Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

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Development of Methodology and Field Deployable Sampling Tools for Spent Nuclear Fuel Interrogation in Liquid Storage

C. J. Berry, C. E. Milliken, M. J. Martinez-Rodriguez, D. J. Hathcock, and M. A. Heitkamp
Savannah River National Laboratory
Savannah River Nuclear Solutions

Abstract

This project developed methodology and field deployable tools (test kits) to analyze the chemical and microbiological condition of the fuel storage medium and determine the oxide thickness on the spent fuel basin materials. The overall objective of this project was to determine the amount of time fuel has spent in a storage basin to determine if the operation of the reactor and storage basin is consistent with safeguard declarations or expectations. This project developed and validated forensic tools that can be used to predict the age and condition of spent nuclear fuels stored in liquid basins based on key physical, chemical and microbiological basin characteristics. Key parameters were identified based on a literature review, the parameters were used to design test cells for corrosion analyses, tools were purchased to analyze the key parameters, and these were used to characterize an active spent fuel basin, the Savannah River Site (SRS) L-Area basin.

The key parameters identified in the literature review included chloride concentration, conductivity, and total organic carbon level. Focus was also placed on aluminum based cladding because of their application to weapons production. The literature review was helpful in identifying important parameters, but relationships between these parameters and corrosion rates were not available. Bench scale test systems were designed, operated, harvested, and analyzed to determine corrosion relationships between water parameters and water conditions, chemistry and microbiological conditions. The data from the bench scale system indicated that corrosion rates were dependent on total organic carbon levels and chloride concentrations. The highest corrosion rates were observed in test cells amended with sediment, a large microbial inoculum and an organic carbon source.

A complete characterization test kit was field tested to characterize the SRS L-Area spent fuel basin. The sampling kit consisted of a TOC analyzer, a YSI multiprobe, and a thickness probe. The tools were field tested to determine their ease of use, reliability, and determine the quality of data that each tool could provide. Characterization was done over a two day period in June 2011, and confirmed that the L Area basin is a well operated facility with low corrosion potential.

Introduction

The objective of this project was to determine the amount of time fuel has spent in a storage basin and the burn time for the fuel based to determine if the operation of the reactor and storage basin is consistent with safeguard declarations or expectations. This project developed and validated forensic tools that can be used to predict the age and condition of spent nuclear fuels stored in liquid basins based on key physical, chemical and microbiological basin characteristics. We developed key parameters based on a literature review, used these parameters to establish test cells for corrosion analyses, purchased instruments to analyze the key parameters, and used these tools in an active spent fuel basin, the L Area basin on the Savannah River Site (SRS).

Existing literature was used to determine key parameters for monitoring a spent fuel basin and determining the corrosion potential in the basin. Focus was also placed on aluminum based cladding because of their application to weapons production. Research was done concerning the relationship between aluminum oxide thickness to reactor temperature profiles and the corrosion rates of the aluminum. Different tools were evaluated to determine oxide thicknesses and different types of coupons were used during the test cell work so aluminum with different oxide thicknesses could be evaluated. The oxide layer formed on aluminum-clad spent nuclear fuel is an important source of forensic information to verify declared fuel service and storage history. The complete service history of fuels stored in foreign basins often comes under scrutiny during international verification to determine if materials have been diverted for illicit use, including potential use in weapons development programs.

Although the literature was helpful in identifying important parameters, relationships between these parameters and corrosion rates were not available. Bench scale test systems were designed, operated, harvested, and analyzed to determine corrosion relationships between water parameters and water conditions, chemistry and microbiological conditions. Water chemistry also plays and important role in aluminum oxide integrity and change during storage. High temperature oxide formed during reactor operations undergoes a slow reversion process during storage in cool (<50 °C) basin water. Additionally aggressive species and high ionic conductivity can alter the oxide through corrosion processes, giving additional clues to the history of the fuel while in storage. The effect of aggressive species, as well as the limited water chemistry information available for several foreign basins was evaluated.

Our experimental approach utilized a test cell system designed to provide conditions that accelerated corrosion of aluminum based materials similar to those used for nuclear fuel storage. Conditions found in foreign and domestic basins were used as conditions in the bench scale experiments. Three different bench scale simulations of aluminum cladding corrosion were developed with small "coin" coupons hanging in 4 liter beakers. Chloride concentration, pH, dissolved oxygen, conductivity and temperature were measured during testing.

The characterization kit was developed and used in an active spent fuel basin to characterize the storage system. The kit contained a handheld multimeter to measure water chemistry parameters and a separate set of instruments to measure total organic carbon concentrations, and coating thickness measurements. Characterization was done over a two day period in June 2011. The tools were field tested to determine their ease of use, reliability, and determine the quality of data that each tool could provide.

Literature Review

Open source literature, SRS information, Department of Energy (DOE), and International Atomic Energy Agency (IAEA) documents were examined to find data related to water chemistry and microbiological conditions of spent fuel storage basins worldwide. The current SRS basin is stable and has minimal corrosion of stored fuel [1,2], but detailed water chemistry data for foreign storage basins is much more difficult to find. The IAEA "Coordinated Research Project", initiated in the 1990s provides the best overview of world-wide storage basin chemistries. A series of corrosion test coupons and rack mounting systems were distributed to nine countries for testing in their respective storage basins. The participating countries were Argentina, Brazil, China, Hungary, India, Pakistan, Russia, United States, and Thailand. Russia pursued testing at two sites; Research Institute of Atomic Reactors, Dimitrovgrad and the Russian Research Institute, Kurchatov Institute, Moscow. Eight countries provided some degree of water chemistry information, with Hungary only providing qualitative information on the condition of the coupons after testing. The water chemistry and degree of corrosion varied widely among the test sites. Some sites had water chemistries comparable to the US in chloride level and overall conductivity while others were higher. Based on the available data, tests using water chemistry similar to that of the US systems should provide an accurate simulation of oxide growth and corrosion for foreign fuel simulants.

The data collected was evaluated to determine if corrosion data was also reported. It was found that chloride and conductivity levels were related to corrosion of aluminum materials in spent nuclear fuel storage basins at SRS and elsewhere. Microbial influenced corrosion was proposed as a corrosion mechanism at Idaho National Laboratory

but specific relations between water parameters and microbial corrosion were not identified.[3] SRS data indicate that an increase in available organic carbon increase microbial densities and the biofilm thickness and density changes over time. Corrosion resulting in the release of fission materials was observed at the SRS K-Basin with a water conductivity 178 μS/cm and a chloride level of 6-9 mg/L.[4] Similar corrosion was reported at the ICPP with many of its materials when chloride levels reached 800 mg/L in the 1970's.[3] Corrosion resulting in the failure of 30% of fuel bundles has been reported in the spent fuel storage pool at the RA research reactor operated by the VINCA Institute of Nuclear Sciences in Belgrade [5], Serbia with water conductivities >300 μS/cm and chloride levels 65-85 mg/L.[5-9] Argentina spent fuel basins showed galvanic corrosion of test coupons after 60 days in water with 74 μS/cm conductivity and 14.8 ppm chloride and pitting and crevice corrosion was noted in water with conductivity >200 μS/cm and chloride content 16 ppm.

Reporting from other spent fuel storage basins include water chemistry data from Chile, Peru, Brazil, Argentina, Thailand, Russia, China, India, and Pakistan. [1,10] Most of the data was obtained as part of the Coordinated Research Project (CRP) on "Corrosion of Research Reactor Aluminum-Clad Spent Fuel in Water."[2] Racks of coupons with various alloy configurations and galvanic couples were installed in basins and periodically examined to measure and monitor corrosion processes. Storage racks in Argentina showed galvanic corrosion after 60 days in water with 74 μS/cm conductivity and 14.8 ppm chloride. In separate monitoring, pitting and crevice corrosion was noted in water with conductivity >200 μS/cm and chloride content 16 ppm. [1] China reported corrosion products in crevices of their test coupon racks and some pitting corrosion on the outer edges of the coupons. Hungary did not report corrosion of any coupons after 1-2 years storage in high quality water. Coupons from India had some corrosion in the crevices but no pitting corrosion was observed. Coupons from Pakistan had some pitting corrosion under washers of the crevice coupons but no other corrosion was observed. No accelerated corrosion was measured in the Russian storage basins. Some pitting corrosion was observed in the Thailand monitoring coupons.

Microbial monitoring has been ongoing at SRS from the early 1990's and some microbial monitoring has been done at the Idaho National Laboratory (INL). Two types of samples were monitored for microbial parameters in the RBOF facility, water samples and coupon samples. Water samples were used to assess the general microbial condition of the basin, assess changes in the microbial population, and monitor bacterial, fungal, and alga populations in the basin. Coupon samples were used to assess biofilm formation on metal surfaces that are similar in grade to the SNF and basin hardware. Coupon examination provides the information that can be related directly to corrosion and continued long term spent fuel storage in an aqueous environment.

The microbiological data indicate that the water conditions were sufficient for minimizing corrosion at the SRS and INL basins. However, microbial densities were relatively high when compared to naturally occurring oligotrophic systems, and basin bacteria were capable of forming biofilms on metal surfaces. The measured density of microorganisms at SRS facilities is 1.5E+05 cells/ml. The development of the biofilm increased over time, and was more dense and thicker for the aluminum-based coupons compared to the stainless steel coupons in SRS basins. The measurement of organisms associated with anaerobic environments demonstrated that pockets of anaerobic bacteria exist in the basin.[11] The presence of acid producing bacteria showed the presence of organisms associated with aluminum corrosion although no corrosion was observed. At INL, sampling of aluminum corrosion coupons placed next to stored fuel elements show that microbial attachment has occurred, and a biofilm has formed. The sampling program was then extended to the surfaces of wet and dry stored fuel elements. Viable cells or spores were found on the surfaces of the ATR fuel elements that were stored under wet and dry conditions. [12]

Key parameter/Measurement Selection

Various parameters of interest were identified based on the literature review to help characterize spent nuclear fuel basins. Three water parameters, chloride concentration, conductivity, and total organic carbon concentration were identified as critical parameters. Oxide thickness, a material property, was also identified as a critical measurement in the characterization of the spent nuclear fuel basin. These parameters and other support measurements and information were used as a basis for developing a test kit to determine storage conditions and fuel storage time based on chemical, physical, and microbiological parameters. The selection criteria for each test component were based on the size, quality of data, analysis time/effort, availability, and cost of each device.

Chloride was identified as a major parameter associated with corrosion in spent fuel basins and chloride measurements between 1-100 ± 5 mg/L are required. Total organic carbon (TOC) and dissolved oxygen have been identified as major parameters associated with microbiological activity in spent fuel basins and concentrations from 1-100 ± 10 mg/L and 0-100%, respectfully, require measurement. Conductivity and pH are also parameters associated with corrosion in spent fuel basins and the kit was designed to measure conductivity concentrations ranging from 1-200 ±5 µS/cm and pH levels from 1-11. Temperature is a parameter that can provide information required to assess the microbiological condition of the basin and oxide condition on fuels. Temperature measurement is required from 5-50 ±5 ºC.

Non-destructive methods such as portable XRF, ultrasonic profiling and eddy current measurements were evaluated for potential integration into the test kit. These methods would provide in-situ analysis of the fuel oxide coating thickness and structure. Portability of these instruments was also evaluated as part of the test kit development. Equipment performance was benchmarked using control samples of oxides grown at pre-defined temperatures to simulate a variety of reactor environments and heat loads.

Basic information on the size, physical configuration, visual condition of the basin, and operation of the basin will also provide information that to help characterize basins. Visual inspection using a calibrated light source and a measuring device can be used with a camera to assess water quality in the basin and examine the spent fuels. Use of these devices will require little training and the measuring devices, rope or string, can be used so they can be left at the facility, as necessary. Important operational information includes a description or sample of the storage source water, information on deionizer or filter beds (as appropriate), water flow, additions and withdrawals, any available historical data to include chemistry, temperature, handling protocols, and cleaning protocols. The radiological activity in the basin can aid in determining the state of the spent fuel. Measuring requirements have not been established at this time. Hand held instrumentation is available that can provide radiation dose levels, contamination levels, and in more expensive models identify and quantify radioactive materials. There are a wide range of options available, but use of existing infrastructure or existing tools at the basin of interest were relied on for this project.

SNF Test Cell

The SNF test cells were designed to provide conditions that accelerated corrosion with conditions that were typically found in foreign and domestic basins. A bench scale simulation of aluminum cladding corrosion was developed with small "coin" coupons hanging in 4 liter beakers. Chloride level, microbial load, total organic carbon, alloys and oxide formation were identified as key parameters to investigate. Chloride concentration, pH, dissolved oxygen, conductivity and temperature were measured every week

The lack of detailed water chemistry information from foreign fuel storage basin necessitates extrapolation of potential test conditions from existing information. The test matrix design for SNF toolkit development has incorporated multiple levels of impurities, oxide types, and alloy composition. Sample coupons with air-formed, water-formed, and steam-formed aluminum oxides were made to accurately simulate oxides formed inside and outside of a reactor environment. These features allowed coverage of a range of fuel oxide scenarios that may be encountered during forensic testing. The dependence of oxide type and thickness on heat flux in the reactor core allows verification of disclosed fuel service history and detection of fuel service anomalies. Non-destructive examination techniques allow the fuel to be characterized and any anomalies in storage or service detected.

Three different oxide coatings were developed on the two types of aluminum alloy based test materials. The air oxide was developed passively and the water oxide was developed over a two and one half month period of storage in deionized water. The steam oxide was developed in an autoclave operating at 129 °C at 1.4 kg/cm2 for 19 hours, twice consecutively with an hour rest between cycles. The Al 1100 and Al 6061 alloys had the same weight change in the autoclave but scanning electron microscopy showed a more developed oxide layer on the Al 6061 materials after autoclaving.

Ten test cells were loaded with sodium chloride, and sediment, some were loaded with an organic carbon source, cellobiose, and all were loaded with a heavy or light amount of a microbial inoculum, and four sediment free test cells were also established. Sodium chloride was added at 0.65 mg, 65 mg, or 325.6 mg, which correlated to a starting concentration of 0.1 ppm, 10 ppm or 50 ppm chloride. Cellobiose is a disaccharide and is a byproduct of cellulose or cellulose rich materials. It was added once (1.25g/L) as complex carbon source that would require biological or enzymatic activity to make it available for cellular growth. The microbial inoculum and sediment were obtained from a fresh water swamp located close to the laboratory called Upper Three Runs. Swamp sediment (approximately 50ml) was chosen because of the highly diverse and complex microbial life represented in this type of eutrophic ecosystem.

SNF Test Cell Results

Major chemical parameters were monitored in each test cell beakers at least once a week using calibrated instrumentation. Readings were taken in the beakers with sediments for 78 weeks and readings were taken for 60 weeks in the beakers without sediment. The temperature of the beakers varied with the temperature of the laboratory and averaged 22.5 °C with a standard deviation of 1.2 degrees. The maximum temperature was 25.2 and the minimum temperature was 19.5 °C. Chloride levels, conductivity, pH, and dissolved oxygen readings were also taken on the beakers. The chloride values showed the smallest variability during the test. The Conductivity, pH, and dissolved oxygen all changed during the test. Table 1 has the average values and standard deviations of measured chloride, conductivity, pH, and dissolved oxygen values for all beakers.

Table 1. Test Cell Water Chemistry: Average Values

Test Cell ID	Chloride (mg/L)	Conductivity (µS/cm)	pH	Dissolved Oxygen (%)
1-0.1 ppm Cl⁻	3 ± 1.0	18 ± 5.3	6.0 ± 0.5	76 ± 12
2-10ppm Cl⁻	8.2 ± 1.8	41 ± 2.1	6.0 ± 0.3	78 ±6
3-50ppm Cl-	42 ± 5.4	186 ± 11	5.6 ± 0.2	81 ± 6.5
4-0.1ppm Cl⁻, Cbs	2.1 ± 1.0	60 ± 38	5.2 ± 1.0	51 ± 26
5-10ppm Cl-, Cbs	8.4 ± 2.2	95 ± 47	5.2 ± 1.0	51 ±24
6-50ppm Cl-, Cbs	41 ± 6.2	247 ± 51	5.0 ± 0.8	52 ±18
7-0.01ppm Cl⁻ low cell#	1.3 ± 0.8	128 ± 80	4.3 ± 0.8	14 ± 17
8-50ppm Cl⁻, low cell#	40 ± 7.1	198 ± 11	4.8 ± 0.5	48 ± 17
9-10ppm Cl-, Cbs, low cell#	10 ± 1.9	106 ± 21	4.5 ± 0.5	36 ±21
10-50ppm Cl⁻, Cbs, low cell#	40 ± 6.7	248 ± 27	4.4 ± 0.4	31 ± 19
13-No Sed. 0.0ppm Cl⁻	1.0 ± 0.3	2.6 ± 0.7	6.5 ± 0.2	85 ±6.3
14-No Sed. 0.1 ppm Cl⁻	2.2 ± 0.5	6.8 ± 0.4	5.9 ± 0.2	85 ± 8.1
15-No Sed. 10 ppm Cl⁻	8.9 ± 1.6	35 ± 1.6	5.5 ± 0.1	86 ± 8.5
16-No Sed. 50 ppm Cl⁻	38 ± 6.9	166 ± 14	5.2 ± 0.2	86 ± 7.1

Kit Description

The kit includes water chemistry measuring devices, an oxide thickness measuring device and a total organic carbon assay. The YSI Professional Plus instrument, see Figure 1 and the YSI manual [13] was chosen to measure water parameters. The YSI handheld multimeter is connected via cables (20 m) to five different probes that will measure and values of chloride, conductivity, dissolved oxygen, pH, and temperature.

The characterization kit will use a handheld multimeter to measure chloride, conductivity, dissolved oxygen, pH, and temperature. A separate test kit will be used to measure the total organic carbon. A YSI Professional Plus instrument, (YSI, Yellow Springs, OH), with the appropriate sensors and ion selective electrodes was chosen to measure these water parameters. Chloride has been identified as a major parameter associated with corrosion in spent fuel basins and chloride concentrations will be measured between 0-100 ± 5 mg/L at depths up to 17 meters using the ion selective electrode. The electrode will require warm-up time, some training, and calibration prior to use but will provide data while in the field. Conductivity and temperature will be measured with the same probe. Chloride is associated with corrosion in spent fuel basins and temperature is important to assess the conditions of the basin and oxide condition on fuels. The meter will measure concentrations that range from 1-200 ±5 μS/cm and temperature from -5 to 70 ˚C. The conductivity probe will require periodic calibration but generally this meter is accurate and can be used without extensive training. The pH will also be measured with the same probe. The range of this probe will be 0-14 for pH. These measurements will be used to supplement the chloride and conductivity data to enhance characterize the water samples for corrosion.

YSI Probe   Total Organic Carbon Instruments

Thickness Guage

Figure 1. Spent Fuel Characterization Kit Components

The HACH system samples were measured by an acid-base indicator affected by infusion of carbon dioxide. The HACH low, middle and high range TOC kit was purchased to determine TOC with a Portable Colorimeter. Total Organic Carbon Reagent Set, Low Range Test 'N Tube that includes: Acid Digestion Solution Vials, low range TOC, buffer solution, micro funnel, indicator ampoules, low range TOC, TOC persulfate powder pillows with a range up to 20 mg/L, and each pack has enough reagents for 50 reactions. The high range is 100-700 mg/L, and the middle range is 15-150 mg/L. Required accessories include the Digital Reactor Block DB 200: 15 x 16 mm vial wells; and TOC Standard Solution, 1000 mg/L, and DR 885 Portable Calorimeter (HACH, Loveland, CO).

A handheld, battery operated, ElektroPhysik Minitest 730 (ElektroPhysik USA, Arlington Heights, IL) coating thickness measurement system with a combined ferrous/non-ferrous sensor is also part of the toolkit, see Figure 1 and the operating manual.[14] This system uses magnetic induction and eddy current measurements to measure coating thickness on both ferrous and non-ferrous materials. The current cable length of this instrument is approximately 4 feet, although other cable lengths are available. The instrument probe end was covered with plastic (Saran™ wrap for easy radiological decontamination), calibrated, and used in the

basin to measure thickness of aluminum based tools, of varying ages, stored in the basin. Measurements consisted of touching the tools with the plastic protected probe multiple times.

Characterization Kit Testing

Each piece of the characterization test kit was evaluated using manufacturer instructions for calibration and used to measure parameters from the bench scale test beakers. The YSI probe was calibrated using vendor supplied standards cross checked using reagent grade American Chemical Society (ACS) chemicals, and compared to reading obtained from the bench scale test beakers for chloride, pH, and conductivity measurements. A 10 µS/cm conductivity standard, a 61 mg/L chloride standard, and three pH buffers (4, 7 and 10) were used to calibrate the instrument. The YSI was then cross checked against laboratory prepared standards and used to measure parameters in the bench scale test cells. Readings from the instrument were deemed accurate and precise enough for use in the field.

The TOC analyzer was calibrated using ACS grade dextrose at different concentration levels. The test kit was accurate to within 5%. The TOC kit also measured a difference between the test beakers loaded with low organic carbon, high carbon levels and beakers with not additional carbon added.

The ElektroPhysik Minitest 730 was calibrated using vendor supplied control standards. The standards consisted of plastic sheets of varying thickness, 28.6, 100.6, 241.8, and 938 µm. Verification testing was done on aluminum coupons with air formed and water formed oxide layers. A difference of an average of 29 µm was measured using the Minitest 730 between the two oxide types. Thickness measurements on water formed oxides had a much larger standard deviation than air formed oxide thicknesses, 20µm compared to 3 µm. This large deviation associated with the water formed oxide was not measured when using the control standards.

SRS L-Area Basin Testing

The purpose of this sampling was to use field deployable tools to analyze the chemical and microbiological condition of the fuel storage medium. The information received from sampling event was used to determine the storage conditions of the SNF' and determine the corrosion potential in the L Area basin. During field testing, water samples were taken, a tool was immersed in the basin at various locations, and a tool was used in direct contact with materials pulled from the basin. The toolkit consisted of a YSI multiprobe, a thickness probe, and a TOC assay kit. The tools characterized the basin chemistry, measured differences in oxide thickness of aluminum tools with different storage lives, and measured the organic carbon levels. This document includes the sampling plan, a general description of the tools, and the results of pool measurements. This document is specific for sampling at a DOE spent fuel storage facility but the information required and the information gained from the sampling could be used as a basis for sampling in other basins or environments.

L Basin sampling occurred in a radiological environment and sampling required coordination with site operations, radiological protection, and basin engineering personnel. All sampling equipment required specially handling, protection, and or decontamination to use and remove from the basin environment. Site operations personnel pulled the water samples for TOC analyses and pulled tools from the basin for measurement using the thickness gauge. Five separate sampling points were selected in the basin, based on location, what was stored in the area, the depth of the sampling point, and operational concerns. The YSI probe also took readings at different depths and the TOC samples were pulled just below the surface of the basin.

Results

Water parameters measured with the YSI probe had consistent values at different sample locations and different sample depths. Total organic carbon was not detected at measurable concentrations using the test kit. Film thickness differences were measured on basin tools with different basin storage times.

The YSI instrument measured chloride concentrations (mg/L), conductivity (µS/cm), dissolved oxygen (mg/L and % saturation), and temperature (°C). Measurements were made at five different locations in the basin at five foot intervals for sample points 1-4 and three foot intervals for sample point 5, Horizontal Tube Storage. Sample points 1-3, the machine basin, VTS west and VTS east were sampled to 25 feet. The sample from the Horizontal tube storage, sample point #5, was sampled to every three feet to 15 feet and another sample was taken at 16 feet. The Dry Cave, sample point #4, was sampled to 30 feet and five foot intervals. All five samples were taken in approximately 32 minutes.

The readings obtained for the four parameters using the YSI probe did not differ much with sample location, sample depth, or sample time. The average values for all of the sample points were quite similar for dissolved oxygen and temperature. The chloride concentration, pH, and conductivity measured in the Dry Cave were slightly lower than the other sample points. The dry cave also had the highest dissolved oxygen level. The ranges of averaged values measured for each parameter at each sample point were relatively small. Chloride averages were between 0.2 and 0.3 mg/L, conductivity ranged from 1.7 to 2.1 µS/cm, dissolved oxygen ranged from 7.9 to 8.3 mg/L or from 92-96% saturation, pH ranged from 5.8 to 6.0, and temperatures ranged from 23.5 to 23.6 °C.

There was little deviation in sample measurements during the 32 minutes of sampling. Liquid samples were taken from sample points 1-3 in the basin and analyzed for organic carbon but none of the samples had measureable levels of organic carbon. The surface thickness of the unknown locking tool had the thickest surface, presumably oxide thickness, and had been stored in the basin for the longest period of time. Samples stored in 2000 and 1996, described as two slowpokes and the dummy fuel bundle by operations personnel, have very similar surface thicknesses. The Cobalt pipe tool had a thickness greater than the slowpoke tools and the dummy bundle but less than the unknown locking tool.

Summary and Conclusions

The water parameters measured during operation of the Test Cell provided direct measurements of key parameters, indirect measurements of biological activity, and allowed the measurement of changes and trends in the test cells. Conductivity levels, pH, dissolved oxygen, and lower chloride levels were measured over the entire operating period for the test cells. In general the test cell operation was consistent with the materials added to the particular beaker. Beakers with added cellobiose material and high microbial load, representative of poorly maintained basins, had the largest measured corrosion rates. Beakers with higher chloride levels also had higher corrosion rates.

The results obtained from the test kit sampling event confirm that the L-Area basin is a well operated spent fuel storage facility. The low levels of chloride, conductivity, and total organic carbon indicated the corrosion potential in the basin is low. There was little variability in the results of sampling for the different parameters with respect to sample location, depth, and the time each sample was taken. This indicates the basin is well mixed and the YSI instrument did not have a large amount of drift during sampling. Total organic carbon levels were below the detection limit of the assay, 1 mg/L. The low TOC levels are due to the sand filters and deionization units used in basin operation. Differences in the surface thickness of basin tools, aluminum tools, were measured using the Elektrophysik instrument.

The YSI instrument worked well. It was simple to calibrate and operate. The calibration procedure used YSI supplied standards poured into containers that were screwed onto the probe. Once the instrument calibrated to the standard value the container was removed the solution was removed, and a new container with a standard for a different parameters was attached. The probe cable length was 30 feet and all portions of the basin that were sampled were within reach of the probe. Marking the probe with plastic cable ties made depth measurements simple. The unit was easy to pre-program and operate in the basin. The buttons responded well while wearing two pairs of gloves. Radiological support personnel and operations personnel were present to wipe down the probe

cable as it was pulled in and out of the basin but were not needed for additional support. Once sampling was completed the results were pulled from the probe using a USB interface onto a PC.

The TOC analyzer gave expected results but the operation of the unit was neither quick nor easy. The equipment was relatively bulky and required a power supply to run the assay. The assay also took time, hours, to allow the sample to incubate per the manufacturer's instructions. The detection limit was 1 mg/L which is adequate to assess corrosion potential but it was not low enough to measure TOC in the L Basin.

The Elektrophysik Minitest 730 provided good results but it was difficult to setup, operation required some precautions, and data transfer was done manually. The instrument can operate on ferrous and non-ferrous samples and settings on the unit must be changed depending on the type of material being analyzed. We set up the instrument and calibrated the instrument for measurements of aluminum but once we were in the basin sampling we had to switch the instrument to different settings that we had used previously for measuring aluminum coupons on the laboratory. Calibration checks were needed between samples and calibrating the unit with the plastic calibration sheets proved difficult when wearing two pairs of gloves. We instead used aluminum pieces with air formed oxides to perform zero point calibrations. When pressing the unit onto the tools the probe tips had to be depressed multiple times to get a reading. This was probably due to the Saran wrapping. The readings that were obtained were consistent and differences in tools stored in the basin for different times were observed. Once the data was collected and the instrument removed from the basin data was transferred from the unit manually. The unit has an infrared port for data transfer but our government PCs do not have that feature turned on. The unit came equipped with a four foot cord which was adequate for our use but a longer cord, different lengths are available, would be helpful to sample other storage basins.

This project achieved the primary objectives of developing methodology and field deployable tools (test kits) that can analyze the chemical and microbiological condition of the fuel storage medium and determining the oxide thickness on the spent fuel basin materials. The terminal objective of this project was to determine the amount of time fuel has spent in a storage basin and the burn time for the fuel using the results of the test kit. The test kit measurements could then be used to determine if the operation of the reactor and storage basin is consistent with safeguard declarations or expectations. We were able to identify key parameters based on a literature review, used these parameters to establish test cells for corrosion analyses, purchase instruments to analyze the key parameters, and use these tools in an active spent fuel basin, the SRS L Area basin. The results showed a low level of corrosion potential in the, well maintained, L basin and differences in oxide thicknesses were measured on tools with varying ages in the basin.

It was found that chloride and conductivity levels were related to corrosion of aluminum materials in spent nuclear fuel storage basins at SRS and elsewhere. SRS data indicate that an increase in available organic carbon increase microbial densities and the biofilm thickness and density changes over time. The primary mechanism of aluminum corrosion occurs when the oxide is penetrated, leading to pitting corrosion and intergranular attack at the material surface. This corrosion is driven by the water chemistry of the fuel storage basin.

Various parameters of interest were identified during the literature review to help characterize spent nuclear fuel basins. Three water parameters, chloride concentration, conductivity, and total organic carbon concentration were identified as critical parameters. Oxide thickness, a material property, was also identified as a critical measurement in the characterization of the spent nuclear fuel basin. These parameters and other support measurements and information were used as a basis for developing a test kit to determine storage conditions and fuel storage time based on chemical, physical, and microbiological parameters.

The selection criteria for each test component were based on the size, quality of data, analysis time/effort, availability, and cost of each device. The kit includes water chemistry measuring devices, an oxide thickness measuring device and a total organic carbon assay. The YSI Professional Plus instrument was chosen to measure water parameters. The YSI handheld multimeter is connected via cables to probes that will measure and values of chloride, conductivity, dissolved oxygen, pH, and temperature. A separate system was selected to measure the TOC and consists of a portable colorimeter, a reaction block, and indicator solutions. The HACH system measured

TOC by an acid-base indicator affected by infusion of carbon dioxide. A handheld, battery operated, ElektroPhysik Minitest 730 coating thickness measurement system with a combined ferrous/non-ferrous sensor is also part of the toolkit. This system uses magnetic induction and eddy current measurements to measure coating thickness on both ferrous and non-ferrous materials.

The outcome of L Basin sampling was that the YSI instrument and the Elektrophysik instruments were successful in the measuring critical water parameters and surface thicknesses. Operational lessons were also learned about the operation of the Elektrophysik instrument. Basin conditions were not conducive for testing the TOC assay but lessons were learned about its utility in a basin environment. Overall, the toolkit was responsive in the system and provided potentially valuable information about the basin environment.

Acknowledgment

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