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Corrosion Evaluation of Aluminum Alloys in Deionized Water

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ABSTRACT

Spent nuclear fuels from foreign and domestic research and test reactors are being returned to SRS are now stored with other nuclear materials in the L-basin at the Savannah River Site (SRS). Recent efforts have consolidated the fuel storage systems and L-basin has become the SRS site for water storage of spent nuclear fuels. Corrosion surveillance of coupons in this basin is being performed to provide assurance of safe storage of spent fuel [1-5]. This paper describes the highlights of recent studies on these aluminum coupons after immersion for more than 7 years in L-basin.

Selected coupons were metallurgically characterized to establish the existence of general corrosion and pitting. Pitting was observed on galvanically coupled samples and also on intentionally creviced coupons, thus demonstrating that localized concentration cells were formed during the exposure period. In these cases, the susceptibility to pitting was not attributed to aggressive basin water chemistry but to local conditions (crevices and galvanic coupling) that allowed the development of oxygen and/or metal ion concentration cells that produced locally aggressive waters. General corrosion was also observed on some of the coupons that had not been treated to enhance the protective oxide prior to exposure in the basin water. These observations demonstrate that, even when the basin water chemistry is rigorously controlled, localized aggressive conditions can develop. Although this demonstration does not suggest significant deterioration of the stored spent nuclear fuels, it does illustrate the potential for corrosion induced degradation and thus the importance of a routine surveillance program.

Keywords: aluminum, deionized water, galvanic corrosion, pitting corrosion, Al 1100, Al 6061, Al 6063, Savannah River Site, SRS, Savannah River National Laboratory, SRNL

INTRODUCTION

Aluminum-clad spent nuclear fuel is stored in a water filled basin at SRS waiting processing or other disposition. L-basin was chosen to receive domestic and FRR fuel due to its greater capacity and better physical condition than the other reactor basins. Corrosion induced-degradation of the spent nuclear fuels stored in L-basin could impact the storage process by causing cladding penetration, exposing fuel core material, and allowing corrosion of the fuel core materials and release of radionuclides to the basin waters. Such releases would lead to high water activity levels, and continued corrosion of the fuel assemblies could impact fuel integrity and present problems in

future fuel handling and transfer operations. Prior to 1995, a portable deionizer was rotated among all the reactor basins to control basin chemistry. In July of that year, a dedicated deionizer was installed in L-basin. By the end of October 1995, conductivity values decreased from an initial level of ~ 100 µS/cm to below 3 µS/cm. Concentrations of Cl^- and other aggressive species were also substantially reduced. As a result, surveillance data after this timeframe has indicated tat the fuel is not degradation. To ensure early detection, however, various aluminum coupons have been immersed in the L-basin at SRS to allow for a continuing surveillance program. This surveillance program permits evaluation of any corrosive effects on the aluminum alloys. Recently, aluminum coupons were pulled from this basin for routine evaluation. Exposed alloys included Al 1100, Al 5086, Al 6061, Al 6063 and 304 stainless steel. The characterization and evaluation of these corrosion coupons, along with the implications as to the condition of the resident fuel assemblies, is the subject of this study.

METHODS

Surveillance Program

Sets of standard corrosion coupons (7 cm and 3.2 cm diameter disks), including coupons representative of the aluminum cladding materials and storage rack materials used at SRS and in the research and test reactors, were placed in the SRS basins (Figure 1). Standard sets of coupons were developed as part of a cooperative assessment of basin corrosion and surveillance programs throughout the DOE complex. Immersion of the coupon sets was initiated in 1995. The surveillance coupons were not treated to increase the thickness of the protective oxide before being placed in the basins. The use of an air-formed film was thought to provide a surface that is more susceptible to corrosion than the irradiated fuel cladding because reactor operations enhanced the protective quality of the oxide film. The use of these non-irradiated coupons allows early detection of corrosion and provides the opportunity to associate that corrosion with changes in the basin water chemistry. Aluminum alloy coupons, including types 1100, 5086, 6061, and 6063 (see Figure 1) were used to represent various fuel cladding and furniture rack alloys. Welding was performed on some of the samples to represent welds expected (autogeneous on the corrosion coupons and R4043 aluminum rod on the furniture rack samples) in the fuel and rack alloys as fabricated. Water quality was maintained in the basins by deionization and conductivity and the level of aggressive species was routinely monitored during the period of time the coupons were immersed.

Coupon Evaluation

The corrosion surveillance samples experienced more than 7 years immersion in L-Basin water. The surveillance samples included furniture rack specimens (flat plates, 6061-T6, and "U" channels, 6063-T5 with R4043 welds), and circular disk coupons. Circular disk coupons (Figure 1) include individual alloys (with and without welds), galvanic couples between large 304 stainless steel (7 cm in diameter) disks and a smaller aluminum disks (3.2 cm in diameter), and crevice coupons. All coupons were electrically isolated from the support rod with a Teflon®[1] washer. The coupons were removed from the storage racks and examined for evidence of pitting, galvanic attack, crevice corrosion and/or general corrosion. Sample observations were compared to those removed from the basins in prior years. A new digital camera system was used in the present evaluation to provide a more detailed examination of the coupons in comparison to prior evaluations. Weight loss measurements used the final weights after withdrawal air drying and comparing it to the originally recorded sample weights prior to immersion.

After the initial examinations, selected samples were cleaned and prepared for metallographic examination. Selected galvanic coupons from 2003, representing the different aluminum alloys in contact with 304, were photographed and then cleaned in an ultrasonic cleaner with a 16N nitric acid solution in order to remove the oxide [6]. Periodically, the coupons were removed, examined, and weighed to ensure the oxide removal by not the removal of metal. Total immersion time was on the order of 90 minutes. Disc coupons and furniture rack coupons with heavy oxide buildup and/or indications of localized corrosion were selected for metallography. The metallographic examinations focused on determining the extent of metal loss to general corrosion and

[1] Teflon is a registered trademark of DuPont

characterizing local corrosion processes (galvanic, crevice and/or pitting corrosion). Pit depth measurements were performed in accordance with ASTM G46 [7] when pitting was observed.

RESULTS

Water Chemistry

The overall water quality in L-basin has been maintained well within operation standards as shown in Figure 2., where water pH and conductivity are shown as a function of time. Both conductivity and pH remained within specified operational limits (< 10 µS/cm and 5.5 – 8.5, respectively) throughout the evaluation period. This period corresponds to the time that the surveillance samples examined in this evaluation were stored in L-basin. However, Figure 3 shows the time dependence of the aggressive ion (Cl^-, Cu^+, and Hg^+) concentrations over the same period reveals that the Cl^- concentration was above target values on occasion.

Coupon Evaluation

Selected images of the individual 2003 surveillance coupons are shown in Figure 4. Overall, the primary corrosion mode was observed to be general uniform corrosion at extremely low rates. Percentage weight gains of approximately 1.2-1.4 % for each sample are graphed in Figure 5. The welded coupons gained slightly more than the non-welded coupons. One of the 1100 coupons did show a lower percentage weight gain, but in general these coupons appear visually comparable to coupons pulled in previous years from L-basin (see Figure 6.). The individual coupons from all three years appear to be undergoing uniform degradation.

The most appreciable oxide buildup observed is in galvanic couples, which is marked by heavy oxidation between the samples of dissimilar metals (see Figure 6 and Figure 7). Howell noted similar behavior in previous years [5]. The coupons from all three years appear similar. Selected galvanic coupons from 2003, representing the different aluminum alloys in contact with 304, were photographed and then cleaned in an ultrasonic cleaner with a 16N nitric acid solution for oxide removal [6]. The cleaned coupons are shown in Figure 8. and Figure 9. Pitting is visible in the areas beneath the Teflon® washer, the serrated Teflon® washer, and also on the mating surface between the aluminum alloy and 304 coupons. Galvanic cell corrosion is expected on the aluminum /stainless steel combination since aluminum is anodic to stainless steel. Although uniform corrosion is still prevalent in these specimens, pitting was also noted in many specimens, which was caused by a crevice condition between the Teflon® washer and the metal and also between the two metal coupons. A sketch of the coupon mounting arrangement is depicted in Figure 10, which shows the position of two coupons and washers. The location of coupon crevices is also shown in Figure 10. Normalized weight gains of only aluminum alloy couples are shown in Figure 11, which is due to oxidation from water immersion. The weights were normalized by dividing by the exposed area of the coupon. Prior to installation in L-basin, the samples, purchased with a 120 grit finish, displayed a uniform, clean surface with no oxidation. In all cases the smaller coupon (3.2 cm diameter) displayed more normalized weight gain than the larger coupon (7 cm diameter), regardless of the alloy combination. There are probably some ongoing galvanic effects, in addition to crevice corrosion, that caused higher corrosion levels on the smaller coupons.

Pit depths were measured on selected aluminum alloys that were either galvanically coupled with 304, were uncoupled, were mated face to face with another aluminum alloy, or were attached with a Teflon® crevice washer. The pit measurements are summarized in Figure 12.. Pit depth averages were greatest in the coupled 6063 coupon. It appears that end grain attack is present in the surface of the 6063 and it is suspected that the 6063 alloy coupon was cut from bar stock since the alloy is only available in that form per ASTM Specifications. All other coupons were fabricated from sheet materials in which the mating surface would not have end grain attack. Pit depth averages were high among the coupled coupons (6061, 6063, and 1100), ranging from 6 to 17 mils. Pit depth averages were low for the uncoupled coupons (5086, 6061, 6063), except for the 1100 coupon where the pit depth average was the second highest. A montage of an 1100 crevice coupon (cross-section) is shown in Figure 13, which reveals pitting in the areas beneath the Teflon® washer, and end grain attack on the ID of the coupon. The visible pitting is the result of a crevice formed between the washer and the coupon. End grain attack is

caused by preferential corrosion of grains exposed by cutting through a cross-section of a mechanically worked material.

The condition of the aluminum support rack coupons, both welded and non-welded, is shown in Figure 14. Corrosion is visible as the white oxide formation in the heat affected zone of the welds with no apparent differences between the long and short term exposures. The visual appearance does not indicate a substantial increase in degradation. Detailed examination of the welds and their heat affected zones reveal different oxide morphology in the root of the weld (Figure 15) versus the remainder of the coupon. The HAZ oxide is rod-like in shape versus the individual particles in the remaining oxide. Electron Dispersive Spectroscopy (EDS) revealed the presence of significant amount of Zn in the rod-like particles of the oxide layer. Repeated EDS on unexposed rack coupons did not show any presence of Zn. The ASTM Specification for alloys [9, 10] indicates that the Zn content is • 0.1% in R4043 and 6063 and • 0.25% in 6061. This is at or below the detectable levels for EDS. When the oxide was removed from the welded rack coupons, extensive, but shallow pitting was revealed. Further analysis is required to determine whether the source of the Zn as a result of trace impurities in the base metal or deposits from basin waters.

CONCLUSIONS

The results in the present study show that corrosion surveillance specimens exhibit uniform corrosion at low rates when conductivity and pH levels remained within specified operational limits (< 10 µS/cm and 5.5 – 8.5, respectively). This reinforces the current position that the present water chemistry controls are sufficiently conservative to mitigate corrosion in L-basin, with one exception. The onset of localized corrosion processes was observed in creviced and/or galvanically coupled corrosion coupons. The presence of this form of corrosion emphasizes the importance of adequate water chemistry control and an active surveillance program to ensure that the interim storage conditions in L-basin continue to inhibit corrosion induced degradation in the stored materials.

No significant difference in corrosion rate was observed among the aluminum alloy corrosion surveillance coupons (i.e., 1100, 6061 and 6063). Uniform surface corrosion was observed on most surveillance coupons and protective surface films are prevalent. However, in-depth cleaning did however (along with improved photographic technology) reveal pitting in the galvanic and crevice coupons. Although, not noted in previous years' inspections, pitting of this type would not be visible without this cleaning and evaluation (which was not done previously). Differences in pitting behavior were observed among the different aluminum alloy coupons. Coupons of alloy 5086 and 6061 revealed no pitting, but pitting was observed in the area below the insulating washer coupons of alloy 1100 and 6063. Pitting was also found beneath the oxide in weld metal of rack furniture specimens from alloy welded 6061 and 6063.

Path Forward

The continued annual withdrawal of Foreign Research Reactor (circular disk shaped) specimens, reporting and inspection is planned in conjunction with Corrosion Monitoring Program activities to demonstrate minimal corrosion in L-basin storage. Additional surveillance specimens, including zircaloy, aluminum alloys, and other metals, will be added to L-basin in order to enable inspection of cladding materials that are currently stored and those added in the future. Further analysis as to the nature and mechanism of corrosion in the heat affected zone of the welded rack furniture samples is planned in the future.

ACKNOWLEDGEMENTS

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Table 1. Composition of Surveillance Coupon Alloys

Aluminum Alloy Designation	Nominal Composition, %				
	Cu	Mn	Mg	Si	Other
1100	0.12				1.0 Max (Si + Fe)
R4043*	0.30 Max			4.5-6.0	0.80 Max Fe/0.10 Max Zn
5086		0.5	4.0	0.4 Max	0.5 Max Fe/0.15 Cr
6061	0.3		1.0	0.6	0.2 Cr/0.25 Max Zn
6063			0.7	0.4	0.35 Max Fe/0.10 Max Zn
8001	0.15 Max				0.6 Fe/1.2 Ni

* Welding rod for furniture rack samples

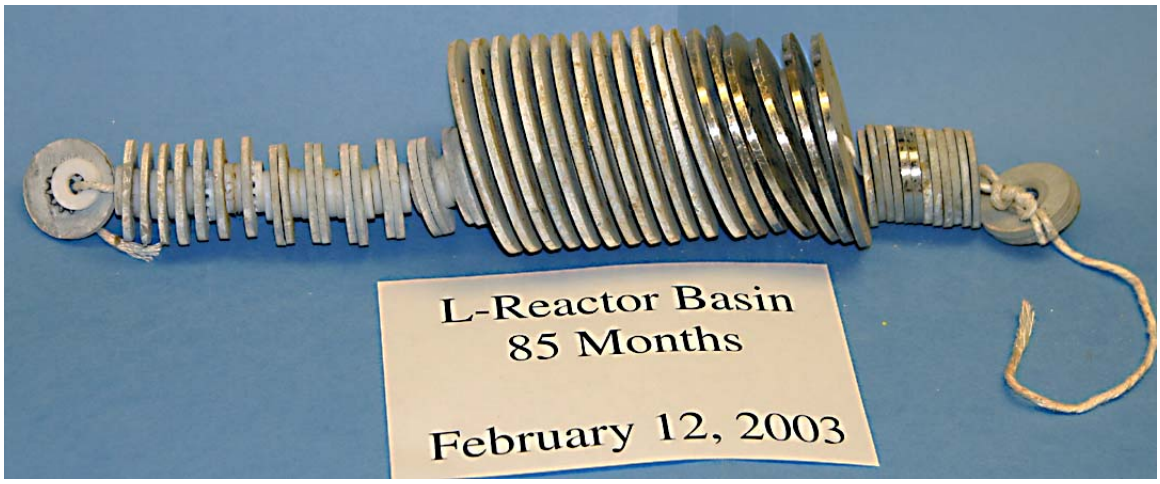


Figure 1. Original coupons are shown in received condition from L-basin.

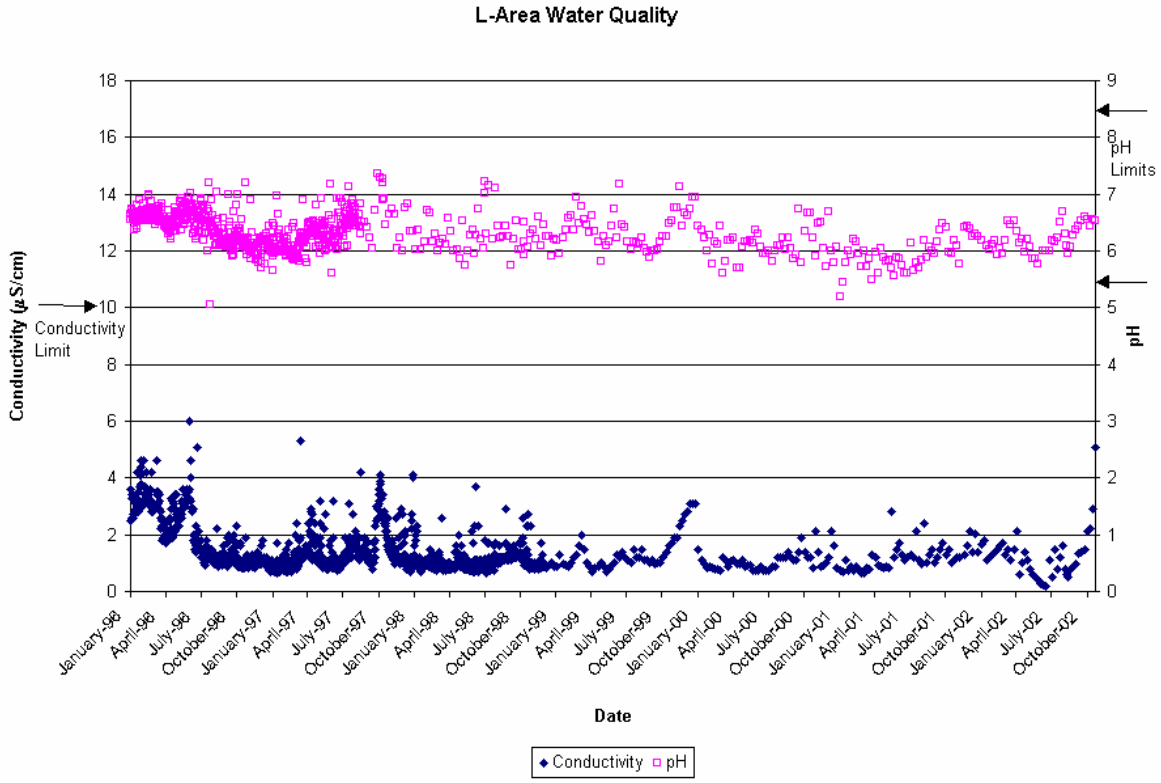


Figure 2. Time dependent water chemistry In L-basin during coupon immersion.

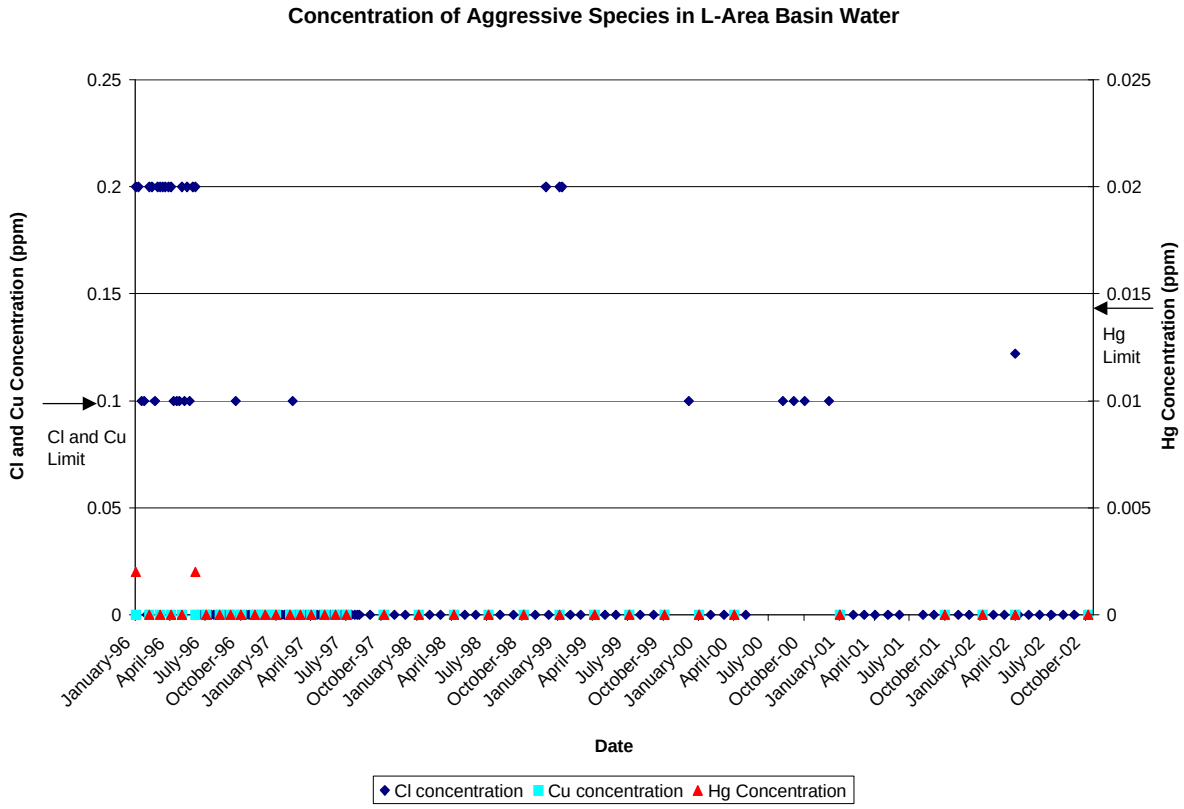


Figure 3. Time dependent concentration of aggressive species in L-basin water during coupon immersion.

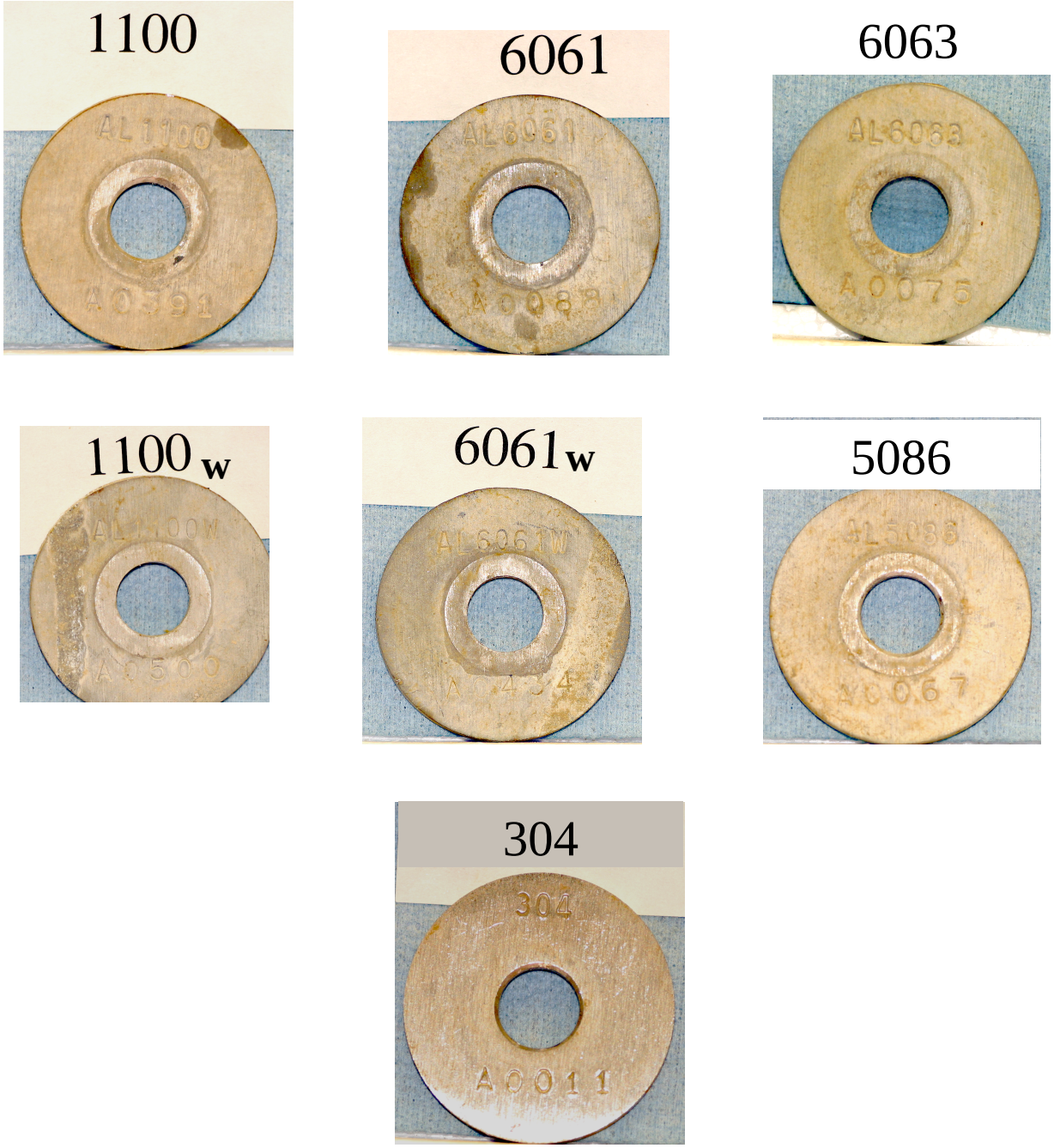


Figure 4. Examples of the individual coupons removed in 2003. Oxide scale in the TFE washer area is visible in all, except for the 304.

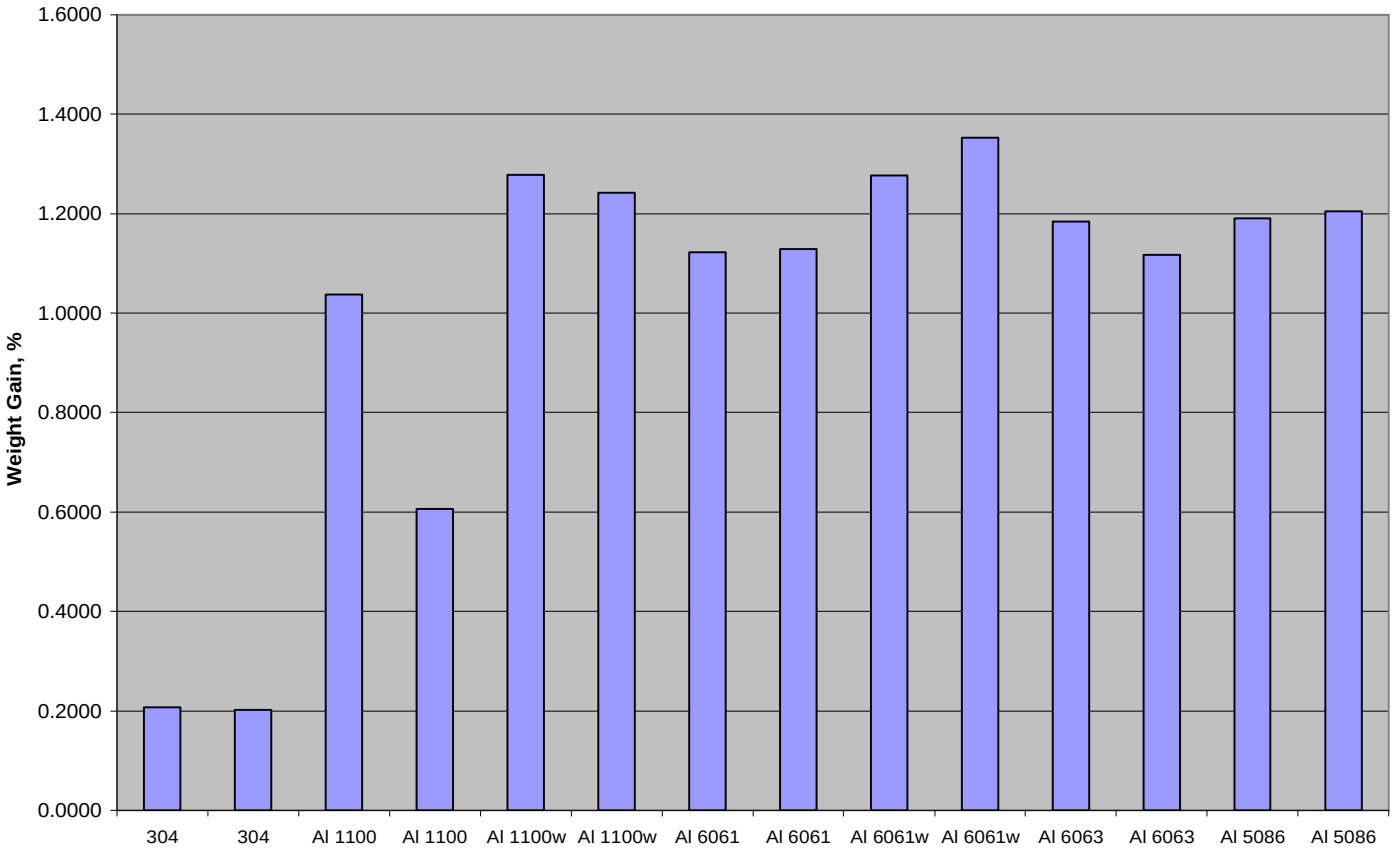


Figure 5. Percentage weight gains (weight gain divided by original weight x 100) from individual metal coupons after 85 months in L-basin. Note the welded samples (alloy designation plus "w") gained slightly more than their non-welded counterparts.

Figure 6. Individual coupons removed from L-basin in 2002 (top) compared to those removed in 2001 (bottom). Note: As in 2003, staining and general corrosion was visible on aluminum coupons at this level of inspection.

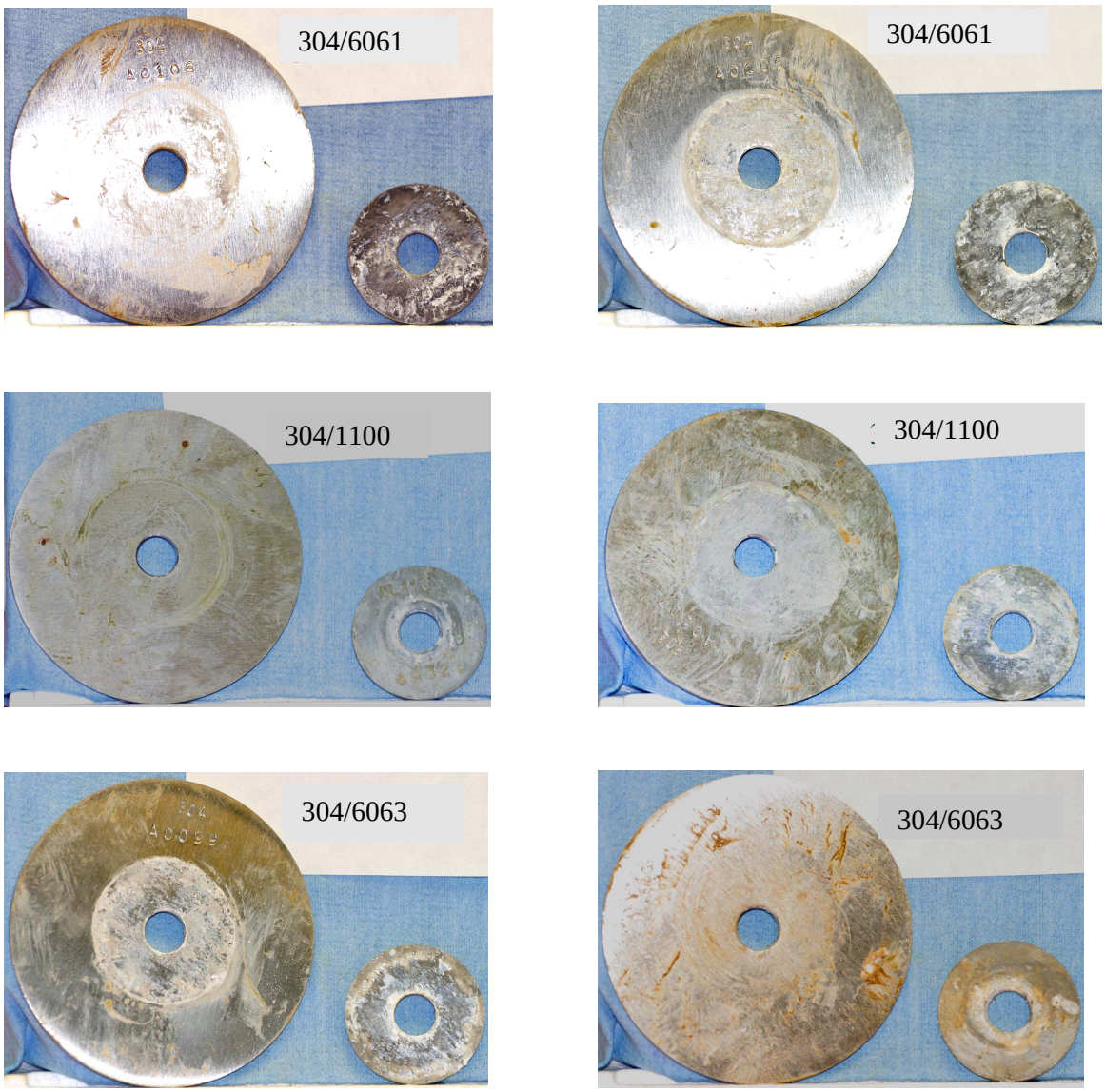


Figure 7. Mating surfaces of galvanic coupons removed in 2003. These surfaces are similar to those removed in prior years.

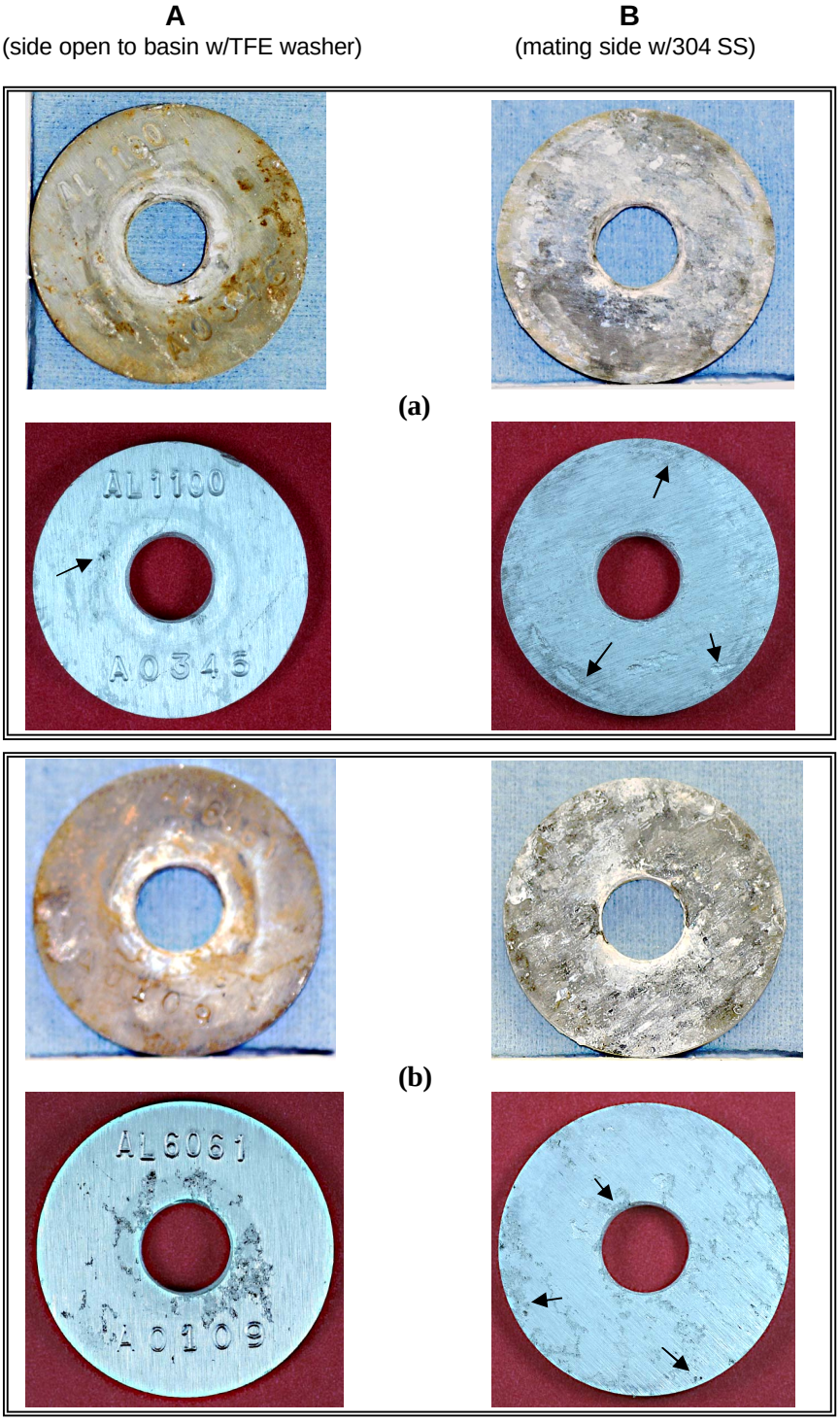


Figure 8. Before and after cleaning photos of aluminum galvanic coupons (1 ¼ inch OD) mated with larger (2 ¾ inch OD) 304 stainless steel coupons revealing pitting from galvanic and crevice effects. Upper coupon group (a) is 1100 aluminum. Lower group is 6061 aluminum. Pitting is located beneath the TFE washer in the "A" column images and on the perimeter, ID and face of the mating surface with 304 in "B" column images.

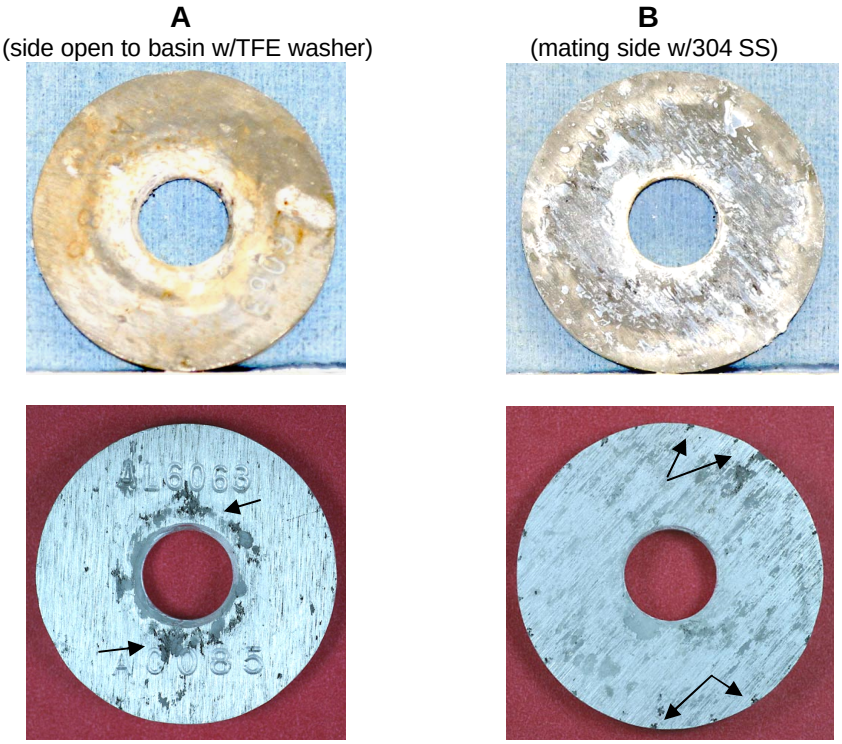


Figure 9. Aluminum 6063 coupon is shown before (upper) and after (lower) cleaning. Extensive pitting is visible in area that was beneath TFE washer (lower left photo) and on edges (lower right photo) where crevice existed and in contact with 304 stainless steel. Original coupon diameter is 3.2 cm.

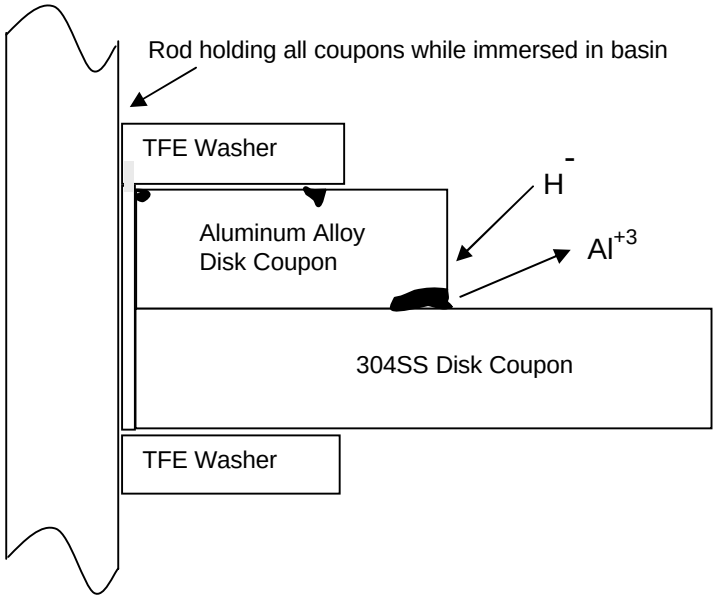


Figure 10. Crevices are formed when the coupons and the TFE insulating washer are mated closely together. A localized concentration cell is formed within the crevice with a lowering of pH at the anode (aluminum at interface) with subsequent corrosion. A current flow between the metal coupons may also be created since aluminum is anodic to the stainless steel.

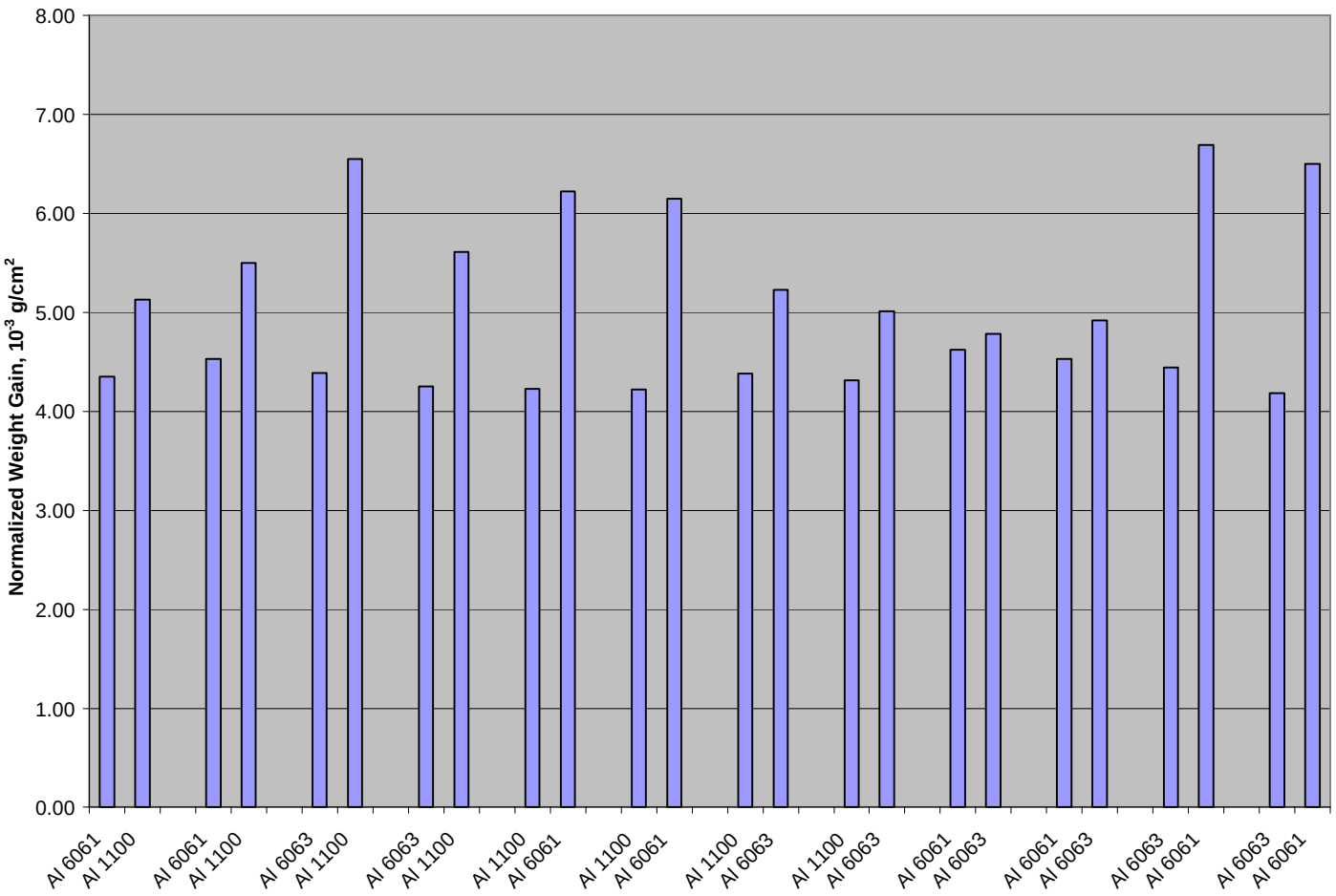


Figure 11. Normalized weight gains from galvanic coupons after 85 months in L-basin. Note the first alloy listed is the largest coupon (2.75 inch diameter). The weight gains were normalized by dividing by the exposed area of the coupon. In all cases, the smaller coupon displayed more weight gain than the larger coupon, regardless of the alloy.

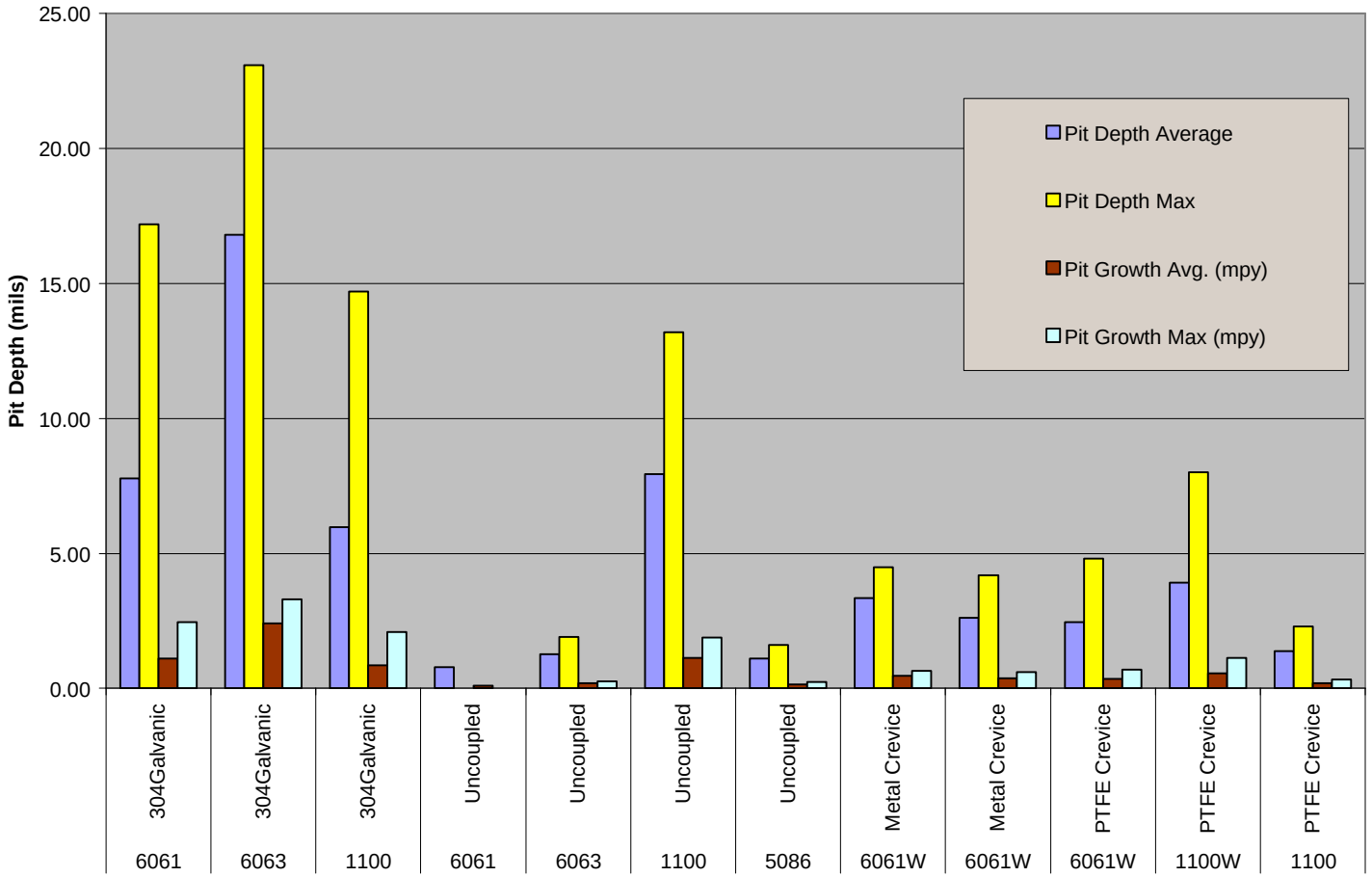


Figure 12. Pit depths as measured in selected aluminum alloys in galvanic couple with 304, uncoupled, and crevice conditions. The average and maximum pit depth and the pit growth rate were highest in the 6063/304 couple. As an individual coupon, 1100 revealed greater pit depths than the other three alloys.

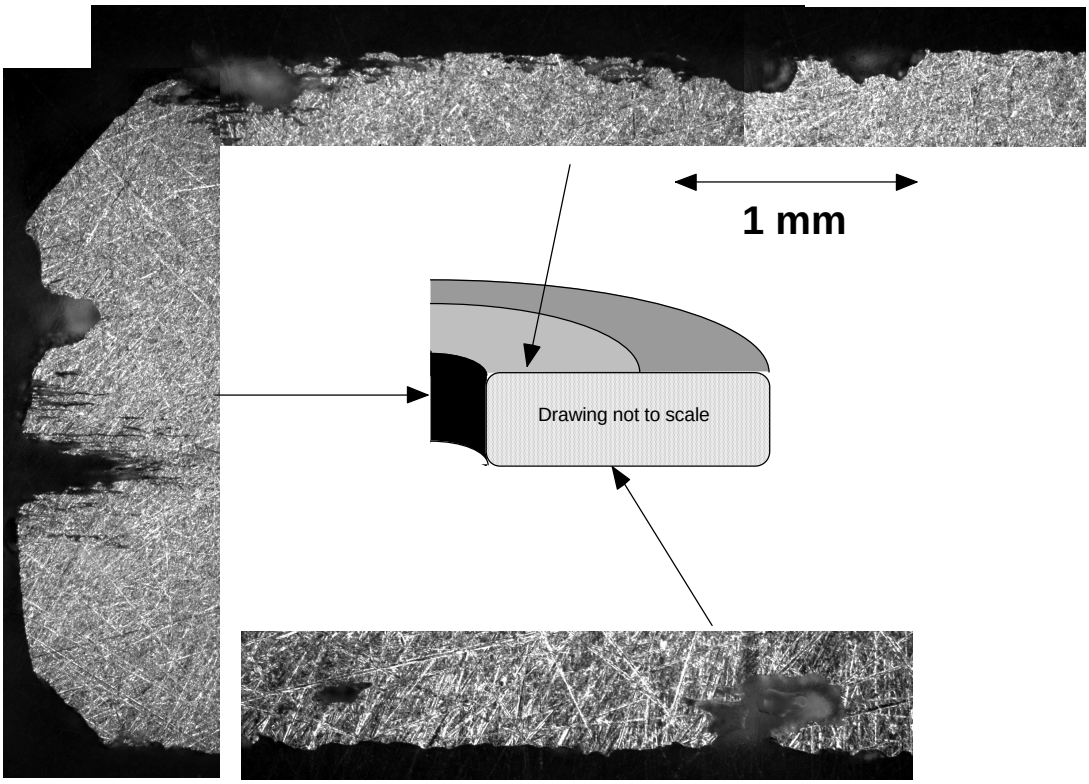


Figure 13. Cross-section montage of pits in 1100 aluminum crevice coupon showing end grain attack in left photo with crevice pitting in upper and lower photos.

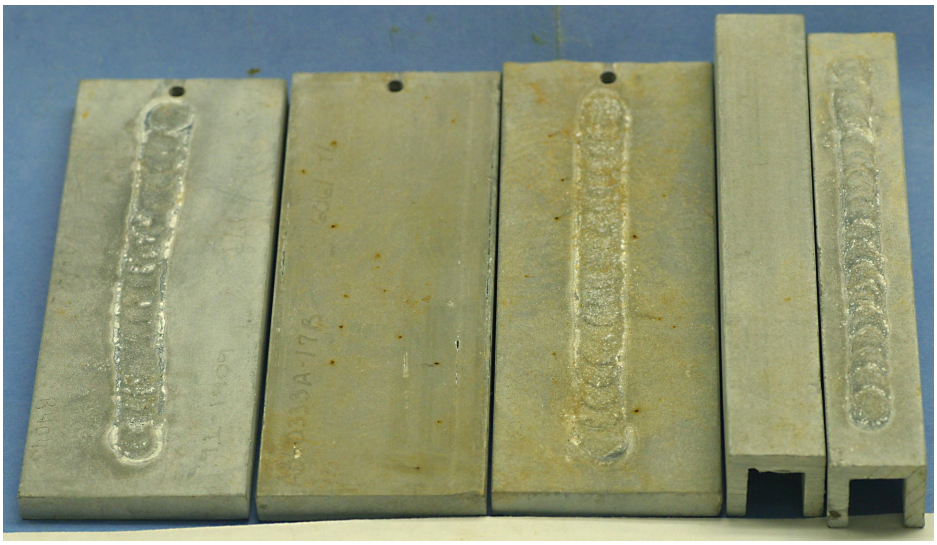
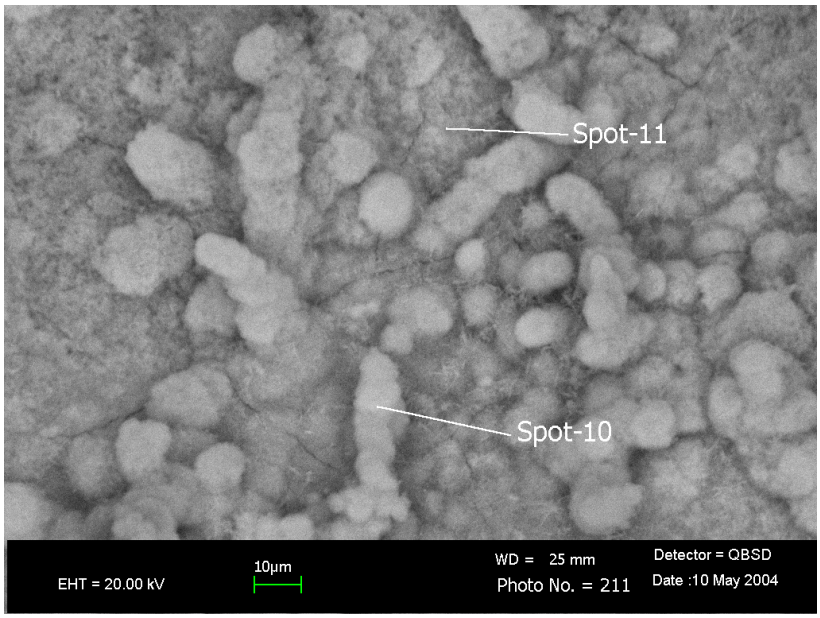
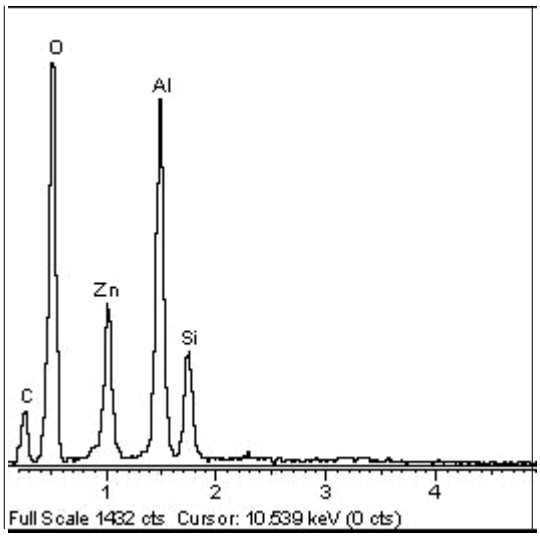


Figure 14. Aluminum rack furniture, with and without welds, removed from L-basin in February 12, 2003 after 85 months immersion. Corrosion is visible as the white oxide formation in the heat affected zone of the welds in addition to an oxide film on the sample surfaces. No differences were observed between shorter term immersions and the above samples. Plate coupons are 6061-T6 and "U" channel coupons are 6063-T5. Welding alloy is R4043.





Weld EDS Spot 10

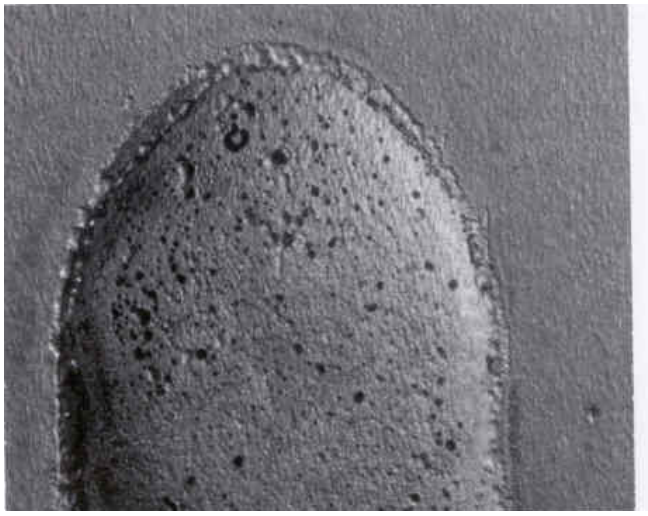


Figure 15. Micrograph of oxide at root of weld revealing rod-like morphology with accompanying electron dispersion spectroscopic analysis (EDS) showing high Zn levels in Al-Si weld metal. Spot 11 also exhibited high Zn levels. Micrograph on lower right shows pitting in surface of weld (~ 1.9 cm wide) with oxide removed.