condition it was in when first exposed to seawater. In previous tests, application of 5% sulfamic acid for 5 minutes lowers OCP to the passive region for Al 6063.

The imaging system automatically images the front face of each sample daily. The samples are scanned ultrasonically at least once a month. The frequency of ultrasonic scanning will be adjusted based on corrosion development. We continue to encounter frequent corrupted data files despite two repair attempts by the manufacturer. They determined it is a problem with all their scanners so they are working on a firmware fix which we still do not have. We have developed a work around where we can re-assemble the corrupted data and we will do so until the manufacturer can provide resolution.

PREVIOUS SAMPLES RESULTS

All previously tested samples except Al 5086 in flowing seawater were removed in May 2015. Results were reported in the November 2015 Shakedown Report. The Al 5086 sample in flowing seawater continues to be tested as the control.

CURRENT SAMPLES DATA COLLECTION

This report contains data collected up to February 17, 2016. As of February 17, 2016, the warm seawater pre-treatment samples have been exposed for a total of 300 days and the control, hypo-chlorination, and acid treatment samples have been exposed for 272 days.

2.1.1. Pitting corrosion

No pits have been observed on any of the new samples. Only a 1.5" x 2.75" rectangle at the center of each sample is analyzed for pitting to minimize the influence of crevice corrosion. Small pits were observed on the Al 5086 control sample in flowing seawater (ut5-1) after 477 days via imaging. Pits were initially reported on the ultrasonic scan at 499 days but subsequent scans do not show pits and the original observation may have been due to noise in the scan. Pits are still visible on images and appear the same size.

In several samples, crevice corrosion has spread from the gasket towards the center of the sample and is within the limits of the rectangle used to identify pits. These points will be manually excluded so they will not be counted as pits.

2.1.2. Crevice corrosion

Crevice corrosion is present on most samples. Most samples with crevice corrosion identified in the images also have crevice corrosion identified in the ultrasonic scans. Of the samples that received warm seawater pre-treatment, only Al 1100 in near stagnant seawater has crevice corrosion. Of the samples receiving daily hypo-chlorination treatment, the Al 1100 samples (in flowing and near stagnant seawater) have crevice corrosion. All samples receiving acid treatment have crevice corrosion. All control samples have crevice corrosion, although, crevice corrosion did not occur on the Al 5086 until 477 days of total exposure. The Al 1100 and Al 3003 control samples in flowing seawater developed crevice corrosion before the Al 5086 sample.

Table 2. Crevice corrosion at the gasket interface. Lateral penetration is the distance from the inner edge of the gasket to the furthest extent of corrosion. The maximum corrosion depth underneath gasket is not necessarily in the same location as the maximum lateral penetration.

Water Flow	Treatment	Sample	Present on image?	Lateral Penetration [mm]	Maximum Depth under Gasket [mm]
Near Stagnant	Control	ut5-18	Yes	3.9	0.5
		ut3-18	Yes	6.9	1.2
		ut1-18	Yes	6.9[b]	0.8
Flowing	Control	ut5-1	No[a]	-	-
		ut3-17	Yes	6.2	1.0
		ut1-17	Yes	n.d.	n.d.
Near Stagnant	Hypochlorination	ut5-16	No	-	-
		ut3-16	No	-	-
		ut1-16	Yes	n.d.	n.d.
Flowing	Hypochlorination	ut5-15	No	-	-
		ut3-15	No	-	-
		ut1-15	Yes	n.d	n.d
Near Stagnant	Acid treatment	ut5-14	Yes	3.9	0.7
		ut3-14	Yes	5.6	1.2
		ut1-14	Yes	4.9	1.0
Flowing	Acid treatment	ut5-13	Yes	1.3	n.d.
		ut3-13	Yes	3.0	0.8
		ut1-13	Yes	3.2	0.8
Near Stagnant	Warm seawater pre-treatment	ut5-12	No	-	-
		ut3-12	No	-	-
		ut1-12	Yes	4.4	0.6
Flowing	Warm seawater pre-treatment	ut5-11	No	-	-
		ut3-11	No	-	-
		ut1-11	No	-	-

n.d. = not detected on ultrasonic scans.

[a] For the same exposure time, no crevice corrosion or pits were detected on the Al 5086 control sample in flowing seawater. Crevice corrosion was detected on images after 477 days. [b] Crevice detectable to the limits of the scan.

The latest ultrasonic scan (middle panel) and associated image (left panel) for each sample are shown in Figures 2-1 through 2-8. The third panel in each figure is the image overlain with 0.1 mm contours from the ultrasonic scan.

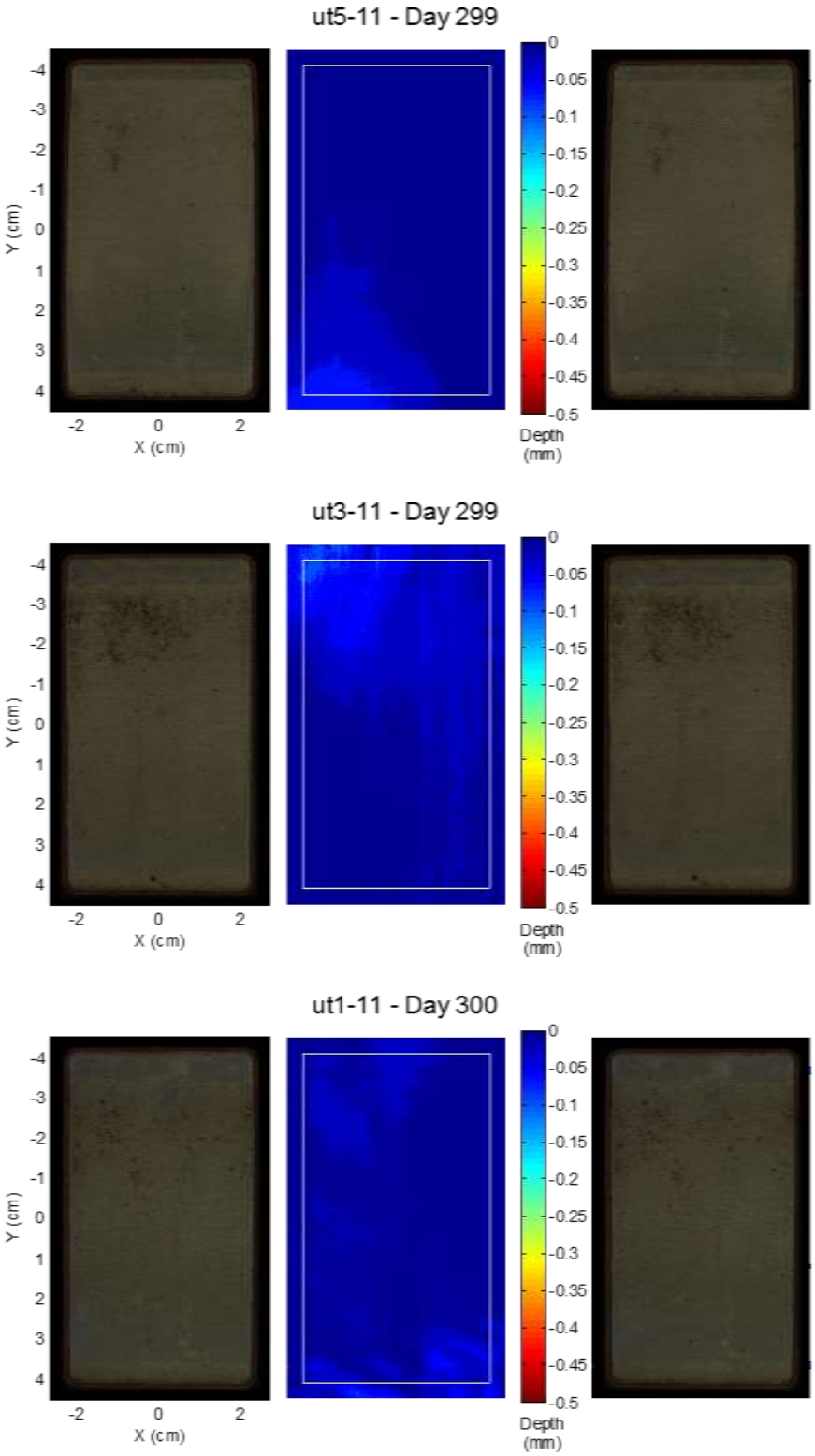


Figure 2-1. Warm seawater pre-treatment samples in flowing seawater. No corrosion features have been observed.

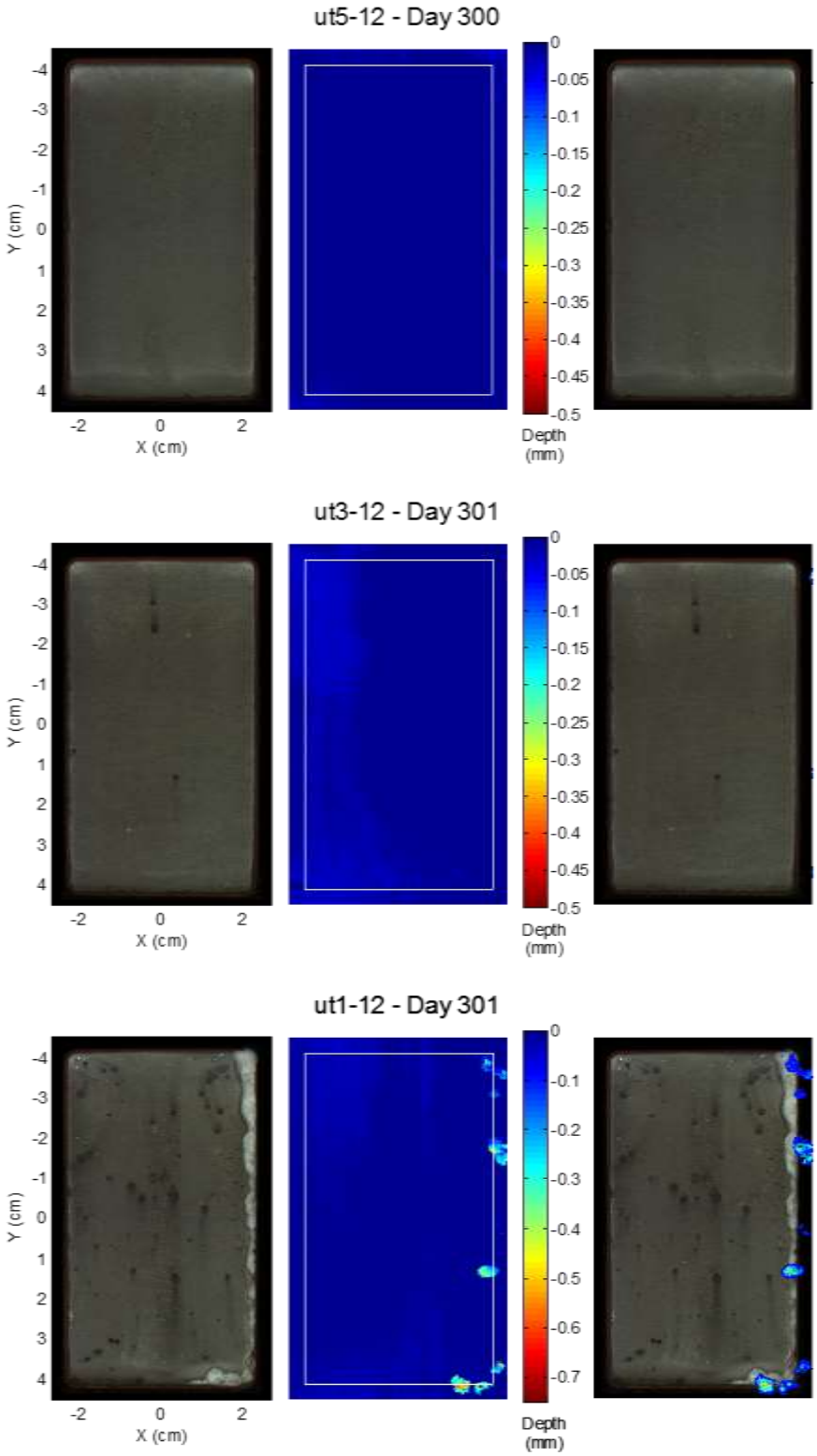


Figure 2-2. Warm seawater pre-treatment samples in near stagnant seawater. Crevice corrosion observed in images and ultrasonic scans on Al 1100.

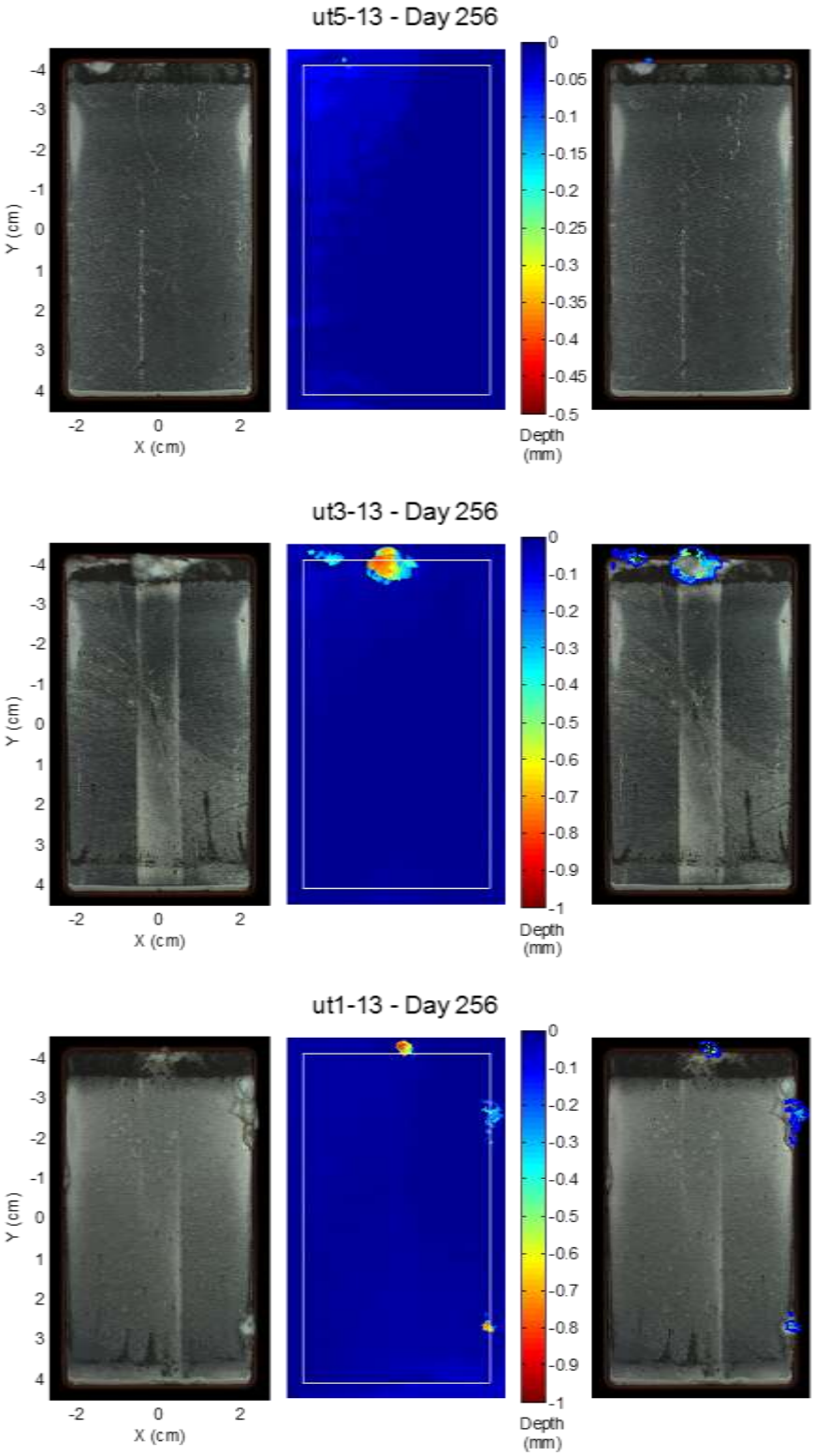


Figure 2-3. Acid treatment samples in flowing seawater. Crevice corrosion is visible in images and ultrasonic scans for all samples.

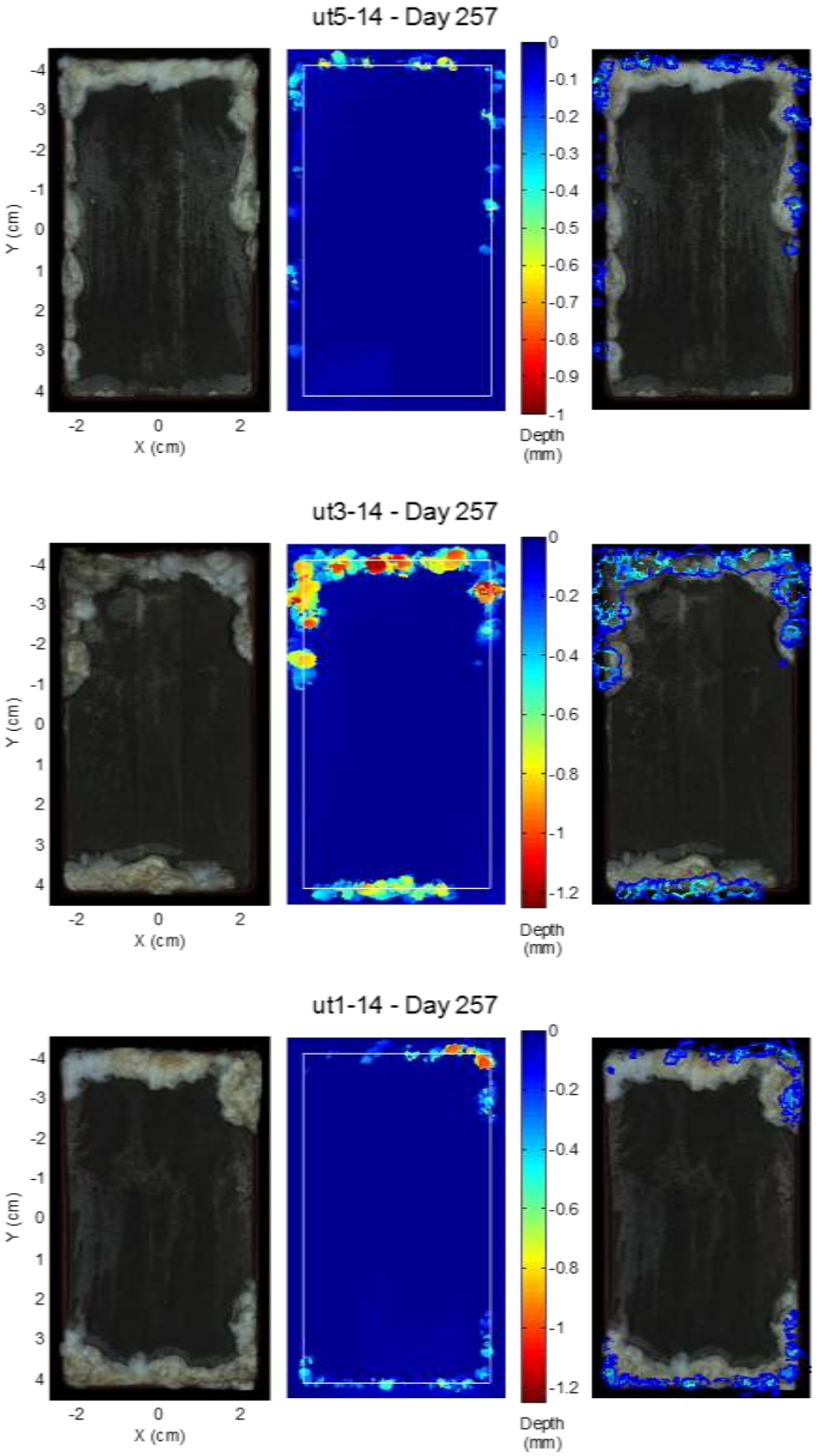


Figure 2-4. Acid treatment samples in near stagnant seawater. Crevice corrosion is visible in imaging and ultrasonic scans for all samples. Dark biofouling on the surface is removed after acid treatment but re-establishes prior to the next treatment.

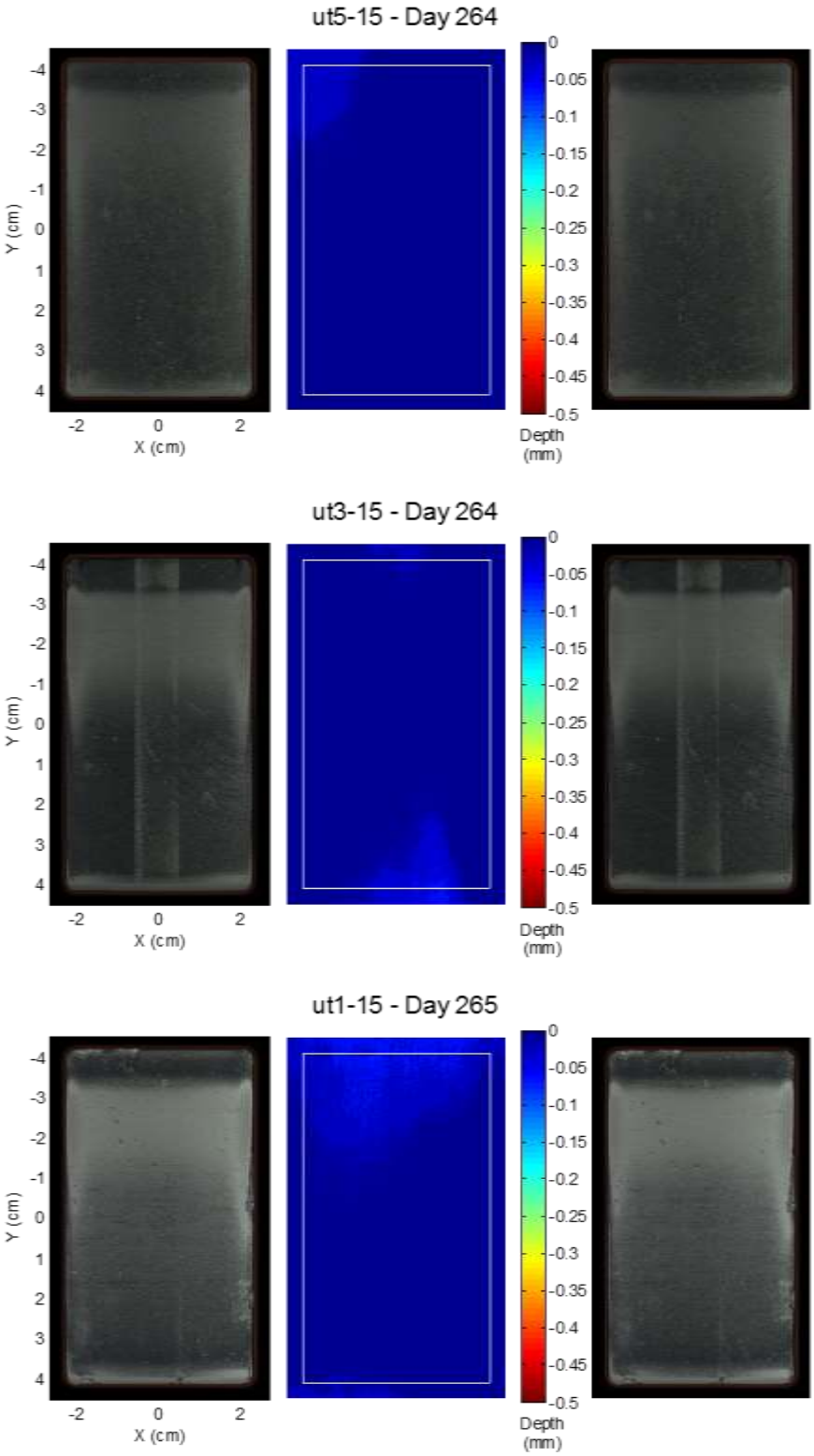


Figure 2-5. Hypo-chlorination treatment in flowing seawater. The beginning of crevice corrosion is visible in images on Al 1100 but not detected on the ultrasonic scan. Al 3003 and Al 5086 do not have observable corrosion features. Surfaces appear new and shiny.

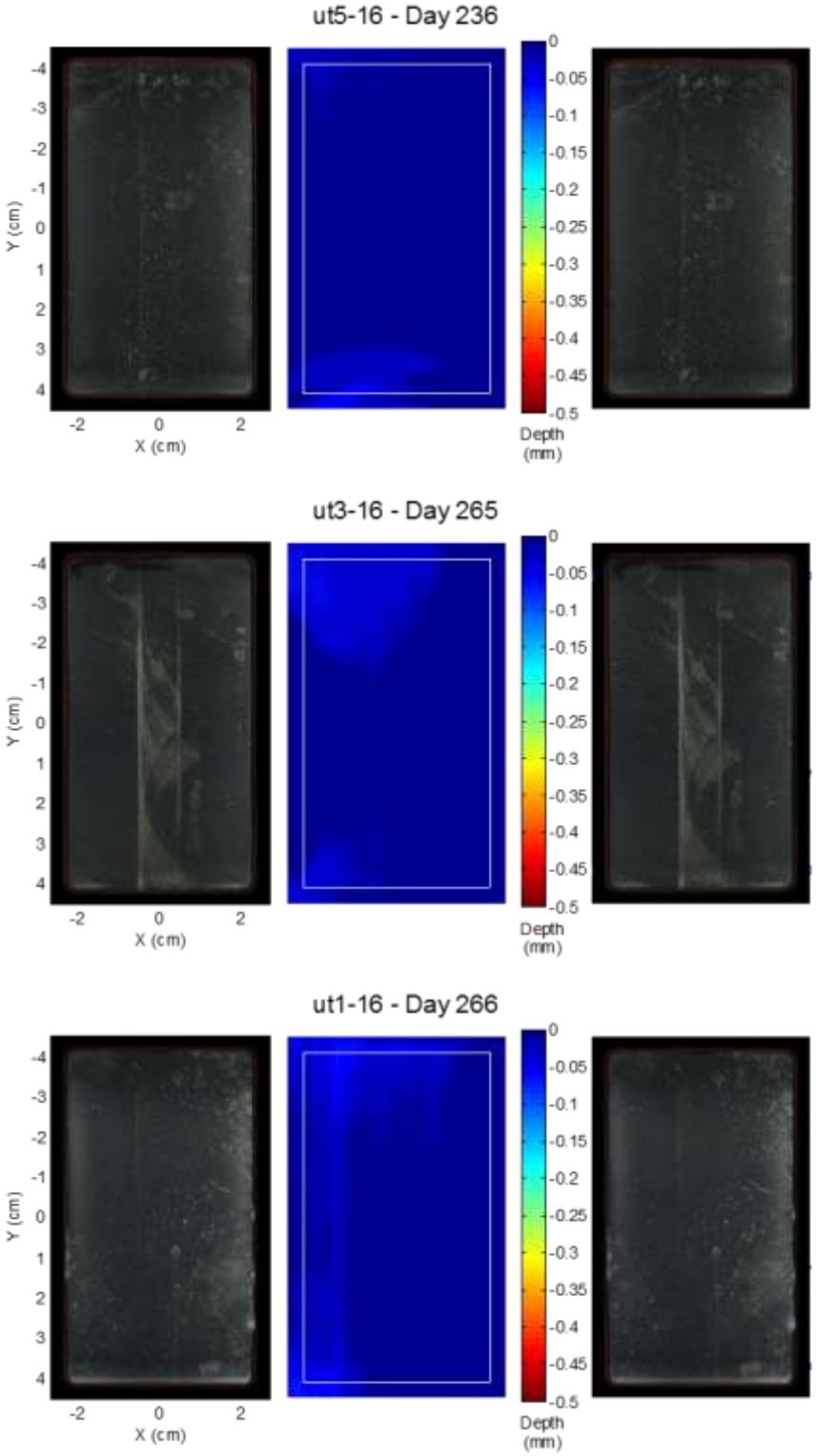


Figure 2-6. Hypo-chlorination samples in near stagnant seawater. The beginning of crevice corrosion is visible in images on Al 1100 but not detected on the ultrasonic scan. Al 3003 and Al 5086 do not have observable corrosion features. Scan quality of ut5-16 at Day 265 was poor and not used; instead, the Day 236 scan and image is shown.

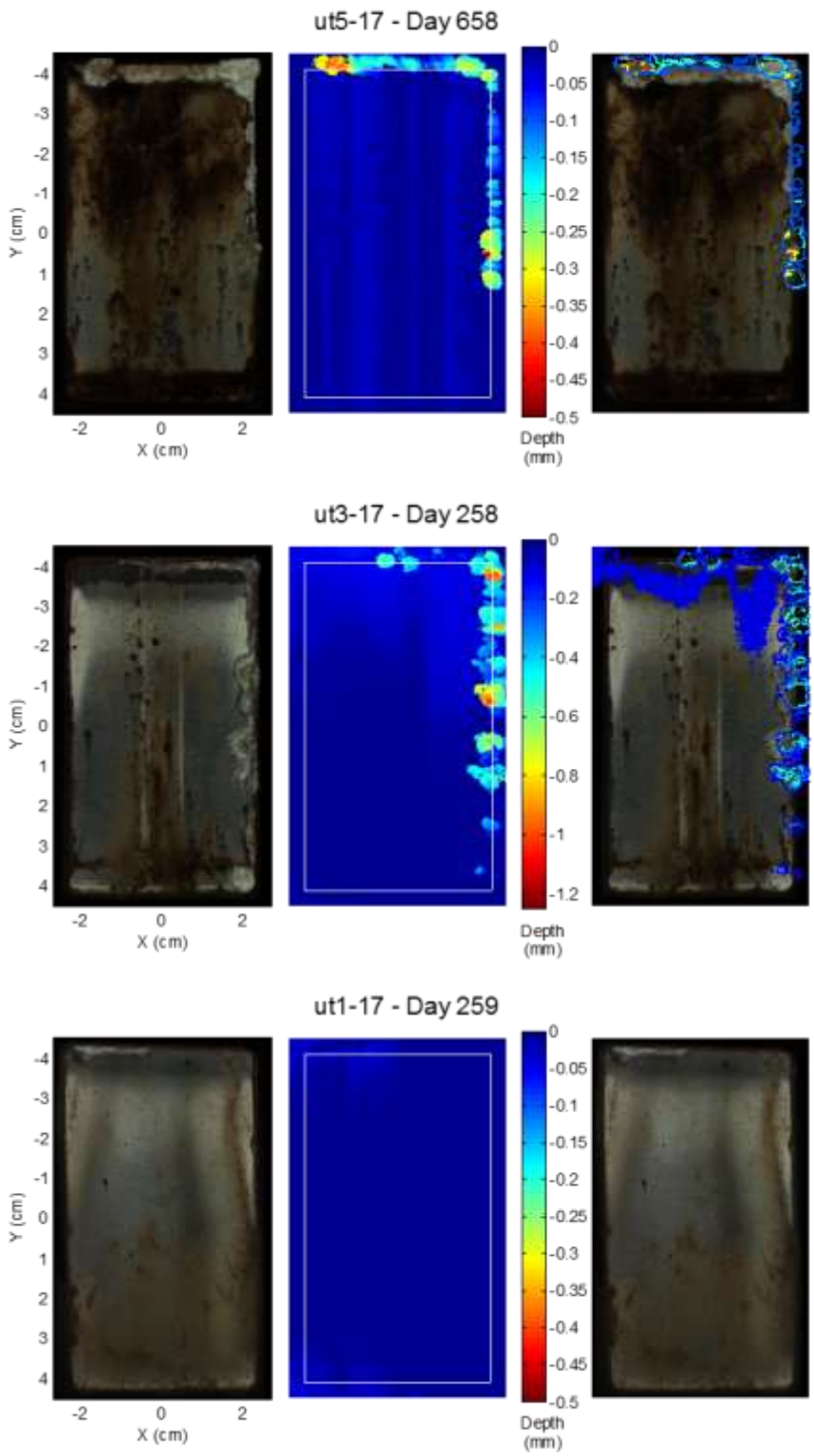


Figure 2-7. Control samples in flowing seawater. ut5-17 is continued from the previous testing. Biofouling on the surface has worsened. Crevice corrosion and biofouling is more severe on Al 3003 than Al 1100. Contour on top edge of ut3-17 is due to uneven thickness. Corrosion has not been detected on Al 1100 via ultrasonic scans.

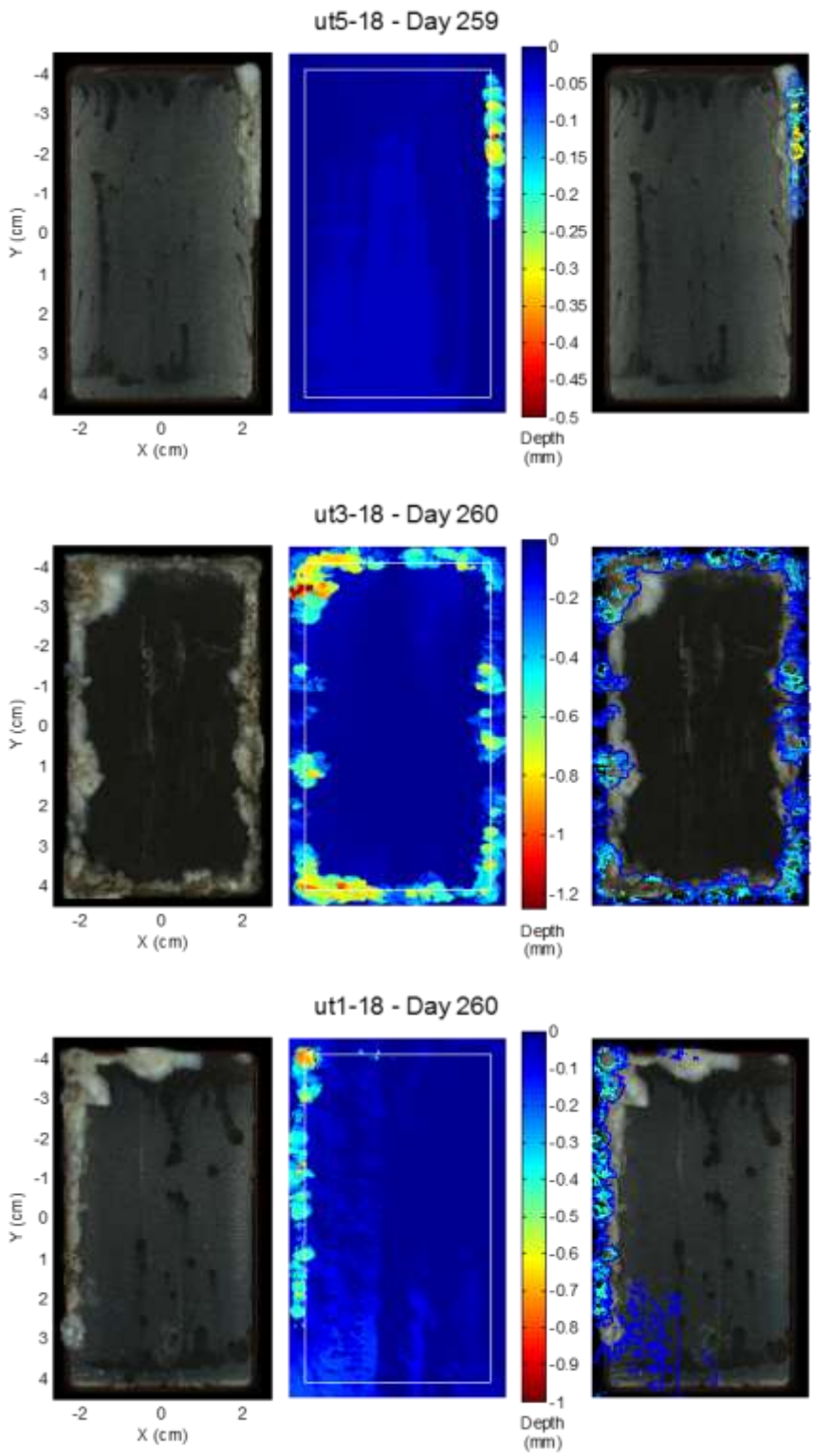


Figure 2-8. Control samples in flow near stagnant seawater. Crevice corrosion is observed on images and ultrasonic scans of all samples; corrosion (and biofouling) is most severe on ut3-18. Contour on the lower left corner of ut1-18 is due to uneven thickness.

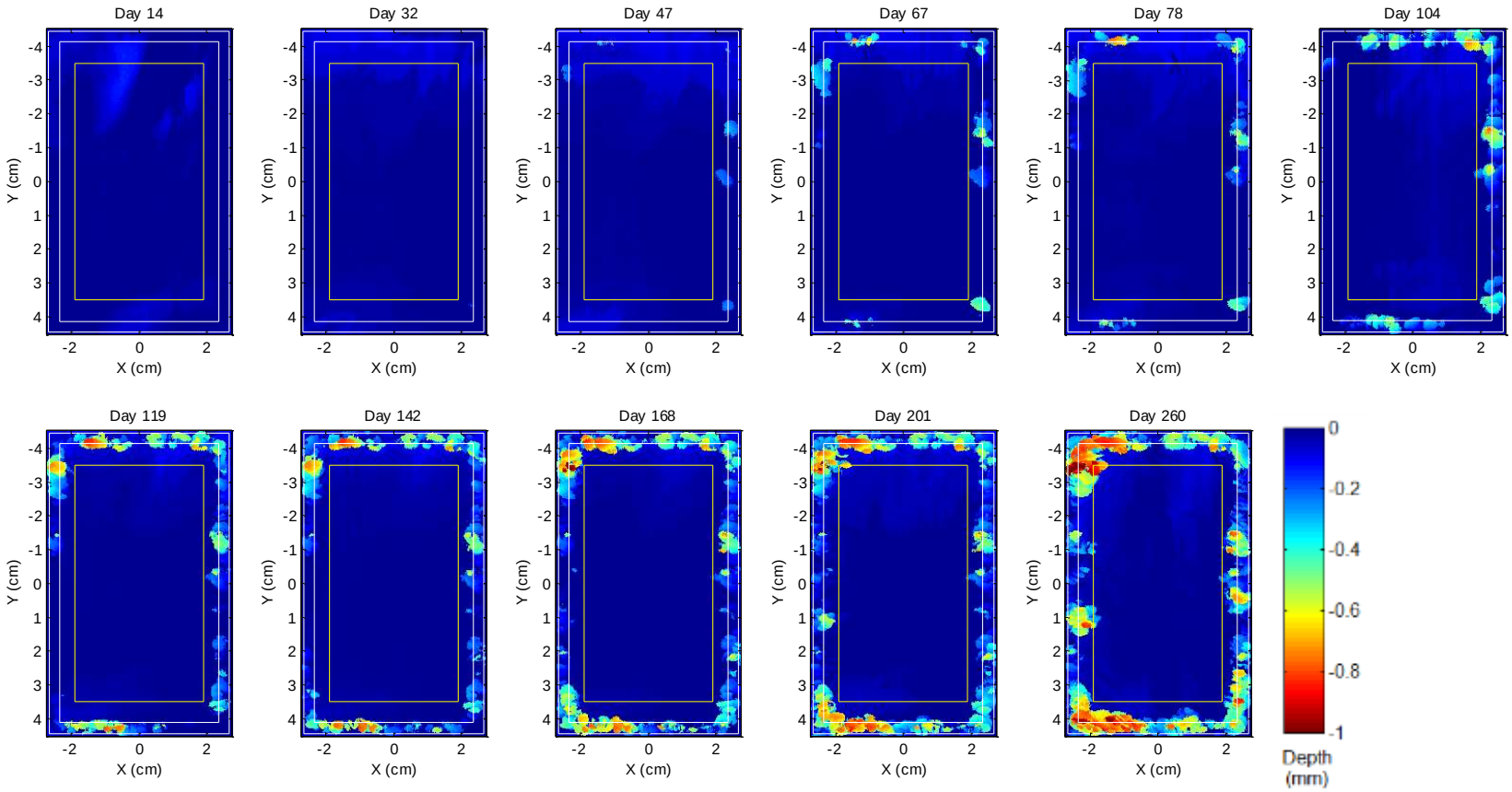


Figure 2-9. Gasket corrosion development on ut3-18 (Al 3003 control sample in near stagnant seawater). The white rectangles are the inner and outer edges of the gasket. Inner yellow rectangle is the area analyzed for pitting. In the several sections along the left and right edges, crevice corrosion is encroaching on the pitting analysis area.

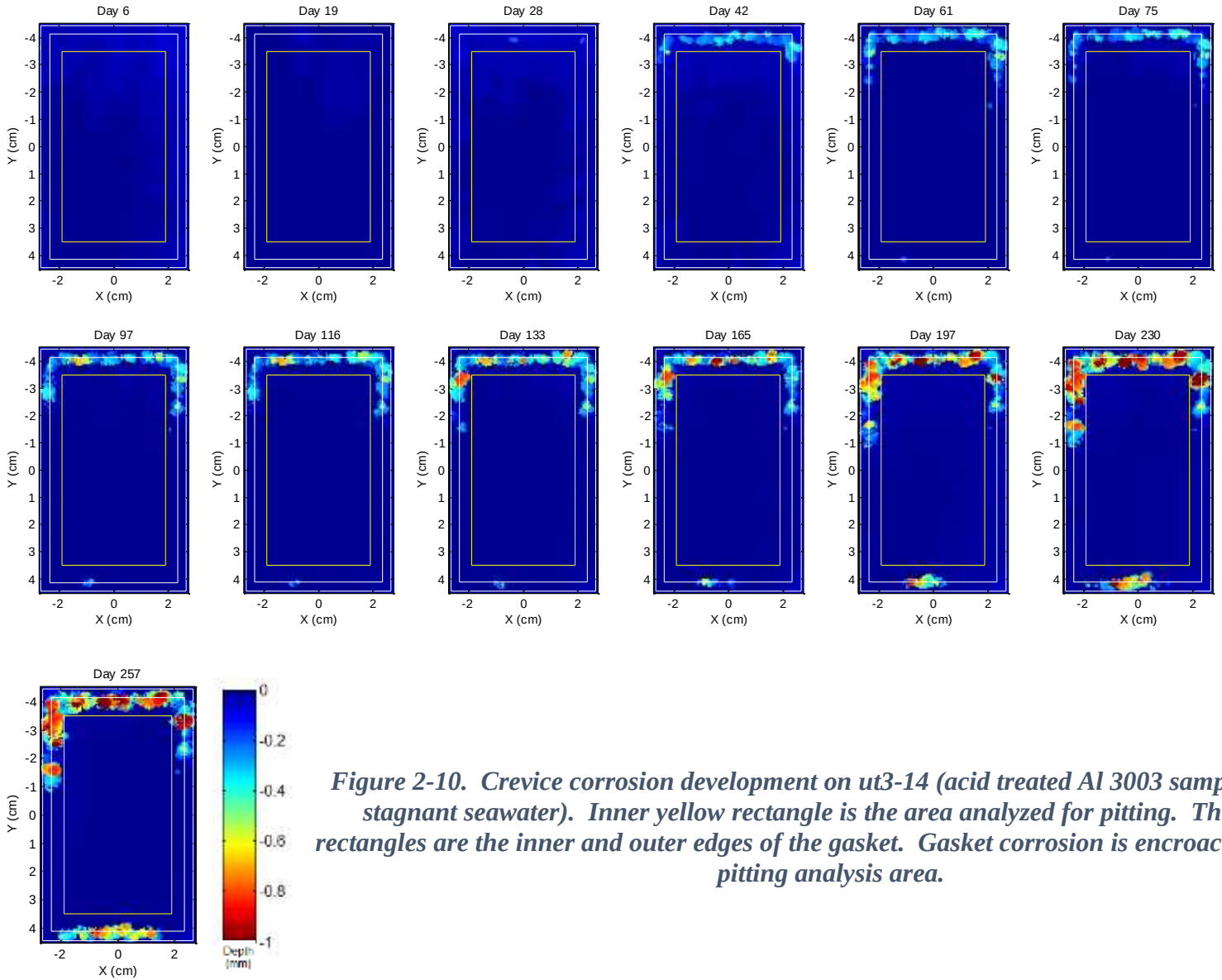


Figure 2-10. Crevice corrosion development on ut3-14 (acid treated Al 3003 sample in near stagnant seawater). Inner yellow rectangle is the area analyzed for pitting. The white rectangles are the inner and outer edges of the gasket. Gasket corrosion is encroaching on the pitting analysis area.

2.1.3. Open Circuit Potential (OCP)

For Al 1100 samples, there is little difference in OCP between the different treatments in either flowing or near stagnant seawater except for the warm seawater pre-treatment sample in flowing seawater (which is free from crevice corrosion). All other samples have some crevice corrosion. No change in OCP was observed after an acid treatment. OCP is not a strong indicator of corrosion for Al 1100.

For Al 3003 samples in flowing seawater, acid treatment and control samples have comparable OCPs, whereas the hypo-chlorination sample has lower OCP. The warm seawater pre-treatment sample OCP is still lowering towards the hypo-chlorination sample OCP. In near stagnant seawater, control, acid treatment, and warm seawater pre-treatment samples have comparable OCPs and the hypo-chlorination sample has lower OCP. The warm seawater pre-treatment sample OCP was initially around -700mV, decreased to -800 mV after 100 days in cold seawater, and began in increase towards -700 mV at 150 days. In both flowing and near stagnant seawater, acid treatments lowered OCP immediately after treatment but OCPs returned to higher values within 20 days post treatment. Crevice corrosion has been detected on all acid treatment and control samples. OCPs of the acid treatment and control samples are in the expected pitting region (around -700 mV) and entered into the pitting region around the same time crevice corrosion was detected via imaging. OCP may be a good indicator of localized corrosion for Al 3003.

For Al 5086, acid treatment samples in flowing and near stagnant seawater and the control sample in near stagnant seawater have OCPs in the pitting region and crevice corrosion has been observed on images and ultrasonic scans. OCP entered the pitting region prior to the appearance of crevice corrosion on images. Crevice corrosion has not been observed on the five other samples. Hypo-chlorination samples have slightly lower OCPs in flowing seawater than in near stagnant seawater. OCP for the warm seawater pre-treatment sample in near stagnant seawater was initially around -700 mV and began to lower to -800 mV after 70 days in cold seawater. In flowing seawater, OCP for the warm seawater pre-treatment sample has remained at -700 mV but no corrosion has been observed in images or ultrasonic scans. As with Al 3003, warm seawater pre-treatment appears to alter OCP behavior. OCP may still be predictive of localized corrosion for Al 5086.

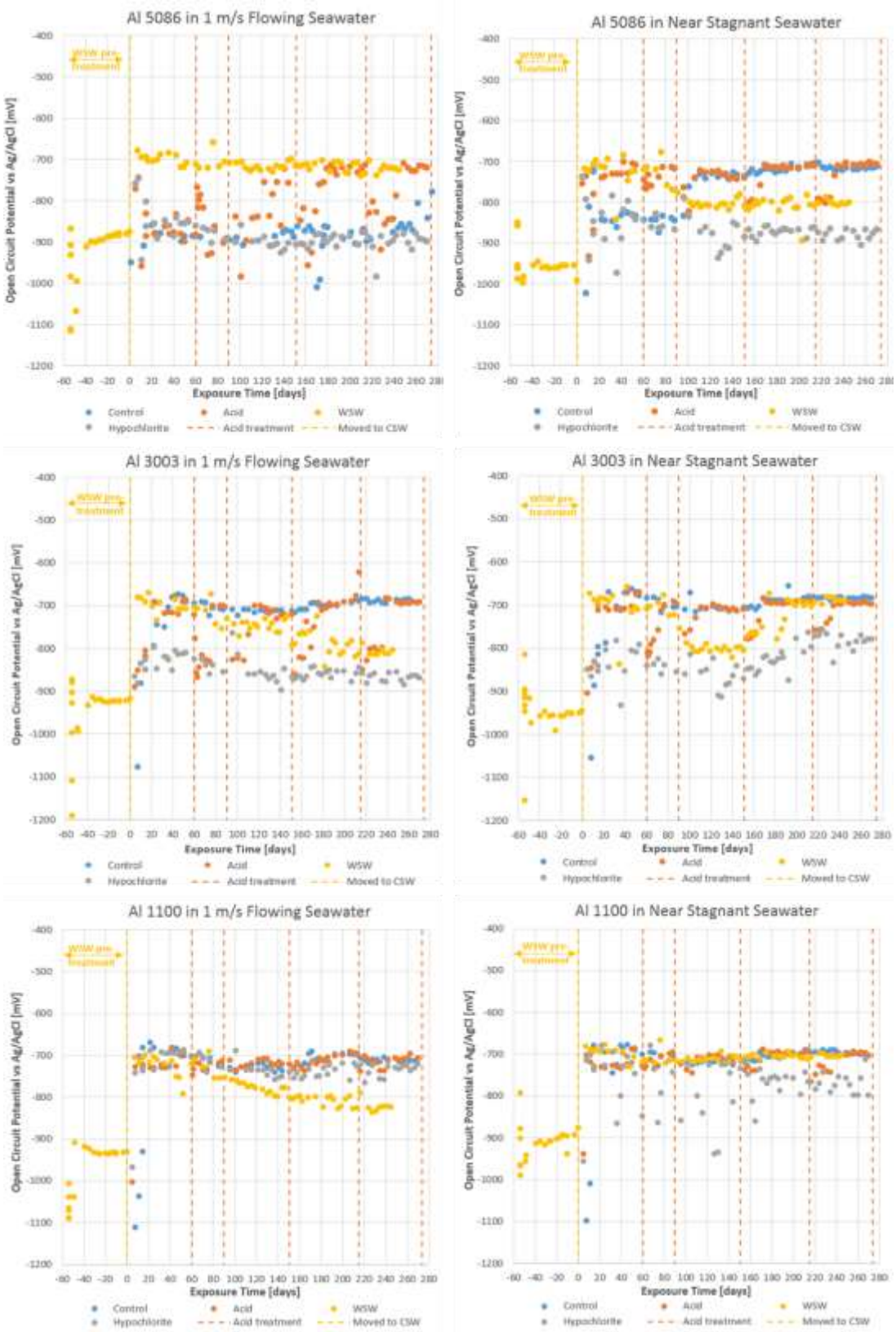


Figure 2-11. Comparison of treatment effects on open circuit potentials of three aluminum alloys.

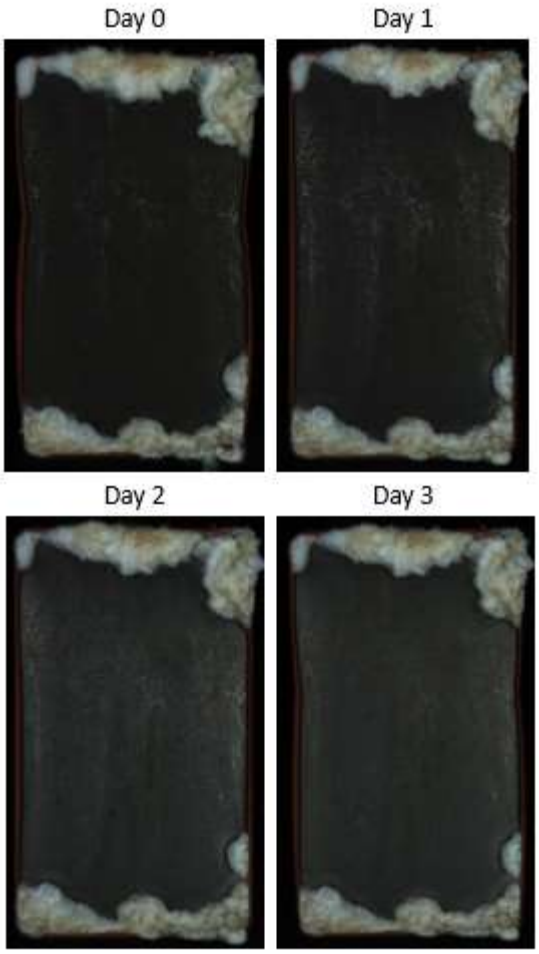


Figure 2-12. Acid treatment removes surface biofouling on ut1-14. Same effect was observed on other acid treated samples. Images were taken before treatment, 1 day, 2 days, and 3 days after treatment.

DISCUSSION

Crevice corrosion continues to expand and deepen. Crevice corrosion continues to be more severe in near stagnant samples than in flowing seawater samples. Acid treated samples were also more susceptible to crevice corrosion than samples receiving hypo-chlorination or warm seawater pre-treatment. Warm seawater pre-treatment samples have performed the best; only the Al 1100 warm seawater pre-treatment sample in near stagnant seawater shows crevice corrosion. Hypo-chlorination appears effective for Al 3003 and Al 5086, neither flowing nor near-stagnant samples have corrosion and the sample surfaces look new. Al 1100 sample surfaces also look new but crevice corrosion is present in both flowing and near stagnant seawater samples.

Pitting has not been observed on images or on ultrasonic scans of new samples, only the Al 5086 control that has been continued from previous testing. For several samples, crevice corrosion is encroaching on the pitting analysis window. These locations were not counted as pits in the analysis.

Biofouling on several sample surfaces has been severe, covering nearly the entire surface. Acid treatment and control samples in near stagnant seawater have the most coverage. Acid treatment removes the visible fouling but biofouling re-establishes coverage before the next treatment (Figure 2-12). Biofouling on the Al 5086 control sample in flowing seawater has developed a rust colored patches (Figure 2-7), unlike the black spots and patches typically observed. The Al 3003 and Al 1100 control samples in flowing seawater have also begun to develop the rust colored patches. Except for the hypo-chlorination samples, which appear free from biofouling, biofouling is worse on near stagnant samples compared to flowing seawater samples.

OCP appears correlated to the onset of crevice corrosion for Al 3003 but not for Al 1100 or Al 5086. Warm seawater pre-treatment appears to alter OCP behavior in Al 3003 and Al 5086. OCP starts high (~ -700 mV) upon exposure to cold seawater and begins to lower after a certain exposure time (varies with alloy and water source).

Cumulative findings of Makai's ongoing corrosion testing program are summarized in Table 3 (draft only, not for publication). Box coupon testing data was also used in the analysis presented in Table 3. One major limitation is that box coupon data collection is discrete and destructive. It is not possible to determine if observed pits were established and continued to deepen over time (as observed for Al 6061) or levelled off and remained at a stable depth (as for Al 2024) or if the observed pits or crevice corrosion could be traced back to a singular disturbance. Continuous, in situ monitoring, as in ultrasonic scanning and imaging, has been advantageous in studying corrosion development.

FUTURE WORK

Daily imaging and as-needed ultrasonic scanning will continue on the samples. Daily hypo-chlorination treatments will continue. Acid treatments will continue to be performed every two months.

Table 3. Cumulative findings corrosion suitability of bare aluminum alloys for use in OTEC heat exchangers.[1]

Alloy	Evaporator	Cumulative Test Exposure	Expected Life Cycle[2]	ANL 1980's Test Results	Condenser	Cumulative Test Exposure	Expected Life Cycle[2]	ANL 1980's 5-years Test Results
3003	Yes[3]	ongoing, ~6 years	at least 6 years	Yes	TBD[4]	ongoing, ~6 years	at least 6 years	Yes with caution
3003 (treated[6])	Not Tested	Not Tested	Not Tested	-	TBD[5]	ongoing, ~6 years	at least 6 years	-
5052	Yes[3]	ongoing, ~6 years	at least 6 years	Yes	TBD[4]	ongoing, ~6 years	at least 6 years	Yes
5052 (treated[6])	Not Tested	Not Tested	Not Tested	-	TBD[5]	ongoing, ~6 years	at least 6 years	-
6063-T5	Yes	ongoing, ~6 years	at least 6 years	Yes	No (pitting)	ongoing, ~6 years	Not suitable	Yes
6063 (treated[6])	Not Tested	Not Tested	Not Tested	-	No (pitting)	ongoing, ~6 years	Not suitable	-
6061	Not Tested	Not Tested	Not Tested	Not Tested	No	~1 year	Not suitable	Not Tested
5086	Not Tested	Not Tested	Not Tested	Not Tested	TBD	ongoing, ~1.5 years	TBD	Not Tested
5086 (treated[6])	Not Tested	Not Tested	Not Tested	Not Tested	TBD	ongoing, ~1.5 years	TBD	Not Tested
1100	Yes	ongoing, ~6 years	at least 6 years	Not Tested	No (pitting)	ongoing, ~6 years	Not suitable	Not Tested

1. These alloys are solely evaluated based on their corrosion and pitting characteristics as determined at Makai Ocean Engineering's Marine Corrosion Lab when coupons are exposed to flowing seawater (~ 1 m/s) ranging from 24 to 28 °C for evaporator uses and 6 to 7 °C (CSW from 674-m) for condenser uses. Alclad alloys are not acceptable for OTEC HXs.
2. Over 30-year life expect losses of TBD micrometers (Makai) in the evaporator and 200 micrometers (ANL) in the condenser.
3. Some pitting has been observed. Pits initially observed after 3 years, pit depths have not significantly increased in samples removed at 5 years. Maximum pit depth observed is ~ 0.75 mm (0.030").
4. Some pitting has been observed. Pits initially observed after 1.5 years, pit depths have not significantly increased in samples removed at 5 years. Maximum pit depth observed is ~ 0.125 mm (0.005").
5. Some pitting has been observed. Pits initially observed after 1 year, pit depths have not significantly increased in samples removed at 5 years. Maximum pit depth observed is ~ 0.2 mm (0.008").
6. Warm seawater pre-treatment is tested on Alloys 3003, 5052, 6063, and 5086. Acid treatment is tested on Al 5086 and Al 6063. Hypo-chlorination is tested on Al 5086.

Caveats:

1. To avoid pitting of braze joints in evaporators, silicon must be removed from surface by, for example, machining off the top layer.
2. Braze joints fabricated using commercial fluxes <u>are not acceptable in the condenser.</u>
3. Avoid stagnant water especially near gaskets.
4. Care must be taken during manufacturing to avoid defects such as extrusion lines or concentrated areas of cold work, e.g., during roller expansion.

Hawaii National Marine Renewable Energy Center (HINMREC)

U.S. Department of Energy Award Number: DE-FG36-08GO18180

Task 6: Supporting Studies

OTEC Heat Exchanger Program: 2016 Ultrasonic Scanning for Corrosion Monitoring Progress Reports

Prepared by:
Makai Ocean Engineering

Prepared for:
Hawaii Natural Energy Institute, University of Hawaii

2015 - 2016

HNEI
Hawai'i Natural Energy Institute
University of Hawai'i at Mānoa

OTEC HEAT EXCHANGER PROGRAM

ULTRASONIC SCANNING FOR CORROSION MONITORING

STATUS REPORT #3

SUBAWARD MA150017

Prepared For

HAWAII NATIONAL MARINE RENEWABLE ENERGY CENTER

LUIS VEGA

1680 East West Road, POST 112A

Honolulu, HI, 96822

USA

Prepared By

MAKAI OCEAN ENGINEERING

PO Box 1206, Kailua, Hawaii 96734

August 2016

1. INTRODUCTION

Aluminum alloys have been proposed for use in Ocean Thermal Energy Conversion (OTEC) heat exchangers for their high thermal conductivity, comparatively low cost, and overall good general corrosion resistance (due to formation of a protective oxide layer) in seawater environments. Although uniform corrosion rates for aluminum alloys are low, aluminum alloys are susceptible to surface pitting and crevice corrosion at gasket interfaces which can initiate when local galvanic cells develop between alloying elements and deposit corrosion product on the surface of the metal. Corrosion product can encase the immediate area and change the local environment which acts to accelerate the corrosion process. It is important to quantify this phenomenon because, in time, pits or crevice corrosion can penetrate the wall of the heat exchanger and cause refrigerant to leak into the seawater. For heat exchangers, this is considered a catastrophic failure and must be avoided.

Makai Ocean Engineering has been studying and quantifying the development of corrosion on aluminum alloys being considered for OTEC heat exchangers. Makai has developed a setup in which pit growth can be observed in-situ by optical imaging and ultrasonic scanning. Pitting sites are identified and corrosion product accumulation on the metal surface is observed using imagery. However, once corrosion product encapsulates a pit, no accurate measurements of pit size or depth can be made with imaging alone. With the addition of ultrasonic thickness scanning, the surface underneath the corrosion product can be observed and the 3-dimensional structure of the pit can be measured. Pit development can now be monitored over time without removal or destruction of samples.

Makai is currently testing three alloys (Al 1100-H112, Al 3003-F and Al 5086-H116) and three corrosion mitigation techniques (warm seawater pre-treatment, hypo-chlorination and exposure to a diluted sulfamic acid) in flowing (1 m/s) and near stagnant cold seawater for a total of 18 samples. Six control samples, one of each alloy in flowing and near stagnant cold seawater, are also being tested.

2. STATUS

Warm seawater pre-treatment samples were exposed to warm seawater on 4/22/15 and moved to cold seawater on 6/15/15. Warm seawater pre-treatment samples have been exposed for 15 months. Control, hypo-chlorination, and acid treatment samples were exposed to cold seawater on 5/21/15. Control, acid treatment, and hypo-chlorination samples have been exposed for 14 months.

Except for the control samples, samples are subjected to one of three treatments: warm seawater pre-treatment, hypo-chlorination, or acid treatment; in either flowing (1 m/s) or near stagnant cold seawater (Table 1). Alloys in each column are arranged in the same order from top to bottom: Al 5086, Al 3003, and Al 1100. Laser profilometer scans of the test surfaces were conducted prior to exposure for each sample. All corrosion samples were degreased, cleaned with simple green, and rinsed with ethanol before installation to remove surface contaminants.

The imaging system automatically images the front face of each sample daily. The samples are scanned ultrasonically once a month. The frequency of ultrasonic scanning will be adjusted based on corrosion development. We continue to encounter frequent corrupted data files despite two repair attempts by the manufacturer. They determined it is a problem with all their scanners so they are working on a firmware fix which we still do not have. We have developed a work around where we can re-assemble the corrupted data and we will do so until the manufacturer can provide resolution.

Table 1. Current test samples.

Column	Sample IDs	Water Flow	Treatment
9	ut5-18, ut3-18, ut1-18	Near Stagnant	Control
10	ut5-1*, ut3-17, ut1-17	Flowing	Control
4	ut5-11, ut3-11, ut1-11	Flowing	Warm seawater pre-treatment
5	ut5-12, ut3-12, ut1-12	Near Stagnant	Warm seawater pre-treatment
6	ut5-16, ut3-16, ut1-16	Near Stagnant	Hypo-chlorination
7	ut5-15, ut3-15, ut1-15	Flowing	Hypo-chlorination
14	ut5-14, ut3-14, ut1-14	Near Stagnant	Acid Treatment
15	ut5-13, ut3-13, ut1-13	Flowing	Acid Treatment

* Original sample, continued from previous round of testing.

This report contains data collected up to 8/1/2016.

2.1. EVENT LOG

On 5/22/15, cold seawater flow was stopped for 3 hours for piping modifications. Samples remained in stagnant seawater.

On 5/28/15, cold seawater flow was mistakenly stopped, samples remained in stagnant seawater overnight.

In July 2015, biofouling on warm seawater samples worsened due to a bleach pump malfunction. The hypo-chlorination samples most likely did not receive the 100 ppb dosage as planned.

On 10/15/15, cold seawater flow was stopped for 2 hours for valve repair. Samples remained in stagnant seawater.

On 6/16/16, cold seawater flow was stopped for ~ 1 hour to prevent over pressurization of the system during NELHA operations. Samples remained in stagnant seawater. After flow restoration, cold seawater temperatures averaged about 9°C (compared to 5.9°C) until 6/30/16 when NELHA system flow was restored to normal conditions.

2.2. TREATMENTS

Treatments are expected to minimize pit depths (and/or presence). The warm seawater pre-treatment protocol was developed on the hypothesis that corrosion resistance in cold seawater would improve if samples exposed in cold seawater had the same protective oxide layer as samples in warm seawater. Initially exposing samples in warm seawater allows the oxide layer to develop and, when performed carefully, the developed oxide layer remains when samples are relocated to cold seawater. Previous testing established 40 days in warm seawater is the sufficient time to build the oxide layer.

The hypo-chlorination treatment protocol is currently used in warm seawater to control biofouling. Bacterial colonies have been observed on samples exposed to cold seawater; while the exact mechanism for pit initiation is unknown, any difference in the local surface environment can accelerate corrosion. Thus, bacterial colonies on a sample's surface may act as pit initiation sites. Samples are exposed to 100 ppb chlorine for 1 hour daily to control the growth of bacterial colonies.

The hypo-chlorination system uses a metering pump that pumps a pre-calculated amount of bleach from a bleach reservoir/tank into the designated seawater header. The amount of bleach to be pumped is based on the desired concentration and the flow rate. We recently discovered the amount of bleach the pump is delivering to seawater headers is affected by the tank level, leading to variability in the chlorine concentration. In general, concentration levels were lower than intended because ORP values were lower than expected. In response, the pumping volume was manually increased to deliver enough bleach that would lower ORP values into the sterilization range. This defect is now corrected programmatically; the pumping volume will take into account the tank level and we will continue to monitor ORP levels as a system check.

The acid treatment protocol was developed based on observations of open circuit potential (OCP) and corresponding corrosion activity. Samples have shown a marked change in

OCP once pitting begins. Treatment of a sample with a mild acid will strip the oxide layer and possibly remove local environments that may have developed, essentially 'resetting' the surface to the condition it was in when first exposed to seawater. In previous tests, application of 5% sulfamic acid for 5 minutes lowers OCP to the passive region for Al 6063. The acid treatment is performed every two months.

2.3. PITTING CORROSION

Only a 1.5" x 2.75" rectangle at the center of each sample is analyzed for pitting to minimize the influence of crevice corrosion. Pits have been observed on the Al 3003 stagnant control sample (ut3-18), the Al 3003 flowing and stagnant warm seawater pre-treatment samples (ut3-11 and ut3-12), and the Al 5086 flowing control sample (ut5-17).

The pit on ut3-11 (Figure 2-1) is relatively small and has not been detected on ultrasonic scans. The pit initially looked similar to biofouling and surface discoloration and was not identified until recent images. By backtracking through the images, the pit was first distinguishable in images taken on 2/11/16.

The pit on ut3-12 (Figure 2-2) has been detected on ultrasonic scans. From the most recent images, the pit appears to be part of crevice corrosion, but backtracking through the images shows the pit developed first and some of the corrosion product buildup spread towards the gasket.

On ut3-18, the pit developed rapidly. No pits were identified in the 2/5/16 ultrasonic scan or image. A small pit first appeared on the 2/20/16 – Day 275 image (Figure 2-7). By the next scheduled ultrasonic scan on 3/22/16 – Day 306, the maximum pit depth was already -0.5 mm (Figure 2-8).

On ut5-17, small pits were observed after 477 days via imaging. A pit (circled on Figure 2-9) was detected on the ultrasonic scan at Day 733 (Figure 2-10). Biofouling began around Day 537 (on 10/6/15 image) and became severe after Day 658. Images after 4/18/16 were indistinguishable due to biofouling coverage.

The maximum pit depths on ut3-12 and ut3-18 are over 0.5 mm deep but do not appear to be getting deeper whereas the maximum pit depth on ut5-17 continues to get deeper (Figure 2-3 through Figure 2-5). The corroded volume per unit area and % corroded surface area have also plateaued for ut3-18 but continue to increase for ut3-12 and ut5-17 (Figure 2-6). The % corroded surface area was calculated by dividing the number of pixels with depths greater than 0.05 mm (pit threshold) by the number of pixels in the pit analysis area. The corroded volume per unit area was calculated by multiplying the average depth of the pitted pixels by the number of pitted pixels divided by the total number of pixels in the pit analysis area.

In several other samples, crevice corrosion has spread from the gasket towards the center of the sample and is within the limits of the rectangle used to identify pits. These points were manually excluded so they would not be counted as pits.

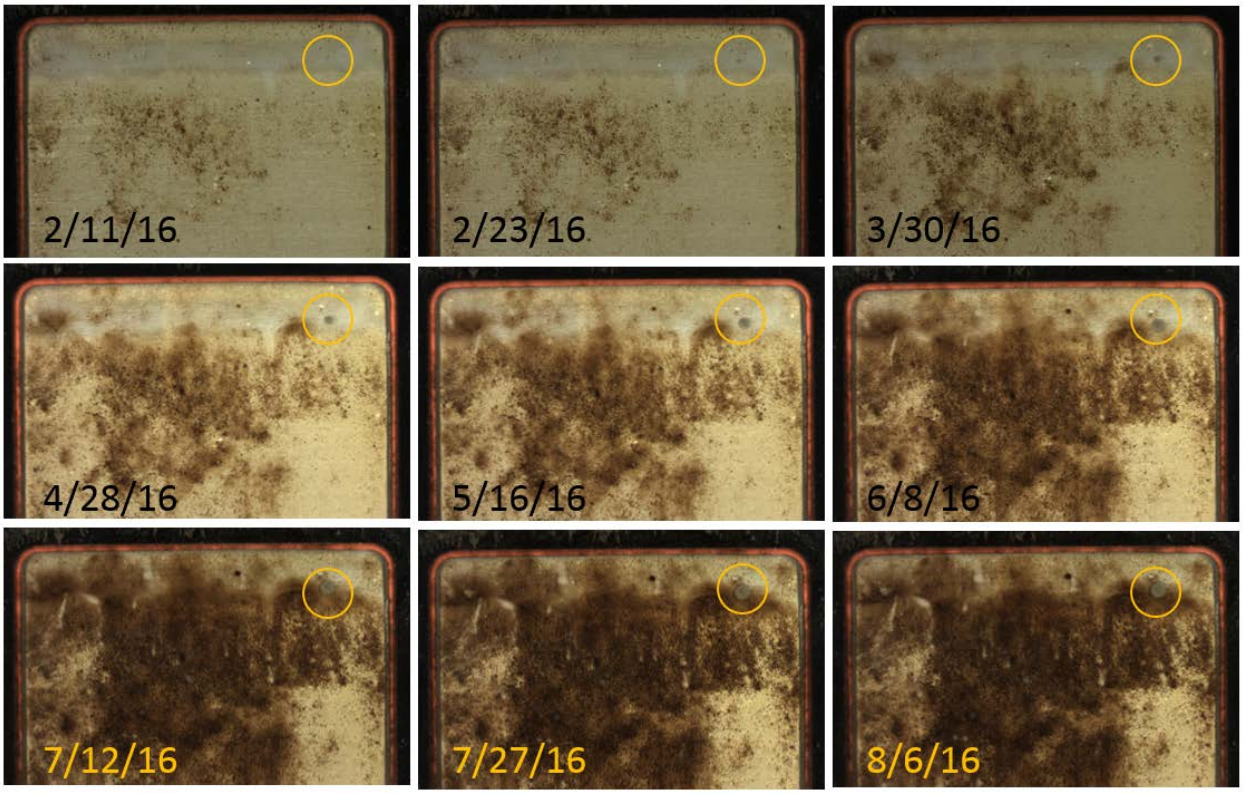


Figure 2-1. Pit development on ut3-11. Pit appears to be a biofouling spot initially. Pit has not been detected on ultrasonic scans.

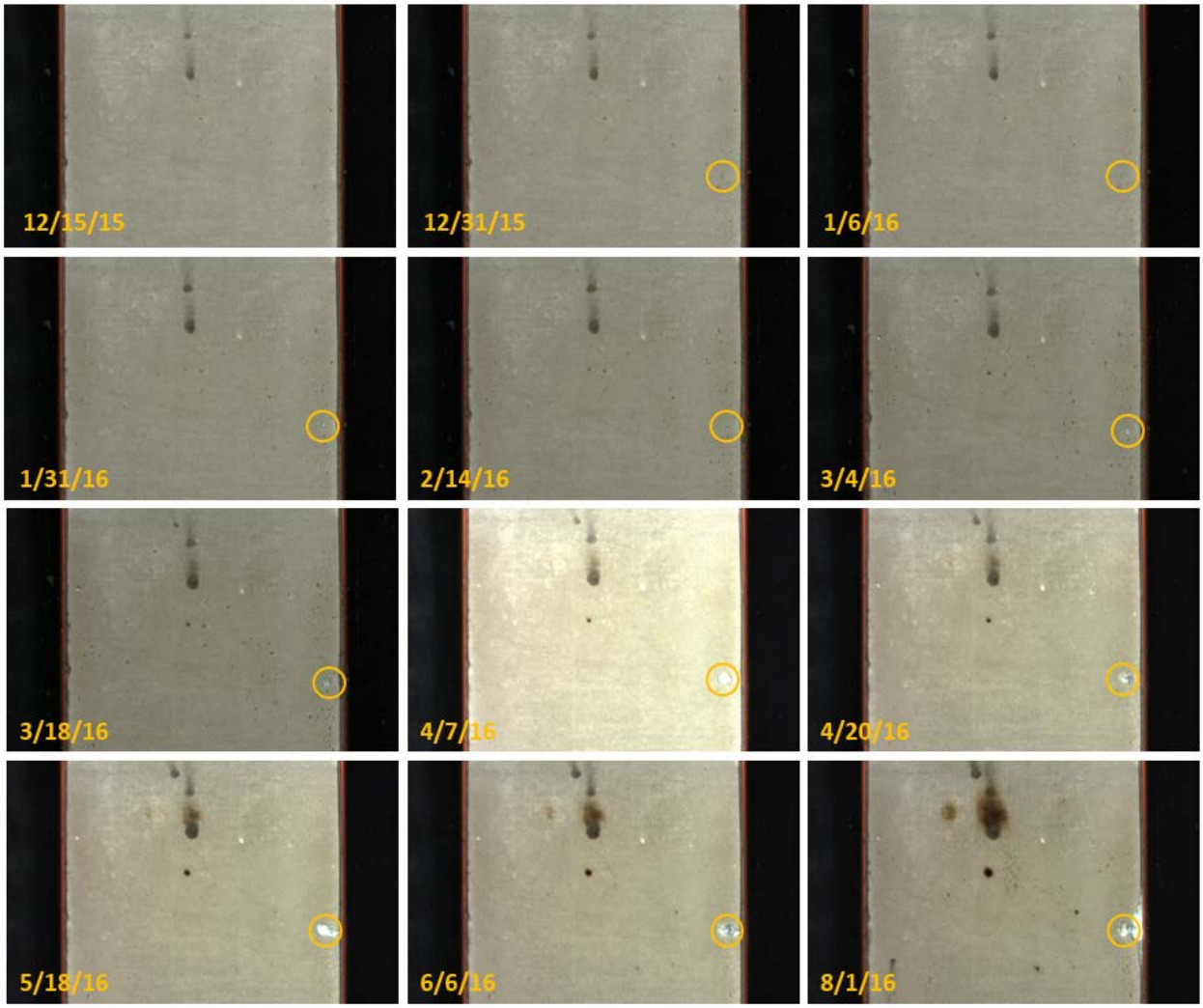


Figure 2-2. Pit development on ut3-12. In images after 4/20/16, the pit appears to be related to crevice corrosion but earlier images confirm that the pit developed first.

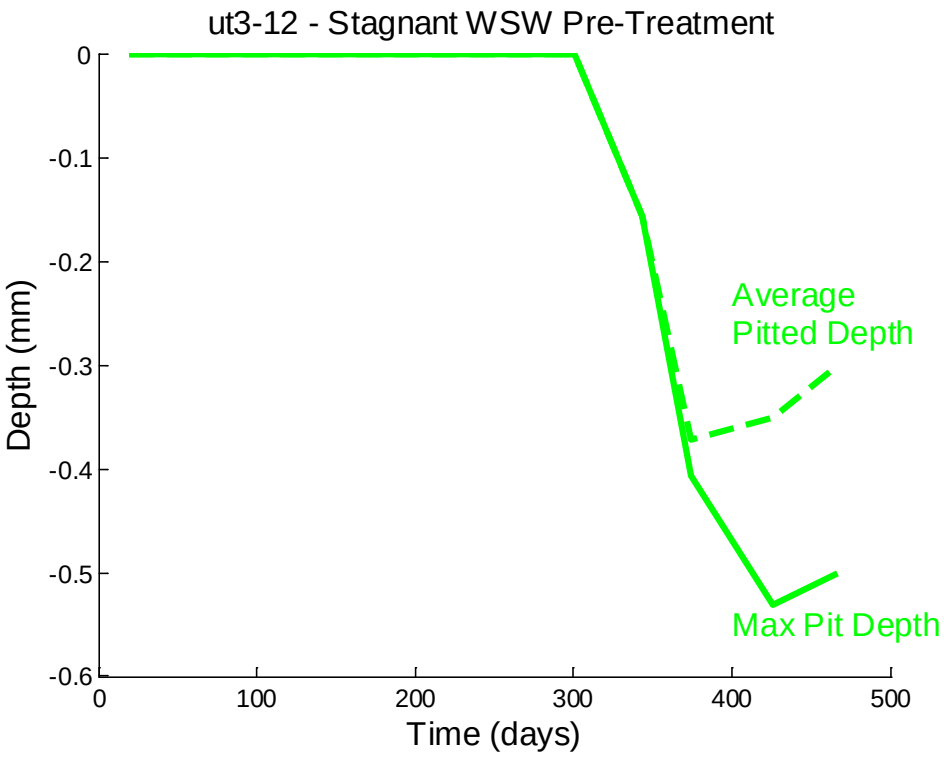


Figure 2-3. Maximum and average pitted depth for ut3-12.

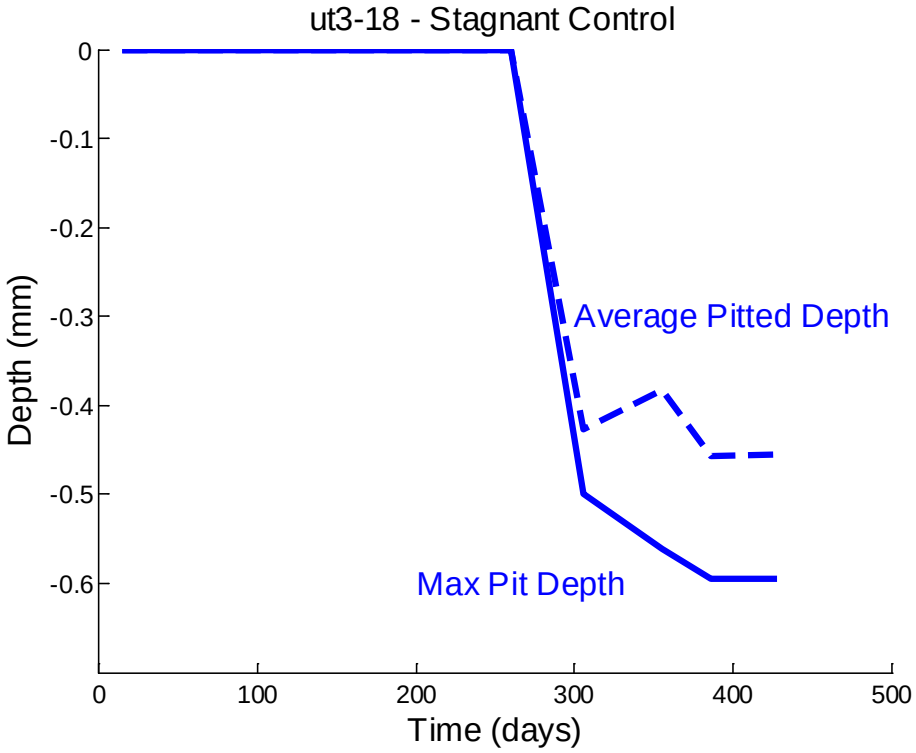


Figure 2-4. Maximum and average pitted depth for ut3-18.

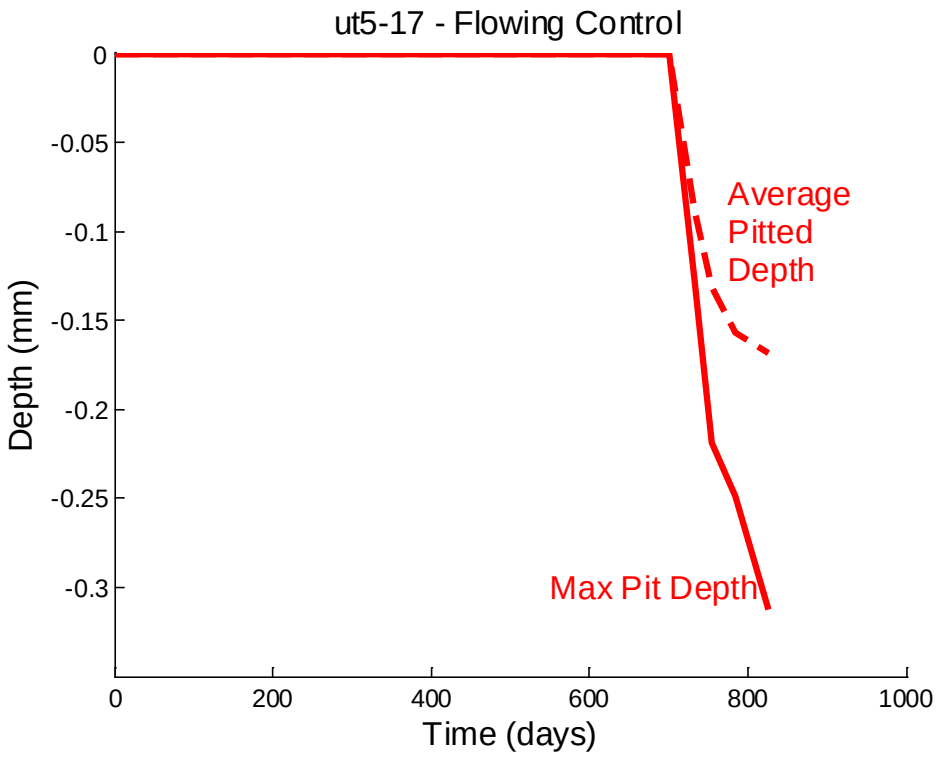


Figure 2-5. Maximum and average pitted depth for ut5-17.

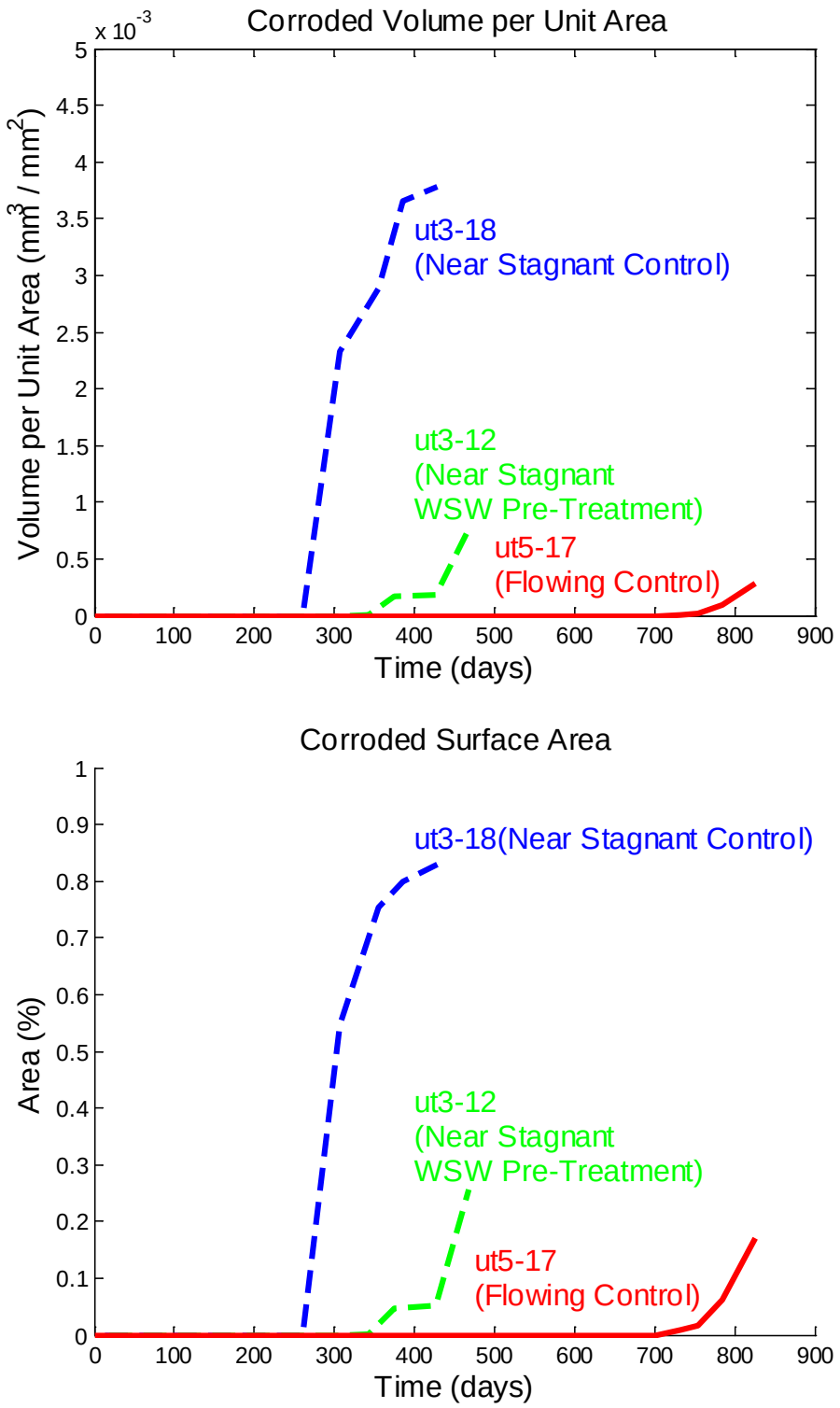
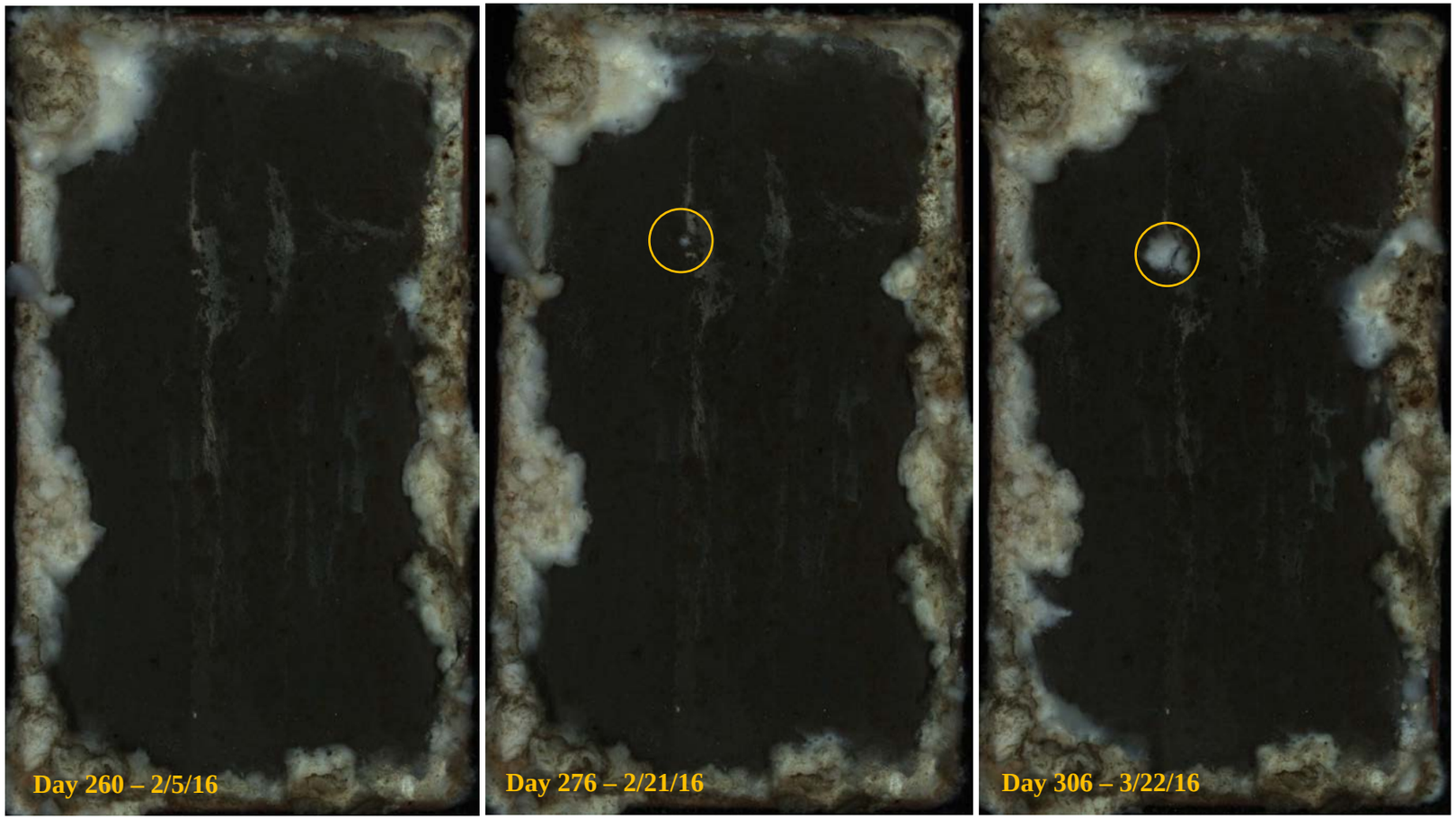


Figure 2-6. For comparison only, the total corroded volume per unit area and percent corroded area. Because the ultrasonic beam is wide, a correction factor was applied to area measurements. It appears that pitting in ut3-18 has plateaued while pits continue to expand and deepen on ut3-12 and ut5-17.


Day 260 – 2/5/16
Day 276 – 2/21/16
Day 306 – 3/22/16

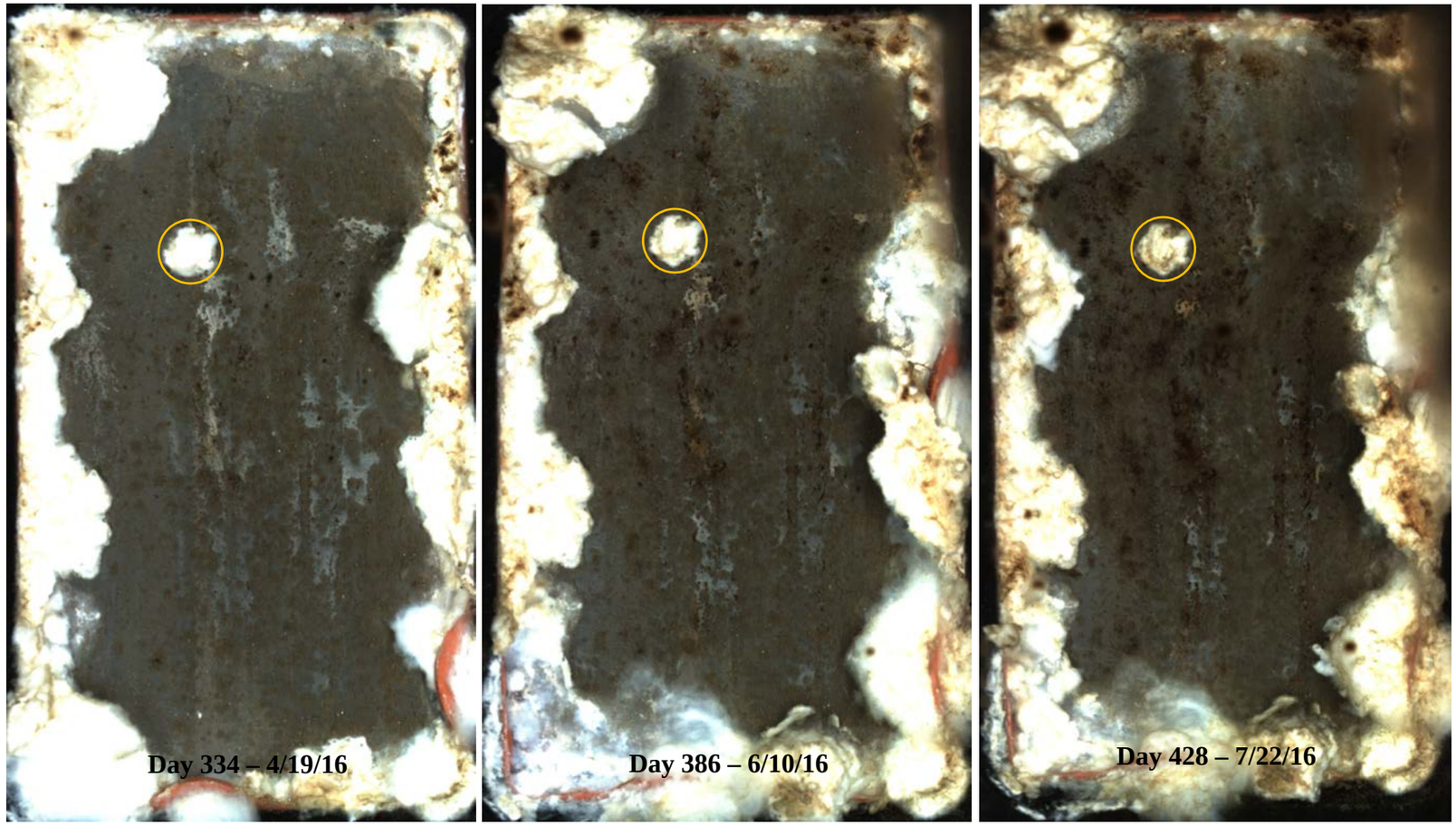
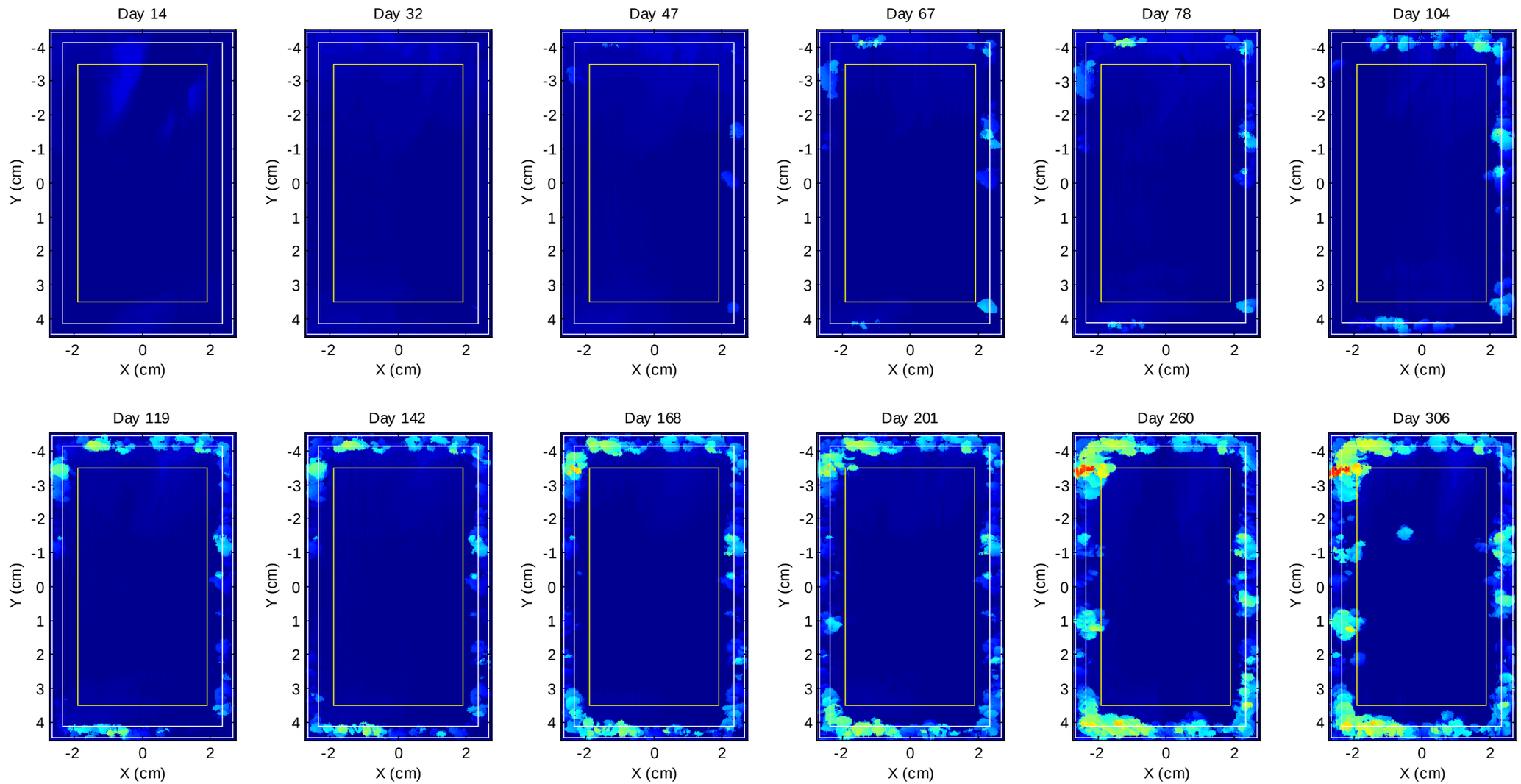


Figure 2-7. Pit development on ut3-18. Pit first identified on images on 2/20/16 (Day 275) and on the next ultrasonic scan (Day 306).


Day 14
Day 32
Day 47
Day 67
Day 78
Day 104
Day 119
Day 142
Day 168
Day 201
Day 260
Day 306
Y (cm)
X (cm)
-4
-3
-2
-1
0
1
2
3
4
-2
0
2

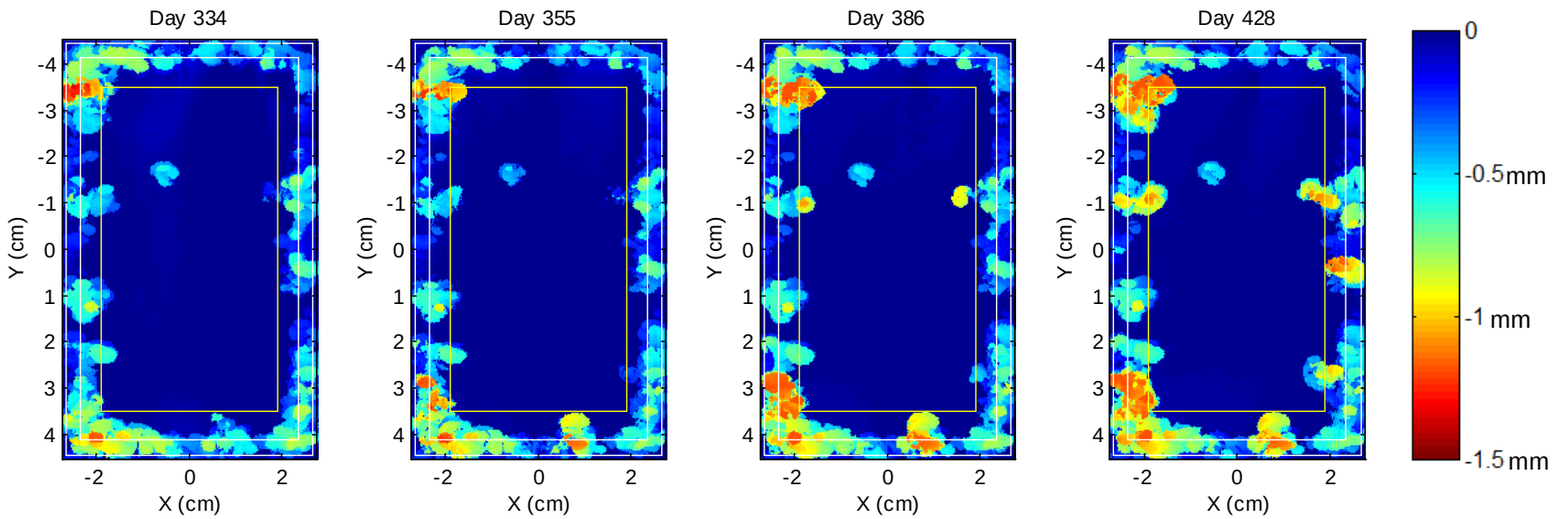


Figure 2-8. Ultrasonic scans of ut3-18. Pitting is first observed on Day 306. Crevice corrosion has encroached on the pitting window and was manually removed from the pitting statistics.

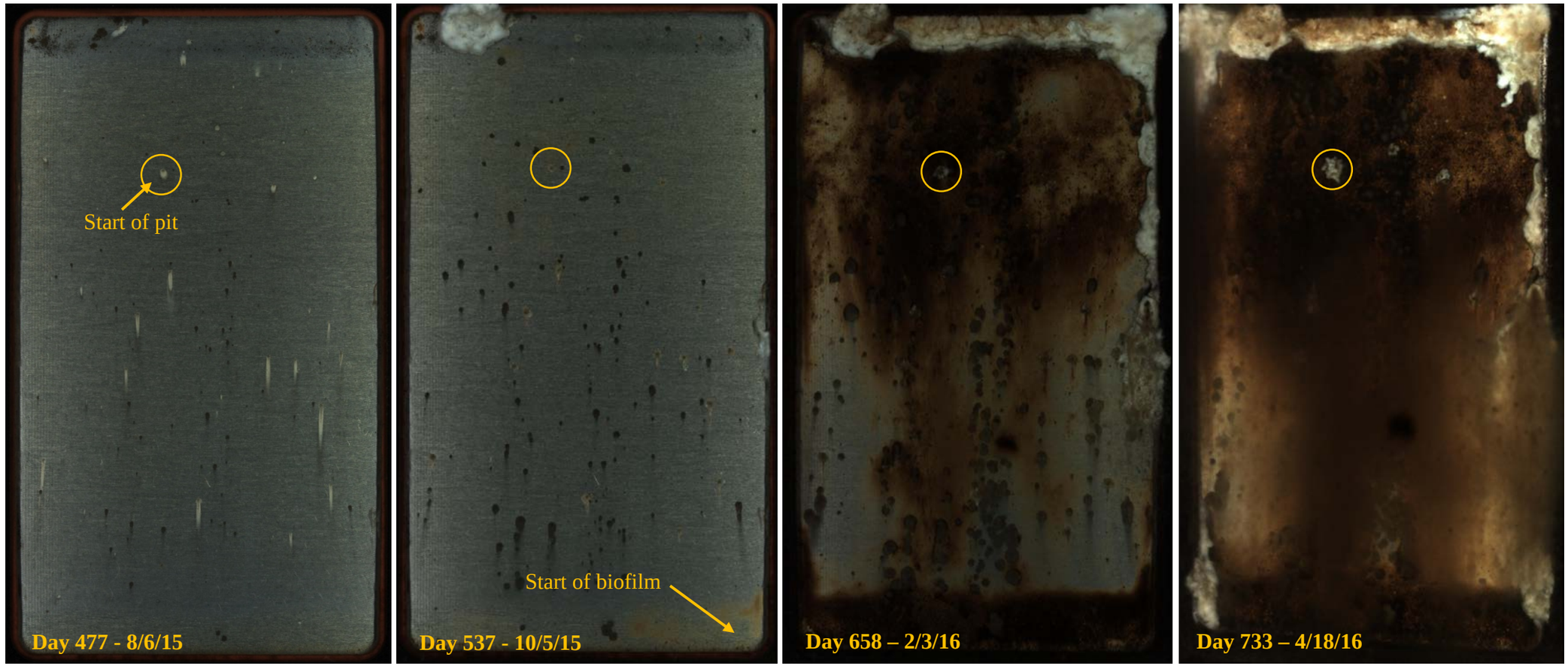


Figure 2-9. Pit and biofouling development on ut5-17. The circled pit is the pit was identified on ultrasonic scans at Day 733.

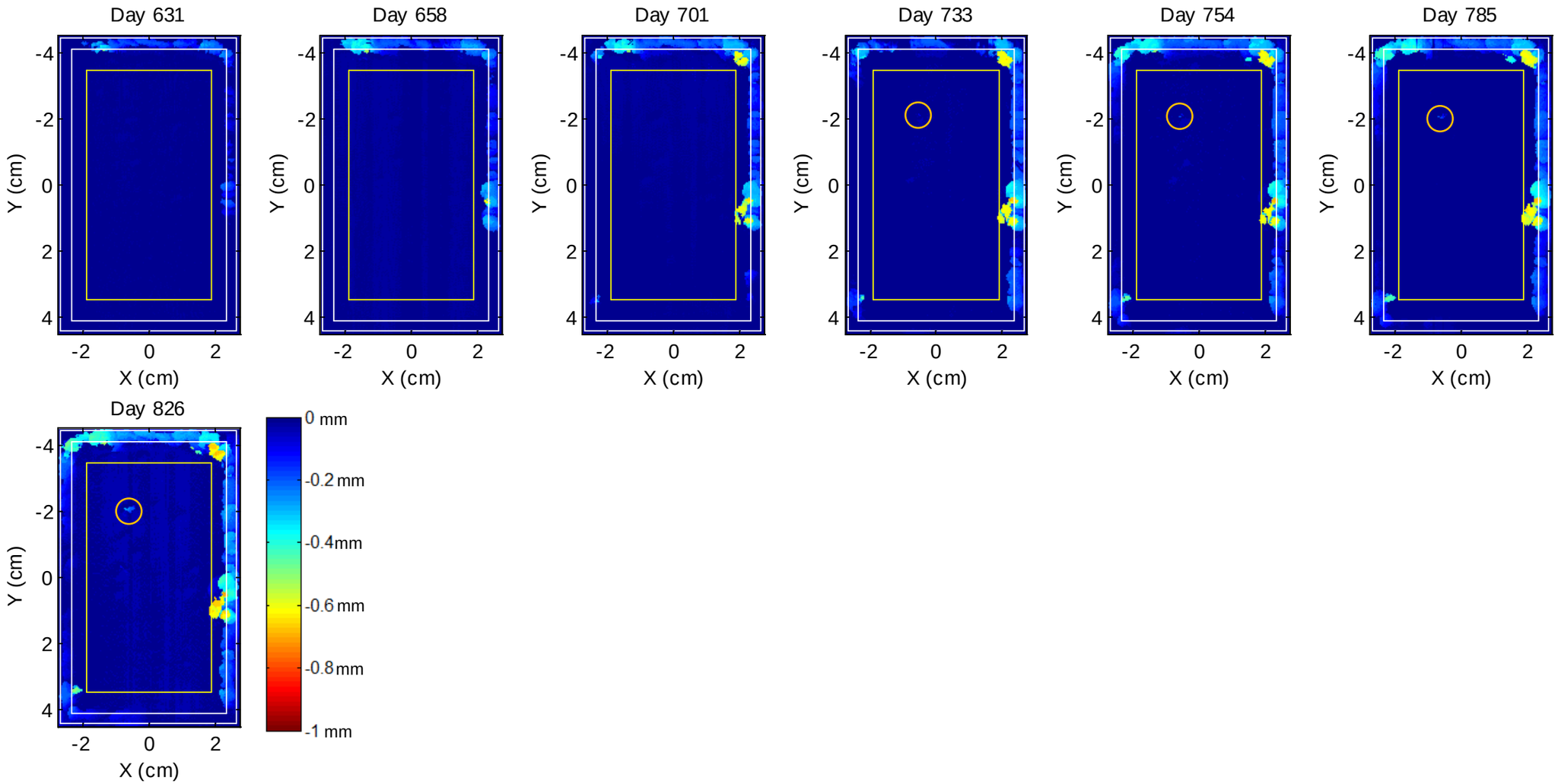


Figure 2-10. Ultrasonic scans of ut5-17. One pit is detected at Day 733. On the Day 754 scan, shadows of additional pits can be seen but they are less than 0.05 mm deep, below the pit identification threshold. Scan at Day 826 is noisy, so only one prominent pit is identified.

2.4. CREVICE CORROSION

Only 7 out of 24 samples do not have crevice corrosion. Except for Al 1100 in near stagnant seawater receiving daily hypo-chlorination treatment, samples with crevice corrosion identified in the images also have crevice corrosion identified in the ultrasonic scans.

Table 2. Crevice corrosion at the gasket interface. Lateral penetration is the distance from the inner edge of the gasket to the furthest extent of corrosion. The maximum corrosion depth underneath gasket is not necessarily in the same location as the maximum lateral penetration.

Water Flow	Treatment	Sample	Present on image?	Lateral Penetration [mm]	Maximum Depth under Gasket [mm]
Near Stagnant	Control	ut5-18	Yes	4.0[b]	0.5
		ut3-18	Yes	11.2	1.2
		ut1-18	Yes	7.0	1.0
Flowing	Control	ut5-1	No[a]	-	-
		ut3-17	Yes	7.5	1.2
		ut1-17	Yes	2.7	0.4
Near Stagnant	Hypochlorination	ut5-16	No	-	-
		ut3-16	No	-	-
		ut1-16	Yes	n.d.	n.d.
Flowing	Hypochlorination	ut5-15	No	-	-
		ut3-15	No	-	-
		ut1-15	Yes	2	0.3
Near Stagnant	Acid treatment	ut5-14	Yes	5.4	1.2
		ut3-14	Yes	6.7	1.3
		ut1-14	Yes	5.4	1.3
Flowing	Acid treatment	ut5-13	Yes	2.0	0.2
		ut3-13	Yes	7.2	1.2
		ut1-13	Yes	3.6	0.9
Near Stagnant	Warm seawater pre-treatment	ut5-12	No	-	-
		ut3-12	Yes	4.0	0.5
		ut1-12	Yes	4.4	0.8
Flowing	Warm seawater pre-treatment	ut5-11	No	2	0.1
		ut3-11	No	-	-
		ut1-11	No	-	-

n.d. = not detected on ultrasonic scans.

[a] For the same exposure time, no crevice corrosion or pits were detected on the Al 5086 control sample in flowing seawater. Crevice corrosion was detected on images after 477 days. [b] Crevice detectable to the limits of the scan.

Of the samples that received warm seawater pre-treatment, Al 5086 in near stagnant seawater, Al 1100 and 3003 in flow seawater do not have crevice corrosion. Al 5086 in flowing seawater has crevice corrosion identified on ultrasonic scans but not visible on images. Of the samples receiving daily hypo-chlorination treatment, only the Al 1100 samples (in flowing and near stagnant seawater) have crevice corrosion. All samples receiving acid treatment have crevice corrosion. All control samples have crevice corrosion, although, crevice corrosion did not occur on the Al 5086 until 477 days of total exposure. The Al 1100 and Al 3003 control samples in flowing seawater developed crevice corrosion before the Al 5086 sample.

2.5. ULTRASONIC SCANS AND IMAGES

The latest ultrasonic scan (middle panel) and associated image (left panel) for each sample is shown in Figures 2-11 through 2-18. The third panel in each figure is the image overlain with 0.1 mm contours from the ultrasonic scan.

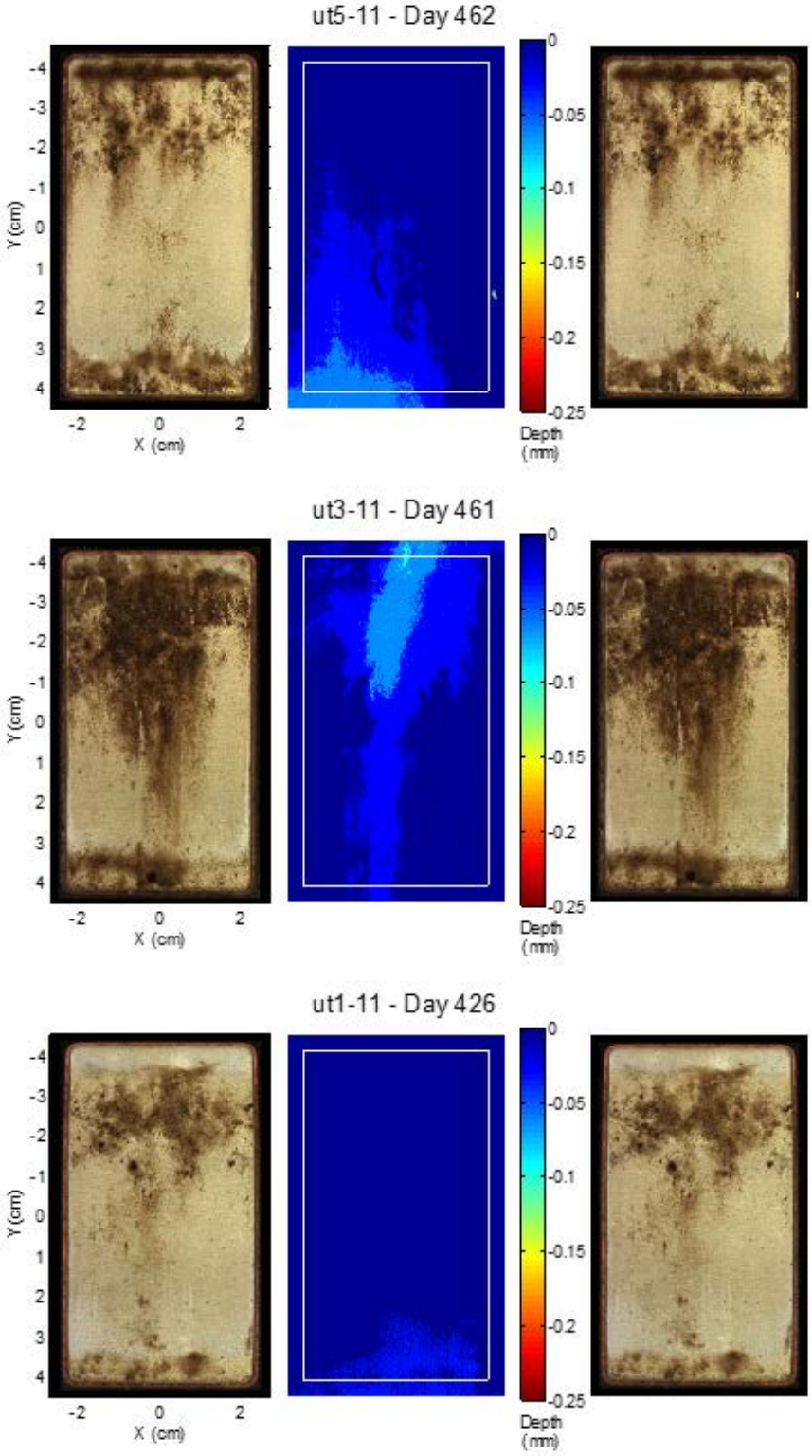


Figure 2-11. Warm seawater pre-treatment samples in flowing seawater. No corrosion features are observed in images but ut5-11 has crevice corrosion detected by ultrasonic scan.

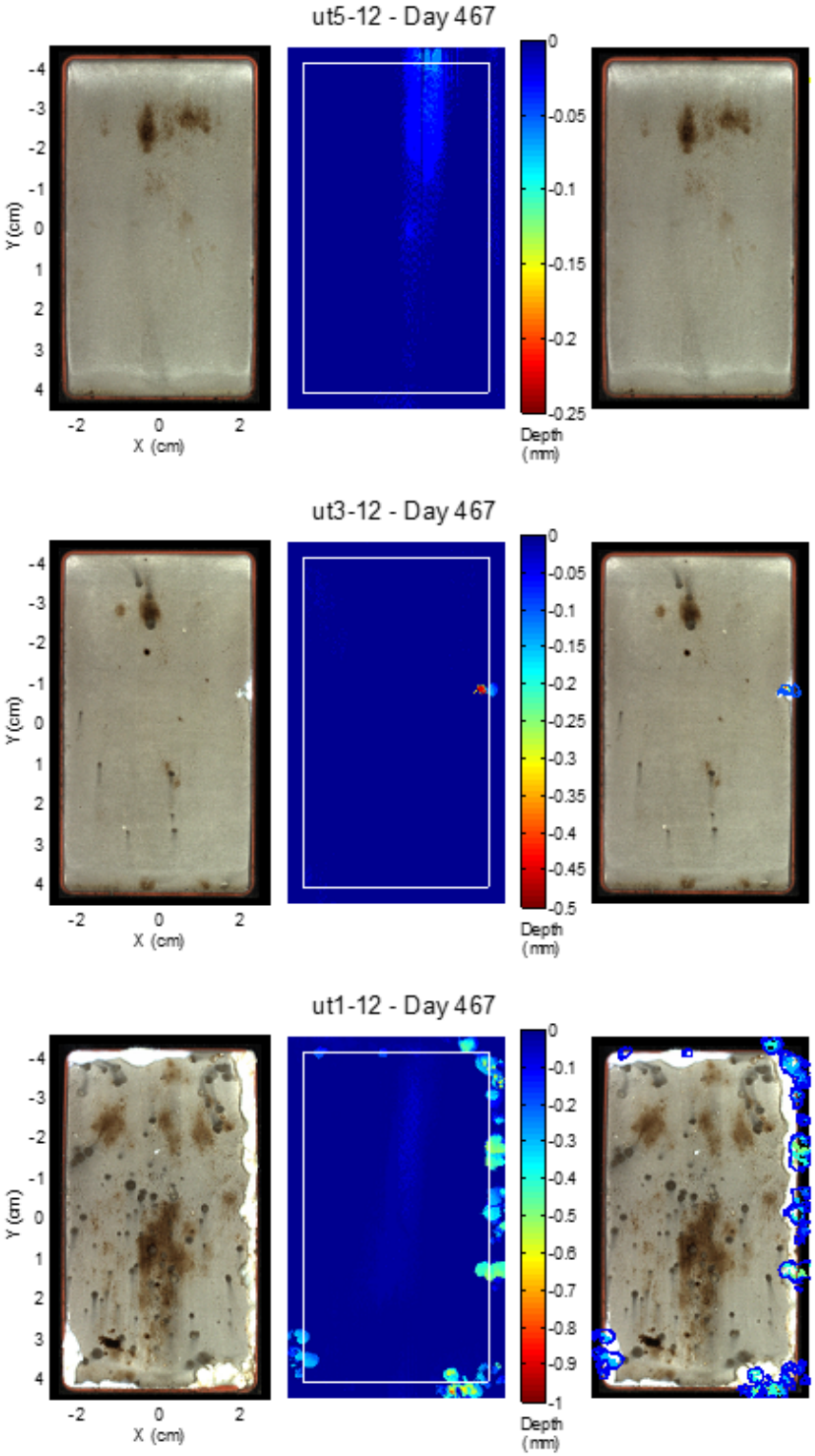


Figure 2-12. Warm seawater pre-treatment samples in near stagnant seawater. Crevice corrosion observed in images and ultrasonic scans on ut3-12 and ut1-12. A pit is visible on ut3-12.

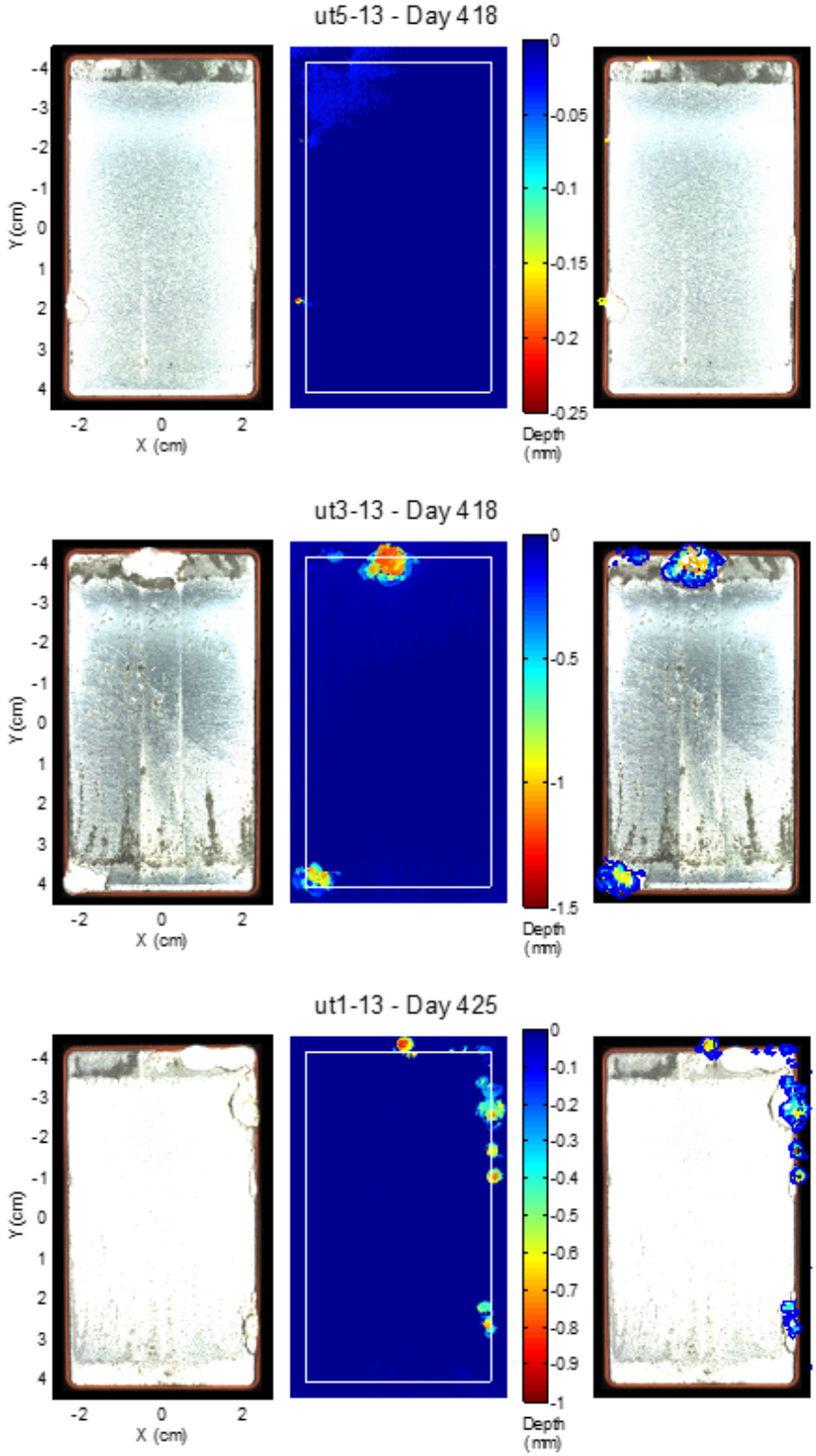


Figure 2-13. Acid treatment samples in flowing seawater. Crevice corrosion is visible in images and ultrasonic scans for all samples.

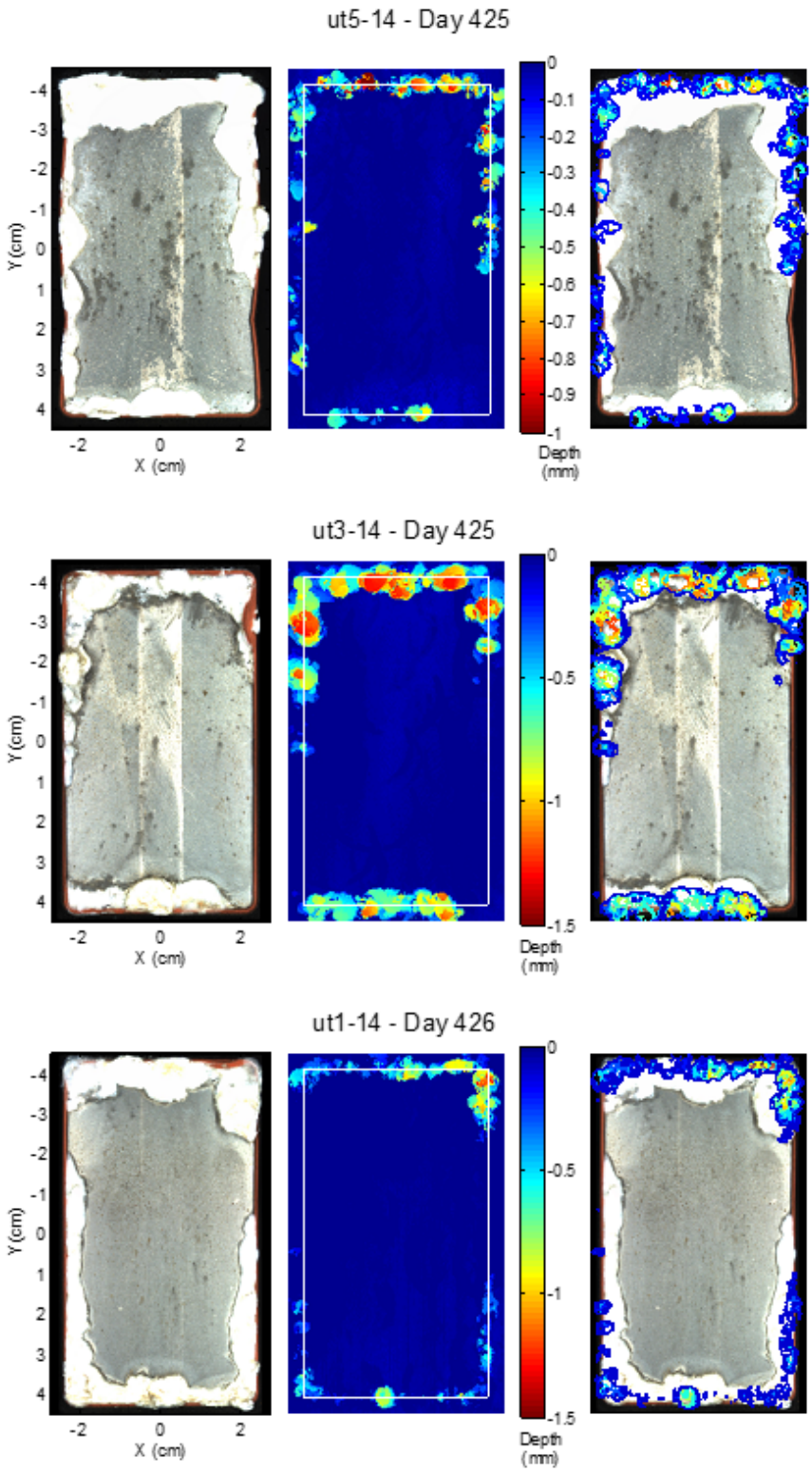


Figure 2-14. Acid treatment samples in near stagnant seawater. Crevice corrosion is severe and visible in imaging and ultrasonic scans for all samples.

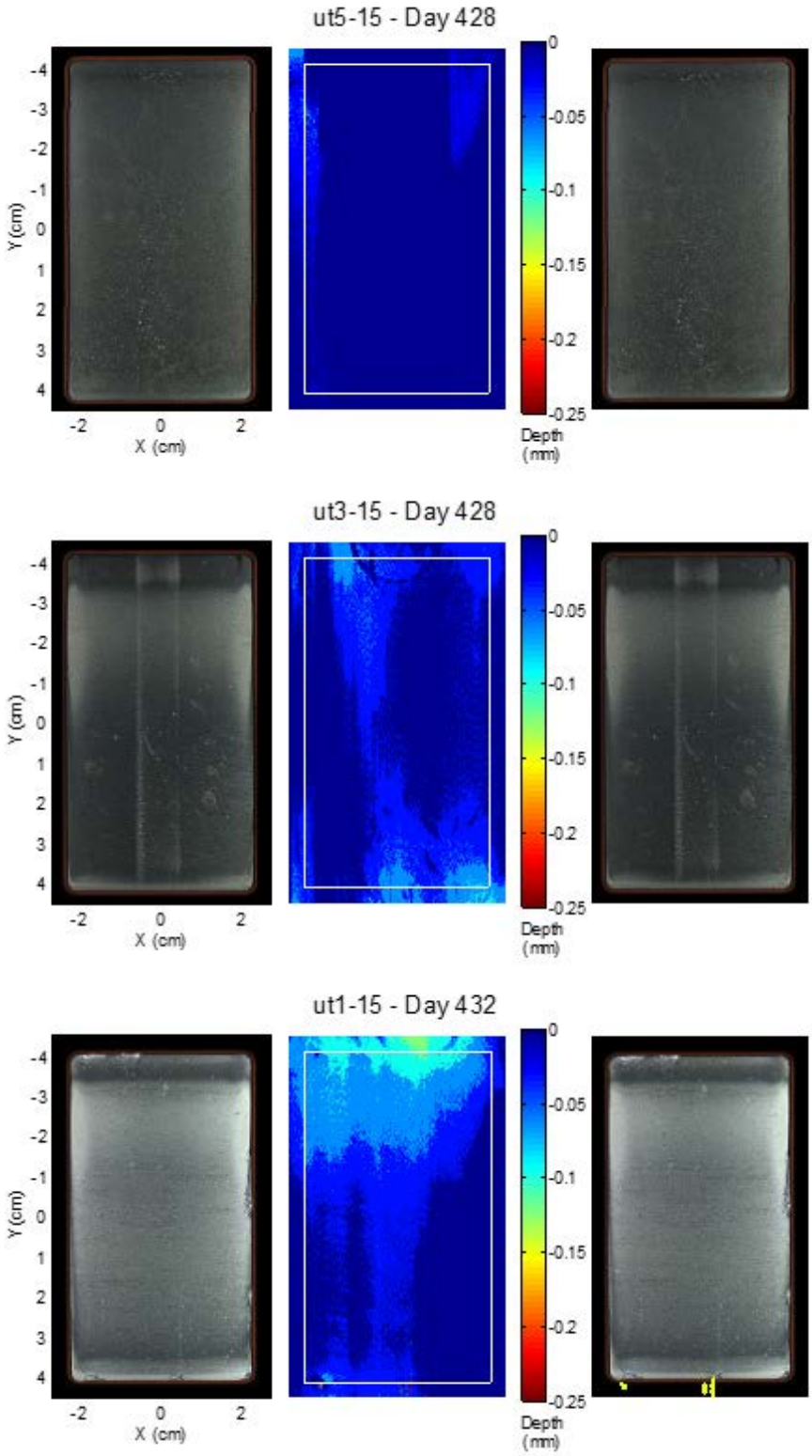


Figure 2-15. Hypo-chlorination treatment in flowing seawater. Crevice corrosion is visible in images and detected on the ultrasonic scan for ut1-15. ut3-15 and ut5-15 do not have observable corrosion features. Surfaces appear new and shiny.

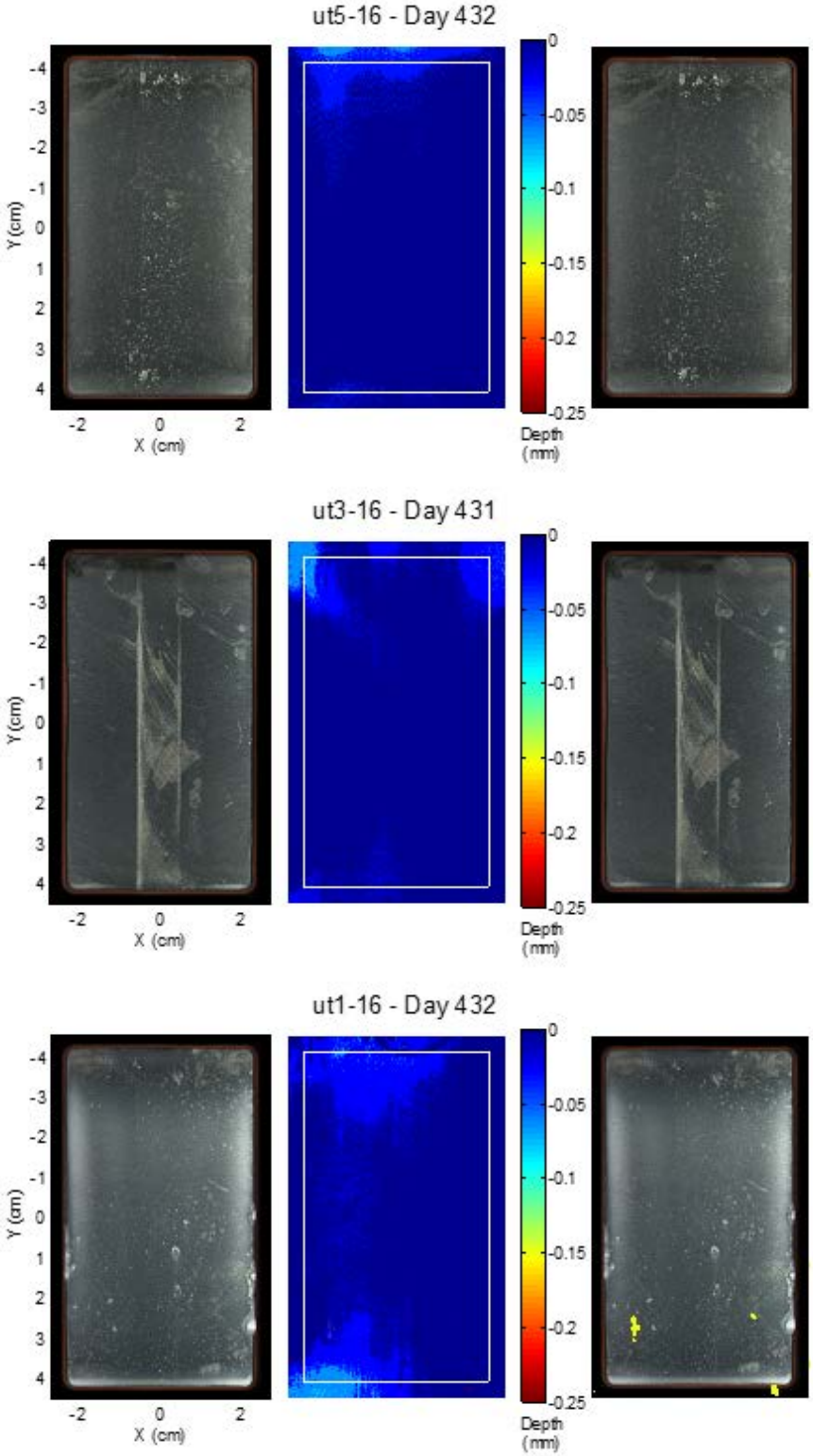


Figure 2-16. Hypo-chlorination samples in near stagnant seawater. The beginning of crevice corrosion is visible in images and on the ultrasonic scan for ut1-16. ut3-16 and ut5-16 do not have observable corrosion features.

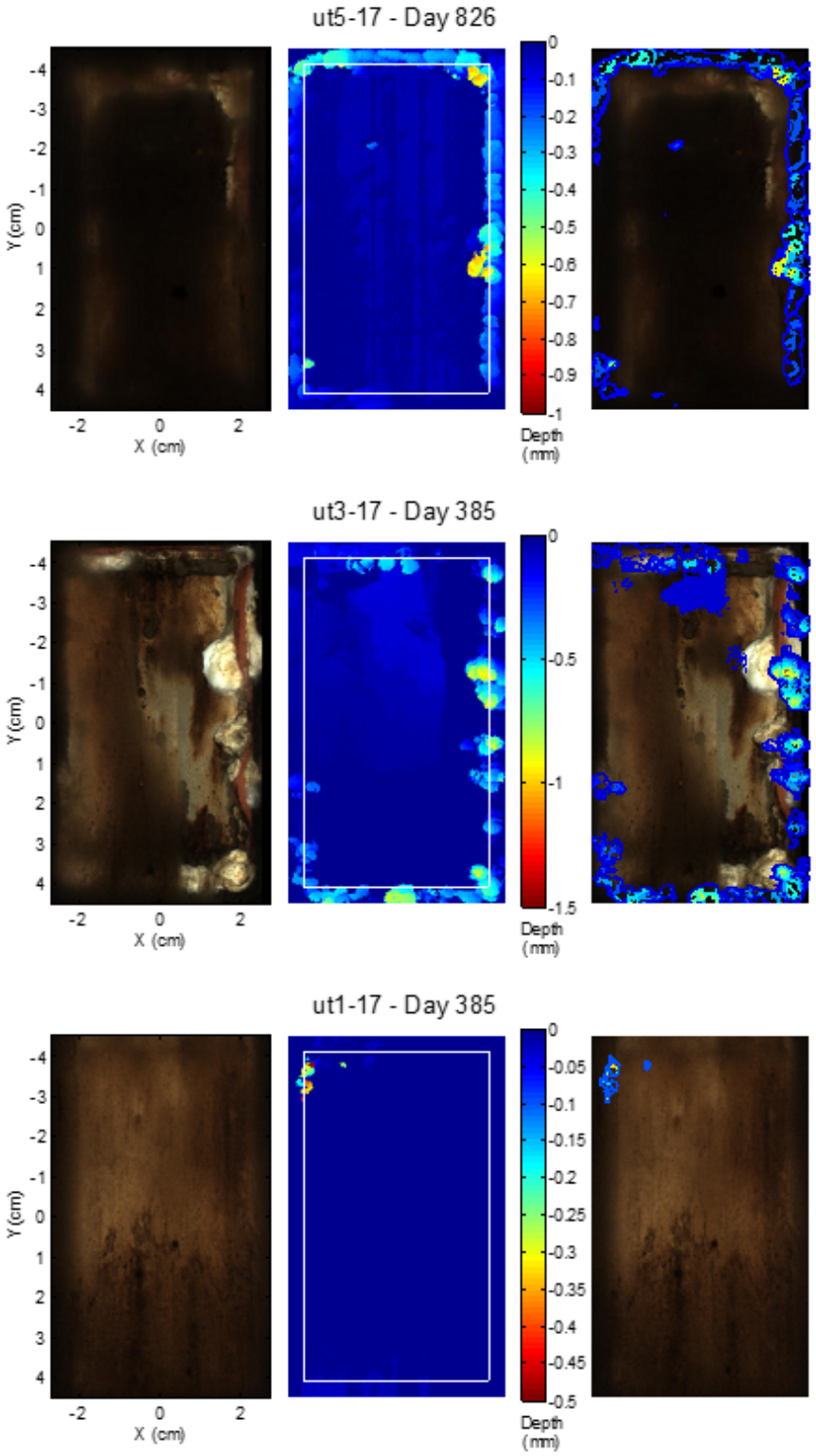


Figure 2-17. Control samples in flowing seawater. Sample surfaces and testing column window is severely biofouled. Crevice corrosion is most severe on ut3-17; the right side of the gasket is distorted from corrosion product. Three pits were visible on earlier images of ut5-17, but now obscured by biofilm. Only one pit is detected on ultrasonic scans.

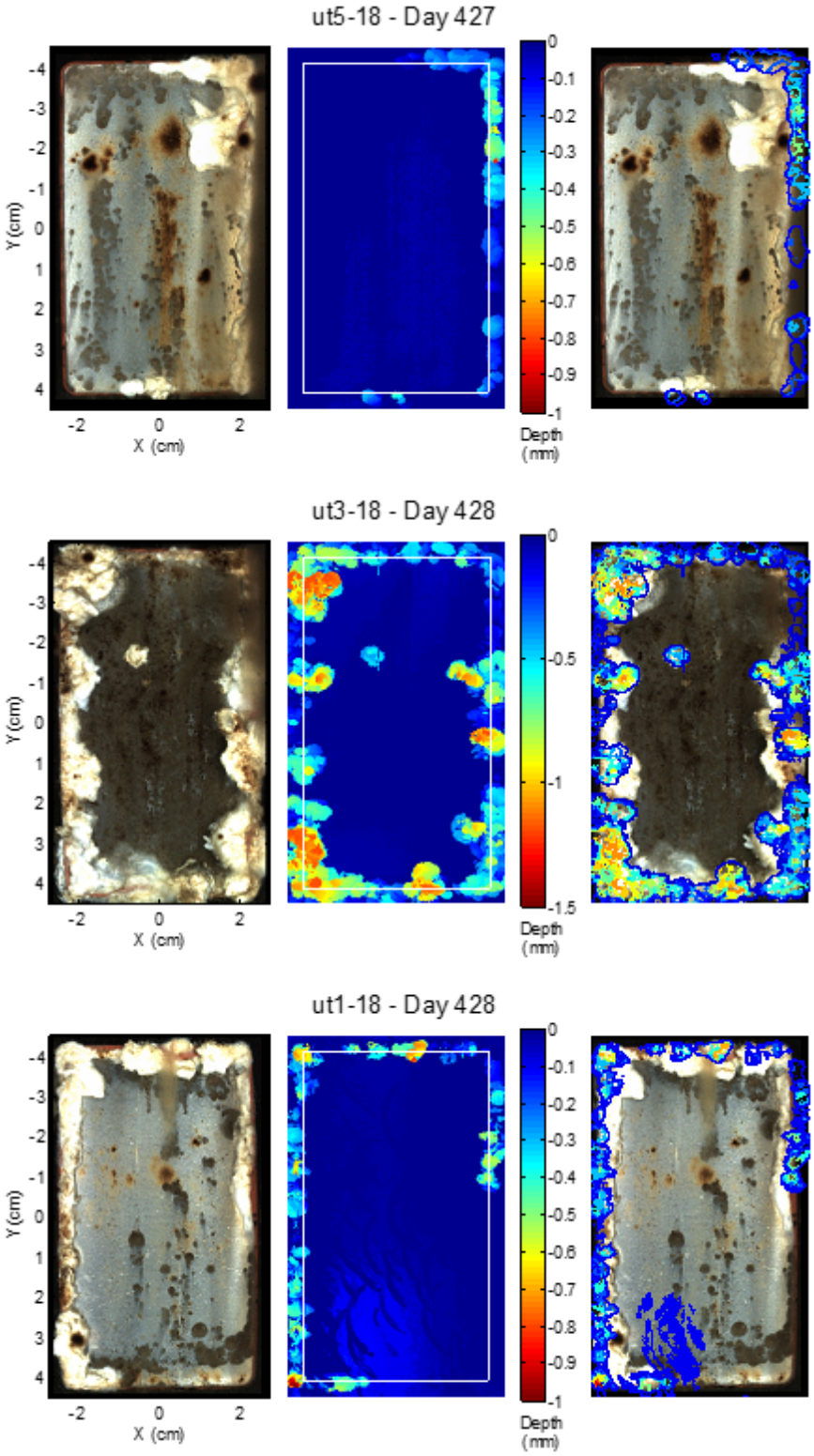


Figure 2-18. Control samples in flow near stagnant seawater. Crevice corrosion is observed on images and ultrasonic scans of all samples; corrosion (and biofouling) is most severe on ut3-18. There is a large pit on in the middle of ut3-18.

2.6. OPEN CIRCUIT POTENTIAL

2.1.1. Al 1100 Samples

For Al 1100 samples, only the warm seawater pre-treatment sample in flowing seawater has OCP outside the pitting region (< -700 mV). It is also the only sample without crevice corrosion or pitting. OCP of the remaining Al 1100 samples reached -700 mV within 15 days after exposure. Crevice corrosion developed rapidly, detectable on images within 20 days for most samples. OCP in the pitting region correlates with the presence of crevice corrosion. Contrary to previous reports, there are small changes in OCP that coincide with acid treatments. In flowing seawater, the sulfamic treatments lower OCP by 50 mV. In near stagnant seawater, acid treatments have resulted in larger and larger OCP changes. The most recent acid treatment lowered OCP by 75 mV.

2.1.2. Al 3003 Samples

For Al 3003 samples in flowing seawater, acid treatment, warm seawater pre-treatment, and control samples have comparable OCPs around -700 mV, whereas the hypo-chlorination sample has OCP around -850 mV. The warm seawater pre-treatment sample OCP was stable at -800 mV between 180 and 330 days in cold seawater but began to increase at 330 days. After 390 days in cold seawater, the OCP reached -700 mV, comparable to that of the control and acid treatment samples. The pit on the warm seawater pre-treatment sample was first observed on images after 241 days in cold seawater when it resembled a biofouling spot. In images after 390 days, the spot looks more like a pit than a biofouling spot.

In near stagnant seawater, control, acid treatment, and warm seawater pre-treatment samples have comparable OCPs around -700 mV and the hypo-chlorination sample has lower, albeit noisy, OCP around -800 mV. The warm seawater pre-treatment sample OCP was initially around -700mV, decreased to -800 mV after 100 days in cold seawater, began to increase after 150 days in cold seawater, and reached -700 mV after 196 days in cold seawater. The start of a pit was observed on images on the warm seawater pre-treatment sample on 12/31/15, after 199 days in cold seawater.

In both flowing and near stagnant seawater, acid treatments lowered OCP immediately after treatment but OCPs returned to higher values within 20 days post treatment. Crevice corrosion has been detected on all acid treatment and control samples. OCPs of the warm seawater pre-treatment, acid treatment, and control samples entered into the pitting region around the same time crevice corrosion/pitting was detected via imaging.

2.1.3. Al 5086 Samples

For Al 5086 samples in flowing seawater, acid treatment and warm seawater pre-treatment samples have OCPs in the pitting region; both samples have crevice corrosion. Crevice corrosion on the warm seawater pre-treatment sample was identified on ultrasonic scans but not in images. The control sample's OCP became noisy after 270 days, but no crevice

corrosion was identified until after 477 days. The hypo-chlorination sample remains around -900 mV; no pits or crevice corrosion have been identified and the sample surface looks shiny and new.

In near stagnant seawater, the acid treatment and control samples have OCPs in the pitting region. Crevice corrosion has been observed on both samples. For the control sample, crevice corrosion was observed in images after 46 days, 40 days before OCP reached the pitting region at 90 days. For the acid treatment sample, OCP was in the pitting region within 20 days after exposure. Crevice corrosion was observed in images after 30 days. Hypo-chlorination and warm seawater pre-treatment samples have OCPs at -900 mV and -800 mV, respectively, and both remain free of crevice corrosion and pitting.

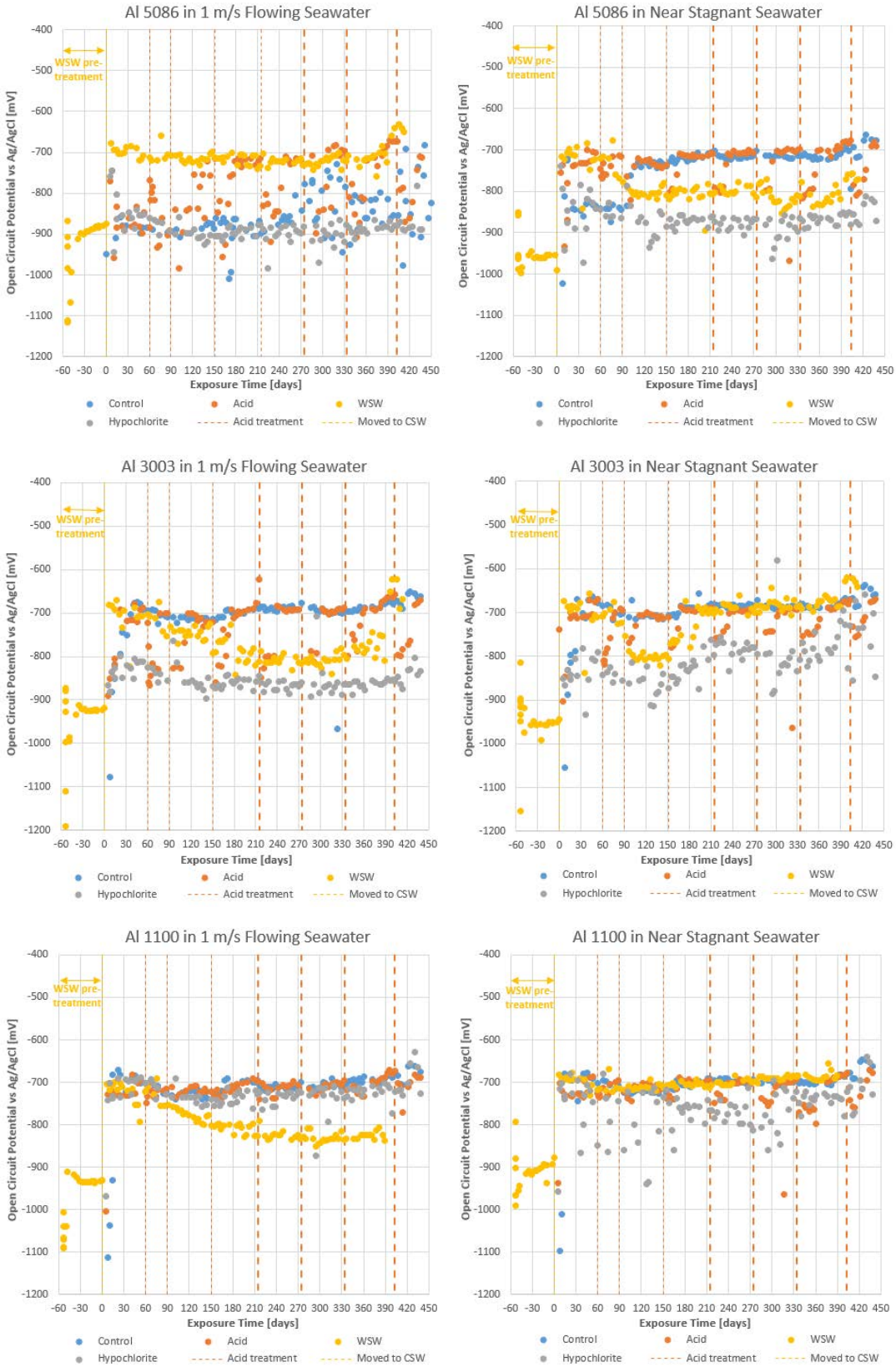


Figure 2-19. Comparison of treatment effects on open circuit potentials.

3. DISCUSSION

Crevice corrosion continues to expand and deepen. In general, crevice corrosion is more severe in near stagnant samples than in flowing seawater samples. Acid treated samples were also more susceptible to crevice corrosion than samples receiving hypo-chlorination or warm seawater pre-treatment. Warm seawater pre-treatment samples have recently been susceptible to crevice corrosion; the Al 5086 sample in flowing seawater has crevice corrosion detected by ultrasonic scan but not on images and the Al 1100 and 3003 samples in near stagnant seawater have crevice corrosion detected both on images and ultrasonic scans. Hypo-chlorination appears the most effective treatment for Al 3003 and Al 5086, neither flowing nor near stagnant samples have corrosion and the sample surfaces look new. Al 1100 sample surfaces also look new but crevice corrosion is present in both flowing and near stagnant seawater samples.

Pits have been observed on four samples: Al 5086 control in flowing seawater, both Al 3003 warm seawater pre-treatment samples, and Al 3003 near stagnant seawater control. For several other samples, crevice corrosion has encroached on the pit analysis window. These locations were not counted as pits in the analysis.

Biofouling on several sample surfaces has been severe, covering nearly the entire surface. Control samples in flowing seawater are the most severely fouled. Rust colored patches have attached to the viewing window and control samples' surfaces in flowing seawater (Figure 2-17). This type of biofouling is unlike the black spots typically observed in cold seawater; the biofouling is more like that observed in warm seawater. The warm seawater pre-treatment samples in flow seawater also have the rust colored coverage. The warm seawater pre-treatment and control samples in near stagnant seawater show the dark spots typically seen in cold seawater and the rust covered patches typically observed in warm seawater. Acid treatment samples are fouled with the dark spots/film seen in cold seawater; acid treatments have been able to remove the biofouling although the biofouling re-establishes prior to the next treatment.

A previous study performed by marine biologist Dale Sarver on biofouling on Makai's cold seawater box beam samples revealed no algal cells or multicellular organisms but large amounts of small motile bacteria. The bacteria excrete a sticky slime (extracellular polymeric substance – EPS) which promotes further colonization and traps other materials. The report concluded that since bacteria are present in deep seawater, the water supply itself is most likely the source of the biofouling, not necessarily contamination from surface seawater – although surface contamination cannot be ruled out. Additionally, sections of the white PVC pipe that supplies cold seawater lies unshielded above ground. It possible for colonies to attach and grow on the supply pipe interior surfaces.

OCP is most closely correlated to the onset of crevice corrosion for Al 3003. OCP changes were within days of pits and crevice corrosion being identified on images. For Al 1100 and Al 5086, OCP did not correspond as closely to the onset of localized corrosion but this could be due to lack of resolution – more frequent OCP measurements may have captured a change.

However, the current OCPs for Al 1100 and 5086 samples are indicative of the presence or absence of localized corrosion. The one Al 1100 and three Al 5086 samples without localized corrosion are the only samples to have OCPs not in the pitting region.

Cumulative findings of Makai's ongoing corrosion testing program are summarized in Table 3 (draft only, not for publication). Box coupon testing data was also used in the analysis presented in Table 3. One major limitation is that box coupon data collection is discrete and destructive. It is not possible to determine if observed pits were established and continued to deepen over time (as observed for Al 6061) or levelled off and remained at a stable depth (as for Al 2024) or if the observed pits or crevice corrosion could be traced back to a singular disturbance. Continuous, in situ monitoring, as in ultrasonic scanning and imaging, has been advantageous in studying corrosion development.

4. FUTURE WORK

Daily imaging and as-needed ultrasonic scanning will continue on the samples. Daily hypo-chlorination treatments will continue. Acid treatments will continue to be performed every two months.

Table 3. Cumulative findings corrosion suitability of bare aluminum alloys for use in OTEC heat exchangers.[1]

Alloy	Evaporator	Cumulative Test Exposure	Expected Life Cycle[2]	ANL 1980's Test Results	Condenser	Cumulative Test Exposure	Expected Life Cycle[2]	ANL 1980's 5-years Test Results
3003	Yes[3]	ongoing, ~6 years	at least 6 years	Yes	TBD[4]	ongoing, ~6 years	at least 6 years	Yes with caution
3003 (treated[6])	Not Tested	Not Tested	Not Tested	-	TBD[5]	ongoing, ~6 years	at least 6 years	-
5052	Yes[3]	ongoing, ~6 years	at least 6 years	Yes	TBD[4]	ongoing, ~6 years	at least 6 years	Yes
5052 (treated[6])	Not Tested	Not Tested	Not Tested	-	TBD[5]	ongoing, ~6 years	at least 6 years	-
6063-T5	Yes	ongoing, ~6 years	at least 6 years	Yes	No (pitting)	ongoing, ~6 years	Not suitable	Yes
6063 (treated[6])	Not Tested	Not Tested	Not Tested	-	No (pitting)	ongoing, ~6 years	Not suitable	-
6061	Not Tested	Not Tested	Not Tested	Not Tested	No	~1 year	Not suitable	Not Tested
5086	Not Tested	Not Tested	Not Tested	Not Tested	TBD	ongoing, ~1.5 years	TBD	Not Tested
5086 (treated[6])	Not Tested	Not Tested	Not Tested	Not Tested	TBD	ongoing, ~1.5 years	TBD	Not Tested
1100	Yes	ongoing, ~6 years	at least 6 years	Not Tested	No (pitting)	ongoing, ~6 years	Not suitable	Not Tested

1. These alloys are solely evaluated based on their corrosion and pitting characteristics as determined at Makai Ocean Engineering's Marine Corrosion Lab when coupons are exposed to flowing seawater (~ 1 m/s) ranging from 24 to 28 °C for evaporator uses and 6 to 7 °C (CSW from 674-m) for condenser uses. Alclad alloys are not acceptable for OTEC HXs.
2. Over 30-year life expect losses of TBD micrometers (Makai) in the evaporator and 200 micrometers (ANL) in the condenser.
3. Some pitting has been observed. Pits initially observed after 3 years, pit depths have not significantly increased in samples removed at 5 years. Maximum pit depth observed is ~ 0.75 mm (0.030").
4. Some pitting has been observed. Pits initially observed after 1.5 years, pit depths have not significantly increased in samples removed at 5 years. Maximum pit depth observed is ~ 0.125 mm (0.005").
5. Some pitting has been observed. Pits initially observed after 1 year, pit depths have not significantly increased in samples removed at 5 years. Maximum pit depth observed is ~ 0.2 mm (0.008").
6. Warm seawater pre-treatment is tested on Alloys 3003, 5052, 6063, and 5086. Acid treatment is tested on Al 5086 and Al 6063. Hypo-chlorination is tested on Al 5086.

Caveats:

1. To avoid pitting of braze joints in evaporators, silicon must be removed from surface by, for example, machining off the top layer.
2. Braze joints fabricated using commercial fluxes <u>are not acceptable in the condenser.</u>
3. Avoid stagnant water especially near gaskets.
4. Care must be taken during manufacturing to avoid defects such as extrusion lines or concentrated areas of cold work, e.g., during roller expansion.