

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied: 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or 2. representation that such use or results of such use would not infringe privately owned rights; or 3. endorsement or recommendation of any specifically identified commercial product, process, or service. Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Spent Nuclear Fuel Storage Basin Water Chemistry: Electrochemical Evaluation of Aluminum Corrosion

D.J. Hathcock, T.R. Murphy, P.R. Vormelker, and Steven Harris
Savannah River National Laboratory
Washington Savannah River Company
Aiken, SC 29808

R.W. Deible
Spent Fuel Operations Engineering
Washington Savannah River Company
Aiken, SC 29808

ABSTRACT

The factors affecting the optimal water chemistry of the Savannah River Site spent fuel storage basin must be determined in order to optimize facility efficiency, minimize fuel corrosion, and reduce overall environmental impact from long term spent nuclear fuel storage at the Savannah River Site. The Savannah River National Laboratory is using statistically designed experiments to study the effects of NO_3^- , SO_4^{2-} , and Cl^- concentrations on alloys commonly used not only as fuel cladding, but also as rack construction materials. The results of cyclic polarization pitting and corrosion experiments on samples of Al 6061 and 1100 alloys will be used to construct a predictive model of the basin corrosion and its dependence on the species in the basin. The basin chemistry model and corrosion will be discussed in terms of optimized water chemistry envelope and minimization of cladding corrosion.

INTRODUCTION

Spent nuclear fuel storage basin in L-Area provides a centralized wet storage area for Al-clad fuels at SRS. In order to preserve fuel and container integrity during long term storage the Corrosion Surveillance program was initiated to monitor the potential for fuel cladding corrosion in the basin. Groups of aluminum test coupons which simulate the alloys (1100 and 6061) and the geometries present

have been placed in the basin and are removed for examination on a regular basis. The coupons are configured such that the effects of galvanic coupling of Al and stainless steel, as well as the effects of crevice corrosion are monitored.^{1,2}

Key to the successful control of fuel corrosion in storage is effective control of the basin water quality and chemistry. During the late 1960s to mid 1990s the K, C, and P reactor basins used portable deionizer systems that helped with aggressive ion and activity removal, but were far less effective than the current permanent system installed in L basin. The permanent system was installed in Through previous work and operating experience at SRS storage basins it has been shown that the presence of aggressive species (i.e. chloride, nitrate, and sulfate), as well as high water conductivity, causes extensive fuel corrosion issues. In order to decrease the aggressive ion concentration and conductivity of the water a permanent deionizer system was installed in L-Basin. The current chemistry control limits are based on practical experience and data from several years of corrosion coupon evaluations. As shown in Figure 1 the operational limits on the concentrations of several species of interest, pH, activity, and conductivity of the basin have been monitored on a regular basis. These values are monitored on a regular basis and tracked to insure that basin conditions are optimum and that any anomalies are detected. The deionizer beds are not in continual service increases in conductivity, Cs-137, and pH occur during these periods; however even with the deionizer inactive for several months in a row the increased levels are still below the maximum allowable levels.

Water Parameter	Quality	Operating Limit	Monitoring Frequency
pH		5.5 to 8.5	Weekly
Conductivity		10 mS/cm	Weekly
Activity		Cs-137: 500 dpm/ml Alpha: 3 dpm/ml Tritium: 0.4 mCi/ml (8.88 x 10 ⁵ dpm/ml)	Weekly Monthly Biannual
Copper Concentration	(Cu)	0.1 ppm	Biannual
Mercury Concentration	(Hg)	0.014 ppm	Biannual
Chloride Concentration	(Cl)	0.1 ppm	Biannual
Iron (Fe) Concentration		1.0 ppm	Biannual
Aluminum Concentration	(Al)	1.0 ppm	Biannual
Temperature		40 C/ 104 F	Weekly

Figure 1 – Spent fuel basin water chemistry parameters

The effects of exposure to aggressive ion levels above those normally allowed in the basin were explored in order to map the water chemistry envelope for potential expansion of the water chemistry limits. Cyclic polarization testing was used to perform accelerated corrosion testing on coupons of 6061 and 1100 aluminum. E_{corr} was measured and used to evaluate the potential impact of the water chemistry on the pitting of the material.

EXPERIMENTAL

The test solutions were prepared using as received Na₂SO₄ (99+% ACS Reagent Grade), NaNO₃ (100%), NaCl (100%), and deionized water according to Table 1. The aluminum coupons were 1 cm² area 6061 and 1100 alloys compliant with ASTM B209-4. Testing was conducted in a standard PAR cell equipped with a condenser, salt bridge, thermometer, SCE reference electrode, Pt counter electrode, and bubbler. A connecting wire was attached to the back of the coupons using conductive silver epoxy. The samples were then mounted in CASTAMOUNT epoxy, polished to an 800 grit finish, and cleaned prior to use. The open circuit potential was monitored for stability prior to beginning the measurements. Cyclic polarization curves were acquired at 0.2 mV/s with an apex voltage of 1 V vs SCE in the solutions of interest.

A 54 run experiment (Table 1) was statistically designed to investigate the factors affecting the corrosion of spent fuel in basin storage. The experimental design was developed for a study of the impact of aqueous chemistry variables on susceptibility to localized corrosion, the primary degradation mechanism in basin storage of spent fuel. Samples of Al 6061 and 1100 alloys will be tested to measure corrosion and its dependence on species and species combinations present in the basin. Better understanding of the basin chemistry and corrosion dependence on the combinations of species present is expected to enable to safely expand the chemistry envelope (operating chemistry limits) and reduce filter-deionizer operations demands.

The statistical design for each alloy (Al 6061 and 1100) was based on a Space Filling Latin Hypercube (SFLH) inscribed in a full 2³ factorial design. The 2³ factorial provides for the testing of extreme processing conditions while the SFLH gives good coverage of the interior design region. In addition, 3 center points were replicated for each alloy. Generally, space filling designs have two criteria for the selection of experimental conditions. The first objective is to spread the design points out to the maximum distance possible between any two points while the second objective is to space the points uniformly. The SFLH is a compromise between the two criteria.

RESULTS & CONCLUSIONS

Cyclic polarization studies were performed on Al1100 and Al6061 coupons under the solution conditions outlined in Table 1. Results for 6061 and 1100 were obtained at the most aggressive chemistries in Table 1 and are shown in Figure 2 and Figure 3 respectively.

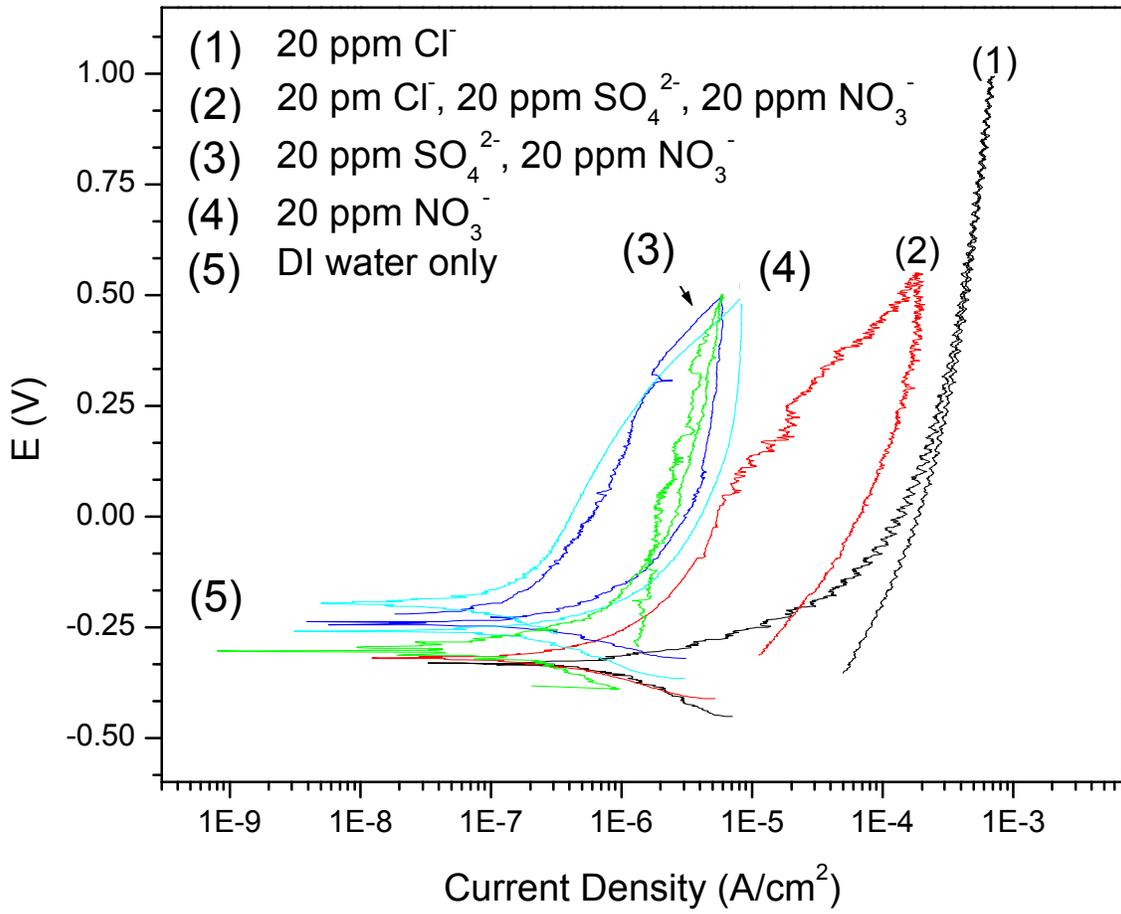


Figure 2- Cyclic polarization results from Al 1100 coupons in aggressive water chemistry.

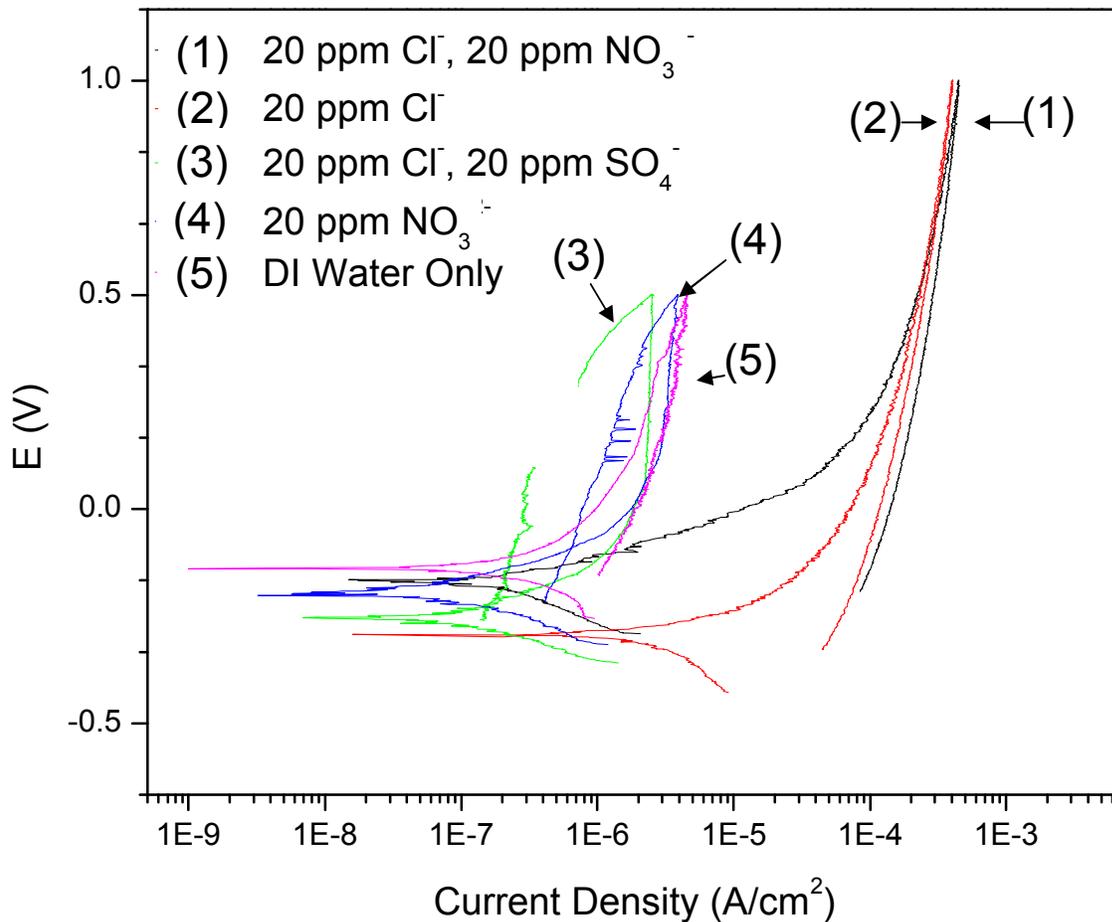


Figure 3- Cyclic polarization results from Al 6061 coupons in aggressive water chemistry.

In the more aggressive water chemistry conditions the E_{corr} for the Al 1100 coupons becomes more positive (Al becomes more noble) with the addition of nitrate and sulfate ions. The E_{corr} becomes most negative when the samples are tested in the chloride only solution. In the intermediate region containing all three ions at high concentration the current density shows a large shift while the E_{corr} only becomes slightly more positive. Post-test metallography has shown surface pitting on the chloride only sample as well as solution containing all three ions, consistent with the high E_{corr} value of -0.319 V for the three ion sample and -0.333 V for the chloride only sample. The shift of the E_{corr} value to more positive potential with the addition of nitrate is consistent with the possibility of nitrate acting as an inhibitor for 1100 corrosion under the experimental conditions. Nitrate is known to be reduced by metallic Al and not the oxide surface. Foley et al³ postulated that the nitrate ion could compete with chloride for defect sites in the passive film. The nitrate then blocks the incorporation of the chloride into the oxide film thus preventing its dissolution at the point of attack.

In the case of Al 6061 the range of E_{corr} values is much broader than found for 1100 in the same solution chemistries. This is likely caused by the increased concentration of impurities in the 6061 alloys vs 1100 alloys. The E_{corr} values tracked with the same general trend as in the 1100 polarization experiments with

the most negative value being the chloride only solution at -0.291 V. The addition of nitrate also increases E_{corr} to -0.161 V thus possibly acting to inhibit the corrosion in the same manner as before, however the current density shift is much less than in the 1100 series.

In conclusion it has been shown that while the chloride is aggressive, it may be tolerable at higher than current concentrations. Additionally, nitrate and sulfate may act as pitting inhibitors for Al 1100 and Al 6061 but further study is warranted to fully understand their effects in solution with respect to pitting and general corrosion.

ACKNOWLEDGEMENTS

The Savannah River National Laboratory is operated for the U.S. Department of Energy by Washington Savannah River Company under contract Contract No. DE-AC09-96SR18500.

REFERENCES

1. J.P. Howell "Corrosion Surveillance in Spent Nuclear Fuel Pools", NACE Corrosion/97, paper 107, (Houston, Texas: NACE 1997)
2. J.P. Howell, Durability of aluminum-clad Spent Nuclear Fuels in Wet Basin Storage", NACE Corrosion/96, paper 609, (Houston, Texas: NACE 1996)
3. T.H. Nguyen, R.T. Foley, "The Chemical Nature of Aluminum Corrosion", J. Electrochem. Soc., (December 1980), pp. 2563 - 2566