A CORROSION MONITORING PROGRAMME FOR RESEARCH REACTOR SPENT FUEL BASINS

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Abstract

A corrosion monitoring programme (CMP) at a spent fuel wet-storage facility helps evaluate the effect of the prevailing water parameters on the corrosion of spent fuel cladding and/or of other structural materials. Hence, a CMP usually involves the exposure of test coupons to the basin water for a pre-determined period followed by corrosion evaluation of the coupons and the determination of water parameters at periodic intervals. A programme of this nature provides insight into the extent of corrosion of the metallic materials. A CMP at a spent fuel storage facility consists mainly of three stages: Planning; Execution; Evaluation. This paper presents the main aspects to be considered and guidelines to conduct a CMP with examples from three IAEA supported projects on the corrosion of aluminium alloys exposed to spent fuel basins in over 15 sites worldwide for periods of up to 6 years.

Introduction

The IAEA's Research Reactor Spent Fuel Database (RRSFDB) indicates that most of the spent fuel are stored in light water filled pools or basins, as shown in Table 1. The at-reactor storage is often in a different section of the reactor pool or in a separate pool within the reactor building and the latter is referred to as the decay pool. Away-from-reactor pools were constructed in many countries for long term storage of research reactor (RR) fuels. The fuels are often stored in racks mounted under water. Most of the RR fuels are clad with relatively pure aluminium or an aluminium (Al) alloy. A large number of these fuels have been stored in pools for periods of up to 50 years. At the time of manufacture of these fuels, such extended wet storage was not foreseen. Corrosion and especially pitting corrosion, is the main form of degradation of Al alloy clad RR fuel. Pitting corrosion of Al alloy cladding is a localized form of attack and could lead to breach of the cladding and release of fissile material to the environment. Besides the hazard of exposure, this often involves contamination of the storage facilities and very expensive clean up procedures. The best option is to avoid this from happening.

Table 1. Spent fuel storage facilities

Type of storage	At reactor	Away from reactor
Pool	154	55
Dry well	25	31
Vault	10	12
Other	18	6

A corrosion monitoring programme (CMP) at a spent fuel wet-storage facility helps evaluate the effect of the prevailing water parameters on the corrosion of spent fuel cladding and/or of other structural materials. A program of this nature provides insight into the extent of corrosion of the metallic materials. It is well known that good quality water is essential to prevent corrosion in a spent fuel basin. However, certain water parameters like conductivity, chloride ion content and some other ions, in quantities well below levels of concern, have a synergistic effect on the pitting corrosion behaviour of Al alloys. Hence, maintenance of water parameters within specified limits is not reason enough for complacency about corrosion of fuel cladding. A well-planned and executed CMP gives the spent fuel basin manager an insight into the state of the fuel cladding and/or metallic structural materials in terms of corrosion. A CMP usually involves the exposure of test coupons to the basin water for a pre-determined period followed by its evaluation to detect for corrosion. The CMP also involves the determination of water parameters at periodic intervals. Other techniques such as electrochemical noise have also been used to monitor corrosion, but to a lesser extent. Thus, a CMP keeps the 'Basin Manager' informed of any transients in water parameters, (which often go unperceived in the absence of a CMP) and its effects, if any, on the corrosion of test coupons, and consequently on that of the fuel cladding and other structural materials.

This paper presents the different stages that constitute a CMP for a spent RR fuel storage facility. Guidelines to be followed during the stages, along with specific examples from two IAEA supported coordinated research projects (CRPs) "Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water" and one IAEA supported Regional Project for Latin America on "Management of Spent Research Reactor Fuel in Latin America" are also presented. [1,2]

The Corrosion monitoring programme (CMP)

The main stages of a CMP at a spent RR fuel storage facility are: (a) The planning stage; (b) The execution stage; (c) The evaluation stage.

The planning stage

In the planning stage it is essential to first list the metallic materials exposed to the spent fuel basin water along with their composition, microstructure, heat treatment condition and surface condition. This helps select the materials for the program. The next step involves the specification of the: (a) type and dimensions of the corrosion test rack, test coupons and insulating separator; (b) duration of the program; (c) frequency of corrosion monitoring; (d) test coupon assembly sequence in the rack; (e) number of racks, coupons and separators; (f) location within the spent fuel basin to place the coupons; (g) water parameters to be monitored and its frequency. Besides these, it is also essential to specify if the program will be complemented with other laboratory studies and the determination of the amount and type of solids that settle on surfaces within the basin. The latter is important as it is well known that settled solids tend to initiate and/or exacerbate the corrosion of Al alloys. [3,4]

A successful CMP is at times compromised by insufficient prior attention to aspects such as availability of sufficient materials in the desired states and to other accessories that may be required during the execution stage. The former refers to a material's supplier adequately equipped to manufacture the test coupons, racks and separators. It is also important to know well in advance about the availability of laboratory facilities for water analysis, sediment analysis, test coupon evaluation etc.

Material selection

A variety of metallic materials are often used in spent fuel basins. For the CMP, only alloys that are of major concern need be selected. These should be representative of the fuel cladding (usually aluminium alloys) and any other thin walled aluminium alloy component, which if corroded could lead to concerns. Other materials that should be included are those that form bimetallic junctions with the fuel cladding leading to corrosion of the latter. Besides knowing the alloy's designation and its nominal composition, it is important to know the metallurgical state of the alloys as inclusions and secondary phases in Al alloys influence its corrosion. The type of heat treatment given to an alloy alters its composition and its stress state. These also influence the corrosion behaviour of the alloy. Usually, the final operation in the manufacturing processes of RR fuel plates is surface treatment as it removes surface defects and helps form a thicker surface oxide. These in turn reduces the number sites at which pits can initiate on the Al surface. Hence, knowledge of the metallurgical state, the heat treatment and surface state of the Al alloys are essential to select, specify and/or produce test coupon material with alloy and surface characteristics similar to that of the fuel cladding.

Many reactor components and spent fuel storage racks are made of stainless steel (SS). It is well known that bimetallic contacts between SS and Al alloys aggravate the corrosion of the latter. [5] Should there be SS-Al alloy contact in a storage basin, it is essential to select a SS with composition close to that of the storage rack material to prepare SS coupons to evaluate the bimetallic corrosion behaviour of Al alloys. Crevice corrosion is another form of localized corrosion and it takes place in crevices. In a spent fuel storage basin, of concern are crevices formed between two Al alloys. In this context the Al alloy used for storage racks is often selected.

Test racks and coupons

A variety of test racks with test coupons of varying shapes and sizes have been used in CMPs. The models used in CRP-II and the RLA are recommended as these racks evolved from other designs. Figure 1 shows a typical corrosion test rack with the coupons and separators. The coupons are made of materials that are identical to or similar to materials used in the spent fuel storage basin. The insulating separator physically isolates one coupon from another and from other metallic parts of the test rack. It should therefore be an insulating, non-porous and resistant to radiation, like dense alpha-alumina. The coupons are usually arranged horizontally even though fuel plates within fuel assemblies are vertical. Experience gained in the CRPs revealed that horizontal coupons are more susceptible to corrosion compared with vertical coupons. Consequently, it is recommended that CMPs use horizontal coupons as the conditions are much more severe and therefore an early warning mode in terms of corrosion of vertical fuel plates and assemblies.

The Al alloys studied in the projects mentioned earlier were AA 1050, AA 1100, AA 6061 and SZAV-1. The coupons were 3 mm thick and 10 cm in diameter with a central hole to enable stacking in an all-stainless steel test rack with a stem and a nut with a hook to suspend the assembled rack in the spent fuel basin. The test rack assemblies also contained coupons to evaluate crevice and bimetallic corrosion.

Figure 1. A typical corrosion test rack with coupons.

The coupon stacking sequence in a test rack is important. Table 2 shows the stacking sequence used by one of the participants of the projects. It is recommended that bimetallic couples be positioned lower down in a vertical test rack to prevent bimetallic corrosion products, if any, from affecting the corrosion of single coupons.

Table 2. Coupon stacking sequence for the different test racks.

CRP racks	**RLA racks**
SZAV-1	AA 1050
SZAV-1 (PS)	AA 6061
SZAV-1/SZAV-1	AA 1050 (PS)
AA 6061 (PS)	AA 1050/AA 1050
AA 6061	AA 6061/AA 1050
AA 6061/AA 6061	AA 6061/AA 6061
SZAV-1/AISI304	SS 304/AA 1050
AA 6061/AISI 304	SS 304/AA 6061

The number of test racks to be used in a CMP would depend on the overall test duration and the frequency at which corrosion is monitored. The number of coupons in each rack would depend on the number of Al alloys and if crevice and bimetallic corrosion are being measured.

Test duration and monitoring frequency

The number of test coupon assemblies or racks to be used in a CMP must be consistent with the expected life of the facility, and with the duration of interim storage of spent fuel. An ideal CMP of a spent fuel basin should envisage surveillance throughout the desired service life of the spent fuel basin. The frequency of corrosion monitoring is the number of times test racks with coupons are withdrawn or removed from the spent fuel storage basin during a CMP. In CMPs at basins with very good quality water, yearly withdrawals of test racks are considered sufficient. At basins with poor quality water or with significant amounts of settled solids, test rack withdrawals should be at three- or six-monthly intervals, until such time the water quality is well under control. It is important to emphasize that at the end of a specific test period, the test rack should be removed, **not to return it to the basin having removed one or more coupons**. Experience has shown that a dry or partially dried coupon, if returned to the basin does not represent conditions similar to that of a fuel cladding or reactor component exposed to the same environment.

Water parameters

At in-reactor spent fuel storage facilities, water parameters such as temperature, pH, conductivity, chloride, sulphate, iron, and a few heavy metal ion content are monitored and recorded at regular intervals. The first 3 parameters are often monitored on-line and recorded at regular once- or twice-daily intervals. At these facilities, the water is separately analysed at fortnightly or monthly intervals. In away-from-reactor spent fuel storage sites, water analysis, if carried out, is often very infrequent. It is recommended that at the CMP site, water of less than desired quality be analyzed twice a month. If no marked variation in ion composition is noted after 6 months, monthly measurements are suggested.

Test rack location

In a spent fuel basin, test racks should be immersed as close as possible to the spent fuels. (Figure 2 (a)) Other aspects to be borne in mind while selecting the location are those in which the test rack assembly: (1) does not hinder regular fuel handling; (2) is not knocked about during regular reactor or basin operations; (3) is not exposed to excessive amounts of settled solids, unless it reproduces conditions similar to that of stored fuels.

(a) (b)

Figure 2. (a) Photograph of test racks close to spent fuel in a storage basin; (b) A spent fuel storage facility with solids floating on the water surface.

Evaluation of settled solids

Most storage basin water surfaces have dust or floating solids as shown in Figure 2(b). Some, if not all these solids are wetted and eventually settle on surfaces inside the basin. The settled solids, depending on their composition, affect the corrosion of Al alloy coupons.[4] It is therefore important, as part of a CMP, to determine the amount and composition of settled solids. Details about the procedure adopted to collect and analyze the solids, their composition at different test sites of the IAEA projects and their effect on corrosion of coupons can be found elsewhere. [4]

The execution stage

The execution stage involves all actions related to preparing the test coupons and racks, conducting the corrosion program and evaluation of the coupons.

Preparation of coupons and racks.

Corrosion test coupon preparation and its assembly to form the test rack consists of a number of steps and this section summarizes the main steps. [1,6,7]

(a) Coupon surface preparation to the same level as that of a fuel plate;
(b) Identification of the coupons with numbers.
(c) Photographic register of the coupon surfaces.
(d) Chemical treatment of the Al alloy coupons to have a clean surface to enable comparison of surface characteristics.
(e) Assembling the coupons in a specified order.
(f) Tightening the top nut to the same extent in all racks.
(g) Photographic register of the assembled rack. (Figure 7 (a))
(h) Attaching a stainless steel rope to the hanger of the rack to suspend it in the basin.

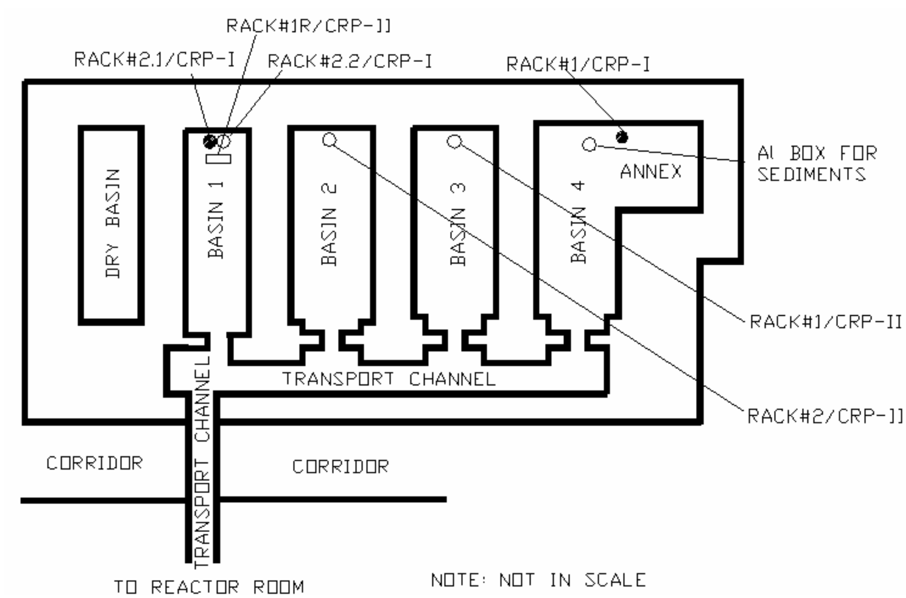


Figure 4. Schematic diagram indicating the position of test racks in the spent fuel storage pool at Vinca, Serbia.

Table 3. Details of test rack location and duration of exposure in the spent fuel storage pool at Vinca, Serbia.

Rack /CRP-phase	Basin no.	Immersion date	Removal date	Exposure (months)
Rack#1 / CRP-I	B-4	July 1996	30 July 2002	72
Rack#2.1 / CRP-I	B-1	26 February 2002	25 July 2003	16
Rack#2.2 / CRP-I	B-1	26 February 2002	2 March 2004	24
Rack#1 / CRP-II	B-3	26 March 2003	26 September 2003	6
Rack#2 / CRP-II	B-2	26 March 2003	6 April 2004	12
Rack#1R / CRP-II	B-1	15 July 2004	19 July 2005	12

The corrosion test

The main steps involved in the corrosion test are:

(a) Suspending the racks at the selected location.

(b) Identification of the test racks with labels containing adequate information about the test rack and about the person carrying out the test. (This also serves to prevent tampering or inadvertent removal or repositioning of the rack).

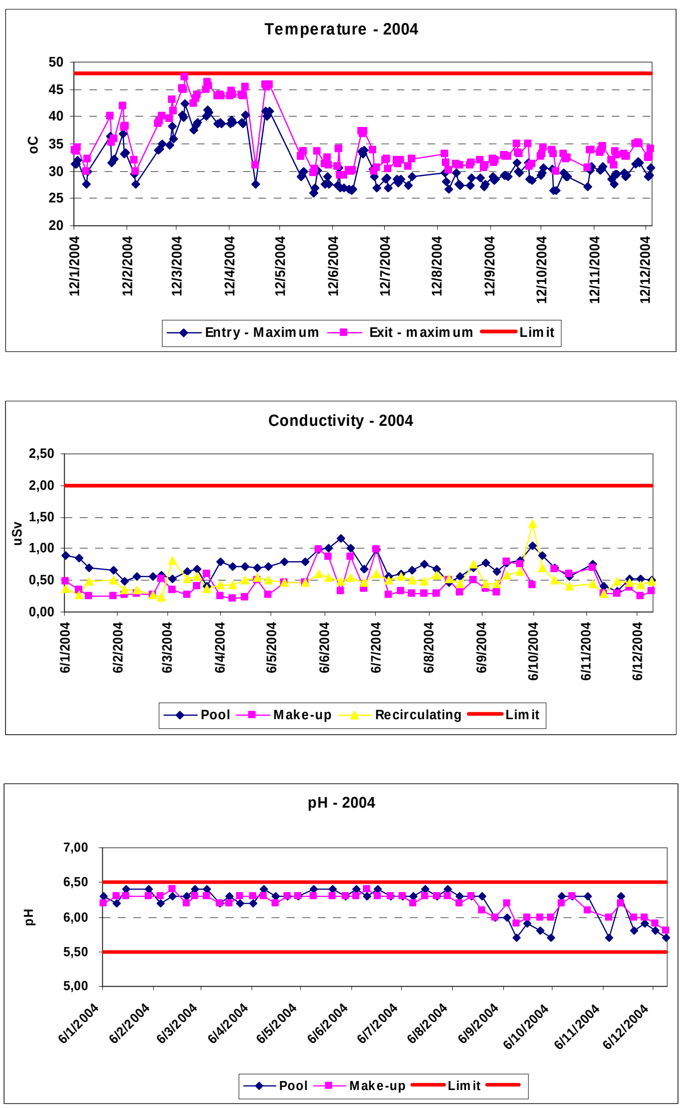


Figure 5. Temperature, conductivity and pH profiles during 2004 in the spent fuel basin of the IEA-R1 research reactor in São Paulo, Brazil.

(c) Recording details of the location and the dates of immersion as exemplified in Figure 4 and Table 3.
(d) Measuring the radiation field intensity near the rack at periodic intervals (in R/h, or Sievert/h).
(e) Monitoring the main water parameters at daily or weekly intervals to plot parameter profiles as shown in Figures 5.
(f) Determining impurities in the basin water at monthly or six monthly intervals. Impurities such as chlorides, sulphates, nitrates, nitrites, carbonates, bicarbonates, iron, copper, silver, mercury, aluminium and other ions which are site-specific. Figure 6 shows changes in impurity content in the RECH-1 reactor in Chile.

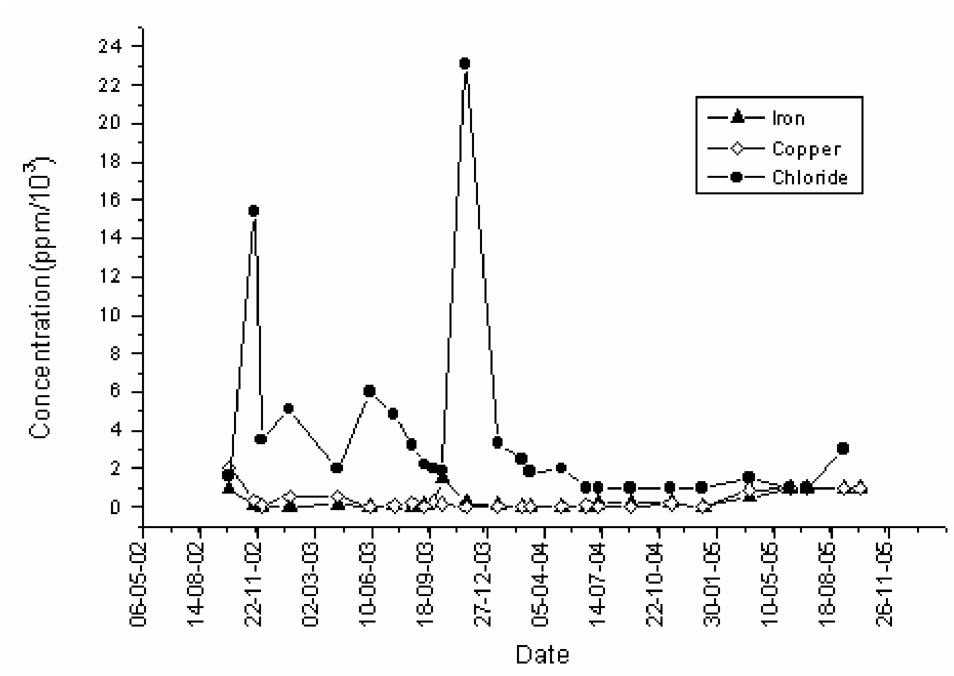


Figure 6. Change in Fe, Cu and Cl contents in RECH-1 reactor pool in Chile.

(g) Registering water flow characteristics near the test rack, rate of or frequency of renewal of water in the basin etc.
(h) Recording activities carried out by reactor or spent fuel basin personnel that could affect test results.
(i) Preparing and immersing a sediment collector in the vicinity of the test rack for a period of 4-6 months to determine the quantity and composition of solids that settle on the surfaces of the coupons.
(j) At the end of the test period withdraw the rack from the basin.

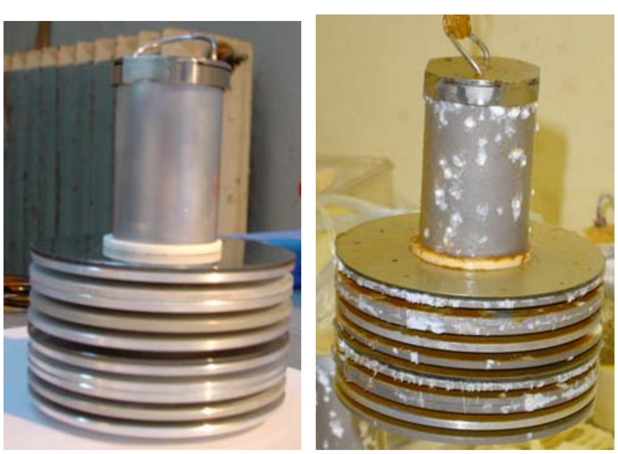


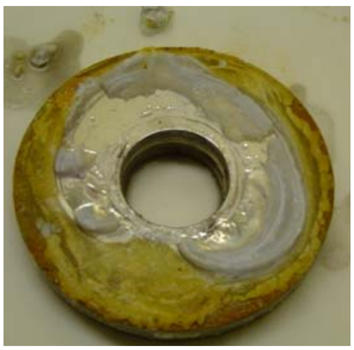
Figure 7. A test rack with coupons, before and after exposure for a year to a spent fuel basin in Serbia.

The evaluation stage

Evaluation of the coupons

Coupon evaluation involves:

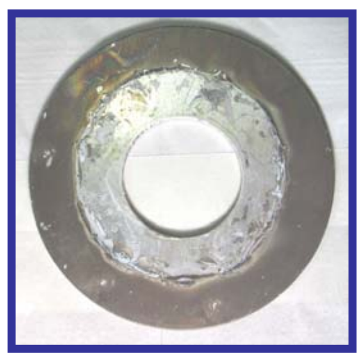
(a) Measurement of pH of water on the external surface of coupons.
(b) Photographing the rack prior to disassembly. Figure 7 shows a test rack of coupons before and after exposure for a year in a spent fuel basin.
(c) Disassembling the rack and removing the coupons.
(d) Photographing the front and back of each coupon. A small card with a note about the material, immersion time and coupon identity should be photographed together with the coupon.
(e) Recording specific surface features for each coupon, such as amount and type of settled deposits, staining, discoloration, pitting, nature of oxide (tenacious or loose), and ease of separation of crevice/bimetallic coupons. Figure 8 (a) show an example of corrosion features on a coupon surface soon after withdrawal.



(a)

(b)

(c)

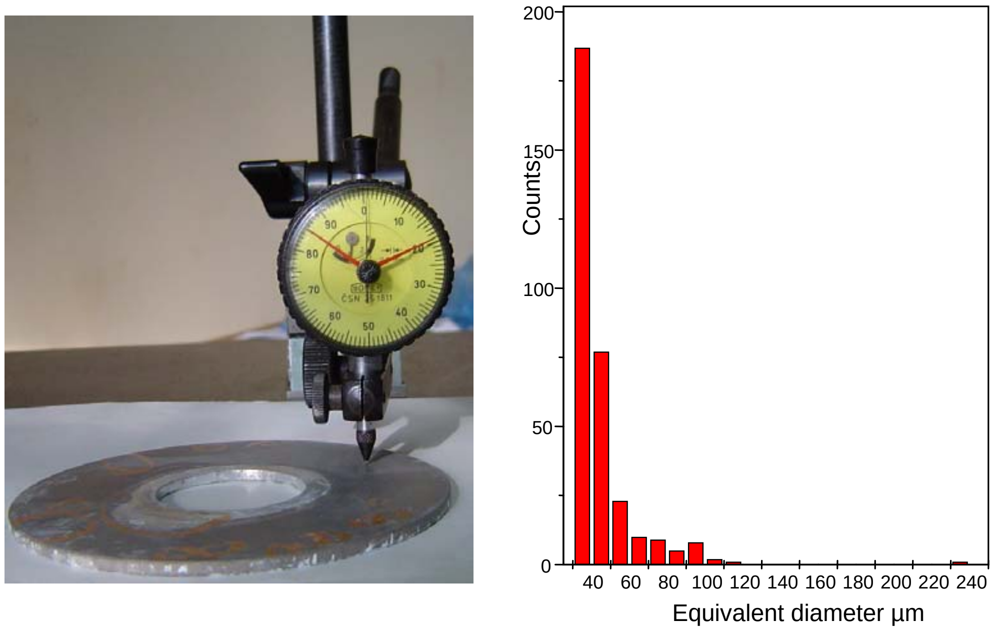


(d)

Figure 8. (a) White jellylike sludge on exposed surface of a AA 6061 coupon exposed for six years. (b) The exposed and contact surfaces of a crevice couple. (c) Corrosion feature on a AA 6061 coupon exposed for a year. (d) Corrosion of AA 6061 coupon at exposed contact region with a SS coupon.

(f) Measuring pH (with pH paper) on the contact surfaces of crevice and bimetallic coupons.
(g) Decontaminating the coupon while still wet.
(h) Examining coupon surfaces to record other corrosion features. (Figures 8 (b-d))
(i) Evaluation of the extent of pitting corrosion with the aid of an optical microscope or an image analysis system.
(j) Determination of pit depths from image analysis data or with a calibrated focusing technique (Figure 9 a) or using standard metallographic techniques (repeated polishing followed by optical microscopy).

(k) Recording the deepest pit and preparing histograms of pit depths and number of pits in different pit depth ranges. (Figure 9 b)
(l) Evaluate the extent of pitting on the contact surfaces of the crevice and bimetallic couples.



(a) (b)

Figure 9. (a) Device used to measure pit depths, with 10 µm resolution. (b) A histogram of number of pits versus pit diameter on a coupon surface.

Reporting CMP results

A report should be prepared about the state of the coupons as a function of water parameters and duration of exposure. The report could include:

(a) Captioned photographs of coupons before and after cleaning.
(b) High magnification photographs of pits if essential.
(c) Photographs to compare and highlight differences.
(d) Pitting density and pit depths (average and maximum) of individual and creviced coupons.
(e) Comparisons with past pit depths data.
(f) An evaluation of possible effects on fuel cladding and other structural components.
(g) Recommendations of appropriate actions to reduce corrosion rates.

Final remarks

Correlation of the results of coupon corrosion evaluation and water parameters is an important step of the whole CMP and this helps predict the surface state of the spent fuel cladding and/or other structural components. On the basis of this appropriate actions could be taken to reduce corrosion rates. This could be alterations in one or more water parameters, changes in housekeeping practices to reduce the extent of settled solids or adoption of procedures to verify fuel cladding integrity at more frequent intervals.

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