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Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water

IAEA
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CORROSION OF RESEARCH REACTOR ALUMINIUM CLAD SPENT FUEL IN WATER

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The Agency's Statute was approved on 23 October 1956 by the Conference on the Statute of the IAEA held at United Nations Headquarters, New York; it entered into force on 29 July 1957. The Headquarters of the Agency are situated in Vienna. Its principal objective is "to accelerate and enlarge the contribution of atomic energy to peace, health and prosperity throughout the world".

CORROSION OF RESEARCH REACTOR ALUMINIUM CLAD SPENT FUEL IN WATER

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 2003

FOREWORD

This report documents the work performed in the IAEA Co-ordinated Research Project (CRP) on Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water. The project consisted of the exposure of standard racks of corrosion coupons in the spent fuel pools of the participating research reactor laboratories and the evaluation of the coupons after predetermined exposure times, along with periodic monitoring of the storage water. The project was overseen by a supervisory group consisting of experts in the field, who also contributed a state of the art review that is included in this report.

The study was carried out in six laboratories in industrialized Member States and four laboratories in developing countries. Besides the basic goal of obtaining insight into the mechanisms of localized corrosion, a secondary goal was the transfer of know-how at the laboratory level from some of the more advanced laboratories and the supervisory group to the four institutes in developing Member States. Localized corrosion mechanisms are notoriously difficult to understand, and it was clear from the outset that obtaining consistency in the results and their interpretation from laboratory to laboratory would depend on the development of an excellent set of experimental protocols.

The basic scope of the programme was originally formulated by the IAEA with the help of the supervisory group in early 1996. The design of the standard corrosion racks and corrosion coupons was based on a corrosion surveillance and monitoring programme for aluminium clad production reactor fuel that had already been established at the United States Department of Energy Savannah River Site (SRS) in Aiken, South Carolina. The CRP began formally with the signing of contracts and agreements in early 1996. The first Research Co-ordination Meeting (RCM) was held in August 1996. At this meeting the participants were briefed, the experimental protocols were developed and the first corrosion racks were distributed. Further RCMs were hosted by two of the participating laboratories in 1998 and 2000. Supervisory group meetings were also held at regular intervals to review the results obtained. The programme was completed and documented in mid-2001.

This report describes all of the work undertaken as part of the CRP and includes: a review of the state of the art understanding of corrosion of research reactor aluminium alloy cladding materials; a description of the standard corrosion racks, experimental protocols, test procedures and water quality monitoring; the specific contributions by each of nine participating laboratories; a compilation of all experimental results obtained; and the supervisory group's analysis and discussion of the results, along with conclusions and recommendations.

CONTENTS

SUMMARY

Aluminium clad spent nuclear fuel from research and test reactors worldwide is currently being stored in water filled basins while awaiting final disposition. Much of this fuel was provided to the various countries by the United States of America as part of the Atoms for Peace programme in the early 1950s. Other fuel was provided by the former Soviet Union. The spent fuel has been in water at the reactor sites for up to 40 years, in some cases, awaiting shipment back to the USA or to the Russian Federation.

As a result of corrosion issues that developed from the long term storage of the aluminium clad fuel, the IAEA implemented in 1996 a Co-ordinated Research Project (CRP) on the Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water. During the initial meeting of experts to develop the CRP, it was discovered that a comprehensive programme on the corrosion of aluminium clad nuclear fuel was already under way at the US Department of Energy (USDOE) Savannah River Site (SRS) in Aiken, South Carolina. This programme did not involve research reactor fuel per se but was set up to address the corrosion of aluminium clad production reactor fuel, which had become caught in the nuclear pipeline when the USA decided to terminate reprocessing of the fuel in question. This programme, begun in the early 1990s to clean up the SRS spent fuel basins and to implement a corrosion monitoring and surveillance programme, was already well established at SRS. It was clear that the CRP would benefit tremendously from the experience of the SRS programme. The SRS joined the CRP, and its chief scientific investigator became a key member of the CRP supervisory group. From the beginning the CRP was designed to complement and enhance the SRS programme and to transfer knowledge gained from studies of the corrosion of production reactor fuel to research reactor fuel and vice versa.

The scientific investigations undertaken during the CRP involved ten institutes in nine countries. The IAEA furnished corrosion surveillance racks with aluminium alloys generally used in the manufacture of nuclear fuel cladding. The individual countries supplemented these racks with additional racks and coupons specific to materials in their storage basins.

The initial corrosion racks provided by the IAEA were immersed in late 1996 in water storage pools with a wide range of water chemistry and environmental conditions, and were monitored for corrosion over a period of time. The results of these early observations were reported after 18 months at the second research co-ordination meeting (RCM) of the CRP, held in São Paulo, Brazil. Pitting and crevice corrosion were the primary corrosion mechanisms observed. Corrosion by deposition of iron and other cathodic particles on the

surface of the aluminium fuel was observed in a number of basins where these particles were seen floating in the water. All corrosion mechanisms were galvanically accelerated in stainless steel–aluminium coupled coupons. Corrosion was not generally observed in those basins whose water conductivity was near 1 µS/cm and whose chloride ion concentration was in the ppb range. Pitting caused by particle deposition was seen in one case, even though the water was of the highest quality.

Additional corrosion racks were provided to the CRP participants in March 1998 at the second RCM. Most of these racks had been immersed in the individual basins by mid-1998. The surveillance racks were monitored visually for corrosion, and when corrosion was detected, the coupons were removed from the water and analysed. As found in earlier testing, water quality proved to be the key to good performance. Crevice corrosion was seen between most of the crevice couples as expected, because the pH was lower by 0.5–1.0 unit in the crevice. In poorer quality water, further corrosion was observed, especially between bimetallic crevice coupons, to the extent that coupons had to be forced apart. The results of the individual participating laboratories were presented at the third and final RCM, held in Bangkok, Thailand, in October 2000.

As already mentioned, corrosion of aluminium clad spent fuel has been studied extensively in the USA at SRS. Corrosion surveillance racks containing a large number of aluminium alloys have been immersed in four different water storage basins under a wide variety of conditions and for long times of exposure. Results similar to those obtained in the CRP were observed and are also presented in this report. Significant pitting and galvanic corrosion were observed in the early 1990s, when water quality was poor. Improved basin management procedures were undertaken and the water quality was quickly improved. Under the improved conditions, no pitting corrosion has been seen in any of the fuel storage basins at SRS since 1994.

OUTLINE OF THE REPORT

The detailed background and designs of the CRP and SRS programmes are presented in Chapter 1.

A thorough state of the art literature review on the corrosion of aluminium alloys was compiled by the IAEA in 1998. This review was published in IAEA-TECDOC-1012, Durability of Spent Nuclear Fuels and Facility Components in Wet Storage. It covered a wide range of quantitative and semi-quantitative data on cladding alloys used in nuclear fuel elements and assemblies, and included separate sections on corrosion of aluminium, zirconium, stainless steel, carbon steels and copper alloys in a wet storage

environment. Relevant sections of this document that apply to the aluminium alloys and fuels predominantly used in fuel for research and test reactors have been updated and are presented in Chapter 2. This chapter contains a discussion of the fundamentals of aluminium alloy corrosion in the wet storage of spent nuclear fuel throughout the world, examines the effects of variables in the storage environment and presents the results of corrosion surveillance testing activities at SRS, as well as discussions of fuel storage basins at other production sites of the USDOE.

On the basis of the knowledge gained during the CRP and the corrosion surveillance programme at SRS, a fundamental understanding of the corrosion of aluminium clad spent fuel has been developed. From this understanding, guidelines for the corrosion protection of aluminium cladding alloys have been developed. These guidelines are presented in Chapter 3.

Chapter 4 presents the details of the corrosion coupons, racks and experimental protocols developed for the CRP.

Chapters 5–13 present the individual reports of the participating institutes, with the exception of SRS results, which have been incorporated into Chapters 1–3. Each report originally contained photographs of the corrosion racks and coupons as well as descriptions of the alloys and their preparation, and the as-received surface features of the coupons. Since this information is discussed in detail in Chapter 4, the participants' reports have been revised to avoid repetition where possible, without removing important technical data. An initial attempt was made to investigate the corrosion weight gain/loss data of individual coupons. This required disassembly of the coupon racks for weighing and reassembling, which disrupted long term localized corrosion data. Since general corrosion has never been a serious problem in fuel storage basins, the early weight gain/loss data have not been included here.

GENERAL COMMENTS ON THE CRP

(a) The pH of the water and the specimens inside the glass ampoules provided to each participant did not show any changes. These specimens were designed to evaluate radiation effects.
(b) The colour of the exposed aluminium alloy surfaces varied from metallic bright to dark grey. The extent to which the surfaces darkened was dependent on the alloy composition.
(c) Sediments were observed on the top surfaces of many coupons.
(d) A number of participants reported corrosion along the outer rim of the coupons. This would be expected from end grain attack on cut surfaces.

(e) The highly polished coupons were more resistant to corrosion than the as-machined coupons.

(f) The crevice/bimetallic couples were often stuck together with corrosion products and required forcible separation.

(g) The pH in the crevice was generally 0.5–1.0 unit less than in the bulk water.

(h) Pits of <0.5 mm diameter were observed on the aluminium at regions in contact with the ceramic separator.

(i) Sediments on the top surfaces of aluminium alloy coupons caused pitting. No pits were observed on the bottom surfaces of these coupons.

(j) Surface features of coupons exposed for 13 months were similar to those of coupons exposed for 25 months. This timescale had no significant effect on aluminium coupon corrosion.

(k) The crevices of the aluminium alloy couples were stained but not pitted, whereas the aluminium–stainless couples were heavily pitted.

CONCLUSIONS

A large database on corrosion of aluminium clad materials has been generated from the CRP and the SRS corrosion surveillance programme. An evaluation of these data indicates that the most important factors contributing to the corrosion of the aluminium are:

(1) High water conductivity (100–200 µS/cm);

(2) Aggressive impurity ion concentrations (Cl⁻);

(3) Deposition of cathodic particles on aluminium (Fe, etc.);

(4) Sludge (containing Fe, Cl⁻ and other ions in concentrations greater than ten times the concentrations in the water);

(5) Galvanic couples between dissimilar metals (stainless steel–aluminium, aluminium–uranium, etc);

(6) Scratches and imperfections (in protective oxide coating on cladding);

(7) Poor water circulation.

These factors operating both independently and synergistically may cause corrosion of the aluminium. The single most important key to preventing corrosion is maintaining good water chemistry. Water conductivity near 1 µS/cm generally ensures that aggressive impurity ions such as chlorides are in the ppb range. When chemistry is maintained in this regime, corrosion of aluminium alloys is minimized.

Good water chemistry alone does not always guarantee that corrosion will be prevented, as shown by the extensive testing conducted in the Argentine

storage pools, where iron oxide particles deposited from the water caused pitting even in high purity water. This has also been seen in other fuel storage basins. Corrosion mechanisms involved in this pitting can be both galvanic and oxygen depletion cells.

The CRP has succeeded in making all the participating countries more aware that the successful wet storage of aluminium clad spent fuel does not come about automatically but requires diligence in maintaining high quality water conditions. Moreover, from papers written and published during the CRP by the participants and from the presentation of some of the results at international conferences, the whole research reactor community is now more fully aware of the susceptibility of aluminium cladding to localized corrosion and the measures that can be taken to minimize it.

RECOMMENDATIONS

Any continuation of the research initiated during this CRP should concentrate on fuel storage basins that have demonstrated significant corrosion problems and will therefore provide additional and much needed insight into the fundamentals of localized corrosion. A better understanding of the fundamental mechanisms will allow the prediction of corrosion rates under different combinations of environmental parameters, enabling storage pool operators to better control those parameters essential to the safe and efficient interim storage of aluminium clad spent fuel.

More comprehensive research is recommended in the following areas:

(a) Evaluation of the effect of dust sediments on the corrosion of coupons and its implication for the corrosion of fuel cladding;
(b) Identification of the different aluminium alloys and other metals presently in use in spent fuel basins and experiments designed to evaluate the effect of specific bimetallic couples;
(c) Evaluation of the effect of hydrodynamic conditions on coupon and fuel cladding corrosion;
(d) Evaluation of the effects of water quality parameters on localized corrosion of aluminium fuel cladding in the wide range that exists between known poor water chemistry conditions and optimum conditions.

Chapter 1

BACKGROUND OF THE IAEA
CO-ORDINATED RESEARCH PROJECT

1.1. INTRODUCTION

Test and research reactor fuel is currently being shipped from within the United States of America and from locations all over the world for interim storage in water filled basins at the Savannah River Site (SRS) in Aiken, South Carolina, USA. The fuel was provided by the USA to many of the countries as a part of the Atoms for Peace programme in the early 1950s. Now, as part of the non-proliferation policy on foreign research reactor spent nuclear fuel of the US Department of Energy (USDOE), much of this fuel is being sent back from research and test reactors in Europe, Asia and Latin America. This fuel has been in water storage at the reactor sites for times ranging from a few years to over 40 years. Most of the fuel assemblies were manufactured from U–Al alloy and clad with aluminium. The quality of water in the fuel storage basins ranges from highly deionized water to untreated and uncirculated water. In the latter extremely aggressive environments, the aluminium clad fuel is very susceptible to pitting corrosion. In the early 1990s, corrosion of aluminium clad fuel was an issue at several of the storage basins in the USA, and has also been seen on materials test reactor (MTR) type research reactor fuel scheduled for shipment back to SRS [1.1].

With aluminium clad fuel corrosion issues starting to appear in wet spent fuel storage basins around the world, the IAEA formulated a corrosion surveillance programme in late 1994. This scientific investigation was implemented in 1996 as part of an IAEA Co-ordinated Research Project (CRP) on Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water. Scientists from countries worldwide were invited to participate [1.2]. The results of the CRP were presented at a final research co-ordination meeting (RCM) in Bangkok, Thailand, in October 2000 and are documented in Chapters 5–13.

This report is a summary and overview of the scientific investigations of this CRP as carried out in the nine participating countries. The results of corrosion surveillance activities in the individual fuel storage basins of these countries are discussed in detail. On the basis of the knowledge gained from the overall results of this project, a set of Guidelines for Corrosion Protection of Research Reactor Aluminium Clad Spent Nuclear Fuel in Interim Wet Storage were developed and are presented in Chapter 3.

1.2. STORAGE OF RESEARCH AND TEST REACTOR SPENT FUEL WORLDWIDE

According to the IAEA database on Nuclear Research Reactors in the World, as of October 2003 there were 272 research reactors in operation, with 214 reactors shut down, 168 decommissioned, 9 under construction and 8 in the planning stages [1.3]. It is instructive to see how these are divided between the developed or industrialized countries of the world and the developing countries. In the industrialized countries, there are 193 research reactors in operation, with 230 reactors shut down, 106 decommissioned, 4 under construction and 3 in the planning stages, while in the developing countries, there are 85 in operation, with 28 shut down, 12 decommissioned, 5 under construction and 5 in the planning stages. The age distribution of operating research reactors peaks at between 35 and 40 years, with 61% of them more than 30 years old. The most common form of spent fuel storage for these research reactors is at-reactor pools or basins. Some of the reactors have auxiliary away-from-reactor pools or dry wells. At some of these auxiliary facilities, the trend has been to shift some fuel from wet to dry storage to avoid the expense of water treatment facilities and maintenance.

Many of the spent nuclear fuel assemblies from Western research reactors are MTR box type, involute plate, tubular, rod cluster or pin assemblies. A typical MTR type fuel assembly is shown in Fig. 1.1. Russian designed research reactors utilize fuel assemblies of different geometrical types, which can be divided into two main groups — multitube assemblies and multirod assemblies. Most of the fuel core is manufactured from U–Al alloy initially enriched to ≥20% (HEU) or <20% (LEU). The cladding alloys of Western fuel types are usually 6061 or 1100 grade aluminium[1.1] ranging in thickness from 0.375 to 0.75 mm. The irradiated aluminium clad assemblies are generally stored in light water filled basins where the corrosion resistance of the aluminium is usually good as long as the water chemistry is maintained at high purity levels. If corrosion is a problem, it is usually in the form of pitting. The most important water parameters affecting the corrosion of these alloys are normally conductivity and aggressive impurity (e.g. chloride ion) concentrations. A tightly adhered aluminium oxide (boehmite) coating formed on the fuel plates during irradiation provides extra corrosion protection in basin storage as long as it remains intact.

As part of the USDOE's programme to bring research reactor fuel back to the USA, engineers from SRS inspected the spent fuel for corrosion and

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[1.1] In this book, the numbers given for aluminium alloys refer to the Aluminum Association (AA) specifications.

FIG. 1.1. Typical MTR type spent nuclear fuel element.

FIG. 1.2. Nodular corrosion products and exposed pits on MTR type spent nuclear fuel.

mechanical damage [1.4]. Over 1700 aluminium clad assemblies were individually examined using video and underwater cameras to record their condition at the fuel storage sites. A wide range of physical conditions of these spent nuclear fuel assemblies were observed. Many of the assemblies after 20 years of storage were in pristine condition. Other fuel assemblies had extensive nodular corrosion products clearly visible on the outer fuel plates, as seen in Fig. 1.2.

Removal of the nodules revealed extensive pitting corrosion that had breached the 0.375 mm aluminium cladding. Pitting corrosion that had penetrated the aluminium cladding to the fuel meat was found on approximately 7% of the total number of assemblies inspected by SRS.

In addition to visual inspection of fuel stored in research reactor basins outside the USA, gamma spectroscopy was used to measure the radionuclide release from the U–Al fuel in water. Water samples were drawn from the

shipping cask, which contained 40 assemblies, before and after a 4 h minimum rest time. Measurements of the ^{137}Cs activity in the cask water were used to determine a difference of about 10 pCi (0.37 Bq)/mL, corresponding to a release rate of 0.9 µCi (3.33×10^4 Bq)/h into a 100 gallon (379 L) cask. Even though the fuel had known cladding penetrations, the release of radioactivity from this U–Al alloy fuel was found to be barely detectable and was far below the SRS site limit of 20.7 µCi (7.66×10^5 Bq)/h per cask [1.5].

1.3. IAEA CO-ORDINATED RESEARCH PROJECT

In December 1994, a meeting of corrosion experts was held at IAEA Headquarters in Vienna as part of an ongoing CRP entitled Irradiation Enhanced Degradation of Materials in Spent Fuel Storage Facilities. During this meeting, spent fuel corrosion issues at SRS and other sites in the USA were discussed by the SRS participant with the IAEA and the European participants.

In the early 1990s, corrosion of aluminium clad spent nuclear fuel stored in light water filled basins became a major concern, and programmes were implemented at the sites to improve fuel storage conditions. The Savannah River Technology Center (SRTC), along with the Spent Fuel Storage Division at SRS, established a corrosion surveillance programme in support of shipment of the research reactor fuel. Details of this 20 year programme were presented. As a result of these discussions and the recommendations of an advisory group, the IAEA established the CRP on Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water. The CRP was designed to address several issues raised by vulnerability assessments conducted at some of the spent fuel storage sites. Its objectives were to:

(a) Establish uniform practices for corrosion monitoring and surveillance;
(b) Provide a technical basis for continued wet storage of research reactor spent fuel;
(c) Collect data to help in the prediction of lifetimes of fuel handling tools and storage racks;
(d) Establish a uniform basis for the characterization of water in fuel storage basins.

Nine countries — Argentina, Brazil, China, Hungary, India, Pakistan, the Russian Federation (two different sites), the USA and Thailand — were invited by the IAEA to participate in the CRP. Research agreements or contracts with institutes in these countries were put in place for work to be performed, and the IAEA provided a detailed work package and standard corrosion test coupons to each participant.

The CRP was based on a corrosion surveillance programme developed and planned for several USDOE spent fuel storage basins in the USA. The proposed US programme was an extensive national effort to monitor the corrosion of different aluminium alloys in racks at storage basins at SRS, the Idaho nuclear site, USDOE Hanford and the West Valley site. The US programme was essentially implemented at SRS, but the other sites opted for smaller individual programmes [1.6]. With a limited budget, the IAEA version of the corrosion monitoring programme was necessarily smaller and was scaled down with respect to the number of racks and coupons. The programme, however, designed to develop basic information on the corrosion of aluminium clad alloys in spent fuel storage environments and to increase awareness of the fact that water quality is the key to successful long term storage of spent nuclear fuel.

1.3.1. Details of the corrosion monitoring programme

The materials selected for testing were representative of typical aluminium cladding alloys used in research reactor fuel, handling tools and storage racks. Aluminium alloy types 5086, 1100, 6061, 6063 and SZAV-1 (throughout this book, aluminium alloys are referred to by their Aluminum Association (AA) numbers), and stainless steel type 316 were produced by the KFKI Atomic Energy Research Institute (AEKI) in Budapest, Hungary, for use by the participants. A single heat of each alloy was used to make the test coupons. In addition to the IAEA rack of corrosion coupons, many of the participants immersed an additional rack in their basins. This rack consisted of coupons of alloys specific to their research reactor fuel and handling tools. Chapter 4 provides a more detailed discussion of the racks and testing protocol.

Test plans for the monitoring were specific to the individual sites and included details for the assembly, exposure, disassembly and evaluation of the coupons. As a minimum evaluation, each site was asked to weigh, clean and photograph each coupon before exposure, and each assembled coupon rack before and after exposure. Detailed metallurgical evaluation of any corrosion was suggested where possible.

Each participant was requested to measure the parameters of their basin water on at least a quarterly basis. The following parameters were to be measured, if possible: temperature, pH, conductivity, chlorides, nitrates, nitrites, sulphates and basin radioactivity. Investigating the correlation between corrosion of the coupons and water parameters was one of the overall goals of this project.

1.3.2. Initiation of the Co-ordinated Research Project

The first RCM of the CRP was held in Budapest on 7–9 August 1996 at AEKI. The nine countries invited to participate were carrying out storage of aluminium clad spent fuel in water filled basins. A presentation was made by each participant describing the current status of the research reactors in their countries and the condition of the spent fuel stored in their basins. The condition of the fuel ranged from being corrosion free in some cases to showing extensive nodular corrosion in others. The SRS corrosion surveillance programme, which served as a model for the IAEA project, was discussed in detail. In addition, a representative from PNNL made a presentation on fuel cladding and storage component corrosion experience at the Hanford site.

Details of the research to be conducted during the CRP were presented by the IAEA and each participant was given one corrosion rack to take back to their individual reactor and fuel storage sites. The first RCM of the CRP was successful in terms of the extensive technical exchange among the scientists from the participating countries. Plans were developed in Budapest to hold the second RCM after about 18 months of research. Communication by e-mail was selected as the means to address issues and answer questions among the scientists and the IAEA during the CRP.

1.3.3. Monitoring corrosion racks at research reactor storage basins

After the first RCM, the participants formulated individual test plans specific to their spent fuel storage basins. A general test protocol for conducting the programme was provided by the IAEA. This protocol included instructions for preassembly, assembly and immersion of the corrosion racks in the storage basin, exposure intervals, and removal and examination.

The individual participants were asked to prepare the corrosion racks and to begin the exposure as soon as possible. Most of the racks were assembled and immersed in fuel storage pools well before the end of 1996. Because of the limited number of racks available, participants were asked to make periodic visual examinations of the coupons to determine whether active corrosion was obvious. If corrosion was visible, the racks were to be removed from the water and the coupons photographed. The racks were then returned to the basin for additional exposure. Water chemistry measurements were made on a periodic basis and monthly visual inspections were performed by most of the participants.

1.3.4. Results

The second RCM was held in São Paulo, Brazil, in March 1998, and the third and final RCM in Bangkok, Thailand, in October 2000. Each participant presented his/her test results at these meetings. A brief summary of the presentations is given below. The final reports of the individual countries are given in Chapters 5–13, with the exception of the SRS results, which have been incorporated into Chapters 1, 2 and 3. Each report originally contained photographs of the corrosion racks and coupons as well as descriptions of the alloys, their preparation and the as-received surface features of the coupons. Since this information is discussed in detail in Chapter 4, the participants' reports have been revised to avoid repetition where possible, without removing important technical data. An initial attempt was made to investigate corrosion weight gain/loss data of individual coupons. This required disassembly of the coupon racks for weighing and reassembling, which disrupted long term localized corrosion data. Since general corrosion has never been a serious problem in fuel storage basins, the early weight gain/loss data have not been included here.

1.3.4.1. Comisión Nacional de Energía Atómica, Centro Atómico Constituyentes (CNEA-CAC), Buenos Aires, Argentina

Rack 1 was immersed in one of the open channels at the Central Storage Facility (CSF), in Ezeiza, at about one metre from a spent fuel assembly and sharing the same water. The rack was inspected after 60 days of exposure and was found to be coated with a thin brownish layer along with some dark particles. Corrosion products were visible on a number of coupons. Several white nodules were observed that, when cleaned, revealed pits in the base metal. Pitting was associated with the particles. Crevice coupons were stuck together and were difficult to separate because of corrosion. Teflon spacers were used to centre the rack in the cylindrical channel. There was extensive crevice corrosion under these spacers. The SZAV-1 aluminium alloy showed a lesser tendency to corrode and the 6061 aluminium–stainless steel galvanic couples showed the highest. The water quality was aggressive for the storage of aluminium clad alloys, with a conductivity of 74 µS/cm and a chloride ion content of 14.8 ppm.

In mid-1998, six additional racks containing aluminium crevice and galvanic couple coupons were immersed at the CSF, in the RA3 decay pool, the RA6 reactor pool and the RA6 decay pool. These different pools provided a wide range of water chemistry conditions. Conductivity ranged from 227 µS/cm at the CSF down to 1.8 µS/cm in the RA6 reactor pool. The chloride ion content ranged from 16 ppm at the CSF to less than 0.5 ppm in the reactor pool. The

racks immersed in the basins included coupons provided by the IAEA and aluminium alloy coupons used in the manufacture of Argentine fuel. Some racks were removed and examined in August 1999 and others in February, July and September 2000. Severe pitting and crevice corrosion were noted on most of the aluminium coupons at the CSF, where the water was the most aggressive. Much of this pitting on the external surfaces was caused by the deposition of what was thought to be iron oxide particles from the corrosion of the carbon steel cover plates.

Some pitting was noted even in the high purity water of the RA6 reactor pool. This pitting was always associated with deposited particles. Pits of 1–2 mm in diameter were produced in waters with no detectable amounts of chloride or sulphate and with a conductivity of less than 2 µS/cm. The particles were thought to be iron oxide and were cathodic to the aluminium. Conditions inside some of the crevices resulted in oxide patches. Other areas seemed pickled, possibly by acidification of the water within the crevices. Small pits (0.1 mm in diameter) were found inside these crevices. The results of these investigations showed that the basin storage environment contained floating particles and it was not always possible to associate the degree of pitting with water composition.

1.3.4.2. *Instituto de Pesquisas Energéticas e Nucleares (IPEN), São Paulo, Brazil*

Some visible nodular corrosion products were observed on the external fuel plates of some assemblies stored in the basin, despite a history of good water chemistry. Galvanic couples from two possible sources may have accelerated the corrosion — the first between stainless steel racks used to store the fuel assemblies and the fuel cladding, and the second due to the presence of silver ions in the water that may have plated out on the aluminium surfaces. The IAEA coupon rack was immersed in September 1996. Water conductivity was maintained at <2.0 µS/cm and the pH was maintained in the range 5.5–6.5. The chloride ion concentration was <0.2 ppm during the exposure period. No corrosion spots were observed on the coupons. The first inspection of the racks was conducted after about six months. All three bimetallic/crevice coupons were stuck together, requiring forcible separation. The aluminium coupons were coated with a grey/white deposit typical of aluminium oxide. The pH was measured inside the crevice and it ranged between 4.0 and 4.5 (acidic). The glass ampoules had a brownish tint, indicative of radiation damage. After these observations, the coupons were reassembled and returned to the basin for continued exposure. After an additional year of immersion, the rack was taken

out of the water at a demonstration during the São Paulo RCM. It was disassembled and examined visually. The white oxide was observed in the crevice. In addition, small metallic particles were embedded on the surface of some of the aluminium coupons. The particles were believed to be cathodic, and possibly iron, as a halo existed around the particle/pit. This halo area was shiny and appeared to be free of corrosion.

IAEA racks 2 and 3 were immersed in the basin in August 1998 and were removed in October 1999. Examination of the coupons revealed a few small pits within the crevices of the bimetallic coupons and more pits at the contact points with the ceramic insulators used to separate the coupons. Some loose deposits were seen on the top surfaces of the coupons. The top surfaces of the 1100/1100 couples had such deposits and more than 50 pits of less than 1 mm diameter. The bottom surfaces were free of pits.

An IPEN rack containing 1060, 6061 and 6262 alloys, used in fuel assembly manufacture, was also immersed in the basin. After 16 months of exposure, it was observed that some pitting had occurred on the uncoupled coupons, mostly on the top surfaces. The aluminium couples were stained inside the crevices but were not pitted. The stainless steel–aluminium galvanic coupons were much more severely corroded. Additional laboratory tests were conducted to determine whether increased levels of silver in the basin water could have increased the corrosion of the aluminium cladding in the IPEN basin. Results indicated no pitting but an increase in darkness of the surface oxide colour with the increase of silver concentration.

1.3.4.3. China Institute of Atomic Energy, Beijing, China

Five racks were immersed in the spent fuel storage pool, including the rack provided by the IAEA in 1996. The basin water was not constantly circulated and it was purified once a year using an ion exchange system. The conductivity of the basin water ranged from 3 to 10 μS/cm and the chloride ion content was <0.1 ppm. A dark grey oxide layer, from general oxidation, developed on most of the outer surfaces of the coupons in contact with the water. The colour darkened and the layer thickened with time. Crevice corrosion products formed in the crevices between coupons. No pitting was observed on coupon surfaces, but some pitting occurred on the outer rim of the coupons owing to the edge effect.

1.3.4.4. KFKI Atomic Energy Research Institute, Budapest, Hungary

The first inspection and evaluation of the coupons was performed after six months of exposure, in November 1997. The second inspection was carried

out after one year of exposure, in May 1998. Racks 2 and 3 were immersed in the basin in May 1998. Rack 2 was removed in May 1999 and rack 3 in May 2000. The results of the inspections carried out after 6, 12 and 24 months of exposure to the basin water are presented and discussed in Chapter 8. The results obtained from racks 2 and 3 revealed no significant differences between the coupons immersed for one and two years in the pool water.

The results obtained from the evaluation of rack 1 coupons indicate that some corrosion processes were taking place. There were differences in corrosion resistance between the different aluminium alloys. Corrosion of these alloys in the water at the KFKI spent fuel storage pool was probably more dependent on the materials than on the duration of exposure to the pool water. The duration of one to two years is probably insufficient to show major differences in high quality water.

1.3.4.5. Bhabha Atomic Research Centre, Trombay, India

Rack 1 was immersed in the Mumbai fuel storage basin on 16 January 1997. It included a sample of Al–1S alloy fabricated at the research centre and used as a galvanic couple sample. After eight months, the rack was removed from the water and inspected. Several of the crevice coupons were taken apart, and the pH inside the crevice was measured and found to be 3–4, while the bulk water pH was 5. Some staining was noted inside the crevice. The Al–1S sample coupled to stainless steel showed some white corrosion products on the rim of the sample. Other coupons showed no visible corrosion. The second inspection was made in February 1998 after 13 months of exposure. The rack and coupons were generally free of corrosion products, except for some white product on the rim of the Al–1S specimen and some corrosion inside the crevice. The water conductivity ranged from 2 to 16 µS/cm and the pH from 5.9 to 6.3 during the test. Chloride ion content was always <2.0 ppm. The two additional racks received at the second RCM were immersed in the pool water in July 1998 and removed in August 2000, with an intermediate visual inspection in July 1999. Individual coupons on these racks had a mirrorlike surface finish. The racks had a total exposure of 742 days.

The coupons were disassembled and photographed during the intermediate inspection. Unlike the coupons received at the Budapest RCM, which had only a machined surface finish, these highly polished coupons showed no deep pits or crevice corrosion. Basin water conductivity was maintained at 3.5–16 µS/cm, with a chloride ion content of less than 2 ppm. The excellent corrosion resistance of these coupons was attributed primarily to the surface finish and the improved purity of the water.

1.3.4.6. Pakistan Institute of Nuclear Science and Technology, Islamabad, Pakistan

Rack 1 was inserted on 12 November 1996 and was withdrawn for a short time on a monthly basis for visual inspection. No pitting corrosion was seen on any coupons during the 12 inspections. The conductivity of the water ranged from 0.1 to 0.8 μS/cm, with a pH between 4.8 and 6.1. The chloride ion content was <0.5 ppm. Racks 2 and 3, which contained two galvanic couples and three crevice sandwiches, were exposed in October 1998. Rack 2 was withdrawn after one year of exposure, in October 1999. The conductivity of the basin water was always <1 μS/cm, the chloride ion content was <0.05 ppm and the pH was 5.5–6.3.

Coupons were examined every month and discoloration was noted as the coupons developed a general oxidation film with time. No pitting was ever seen on any of the exposed surfaces. Once the coupons were disassembled, some pitting was seen under the ceramic washers of the galvanic coupons. Pitting was also observed under the washers of the crevice coupons. There was no detectable visual change in the stainless steel coupons. The water conductivity was maintained at between 0.1 and 0.7 μS/cm.

1.3.4.7. Research Institute of Atomic Reactors, Dimitrovgrad, Russian Federation

The steel lined storage basin at the research reactor uses ion exchange technology to keep the water purified to a conductivity of 1.4–1.7 μS/cm and a chloride ion content of <20 ppb. Inspections of rack 1 were made after 6 and 14 months. The rack was removed from the pool and dismantled, the coupons were weighed, photographed and reassembled, and the rack was reimmersed in the basin. The coupons freely exposed to water had a uniform grey colour that is typical of general corrosion on some aluminium alloys. Some 0.02 mm deep pits were seen on the exposed surface as well as some small red and brown particles protruding from the coupon surfaces. In addition, a few small, 0.03 mm deep pits were seen at the contact line between the 100 mm disc and the 70 mm disc. There was evidence of crevice corrosion between the coupled coupons. The weight gain of the alloys as a function of time showed a parabolic behaviour in accordance with the equation $Y = ax^2 + bx + c$.

Racks 2 and 3 were disassembled, and the coupons were examined, weighed and reassembled for continued exposure. Pitting was detected only at the grain boundaries of polished coupons. This was thought to be due to grain boundary etching and not to be caused by the storage pool environment. Some crevice corrosion was noted between the crevice coupons, and some impurities

were seen on the top sides of some of the coupons without pitting. The change in mass of all aluminium coupons was measured and found to be parabolic with time, as expected from the conductivity of the water and the general corrosion or oxidation of the alloys.

1.3.4.8. Russian Research Centre, Kurchatov Institute, Moscow, Russian Federation

During the first 18 months of exposure of the rack, the water conductivity ranged from 1.9 to 7.6 µS/cm and the chloride ion concentration was between <0.05 and 0.3 ppm. The corrosion rack was immersed in the RR-8 fuel storage basin, and interim inspections were conducted after 6 and 12 months. The basin is lined with stainless steel and has aluminium storage racks. The purification system uses ion exchange filters. A uniform surface oxide with no pitting corrosion was observed during these two inspections. Subsequently, rack 1 was withdrawn at periodic intervals, disassembled and photographed up to a total exposure time of 1254 days. The coupons were weighed, examined, reassembled and immersed again. Two additional racks furnished by the IAEA were immersed in April 1998. The coupons in rack 2 were examined after 367 and 551 days of exposure and those in rack 3 after 725 days of exposure. These coupons were also weighed, photographed and examined for corrosion.

On most of the coupons, general corrosion resulted in a dull grey–white film, with additional corrosion products within the crevices. No pitting corrosion was seen on the outer surfaces of the coupons, except on the outer rim of some of the 6061 crevice coupons and the 6063–AISI 316 galvanic coupons. Corrosion along the rim is quite common, as machined, high energy surfaces are more prone to corrosion. No corrosion was observed on the aluminium specimens inside the glass ampoules. The water and glass were clear, indicating no radiation effects.

1.3.4.9. Office of Atomic Energy for Peace, Bangkok, Thailand

The rack was immersed in the fuel storage pool in November 1996. The coupons were examined visually every 30–40 days for the first six months. During the first inspection, carried out after 40 days, the crevice coupons were found to be stuck together. A few corrosion nodules were detected after about four months. After six months of exposure, metallographic examination of three coupons was carried out, and the maximum pit depth was found to be 10–40 µm. On the crevice side, the pit density was higher (4–6 pits/cm^2) than on the non-crevice side (1 pit/cm^2). However, the pits on the non-crevice side were deeper. The 1100 coupons had higher corrosion resistance than the SZAV-1

alloy, and 6061 exhibited the highest corrosion of the three aluminium alloys. The water conductivity ranged between 1.5 and 4.8 μS/cm, the pH between 6 and 8, and the chloride ion concentration between 0.1 and 0.8 ppm.

Two additional racks of corrosion coupons were immersed in the fuel storage pool in March 1998. The conductivity of the water ranged between 1 and 6 μS/cm during the exposure period and the chloride ion content was between 0.1 and 0.5 ppm. No pitting corrosion was observed on the exposed surfaces of the coupons, except along the outer rim.

1.3.5. General comments on the CRP

(a) The pH of the water and the specimens inside the glass ampoule did not show any change. These specimens were designed for the evaluation of radiation effects.
(b) The colour of the exposed aluminium alloy surface varied from metallic bright to dark grey. The extent to which the surface darkened was dependent on the alloy composition.
(c) Sediments were observed on the top surfaces of many coupons.
(d) A number of participants reported corrosion along the outer rim of the coupons. This would be expected from end grain attack on cut surfaces.
(e) Highly polished coupons were more resistant to corrosion than the as-machined coupons.
(f) The crevice/bimetallic couples were often stuck together with corrosion products and required forcible separation.
(g) The pH in the crevice was generally 0.5–1.0 unit less than in the bulk water.
(h) Pits of less than 0.5 mm diameter were observed on the aluminium in regions in contact with the ceramic separator.
(i) Sediments on the top surfaces of aluminium alloy coupons caused pitting. No pits were observed on the bottom surfaces of these coupons.
(j) The surface features of coupons exposed for 13 months were similar to those of coupons exposed for 25 months. This timescale had no significant effect on aluminium coupon corrosion.
(k) The crevices of the aluminium alloy couples were stained but not pitted, whereas the aluminium–stainless steel couples were heavily pitted.

1.4. SRS CORROSION SURVEILLANCE PROGRAMME

The corrosion surveillance programme at SRS was established in 1992 to monitor production fuel in on-site spent fuel storage basins [1.7]. This extensive

programme, still in progress, has helped to increase understanding of the corrosion of aluminium clad spent fuels. The data from corrosion surveillance coupons in the SRS basins, the SRTC laboratory tests and detailed reviews of aluminium alloy corrosion from the literature have been documented in a number of publications. Some of the data are included in this report. The data from the SRS surveillance programme have been shared with the IAEA CRP with a view to increasing the understanding of aluminium corrosion and developing a basis for corrosion protection of spent fuels. A description of the SRS programme and the main results are presented below.

1.4.1. Background

In 1989, processing of aluminium clad production fuel was suspended at SRS in order to carry out safety upgrades at reprocessing facilities located in Canyon F and because of issues related to US non-proliferation concerns. The irradiated fuel and target materials were caught in the back end of the nuclear pipeline with no plans for processing. Normal water storage times of 9–18 months became years. Also, with less than optimum water quality during the early 1990s, pitting corrosion of the fuel (Fig. 1.3) became an issue at SRS and at other USDOE sites [1.8]. An extensive programme was initiated at SRS to clean up the storage basins and to install new water purification equipment. At the same time, a corrosion surveillance programme was started to monitor the fuel stored in the basins and to measure the effectiveness of the cleanup activities. The results of these surveillance activities up to 2000 are reported in a number of publications [1.9–1.11].

FIG. 1.3. Nodular corrosion on aluminium clad U–Al alloy fuel.

The SRS corrosion surveillance programme was expanded in 1996 to support the decision of the USA to bring back about 15 000 foreign research reactor fuel assemblies for storage in the Receiving Basin for Off-Site Fuel (RBOF) and the L Reactor basin. In addition, the IAEA extended the scope of its spent fuel management programme to include programmes focused specifically on spent fuel from research and test reactors.

1.4.2. Component immersion tests

The corrosion surveillance programme at SRS, established in 1992, was initiated at a time when corrosion of fuel cladding and aluminium components became evident for the first time. Detailed discussions of the surveillance activities have been presented in Ref. [1.9]. The programme was initially set up to monitor the production fuel and target material from the last irradiation campaigns in the P, K and L Reactors at SRS. The programme was expanded to include the RBOF, in which all the fuel received from off-site locations around the world was stored.

The initial corrosion test racks were made with tube ends cut from unirradiated fuel and target tubes (Fig. 1.4) They were pretreated to 95°C in deionized water for 30 h to develop a 1 μm thick high temperature boehmite (aluminium oxide) layer on the surfaces.

The racks were initially placed in the K Reactor basin only. There were five withdrawals during 1992, and aggressive pitting corrosion was detected on the surveillance coupons. Pitting corrosion penetrated 0.75 mm, equivalent to a
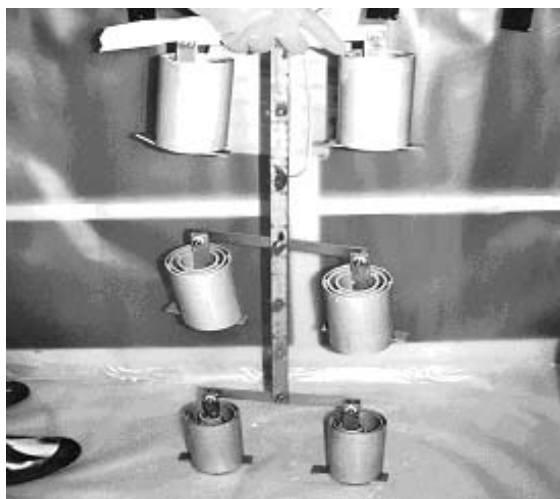
FIG. 1.4. Component immersion test rack.

fuel cladding thickness, into 8001 alloy in 45 days and into 1100 alloy in about six months. During this time the basin water conductivity was approximately 200 µS/cm and the average chloride content was about 8 ppm. Owing to the aggressiveness of the water towards aluminium components stored in the basin, a new basin management programme was initiated to improve the quality of the environment.

A major effort was initiated to deionize all three reactor basins on a continuous basis using portable deionizing systems, which had been in use since the mid-1960s. This effort resulted in some improvements in all three basins, but because of the limited number and availability of portable deionizers for the three basins, the improvements were slow, and new mixed bed deionizers were acquired for the K and L basins.

The component immersion tests were expanded to include the RBOF and the P and L basins in 1993. In addition, tests were continued in the K basin. Surveillance coupons were withdrawn periodically from the four basins during 1993–1995, while continuous deionization of the water was being carried out. With water conductivity lowered to 100–125 µS/cm or less in the L and K basins and the aggressive impurity ion content reduced, no pitting corrosion was seen on corrosion coupons in these basins. The water conductivity in the RBOF has always been maintained in the 1–3 µS/cm range, with the chloride ion content in the ppb range. No pitting corrosion of surveillance coupons has ever been seen in the RBOF under these high quality water conditions. With limited deionizer availability, the water conductivity of the P basin increased to 160 µS/cm, and once again some pitting was observed. A decision was subsequently made to close the P basin and transfer the fuel stored in that basin to the L and K basins.

In the interim period before the new deionization equipment for the L and K basins was received, portable equipment was installed in July 1995 and used to lower the L basin water conductivity from 110 to below 8 µS/cm in 2.5 months. The equipment was then moved to the K basin, and within three months the conductivity was lowered to below 10 µS/cm. Continued deionization in both basins for two more months lowered the conductivity further, to less than 3 µS/cm, and the chlorides, nitrates and sulphates were lowered to about 0.5 ppm. The corrosion surveillance programme continued in the three reactor basins and in the RBOF while the basin and water quality improvements were being carried out, i.e. until mid-1996. Results of the component immersion tests through September 1997 (the last withdrawal) showed no pitting corrosion on any of the corrosion coupons. These coupons were exposed to a variety of conditions for 37–49 months as conditions improved in the basins. Table 1.1 presents a summary of component immersion tests for the period 1992–2000, when corrosion coupons accumulated exposure time in extremely high quality water and withdrawal intervals were extended.

1.4.3. Research and test reactor spent fuel corrosion surveillance

The L Reactor basin at SRS was refurbished in 2000 to receive a large number of aluminium clad research reactor assemblies from both domestic and foreign sources over the next 20 years. With this refurbishment, a comprehensive corrosion surveillance programme was developed to directly support the new extended fuel storage activity at SRS. This programme was initially intended to demonstrate that the L basin could provide a suitable environment for the long term interim storage of aluminium alloys after the basin upgrades during 1994–1996. The coupons in the RBOF, with its superb water quality, did not reveal the pitting corrosion seen earlier, in the period 1992–1993. However, the new surveillance programme was implemented in this basin to provide additional data to supplement the existing component immersion test programme.

The research reactor corrosion surveillance programme was designed to support the receipt of both domestic and foreign research reactor (FRR) fuel. The corrosion monitoring programme concentrated on aluminium alloys that are typical of the cladding materials of spent foreign reactor fuel. Fuels clad with other alloys, such as Zircaloy and stainless steels, are expected to go to another USDOE storage basin in Idaho and are not included in this programme. In addition to providing data to support fuel receipts at SRS, results from this programme complement the IAEA sponsored corrosion surveillance activities for research reactor aluminium clad spent fuels.

Tests within this programme began in both the L Reactor basin and in the RBOF in January 1996. The exposure time for alloys in the test racks was deemed adequate to determine the suitability of the reactor basin water for extended storage of the FRR aluminium clad materials. Data from this programme and laboratory corrosion testing programmes provide a technical basis for maintaining and improving basin management practices and establishing operational limits, and could aid in the prediction of fuel performance in storage basins.

1.4.3.1. Corrosion racks and test coupons

The corrosion coupons are 31.75 mm diameter discs 3.175 mm thick and with a hole in the centre to fit over an insulated stainless steel rod. Plastic insulators separate individual coupons. The coupons are not preoxidized at elevated temperature in water but have the normal air formed oxide. This condition should make them more sensitive to any water chemistry changes. Four basic types of corrosion coupon are being tested in the L basin and RBOF water environments:

TABLE 1.1. COMPONENT IMMERSION TESTS 1992–2000

Basin	Date	Exposure (d)	Maximum pit depth (mm)		Pit density (pits/cm²)		Average Cl⁻ (ppm)	NO_3 (ppm)	SO_4 (ppm)	pH	Average conductivity (µS/m)
			1100	8001	1100	8001					
1992											
K	Jul. 1992	45	0.05	1.34	0.125	0.01	8	20	15	7.5	175
K	Jun. 1992	75	0.33	1.14	0.125	0.01					
K	Mar. 1992	107	0.58	0.99	0.125	0.01					
K	Jun. 1992	182	1.47	0.70	0.125	0.01					
K	Dec. 1992	365	2.54	1.45	0.125	0.05					
1993–2000											
K	Mar. 1994	65	No pitting								
K	Jul. 1994	181									
K	Feb. 1995	403					6	18	9	7.3	125
K	Aug. 1995	590									
K	Aug. 1997	1091					<0.1	<0.1	<0.1	7.25	2.5
K	Feb. 1999	1240	No pitting							6.9	3.5
K	Jan. 2000	1590	No pitting				<0.1	<0.1	<0.1	6.8	2.7
L	Nov. 1993	61	No pitting								
L	Mar. 1994	127									
L	Jul. 1994	241									
L	Feb. 1995	336					14	20	2	6.6	102

TABLE 1.1. (cont.)

Basin	Date	Exposure (d)	Maximum pit depth (mm)		Pit density (pits/cm^2)		Average Cl$^-$ (ppm)	NO$_3$ (ppm)	SO$_4$ (ppm)	pH	Average conductivity (µS/m)
			1100	8001	1100	8001					
L	Aug. 1995	340									
L	Aug. 1997	1114					<0.1	<0.1	<0.1	6.6	1.8
L	Feb. 1999	1240	No pitting							6.5	1.0
L	Jan. 2000	1470	No pitting				<0.1	<0.1	<0.1	<0.1	0.84
P	Nov. 1993	61	No pitting								
P	Mar. 1994	127									
P	Jul. 1994	241									
P	Feb. 1995	336	1 mm pits in 8001				10	9	18	7.5	160
P	Sep. 1995	715	No pitting								
RBOF	Sep. 1997	1222	No pitting				0.1			6.19	1.18
RBOF	Mar. 1999	1290	No pitting							6.5	1.0
RBOF	Aug. 1995	480	No pitting				0.2	1.5	0.5	7.4	1
RBOF	Apr. 1996	723	No pitting								
RBOF	Feb. 2000	1260	No pitting				<0.1	<0.1	<0.1	6.9	<0.1

(a) Standard alloy — circular disc;
(b) Welded alloy — circular disc;
(c) Galvanic couples — circular discs with a 4:1 cathode to anode area ratio;
(d) Crevice — pairs.

On the basis of the current inventory of fuel in the RBOF and the information about incoming research reactor fuel, alloys 1100, 6061 and 5086 are the main fuel cladding alloys expected to be stored in the basin. The welded and galvanic coupons will be mainly 1100 and 6061. Some 304L stainless steel coupons are included in the galvanic couple tests to represent potential interactions encountered in most storage basins around the world. Several examples of each type of coupon are included in each corrosion rack. Each rack contains 60 coupons. Figure 1.5 is a photograph of the FRR corrosion surveillance rack.

1.4.3.2. Schedule for withdrawal and analysis

Eighteen corrosion racks were initially available for the SRS research reactor corrosion surveillance programme. Twelve racks were immersed in two different areas of the L basin. Six racks were immersed in the RBOF to support the programme, which is currently scheduled to last for 20 years. The corrosion monitoring programme was initially designed to provide data after six months, one year, two years, five years, ten years and 20 years of exposure. Duplicate racks are scheduled for examination at the end of each predetermined exposure time. The first three withdrawals up to the end of two years of exposure were designed to provide an early indication of the aggressiveness of the storage environment for the aluminium coupons.

FIG. 1.5. FRR corrosion surveillance rack.

A new, simplified corrosion rack was designed in early 1999 to supplement the existing programme. The new rack contained fewer coupons of the aluminium alloys, with crevice and some galvanic coupons. This rack was designed for withdrawals in years where no scheduled withdrawals were planned in the original programme. Fifteen additional racks were immersed in the RBOF and the L Reactor basin in February 1999, and a new schedule of withdrawals was drawn up. It calls for a minimum of one withdrawal per year over the 20 year programme. Along with colour photography and metallurgical examination of the coupons, a detailed characterization of the basin water during the exposure period will be obtained from the existing water sampling and analysis programme. The water conductivity, pH, and chloride, nitrate, nitrite and sulphate contents will be recorded.

1.4.3.3. Results

A total of six racks were withdrawn from the two basins during 1996–1997. These racks were withdrawn after six and 12 months of exposure. Out of the 360 individual coupons examined during the first year of exposure, pitting was observed on four coupons, as shown in Fig. 1.6. Further detailed investigations on these coupons using scanning electron microscopy showed iron filings embedded on the surface of the aluminium. These iron particles were cathodic with respect to the aluminium coupon, causing localized attack on the aluminium and shallow pitting. Once a pit developed in the aluminium, the iron particle dropped out, leaving a round, shallow pit. Subsequent

FIG. 1.6. Pitting caused by embedded iron filings.

discussions with the vendor that supplied the corrosion coupons indicated that the iron particles were probably embedded during the polishing process. No pitting was seen on any coupons without embedded iron filings.

Three additional racks were removed from the L basin and from the RBOF in early 1998 after two years of exposure to water with a conductivity of 1–3 μS/cm and a chloride ion content in the ppb range. No pitting was observed on the other 180 coupons in these racks. Some mild oxidation of the surfaces was seen on all coupons. Some mild surface reaction was seen in the crevice area of the stainless steel–aluminium galvanic couple coupons. A number of the large aluminium coupons had areas on which the surface appeared to be protected from oxidation during immersion in the basin water. These areas can be seen in Fig. 1.7. In these areas, the aluminium surface was similar in colour to the areas of the specimen covered by an insulator or between crevice specimens that had not been exposed to the water. The remainder of the coupon surface exposed to the water was dark grey in colour.

On these coupons, protection from surface oxidation may possibly have been provided by a tightly adhered biofilm or by some coating left over from coupon manufacturing. The existence of a biofilm on aluminium coupons has been shown in other microbiological characterization work done in the RBOF [1.12]. No localized attack was observed in these passivated areas of the coupon.

Additional coupons were withdrawn from the K and L Reactor basins and from the RBOF in January 2000. After more than four years of exposure, the coupons were generally oxidized and discoloured, but no unexpected pitting was observed. A few coupons from the RBOF showed shallow pits due

FIG. 1.7. Possible biofilm passivation on aluminium top external surfaces.

to embedded iron particles. As expected, the galvanic couples showed some crevice corrosion within the stainless steel–aluminium couples and a slight increase in corrosion products on the aluminium–aluminium crevice coupons.

1.4.4. Myth of microbially influenced corrosion in the RBOF at SRS

In May 1998, a number of articles in the press reported that microbiologically influenced corrosion (MIC) was active on aluminium clad spent fuel stored in the RBOF at SRS. The source of the story was a reporter from a national news service who attended a poster session at a meeting of the American Society for Microbiology (ASM) in Atlanta, Georgia. The reporter wrote a story based on a paper presented by four microbiologists from SRS. The story was sent to all subscribing news services around the world. Stories appeared in national publications about 'metal munching' microbes in fuel storage pools, microbes corroding nuclear waste storage containers and the 'bugging of nuclear fuel'. These articles attracted much attention, as might be expected, but contained a number of inaccuracies. The issues were immediately reviewed by SRS and actions were taken to clarify the information before the written paper was released.

The study conducted in the RBOF at SRS and presented at the ASM meeting found microbial densities of 10^4–10^7 cells/mL in the water samples collected from the basin and identified the presence of acid producing, aerobic, anaerobic and sulphate reducing bacteria. Average microbial densities were about 10^5 cells/mL, with seasonal variation. Small cylindrical aluminium alloy coupons submerged in the water of the storage basin developed a biofilm attached to their surface in as little as 21 days. Microbial densities increased with time, with microbes appearing to cover the surface upon inspection of the coupons after 12 months. The biofilms on the stainless steel coupons were less dense than those on the aluminium.

The hypothesis that was put forth from this study was that the biofilm caused cracks and pitting corrosion in the alloy, as shown by the scanning electron micrograph in Fig. 1.8. On closer examination and review of the data by materials and corrosion specialists from SRTC, the findings were clarified. The cracks that had been reported in grain boundaries of the surface oxide of the coupons were caused by stresses from the volume expansion of the oxide, which were produced during the autoclaving preconditioning process. The cracks were seen in areas on the surface that were not under the patchy biofilm. No pitting corrosion was seen on the surface of the metal sample itself as initially reported.

It is well known that MIC cannot be predicted from bulk water microbial densities. Microbes in the bulk water have little influence on interactions on

metal surfaces. The attachment of bacteria and fungi (in a biofilm) to metal surfaces can set up an environment that has the potential to influence corrosion. When corrosion does occur, it is by standard corrosion mechanisms. This biofilm, however, can also be protective and prevent corrosion from occurring [1.13]. There is no evidence at SRS that the microbes in the basin water played any role in the corrosion of the spent fuel in the RBOF or in any of the other on-site storage basins. Internal studies carried out at the reactor basins in the 1960s indicate that microbiological activity has always been present in these basins, with seasonal variation in microbial densities, which are highest in the summer. Temperature change was found to be the most important factor causing these microbial density changes. No corrosion in any of these basins has ever been attributed to MIC.

Although laboratory tests have shown aluminium corrosion to be accelerated by bacteria and fungi, cases of MIC of aluminium alloys in service in high purity water are very limited [1.14]. There have been a number of cases related to jet aircraft fuel tanks and in petrochemical fuel environments. In these cases of microbiologically influenced pitting, the pits were crystallographic in nature, with faceted pit walls, even though the service environments were quite different. No faceted pits, or even a tendency towards faceted pits, were observed when metallography of pitted aluminium alloy coupons in the SRS corrosion surveillance programme was carried out.

Pitting of the aluminium alloys in the SRS reactor basin water can be attributed to the conductivity and impurity concentration of the basin water and to the thickness of the oxide films on the aluminium components. This is
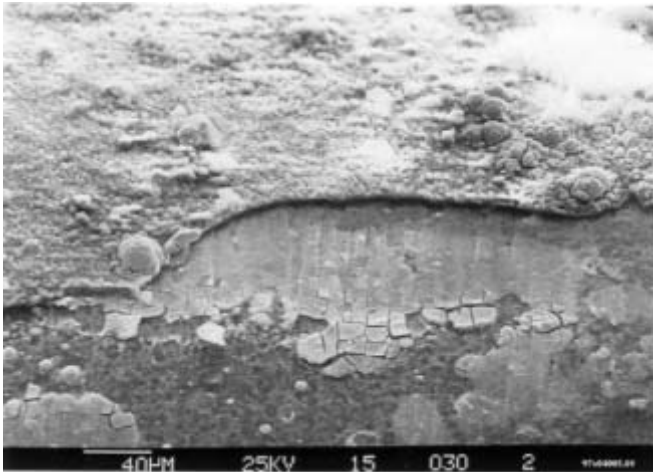
FIG. 1.8. Biofilm on aluminium alloy in high purity water.

consistent with the effects of water chemistry and oxide quality on standard corrosion processes. The introduction of MIC is not required to explain the pitting tendency of the aluminium components. At SRS, the basin water quality was improved, and pitting of the aluminium corrosion surveillance coupons in the reactor basins was eliminated, despite the presence of microbes in the water and the formation of a biofilm on the coupons in the RBOF. In low conductivity (and high purity) water in the RBOF, no pitting has been observed on any component immersion test coupons since 1994. Embedded iron filings in a few corrosion surveillance coupons caused the only pitting seen on any RBOF corrosion surveillance coupons.

Samples of the RBOF water will continue to be analysed on a periodic basis as fuel comes in for interim storage from the FRR sites. This will allow SRS to develop a database on the diversity of the microbiological activity at the different research reactor sites. Corrosion of the spent fuel initiated by any mechanism will continue to be monitored in all basins at SRS through the corrosion surveillance programme.

1.5. CONCLUSIONS

The CRP and the extensive corrosion surveillance programme at SRS have resulted in the development of a basic understanding of the corrosion of aluminium clad spent nuclear fuel. Tests have been conducted in water storage pools with a wide range of purity and environmental conditions. Analyses of the data reveal that the most important factors contributing to the corrosion of the aluminium are:

(a) High water conductivity (100–200 μS/cm);
(b) Aggressive impurity ion concentrations (e.g. Cl^-);
(c) Deposition of cathodic particles on aluminium (Fe, etc.);
(d) Sludge, which contains Fe^{3+}, Cl^- and other ions in higher concentrations than in the water;
(e) Galvanic couples between dissimilar metals (stainless steel–aluminium, aluminium–uranium, etc.);
(f) Scratches and imperfections in the oxide coating;
(g) Poor water circulation.

These factors, operating both independently and synergistically, may cause corrosion of the aluminium. The single most important key to preventing corrosion is maintaining good water chemistry. Water conductivity near 1 μS/cm generally ensures that the concentrations of aggressive impurities such

as chlorides are in the ppb range. When water conductivity is maintained in this regime, corrosion of aluminium alloys is minimized.

Good water chemistry does not always guarantee that corrosion of aluminium clad spent fuel will be prevented, as was seen from the extensive tests conducted in storage pools in Argentina. There, deposited iron oxide particles (from the water) caused pitting even in the high quality water. This has been seen in other fuel storage basins. The corrosion mechanisms involved in this pitting can be both galvanic and oxygen depletion cells.

Some of the CRP participants saw no corrosion of their aluminium alloy coupons, while others saw significant pitting. Pitting, crevice and galvanic corrosion were the main forms of corrosion observed. Crevice corrosion was not always accompanied by pitting of the aluminium surfaces within the crevice. Bimetallic corrosion of aluminium alloys coupled to stainless steel generally resulted in accelerated corrosion with pitting.

Some of the participants did not carry out immersion and withdrawal of their corrosion racks in the manner stipulated. This made it difficult to compare all the results. An important lesson from these tests conducted in fuel storage basins of various countries was the need to improve basin water quality. Reduction of water conductivity and chloride ion content, in particular, was found to be essential to maintain low corrosion rates. All the participants became more aware of this as the CRP progressed and greater emphasis was placed on improving basin water chemistry. The knowledge gained from this CRP has resulted in proposed guidelines for corrosion protection of aluminium clad spent nuclear fuel. A draft of these guidelines is presented in Chapter 3.

Some understanding of the corrosion of aluminium alloys used as cladding on research and test reactor fuel has been obtained from the CRP. Aluminium corrosion is extremely complex and the variables affecting localized corrosion (pitting and crevice corrosion) act both independently and synergistically. Additional information about the effects of deposited particle composition on the corrosion behaviour of aluminium alloys is needed. Surface finish affects the corrosion of aluminium alloys, and more information is required with respect to this parameter. Additional data on the effects of certain impurity ions in basin water on localized corrosion behaviour are necessary to better identify the ions that cause corrosion. A goal would be to develop an equation for pitting as a function of water chemistry parameters.

Continuation of this CRP concentrating on fuel storage basins that have demonstrated significant corrosion problems will provide additional and much needed insight into this issue. The final results will enable storage pool operators to better control those environmental parameters key to long term storage of aluminium clad spent fuel.

REFERENCES TO CHAPTER 1

[1.1]   BURKE, S.D., HOWELL, J.P., "The impact of prolonged wet storage of DOE reactor irradiated nuclear materials at the Savannah River Site", Proc. Topical Mtg on DOE Spent Nuclear Fuel — Challenges and Initiatives, Salt Lake City, 1994, USDOE, Washington, DC (1994) 118–124.

[1.2]   HOWELL, J.P., "Corrosion surveillance for research reactor spent nuclear fuel in wet basin storage", Corrosion/99, Natl Assoc. of Corrosion Engineers, Houston, TX (1999) paper 462.

[1.3]   RITCHIE, I.G., ERNST, P.C., "Overview of spent fuel management and problems", Proc. 2nd Int. Topical Mtg on Research Reactor Fuel Management, Bruges, Belgium, 1998, European Nuclear Soc., Brussels (1998) 105–109.

[1.4]   BROOKS, P., SINDELAR, R.L., "Characterization of FRR SNF in basin and dry storage systems", Proc. 3rd Topical Mtg on DOE Spent Fuel and Fissile Materials Management, Charleston, SC, 1998, USDOE, Washington, DC (1998) 542–549.

[1.5]   SINDELAR, R.L., BURKE, S.D., HOWELL, J.P., "Evaluation of radionuclide release from aluminum based SNF in basin storage", ibid., pp. 259–264.

[1.6]   HOSKINS, A.P., et al., Fuel Performance in Water Storage, Rep. WINCO-1167, Idaho Natl Engineering Lab., Idaho Falls (1993).

[1.7]   AMERICAN SOCIETY FOR TESTING AND MATERIALS, Standard G31-72 (Reapproved 1995), Standard Practice for Laboratory Immersion Corrosion Testing of Metals, ASTM, Philadelphia, PA (1995) 1–8.

[1.8]   HOWELL, J.P., "Criteria for corrosion protection of aluminum-clad spent nuclear fuel in interim wet storage", Corrosion/2000, Natl Assoc. of Corrosion Engineers, Houston, TX (2000) paper 200.

[1.9]   HOWELL, J.P., "Corrosion surveillance in spent fuel storage pools", Corrosion/97, Natl Assoc. of Corrosion Engineers, Houston, TX (1997) paper 07.

[1.10] HOWELL, J.P., "Durability of aluminum-clad spent nuclear fuels in wet basin storage", Corrosion/96, Natl Assoc. of Corrosion Engineers, Houston, TX (1996) paper 128.

[1.11] HOWELL, J.P., "Corrosion of aluminum alloys in a reactor disassembly basin", Corrosion/93, Natl Assoc. of Corrosion Engineers, Houston, TX (1993) paper 609.

[1.12] DOMINGO SANTO, J.W., BERRY, C.J., SUMMER, M.S., FLIERMANS, C.B., Microbiology of spent nuclear fuel storage basins, Curr. Microbiol. **37** (1998) 387–394.

[1.13] VIDELA, H.A., Manual of Biocorrosion, CRC Press, Boca Raton, FL (1996).

[1.14] LOUTHAN, M.R., Jr., "The potential for microbiologically influenced corrosion in the Savannah River spent fuel storage pools", Proc. NATO Workshop on Microbial Degradation Processes in Radioactive Waste Repositories and in Nuclear Fuel Storage Areas, Budapest, 1996, Kluwer, Dordrecht (1997).

Chapter 2

STATE OF THE ART REVIEW ON
ALUMINIUM CORROSION

2.1. INTRODUCTION

This chapter presents a discussion of the fundamentals of aluminium alloy corrosion applicable to the wet storage of spent nuclear fuel throughout the world. It examines the effects of variables on corrosion in the storage environment and presents the results of corrosion surveillance testing activities at SRS, as well as discussions of corrosion at fuel m storage basins at other production sites of the USDOE. Aspects related to the corrosion of aluminium clad fuel at SRS apply to research and test reactor fuel worldwide.

The IAEA compiled a thorough state of the art literature review on corrosion of aluminium alloys in 1998. This review was published in IAEA-TECDOC-1012, Durability of Spent Nuclear Fuels and Facility Components in Wet Storage [2.1]. It presented a wide range of quantitative and semi-quantitative data on nuclear fuel cladding alloys and included sections on corrosion of aluminium, zirconium, stainless steel, carbon steels and copper alloys in wet storage environments. Sections of the book that apply to aluminium alloys used in fuels for research and test reactors have been updated and presented in this review.

Aluminium alloys have been used as cladding materials for nuclear fuel and targets because of their low thermal neutron absorption cross-section. The corrosion resistance of aluminium is generally very good. Water quality plays a key role and is closely controlled in high temperature reactor operations. After irradiation in a defence production reactor, the aluminium clad fuel and target assemblies are stored in large water filled basins to cool while awaiting processing. In the past, the spent fuel was usually processed before corrosion became a problem.

Under the non-proliferation policy for nuclear materials, the USDOE halted processing of nuclear materials for defence purposes at its production sites during the late 1980s. At this point, about 2800 metric tonnes (t) of spent nuclear fuel were caught in the pipeline, awaiting processing while stored in light water filled basins [2.2]. At SRS, where most of the 200 t of stored fuel was aluminium clad, processing in the F Canyon facilities was suspended in 1989. As of 1996, aluminium clad fuel stored in stainless steel buckets, as well as fuel and target materials stored on stainless steel hangers, had been immersed in SRS

reactor basins for over seven years and were showing extreme signs of corrosion. Similar extended storage scenarios pertained at the Hanford Site, Idaho Technologies Co., Oak Ridge National Laboratory and other spent fuel storage sites in the USDOE production complex. Significant corrosion problems existed with the spent aluminium clad fuel at some sites, while at others corrosion was minimal or undetectable [2.3–2.5].

The factors promoting the corrosion of aluminium are complex. In many cases, they operate synergistically and are not well understood. This chapter presents a discussion of the fundamentals of aluminium alloy corrosion, including mechanisms and the effects of variables in the storage environment, as well as results of corrosion testing related to aluminium clad spent nuclear fuel in wet basin storage.

2.2. FUNDAMENTAL FACTORS AFFECTING CORROSION

There are a number of factors that affect the corrosion of aluminium clad spent nuclear fuels in wet storage.

2.2.1. Oxide films on aluminium

Aluminium is one of the most thermodynamically reactive metals. Aluminium owes its excellent corrosion resistance in most environments to the protective oxide barrier film formed on and strongly bonded to its surface. This aluminium oxide film is relatively inert and tends to prevent further oxidation of the aluminium. The film can dissolve in the presence of some chemicals and this can lead to dissolution of the metal. When the film is damaged under conditions where normal self-healing does not occur, localized corrosion in the form of pitting or intergranular attack can occur [2.6].

The formation of protective oxide films on aluminium at moderate temperatures occurs in three distinct stages [2.7]. These stages are a function of time and temperature. Upon immersion in water at temperatures of between 60 and 70°C, the existing amorphous oxide barrier film on aluminium thickens to form the crystalline hydrated aluminium oxide phase, boehmite ($Al_2O_3 \cdot H_2O$). Continued immersion, ranging from hours to days, results in the formation of the crystalline phase, bayerite ($Al_2O_3 \cdot 3H_2O$). By mechanically removing the bayerite outside layer and identifying the film beneath it to be boehmite, using electron diffraction, it can be seen that the films form in a layered manner. At temperatures of about 70°C, the films are predominantly boehmite. However, some films showed both bayerite and boehmite in electron diffraction patterns.

2.2.2. Kinetics

From an engineering standpoint, the kinetics or rate of corrosion of a system is usually of primary importance. Corroding systems are not in equilibrium and therefore thermodynamic calculations cannot be applied. For metal corrosion to occur, an oxidation reaction (generally metal dissolution or oxide formation) and a cathodic reduction reaction (such as oxygen reduction) proceed simultaneously. In most normal water environments, the overall reaction for aluminium corrosion is reaction with water to form aluminium hydroxide and hydrogen. The aluminium hydroxide has very low solubility in water and precipitates as bayerite or boehmite, depending on the temperature of the water [2.8].

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \tag{2.1}$$

The oxidation (anodic) reaction is given by:

$$Al \rightarrow Al^{3+} + 3e^- \tag{2.2}$$

The reduction (cathodic) reaction is given by:

$$2H^+ + 2e^- \rightarrow H_2 \tag{2.3}$$

In the electrochemical reaction, the positively charged ions leave the surface of the anode and enter the electrolyte solution, leaving electrons behind to flow through the metal to the cathode. At the cathode, the electrons are consumed by the hydrogen ions at the surface, and hydrogen gas is liberated. The oxidation and deterioration of the anode surface causes corrosion to occur.

2.2.3. Types of corrosion

In wet storage of aluminium clad spent nuclear fuel, different types of corrosion can occur. A short discussion of the more important types of corrosion as they pertain to the aluminium alloys is provided below.

General corrosion. The general corrosion resistance of aluminium in high purity water is very good. There is no significant general corrosion or gradual thinning of aluminium as may occur with steel [2.9]. General corrosion has not been a problem during storage of aluminium clad alloys at many of the basins in the USA, as long as the protective oxide on the aluminium remains intact. As a general rule, the protective oxide film is very stable in aqueous solutions in the pH range 4.0–8.5 [2.10].

Galvanic corrosion. Galvanic corrosion occurs when a metal or alloy is electrically coupled to another, usually dissimilar, metal in the same electrolyte. In the case of spent nuclear fuel storage, galvanic corrosion is evident throughout the basins. During galvanic coupling, corrosion of the less corrosion resistant metal increases, this metal becoming the anode, while corrosion of the more corrosion resistant metal decreases, and this metal becomes the cathode. The driving force for the corrosion or current flow is the potential that develops between the dissimilar metals.

Some of the other factors affecting galvanic corrosion are area ratios, distance between electrically connected materials, and geometric shapes. Galvanic corrosion of the anodic metal takes the form of general or localized corrosion, depending on the configuration of the couple, the nature of the protective films formed and the nature of the metals.

Aluminium and its alloys occupy active positions in the galvanic series and thus are highly susceptible to failure by galvanic attack [2.10]. In solutions containing chloride ions, aluminium alloys are susceptible to galvanically induced localized corrosion, especially in dissimilar metal crevices. Severe attack is often seen when the aluminium alloys are coupled with more noble metals. The galvanic corrosion behaviour of stainless steels is difficult to predict because of the influence of passivity of the protective oxide film. In general, stainless steel is nobler than the aluminium in the galvanic series and, depending on the environment and other factors, may promote corrosion of the aluminium. At SRS, some of the fuel tubes are fabricated from different aluminium alloys joined together by a weld or mechanically bonded. Galvanic effects promoting corrosion between the two alloys have been noted in basin corrosion tests and in storage [2.11]. In addition, underwater photographs of bundled 1100 alloy fuel tubes in contact with 6061 alloy spent fuel storage racks have shown the tubes to remain free of corrosion while the storage racks appear to corrode sacrificially.

Galvanic corrosion of spent nuclear fuels in storage basins is active and can be reduced considerably by removing the couple whenever possible and by lowering the basin water conductivity. At low conductivity, in the range 1–3 µS/cm, the galvanic effect should be minimized. Basin water deionization will remove the corrosion-causing anions and cations from the water and will increase the resistance to current flow.

Crevice corrosion. Crevice corrosion is a highly localized form of corrosion and occurs on closely fitted surfaces upon entry of water into the crevice [2.6]. Recent work has shown that the mechanism is complex. Chloride ions are drawn into the crevice as metal dissolution occurs and the conditions inside the crevice become acidic. Metals like aluminium that depend on oxide films or passive layers for corrosion resistance are particularly susceptible to crevice corrosion.

Crevices exist in many locations in storage basins where nuclear fuel is supported by hangers and storage racks. These locations provide the environment for localized corrosion to occur, because of the stagnant areas and the setting up of differential oxygen cells. At SRS, the slug bucket storage, used for the storage of aluminium clad Mark 31A target slugs, provides an environment that promotes crevice corrosion. In this situation, the stacking of slugs, combined with the sludge and corrosion product accumulation within the bucket, creates many possibilities for crevice aided corrosion.

Stress corrosion cracking (SCC). Stress corrosion cracking has not played a major role in the corrosion of the fuel stored in the basins. The alloys used as cladding materials are pure aluminium — 1100, 6061 and 6063 — and these are not susceptible to SCC.

Pitting corrosion. Pitting of the aluminium clad fuel and target materials in wet basin storage is the main mechanism of corrosion in basins around the world. Pitting is a localized form of corrosion in which metal is removed preferentially over very small areas on the surface to develop cavities or pits. The attack is generally limited to extremely small areas, while the remaining surface is relatively unaffected. The pits usually start at small points on the surface and enlarge with time. This enlargement of the surface area of a pit is usually small in comparison with its increase in depth and volume [2.12]. Pitting requires the presence of an electrolyte, and in the case of most storage basins, inadequately deionized water serves this purpose. While many pits are hemispherical or conical, the shapes vary considerably. The shape of the cavity at the metal surface tends to be round, but the pit walls tend to be very irregular. Pitting is most common on metals that are covered with an adherent surface film. The pits tend to develop at defects or flaws in the surface film and at sites where the film has been mechanically damaged and does not self-heal. In structures, the occurrence of pits is not always detrimental, since the amount of metal removed is usually small and the rate of penetration decreases with time in most cases. On the other hand, under special conditions, the rate of pitting can be quite rapid [2.13]. When this occurs, it can be one of the most destructive forms of corrosion. The most common undesirable result of pitting corrosion is perforation of the metal. In the case of stored aluminium clad spent nuclear fuels, pitting can be extremely undesirable, as perforation of the clad material can lead to release of uranium, plutonium, ^{137}Cs and other radionuclide activity to the basins. Buildup of this activity in the basin water can ultimately lead to high radiation levels and exposure to personnel working around the basins.

Pitting, like general corrosion, has also been shown to proceed by an electrochemical mechanism. The pitting is caused by electrochemical differences at two adjacent locations on the surface. An individual pit is therefore a local cell with its own anode and cathode. Electrical current flows through the liquid

medium from the local anode (the site of metal removal) to the adjacent local cathode. Pitting may also be caused by current entering a solution from the metal surface owing to an external cause, such as an impressed electromotive force or galvanic corrosion produced by contact with a dissimilar metal.

In the life cycle of a pit, there are generally four possible stages: initiation, propagation, termination and reinitiation [2.13]. The pitting of aluminium can be described as an autocatalytic process. The functioning of local cells in an electrolyte produces changes at local anode and cathode sites that increase the potential between them and therefore the activity of pits. The corrosion processes within a pit produce conditions that are both stimulating and necessary for pit growth to occur. In a situation where a metal is being pitted by an aerated chloride-containing electrolyte, rapid dissolution occurs within the pit, while oxygen reduction takes place on the adjacent surfaces. The rapid dissolution within the pits tends to produce excess charge in this area and results in the migration of chloride ions into the pit to maintain neutrality. Thus there is a high concentration of metal chloride and of hydrogen ions in the pit. As a result, the pits become more acidic, reaching low pH levels. This process stimulates metal dissolution.

The rate of penetration of pits in aluminium has been shown to decrease rapidly with time. Aziz and Godard found that in field test coupons the pitting rate curve follows a cube root law [2.14]:

$$d = Kt^{1/3} \tag{2.4}$$

where d is maximum pit depth, t is time and K is a constant depending on the alloy and the water conditions (composition, temperature, velocity, etc.). The depths of pits in water pipe sections were measured at various time intervals and the maximum pit depths at specific times in the future were calculated using the cube root law. Actual pit depth measurements verified the validity and accuracy of the equation. From the equation, one can see that doubling the wall thickness can increase the time for perforation by a factor of 8.

2.3. ENVIRONMENTAL FACTORS AFFECTING ALUMINIUM CORROSION

The corrosion of aluminium alloys in high purity water is complex and many of the factors responsible for this corrosion are interrelated. In high purity, deionized water, general thinning of the cladding caused by uniform corrosion is very low. The fuel enters the basin with, in some cases, several millimetres of protective oxide coating formed at high temperatures. When corrosion by water

does occur, it generally takes the form of pitting and is associated with the breakdown of the protective oxide coating. The number of pits formed and their rate of penetration depend on the water composition and the conditions of service [2.14]. Pitting, which tends to occur in stagnant waters, can often be prevented by keeping the water in constant motion. This section contains a discussion of some of the most important factors affecting the corrosion of aluminium alloys as related to the water chemistry and the service environment.

2.3.1. Influence of water composition

In general, soft water is less aggressive than hard water with respect to pitting corrosion of aluminium. The hardness of water is due to the presence of calcium carbonate ($CaCO_3$) and other ions such as sulphates and chlorides. Water with a $CaCO_3$ content of about 1–60 ppm is considered soft, with over 60 ppm hard and with over 181 ppm very hard.

The major factors believed to influence the pitting of aluminium alloys are conductivity, pH, and bicarbonate, chloride, sulphate and oxygen content [2.6]. Because of the interrelationship of the composition and service factors, it is difficult to predict the influence of water on aluminium corrosion from a table of water composition alone. A number of studies have been conducted of synthetic waters containing several metal and salt ions alone and in combination [2.15–2.17]. They found that the corrosion of aluminium was accelerated when salts of copper, chlorides and bicarbonates were present together, compared with cases where only a single impurity was present. In some cases where two of the three constituents were present, there was little corrosion, but with the three species present together, nodular corrosion occurred.

2.3.2. Conductivity of water

As corrosion processes associated with aluminium fuels in storage basins are electrochemical, the nature of the electrolyte, or basin water, plays a key role in the flow of electric current and electrons in the process. The amount of metal removal by corrosion is directly related to the current flow. By increasing the resistance of the water, the corrosion of the aluminium can be reduced. Very pure water has a high resistance and is much less corrosive than impure or natural waters. The low corrosiveness of high purity water is primarily due to its high electrical resistance (low conductivity) [2.12].

The electrical resistivity of water is measured in ohm centimetres, and conductivity, given by the reciprocal of resistivity, in mho/cm. In international units, 1 μmho/cm = 1 μS/cm, where S is the unit siemens. Extremely pure water is produced by deionization. This water has a conductivity of less than 1 μS/cm.

Type I reagent grade water can be produced by deionization, distillation, reverse osmosis or combinations of these techniques to a conductivity level of less than 0.1 µS/cm. Some natural lake waters, such as Lake Ontario, Canada, have a typical conductivity of about 270 µS/cm. Sea water has a conductivity of about 40 000 µS/cm [2.18].

Storage basins around the USA that are storing aluminium clad spent nuclear fuels without corrosion problems operate deionization equipment continuously and maintain conductivity levels of typically less than 10 µS/cm. Storage times for aluminium clad alloys of up to 25 years without corrosion in low conductivity waters have been reported [2.5].

At Brookhaven National Laboratory, the aluminium clad fuel elements are stored in a canal (pool) and subjected to continuous bypass demineralization [2.19]. The conductivity is maintained at about 0.5 µS/cm, and when it reaches 1 µS/cm, the resins are regenerated. Fuel elements have been stored continuously in the canal without any evidence of cladding breaches. At Oak Ridge National Laboratory, the conductivity is routinely maintained at 1 µS/cm but at times it has been as low as 0.5 µS/cm, and again no evidence of corrosion in fuel stored for eight years has been reported. The Georgia Institute of Technology has reported successful storage of 1100 clad fuel in its pool for over 25 years, where continuously deionized water at typically 1 µS/cm or better has been used [2.19].

For the larger fuel storage basins in the USDOE complex, the ones that are not experiencing corrosion problems are operating deionizers continuously and are routinely achieving conductivity levels of 1–3 µS/cm. The RBOF facility at SRS operates at 1–3 µS/cm. At the Idaho Technologies CPP-666 basin, the deionization system routinely maintains the basin water at about 1–2 µS/cm. At the Westinghouse Hanford Company K-East and K-West basins, each basin currently uses mixed bed resin ion exchange technology for continuous deionization. The K-East basin, with its bare, uncoated concrete walls, is now operating at 3–5 µS/cm, down from the typical 250 µS/cm of the mid-1970s to 1980s, before the ion exchange columns or mixed bed resins were used. K-West is currently operating at 1–2 µS/cm.

As can be seen from the surveys of the best basins in the USA, the conductivity of the basin water plays a key role in minimizing the corrosion of aluminium alloys. In basins with conductivity in the range 1–3 µS/cm, aluminium clad alloys can be stored with little or no pitting corrosion. To achieve these low levels of anion and cation concentrations, the corrosion-inducing impurities such as chloride ions are generally reduced to the ppb range, where they make the water significantly less aggressive.

While coupon data from the SRS basins indicate that corrosion performance has improved with cleanup of the basins, there is no evidence that

lowering the conductivity to 100 µS/cm is adequate for 10–20 years of continuous storage of aluminium alloys. On the basis of the available information, engineering judgement indicates that a level of about 50 µS/cm may be adequate for a few years. However, there are no available field data or coupon test data based on 25 year test exposures to help establish whether this level of purity will protect aluminium from pitting corrosion during long term storage. There is evidence based on data from a number of storage basins around the world that aluminium clad spent nuclear fuel can be stored successfully in basins with a water conductivity of less than 10 µS/cm, and generally in the 1–3 µS/cm range, for times exceeding 25 years without cladding corrosion. Basin deionization systems should be designed and operated to achieve these extremely low conductivity levels in order to ensure successful long term storage of aluminium clad spent nuclear fuels.

2.3.3. Effect of pH

Aluminium is passive and is protected by its oxide film in the pH range 4–8.5. The limits of this range vary somewhat with temperature, the form of oxide present and the presence of substances that form soluble complexes or insoluble salts with aluminium. The oxide film is soluble at pH values below 4 and above 8.5. General corrosion in distilled water at 60°C has been shown to be at a minimum at pH4. It increases slightly in the passive range and is higher in the pH range 9–10. In chloride solutions, the pitting potential of aluminium, like that of iron and steel, has been found to be relatively independent of pH in the range 4–9 [2.20]. Godard reported that a deviation from neutrality (pH7), on both the acid and the alkaline side, increased the pitting rate in natural fresh waters [2.6].

The corrosion rate often depends more on the ion that alters the pH than on the pH itself. For example, aluminium is not rapidly attacked by concentrated nitric acid at a pH of 1, or by glacial acetic acid at a pH of 3, but is corroded rapidly by hydrochloric or phosphoric acid at a pH of 4. On the alkaline side, aluminium is resistant to ammonium hydroxide at pH13, but is rapidly corroded by sodium hydroxide at pH11. The reason for this behaviour is probably the composition of the corrosion product and its ability to form protective films on the surface of the aluminium [2.6].

2.3.4. Effect of impurities

The protective oxide film on the surface controls the corrosion rate and pitting tendency of aluminium alloys. The corrosiveness of basin water is due to the ability of impurity ions to penetrate the oxide film to attack the aluminium

metal. Sverepa reported the oxide film penetrating power of anions to be, in decreasing order, chloride, bromide, iodide, fluoride, sulphate, nitrate and phosphate [2.21].

The pitting corrosion of aluminium is often caused by halide ions, of which chlorides are the most common. An increase in the chloride concentration of a solution leads to a decrease in the pitting potential of aluminium. Chlorides break down the protective oxide film and inhibit repassivation. They stimulate metal dissolution. Chlorides from the bulk electrolyte solution migrate into pits and crevices, causing rapid dissolution. Pitting occurs in the presence of oxygen because the metal is readily polarized to its pitting potential [2.20]. In the absence of oxygen, aluminium does not corrode by pitting because the metal is not polarized to its pitting potential. In general, aluminium does not pit in aerated solutions of most non-halide solutions because its pitting potential is much more noble (cathodic) than in halide solutions.

The chloride content of storage basin water should be kept low to prevent pitting corrosion. It is difficult to specify a chloride ion limit below which pitting corrosion does not occur, because of the synergistic reactions that take place with other anions in the water. Sverepa found that increasing the chloride content from 0 to 50 ppm in water containing 116 ppm bicarbonate ions increased the number of pits but not their depths [2.21]. The effect was much higher in the presence of copper. Very little attack occurred in the presence of 10 ppm chloride and 116 ppm bicarbonate at pH8.0, while in the presence of 50 ppm chloride and 232 ppm bicarbonate, 0.1 mm deep pits occurred at the same pH. At a lower pH of 6.4, corrosion occurred with only 20 ppm chloride and 116 ppm bicarbonate.

Severe corrosion of fuels in the Idaho CPP-603 basin was reported when the chloride content was about 800 ppm in 1976. The basins at SRS have maintained chlorides at 20–25 ppm over the years, and this has permitted the addition of hypochlorate for algae control. However, over long storage times at these chloride levels, pitting corrosion may occur, as galvanic couples exist throughout the basins. Storage basins throughout the USDOE complex that are successfully storing aluminium clad spent fuel have chloride contents of less than 1 ppm or in the ppb range. The RBOF at SRS is typically operated at less than 10 ppb Cl^- and the CP-666 basin at Idaho operates at about 50 ppb.

2.3.5. Copper

Heavy metal ions such as copper and mercury are very aggressive with respect to pitting corrosion of aluminium alloys [2.8]. The aluminium reduces the ions of copper, mercury, lead, etc. The heavy metal ions can also plate out on the aluminium surface and form galvanic cells where the aluminium becomes the anode and the heavy metal a very effective cathode. The threshold

concentration for reduction of the copper ions by aluminium is about 0.02 to 0.05 ppm in neutral and acidic solutions. These levels are considered the threshold for initiation of pitting on aluminium. A specific value is not normally proposed because the pitting tendency also depends on a number of other factors, including the concentrations of other ions (particularly chloride, bicarbonate and calcium), the pH of the water, the aluminium alloy and whether the pits are open or occluded [2.10]. The influence of copper is less at a pH of 8.0 than at 6.4, because of the lower solubility of copper in water at the higher pH level. On the basis of two case histories, Godard reported that about 0.10 ppm of copper in distilled water was sufficient to cause pitting of aluminium [2.8]. Copper and mercury ion concentrations in storage basins are usually low. However, some basins have copper tube heat exchangers, copper thermo-couples or mercury thermometers, which are the sources of heavy metal ions. The RBOF usually operates at about 2 ppb copper content. In the early 1980s, an algaecide added to the basin water at Hanford's K-East basin resulted in dissolution of the copper from the heat exchanger tubes, causing nodular pitting corrosion on the aluminium canisters containing the spent fuel.

2.3.6. Bicarbonate

An important factor in determining the aggressiveness of water with respect to pitting corrosion of aluminium is the hardness (or softness) of the water, as measured by the carbonate content [2.6]. In an unlined concrete basin it is likely that calcium carbonate continuously leaches into the water, causing buildup of carbonate hardness. In addition, at the large surface areas associated with the basins, atmospheric carbon dioxide can react with the water to form bicarbonate ions. The bicarbonate ion alone does not cause pitting at concentrations of up to 300–400 ppm, but in the presence of chloride and copper ions, it causes intensive pitting [2.17, 2.18, 2.21]. Sverepa found that at low bicarbonate levels, voluminous corrosion products were dispersed in solutions around the pits. At higher bicarbonate concentrations, harder, thicker nodules formed that adhered firmly to the pits.

Continuous deionization of the storage basin water softens the water, as it removes the calcium bicarbonate and other ions contributing to hardness. Godard, however, found that zeolite softened, deionized water influenced the pitting behaviour of aluminium to the same extent as untreated water [2.6].

2.3.7. Sulphates

Studies by Draley have shown that at 50–70°C, the presence of sulphate ions reduced the corrosion rate of aluminium [2.22]. Rowe and Walker found

that up to 300 ppm of sulphate ions only did not increase the corrosion of aluminium [2.17]. Godard and Torrible, however, found that the oxide film thickness decreased as the concentration of sulphates increased. They also obtained evidence that the pitting rate increased with the sulphate/chloride ratio [2.23]. Godard concluded that the pitting corrosion, i.e. pitting density and pitting rate, was influenced by the film thickness [2.18]. The thinner the oxide film, the more susceptible the metal was to corrosion. In a later work, Pathak and Godard's data showed that the increase in sulphate concentration reduced the time to form a 1 mm pit in aluminium [2.24].

2.3.8. Oxygen

Surface waters and storage pools at SRS are normally saturated with oxygen. Hence oxygen is not a variable in many of the corrosion problems associated with wet stored fuel. Godard has shown that complete elimination of oxygen from Kingston (Ontario, Canada) tap water markedly reduced the corrosion of aluminium [2.6]. Rowe and Walker reported that in water containing copper, bicarbonate and chloride ions, the exclusion of air reduced the corrosion to one third of that in oxygen saturated water [2.17]. Measurements of the oxygen content of L-Basin water at SRS at 15°C revealed it to be constant with depth in the basin, and saturated at 10.9 ppm.

2.3.9. Temperature

Mears and Brown studied the influence of temperature on the pitting of aluminium alloys in chloride solutions [2.25]. They found that as the temperature increased, both the density and the probability of pitting increased, while the pitting rate or average depth of pits decreased. Godard studied the influence of temperature on the pitting of 1100 alloy by determining pit density and maximum pit depth in tap water at up to 70°C [2.8]. He found that the pitting rate–temperature curve for some pits had a maximum at about 40°C. The rate of pitting at this point was five times that at 25°C.

An increase in temperature affects pitting rates by: (1) reducing the solubility of oxygen in the solution, and (2) stimulating the initiation of pitting, which in turn reduces the pitting rate. Most basin operations are aimed at maintaining low basin temperatures. Much of the fuel in the basins in the USA has been there for several years, and the radioactive decay heat is low and is diminishing. It is extremely important to maintain low temperatures in the basins, as corrosion of the uranium metal cores has been seen during temperature excursions at the Hanford basins.

2.4. PITTING RATE INDEX

Although the prediction of the corrosivity of natural and other waters from the values of specific compositional parameters has proven to be extremely difficult, Pathak and Godard developed an empirical relationship for predicting the corrosivity of natural fresh waters to aluminium in 1967 [2.24]. Using 67 natural waters where analyses were available and 3003 alloy, they conducted tests to determine the maximum pit depth as a function of exposure time. From the data, the time required to develop a 1 mm pit was extrapolated.

The pitting rate index (PRI) is defined as the number of weeks needed to obtain a maximum pit depth of 1 mm. The equation is shown below:

$$\log \text{PRI} = 2.5 - 0.28 \log (\text{sulphate}) + 0.18 \log (\text{chloride})$$
$$- 0.20 \log [(\text{pH} - 7)^2 \times 100] - 0.42 \log (30\,000/R) \qquad (2.5)$$
$$- 0.064 \log (\text{copper} \times 10^3)$$

where $R = 1/C$ (conductivity, µS/cm). A PRI of less than 25 weeks is indicative of aggressive water.

The pitting rate equation was used on the water quality data available from an analysis carried out at SRS in 1992–1995 to determine the relative aggressiveness of the storage basins at SRS, especially since the water chemistry of the basins varied during cleanup activities over this time period. The PRI was calculated on the basis of analyses of water samples taken from the basins. Comparisons of the maximum pitting depths of the component immersion test coupons removed from these basins at various times in the period 1992–1995 provide some benchmarks for the equation. The effects of the extremely low conductivity and low impurity concentrations of the RBOF at SRS on the PRI were evident. Using the low range of conductivity at 1 µS/cm, the PRI was calculated to be greater than ten years, and using the highest value of 200 µS/cm, the PRI was calculated to be a few months. Fuel that has been stored in this basin under the lowest conductivity was inspected and no signs of corrosion were seen after almost 12 years.

On the basis of the extent of pitting of fuel in the SRS basins, the pitting rate equation seems to predict when basin water is aggressive with respect to pitting corrosion of aluminium or when aluminium alloys can be stored in water of a given purity for extended time periods. Godard indicates that the PRI is more accurate for aggressive waters than for non-aggressive waters. It appears to be a reasonable indicator for comparison of basin waters and for following the cleanup and deionization activities of a given basin. It does not predict with accuracy the time required to form 1 mm pits in deionized waters of fuel storage basins, and the equation is not valid for a pH of exactly 7.0.

2.5. CONCLUSIONS

The key to long term storage of aluminium clad spent nuclear fuels in wet storage is water quality. Experience has shown that successful storage without significant corrosion for times exceeding 25 years can be accomplished by control of the variables affecting water quality and by good engineering design. Although complex and not always well understood, a number of factors that influence corrosion are believed to operate both independently and synergistically. These factors have been discussed in detail in this chapter. The most important factors are believed to be water conductivity, chloride ion content and dissimilar metal contact, which accelerates corrosion mechanisms.

The quality of water in the basins at SRS and other facilities around the USA that are successfully storing aluminium clad fuel without corrosion has similar characteristics. The water in these basins has extremely low conductivity and low chloride ion content. These basins use mixed bed resin deionizer systems to achieve low conductivity and impurity content in the storage pools. The conductivity of basins at SRS where pitting corrosion of aluminium was evident was about 200 times higher than in basins where pitting corrosion was not observed (1–3 μS/cm). In addition, levels of aggressive ions such as chlorides were 1000 times lower (20 ppb). This water quality cannot generally be maintained unless the purification systems are designed to operate continuously. At SRS, no new pitting corrosion has been observed on aluminium clad fuel since the new deionization equipment was installed and the water was continuously deionized to conductivity levels of 1–3 μS/cm.

Experience at the SRS basins has shown that the galvanic couples between stainless steel and the aluminium alloy clad fuels play a more significant role in accelerating the pitting processes on the fuels than originally anticipated. Even though the area ratios between the dissimilar metals may not be too unfavourable, the pitting potential of the aluminium fuel assembly/dissimilar metal couple may be lowered enough to initiate pitting.

The pitting rate equation discussed in this chapter, although not accurate, gives a reasonable evaluation of the aggressiveness of the water quality in fuel storage basins. It has been used to monitor the basin water cleanup activities at SRS, and improvements in water chemistry have been verified by corrosion coupon tests. Additional work is needed to improve this correlation.

At SRS and other basins storing US defence related spent nuclear fuel, extensive efforts are under way to improve fuel storage conditions. These efforts should result in extended storage capability. This interim wet storage, however, cannot be extended indefinitely, and provisions must be made for other disposition. The ultimate solution for this problem is processing the fuel to a more stable form using standard techniques readily available and utilized

at SRS for over 35 years. Other methods, such as dry storage or melt–dilute, are viable but will require development over years.

REFERENCES TO CHAPTER 2

[2.1] INTERNATIONAL ATOMIC ENERGY AGENCY, Durability of Spent Nuclear Fuels and Facility Components in Wet Storage, IAEA-TECDOC-1012, Vienna (1998).

[2.2] BURKE, S.D., HOWELL, J.P., "The impact of prolonged wet storage of DOE reactor irradiated nuclear materials at the Savannah River Site", Proc. Topical Mtg on DOE Spent Nuclear Fuel — Challenges and Initiatives, Salt Lake City, 1994, USDOE, Washington, DC, (1994) 118–124.

[2.3] BURKE, S.P., 100-K Basins Historical Corrosion Data, Rep. WHC-SD-NR-TRP-023 Rev. 0, Westinghouse Hanford Co., Richland, WA (1994).

[2.4] HOSKINS, A.P., et al., Fuel Performance in Water Storage, Rep. WINCO-1167, Idaho Natl Engineering Lab., Idaho Falls (1993).

[2.5] COOK, D.H., et al., "Achieving increased spent fuel storage capacity at the High Flux Isotope Reactor (HFIR)", Proc. Topical Mtg on DOE Spent Nuclear Fuel — Challenges and Initiatives, Salt Lake City, 1994, USDOE, Washington, DC, (1994) 163–169.

[2.6] GODARD, H.G., The Corrosion of Light Metals, Wiley, New York (1967) 3.

[2.7] HART, R.K., Trans. Faraday Soc. **53** (1957) 1020–1027.

[2.8] GODARD, H.G., Mater. Performance **20** (1981) 9–15.

[2.9] GODARD, H.G., Can. J. Chem. Eng. **38** (1960) 167–173.

[2.10] Metals Handbook, 9th edn, Vol. 13, ASM International, Metals Park, OH (1987) 18–44.

[2.11] HOWELL, J.P., "Corrosion of aluminum-clad spent fuel in reactor basin water storage", Corrosion/95, Natl Assoc. of Corrosion Engineers, Houston, TX (1995) paper 429.

[2.12] FONTANA, M.G., Corrosion Engineering, 3rd edn, McGraw-Hill, New York (1986).

[2.13] HAMPEL, C.A., Ed., Encyclopedia of Electrochemistry, Reinhold, New York (1964) 925–929.

[2.14] AZIZ, P.M., GODARD, H.P., J. Ind. Eng. Chem. **44** (1952) 1791–1795.

[2.15] PORTER, F.C., HADDEN, S.E., J. Appl. Chem. **3** (1953) 385–409.

[2.16] DAVIES, D.E., J. Appl. Chem. **9** (1959) 651–660.

[2.17] ROWE, L.C., WALKER, M.S., Corrosion **17** (1961) 105–108.

[2.18] GODARD, H.P., Mater. Performance **18** (1979) 21–27.

[2.19] GIBBS, A., SRS Reactor Corrosion Handbook (U), Rep. WSRC-TR-93-42-022, Rev. 0, Westinghouse Savannah River Co., Aiken, SC (1993) 141–142.

[2.20] SZKLARSKA-SMIALOWSKA, Z., Pitting Corrosion of Metals, Natl Assoc. of Corrosion Engineers, Houston, TX (1986).

[2.21] SVEREPA, O., Werkst. Korros. **9** (1958) 533.

[2.22] DRALEY, J.E., US Atomic Energy Commission T.I.D. 7587 (1960) 165.

[2.23] GODARD, H.P., TORRIBLE, E.G., Corros. Sci. **10** (1970) 135–142.

[2.24] PATHAK, B.R., GODARD, H.P., Nature (London) **218** (1968) 893–894.

[2.25] MEARS, R.B., BROWN, R.H., Ind. Eng. Chem. **29** (1937) 1087.

Chapter 3

GUIDELINES FOR CORROSION PROTECTION OF RESEARCH REACTOR ALUMINIUM CLAD SPENT NUCLEAR FUEL IN INTERIM WET STORAGE

3.1. INTRODUCTION

On the basis of the knowledge gained during the CRP and the corrosion surveillance programme at SRS, an understanding of the corrosion of aluminium clad spent fuel has been developed. From this understanding, the participants in the CRP have drawn up guidelines for the corrosion protection of aluminium cladding alloys. The proposed guidelines provide practical guidance for spent fuel pool operators, and for this reason they are reproduced below.

About 700 nuclear research and test reactors (hereinafter simply referred to as research reactors) have been constructed around the world since the beginning of the nuclear age. More than 250 of these reactors are still in operation, and many of those permanently shut down are still managing spent fuel in interim storage [3.1]. The most common storage location for spent fuel from research reactors is in at-reactor water pools or auxiliary away-from-reactor pools. Most of the fuel used in research reactors in both eastern and western countries is fabricated with a core consisting of uranium–aluminium alloys and protected by an aluminium alloy cladding. A small percentage of the fuel is clad with stainless steel, zirconium or other alloys. Fuel is regarded as spent nuclear fuel, regardless of burnup, when it is discharged from the reactor core for the final time. It is then normally placed in pools for cooling and interim storage until a final disposition is made. Some of these aluminium clad spent fuels have been in water storage for more than 40 years and remain in pristine condition, while others are severely degraded by pitting corrosion. Pitting corrosion of the fuel can lead to breach of the cladding material and release of radioactivity to the storage basin. This chapter contains guidelines for increasing corrosion protection of aluminium clad spent nuclear fuel in wet storage pools and includes recommendations concerning water chemistry, operational practices and other basin management techniques during extended interim storage. Following the recommendations in these guidelines for obtaining optimum water quality will also help lower the corrosion rates of other cladding alloys used with research reactor fuel.

3.2. SCOPE

These guidelines apply to the interim wet storage of aluminium clad research reactor spent nuclear fuel. They specify recommended water chemistry parameters and other operational practices to minimize corrosion degradation of the fuel in long term extended water storage environments. More than 15 000 research reactor fuel assemblies will be returned to the USA over the next 20 years for ultimate disposition, while other fuel will remain in pools around the world for continued storage. Implementation of these guidelines should enhance storage performance, minimize release of fission products to the storage water and surrounding facilities, and permit safe transport of this fuel to other destinations without using expensive canning techniques.

3.3. CORROSION EXPERIENCE WITH ALUMINIUM CLAD SPENT FUEL IN WET STORAGE

In the past decade many research and production reactors around the world have been shut down. In some cases their fuel and target material has been caught in the back end of the nuclear pipeline while waiting for processing. With the suspension of processing at many of these sites, aluminium clad material that had normally been stored for 12–18 months remained in water for times up to eight years. In some countries, fuel has been stored for up to 40 years. During these storage periods under varying water purity conditions, general corrosion was insignificant. However, pitting corrosion in some cases significantly damaged the aluminium cladding. Pitting corrosion of nuclear fuel can result in a breach of the 0.375–0.750 mm cladding, with subsequent release of caesium isotopes, transuranics and other fission products to the water.

Comprehensive corrosion surveillance programmes at some of these storage basins with aluminium clad fuel have provided insight into corrosion mechanisms involved in the long term wet storage of nuclear fuel [3.2]. In less than optimum quality deionized water with a conductivity of about 200 µS/cm and with a chloride ion content of 10 ppm, severe nodular corrosion developed on the aluminium cladding. Pits that penetrated the aluminium cladding led to release of radionuclides to the water. Routine operations in previous years at 85 µS/cm resulted in insignificant corrosion problems, but fuel was then in storage for much shorter times before being processed. In contrast, fuel stored in another basin on-site where water conditions were strictly maintained at 1–3 µS/cm with a chloride ion content of less than 20 ppb never had pitting corrosion problems over the 35 years of the basin's operational history. An extensive basin cleanup campaign at this site, along with installation of new

basin water deionizers, resulted in high quality storage water with a conductivity of 1–3 μS/cm in all basins, and with chlorides at less than 100 ppb. No new pitting corrosion has been observed in these basins after five years.

Research reactor spent fuel is being stored in water filled basins around the world under a wide variety of conditions. Many of the pools have water purification equipment that maintains the water at high purity levels. In these basins, aluminium clad fuels have been stored for 25–35 years without corrosion problems. Other storage pools are small and do not have high quality water. In these pools, corrosion of aluminium clad spent nuclear fuel has been a problem. As a consequence of the USDOE's decision to have foreign research reactor spent fuel returned to the USA, over 1700 aluminium clad assemblies have been inspected for corrosion and mechanical damage [3.3]. The condition of the assemblies has ranged from pristine, with no visible corrosion, to severely corroded, with nodular corrosion and pitting. Approximately 7% of the assemblies inspected showed pits that had breached the aluminium cladding.

3.4. TYPES OF CORROSION ENCOUNTERED IN SPENT FUEL STORAGE BASINS

The factors promoting corrosion of aluminium alloys are complex and interrelated. They often operate synergistically, making prediction of corrosion difficult. In wet storage of aluminium clad spent fuel, there are a number of corrosion mechanisms involved. The most important mechanisms as related to spent nuclear fuel are briefly discussed here. Other details and definitions related to aluminium corrosion can be found in the normative publications and ISO standards provided therein.

3.4.1. Uniform corrosion

Uniform attack or general corrosion is the most common form of corrosion. It is normally characterized by a chemical or electrochemical reaction that proceeds uniformly over the entire exposed surface or a very large area. This mechanism has not been a significant concern with spent nuclear fuel in wet storage.

3.4.2. Galvanic corrosion

Galvanic corrosion occurs when a metal or alloy is electrically coupled to another, usually dissimilar, metal in the same electrolyte. Severe localized attack is often seen when aluminium alloys are coupled with more noble metals. As this

corrosion is an electrochemical process and depends on the flow of current through the electrolyte (basin water), high purity water offers resistance to this flow and minimizes the corrosion. Galvanic corrosion in spent fuel basins is readily apparent, as dissimilar metallic storage racks, steel buckets, steel hangers and other components are often used and are in direct contact with the aluminium clad fuel and target assemblies. Stainless steel is the main dissimilar metal used in these storage applications and it accelerates the galvanic corrosion of the aluminium clad fuel even in pure, low conductivity water. Storing aluminium clad fuel in aluminium storage containers and aluminium storage racks can minimize corrosion damage.

3.4.3. Crevice corrosion

Crevice corrosion of aluminium alloys is highly localized corrosion occurring on closely fitted surfaces upon entry of water into the crevice. In this type of corrosion, chloride ions are drawn into the crevice, where metal dissolution occurs and acidic conditions exist. Similar to galvanic corrosion, crevice corrosion relies on the flow of current through an electrolyte. Thus crevice corrosion is reduced in low conductivity water. There are a number of locations in spent fuel storage pools where crevice corrosion attack can occur on spent nuclear fuel. Crevices form at the interfaces of fuel elements supported on hangers or resting on storage racks, and also exist between storage racks and metal pool liners. It is not unusual in some fuel storage basins to see aluminium clad target elements stacked in stainless steel buckets, creating conditions for both crevice and galvanic corrosion.

In existing storage facilities, means to minimize crevices are limited. Much of the work needs to be done up front, in the initial design and construction stage of the facility. Storage racks and storage bucket designs should minimize crevices between the aluminium cladding and the storage surface, and permit flow of water across the fuel elements.

3.4.4. Pitting corrosion

Pitting corrosion is an extremely localized form of corrosion that results in holes being produced in the metal. This type of attack is generally limited to small areas, with the large areas remaining passive. Pits, or cavities, can be isolated or can be so close together that they appear as a rough surface. They are often hard to detect, as corrosion products usually cover them. The hydrated aluminium oxide (corrosion product) produced during pitting has a much larger volume than the metal corroded. Pitted aluminium cladding surfaces therefore often reveal small white nodules.

Pitting is one of the most destructive and insidious forms of corrosion and is the main form of degradation of aluminium clad spent fuel in fuel storage basins around the world. It is electrochemical in nature, and the pitting process is autocatalytic. The corrosion processes within a pit produce conditions that are both stimulating and necessary for the pit to grow. The depth of a pit can increase with time and progress through the metal thickness. In the case of aluminium clad spent fuel, penetration of the aluminium cladding results in corrosion of the uranium or uranium–aluminium alloy fuel core and the release of fission products to the storage pool water. The increase in α and β–γ radioactivity can be measured in water specimens taken from the storage basin.

Pits can exist on some fuel when it enters the storage basin. Not all spent fuel cladding is initially in pristine condition. A more severe environment exists in the pit beneath the nodule or crusted oxide corrosion product. Corrosion will likely continue beneath the nodular oxide. However, high quality basin water could minimize or eliminate any new corrosion. In addition, the high quality water could slow pit growth by dilution of the severe environment within the pit.

3.4.5. Hydrogen blisters

Blister formation or raised areas in the cladding of spent nuclear fuel can lead to breach of the aluminium cladding and subsequent corrosion of the fuel core. This blistering is a manifestation of internal gas pressurization and/or internal oxide formation. Blistering is facilitated under coatings and oxides because hydrogen has low diffusion rates in aluminium, so trapped hydrogen disperses slowly. Blisters can be formed by several mechanisms.

(a) *Blisters formed during manufacturing.* Trapped air or inclusions of intermetallic particles formed during the fabrication process.
(b) *Blisters formed from agglomeration of fission gas products.* Fission gases can agglomerate at local unbounded regions at the fuel–clad interface during irradiation. Higher than normal temperature in the reactor or heat buildup in the shipping cask can result in blistering.
(c) *Blisters formed due to corrosion.* This is the most common form of blistering seen on the surface of spent fuel elements and is caused by hydrogen gas formation from normal corrosion reactions of aluminium in the cladding and the fuel core with water. Alloying elements in the aluminium alloy, such as nickel, or impurities trapped in the surface can act as cathodes for hydrogen evolution. If a local unbounded area is located in the proximity of the corrosion pit, hydrogen and/or voluminous

corrosion products can be trapped and result in blister-like morphology in this region.

3.5. PROPOSED GUIDELINES FOR CORROSION PROTECTION OF ALUMINIUM CLAD SPENT FUEL IN WET STORAGE

The corrosion of spent nuclear fuel is dependent on a number of inter-related factors. These factors may operate singly or synergistically, making predictions difficult. Many of the metallurgical factors are already inherent in the spent fuel when the reactor operator receives the fuel from the fuel manufacturer for irradiation. Factors such as alloy composition, heat treatment, microstructure, nature and thickness of the protective oxide coating, inclusions and impurities in the alloy, and cold work play a role in the corrosion process. These factors cannot be controlled during wet storage. The guidelines presented in this chapter refer mainly to the environmental and service related factors that can be controlled and used to optimize corrosion protection of the aluminium clad fuel during interim wet storage.

These guidelines are for corrosion protection of the aluminium cladding, to prevent breach of this cladding and subsequent corrosion of the fuel core. Most research reactor fuel is fabricated from uranium–aluminium alloys, and this type of fuel exhibits corrosion behaviour similar to that of aluminium. Therefore implementation of these guidelines should also minimize corrosion of the fuel core. The corrosion of a metallic uranium core is much more rapid than that of a uranium–aluminium alloy core. Implementing the guidelines to protect aluminium cladding will also reduce the corrosion of this type of fuel core.

3.5.1. Water chemistry

Maintaining high quality water in the fuel storage pool is the single most important factor in controlling corrosion of aluminium clad spent fuel assemblies and other aluminium alloy components stored in the pool. Treatment and purification of the water in the pool and any make-up water with the aid of filters and ion exchange resins is essential to achieve optimum storage performance. The recommended water parameters to minimize pitting and other forms of corrosion on aluminium clad spent fuel during extended interim wet storage are as follows:

Conductivity. The conductivity of the water in the fuel storage basin should be maintained as low as achievable and in the range 1–3 µS/cm for optimum corrosion protection. This level may be difficult to achieve in unlined

pools. Conductivity in the range 3–10 µS/cm may yield satisfactory results provided the concentration of impurities such as chloride ions is low. There is some evidence that pitting may be suppressed below 50 µS/cm, depending on other parameters. Values near 200 µS/cm are known to be aggressive for aluminium and lead to pitting.

pH. The pH should be maintained in the range 5.5–6.5 in reactor pools. This pH level will minimize uniform corrosion. Pitting corrosion is not affected by pH in this range. Tight control of pH is essential in reactors where the same cooling water is shared by the core and the fuel storage basin. In away-from-reactor storage pools, a wider range of pH, 5.0–8.0, may be permissible. Irradiation is known to reduce the range within which the protective aluminium oxide is stable and can result in increased turbidity from precipitation of aluminium hydroxide from the water.

Chloride (Cl). The chloride ion content of the water should be maintained as low as achievable and at less than 1 ppm for optimum corrosion protection. This level is generally achievable if water conductivity is maintained in the 1–3 µS/cm range. Chloride ions break down the passive film on aluminium and promote metal dissolution.

Sulphates (SO_4). The total sulphate ion content of the water should be maintained at less than 1 ppm for optimum corrosion protection. However, for unlined pools where water quality is difficult to control, sulphates at or below 10 ppm should give satisfactory protection. An increase in sulphate concentration results in a decrease in thickness of the protective oxide film, with a corresponding increase in susceptibility to pitting corrosion.

Heavy metals. The concentration of copper, mercury, silver and other heavy metal ions should be maintained at or below 0.02 ppm. Heavy metal ions are extremely aggressive in causing pitting corrosion of aluminium, as they deposit readily, forming strong galvanic cells. These ions have strong synergistic reactions with chloride, bicarbonate and calcium ions. Reduced metals in the basin sludge or particles in the basin water can deposit and form galvanic cells, leading to localized corrosion of aluminium cladding.

Other impurities. Impurity ions such as iron, aluminium, nitrates and nitrites should be maintained at levels as low as possible. Normal deionization of the water in the storage pool to conductivity levels of 1–3 µS/cm should keep these impurities at or below the 1 ppm level. The presence of impurity ions increases water conductivity and the flow of corrosion current, thereby increasing the corrosion of the aluminium cladding.

Hardness. The carbonate hardness of the water should be maintained at 60 ppm or less when possible. Carbonate and bicarbonate ions can react synergistically with chloride and copper ions, resulting in increased pitting of aluminium. Soft water, defined by a carbonate content of 60 ppm or less, is not

as aggressive in causing aluminium corrosion as hard water. Continuous deionization of the basin water softens the water, as it removes calcium carbonate and other ions contributing to the hardness.

Temperature. The water temperature should be maintained at 40°C or below. The rate of pitting at 40°C has been found to be five times that at 25°C. The density and probability of pitting have been found to increase with temperature. The corrosion rate of uranium metal increases dramatically with increasing temperature.

Radiation effects. Gamma radiation from irradiated fuel assemblies, ^{60}Co or radioactive caesium sources can have some effect on materials stored in fuel storage pools. Gamma fluxes have little effect on the properties of the cladding, and the radiation field does not promote any significant increase in corrosion of the metals in wet storage. Gamma fields can degrade components subject to radiolytic decomposition, such as neutron absorbers that contain organic materials and rack configurations that trap water. In the latter case, radiolytic decomposition can result in gas formation and a consequent buildup in pressure.

3.5.2. Operational practices

Water circulation. Regions of stagnant water in the fuel storage basin should be avoided. It should be ensured that the water is circulated and in movement over the stored fuel assemblies. For example, a linear flow rate of about 2.4 m/min over the aluminium surface has been shown to suppress pitting on some aluminium alloys.

Sludge removal. Sludge should not be allowed to accumulate in the fuel storage basin but should be removed periodically by vacuuming or other methods. This material can contain chlorides, heavy metals, etc., and deposit on fuel assemblies, initiating pitting of the aluminium cladding.

Filtration. Mechanical filters or resin beds should be used to control the amount of suspended solids or particulate material in the basin water, before they turn into sludge. Deionization of the water helps to accomplish this.

Skimmer system. Debris and other species floating on the water surface of fuel storage pools should be removed by a skimmer system or other means. This material can settle on the surfaces of fuel cladding and cause pitting corrosion.

Crevices. Crevices between the aluminium clad assemblies and fuel storage racks or hangers should be avoided. Reduced pH, concentration of chloride ions and oxygen concentration cells in these crevices can lead to accelerated corrosion of the cladding.

Galvanic couples. Contact between aluminium clad fuel assemblies and dissimilar metal storage racks or hangers should be avoided. Aluminium storage racks should be used or non-conducting insulators provided whenever

possible. Aluminium clad fuel assemblies coupled to stainless steel racks or hangers can accelerate pitting corrosion of the aluminium.

Handling of spent fuel. Fuel assemblies should not be handled with sharp edged tools, as scratches in the oxide coating of irradiated fuel serve as pit initiation sites in the storage basin. Mechanical damage and surface scratches on fuel element surfaces should be minimized as much as possible during discharge from the reactor core and during subsequent fuel handling and storage operations.

Microbiological activity. Chemicals containing chlorides or other halogens such as sodium hypochlorite should not be added to storage basin water to control algae, bacteria or turbidity without first testing for compatibility with the fuel, the basin lining and other basin components. The chloride ions in these chemicals will destroy the passive film on aluminium and cause aggressive pitting corrosion.

Biofilm formation at the air–water interface. The 'bathtub ring' often formed at the air–water interface around the sides of the basin is likely to be a biofilm due to microbial activity. This film acts like a trap and is known to concentrate caesium and other radioactive isotopes contained in the basin water. This biofilm should be removed mechanically by wet brushing, using water to hold down any airborne activity. A 35% solution of hydrogen peroxide has proven effective in suppressing microbial activity and could be used to assist in biofilm removal without corrosive attack on aluminium alloys.

Basin lighting conditions. The lighting level should be maintained as low as practical in and around the basin area. High levels of lighting promote microbiological growth in the water. Ultraviolet lighting can be used to suppress the microbiological activity associated with filters, etc. However, sidestream ultraviolet systems are used primarily against planktonic activity and are not effective against sessile colonies.

Make-up water. Make-up water added to the fuel storage pool should be of a quality that is equal to or better than that of the existing pool water. Deionized water should be used whenever possible.

Radionuclide activity in the basin water. Radionuclide activity in the basin water (leached from the spent fuel) should be monitored and controlled to levels deemed to be safe for personnel working in the surrounding area. Continuous deionization of the water removes α and β–γ radioactivity from the water. Fission products such as ^{137}Cs and other radionuclides may be found in the water where failed spent fuel elements or cladding breached fuels are stored. Special materials such as zeolite can be used in ion exchange type purification systems to specifically remove these radionuclides.

Water sampling plan. Maintaining water purity levels as recommended here is vital for successful operation of a wet fuel storage facility. Basin water quality is monitored through sampling. All the major water parameters, such as pH,

conductivity and chloride ion content, should be measured on a periodic basis, consistent with good basin management practices. Weekly monitoring is recommended, but the basin operator can establish this interval according to pool conditions. Other impurity ions such as sulphates, nitrates, nitrites, copper, mercury, iron and aluminium should be measured at least quarterly. Temperature should be monitored daily. Measurement of α and β–γ radioactivity in basins storing spent fuels should be made at intervals established according to individual requirements. An increase in radioactivity is an indication of corrosion. Permanent records should be kept and analytical results trended.

A sampling of the basin water should be used to make a baseline evaluation of microbiological activity in the basin. This analysis should include counts of hetrotrophic, acid producing, anaerobic and sulphate reducing bacteria. These baseline data can be used for comparison with subsequent bacterial analysis data.

Corrosion surveillance programme. A long term corrosion surveillance programme should be implemented in the fuel storage pool to monitor the aggressiveness of the basin water in causing the corrosion of aluminium alloys. Details for specific site programmes can be tailored to the individual sites but should contain the main elements described in these guidelines. A typical programme that has been implemented in a number of countries with research reactor fuel is described in Ref. [3.4]. Corrosion racks with coupons manufactured from aluminium alloys typical of the spent fuel cladding should be immersed in the water near the stored aluminium clad spent fuel. Standard corrosion coupons, either round or rectangular in shape, should be used. Each rack should comprise multiple coupons representing individual aluminium alloys, crevice corrosion coupons and galvanic coupons. The coupons should not be preoxidized and should have air formed oxide only on the surface. This ensures some conservatism.

A schedule for withdrawal of these coupons should be formulated on the basis of the length of time the fuel is expected to be in the basin and the total number of corrosion racks available for testing. As a minimum, there should be enough racks available to obtain data after six months, one year and two years, to provide an early indication of the aggressiveness of the storage environment with respect to the aluminium coupons. The surveillance programme should continue for a length of time depending on the expected storage life of the fuel. For a 20 year programme, withdrawals could be extended to five, ten and 20 years of exposure time. If the water conditions are more aggressive, additional racks may be required and more frequent intervals of withdrawal may be necessary.

Metallographic evaluation of the corrosion coupons should include determination of pitting density and maximum pit depth. With knowledge of the pitting depth and exposure time, the pitting rate may be calculated. Video and

still colour photography should be used to document the withdrawals. Data from the water analyses performed during the exposure periods should be correlated with the corrosion observed on the coupons to explain the test results.

Records management programme. Data on basin water chemistry and the corrosion surveillance programme should be maintained at each basin site.

REFERENCES TO CHAPTER 3

[3.1] RITCHIE, I.G., ERNST, P.C., "Overview of spent fuel management and problems", Proc. 2nd Int. Topical Mtg on Research Reactor Fuel Management, Bruges, Belgium, 1998, European Nuclear Soc., Brussels (1998) 105–109.

[3.2] HOWELL, J.P., BURKE, S.D., "The corrosion of aluminum-clad spent nuclear fuel in wet basin storage", Proc. Embedded Topical Mtg on DOE Spent Nuclear Fuel and Fissile Material Management, Reno, 1996, American Nuclear Soc., La Grange Park, IL (1996) 49–56.

[3.3] BROOKS, P., SINDELAR, R.L., "Characterization of FRR SNF in basin and dry storage systems", Proc. 3rd Topical Mtg on DOE Spent Fuel and Fissile Materials Management, Charleston, SC, 1998, USDOE, Washington, DC (1998) 542–549.

[3.4] HOWELL, J.P., "Corrosion surveillance for research reactor spent nuclear fuel in wet basin storage", Corrosion/99, Natl Assoc. of Corrosion Engineers, Houston, TX (1999) paper 462.

Chapter 4

CRP TEST MATERIALS, RACKS AND EXPERIMENTAL PROTOCOLS

4.1. INTRODUCTION

Spent nuclear fuel assemblies from Western research reactors are mostly of the MTR box type with fuel plates. There are also fuel assemblies with involute cores, tubular configurations, rod clusters and pin assemblies. The Russian designed spent nuclear fuel assemblies have different geometries and can be divided into two main groups: multitube or multirod assemblies. The fuel core in all these fuel assemblies consists of U–Al alloys, or $UAl_x + Al$, U_3O_8 or U_3Si_2 dispersions in an aluminium matrix. The uranium in the fuel assemblies is enriched to <20% (LEU) or ≥20% (HEU), and the cladding alloys are usually 1100, 6061 or 6063 alloys[4.1]. The thickness of the cladding in the different assemblies varies in the range 0.35–0.75 mm. In the box type MTR fuel assemblies, the support plates are made of either 6063 or 6061. The interim storage of these different types of fuel assembly is mainly in light water filled basins, either at the reactor site or away from the reactor site, often in racks made of aluminium alloys or stainless steels.

Two of the main objectives of this CRP were:

(1) To establish uniform corrosion monitoring and surveillance practices,
(2) To provide technical guidelines for continued wet storage of spent fuels.

In order to achieve these objectives, standard coupons assembled in racks were exposed for extended periods in the spent fuel storage basins of the nine participating countries. These specimen racks were withdrawn for interim and final inspections. This chapter provides details about (a) the materials, coupons and racks; and (b) the protocol.

Two sets of racks with test coupons were prepared and distributed to the participants of this CRP at the first RCM, held in Budapest in 1996, and at the second RCM, held in São Paulo in 1998.

[4.1] In this book, the numbers given for aluminium alloys refer to the Aluminum Association (AA) specifications.

4.2. MATERIALS, COUPONS AND RACKS

The materials were selected to represent typical aluminium alloys used for fuel cladding, handling tools and fuel assembly storage racks. The alloys were: 1100, 5086, 6061 and 6063; SZAV-1; and stainless steel AISI 304 (or AISI 316) (hereafter referred to as SS 304 or SS 316). The test coupons were prepared from a single source to be representative of the alloys used in research reactors worldwide. A commercial aluminium smelter company, contracted by KFKI in Hungary, supplied the coupons. The compositions of the as-cast alloys are shown in Table 4.1. The alloys were produced in sufficient quantities to provide coupons to be used throughout the programme by all the participants. The requirements that were taken into consideration for producing the coupons and the racks included:

(a) Testing the effect of the basin water environment;
(b) Testing crevice corrosion between aluminium alloy coupons;
(c) Testing galvanic corrosion between aluminium alloys and stainless steel coupons;
(d) Ease of transport of the coupons and the racks;
(e) Allowing site specific test coupons to be included in the overall test rack.

With these factors in mind, disc type coupons were chosen. These were similar to the American Society for Testing and Materials (ASTM) test coupons but smaller in diameter (100 and 70 mm) to facilitate transport. Single sheet coupons were used to evaluate pitting corrosion on exposed surfaces, and couples or sandwich type coupons were used to simulate crevice and/or galvanic corrosion. The coupons were cleaned and numbered, and the alloy type was identified using a laser scriber. The coupons were stacked in a stainless steel rack. This consisted of a steel pipe welded to a stainless steel base plate and threaded at the other end to hold the coupons in place with a stainless steel nut welded to a hook to enable the rack to be suspended with a nylon rope. A

TABLE 4.1. CHEMICAL COMPOSITION (wt%) OF ALUMINIUM ALLOYS

	Cu	Mg	Mn	Si	Fe	Ti	Zn	Cr	Be
1100	0.16	<0.1	0.05	0.16	0.48	0.005	0.03	0.005	
5086	>0.2	4.1	0.43	0.19	0.33	0.04	0.045	0.10	0.004
6061	0.25	0.94	0.12	0.65	0.24	0.04	0.03	0.04	
6063	0.16	0.73	<0.05	0.37	0.24	0.04	0.03	0.055	
SZAV-1	<0.01	0.53	<0.05	0.71	0.09	<0.005	0.03	<0.005	
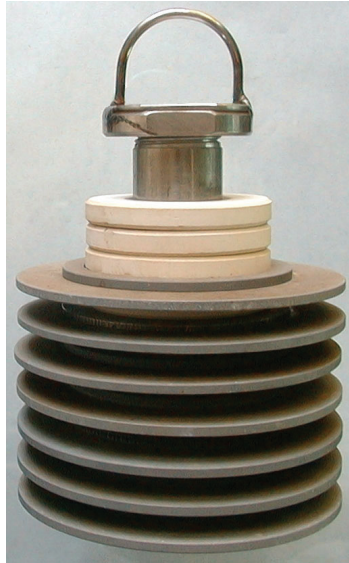
FIG. 4.1. A Batch I rack.

tubular ceramic sleeve was used to encase the stainless steel tube and to avoid contact between the tube and the coupons. Ceramic rings (alumina) were used to insulate the coupons from each other. Racks containing these coupons were distributed to the participants at the first RCM in 1996 (these racks are referred to here as Batch I), and during the second RCM in 1998 (Batch II). A photograph of a Batch I rack is shown in Fig. 4.1.

4.2.1. Batch I racks

The coupons of Batch I were made of 1100 and 6061, the crevice couples were 6063–6063 coupons and the galvanic couples were made up of 6061–SS 316. Small glass ampoules containing 9 mL of high purity water (pH7.2, conductivity 0.39 μS/cm) and small, riveted 1100–6063 tensile test type coupons were inserted into the hollow of the central stainless steel tube of the rack. (Fig. 4.2.) These coupons were included to evaluate the effects of temperature and radiation on the corrosion behaviour of the encapsulated crevice coupons. The assembled racks were approximately 150 mm high and 100 mm in diameter. The height of the racks was designed to permit further site specific alloy coupons to be included, besides the standard set of coupons, to test general, crevice and galvanic corrosion.
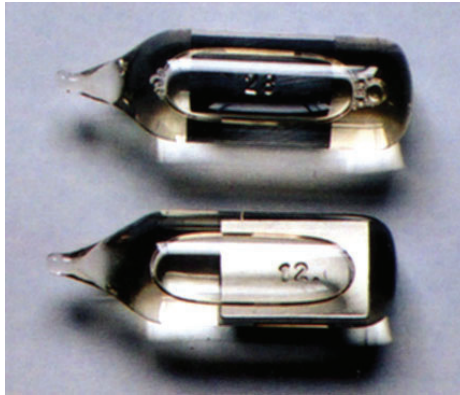
FIG. 4.2. Glass ampoules with crevice coupons.

One or two racks were handed out to each of the participants. The kits included the rack with the coupons, the insulating rings and two ampoules containing the tiny coupons. The rack components were degreased in alcohol, rinsed in deionized water, dried in air at room temperature and assembled. The participants were advised to handle the rack and the coupons with gloves during disassembly for weighing, photographing and reassembling prior to exposure in their storage basins.

Though the original information package for the proposed CRP specified six base metals, two crevice sandwiches and four galvanic couples for exposure, the racks of Batch I contained fewer coupons.

The specimen stacking sequence was as follows, from top to bottom in the racks of Batch I: 1100, 1100, 6061, 6061, SZAV-1, SZAV-1, 6063–6063, 6063–6063, SS 316–6063, SS 316–6063.

The participants were instructed to expose these racks in representative spent nuclear fuel assembly storage basins. They were also encouraged either to add coupons made of site specific alloys to these CRP racks or to fabricate similar racks with site specific alloy coupons. None of the participants added site specific alloy coupons to the racks of Batch I. China, however, prepared and exposed a separate rack with Chinese alloy coupons. This rack was exposed prior to the second RCM. The Chinese rack included coupons of the aluminium alloys 305 and LT24L and of SUS 304-8K; the composition of these alloys is given in Table 4.2. A photograph of this rack is shown in Fig. 4.3. Table 4.3 shows the position of these alloy coupons in their additional rack. Brazil manufactured a separate rack (the IPEN rack) of coupons. This included a large number of coupons in different configurations, to allow evaluation of the effect of fuel

TABLE 4.2. CHEMICAL COMPOSITION (wt%) OF COUPONS IN THE CHINESE RACK

	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	C	P	S	Ni
LT24[a]	0.4–0.8	0.7	0.15–0.4	0.15	0.8–1.2	0.04–0.35	0.25	0.15				
305[b]	0.17	0.45–0.7	0.15				0.05					
SUS 304-8K	<1.0			<2.0		17.0–19.0			<0.07	<0.035	<0.03	8.0–11.0

[a] Quenched.
[b] Annealed.

TABLE 4.3. POSITION OF SPECIMENS IN THE CHINESE TEST RACK

Specimen configuration	Position in rack[a]	Alloy	Size (mm)
Uncoupled	1 (5-1)	SUS 304-8K	$\varnothing$ 70/31 × 1
	2 (6-2)	SUS 304-8K	$\varnothing$ 100/31 × 1
	(6-1)	SUS 304-8K	$\varnothing$ 100/31 × 1
Crevice couple	3 (1-2)	305	17 × 10 × 2
	(1-1)	305	17 × 10 × 2
	4 (4-2)	LT24	32 × 10 × 2
	(4-1)	LT24	32 × 10 × 2
Galvanic couple	5 (2-1)	305	32 × 20 × 2
	(3-1)	LT24	17 × 10 × 2
Uncoupled	6 (3-2)	LT24	17 × 10 × 2
	7 (2-2)	305	32 × 10 × 2

[a] From bottom to top.

TABLE 4.4. CHEMICAL COMPOSITION OF ALUMINIUM ALLOYS USED IN THE IPEN RACK

Element	1060	6061	6262
Si	<0.25%	0.4–0.8%	0.4–0.8%
Cu	<0.05%	0.15–0.4%	0.15–0.4%
Fe	<0.35%	<0.7%	<0.7%
Mn	<0.03%	<0.15%	<0.15%
Mg	<0.03%	0.8–1.2%	0.8–1.2%
Zn	<0.05%	<0.25%	<0.25%
Ti	<0.03%	<0.15%	<0.15%
Cr		0.04–0.35 ppm	0.04–0.14 ppm
B	<10 ppm	<10 ppm	<10 ppm
Cd	<10 ppm	<10 ppm	<10 ppm
Co	<30 ppm	<30 ppm	<30 ppm
Li	<80 ppm	<80 ppm	<80 ppm
Others	<0.03% individual	<0.15% total	
Al	>99.6%	Balance	Balance

TABLE 4.5. SEQUENCE OF SPECIMENS IN THE IPEN RACK[a]

Configuration	Alloys	Condition
Uncoupled	1060	
Uncoupled	6061	
Uncoupled	6262	
Coupled	1060–6061	
Coupled	6061–SS 304	
Coupled	6262–SS 304	
Coupled	1060–SS 304	
Coupled	1060–1060	
Coupled	6061–6061	
Uncoupled	1060	Preoxidized
Uncoupled	1060	Preoxidized and scratched

[a] Four specimens of each configuration; from top to bottom of the rack.

plate processing conditions on pitting, crevice and galvanic corrosion of Brazilian alloys used in the manufacture of fuel elements for the IPEN IEA-R1 research reactor. The processing conditions included preoxidation and scratching of preoxidized coupons to simulate surface oxide damage during handling.

The IPEN rack exposed aluminium alloys 1060, 6061 and 6262, used in the fabrication of fuel assemblies for IPEN's IEA-R1 research reactor. The composition of these alloys is given in Table 4.4. Besides 80 mm diameter coupons of the three alloys, the rack included coupons of 1060 in the processed and scratched condition (to simulate the effect of scratches formed on fuel assemblies during handling in the reactor) and various combinations of galvanic and crevice couples. Table 4.5 lists the sequence of the coupons in the IPEN rack.

The participants were instructed to disassemble the racks, weigh the coupons, photograph the two sides of the coupons, assemble the rack, photograph the assembled rack and then introduce the rack into the spent fuel storage basins. The coupons were to be exposed in the fuel storage basins in the as-received condition. The racks and coupons issued to Brazil were disassembled and handled without gloves during demonstration at the Budapest meeting. Consequently the surfaces of the coupons of these racks were treated using the following procedure: cleaning/washing in deionized water, degreasing in analar grade ethanol, rinsing in deionized water and drying in forced air at room temperature.

The number of racks distributed to each participant was limited (just one or two). This precluded the removal of one rack after increasing periods of

FIG. 4.4. A Batch II rack.

exposure. Consequently the participants were asked to remove the rack from the basin water, inspect and photograph the coupons, reassemble the rack and return the rack to its original position in the storage basin, all this while preventing, if possible, the coupons from drying out.

The various participants adopted different procedures for interim inspection, in many cases invalidating their results. To avoid this in subsequent tests and to obtain more meaningful information, a test protocol was elaborated at the second RCM.

4.2.2. Batch II racks

Another set of racks manufactured by KFKI from the original batch of alloys was handed out at the second RCM.

The procedure adopted for preparing the coupons of this batch was slightly different. The surfaces of the coupons were mechanically polished, as opposed to the plain machine finishing that had been adopted for the coupons of Batch I. The racks of Batch II (Fig. 4.4) did not contain the glass ampoules with the tiny tensile test type coupons, and the coupons in each rack of Batch II

were fewer in number and were arranged in the following order: galvanic: SS 316–6063; galvanic: SS 316–6061; crevice: 6063–6063; crevice: 6061–6061; crevice: 1100–1100.

The 6063 coupons of this batch were passivated in water at 95°C for 24 h and were scratched to simulate the effect of surface oxide damaged during handling. Two or more racks were handed out to each of the participants. The racks were to be removed after one and two years of exposure in the storage basins.

The Argentine experience included the exposure of six racks at various storage sites. Four of the six racks (from Batch II) included some Argentine alloy coupons and two of the racks contained only Argentine coupons. Table 4.6 gives the position of the coupons in the racks.

In order to maximize the amount of information that could be obtained with the limited number of racks handed out to each participant, interim inspections of the racks and the specimens were recommended, especially without disassembly of the racks and without allowing the racks to dry out. These instructions constituted the test protocol. Guidelines for specimen evaluation also formed part of this test protocol.

4.3. TEST PROTOCOL

Definitions: The corrosion rack is the assembled set of coupons, spacers, central support tube and hanger. A basin, pool or pond is the contained volume of water used for storage of spent fuel. In some cases the pool also contains the reactor core.

4.3.1. Preassembly

(a) Unpack and handle the components with surgical gloves (with any talcum powder on the outside washed off).
(b) The weighing of individual coupons is optional.
(c) The rack numbering system is up to the individual participant, because site specific coupons of either large or small size may be added. The numbering system chosen should be logical, carefully recorded at the beginning of testing and adhered to throughout the programme.
(d) Photograph the front and back of each coupon and the overall assembled rack.
(e) No cleaning of coupons is required if the rack was received in a sealed plastic bag. If, however, the rack has been handled without gloves, cleaning will be necessary.

TABLE 4.6. POSITION OF ARGENTINE 6061 (A) AND OTHER COUPONS IN THE RACKS

Position in rack from top	Rack number	2	3	4	5	6	7
Top	Crevice	A	A	A	A	A	A
Bottom	couple	A	A	A	A	A	A
Top	Crevice	A	A	A	A	A	A
Bottom	couple	A	A	A	A	A	A
Top	Crevice	A	A	A	A	A	A
Bottom	couple	A	A	A	A	A	A
Top	Crevice	6063	6063	6063	6063	A	A
Bottom	couple	6063	6063	6063	6063	A	A
Top	Crevice	6061	6061	6061	6061	A	
Bottom	couple	6061	6061	6061	6061	A	
Top	Crevice	1100	1100	1100	1100	A	
Bottom	couple	1100	1100	1100	1100	A	
Top	Galvanic	6063	6063	6063	6063	A	A
Bottom	couple	SS 316	SS 316	SS 316	SS 316	SS 304	SS 304
Top	Galvanic	6061	6061	6061	6061	A	A
Bottom	couple	SS 316	SS 316	SS 316	SS 316	SS 304	SS 304
Top	Galvanic	A	A	A	A	A	A
Bottom	couple	SS 304	SS 304	SS 304	SS 304	SS 304	SS 304
Top	Galvanic	A	A	A	A	A	A
Bottom	couple	SS 304	SS 304	SS 304	SS 304	SS 304	SS 304
Top	Galvanic	A	A	A	A	A	
Bottom	couple	SS 304	SS 304	SS 304	SS 304	SS 304	

4.3.2. Assembly

(a) Assemble the coupons in the specified order — large coupons on top with the deliberately scratched side facing up.

(b) Add extra coupons of site specific materials, noting their position and recording all relevant information on them.

(c)   Tighten the top hanger nut by hand until tight and then give a further 10°
turn.

(d)   Attach wire/nylon rope to the hanger on the rack (remember that
aluminium and steel form a galvanic couple).

4.3.3. Immersion in the storage basin

(a)   Position the corrosion rack in the water in the vicinity of the spent fuel if
possible.

(b)   Position the rack below the water surface and above the basin floor. Do
not allow it or any of the coupons to touch the side walls, the floor, sludge
or metallic components.

(c)   Record the location (depth, distance from walls, etc.). Make a sketch as a
reminder and for the final report.

(d)   Measure the radiation field intensity at periodic intervals underwater
near the rack (in R/h or Sv/h).

(e)   Sample the water at the immersion depth as near to the rack as possible.

(f)   Indicate flow conditions near the rack (flowing or static), and rate or
frequency of renewal of water in the basin.

(g)   Observe if loose particles are present on the coupon surface, and if they
appear to be causing a corrosion problem, describe it.

4.3.4. Exposure interval

(a)   Place racks 2 and 3 into the water as soon as possible.

(b)   Record the date of immersion.

(c)   Leave rack 2 in the basin water for one year from the immersion date.

(d)   Leave rack 3 in the water for continued exposure. You will be notified
when to remove this rack after an evaluation of the results from rack 2
examinations has been carried out.

4.3.5. Removal and examination of coupons

(a)   Withdraw the rack assembly from the basin.

(b)   Measure the pH of water on the external surfaces of the coupons.

(c)   Compare with the pH of the bulk water sample.

(d)   Photograph the overall rack assembly prior to disassembly. Photograph
all points of interest showing significant corrosion phenomena, including
any corrosion of the edges.

(e)   Remove the individual coupons from the rack assembly.

(f)   Photograph the front and the back of each individual coupon. A small card with a note of the material, immersion time and identity number, photographed together with the coupon surface, would be very useful.
(g)   Count the number of pits.
(h)   Provide written observations of specific corrosion phenomena for individual coupons, including ease of removal (ease of separation of crevice/bimetallic coupons), amount and type of loose deposits, staining, discoloration, pitting, tenacious or loose oxides, raised embedded particles felt with a gloved finger, etc.
(i)   Separate crevice coupons and measure the pH on their inside faces; compare with the pH of the bulk basin water and of the water on the outside surfaces.

4.3.6. Post-storage detailed examination

(a)   Decontaminate the coupons with a chloride free detergent and rinse with deionized water.
(b)   Air dry/wipe.
(c)   Use a 50% solution of phosphoric acid, if necessary, to clean/dissolve oxide from pits in order to conduct a metallographic evaluation. Immerse for a short interval only. Remove from the solution as soon as bubbles start to increase. Further exposure will dissolve the base metal.
(d)   Ensure that there are no oxides in the pits before determining the true pit depth.
(e)   Conduct a metallographic evaluation of the deepest pits. Measure pit depth with a stylus or using the calibrated focusing technique.

4.3.7. Final report

4.3.7.1. Preparation

Weighing of the coupons is at the discretion of the participant. No further cleaning is necessary prior to immersion in the pool. However, all handling should be carried out with clean gloves. No further surface treatment is necessary. Each rack has one disc that was passivated at 95°C for 24 h in water. The surface of this passivated disc was scratched with a 1 mm wide scriber (on the side without the identification number). A quality assurance document is enclosed in each shipping box. All participants should, if possible, include further coupons on the racks, especially if their aluminium alloy is of a different composition or microstructure from the coupons supplied.

4.3.7.2. Evaluation

All participants are requested to focus on localized corrosion mechanisms and to remember that the primary purpose of the CRP experiments is to relate what is seen on the racks to the performance of the fuels in the storage basins.

Pitting corrosion

(a) Pits should be photographed.
(b) Pit depth should be determined, if a stylus device or a calibrated microscope stage is available.
(c) Final evaluation should focus on the deepest pits and should be carried out by sectioning and polishing, as in the preparation of all metallographic coupons.
(d) The section should be through the deepest part of the pit.
(e) Some attempt should be made to count the pits along with measurement of their diameters and depths. A stochastic approach can be used.

Crevice corrosion

Opening a crevice couple destroys or drastically changes the crevice features. Therefore a crevice couple should be opened and evaluated only once. If you reuse the couple, the surfaces should be machined and/or polished to reproduce the surface finish of the coupons.

(a) Visual and photographic inspection, together with the determination of the pH using pH paper, is the first step.
(b) Metallographic evaluation should be carried out and some evaluation of the area of attack should be made.
(c) Evaluation of pitting in the crevice should follow the above instructions for pitting corrosion.

Galvanic corrosion

Galvanic couples should be treated in precisely the same way as crevice couples.

4.4. CONCLUDING REMARKS

The information provided in this chapter served as the basis for the corrosion surveillance tests carried out by the participants in the storage basins in their countries. The results of these tests are reported in Chapters 5–13.

Chapter 5

CORROSION OF RESEARCH REACTOR
ALUMINIUM CLAD SPENT FUEL IN WATER
AT VARIOUS SITES IN ARGENTINA

5.1. GENERAL INTRODUCTION

Several experimental nuclear reactors have been put into service in Argentina since the early 1960s. All of them use aluminium clad fuel, most of the MTR type. RA3, located at the Ezeiza Atomic Centre (near Buenos Aires) is the most powerful of these experimental reactors. It started up burning 90% enriched uranium, and the fuel plates were made of pure (99.7%) aluminium. It was converted to use 20% enriched uranium at the end of the 1980s, and at that time the fuel plates started to be manufactured with 6061 alloy. Some of the earliest irradiated fuel elements were inserted into RA6 in Bariloche (some 1700 km south-west of Buenos Aires), a zero power reactor, where they have been in service for almost 20 years.

RA3 spent fuel elements are normally maintained in a decay pool for a limited time before being stored in the Central Storage Facility (CSF) in Ezeiza. In the case of RA6, the bundles that are not in use are kept in this reactor's decay pool (DP). In all cases, the fuel has to sustain long periods of immersion in water. In aqueous environments, aluminium and its alloys are known to be subject to corrosion processes, which are strongly dependent on the water quality. In the RA6 reactor pool (RP) the water is continuously monitored for conductivity. Whenever this value reaches a level of about 0.8 µS/cm, the purification procedure is initiated and is continued until the value has decreased to 0.4 µS/cm. In the RA3 and RA6 DPs, however, the monitoring is not on-line.

The CSF consists of an interconnected array of steel tubes buried in the ground. It has two sections with 16 lines of eight tubes each; two fuel elements fit into every channel. The water can circulate through the channels of each line to be purified by an external device. However, owing to the room activity increase produced when this operation was performed, the purification procedure was discontinued and the water became stagnant.

Given the different water control conditions in each of the sites, it was decided to conduct the CRP monitoring programme in the CSF, RA3 DP, RA6 DP and RA6 RP. A total of seven racks were used. The programme was divided into two stages. In the initial stage, the first rack (rack 1) was used to monitor only one of the facilities, in order to gather data to improve the surveillance routine. In the second phase, the work was extended to all the locations.

5.2. FIRST STAGE: RACK 1

5.2.1. Introduction

The assembly rack distributed during the first RCM, in 1996, was immersed in one of the open channels (channel 46) at the CSF, in order to study the corrosion behaviour of the different alloys in the water of that basin. The procedure for the preparation, immersion and corrosion analysis of the samples is described below.

5.2.2. Experimental set-up

Before immersion, both sides of the samples were photographed at sufficient magnification to allow them to be identified and to establish the initial surface condition. Then they were cleaned, weighed in a precision balance and degreased, and finally the rack was assembled and stored up until the immersion time.

The cleaning of the samples was conducted using detergent and water, and the drying was done with the help of alcohol and a warm air blower, to ensure a proper weight measurement. This was conducted with a balance with a precision of 0.01 g, although only the first decimal place was recorded. Table 5.1 shows the values obtained for each sample.

After weighing, all the material was degreased with acetone and dried with a warm air current, and the rack was assembled with the samples following the order indicated in Table 5.2. Finally, the full ensemble was stored in a sealed plastic envelope until time for immersion.

In order to avoid electric contact between parts of the rack and the channel wall, six Teflon separators were installed on two samples, providing three points of insulation at two different heights. Alterations of the sequence order with respect to the test plan were needed to have enough room for the pieces. Besides the samples listed in Table 5.2, two encapsulated galvanic couples were placed inside the assembly. The whole system was hung above the basin tube using a 0.5 inch (1.27 cm) diameter nylon rope; then it was lowered inside the channel down to 20 cm above the bottom of the channel. In this position, the rack shares the water with the stored fuel; however, the nearest fuel element is in the next channel, about 1 m away through the ground.

Samples of the water contained in the test channel were taken in order to conduct a chemical analysis for the following: pH; conductivity; and chloride, nitrate, nitrite and sulphate contents.

TABLE 5.1. WEIGHT VALUES OF THE SAMPLES

Material	Identification number	Weight (g)
6063	15	18.2 ± 0.1
6063	16	18.3 ± 0.1
6063	64	50.0 ± 0.1
6063	65	50.1 ± 0.1
6061	08	18.3 ± 0.1
6061	09	18.3 ± 0.1
6061	69	50.1 ± 0.1
6061	70	50.4 ± 0.1
1100	03	18.6 ± 0.1
1100	72	51.0 ± 0.1
1100	77	48.8 ± 0.1
1100	79	49.5 ± 0.1
1100	80	49.5 ± 0.1
SZAV-1	07	18.5 ± 0.1
SZAV-1	51	48.3 ± 0.1
5086	13	17.9 ± 0.1
SS 316	08	49.1 ± 0.1
SS 316	09	49.4 ± 0.1
SS 316	10	49.3 ± 0.1
SS 316	27	49.0 ± 0.1
SS 316	28	49.1 ± 0.1

TABLE 5.2. DESCRIPTION OF THE RACK

Position (from top to bottom)	Sample arrangement
1	1100, large, single
2	6063–6063, small, crevice
3	1100, large, single
4	6061, large, single
5	6061, large, single
6	6063–6063, large, crevice
7	SZAV, small, single
8	SZAV, large, single
9	6061–SS 316, small, couple
10	6061–SS 316, small, couple

Note: Large and small refer to the diameter of the individual samples. Crevice: an Al–Al sandwich; couple: an Al–SS galvanic couple.

5.2.3. Results of evaluation of rack 1

After 60 days of exposure to the water of channel 46 of the CSF, rack 1 was taken out of its position for a routine inspection. Since the samples showed clear signs of corrosion attack when inspected visually, the whole rack was withdrawn in order to assess its condition. When extracted, the rack was found to be partly covered by a brownish layer and scattered black particles. Several samples showed signs of corrosion. Figures 5.1–5.3 show the rack after being extracted. The Teflon separators can be seen. In all three figures, signs of corrosion are detectable. In the top coupon, several white blisters were observed. After a gentle cleaning of part of the surface, a pit was found underneath each of them, as shown in Fig. 5.4. Figure 5.5 shows a larger magnification of the side view, in which corrosion products are seen emerging from inside the galvanic couples.

5.2.3.1. Disassembling and decontamination

During disassembly of the rack, it was noted that the plates of the large crevice sandwiches were stuck together, and it took a fairly strong shock to separate them. After the coupons were thoroughly rinsed with tap water, they were washed using a general purpose detergent and rinsed again, and their activity was measured (Table 5.3).

TABLE 5.3. SURFACE CONTAMINATION (Bq/cm^2)

Material	Identification number	Front	Back
6063	15	1.00	1.00
6063	16	0.75	2.00
6063	64	1.75	0.50
6063	65	1.00	2.50
6061	08	1.00	3.25
6061	09	2.00	12.5
6061	69	3.75	2.50
6061	70	4.00	2.00
1100	72	1.50	2.50
1100	77	0.75	3.50
SZAV-1	07	1.00	1.00
SZAV-1	51	0.75	1.00

Note: Front: side with step; back: smooth side.

FIG. 5.1. Rack 1 as extracted from channel.

FIG. 5.2. Top view of rack 1 after extraction.

FIG. 5.3. Side view of rack 1 after extraction. Corrosion products can be seen emerging from inside the two galvanic couples at the bottom of the assembly.

FIG. 5.4. Pits in the middle of the zone where white blisters were found.

FIG. 5.5. Corrosion products emerging from inside the galvanic couples.

After the samples were dried, sweep tests were conducted, with negative results. Since the samples were not easily decontaminated, all the metallographic work was conducted in a controlled laboratory. Before this, all coupons were weighed again in the same balance used before testing; the determinations showed no appreciable difference between the values obtained before and after the immersion tests.

5.2.3.2. Metallographic examination

The samples were photographed in detail and their state was assessed from the corrosion point of view. Some of them presented pits, some were stained, some had both effects and some were apparently clean. Some of the pits seen at the time the rack was withdrawn from the basin were no longer visible because they had been filled with corrosion products wiped in during the decontamination work. Also, pitting became evident in zones covered with white deposits. Table 5.4 presents the detailed observations relating to the samples prior to the chemical cleaning and destructive analysis. The samples that showed the highest degree of corrosion were selected for destructive testing, in order to determine the depth of the attack. These were: 1100/77 (pitting associated with dust particles that had fallen onto the surface), 6063/16 (crevice corrosion), 6061/09 (galvanic corrosion) and 6061/69 (single sample).

Figures 5.6–5.9 correspond to coupon 1100/77. Figure 5.6 shows the corrosion produced inside the square zone covered by a Teflon separator. Figure 5.7 shows the massive pitting that can be encountered inside, at a higher magnification. Figures 5.8 and 5.9 show the cross-section metallography of one of the isolated pits encountered that were associated with dust particles. Figures 5.10–5.12 show the attack affecting sample 6063/64 inside the artificial crevice between coupons 6063/63 and 64, at three different

TABLE 5.4. STATE OF THE SAMPLES AFTER EXPOSURE TO BASIN WATER

Position	Type	Alloy	Identification number	Side	Observations
1	Single	1100	77	Top	95% of surface stained brown, with several isolated pits. Three squared sections that were in contact with the Teflon separators and the central portion, where the Al support FRL-O27-14 was located, show signs of crevice corrosion, with white deposits
				Bottom	Crevice corrosion in the central portion where the alumina and Teflon separators were located. The rest of the sample looks quite clean and free of attack
2	Crevice	6063	15–16	Inner	White and black stains, deposits and general attack over 80% of the surface
				Outer	Corrosion, mainly in the central portion, under the alumina separator
3	Single	1100	72	Top	Signs of corrosion in the central portion, under the alumina separator
				Bottom	Clean
4	Single	6061	69	Top	Dark and white stains mainly in the central part (contact with alumina). Small isolated pits
				Bottom	Corrosion in the alumina lodge. Otherwise clean
5	Single	6061	70	Top	Slightly corroded around the identification (ceramic position), with pitting. Mostly clean
				Bottom	Mostly clean. A bit of stain near the identification, with some pitting
6	Crevice	6063	64–65	Inner	Corrosion on 40% of both surfaces, preferentially in the middle
				Outer	Corrosion only where the alumina separator was placed
7	Single	SZAV-1	07	Top	Slightly stained in brown, otherwise clean
				Bottom	No visible corrosion signs

TABLE 5.4. (cont.)

Position	Type	Alloy	Identification number	Side	Observations
8	Single	SZAV-1	51	Top	Change in colour only in the Teflon separator zones. The rest is clean
				Bottom	Change in colour only in the Teflon separator zones. The rest is clean
9	Couple	6061	08	Inner	Heavily corroded. White and black deposits. Pitting
				Outer	Brown stains over 20% of the surface. Mostly clean
10	Couple	6061	09	Inner	Heavily corroded. White and black deposits. Pitting
				Outer	Brown stains over 20% of the surface. Mostly clean
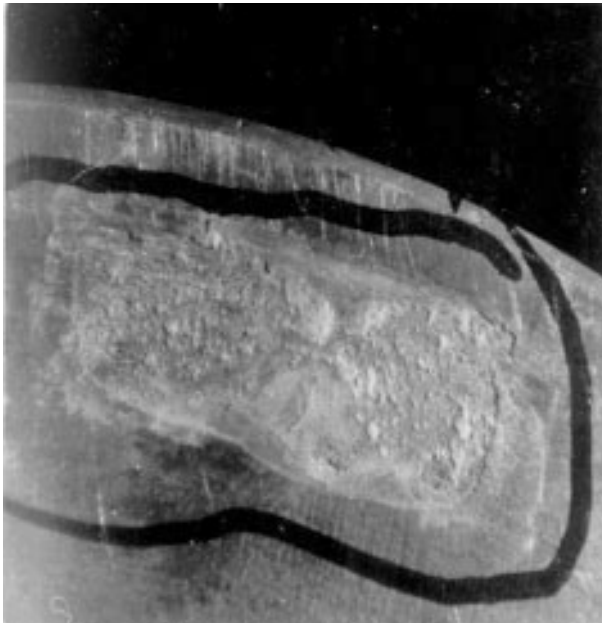
FIG. 5.6. Coupon 6061/77. Attack under Teflon separator (6 ×).
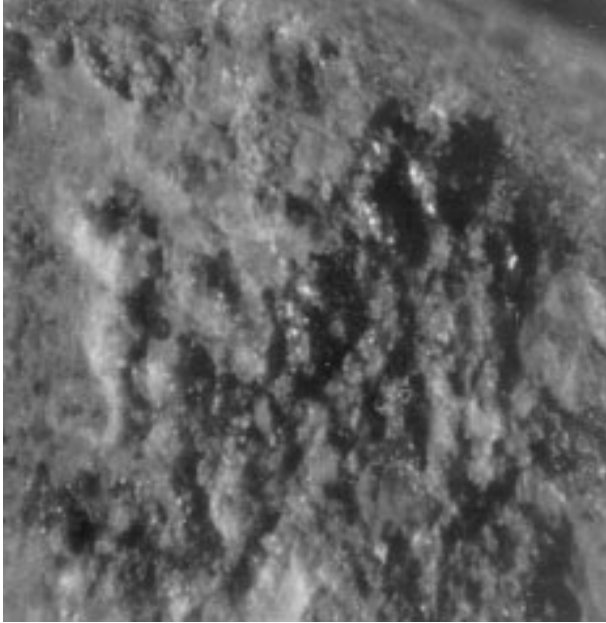
FIG. 5.7. Higher magnification of Fig. 5.6, showing pitting (50 ×).
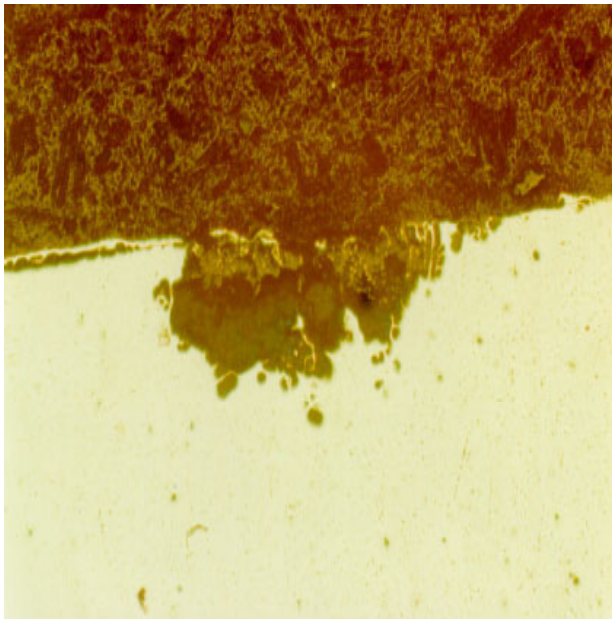
FIG. 5.8. Cross-section of isolated pit (50 ×).
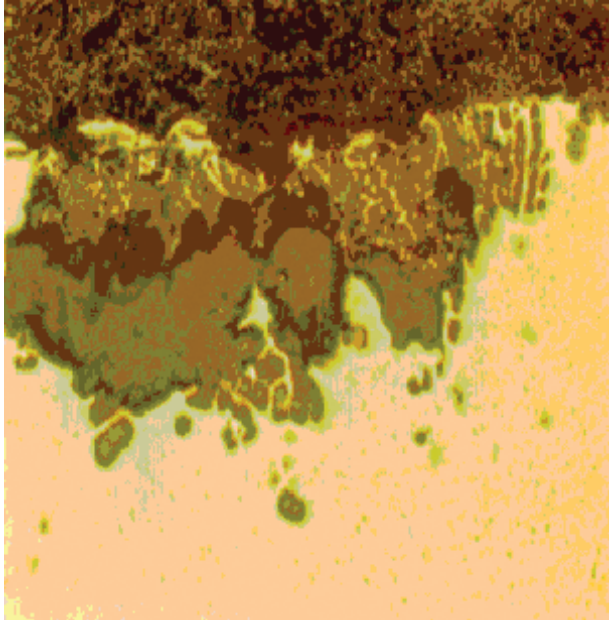
FIG. 5.9. Higher magnification of Fig. 5.8 (100 ×).

FIG. 5.10. Coupon 6063/64, crevice corrosion (6 ×).
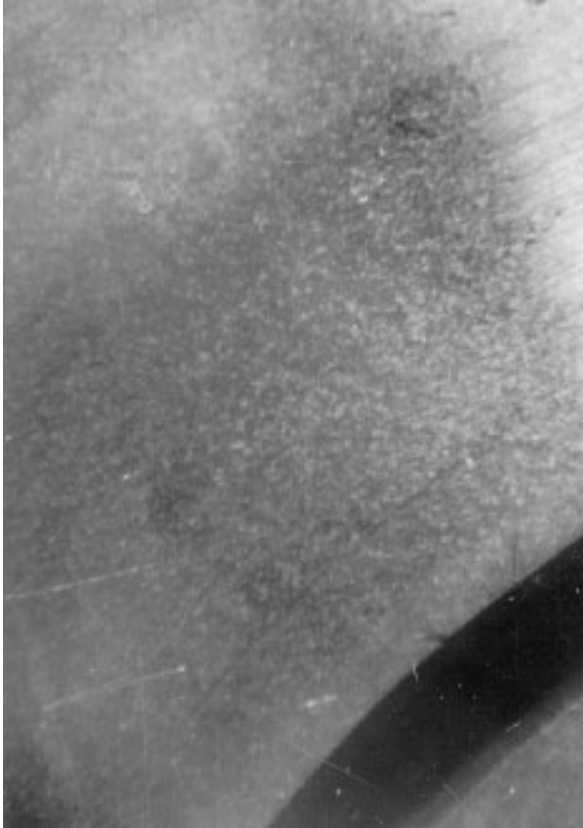
FIG. 5.11. Coupon 6063/64, outside the crevice (6 ×).

FIG. 5.12. Coupon 6064/64, crevice corrosion (18 ×).
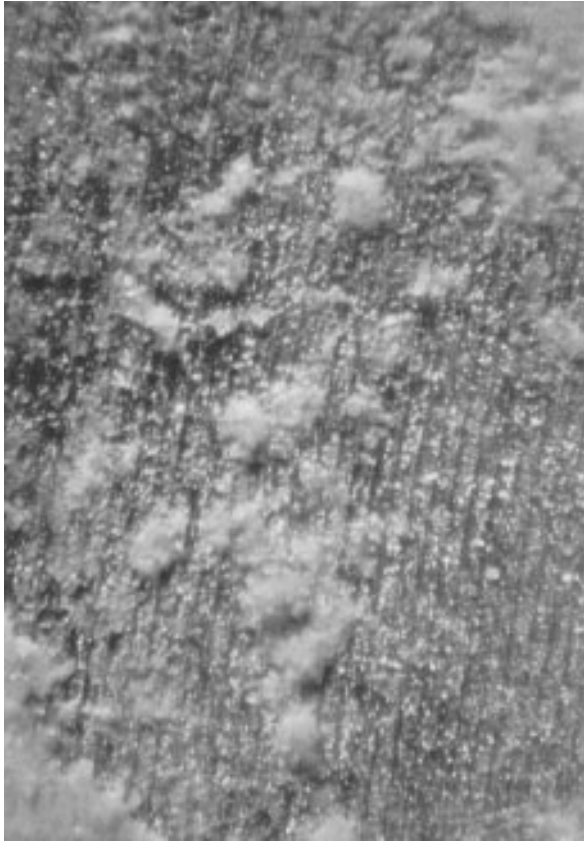
FIG. 5.13. Coupon 6064/64, crevice corrosion (50 ×).

magnifications, whereas Fig. 5.13 shows the outer surface of the same sample, which is virtually clean. In Figs 5.14 and 5.15, massive pitting produced on sample 6061/08 at the inner side of the galvanic couple can be seen at two magnifications, whereas in Fig. 5.16 the clean outer surface of the same coupon can be seen.

5.2.3.3. Water chemistry

A sample taken from the channel at the time of immersion was analysed. Table 5.5 shows the data obtained.

TABLE 5.5. ANALYSIS OF BASIN WATER AT THE POSITION OF RACK 1

	Value	Error	Units
pH	7.5 (22°C)		
Conductivity	74	10%	µS/cm
Chloride ions	14.8	0.5	ppm
Nitrate ions	Not detectable	0.5	ppm
Nitrite ions	Not detectable	0.5	ppm
Sulphate ions	3.3	0.2	ppm
Cu ions	Not detectable	0.5	ppm
Ag ions	Not detectable	0.5	ppm
Total dissolved solids	8.8		mg/100 mL
Temperature range	15–20		°C
γ activity			
Cs	9000[a]	200	Bq/L
Co	58[b]	5	Bq/L

[a] Values in other channels range up to 12×10^4 Bq/L.
[b] Real values at rack position may be considerably higher.

FIG. 5.14. Coupon 6061/08, galvanic corrosion (6 ×).

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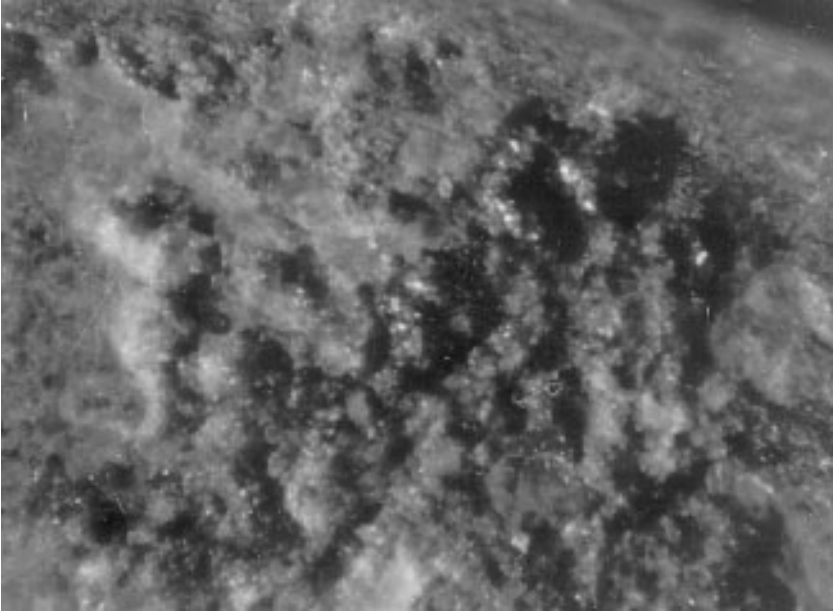
FIG. 5.15. Coupon 6061/08, galvanic corrosion (50 ×).
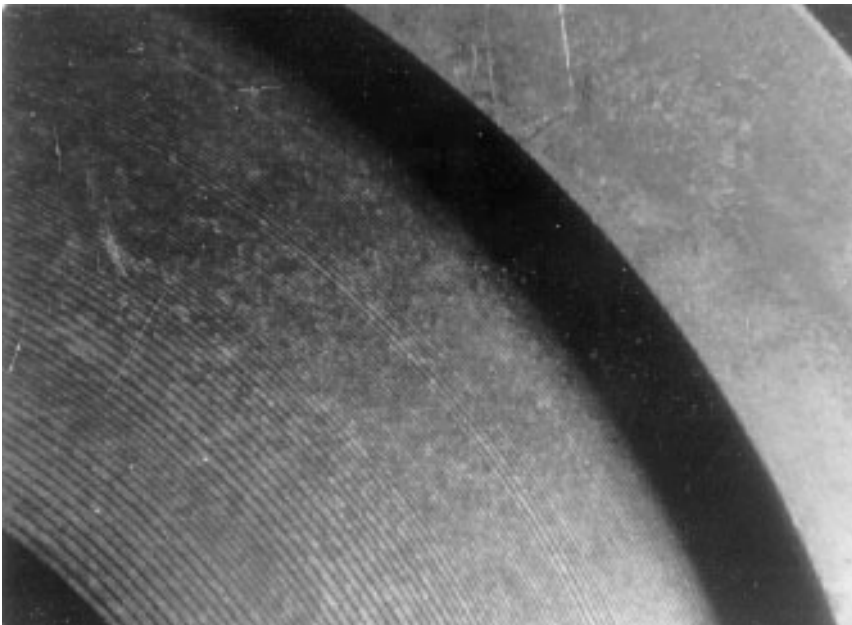
FIG. 5.16. Coupon 6061/08, outside of galvanic couple (6 ×).

5.2.4. Discussion

After 60 days of immersion in the water of the basin, several coupons were affected by corrosion processes leading to pitting, crevice and galvanic corrosion. Although no weight loss was recorded, the degradation was evident from visual inspection and metallography. The strongest attack occurred inside the galvanic couples, followed by that in the crevice sandwiches; in both cases, a fair amount of corrosion products, mainly a white gel most probably composed of aluminium hydroxide, was found emerging from the interstices. Generally the upper sides of the samples were more affected than the lower, probably owing to the effect of dust particles falling and depositing on them. This shows quite clearly in coupon 1100/77 in position 1, at the top of the rack, where numerous particles randomly distributed were associated with pits. Virtually all points of contact between samples and other objects (other samples, ceramic or Teflon separators, aluminium support) were preferential sites for corrosion.

The analysis of the water showed a chloride content of 14.8 ppm, much higher than what is normal in basins without reportable corrosion problems [5.1]; also, the conductivity (74 μS/cm) was too high compared with what is expected for an installation of this kind. Normal specifications for the water quality of a basin should state a chloride content below 1 ppm and conductivity below 2 μS/cm; the measured values could compare with normal values for tap water.

In these conditions, the possibility for the onset of corrosion processes is high, and these will occur preferentially in places in contact with cathodic species, such as stainless steel or iron rich dust particles, and inside the artificial crevices. In this last case, when a region of a sample is undergoing a massive dissolution process, it tends to act as a sacrificial anode because the rest of the surface is needed for the cathodic reaction. As all the central portions of the coupons have undergone this type of attack, owing to the crevices formed with the ceramic separators, etc., it is possible that corrosion of the free portions has to some extent been inhibited by this effect.

Three single samples of different materials, exposed in the same conditions, showed different corrosion behaviours. Both 1100 and 6061 coupons were affected by crevice attack in the region of contact with the ceramic isolator. Although the first alloy also sustained a considerable pitting attack, this occurred mainly on the upper side of the sample in position 1, at the top of the rack, where the majority of the dust had fallen. The SZAV-1 coupons do not show the same degree of crevice corrosion, and they are only slightly stained in both the central and the peripheral region, having no other visible sign of corrosion.

All the results mentioned are obtained consistently, with the duplicated samples behaving similarly. The contamination level of each coupon also seems to be related to the degree of corrosion, being higher the stronger the level of

degradation. The surfaces of 6061 in contact with stainless steel have the maximum level of activity, followed by the crevices produced in the 6061 single coupons, the pitted side of the 1100, the inner sides of the 6063 crevices and the two SZAV-1 coupons. This could be related to the amount of corrosion products formed, which may retain some of the active species present in the water.

Taking into account the limited amount of exposure, it is easy to assume that the fuel elements stored in the facility for many years must have sustained a considerable degree of degradation, owing to poor water quality. All the probabilities are on the negative side. The fuel elements are placed inside the steel tubes, touching the bottom, forming galvanic couples. Many kinds of crevice exist, between fuel elements and steel tubes, between the aluminium plates and the tubes, etc. Although the occupied positions are covered at the top by stainless steel clad caps, it was reported at the first RCM that these were made of carbon steel, which corroded significantly, covering the upper part of the elements with a brown dust, mainly composed of iron oxide. Taking into account the measured effect of dust particles on the corrosion of the aluminium coupons, the fuel elements themselves would also have become pitted in the same time frame.

5.3. CONCLUSIONS OF THE FIRST STAGE

(a) The aluminium coupons of rack 1 immersed in the water of channel 46 of the CSF have been affected by corrosion processes: galvanic corrosion, crevice corrosion and pitting, in decreasing order of importance. No general corrosion measurable by weight loss has occurred.

(b) These effects are due to the poor quality of the water, with high chloride content and conductivity.

(c) It is reasonable to assume that the fuel elements stored in the facility must have undergone a high degree of deterioration.

(d) On the basis of the observations, the alloys tested could be ranked in order of resistance to corrosion in this environment as follows: SZAV-1, 6061, 1100.

5.4. EXTENDED PROGRAMME

5.4.1. Introduction

New sets of experiments have been performed at three different sites using six racks, four of them filled with samples distributed for the CRP and the other two fully assembled with coupons manufactured in Argentina. Water

TABLE 5.6. SITE DISTRIBUTION OF RACKS

Site	CSF	RA3 (CAE)	RA6 (CAB)
Pool/channel	46 113	DP	DP RP
Rack number	2 3	4 (A), 5 (B)	6 7
Immersion date	1998-05-21	1998-06-18	1998-07-29

analyses have been periodically conducted in all the cases. Coupon extractions were carried out in four steps over a period of four years.

5.4.2. Experimental set-up

Six new racks have been immersed at selected positions at three different sites: channels 46 and 113 of the CSF; two positions (A and B) at the DP of the RA3 reactor at the Ezeiza Atomic Centre (CAE); and the RA6 DP and RP at the Bariloche Atomic Centre (CAB), as seen in Table 5.6.

Position 46 of the CSF is the same one used with rack 1, known to be in a poor condition, as reported at the second RCM. Channel 113 belongs to a newer set of lines, built with a higher quality steel and with stainless steel channel caps. It is believed that in these lines the fuel is stored in better condition; however, no water treatment is being carried out.

Racks 2 to 4 are those distributed during the second RCM and completed with locally manufactured samples (one sample is composed of two coupons placed together, in electric contact, forming either a crevice sandwich or a galvanic couple); they were reordered, as agreed, to place the galvanic couples at the bottom. Racks 5 and 6 are filled only with Argentine coupons, using the structural components of rack 1 and a spare piece. In all cases the Argentine material is the same 6061 alloy used to make nuclear fuel. The samples are machined from a cold rolled sheet, thoroughly cleaned and degreased using pure acetone. All the insulators needed to complete the assemblies were made of high density polyurethane. To ensure separation of the samples from the steel channel wall, aluminium spacers were installed in racks 2 and 3 instead of those used in rack 1, which were made of Teflon. Figures 5.17 and 5.18 show these racks just before immersion. Figure 5.19 shows rack 5 prior to the test and Fig. 5.20 shows racks 4 and 5 in their final positions inside the RA3 DP, denoted A and B, above and beside a fuel canister. Table 5.7 contains detailed information on how the racks were assembled. In order to obtain the best possible statistics, as many coupons as possible were included in these tests. In total, 126 coupons have been tested, 40 produced by the host laboratory and
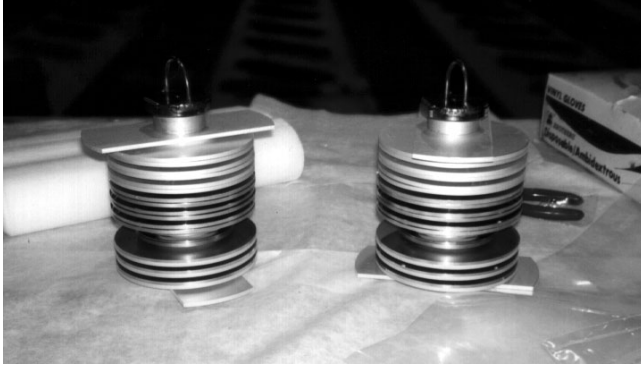
FIG. 5.17. Racks 2 and 3 before immersion.
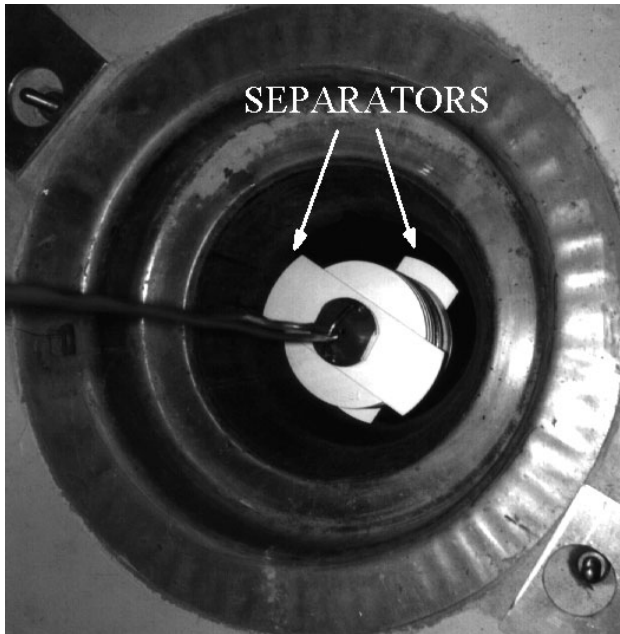
FIG. 5.18. Rack 3 during positioning in pool.

FIG. 5.19. Rack 5 before positioning in pool.

RACK #4

RACK #5
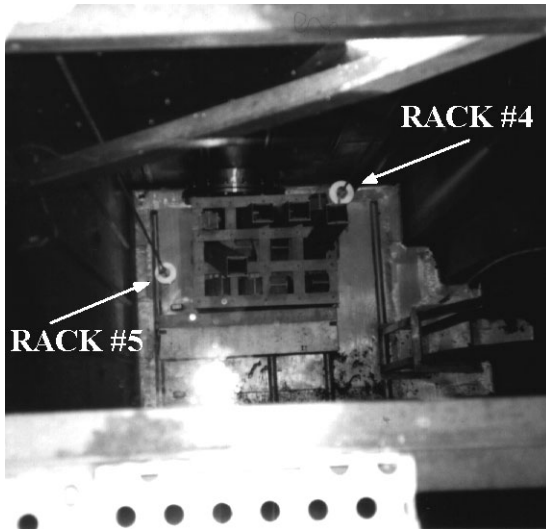
FIG. 5.20. Racks 4 and 5 in place.

TABLE 5.7. ASSEMBLY INFORMATION

Position in rack from top		Rack number	2	3	4	5	6	7
		Sample type	Coupon identification (marks on the metal)[a]					
1	Top	Crevice sandwich	A/10	A/19	A/25	A/36	A/43	A/56
	Bottom		A/11	A/20	A/22	A/32	A/44	A/63
2	Top	Crevice sandwich	A/9	A/6	A/24	A/30	A/45	A/58
	Bottom		A/16	A/7	A/26	A/31	A/46	A/57
3	Top	Crevice sandwich	A/17	A/12	A/21	A/23	A/47	A/59
	Bottom		A/18	A/13	A/27	A/28	A/48	A/55
4	Top	Crevice sandwich	6063/169	6063/162	6063/190	6063/189	A/49	A/60
	Bottom		6063/181	6063/179	6063/168	6063/158	A/50	A/61
5	Top	Crevice sandwich	6061/244	6061/243	6061/208	6061/214	A/53	—
	Bottom		6061/245	6061/247	6061/203	6061/226	A/51	—
6	Top	Crevice sandwich	1100/243	1100/242	1100/215	1100/219	A/52	—
	Bottom		1100/249	1100/230	1100/224	1100/220	A/54	—

TABLE 5.7. (cont.)

7	Top	Galvanic couple	6063/134	6063/118	6063/146	6063/149	A/34	A/62
	Bottom		SS 316/105	SS 316/141	SS 316/110	SS 316/124	SS 304	SS 304
8	Top	Galvanic couple	6061/127	6061/144	6061/134	6061/120	A/41	A/64
	Bottom		SS 316/108	SS 316/141	SS 316/125	SS 316/142	SS 304	SS 304
9	Top	Galvanic couple	A/15	A/3	A/35	A/38	A/40	A/65
	Bottom		SS 304	SS 304	SS 304	SS 304	SS 304	SS 304
10	Top	Galvanic couple	A/14	A/2	A/5	A/33	A/39	A/42
	Bottom		SS 304	SS 304	SS 304	SS 304	SS 304	SS 304
11	Top	Galvanic couple	A/8	A/1	A/4	A/29	A/37	—
	Bottom		SS 304	SS 304	SS 304	SS 304	SS 304	—

[a] A: Argentine (6061 alloy); others supplied by the IAEA. Total IAEA coupons: 40; total Argentine coupons: 86.
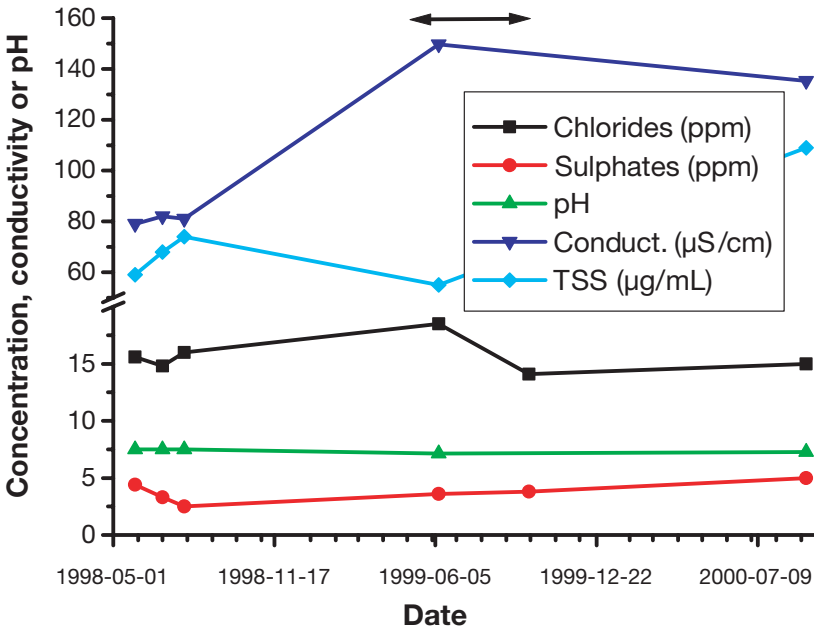
FIG. 5.21. Evolution of chemical variables in CSF channel 46. TSS: total soluble solids.

86 manufactured in CNEA, forming 63 sandwiches mounted in six racks. In order to monitor the water quality, chemical analysis of the different waters was conducted periodically.

5.4.3. Results

5.4.3.1. Water chemistry

　　Table 5.8 presents details of the chemical analysis conducted at all the sites. Silver is not measured, because of the absence of copper ions (AgCl is even more stable than CuCl). Analyses of nitrites and nitrates were also discontinued after very negative initial results.

　　As can be seen, the results are site dependent, which is consistent with the way the control is performed in each case. Figures 5.21–5.25 show the variation in time of all the measured parameters.

5.4.3.2. Appearance of the samples

　　Three different types of feature have been observed on the coupons' surfaces — uneven oxidation, even oxidation and pitting — as is shown in
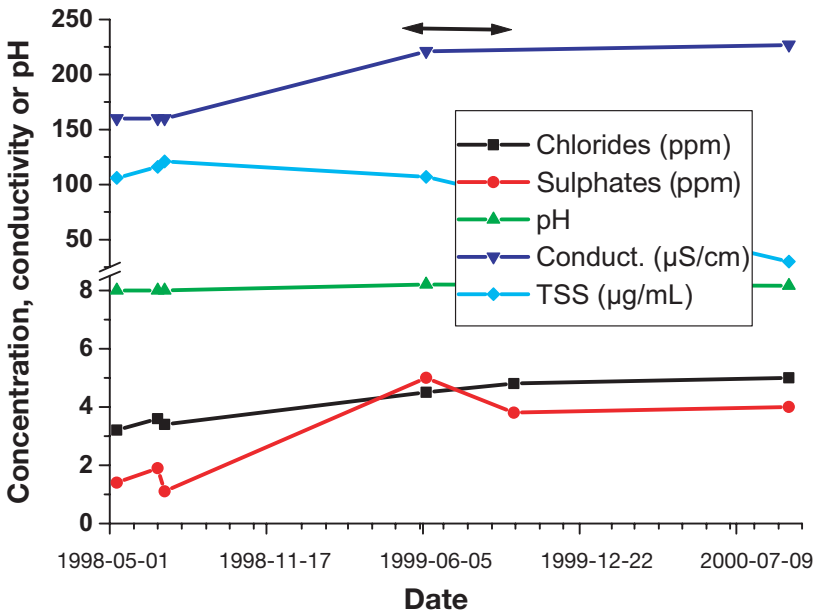
FIG. 5.22. Evolution of chemical variables in CSF channel 113. TSS: total soluble solids.
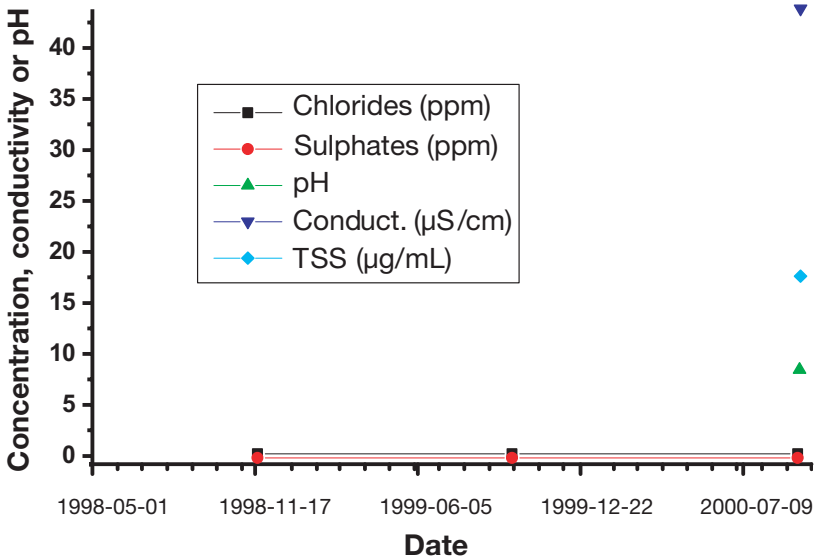
FIG. 5.23. Evolution of chemical variables in the RA3 DP. TSS: total soluble solids.
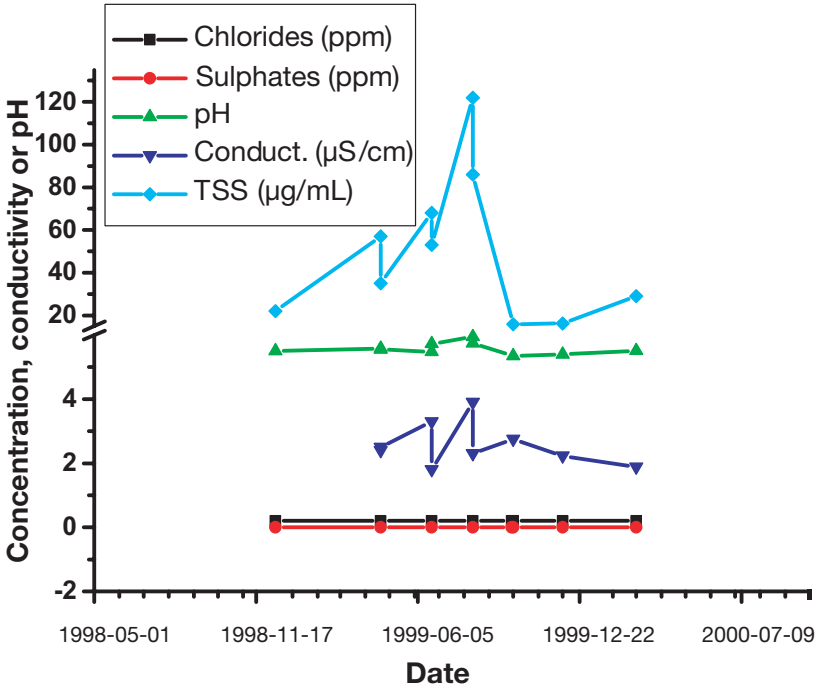
FIG. 5.24. Evolution of chemical variables in the RA6 RP. TSS: total soluble solids.
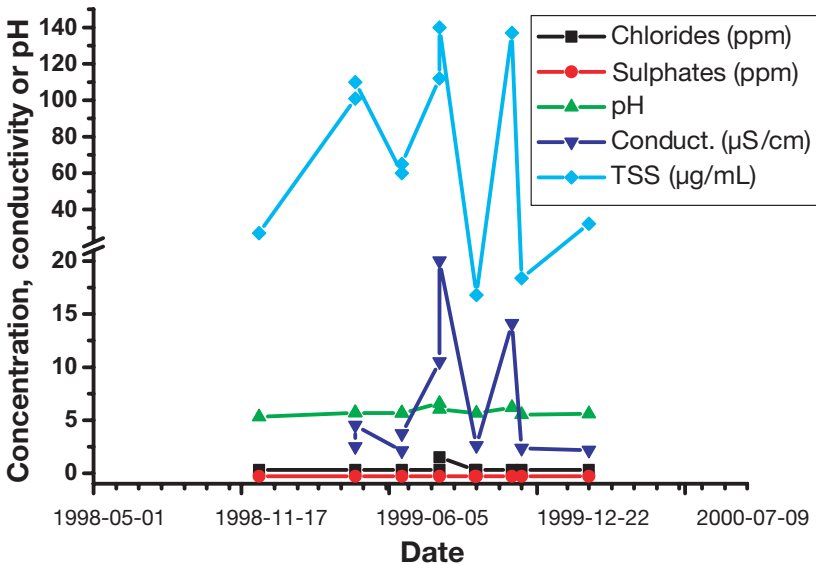
FIG. 5.25. Evolution of chemical variables in the RA6 DP. TSS: total soluble solids.

FIG. 5.26. Thick oxide covering surface of sample (1 ×).

FIG. 5.27. Uneven oxidation (1 ×).
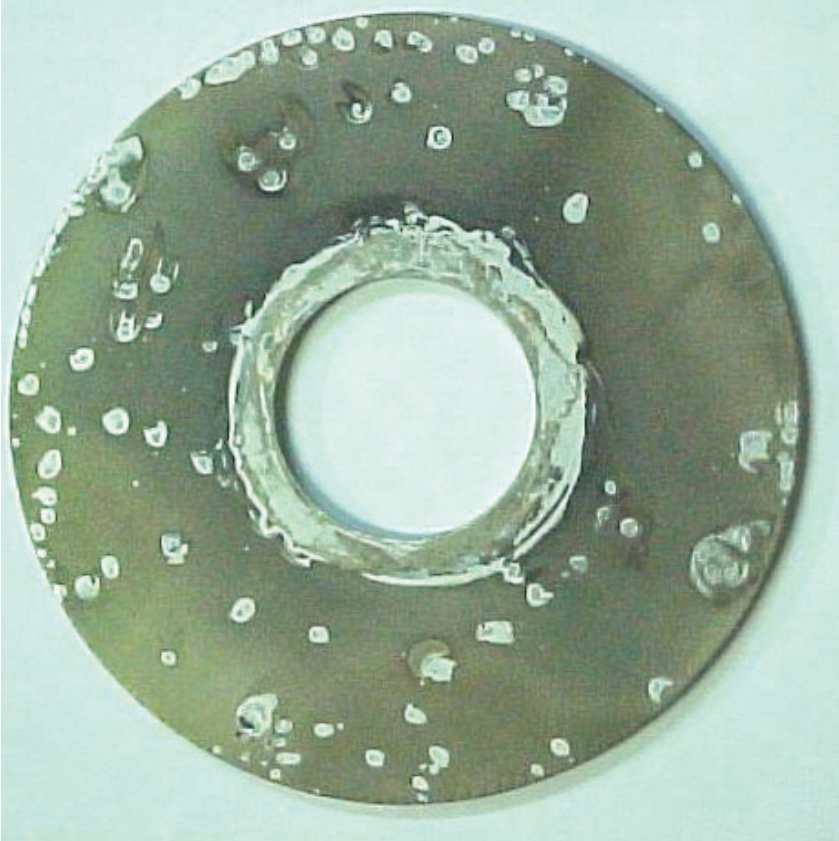
FIG. 5.28. Pitted surface (1 ×).

FIG. 5.29. Islands of pits on an otherwise intact sample (1 ×).

FIG. 5.30. Magnification of island (2 ×).

FIG. 5.31. Detailed view of one pit inside the island (20 ×).
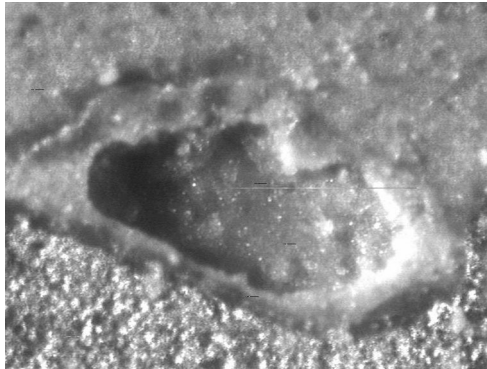
FIG. 5.32. Magnification of Fig. 5.31 (50 ×).
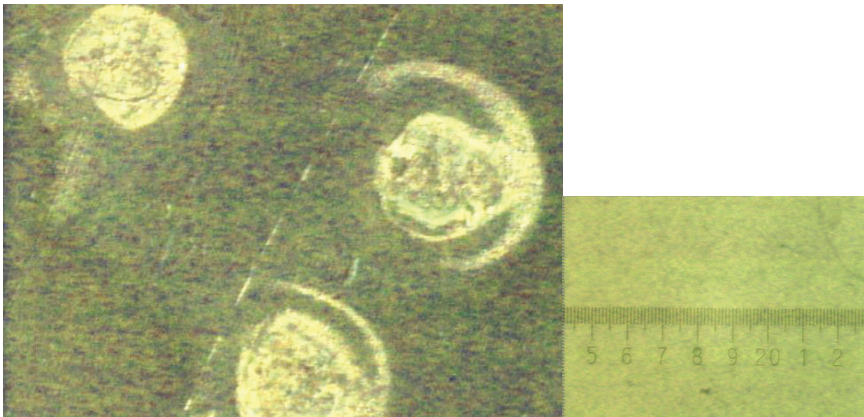
FIG. 5.33. Large pits. One main division equal to 100 μm.

Figs 5.26–5.28. In Fig. 5.29 a type of pitting can be seen that consists of a cluster of pits covering an isolated region. Figures 5.30–5.32 show this feature in detail.

The first type of feature, uneven oxidation, relates to the internal sides of sandwiches (either crevices or galvanic couples). The inhomogeneous coloration indicates uneven matching of the two surfaces, which leaves zones with more or less access of water; in these surfaces only small pits have been found.

The results indicate a much better water quality in both the RA6 RP and the RA6 DP than in the CSF lines.

Oxidation of aluminium coupons is dependent on water quality. It is observed that the higher the conductivity the darker the coloration. However, pitting was found in every type of environment. The large pits observed seem to be associated with particles deposited on the surface, probably iron oxide coming from rusted caps in the CSF channels, dispersed cement fragments produced in civil works performed in the surrounding area of the RA6 DP or debris from failed fuel stored in the RA3 DP. The islands of pits shown in Figs 5.29–5.32 relate to the RA6 DP. From Table 5.8 it is evident that the water at this site is well maintained, with low conductivity levels and no dissolved aggressive ions. No pitting was observed in any sample immersed in the RA6 RP, probably because the continuous water movement prevents sedimentation.

5.4.3.3. Metallography

Figure 5.33 shows a top view of the large pits encountered on coupon 15 (belonging to rack 3, which was immersed in channel 113 of the CSF), onto which particles had fallen. The size of the pits appears to be less than 0.3 mm in diameter. However, when a cross-section metallography was performed, it became clear that the attack had propagated underneath the exposed surface, extending over regions as wide as 1 mm, as seen in Figs 5.34–5.36. In Fig. 5.34 three pits can be seen that were found in the same line of the cross-section. Magnifications of two of them are shown in Figs 5.35 and 5.36.

Figures 5.37 and 5.38 present side views of pits in sample 45, which also sustained some particle pitting where it was immersed in the RA6 DP. The pits seem to be between 100 and 200 μm deep. Unfortunately, the precise location of the pit shown in Fig. 5.31 could not be found.

Figures 5.39 and 5.40 show other features observed on the internal side (inside crevice sandwich) of sample 11 of rack 3, exposed to water in channel 113 of the CSF. The pits appear shallow and extended; with only one exception, their measured depth is less than 50 μm.

5.4.4. Discussion

Corrosion effects have been encountered. They are mainly related to the water quality of the sites studied. The three main consequences are oxidation, crevice attack, and galvanic corrosion and pitting.

Thicker oxide layers have appeared in sites where the conductivity was higher. On the outer surfaces of coupons the layers are even. On the inner surfaces, however, uneven coloration was produced, probably owing to different levels of water access from the outside. General corrosion has occurred mainly on the inside of galvanic couples immersed in higher conductivity waters. Crevice effects have not been very strong; they also depend on conductivity.

None of the effects described in the previous paragraph seem to be relevant to the containment of the fissile material, because the penetration they promote is very small. In no case was a relevant amount of weight loss measured. What does matter is the probability of cladding perforation due to pitting. Two main types of pitting were found: the type that takes place inside the sandwiches, together with general attack, and that produced by particles deposited on the surface of the coupons. Pits of the first type appear to be smaller, open and shallow, whereas the particle pitting is more extensive and tunnels underneath the surface, propagating over distances of the order of a millimetre or more. They are seen to grow with time, when metallography performed in the first stage of the work is compared with that in the final stages (Figs 5.8 and 5.9 compared with Figs 5.35 and 5.36).

This phenomenon is also affected by the quality of the water, but it is still important in very good quality waters, as demonstrated by coupon 45, which sustained this type of pitting in conditions of conductivity of the order of 1 μS/cm. It is important to remark that apparently no chloride is needed. Laboratory investigations in progress show that 6061 undergoes strong corrosion attack related to cathodic reactions of hydrogen and oxygen, even at a potential below the corrosion potential, in the absence of any aggressive anion, as in citrate solutions, where no pitting is produced even above the oxygen evolution potentials. The role of particles may be related to the higher reaction rate for cathodic reactions on materials other than aluminium, particularly iron, iron oxide and iron-containing particles. The onset of this mechanism is coincident with excursions verified in the chemical parameters in all the locations, being particularly clear in the case of the RA6 DP, where the pitting appeared only after a sudden increase in total soluble solids values. This demonstrates the usefulness of the monitoring programme, because it permits the start of the process to be prevented just by analysing the water periodically. These results also serve to improve the design criteria, because they indicate

TABLE 5.8. CHEMICAL ANALYSIS OF THE DIFFERENT WATERS

Site	Channel	Date	Cl^- (µg/mL)	NO_2^- (µg/mL)	NO_3^- (µg/mL)	SO_4^{2-} (µg/mL)	Cu^{2+} (µg/mL)	pH ± 0.2	Conductivity (µS/cm)	Total dissolved solids (µg/mL)
CSF	46	1998-05-28	15.6 ± 0.1	ND	ND	4.4 ± 0.1	ND	7.5	79 ± 7	59 ± 1
CSF	113	1998-05-28	3.2 ± 0.2	ND	ND	1.4 ± 0.1	ND	8	160 ± 5	106 ± 2
CSF	113	1998-07-01	3.6 ± 0.2	ND	ND	1.9 ± 0.1	ND	8	160 ± 5	116 ± 2
CSF	113	1998-07-28	3.4 ± 0.2	ND	ND	1.1 ± 0.1	ND	8	160 ± 5	121 ± 2
CSF	46	1998-07-01	14.8 ± 0.1	ND	ND	3.3 ± 0.1	ND	7.5	82 ± 7	68 ± 1
CSF	46	1998-07-28	16.0 ± 0.1	ND	ND	2.5 ± 0.1	ND	7.5	81 ± 7	74 ± 1
RA6	RP	1998-12-11	ND	—	—	ND	—	5.5	—	22 ± 1
RA6	DP	1998-12-11	ND	—	—	ND	—	5.31	—	27 ± 1
RA3	DP	1998-11-20	<1	—	ND	ND	—	—	—	—
RA6	DP	1999-04-20	<1	—	<1	<1	—	5.69	2.5	101 ± 0.05
RA6	DP	1999-04-20	<1	—	<1	<1	—	5.67	4.5	110 ± 0.05
RA6	RP	1999-04-20	<1	—	<1	<1	—	5.58	2.4	57 ± 0.5
RA6	RP	1999-04-20	<1	—	<1	<1	—	5.55	2.5	35 ± 0.5
RA6	DP	1999-06-22	<1	—	<1	<1	—	5.68	2.1	60 ± 0.5
RA6	DP	1999-06-22	<1	—	<1	<1	—	5.66	3.7	65 ± 0.5
RA6	RP	1999-06-22	<1	—	<1	<1	—	5.48	3.3	68 ± 0.5
RA6	RP	1999-06-22	<1	—	<1	<1	—	5.73	1.8	53 ± 0.5
RA6	RP	1999-08-12	<1	—	<1	<1	—	5.94	3.9	122 ± 0.05
RA6	RP	1999-08-12	<1	—	<1	<1	—	5.74	2.3	86 ± 0.5
RA6	DP	1999-08-12	<1	—	<1	<1	—	6.58	10.5	112 ± 0.05
RA6	DP	1999-08-12	1.5 ± 0.2	—	<1	<1	—	6.04	20	140 ± 0.05

TABLE 5.8. (cont.)

Site	Channel	Date	Cl^- (µg/mL)	NO_2^- (µg/mL)	NO_3^- (µg/mL)	SO_4^{2-} (µg/mL)	Cu^{2+} (µg/mL)	pH ± 0.2	Conductivity (µS/cm)	Total dissolved solids (µg/mL)
CSF	46	1999-06-09	18.5	—	ND	3.6	—	7.14	149.7	55
CSF	113	1999-06-09	4.5	—	ND	5.0	—	8.20	221	107
CSF4	46	1999-09-29	14.1	—	—	3.8	—	—	—	—
CSF	113	1999-09-29	4.8	—	ND	3.8	—	—	—	—
RA6	RP	1999-09-29	ND	—	ND	ND	—	—	—	—
RA6	DP	1999-09-29	ND	—	ND	ND	—	—	—	—
RA3	DP	1999-09-29	<1	—	ND	ND	—	—	—	—
RA6	RP	1999-10	ND	—	ND	ND	—	5.35	2.75	15.8
RA6	DP	1999-10	ND	—	ND	ND	—	5.66	2.59	16.8
RA6	DP	1999-11-18	<1	—	<1	<1	—	6.18	14.1	137 ± 0.5
RA6	RP	1999-12	ND	—	ND	ND	—	5.40	2.23	16.2
RA6	DP	1999-12	ND	—	ND	ND	—	5.53	2.34	18.4
RA6	DP	2000-03	ND	—	ND	ND	—	5.58	2.16	32.2
RA6	RP	2000-03	ND	—	ND	ND	—	5.51	1.88	29
CSF	46	2000-09-07	15	—	ND	5	—	7.28	135.3	109
CSF	113	2000-09-14	5	—	ND	4	—	8.16	227	30
RA3	DP	2000-09-14	ND	—	ND	ND	—	8.4	43.8	17.7

Note: ND: not detectable (<0.5 ppm); —: not measured.
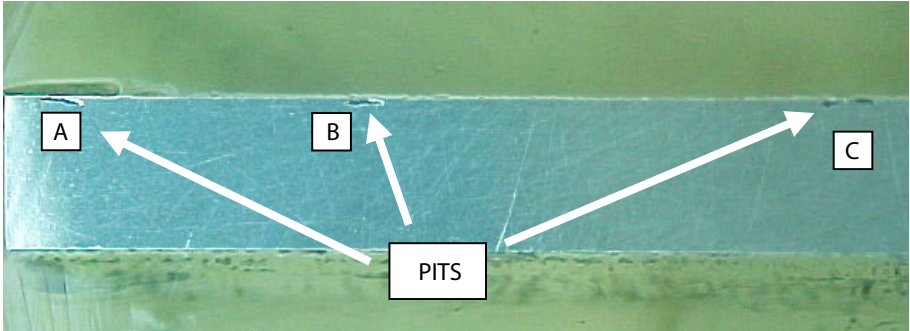
FIG. 5.34. Cross-section metallography showing pits. Coupon thickness 3 mm.
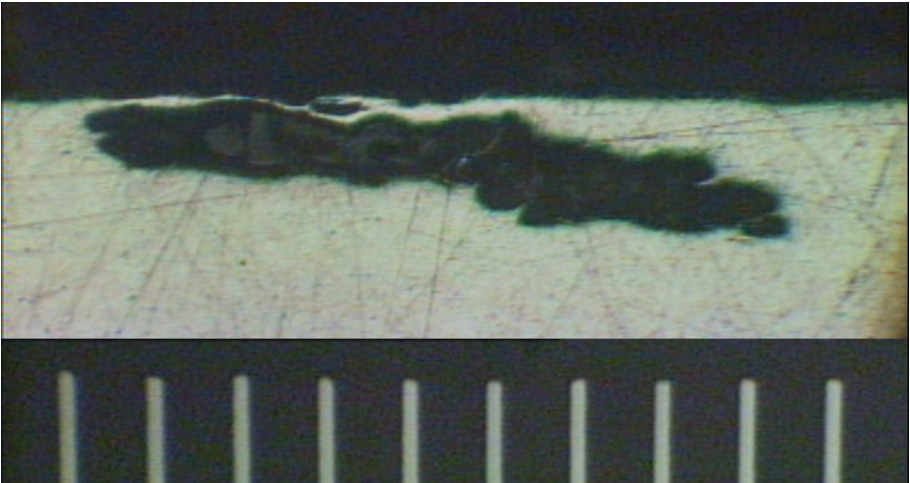
FIG. 5.35. Magnification of pit A. One division equal to 100 μm.
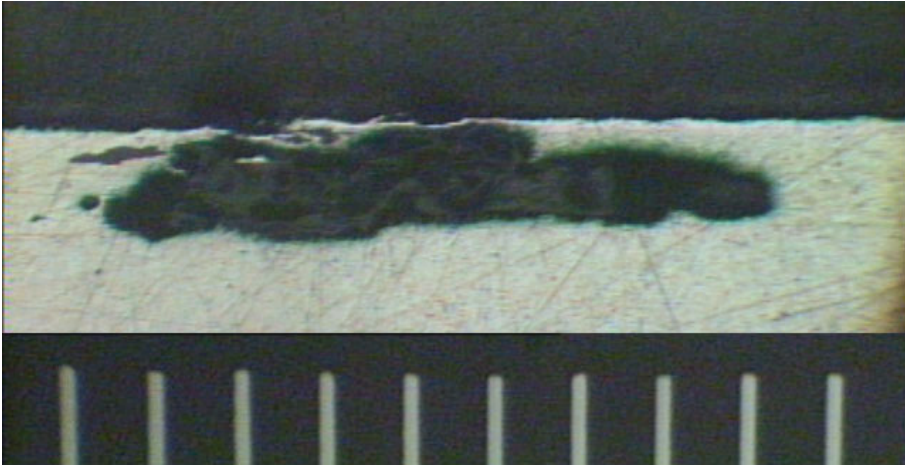
FIG. 5.36. Magnification of pit B. One division equal to 1 μm.

that the use of certain materials in the vicinity of the basin should be restricted, for example carbon steel components that could corrode, thereby producing iron oxide that could disperse and reach the stored fuel.

These observations are quite consistent with the results of inspections performed on the fuel deposited in the CSF [5.2] that made evident the degradation sustained by the fuel elements, mainly in zones where they were in contact with steel (galvanic couples). Pitting was verified, and several perforations on plates were seen.

5.5. CONCLUSIONS

(a) The monitoring programme implemented was able to detect situations that would threaten the integrity of stored fuel owing to corrosion processes.

(b) The first rule for the storage of spent fuel for long times is to maintain the water quality at an optimum level.

(c) Special attention must be given to the effect of particles that may fall onto the aluminium plates, especially particles that might contain iron.

(d) The use of carbon steel components or the conducting of any activity in the vicinity of the basins that could promote the fall of particles onto the water should be avoided.

(e) The results are consistent with the real state of the stored spent fuel.

(f) These observations will help in the redesign of the Argentine facilities that is in progress.
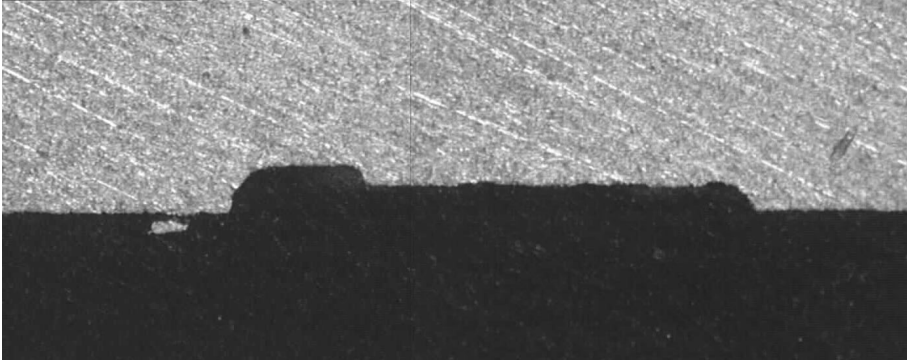
FIG. 5.37. Shallow attack on external face of crevice sandwich. Dimensions of the attack 5.5 mm × 0.5 mm.
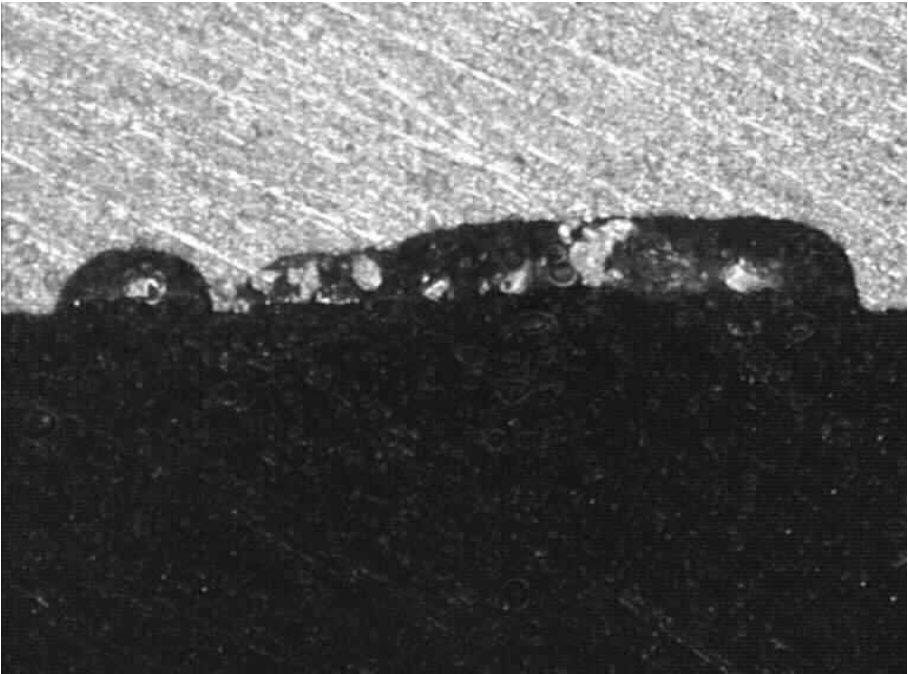
FIG. 5.38. Particle pitting on coupon 11. Size of area pictured 5.4 mm × 4 mm.
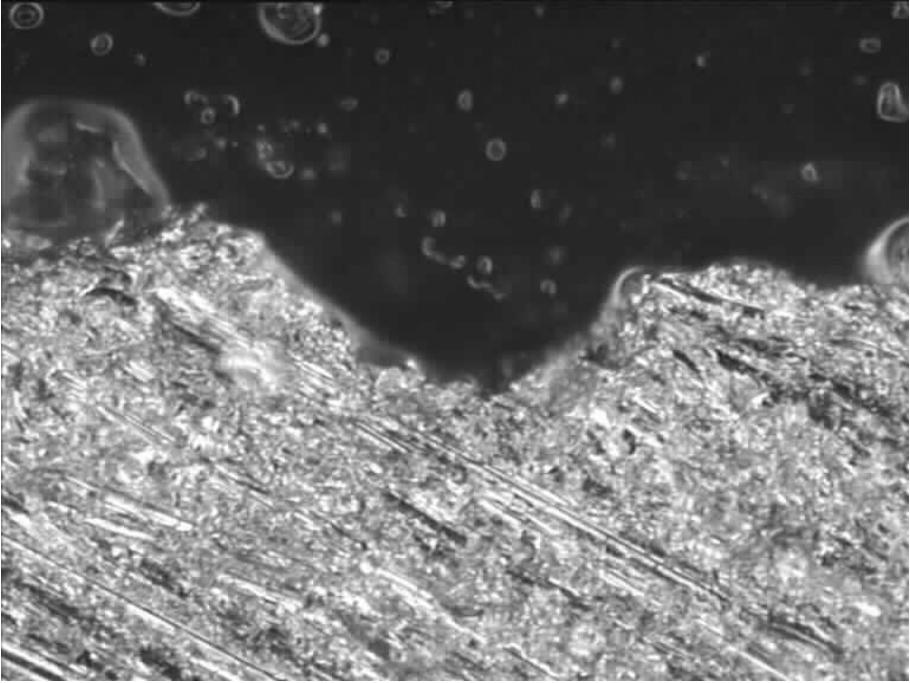
FIG. 5.39. Small pit on inner side of crevice. Size of area pictured 1.35 mm × 1 mm.
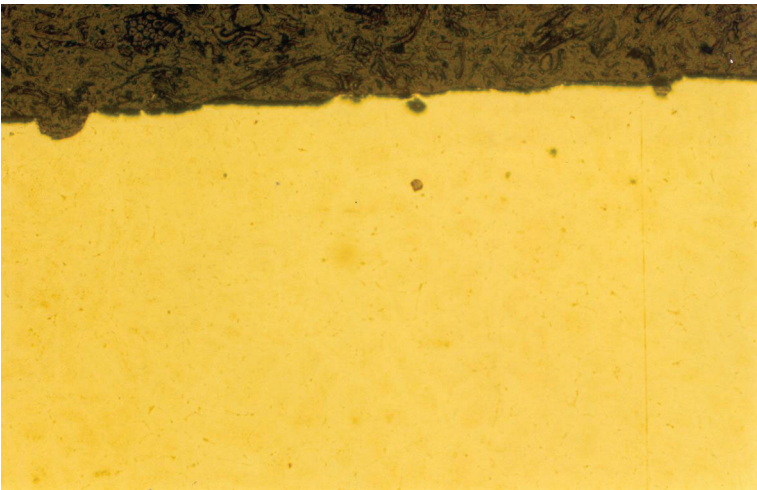
FIG. 5.40. Small pits on inner side of crevice. Size of area pictured 750 μm × 500 μm.

REFERENCES TO CHAPTER 5

[5.1] HOWELL, J.P., BURKE, S.D., "The corrosion of aluminum-clad spent nuclear fuel in wet basin storage", Proc. American Nuclear Society Embedded Topical Mtg on DOE Spent Nuclear Fuel and Fissile Material Management, Reno, 1996, pp. 49–56.

[5.2] VINSON, D., SINDELAR, R.L., HOWELL, J.P., ANDES, T.C., Impact of Degraded RA-3 Fuel Condition on Transportation to and Storage in SRS Basins, Rep. WSRC-TR-2000-00152, Westinghouse Savannah River Site, Aiken, SC (2000).

Chapter 6

CORROSION BEHAVIOUR OF ALUMINIUM ALLOYS IN THE SPENT FUEL STORAGE SECTION OF THE IEA-R1 RESEARCH REACTOR, IPEN, SÃO PAULO, BRAZIL

6.1. INTRODUCTION

6.1.1. The IEA-R1 research reactor

IEA-R1 is a pool type, light water moderated and graphite reflected research reactor at the Instituto de Pesquisas Energéticas e Nucleares (IPEN), which is part of the Brazilian Nuclear Energy Commission. This reactor was designed and built by Babcock & Wilcox Company (B&W) according to specifications furnished by the Brazilian Nuclear Energy Commission, and was financed by the US Atoms for Peace programme. Although designed to operate at 5 MW, IEA-R1 has been operating at 2 MW. Since startup, 181 core configurations have been installed and around 150 fuel assemblies (FAs) used. The reactor was operated for 40 hours per week (8 hours per day) during most of its life. Since 1996, it is being operated in one continuous cycle of 64 hours per week.

In terms of the fuel used in this reactor, four stages can be visualized.

The first stage corresponds to the first core of the reactor. It was composed of U–Al alloy fuel with 20 wt% enrichment. Each FA had 19 curved fuel plates produced by B&W. These FAs failed in the very early stages of reactor operation, owing to pitting corrosion caused by the brazing flux used to fix the fuel plates to the support plates. In 1958 these FAs were replaced by a second batch, also produced by B&W, that was identical to the first (U–Al alloy, 20 wt% enrichment, 19 curved fuel plates) except that brazing was not used for assembling. The fuel plates were fixed mechanically to the support plates. The second batch of FAs performed well up to their discharge burnup.

The second stage corresponds to complete replacement of the core. Fuel assemblies bought from UNC (USA), with U–Al alloy (93% enrichment) and 18 flat fuel plates, were used. In this stage, the core was converted from LEU to HEU. Also during this stage, the control rods were changed from rod type to fork type (plates). The control FAs were made by CERCA (France), using U–Al alloy (93% enrichment) and flat plates.

The third stage was characterized by restrictions in HEU fuel supply. IPEN bought five FAs from NUKEM (Germany). These were of the UAl$_x$–Al dispersion type, with 20% enriched fuel and with 18 flat fuel plates per fuel assembly. The amount of ^{235}U in an LEU fuel plate was almost the same as in an HEU fuel plate, and the geometry of the fuel element assembly was the same. In this stage, with partial LEU core load, the HEU FAs began to have higher burnup, and the number of FAs used in the reactor core increased.

The fourth stage began with IPEN's decision to manufacture its own fuel and to gradually replace the high burnup HEU fuel in the core. IPEN had at that time sufficient knowledge and experience in core engineering, fuel engineering and fuel fabrication to produce MTR FAs for IEA-R1. The IPEN FAs are of the U_3O_8–Al dispersion type, with 20 wt% enrichment, and are geometrically identical to the LEU fuel from the third cycle. Table 6.1 summarizes the different FAs used in the IEA-R1 core.

6.1.2. Spent fuel storage

The dry storage is located on the first floor of the reactor building and consists of horizontal silos in a concrete wall. The spent FAs in dry storage were those of the first load that had corroded and had released fission products in the early stages of reactor operation. Their burnups were almost nil, but some of them had a dose rate of more than 1 R/h on the FA surface. These FAs were wrapped in plastic bags.

The reactor pool is divided into two sections. The first section is the core pool, where the core and irradiation facilities are located. The second section is the spent fuel pool, where the spent fuel storage racks are located. Some of the FAs in this section of the reactor pool had been in storage for only a short time; others had been in the pool for almost 40 years, 30 of these years in the spent fuel racks. Some of these FAs had pit nodules visible to the naked eye. The pool water quality was and continues to be excellent; pH is always maintained at between 5.5 and 6.5, the conductivity at below 2 µS/cm and the chloride content at less than 0.5 ppm.

Over the years, radiochemical analysis of the pool water showed low ^{137}Cs activity (less than 5 Bq/L), indicating that there were some leaking FAs. This activity was also low because the water cleaning system was always in operation. It is possible that some of the corrosion nodules may have reached the fuel, exposing fission products to the pool water.

In the 1970s, the reactor pool wall lining was changed from ceramic to stainless steel, and the spent fuel rack from aluminium alloy to stainless steel. At that time, the possibility of galvanic corrosion between the FAs and the storage rack had not been considered.

TABLE 6.1. FUEL ELEMENT ASSEMBLIES OF THE IEA-R1 RESEARCH REACTOR

		First stage		Second stage		Third stage	Fourth stage
		1st core	2nd core	Original	Modified		
First year in reactor		1957	1959	1968	1972	1981	1985[a]–1988
FA ID number		1–40	41–79	80–118	119–122	123–127	128–134
Dry storage	Standard	34					
	Control	5					
	Partial	1					
Wet storage	Standard		33	25		3	
	Control		4	6	4		
	Partial		2				2
In-core	Standard			8		2	16
	Control						4
	Partial						
Original enrichment (%)		20	20	93	93	20	20
Manufacturer		B&W (USA)	B&W (USA)	UNC (USA)	CERCA (France)	NUKEM (Germany)	IPEN (Brazil)
Fuel type		U–Al alloy	U–Al alloy	U–Al alloy	U–Al alloy	UAl_x–Al	U_3O_8–Al
Number of plates per FA	Standard	19	19	18		18	18
	Control	9	9	9	12		12
	Partial	10	9 or 10				2–10
Type of fuel plate		Curved	Curved	Flat	Flat	Flat	Flat
Burnup (% ^{235}U)	Control	0	~40		~50		~20[b]
	Partial	0	~10	~43			~20

[a] Partial fuel element assembly.
[b] Up to September 1996.

6.1.3. Fuel assessment — visual inspection of spent fuel assemblies

The visual inspection of FAs was originally carried out with unaided eyes. The FAs were held at a depth of 2 m in the pool. This inspection helped to

locate corrosion pits on the outer surfaces of the external fuel plates and to show their distribution. The surfaces of the internal fuel plates could not be examined. The FAs inspected were the LEU FAs of the second core of the first stage (FAs IEA-41 to 80) and the HEU FAs of the second stage (FAs IEA-81 to 118). Pits were observed on many FAs.

(a) Some pits were observed in specific regions on the fuel plate along the interface with the side plate. These regions were away from the fuel region of the plate.
(b) On some FAs, the corrosion pits were on the external fuel plates in regions close to the stainless steel rack.
(c) On LEU FAs with curved fuel plates, some pits were found on the convex side (the side that was in contact with the stainless steel rack) but very few on the concave side (no contact with the rack). This provided evidence of pitting corrosion by galvanic action with stainless steel.
(d) In some FAs the lateral support plates showed few corrosion pits, and most of these were in regions in contact with the rack. Table 6.2 summarizes the results of visual inspection.

The pitting corrosion was due mainly to galvanic action between the FA and the stainless steel support rack. The fuel plate cladding (1060) and the side plate (6061 T6) also formed a galvanic pair, and the corrosion associated with this pair was less intense. Many FAs were inspected later with an underwater video camera. The pitting corrosion nodules, their sizes, distribution and location were investigated.

TABLE 6.2. SUMMARY OF VISUAL INSPECTION OF FAs

	20% enriched FA number	93% enriched FA number
Pits on external fuel plates	42, 43, 48, 49, 53, 55, 58, 61, 62, 64, 66, 69, 70, 78, 79	103, 106
Few pits on external fuel plates	41, 44, 45, 46, 47, 50, 51 52, 54, 56, 57, 59, 60, 63, 65, 67, 68, 71, 72	93, 95, 96, 97, 99, 100, 102, 104, 105, 109
No pits	73	80, 81, 83, 84, 88, 91, 92, 98, 101, 107, 108, 111, 112

The conclusions of the fuel assessment, which included sipping tests, were:

(1) Visual inspection of the FAs in the pool showed pitting corrosion on the external fuel plates. Those stored for almost 40 years were the worst. The pitting corrosion was due to galvanic effects between the aluminium fuel plate cladding and the stainless steel rack.
(2) The sipping test method developed by IPEN was found to be efficient for determining fission product leakage from FAs.
(3) A ^{137}Cs leak rate of 14 Bq/min for the FA in the worst state was far below the DOE–SRS criteria for canning MTR FAs that have leaked.
(4) Gamma ray spectrometry of pitting corrosion nodules indicated the presence of Cs, U and Eu isotopes. The ^{137}Cs activity was much higher than that in the sipped water specimen. Isotopes of U and Eu were not detected in the water. This confirmed the presence of through-clad pits in some FAs.

6.1.4. Corrosion experience related to IEA-R1 reactor fuel and aluminium alloys

This section presents some of the projects carried out, observations made or actions taken that were related to corrosion of the IEA-R1 reactor fuel cladding.

(a) The effect of surface inclusions on the corrosion behaviour of MTR type fuel plates was studied. The nature and composition of the inclusions were linked to the type, size and distribution of pits on the fuel plate surface [6.1].
(b) The aqueous corrosion behaviour of U_3O_8–Al cermet cores was investigated. In this investigation, the effect of core composition and coolant temperature on the corrosion behaviour of the cermets was studied. The corrosion rate was evaluated in terms of the volume of hydrogen evolved, and a mechanism was proposed [6.2].
(c) A few years ago, certain FAs (manufactured at IPEN), when exposed to the reactor coolant, released significant quantities of hydrogen. This was mostly from the regions close to the fuel plate–side plate joint and was the product of passivation of the FA surface. The H_2 release rates were measured. On the basis of this experience, prepassivation of all new FAs in the reactor coolant prior to their introduction into the core was adopted.
(d) The surfaces of the external fuel plates of FAs FE-142 and FE-146 revealed pits following their exposure to the reactor coolant (in storage

racks) for 57 and 47 days, respectively. Pit clusters were observed on the fuel plate surfaces, at regions that were close to the stainless steel support rack. The FAs were rejected and were subsequently dismounted. The surfaces of the inner fuel plates did not show the same level of pitting as the external plates. The pits on the outer surfaces of the outer fuel plates were attributed to galvanic effects, due mainly to possible contact with the stainless steel rack.

(e) The surfaces of the external fuel plates in FAs exposed to the IEA-R1 core operated at 5 MW showed specific corrosion patterns. Oxides of different shades were observed. The different shades of surface oxide could be attributed to differences in oxide thickness. The oxide was darker in the middle of the plate and lighter towards the edges. Increased oxide thickness was attributed to increased temperature and the higher neutron flux.

6.2. THE IAEA CRP

In 1996 the IAEA initiated a CRP on the corrosion of aluminium clad spent research reactor fuels to help evaluate the state of the spent fuel assemblies and to inform pool/basin operators regarding maintenance and housekeeping procedures to extend the lives of the FAs. The main activities of this programme are related to exposing racks of aluminium alloy specimens (coupons) in different spent fuel basins around the world. Five racks were suspended in the IEA-R1 reactor pool and were subsequently withdrawn after different time spans to evaluate the extent of corrosion of the coupons as a function of alloy composition, crevices, bimetallic effects and water chemistry. During this period the pool water was monitored for pH, conductivity, chloride ion content and radiometry (Table 6.3). The IAEA CRP racks are denoted as racks 1, 2A, 2B, 3A and 3B.

6.2.1. IAEA rack 1

The rack 1 coupons were prepared by rinsing in deionized water; degreasing with analar grade alcohol, followed by drying; then rinsing in deionized water and drying in forced air at room temperature. The coupons were weighed and photographed, and the rack was mounted. Glass capsules containing aluminium alloy bimetallic specimens were also mounted in the cylindrical hollow of the specimen support. The rack was stored in a dessicator.

This rack was immersed in the IEA-R1 research reactor pool on 1996-09-23 and was positioned close to a storage rack.

TABLE 6.3. REACTOR POOL WATER PARAMETERS

Date	pH	Conductivity (μS/cm)	Chloride content (ppm)
1997-04-14	6.1	1.56	0.00
1997-08-08	6.0	2.0	0.01
1997-12-11	6.2	1.46	0.00
1998-04-14	6.3	1.25	0.01
1998-07-27	6.3	1.25	0.01
1998-12-15	6.2	1.47	0.00
1999-03-30	6.1	1.33	0.02
1999-06-30	5.8	1.10	0.01
1999-09-15	6.1	1.37	0.00
1999-12-08	5.7	1.25	0.00
2000-03-20	6.0	0.60	0.00
2000-06-20	6.3	1.25	0.01
2000-08-30	6.24	1.30	0.00

The reactor water parameters, such as conductivity, pH and chloride ion concentration, were monitored periodically, and radiometric analysis of the water was also carried out (Table 6.3). The conductivity was determined directly (but intermittently) by the probe in the deionizing circuit. Conductivity was maintained at <2.0 μS/cm. The pH was always in the range 5.5–6.5 and the chloride ion concentration was <0.2 ppm. When the conductivity came close to 2.0 μS/cm or the chloride content came close to 0.2 ppm, the deionization resins were regenerated. The water specimens for radiological analysis were collected once a week after the reactor was switched off. Gamma spectroscopy was carried out to determine the nuclides ^{140}Ba, ^{58}Co, ^{60}Co, ^{51}Cr, ^{137}Cs, ^{131}I, ^{133}I, ^{99}Mo, ^{24}Na, ^{239}Np, ^{132}Te and ^{187}W.

6.2.2. Results of the first inspection of rack 1

Rack 1 was examined after six months of exposure to the IEA-R1 reactor pool water. This rack was dismounted to enable the pH between the crevice and the bimetallic couple coupons to be measured. The three couples were stuck together and had to be forced apart. The pH of the water in the crevice was found to be approximately 4–4.5. The pH of the water on other parts of the rack measured 5 or more. All the aluminium coupons in the crevice showed white/grey staining typical of aluminium oxide, regardless of whether the

couple was SS–Al or Al–Al. The aluminium surfaces within the crevice were stained with white/grey oxide. The coupons were photographed and filmed. They were then remounted as a rack and introduced into the reactor coolant. The water within the glass ampoules was yellow/brown. This was attributed to the effect of radiation from the cooling fuel elements. One ampoule was retained outside for measuring the pH of the water within, and the other was reintroduced into the rack.

6.2.3. IAEA racks 2A, 2B, 3A and 3B

At the RCM held in São Paulo in March 1998, racks 2A, 2B, 3A and 3B were received from the IAEA. A test protocol concerning specimen (coupon) preparation and handling, test duration, etc., was defined. The use of site specific alloys was also encouraged. These four racks contained coupled coupons. The coupons were photographed, and the rack was reassembled and introduced into the IEA-R1 reactor pool, close to the spent fuel racks, on 1998-08-25. Racks 2B and 3B were removed on 1999-10-20 and racks 2A and 3A on 2000-09-27, after 13 and 25 months, respectively.

The racks were photographed as they were removed from the pool, they were disassembled, and the pH of the water on the surface of the coupons as well as in the crevice of the couples was measured. The two sides of the coupons were photographed, then cleaned in deionized water and air-dried, and their surfaces were examined with a magnifying glass. Figures 6.1(a)–(c) show the main features of the coupons after exposure to the spent fuel pool.

The overall conclusions from the examination of coupons in racks 2A, 2B, 3A and 3B are as follows.

(a) In all the SS 316–aluminium alloy couples, the aluminium alloys were stained on the contact side with white/grey aluminium oxide. Very few pits (fewer than three, and these of <0.5 mm diameter) were observed.

(b) On many aluminium alloy coupons, pits of <0.5 mm diameter were observed in regions in contact with the ceramic separator.

(c) In the 6063–6063 couples, the top surface, although quite bright, contained more sediments than the bottom surface (non-contact surface), which was dull and non-reflecting. A few pits were observed, and these were always on the top surface. The contact surfaces were stained but revealed no pits when observed with a magnifying glass.

(d) In the 6061–6061 couples, the top and the bottom surfaces (non-contacting surfaces) were quite similar in appearance. The surfaces were dull and non-reflecting. Two tiny pits, both crystallographic in nature, were observed on the contact surface of one of the coupons.

(a)

(b)

(c)
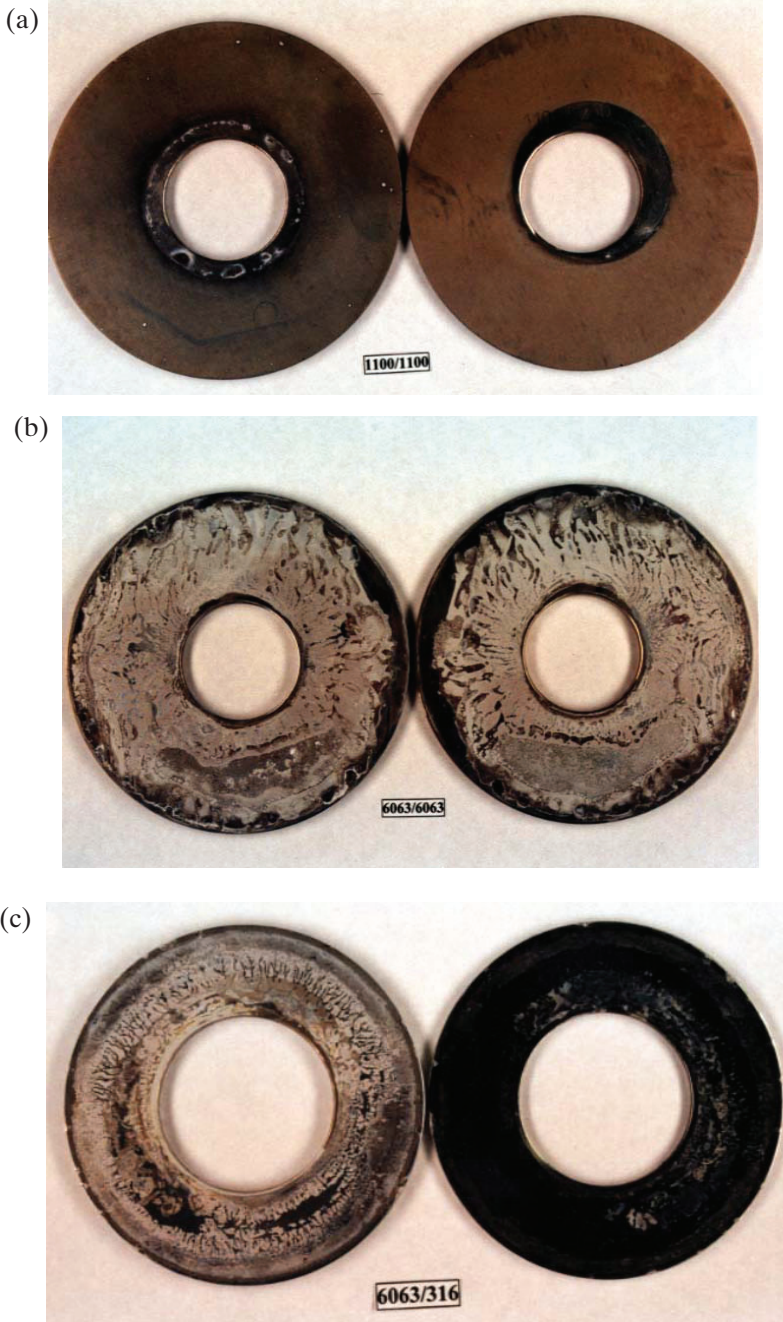
FIG. 6.1. Surface features on (a) an 1100–1100 crevice couple, (b) a 6063–6063 crevice couple, and (c) a 6063–SS 316 galvanic couple from rack 2A.

(e) In the 1100–1100 couples, the top surface with the sediments revealed a large number (>50) of tiny pits, but none larger than 0.25 mm in diameter. The bottom surface had no pits.

(f) The contact surfaces of the aluminium coupons, independent of the couple, showed very similar features. They were stained and contained white or grey oxides.

(g) The duration of exposure did not have any significant effect. The surface features of coupons exposed for 13 months were similar to those on coupons exposed for 25 months.

(h) No significant variation in pH was observed between the water from inside the crevice and that on the outer surface.

6.2.4. The IPEN rack

Alloys 1060, 6061 and 6262 are presently being used in IPEN for the manufacture of FAs for the IEA-R1 reactor. The compositions of the alloys are given in Table 6.4. Coupons of the three alloys, 1060 in the processed and scratched condition (to simulate the effect of scratches formed during handling of fuel elements in the reactor coolant), and various combinations of bimetallic couples were mounted in the rack (Fig. 6.2). Four coupons under each set of conditions were exposed. Coupon preparation and pretreatment were as mentioned earlier. This rack was also introduced into the IEA-R1 reactor, close
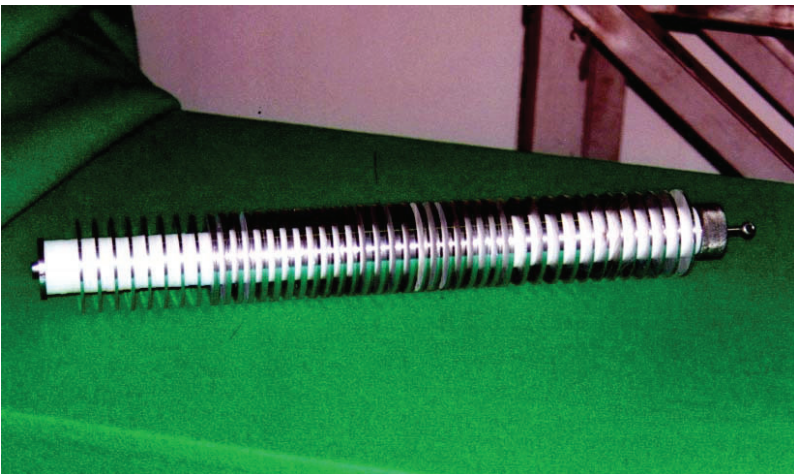
FIG. 6.2. The IPEN rack of test coupons.

(a) (b)
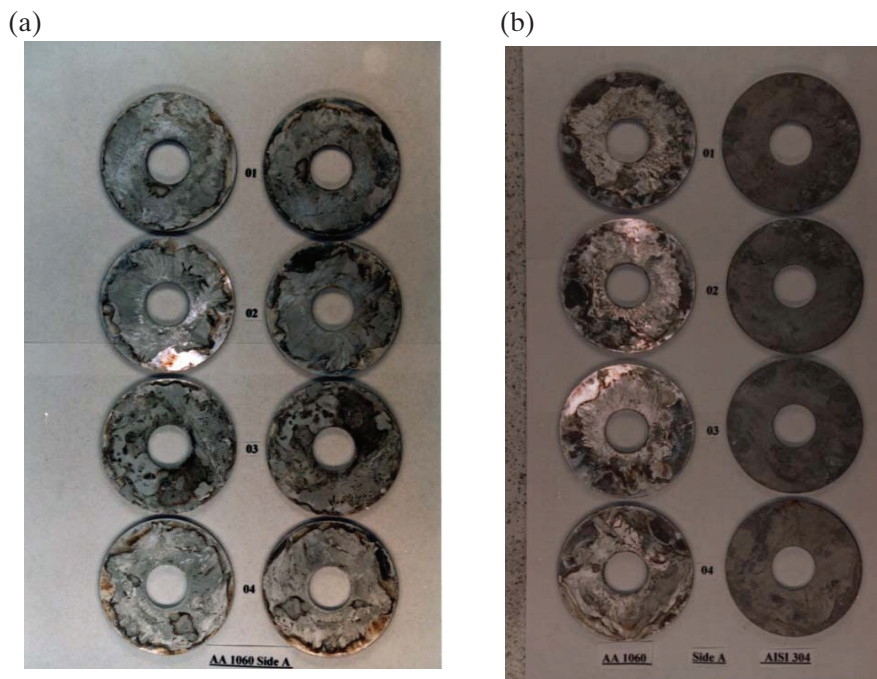
FIG. 6.3. Surface features on the facing surfaces of (a) 1060–1060 crevice couple coupons and (b) 1060–SS 304 galvanic couple coupons.

to the spent fuel racks. The rack was exposed for 16 months (1997-04-08 to 1998-08-25). The pH, water chemistry and conductivity of the pool water were monitored periodically and the values are given in Table 4.4 in Chapter 4. The main features of some of the coupons are shown in Fig. 6.3.

The observations made from the IPEN rack of coupons after 16 months of exposure to IEA-R1 reactor pool water in the spent fuel section can be summarized as follows.

(a) Uncoupled 6061 and 6262 coupons had fewer pits than uncoupled 1060 specimens.
(b) The top surfaces of uncoupled coupons had more pits than the bottom surfaces.
(c) The crevice surfaces of 1060–1060, 6061–6061 and 6061–1060 couples were stained but not pitted.
(d) The surfaces of the aluminium alloys within the crevices of 6061–SS 304 and 6262–SS 304 couples were heavily pitted. The steel surfaces were only stained and revealed rust marks.

(e) The crevice side of the 6061 coupon was much more severely corroded when coupled to SS 304 (compared with 6061–6061 couples). The severe corrosion observed on 6061 coupled to SS 304 was not seen to the same degree on 6061–6061 couples.

(f) The 1060 surface within the crevice of 1060–SS 304 couples was stained but not pitted. No rust stains were seen on the steel surface within the crevice.

(g) Aluminium alloys coupled to stainless steel corroded at a higher rate.

(h) Further tests are required to evaluate the effect of preoxidation of 1060.

6.3. RESULTS

The results obtained from evaluation of the five CRP racks and the IPEN rack can be summarized as follows.

(a) Pitting was the main form of corrosion.

(b) Crevice corrosion and galvanic effects predominated.

(c) Reduction in conductivity and chloride ion content of the pool/basin water was essential to maintain low corrosion rates.

(d) Dust sediments on aluminium alloy specimens contributed to pit initiation.

(e) Alloys 6061 and 6262 were more resistant to pitting than 1100 or 1060.

(f) Crevice corrosion was not necessarily accompanied by pitting of the aluminium surfaces within the crevice.

(g) Bimetallic corrosion of alloys 6061 or 6262 coupled to SS 304 was more severe than that of 1060 coupled to SS 304.

(h) Results concerning the effect of preoxidation on corrosion of aluminium alloys are still inconclusive.

(i) The surface and pitting features observed on coupons exposed to the IEA-R1 pool water for 13 months were similar to those on coupons exposed for 25 months.

6.4. RECOMMENDATIONS BY THE CRP PARTICIPANTS FROM IPEN

In the light of the above, further research should be conducted to:

(a) Evaluate the effect of dust sediments on the corrosion of coupons;

(b) Determine the different aluminium alloys and other metals presently in use inside spent fuel basins and design experiments to evaluate the effect of specific bimetallic couples;

(c) Evaluate the effect of hydrodynamic conditions on coupon corrosion.

REFERENCES TO CHAPTER 6

[6.1] RAMANATHAN, L.V., "The influence of surface inclusions on the corrosion behavior of MTR type fuel plates", Proc. 9th Int. Congr. on Metallic Corrosion, Toronto, 1984, Vol. 2, Natl Research Council of Canada, Ottawa (1984) 578.

[6.2] DURAZZO, M., RAMANATHAN, L.V., "Aqueous corrosion of U_3O_8–Al cermet cores", Proc. 10th Int. Congr. on Metallic Corrosion, Madras, 1987, Vol. 2, Oxford and IBH Publishing, New Delhi (1987) 1577.

Chapter 7

CORROSION BEHAVIOUR OF ALUMINIUM ALLOY TEST COUPONS IN THE SPENT FUEL BASIN OF THE CHINA INSTITUTE OF ATOMIC ENERGY, BEIJING

7.1. INTRODUCTION

Aluminium and aluminium alloys have low thermal neutron cross-sections, and good tensile strength and thermal conductivity. These alloys are widely used as fuel cladding and as construction material in research reactors. A large number of spent fuel assemblies clad with aluminium or aluminium alloys are stored under water in basins, and one of the main considerations is the extension of storage time of these spent fuel assemblies. Corrosion can induce degradation of the fuel cladding, the fuel itself and the storage facility [7.1, 7.2]. Hence it is important to study the corrosion behaviour of aluminium and its alloys, mainly from the point of view of safety in operation, reduction in radiation exposure and reduction of radioactive waste. The IAEA CRP on Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water was initiated at the end of 1995. A number of tests have been conducted within the framework of the CRP and have been reported in successive progress reports and presented at the RCMs. The results of some of these tests carried out at the China Institute of Atomic Energy (CIAE) and some of the main conclusions reached by the Chinese participants are summarized in this chapter.

7.2. EXPERIMENT

7.2.1. Test coupons and racks

Five racks of test coupons were immersed in the spent fuel basin of the swimming pool research reactor at the CIAE. The rack numbers, the coupon materials and the immersion dates are listed in Table 7.1. The coupons were assembled in the rack to evaluate general corrosion, crevice attack and galvanic effects.

The coupons were assembled in the racks with clean surgical gloves in the order specified and according to the test protocol. The racks were photographed before and after immersion. The coupons of the first and the fifth rack were pretreated by washing in deionized water, scrubbing with grease

free cotton and alcohol, and drying in an oven at 110°C until the weight was constant. They were then assembled in the rack. The coupons of racks 2, 3 and 4 were not given any pretreatment before they were assembled in the racks and placed in the basin water. The coupons were assembled in the specified order; the nut holding the coupons in place was tightened by hand until hand-tight and then given a further 10° turn.

7.2.2. Spent fuel basin

The spent fuel basin used for the corrosion tests was constructed of reinforced concrete and lined with aluminium. The size of the basin was 3114 mm (length) × 2114 mm (width) × 5430 mm (depth) and the basin contained 31.6 m^3 of deionized water. The racks were suspended in the spent fuel basin water on stainless steel wires. The racks were positioned 2.5 m below the water surface, and were 0.8 m and 1.5 m away from the basin walls, to avoid contact with the fuel racks (Fig. 7.1).

There are 24 fuel racks in this basin and 14 assemblies in each fuel rack. At present, 236 assemblies with 3628 rods of spent fuel are stored in this basin,

TABLE 7.1. TEST COUPONS AND RACKS

Rack No.	Origin	Materials	Date of first immersion	Duration of test (d)
1	First RCM[a]	1100	1996-09-20	1374
		6061		
		6063		
		SEAV-1		
		SS 316		
		305 (~Al 8081)		
5	CIAE[b]	LT24 (~Al 6061)	1997-11-27	904
		SUS 304-8K		
		1100		349
2	Second RCM[c]	6061		772
3		6063	1998-04-02	Racks have been
4		SS 316		left in basin water

[a] Provided by the IAEA and received in Budapest in August 1996.
[b] Made by CIAE with coupons of site specific material.
[c] Provided by the IAEA and received in São Paulo in March 1998. Besides the two racks given to each participant, CIAE received an extra rack.

and they occupy over two thirds of the basin's storage capacity. The first assembly was introduced into the basin in 1966. The most recent addition to the pool was on 1998-06-13. In this basin, no failures in the spent fuel assemblies have been observed. The radiation field on the basin surface is 200 µR/s, and around the basin it is about 5 µR/s.

The basin water is mainly stagnant, except during purification. Basin water purification is not periodic and depends on the extent of deterioration of the water quality; it is carried out about once a year. The purification system is a mobile mixed ion exchange column 1.5 m high and 200 mm in diameter.

The last cleaning of the spent fuel basin was in 1995 and included the bottom and the walls of the basin. The basin sludge was not analysed. The materials of the basin components are: fuel rack — aluminium; graphite rack — aluminium; test target — stainless steel and aluminium.
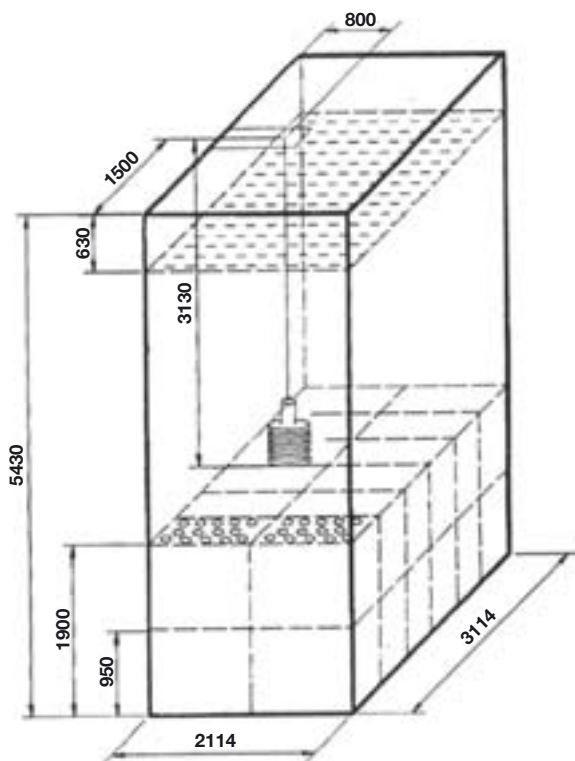
FIG. 7.1. Spent fuel basin and position of rack. Dimensions in millimetres.

7.2.3. Reactor and spent fuel

Relevant data about the reactor and its spent fuel are given below.

Reactor type	Swimming pool research reactor
Major functions	Radioisotope production, material irradiation, physics research
Commissioned	1964-12-20
Power	3.5 MW
Thermal neutron flux	3.5×10^{13} (av.), 5×10^{13} (max.) $n \cdot cm^{-2} \cdot s^{-1}$
Coolant	Light water
Moderator	Light water
Reflector	Be and graphite
Fuel core	UO_2
U-235 content	10%
Fuel cladding	LT21 (Al–Mg–Si system)
Cladding thickness	1.5 mm

7.2.4. Basin water monitoring

The basin water chemistry was analysed using the following instruments:

Mass	Mettler electronic balance, made in Switzerland;
pH	pH M26, made in Denmark;
Conductivity	DDS-11 conductivity meter, made in China;
Anions	Dionex 4000I ion, made in China;
Cations	PQ2 ICP/MS, made in the United Kingdom;
Algae	XPA-1 polarized light microscope (100 ×, 500 ×), made in China.

The radioactivity of the basin water was measured as follows:

γ activity: Low background coaxial HPGe spectrometer, made in the USA; relative efficiency 30%, 70 keV to 2.7 MeV, background 1.9 counts/s.

β activity: Low background β spectrometer, FH 1914, made in China; detection efficiency 26%, background 1.1–1.5 counts/min.

α activity: Parallel-plate barrier chamber α spectrometer, made in China; detection efficiency 45%, 4–6 MeV, background 13 counts/h.

7.3. EXPERIMENTAL DETAILS

7.3.1. Water chemistry parameters, radioactivity and radiation level

The basin water was periodically analysed. The water was sampled at the appropriate depth, near the test rack. The parameters are listed in Table 7.2. These parameters indicate that the basin water quality did not change significantly.

The radiation dose rate near the test rack was 0.4–3.9 Gy/h. The dose rate also varied with distance between the test racks and the spent fuel (Table 7.3).

TABLE 7.2. TYPICAL PARAMETERS OF BASIN WATER

pH	6.0–7.0
Conductivity	3–10 µS/cm
Cl^-	<0.1 ppm
NO_3^-	<1 ppm
SO_4^{2-}	<1 ppm
F^-	<0.05 ppm
Temperature	17–25°C
Cu^{2+}	<5 ppb
Hg^{2+}	<1 ppb
Al^{3+}	<30 ppb
Fe^{3+}	<2 ppb
Ag^+	<25 ppb
α activity	10^{-1} Bq/L
β, γ activity	10^4 Bq/L
Algae	None

TABLE 7.3. RADIATION DOSE RATE AROUND THE TEST RACK

Detecting position	Apparatus	Uncertainty	Absorption dose (Gy)		Dose rate (Gy/h)
			Measurements	Average	
Rack 2	$Ag_2Cr_2O_7$	<3% (40–400 Gy)	1066, 1099, 1403, 1321, 1197	1217	3.9
Rack 5	Fricke	<5% (0.4–400 Gy)	110, 102, 112, 120, 103	109	0.4

The temperature near the racks was measured and found to be 1°C higher than the temperature of the bulk water.

7.3.2. Visual observation and inspection with a magnifying glass

Visual observation or inspection with a magnifying glass of the test coupons/racks was conducted before and after drying. The visual observations at the basin site did not reveal any significant change. The racks were removed from the water basin and disassembled, and the coupons were sealed in plastic bags at ambient temperature for inspection with a magnifying glass. The disassembly was carried out using clean gloves. The fronts and backs of the coupons were photographed. The results are presented in Table 7.4. The main observations are:

(a)   The coupon surface in contact with the basin water turned dull gradually and with immersion time. The general corrosion was quite uniform on the

TABLE 7.4. RESULTS OF VISUAL OBSERVATIONS — RACK 5 (IMMERSION FOR 481 d)

	Order in rack[a]	Specimen material	Visual and 5 × observations
Uncoupled coupon	1	SUS 304-8K	Smooth, bright, NOC[b]
	2	SUS 304-8K	Smooth, bright, NOC[b]
	2	SUS 304-8K	Smooth, bright, NOC[b]
Crevice sandwich	3	305	Light, white spots, two pits on the back
	3		
	4	LT24	White spots on the back
	4	LT24	White spots with pit on the back
Galvanic couple	5	305	White spots on the back
	5	LT24	NOC, pit on the back
	6	LT24	NOC
	7	305	Pit on the back

[a] From bottom to top; the front side is the side with the identification number.
[b] NOC: no obvious change.

outer surface. The extent of greying of the surface varied with alloy composition and was in the following order: 6063 > 6061 > 1100 > SEAV-1 > SS 316.

(b) Stains and water spots, both inhomogeneously distributed, were observed on the crevice side of crevice sandwiches or galvanic couples. Some areas on the crevice side remained bright, especially the stainless steel coupons.

(c) Sediments were observed on the top surfaces of coupons high up in the rack and on the edges. These sediments were impurities from the basin. Some white sediment was also found on the coupon surfaces. The sediments could be removed easily.

(d) The stains on the aluminium coupons were more difficult to remove than those on the stainless steel coupons.

(e) Areas of the coupon surface in contact with the ceramic separator revealed white deposits. These were inhomogeneously distributed and could be easily removed. The deposits probably came from the separator.

(f) The water and the two coupons (1100 and 6063) within the small glass ampoule (in 9 mL H_2O, pH7.2, conductivity 0.39 µS/cm) that were received at the Budapest RCM (and placed in rack 1) did not reveal any change. The coupons retained their original light appearance.

(g) The pH of the water within the crevice of crevice couples was 5.2–5.8, about one unit lower than that of the bulk water. (The pH was measured with pH papers of the range 4–8.)

(h) The scratched coupons (6053 (coupon 173) and 6063 (coupon 164)) that were passivated at 95°C for 24 h in water to form the passive layer did not reveal any obvious change.

No problems were encountered while separating the crevice couples, nor were nodules and gas bubbles observed on the coupon surfaces. Overall, rack 1 did not reveal much corrosion attack, owing probably to the coupons and rack having been pretreated at 110°C before immersion. Rack 5 revealed more corrosion attack, and the Teflon isolator, which undergoes radiation induced degradation, may have caused this.

7.3.3. Photographic record

The front and back of each coupon, as well as the overall assembled rack, were photographed. A photograph of the coupons of rack 2 is shown in Fig. 7.2. Comparative examination of these photographs revealed the following:

(a) There were stains and spots on the immersed coupons. These were inhomogeneously distributed.
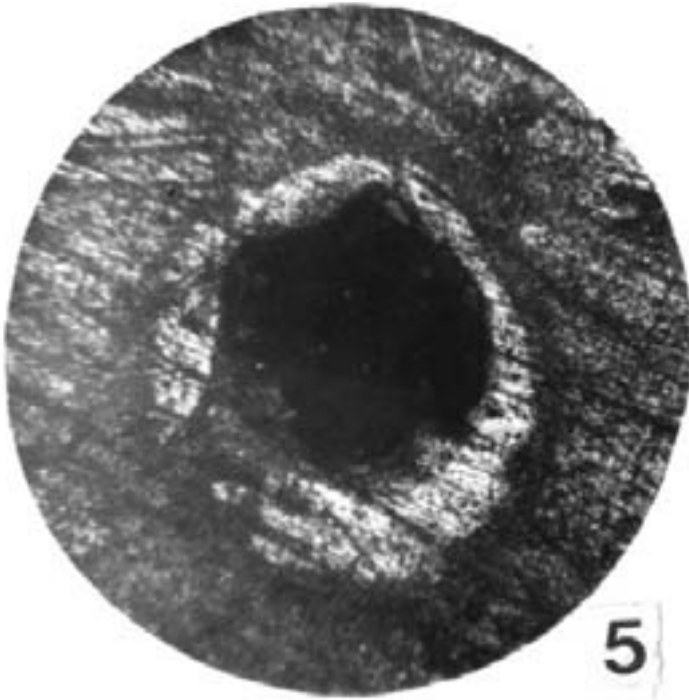
FIG. 7.2. Surfaces of coupons from rack 2.

FIG. 7.3. Pits on coupon surface from rack 5.

(b) Aluminium coupons had many more stains and spots than the stainless steel coupons.

(c) The number of stains and spots on the facing surfaces of crevice couples and galvanic couples far exceeded those on the individual coupons.

7.3.4. Metallographic analyses

Metallographic evaluation was conducted with a shielded microscope, XJB-1. The pits were observed at a magnification of $120 \times$ and photographs taken at $180 \times$. The pit depth measurements were made by the calibrated focusing technique. The coupons were removed from the rack assemblies, washed with running water and deionized water, treated with 50% H_3PO_4 solution to clean/dissolve the oxide from pits and dried prior to metallo-graphic analyses. Figure 7.3 shows typical pits on the surface of a coupon from rack 5.

(a) The 6061 coupons revealed a large number of corrosion pits (>30, with different depths and a maximum depth of 232 µm) along the circular edge. Some pits were observed along the circular edge of 6063 coupons (1–5 pits, with different depths and a maximum depth of 270 µm). There were no corrosion pits on the 1100 coupons. Since pit depth is an important factor, in terms of corrosion attack, the aluminium alloys can be graded in the following order: 6063 > 6061 > 1100.

(b) The stainless steel coupons did not reveal any obvious change when exposed to the spent fuel basin water for four years, even as part of a galvanic couple. The single pit observed on the top SS 316 coupon of rack 1 may have been caused by mechanical damage, as this pit did not increase with immersion time from 588 to 951 days. The pit on the top 305 specimen in rack 5 may have been caused by corrosion under a particle.

(c) In rack 5, three pits were observed after 118 days of immersion, and this number increased to five with immersion for 481 days. This indicates that the extent of corrosion increases with immersion time. The pits appeared mainly on the crevice coupons and galvanic couples, thereby indicating that crevices and galvanic coupling promote corrosion attack.

(d) In rack 3 the corrosion pits appeared only on the circular edges of the coupons. No pits were observed on the coupon surfaces in the case of either crevice or galvanic coupling. The pits that occurred along the edges are not important and are the result of mechanical stresses caused at these regions during manufacture.

7.4. CONCLUSIONS

This section presents the conclusions drawn on the basis of the work carried out during the CRP by the participants from CIAE.

Basin water chemistry and radioactivity monitoring showed that the basin water of the CIAE research reactor is quite good. The main parameters having a significant effect on corrosion attack are as follows:

pH	6.0–7.0
Conductivity	3–10 µS/cm
Temperature	17–25°C
Cl^-	<0.1 ppm
Cu^{2+}	<5 ppb
Hg^{2+}	<1 ppb

Corrosion of the coupons is sensitive to water quality. It is therefore important to control water quality in the spent fuel storage basin. The results of visual inspection and metallographic analyses revealed that corrosion attack also increased with duration of immersion in optimum quality basin water.

The aluminium coupon surfaces gradually turned dull and this increased with immersion time. The outer surface of almost every aluminium alloy coupon was covered with a dark grey layer consisting of a relatively thin oxide film. This oxide film protects the coupon from further corrosion. The facing surfaces of all the crevice and galvanic couples appeared stained or showed white/grey spots that were loosely adhered. This could have been a kind of scale formed by the water.

The two coupons in the glass capsules did not show any change in appearance even after 1374 days of immersion. This gave further evidence that corrosion can be prevented in high purity water.

The pH of the water inside the crevice of crevice couples was in the range 5.2–5.8. This was about one pH unit lower than the pH of the bulk water. Water of reduced pH promotes dissolution of the aluminium oxide film on the crevice surfaces and increases the corrosion of aluminium.

Aluminium coupons coupled to stainless steel corroded more, owing to galvanic effects. The particulate material on coupon surfaces may have contributed to pit initiation.

The extent of corrosion of coupons was affected by their composition and geometry. A comparison of the test results revealed that the extent of corrosion varied in the following order: 6063 > 6061 > 1100; top coupon > bottom coupon; galvanic couples, crevice couples > individual coupons.

General corrosion has no significant effect on fuel clad degradation. However, localized corrosion, such as pitting, can lead to a breach of fuel

cladding and release of radioactive material. Therefore greater attention has to be paid to localized corrosion.

REFERENCES TO CHAPTER 7

[7.1] RITCHIE, I.G., ERNST, P.C., "Research reactor spent fuel status", Research Reactor Utilization, Safety and Management (Proc. Int. Symp. Lisbon, 1999), IAEA-CSP-4/C, IAEA, Vienna (2000).

[7.2] DODD, B., "Current status of the world's research reactors", ibid.

Chapter 8

CORROSION OF ALUMINIUM ALLOY
TEST COUPONS IN THE SPENT FUEL BASIN
OF THE BUDAPEST RESEARCH REACTOR
AT AEKI, BUDAPEST, HUNGARY

8.1. INTRODUCTION

The object of the study presented in this chapter was to assess the corrosion rates of typical aluminium alloys used for fuel cladding, in a variety of research reactor spent fuel pools with different water chemistry regimes. To do this, a unified set of coupons was required. The CRP activities started in August 1996, with the first RCM at the Atomic Energy Research Institute (AEKI) in Budapest. At this meeting, it was decided that AEKI would prepare the test coupons to be used in this study. It was also decided that four aluminium alloys (1100, 6061, 6063 and SZAV-1) and one stainless steel (SS 316) would be studied. AEKI prepared the test rack with the aluminium and stainless steel coupons. One set was given to all the participants of the CRP. A test manual, including the test procedure and a detailed description of the coupons, was also prepared and given to the CRP participants.

This chapter contains the results of the investigations carried out in the Budapest Research Reactor, operated by AEKI. The results correspond to the entire investigation period, i.e. coupons that were taken out of the pool in May 1998 (after 6 and 12 months of exposure), in May 1999 (12 months of exposure) and in May 2000 (24 months of exposure). Some of the earlier results were presented in progress reports and at the second RCM in São Paulo.

8.2. REACTOR AND SPENT FUEL STORAGE POOL

A description of the fuel basin is given to help in drawing conclusions from the results. The basin was built during the last reconstruction of the reactor, i.e. between 1986 and 1992. The reconstructed reactor went critical for the first time in December 1992. Regular operations started in November 1993, and the basin has been in use since then, i.e. the first spent fuel elements were removed from the reactor core and immediately put into the basin in 1994. The fuel elements are normally used up to a relatively high burnup of 60%. They are exposed to temperatures of up to 60°C in the reactor. The temperature of the storage pool is about 20°C, with very limited seasonal variations.

The spent fuel storage basin is a stainless steel pool, located in the reactor hall. The inner storage racks are made of aluminium. The racks have stainless steel legs to avoid contact of aluminium with the stainless steel pool walls. Other structures of the pool are made of stainless steel. The pool contains 370 spent fuel elements. The oldest element has been in the basin since 1994, and the latest was put into the basin in 2000. The fuel elements are of the VVR-SM and VVR-M2 type. In both cases, the cladding material is aluminium (SZAV), and the meat contains 36% enriched uranium (U–Al alloy for the VVR-SM type and UO_2 granulates in aluminium for the VVR-M2 type). The fuel elements have a hexagonal cross-section, with an active length of 600 mm, a total length of 865 mm (including legs, etc.) and a key size (width of the hexagon) of 35 mm. Fifty-four beryllium elements are stored in the pool as well, and their shape and size are identical to those of the fuel elements. The legs and the upper ends of the beryllium elements are made of aluminium (SZAV), and the beryllium, being uncovered, is in contact with the water. The beryllium elements were placed in the pool between 1994 and 2000. Most of the beryllium elements were removed from the reactor core between 1994 and 1997, and only a few in the period 1998–2000. The fuel storage racks contain 230 absorber elements made of B_4C and are covered by aluminium (SZAV). The absorbers are fixed, according to the requirements of the regulatory body. The storage pool contains only the fuel, the absorber and the beryllium elements. The fuel elements are 4 m below the water level. The numbers given above reflect the contents of the pool in the summer of 2000.

The coupon racks were positioned about 2 m above the fuel elements and 2 m below the water surface. The γ radiation dose was measured only occasionally. The dose rates at the upper ends of the fuel elements were last measured on 2000-02-23. They were 10, 16 and 22.8 Sv/h at three different positions just above the relatively fresh fuel elements. The dose rate near the rack could not be measured with low sensitivity devices. An upper limit was nevertheless determined, and the dose rate did not exceed a few millisieverts per hour. The pool water is continuously recirculated by pumps. There are no stagnant areas within the pool. Water parameters such as pH, conductivity and radioactivity were measured regularly, some on a monthly basis and some more frequently. Summaries of these measurements are given in Table 8.1. Chemical analyses were carried out approximately every three months. The results of the chemical analyses are given in Table 8.2.

Table 8.1 shows that all the measured activities were quite low, i.e. less than 1 Bq/mL. The accuracy of the radioactivity measurement at this low level is not great. Hence the results presented in Table 8.1 can be considered to be constant. The electrical conductivity varied between 1.2 and 4.2 μS/cm. The average value is 2.34 μS/cm, with a standard deviation of 0.81. This value can be

considered low and stable. The pH of the basin varied between 4.1 and 6.3, with an average of 5.2 and a standard deviation of 0.6. This variation in pH could be a consequence of the filtration process that was performed occasionally (usually twice a year) with a mobile filter. The data in Table 8.2 show low metal concentrations and a somewhat high chloride ion concentration. Among the aggressive ions, only chlorides could be detected. Other aggressive ions, such as sulphates or nitrates, were not detected.

On the basis of the results presented in Tables 8.1 and 8.2, it can be concluded that the quality of the water in the storage basin was good during the entire period of the CRP investigations, i.e. from May 1997 to May 2000.

TABLE 8.1. SUMMARY OF BASIN WATER PARAMETERS

Date	Total β activity (Bq/mL)	^{137}Cs γ activity (Bq/mL)	^{60}Co γ activity (Bq/mL)	Electrical conductivity (μS/cm)	pH
1997-05-27	0.32	0.20	0.26	3.0	6.0
1997-09-23	0.00	0.20	0.10	1.2	5.6
1997-12-09	0.69	0.00	0.00	3.0	6.3
1998-04-09	0.34	0.18	0.22	2.0	5.6
1998-08-11	0.05	0.17	0.17	2.5	5.2
1998-12-16	0.43	0.06	0.28	2.2	5.5
1999-03-16	0.10	0.10	0.20	1.5	5.1
1999-07-07	0.72	0.06	0.38	1.5	4.6
1999-10-21	0.07	0.09	0.16	2.5	4.4
1999-12-20	0.14	0.06	0.20	2.5	5.1
2000-03-16	0.70	0.06	0.21	1.5	4.3
2000-05-25	0.33	0.13	0.23	2.5	4.1

TABLE 8.2. RESULTS OF QUARTERLY WATER ANALYSES (CONCENTRATIONS IN mg/L)

Date	Cl	Cu	Fe	Mg	Mn	Zn
1997-06-04	36.5	4.30	<10	<12	0.63	36.4
1997-10-09	20.1	1.50	<10	<12	0.04	6.42
1998-05-13	35.5	1.44	<10	14.8	0.29	6.42
1998-10-19	22.9	2.90	<10	10.6	0.45	5.71
1999-06-22	61.3	1.78	<10	14.5	0.82	20.6
1999-12-10	35.7	1.97	<10	<8	0.29	29.5
2000-05-09	27.5	5.94	<10	13.6	0.40	18.2

8.3. INVESTIGATIONS

8.3.1. Inspection and evaluation of rack 1 (after 6 and 12 months)

The first inspection was performed after six months of exposure, i.e. in November 1997. The details of the visual inspection were given in the answers to the questionnaire distributed in November 1997. On most of the coupons, no real corrosion was seen. This corresponded to expectations. However, each coupon was covered with a dark grey layer. In a few cases, different colours (e.g. yellow) could be seen as well. In some other cases, definite traces of corrosion could be observed. In the case of SZAV-1 coupons, a lot of corrosion products were observed. Traces of corrosion products were even seen on adjacent coupons. The second inspection was carried out after one year of exposure.

Visual inspection of the disc shaped coupons showed that the surface deposit on almost every coupon was less than that observed during the first inspection. The grey layer covering the coupons could be easily removed by washing. After washing, no sign of corrosion was visually detected. After inspection, the second stage of investigation consisted of polishing the coupons for examination under the microscope. The polishing was performed in different directions.

Photographs of the coupons were taken to record some of the visual observations and the status after polishing as well. The black and white photographs demonstrate the relevant surface features well. All the polished surfaces were quite similar. The largest pits were seen on SZAV-1. On the other alloys, pitting was negligible. Typical polished surfaces of SZAV-1 are shown in Fig. 8.1. The average and maximum pit sizes observed on SZAV-1 were 10 and 70 μm, respectively.

One can conclude that 12 months of exposure to the basin water did not result in initiation of corrosion on most of the aluminium alloys. On SZAV-1, a few spots indicating the start of pitting were observed.

Insufficient polishing of the coupons could be a possible reason for the grey layer on the surface of the coupons observed during the first inspection. The coupons of racks 2 and 3 (immersed in the pool in 1998) seemed more polished than those of rack 1.

8.3.2. Inspection and evaluation of racks 2 and 3 (after 12 and 24 months)

Racks 2 and 3 were placed in the basin in May 1998 and were removed in May 1999 and May 2000, respectively.
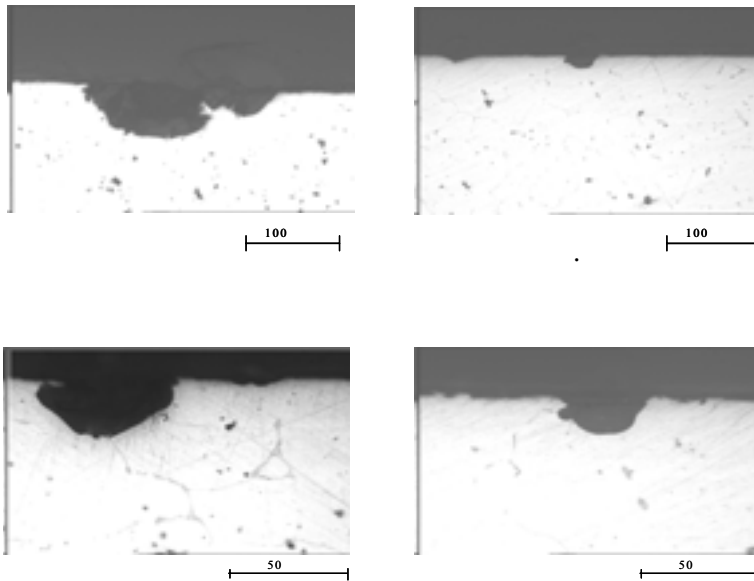
FIG. 8.1. Pits on SZAV surfaces exposed to the basin water.

8.3.3. Preparation of the second set of racks

The same stock of alloys as used for making the coupons of rack 1 was used for the coupons of racks 2 and 3. However, the aluminium oxide tubes and rings that were used in rack 1 were no longer available from the same vendor. Consequently these parts were made from a different lot of materials, and this resulted in some delay and additional costs. The aluminium and stainless steel coupons were marked using a laser scriber. These marks indicated the material and identified the coupon. The following changes were also introduced during the manufacture of coupons for racks 2 and 3.

(a)   Every coupon was polished to improve the surfaces for the investigations and to ensure easy detection of the start of corrosion.
(b)   The surfaces of many 6063 coupons were passivated at 95°C for 24 h. One of the surfaces (that without identification marks) was scratched to introduce a defect.
(c)   The manner in which the racks were packaged was also altered, i.e. two preassembled racks were packed in a cardboard box. Complete documentation was also enclosed in every box.

Two coupon racks corresponding to the above description were suspended in the pool on 1998-05-25.

8.4. RESULTS

8.4.1. Rack 2

Rack 2 was in the pool for exactly one year, and a 6063 coupon from this rack is shown in Fig. 8.2. Colour photographs of coupons from racks 2 and 3 were taken before and after immersion in the pool. The deposit (surface layer) on the 6063 coupon, seen in Fig. 8.2, could be easily removed by simple washing.

The coupons were covered with a grey layer similar to that observed on the coupons of rack 1 but of a lesser extent. This layer also could be removed by simple washing in water.

Photographs of the coupons were taken, and although in black and white, they reveal the different features. The rack and the coupons were
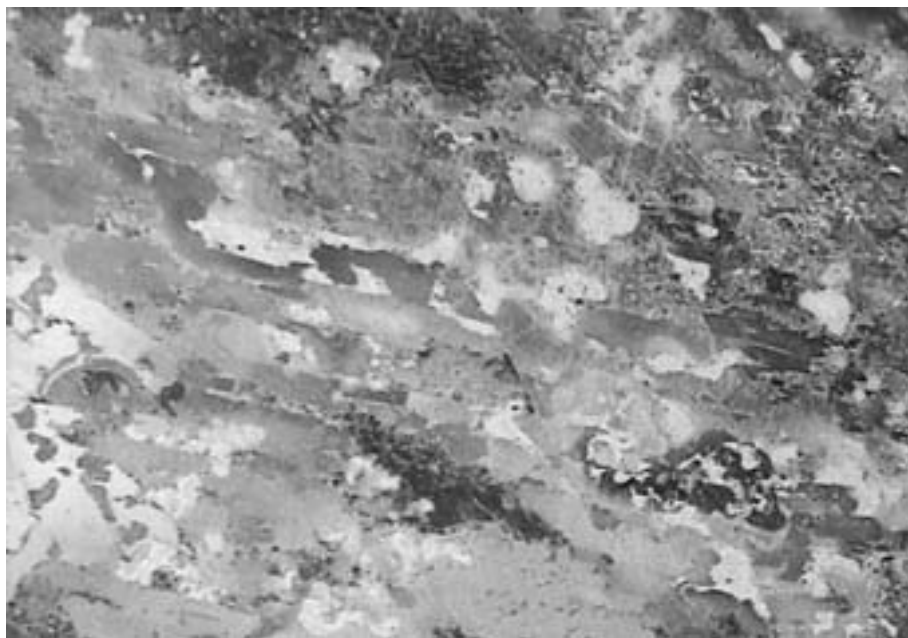
FIG. 8.2. Deposit on a 6063 coupon from rack 2 after exposure to the basin water for one year.

photographed before immersion in the pool and after one year of exposure. The photograph of a 6063 coupon taken in 1999 is shown in Fig. 8.3.

8.4.2. Rack 3

Rack 3 was in the pool for two years. The rack was immersed on 1998-05-25 and taken out on 2000-05-30. A photograph of a 6063 coupon from rack 3 following exposure to the basin water for two years is shown in Fig. 8.4. The deposit (surface layer) on the coupon surface could be easily removed by simple washing.

The coupons were covered with a grey layer similar to that observed on the rack 2 coupons and also similar to that on coupons removed in 1999 from the pool. The layer could be removed by simple washing with water.

Photographs of the coupons were taken to demonstrate the features observed visually as well as the status after polishing. These black and white photographs reveal the different features well. The rack and coupons were photographed both before immersion in the pool and after their removal after two years.

Some pits were seen on the surfaces of the coupons (Fig. 8.5). A few seemed deeper than the others. To study this in detail, metallographic coupons were prepared (polished) to examine the pits. All the coupons were carefully evaluated. These pits were neither deeper nor larger than those observed on coupons from rack 1. Hence no pictures of these pits have been presented.
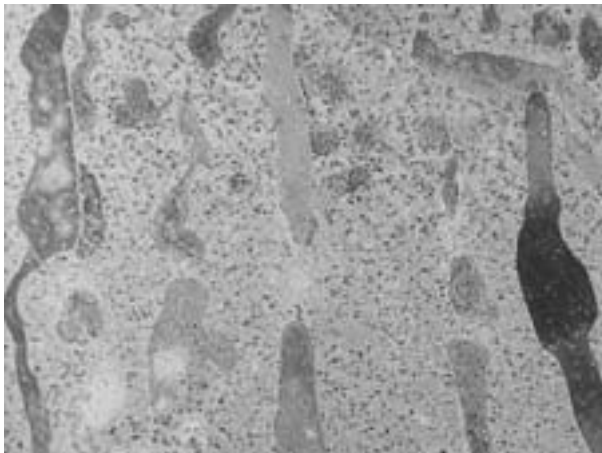
FIG. 8.3. Surface of a 6063 coupon from rack 2 after exposure to the basin water for one year.

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FIG. 8.4. A 6063 coupon from rack 3 after exposure to the basin water for two years.
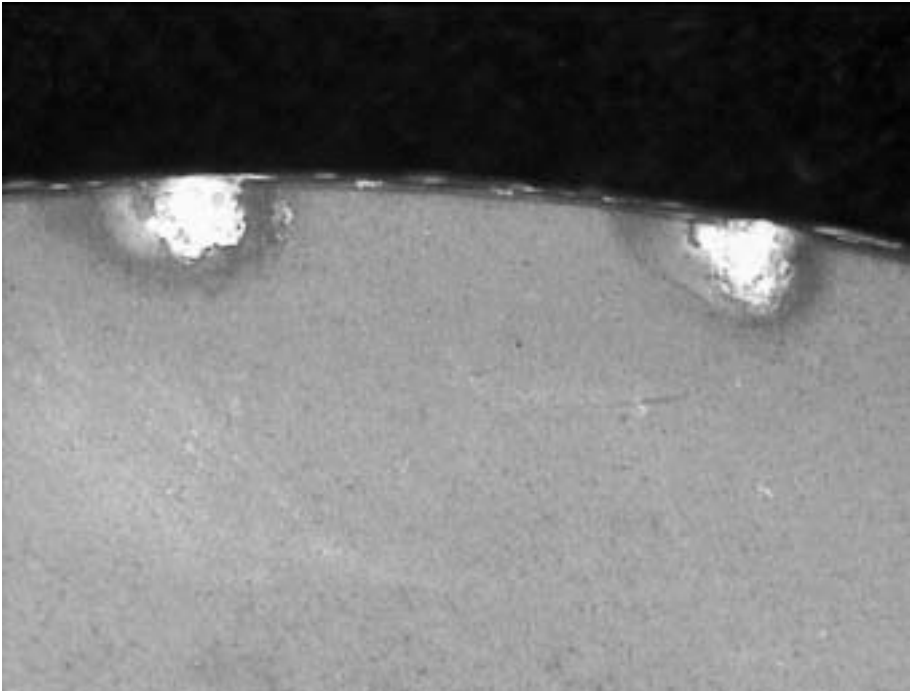
FIG. 8.5. Surface of a 6063 coupon from rack 2.

8.5.   CONCLUSIONS

The results obtained from the evaluation of rack 1 coupons indicate that some corrosion processes were taking place. There were differences in corrosion resistance among the different aluminium alloys. Most of the alloys did not reveal corrosion after one year of exposure in the pool.

The results from the evaluation of coupons from racks 2 and 3 showed that there were no significant differences between those exposed for one and two years to the pool water. A comparison of photographs from rack 2 and rack 3 shows a number of similarities between the corresponding samples. Corrosion of these alloys was probably more dependent on the materials than on the duration of exposure to the pool water. The duration of one to two years is probably insufficient for differences to be observed.

Chapter 9

CORROSION OF ALUMINIUM ALLOY COUPONS EXPOSED IN THE TROMBAY SPENT FUEL STORAGE POOL AT BARC, MUMBAI, INDIA

9.1. INTRODUCTION

Aluminium and its alloys are used extensively in research reactors as core components such as fuel element claddings, channel tubes and pipes, and this is mainly because of aluminium's low thermal neutron absorption cross-section and low density, and the absence of any structural transformation up to its melting point. In addition, upon irradiation it does not produce any long lived radionuclides except for ^{28}Al, which has a half-life of only 2.24 minutes. Radiation damage in aluminium and its alloys is insignificant because of their low recrystallization temperatures.

Although aluminium and its alloys have attractive nuclear properties, they have limited strength, poor compatibility with uranium at high temperatures and low corrosion resistance in water or steam at temperatures above 523 K. Hence their use is restricted to core components in research reactors, where temperatures do not exceed 423 K. However, various parameters, such as water quality, structural design (crevices, galvanic contact with other materials), alloy composition and irradiation, have significant influence on the corrosion resistance of aluminium in research reactors.

In many countries, aluminium clad spent fuels are stored under water for extended periods. The release of fission products could take place through breaches in the cladding and could be a matter for serious concern. In view of this, the IAEA initiated a CRP within the framework of which coupons made from various aluminium alloys would be exposed in a number of spent fuel storage pools.

In this CRP, standard aluminium alloy test coupons mounted in racks were distributed to representatives of the participating countries during the first RCM in Budapest and during the second RCM in São Paulo. These racks were exposed in the Trombay spent fuel storage pool of the Bhabha Atomic Research Centre (BARC), Mumbai. These racks and coupons were examined as per the guidelines of the CRP, and the observations are summarized in this chapter.

9.2. EXPERIMENTAL PROCEDURE

9.2.1. Coupons received at the Budapest RCM

The coupons and the rack were cleaned with a soap solution and running tap water and were degreased in alcohol. They were then rinsed in deionized water and air-dried. The coupons were inspected using a stereomicroscope, their dimensions were measured, and their weights were determined before immersion in the pool. An additional coupon of 1-S (1050) aluminium (99.5% Al), fabricated at BARC, was added to the rack. Details were given in progress reports submitted by BARC within the framework of the CRP. The rack contained coupons made of different aluminium alloys, such as 1050, 1100, 6061, 6063 and SZAV (a Russian alloy), as well as stainless steel. The coupon surfaces were in the as-machined condition and no further polishing was carried out. The rack was assembled as per the guidelines, forming sealed crevices, galvanic couples, etc., as shown in Fig. 9.1. In addition, two glass ampoules containing tensile test coupons in demineralized water were placed within the central cavity of the rack. The glass ampoules were introduced to evaluate the effect of radiation on the mechanical and corrosion behaviour of the aluminium alloy coupons. The rack was immersed in the pool on 1997-01-16 at a location which was about 4 m below the water surface, 1 m away from the sides of the pool and

FIG. 9.1. Rack 1 just prior to the second immersion.

3 m from the stored fuels. The demineralized water of the pool was continuously circulated at 100 L/min and there was an on-line purification system. Pool water samples were collected from regions close to the rack in the pool and analysed. The results of these analyses are given in Table 9.1. The rack was removed on 1998-07-22 after 550 days of exposure. Before final removal, two interim inspections were carried out, the first on 1997-09-18 and the second on 1998-02-18.

9.2.2. Coupons received at the São Paulo RCM

Two racks (racks 2 and 3) containing aluminium and stainless steel coupons were received during the second RCM in São Paulo. These coupons consisted of three pairs of large discs of the aluminium alloys 1100, 6061 and 6063, and two pairs of small discs of the aluminium alloys 6061 and 6063, in galvanic contact with 316 type stainless steel. The large discs were used to form the crevice couples, while the smaller discs were used to form both crevice and galvanic couples. The chemical compositions of the coupons were assumed to

TABLE 9.1. CHEMICAL ANALYSIS OF THE SPENT FUEL POOL WATER AND RADIATION FIELD MEASUREMENTS CARRIED OUT DURING EXPOSURE OF TEST COUPON RACKS TO THE POOL WATER

	1997-09-18	1998-02-11	1998-07-22	1998-09-04	1998-11-30	1999-07-10	2000-03-04	2000-08-04
Temperature (ºC)	28	27.5	28	27	27.5	28	28	28.0
pH	5.9	6.3	6.1	6.3	5.8	6.8	5.9	6.38
Conductivity (µS/cm)	2	16.2	14.5	2.6	1.7	3.4	3.0	3.8
Chloride (ppm)	<2	<2	<2	1.7	1.3	1.6	1.5	1.5
Sulphate (ppm)	89	169	149	—	—	—	—	—
α (Bq/g)	—	—	0.2	—	0.2	0.2	—	0.2
β (Bq/g)	—	—	4.5	—	3.1	5.8	—	4.0
γ (Bq/g)	—	—	1.5		1.0	2.0	—	1.3

Note: —: no measurements made.

be the same as those used in the first rack. The coupons of racks 2 and 3 had a mirror-like finish, suggesting that these coupons may have been polished using a special technique after surface machining. Ceramic spacers were placed between the coupons of each pair. These racks were neither touched by hand nor disassembled before their exposure to the pool water at the same location where rack 1 had been exposed. Details were given in progress reports submitted by the BARC participants within the framework of the CRP. These racks were immersed in the pool water on 1998-07-22 and were removed on 2000-08-04, with an intermediate visual inspection on 1999-07-07. These racks were thus exposed to the pool water for a total period of 742 days.

9.3. OBSERVATIONS

9.3.1. Coupons received at the Budapest RCM

After removal from the pool, the rack and the coupons were extensively photographed to record the surface features. In addition, the pH within the crevices was measured. Figure 9.1 shows the first set of coupons just prior to the second immersion. Figure 9.2 shows racks soon after removal from the pool after 550 days of exposure. Some pits were seen on the coupon surfaces. All the

FIG. 9.2. Racks after removal from the basin.

FIG. 9.3. Surface features on coupons after decontamination.

coupons were decontaminated in a 50% phosphoric acid solution and then examined. Figure 9.3 shows the surface features after decontamination. Pits and machining marks are clearly visible. One of the coupons was sectioned close to a pit and the coupon cross-section was polished to measure the depth of the pit.

In the final inspection, severe crevice and pitting corrosion was observed on the aluminium alloys. Pits as deep as 0.5 mm and as wide as 1.1 mm were observed on coupon 1100/57 (Fig. 9.4). The SZAV coupons showed only crevice corrosion. The results of the three inspections showed that:

(a)   There was an incubation period for crevice/pitting attack to occur on the aluminium alloys.

(b)   In the as-machined surface condition, these alloys were prone to localized corrosion, even in the relatively benign environment of the spent fuel storage pool water, which had a chloride content of <2 ppm and a conductivity of <16 µS/cm. Pits initiated even at the identification marks on the coupons and were either elliptical or undercut.

9.3.2. Coupons received at the São Paulo RCM

As mentioned above, the two racks received in São Paulo were exposed in the same pool for 742 days. The coupons were inspected before and after decontamination. The chloride ion content was maintained at <2 ppm and the conductivity at <16 µS/cm. There were no deposits or corrosion products on the coupon surfaces and the pH values within the crevices were near neutral. Neither crevice corrosion nor galvanic corrosion was observed (Fig. 9.5). After
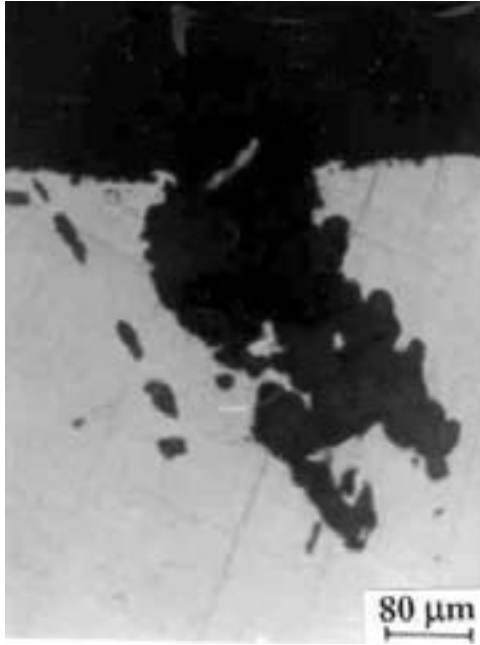
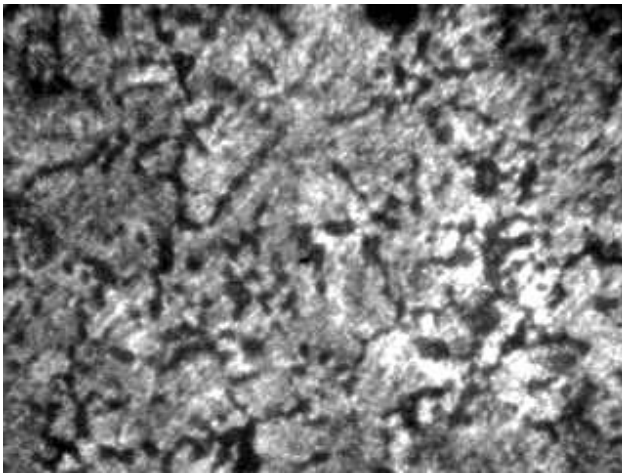FIG. 9.4. Coupon surface showing a pit.

FIG. 9.5. Surface of coupon from rack 2 showing grain boundaries after decontamination.

decontamination, the crevice surfaces had a bright silvery appearance. The outer surfaces of the coupons exhibited some roughening. The extent of roughness was greatest for 1100 and least for 6061 coupons. Microscopic examination revealed grain boundaries (Fig. 9.5). The deepest pit was found on the exposed surface of 1100 and the maximum pit depth was only 7.2 µm. No crevice or galvanic attack was observed. In general, the surfaces of the coupons of racks 2 and 3 were significantly better than those of rack 1.

9.4. DISCUSSION

The spent fuel storage pool at BARC contains low conductivity water (Table 9.1) and an on-line purification system. The specific conductivity was quite low (3.5–16 µS/cm) and the chloride content was <2 ppm. Even in such a benign environment, the aluminium alloys were prone to pitting and crevice attack, depending on the surface condition. Even though uniform corrosion rates were low (1–2 mdd)[9.1] for all the aluminium alloys, crevice/pitting corrosion was observed on all aluminium alloy coupons with machined surface finishes (coupons of rack 1). The results obtained with the coupons of racks 2 and 3 were quite different: no deep pits or crevice corrosion was observed, even after exposure for over two years (742 days). This difference could be attributed to the lower conductivity (except for a short duration) of the pool water to which the coupons of racks 2 and 3 were exposed, to the polished surfaces of these coupons, or to both. The coupons of the racks received in São Paulo had a polished surface, achieved by either chemical or electrolytic polishing. A mirror-like surface finish was observed on the facing crevice surfaces even after 742 days of exposure.

During chemical or electrolytic polishing, an anodic condition is created either by environmental control (chemical polishing) or by the application of a potential (electrolytic polishing). In either case, a thin layer of oxide (an anodized film) forms uniformly over the specimen surfaces. This film forms on the matrix phase as well as on the precipitates or inclusions, and it acts as a passivating layer. The crevice couple coupons from racks 2 and 3 were so tightly pressed together that the crevice remained almost dry. Hence no crevice or pitting damage was observed on these coupons. However, the outer surfaces of these coupons showed grain boundary etching, indicating that this thin oxide film was unable to provide complete protection over an extended period. Intergranular corrosion of aluminium alloys occurs owing to segregation of

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[9.1] mdd: milligrams per square decimetre per day.

impurity or alloying elements to grain boundaries. Differences in electrode potential between the matrix and the precipitates result in intergranular attack. These alloys should therefore be heat treated to bring about uniform distribution of precipitates and reduction in impurity segregation to grain boundaries.

The presence of a thin oxide/anodized layer on aluminium alloy surfaces may shift the electrochemical potential (ECP) to more noble values (passive state). In another CRP, ECPs on 1050 (99.5% aluminium) coupons exposed in the same spent fuel storage pool [9.1] were measured. These ECP values (with respect to a saturated calomel electrode) varied in the range 107–382 mV, depending on sample location with respect to the stored spent fuels. Although no definite trend could be observed, all the ECP values were positive, indicating immediate passivation of the coupons upon immersion in the pool water. Detailed ECP measurements on aluminium alloy coupons with surfaces polished by different techniques could help substantiate the observations made in this study.

At room temperature, corrosion of aluminium and its alloys proceeds mainly by the oxygen depolarization reaction, and this is limited by diffusion. The critical diffusion current on aluminium is one tenth of that on iron and copper. Hence no cathodic reactions occur on most of the aluminium surface. At room temperature, aluminium and its alloys are at a corrosion potential that corresponds to the passive state. The corrosion rate is quite low, about $0.0028 \text{ g·dm}^{-2}\text{·d}^{-1}$. In de-aerated electrolytes, the cathodic process involves the discharge of hydrogen ions. A part of this hydrogen could dissolve in the metal, and subsequently hydrogen atoms could recombine to form hydrogen molecules. This would generally be accompanied by volume expansion, leading to the buildup of internal pressure. As a result, blisters could form on the aluminium alloy surface and destroy the protective oxide film, and thereby enhance corrosion. Grain boundaries are sinks for defects, microporosity, etc. Thus aluminium corrosion could be more intense at grain boundaries, as observed in this study. A small amount of iron in aluminium helps improve the corrosion resistance of the aluminium alloy, even at elevated temperatures.

9.5. CONCLUSIONS

On the basis of the results obtained from exposing the test coupon racks to the Trombay spent fuel storage pool water, the following conclusions can be drawn:

(a)   The pool water parameters, such as specific conductivity and chloride ion concentration, have a significant effect on both uniform and localized corrosion.

(b)   Aluminium alloy coupons in the as-machined surface condition are more prone to localized attack, such as pitting and crevice corrosion.

(c)   Aluminium alloy coupons with smooth and mirror-like surfaces are resistant to crevice corrosion and pitting attack.

(d)   Coupons of 1050 are more prone to pitting attack.

ACKNOWLEDGEMENTS

REFERENCE TO CHAPTER 9

[9.1]   KAIN, V., AGARWAL, K., DE, P.K., SEETHARAMAIH, P., Environmental degradation of materials during wet storage of spent nuclear fuel, ASM J. Mater. Eng. Perform. **9** 3 (2000) 317–329.

Chapter 10

CORROSION OF ALUMINIUM COUPONS IN THE FUEL STORAGE BAY OF PINSTECH, ISLAMABAD, PAKISTAN

10.1. INTRODUCTION

This chapter reports the work carried out at the Pakistan Institute of Nuclear Science and Technology (PINSTECH) under the CRP, the aims of which were to:

(a) Assess the corrosion rate of aluminium cladding alloys for research reactor fuels in storage basins;
(b) Achieve an understanding of the corrosion mechanisms involved.

10.2. DESCRIPTION OF PROCEDURES

The IAEA distributed racks 2 and 3, containing aluminium and stainless steel coupons, during the second RCM, in March 1998, to participants of the CRP, along with the test protocol. As the Pakistani representative could not attend the second RCM, the racks and the relevant literature were sent by mail by the IAEA and were received in July 1998. These racks were handled according to the test protocol and were immersed in the fuel storage bay in October 1998. Rack 1, received at the first RCM, had been immersed in the same bay since November 1996.

In this chapter the procedures used for preparing the racks and coupons, for immersion and corrosion evaluation (after exposure) of the coupons of rack 2, for pool water chemistry determinations, for periodic inspections and for determination of radiation levels near the racks are described. Rack 2 contained eight aluminium alloy coupons and two stainless steel coupons.

Aluminium and its alloys have low thermal neutron capture cross-sections, and good tensile strength and thermal conductivity. They are commonly used as fuel cladding and as construction materials in water cooled research reactors. Aluminium owes its excellent corrosion resistance in most environments to the protective barrier oxide film that forms and strongly bonds to its surface. This oxide film is relatively inert and tends to resist further oxidation. During wet storage of aluminium clad spent fuels, a number of corrosion mechanisms

potentially play a role. The general corrosion behaviour of aluminium in high purity water is extremely good. As a general rule, the protective oxide film is very stable in aqueous solutions in the pH range 4–8.5 [10.1].

Aluminium and its alloys occupy positions in the galvanic series that are considered active, and they are therefore highly susceptible to failure by galvanic attack [10.1]. In chloride-containing solutions, aluminium alloys are susceptible to localized corrosion, pitting and galvanic corrosion, especially in dissimilar metal crevices. Severe attack is often seen when the aluminium alloys are coupled to more noble metals. The galvanic corrosion behaviour of stainless steel is difficult to predict because of its passive nature. In general, stainless steel is more noble than aluminium in the electrochemical series and, depending on the environment and other factors, it may promote corrosion of aluminium. Howell [10.2] studied the galvanic corrosion of different aluminium alloys that were joined by welding or were bound mechanically. He noted that the galvanic effects promoted corrosion between two alloys in basin corrosion tests and during storage. Godard et al. [10.3] have studied the crevice corrosion of aluminium alloys and reported significant localized corrosion on closely fitted surfaces upon entry of water into the crevice.

Pitting is the main form of corrosion of aluminium alloy clad fuels in wet storage basins around the world. It has been observed that pits usually start at small points on the surface and enlarge with time [10.4]. The areas of these pits are generally small compared with their depth and volume. Hampel [10.5] pointed out that in the life cycle of a pit, there are four possible stages: initiation, propagation, termination and reinitiation. Howell [10.6] observed in his study that the pitting corrosion of aluminium is an autocatalytic process. The operation of local cells in an electrolyte produces changes at local anode and cathode sites that increase the potential between them, and therefore increase the activity of pits. The major factors believed to influence the pitting of aluminium alloys are: conductivity; pH; bicarbonate, chloride and sulphate ion levels; and dissolved oxygen content [10.3].

The corrosion processes associated with aluminium clad fuels in storage basins are electrochemical. Hence basin water plays a key role in the flow of electric current and ions in the process. The amount of metal removed by corrosion is directly related to the current flow. By increasing the resistance of the water, the corrosion of aluminium can be reduced. Fontana [10.4] pointed out that the low corrosion rates in high purity water are primarily due to the low conductivity of the water. Aluminium is passive and protected by its oxide film in the pH range 4–8.5. It has been observed that the pitting potential of aluminium in chloride solutions is independent of pH in the range 4–9 [10.7].

The protective oxide film plays a key role in avoiding general and pitting corrosion of aluminium alloys. The corrosiveness of basin water is influenced to

a large extent by the ability of impurity ions to penetrate the oxide film on the aluminium surface. Sverepa [10.8] reported on the penetrating power of anions into passivating oxides, and these were, in decreasing order, chloride, bromide, iodide, fluoride, sulphate, nitrate and phosphate. The pitting corrosion of aluminium is often produced by halide ions, and chlorides are most frequently encountered. Chloride ions break down the protective oxide film and inhibit repassivation. Chloride ions from the bulk electrolyte migrate into pits and crevices, causing rapid dissolution of aluminium within these regions. Pitting occurs in the presence of oxygen because the metal is readily polarized to its pitting potential [10.1]. In general, aluminium is not pitted in aerated, non-halide solutions, because its pitting potential is nobler (cathodic) than in halide solutions. Hence it is recommended that the chloride content of basin waters be maintained as low as possible, to prevent pitting corrosion. It is difficult to specify a limit for the chloride ion content below which pitting will not occur, and this is because of the synergistic reactions that take place with other anions in the water. Sverepa [10.8] observed that increasing the chloride content from 0 to 50 ppm in water containing 116 ppm of bicarbonate ions increased the number of pits but not their depth. Also, with 0.1% copper, the effect was much greater. In the presence of 10 ppm of chloride ions and of 116 ppm bicarbonate ions at pH8, very little attack occurred, whereas at pH8, with 50 ppm of chloride ions and 232 ppm of bicarbonate ions, pits occurred.

Mears and Brown [10.9] studied the influence of temperature on pitting of aluminium alloys in chloride solutions. They found that as the temperature increased, the density of pits and the probability of pitting increased, while the pitting rate or average pit depth decreased. Consequently it has been observed that it is extremely important to maintain basin water temperatures as low as possible to avoid corrosion.

10.3. EXPERIMENTAL PROCEDURE

10.3.1. Preparation of rack assembly

Ten coupons preassembled on rack 2 were received from the IAEA. This rack was disassembled and all the coupons, the rack and the insulators were degreased ultrasonically using alcohol, rinsed with water and dried. The two sides of the coupons were photographed. All the coupons were weighed in a single pan digital balance (0.0001 g accuracy). All the dimensions of the coupons were measured with vernier callipers. The coupons were reassembled in the rack in the same sequence.

Photographs of the rack and the coupons were taken at different stages — as-received, the individual coupons, and rack and coupons after reassembly.

10.3.2. Immersion of rack 2 in the pool

A nylon cord was used to suspend the rack in the basin pool. The rack was lowered into the pool on 1998-10-15. This rack was allowed to remain immersed for one year.

10.3.3. Basin water chemistry

The first rack (rack 1) was immersed in the storage fuel bay in November 1996. Before its immersion, weekly monitoring of basin water chemistry had been started. The water samples were measured/analysed for their pH, conductivity, temperature and content of anions such as chloride, sulphate, nitrates and nitrite. The following analytical instruments were used to carry out these measurements:

pH   A combination type pH electrode
Conductivity   A laboratory conductive meter
Anions   An ion chromatograph
Temperature   A thermometer

The basin water was recirculated daily for 7 h, at a flow rate of 67 L/min. The pool water was purified in a mixed bed demineralizer with a strong acid cation exchanger and a strong base anion exchanger.

10.3.4. Radiation measurements

The radiation level near the rack was measured during regular inspections carried out by the Health Physics Division of PINSTECH.

10.4. RESULTS AND DISCUSSION

10.4.1. Monthly inspections

The first visual inspection of rack 2 was conducted after one month of exposure to the basin water. Each inspection was carried out after withdrawing the rack from the pool for a very short time. No pitting corrosion was observed on any of the coupons. However, some discoloration of the coupons was

noticed. Subsequently, rack 2 coupons were visually inspected every month. The overall observations are presented in Table 10.1.

10.4.2. Basin water chemistry

Water coupons were collected weekly and their pH and conductivity were measured, along with anions such as chloride, sulphate, nitrates and nitrite. The data obtained during 1998–1999 are given in Table 10.2.

TABLE 10.1. SUMMARY OF VISUAL OBSERVATIONS

Inspection date	Total exposure (d)	Observations
1998-11-15	31	Pitting not observed, some discoloration noticed
1998-12-15	61	Corrosion not observed, all coupons slightly bright in colour
1999-03-15	151	Coupons dull, no corrosion found
1999-06-15	243	No pits on coupons, some coupons dull in colour
1999-09-15	335	Coupons dull, no corrosion
1999-10-15	365	No corrosion

TABLE 10.2. SUMMARY OF BASIN WATER PARAMETERS

Date	pH	Temperature (°C)	Conductivity (µS)
1998-10-09	5.50		0.3
1998-12-07	5.60		0.3
1999-02-26	5.9	21	0.8
1999-04-05	5.9	22	0.8
1999-06-02	6.2	24	0.3
1999-08-04	6.0	28	0.4
1999-10-15	5.5	26	0.5

Notes: Using the ion chromatography technique, F^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-} were not detected, and Cl^- was <0.05 ppm.

The lowest detection limit of the different anions in ppm was as follows: F^-: 4; Br^-: 5; Cl^-: 1; NO_2^-: 4; NO_3^-: 4; PO_4^{3-}: 6; SO_4^{2-}: 5.

Chloride content was determined by a preconcentration procedure.

10.4.3. Radiation measurements

The radiation level near the specimen racks was continually checked during inspection by the Health Physics Division of PINSTECH, and was always nil.

10.4.4. Removal of rack 2

According to the test protocol, rack 2 was withdrawn on 1999-10-15 from the basin water, after one year of exposure. The following procedure was adopted at the site and in the laboratories.

10.4.4.1. Observations at the site

(a) The rack 2 assembly was withdrawn from the basin water.
(b) The pH of the bulk water and on the external and internal surfaces of the coupons was measured with (i) Aclit pH0–6 papers (Merck) and (ii) Neutralit pH5–10 papers (Merck). The pH values are given in Table 10.3.
(c) Photographs were taken of the overall rack and all other aspects of interest.

10.4.4.2. Detailed examination in the laboratory

(a) The rack was disassembled using clean cotton gloves to avoid contamination of the coupons with oils, salt and other deposits.

TABLE 10.3. pH VALUES DETERMINED USING pH PAPERS AT THE TIME OF WITHDRAWAL OF RACK 2

	pH
Bulk water	5.5
Surface of upper coupon	5.5
Galvanic couple (316/112 + 6063/11) inside surface	5.5, 6 with time
Galvanic couple (316/119 + 6061/143) inside surface (few drops of water)	5.5
Crevice sandwiches (6063/167 + 6063/187) inside surface (few drops of water)	5.5
Crevice sandwiches (6061/241 + 6061/237) inside surface (few drops of water)	5.5
Crevice sandwiches (1100/28 + 1100/21) inside surface (more drops of water)	5.5

(b) The coupons were removed from the rack. During removal, every coupon was thoroughly examined and observations were made. The observations included the following, and some of these are shown in Table 10.4:

— Ease of removal (separation of crevice/galvanic coupons).
— pH on the facing surfaces of coupons. This was 5.5 in all cases.
— Amount and type of loose deposits. This was nil.
— Staining.
— Discoloration.
— Pitting. None was found.
— Tenacious or loose oxides. None were found.
— Embedded particles. None were found.

(c) Photographs were taken of the crevice and galvanic couples (front and back faces).

10.4.4.3. Post-exposure detailed examination

The following procedure was adopted during the detailed examination:

(a) All the coupons of rack 2 were decontaminated using 5% phosphoric acid for a few seconds and were then air-dried to remove moisture from the surface.
(b) The coupons were weighed in a digital balance.

TABLE 10.4. OBSERVATIONS MADE DURING SEPARATION OF GALVANIC AND CREVICE COUPLE COUPONS

Pair No.	Marking	Ease of removal	Staining	Discoloration
1	316/112	Not easy, removal by sliding	On surface	No
	6063/114		On surface	Yes
2	316/119	Easy removal	Inside edge	No
	6061/143		On surface	Yes
3	6063/167	Easy removal by sliding	On surface	Yes
	6063/187		On surface	Yes
4	6061/241	Removal not easy by either	On surface	Yes
	6061/237	sliding or pulling	On surface	Yes
5	1100/228	Easy removal by sliding	On surface	Yes
	1100/228	or pulling	On surface	Yes

(c)   All the coupons were immersed in a 50% phosphoric acid solution to clean/dissolve oxide from within the pits and the coupons were removed from the solution when bubbles started to form. The weights of the coupons after cleaning were also measured in a digital balance.

(d)   The two surfaces of the coupons were examined, and the details are given in Table 10.5.

(e)   The surface condition of each coupon was also observed using an optical microscope, and the observations are summarized in Table 10.6.

10.4.5.   Permanent withdrawal of rack 3

Rack 3 was permanently withdrawn from the basin water in October 2000. The same procedures as described above were used to disassemble and investigate the coupons. Photographs of the front (exposed to water) and back (coupling side) are shown in Fig. 10.1.

10.5. CONCLUSIONS

The following conclusions were drawn:

(a)   Galvanic and crevice couples could be separated by sliding them apart.
(b)   The crevice pH was ~5.5.
(c)   There were no loose deposits.
(d)   There were no pits on the exposed surfaces.
(e)   Pits were found in the crevices with the ceramic washer.

TABLE 10.5. VISUAL OBSERVATIONS MADE AFTER DECONTAMINATION OF COUPONS

Marking	Top, front (exposed to water)	Bottom, back (coupled surface)	Outer edge	Inner edge (with hole)
Galvanic couples				
316/112	Almost shining surface and white, thin, circular line indicating mark of washer	Shining surface, some stains of scale initiation	Almost clean. Very minute black spots in some areas	Very thin rust layer
6063/114	Dull, surface exposed to water. Deposition of scale. Corrosion (general) mainly under washer	White deposits, water stains and thin, irregular scale due to water seepage between crevice faces. Shining surface compared with front	Dull in colour	White deposits
Comparison	In a galvanic couple (316/112 + 6063/114), the aluminium sample 6063/114 had more deposited scale on the coupled surface than did the stainless steel coupon 316/112			
316/119	Almost shining surface. Broken thin line along washer boundary. One brown spot near the inner edge (hole), indicating some corrosion around the inner edge	White deposit with irregular shape covering 60% of the surface	Clean	Clean
6061/143	General corrosion on some areas under washer. Discoloration due to scale on the rest of the area	White, irregular deposits of scale	No corrosion. Covered with white scale	White deposits

TABLE 10.5. (cont.)

Marking	Top, front (exposed to water)	Bottom, back (coupled surface)	Outer edge	Inner edge (with hole)
Comparison	In a galvanic couple (316/119 + 6063/143), the aluminium coupon 6063/114 developed more scale than the stainless steel coupon 316/119			
Comparison between steel coupons	Coupon SS 316/119 had more scale than SS 316/112			

| Marking	Front (outer surface)	Back (coupled surface)	Outer edge	Inner edge (with hole)
Crevice couples				
6063/167	Identification marks had scale. Some bright spots without scale found under washer. Exposed surface dull in colour owing to scale	White deposits where water entered from inner edge	Outer edge clean	White inner edge due to scale
6063/187	Fully covered with scale, 60% bright and 40% black, irregular. Similar scale deposit under washer, white in colour with some bright spots under washer	Irregular scale (white) deposits. Bright lines indicating points of entry of water from inner edge	Almost clean	Clean edge
Comparison	In crevice couples of aluminium alloys (6063/167 + 6063/187), both coupons showed almost identical levels of brightness			

TABLE 10.5. (cont.)

Marking	Front (outer surface)	Back (coupled surface)	Outer edge	Inner edge (with hole)
6061/241	Fully covered with white scale, 70% dull bright and 30% black. Some bright spots without scale found under washer	30% of contact area unattacked and bright. White deposits (70%) in the form of streaks	Outer edge clean	White deposit
6061/237	Exposed area covered with scale, about 40% dull bright and 60% dark black. Some white spots under washer	Unattacked bright area (30%), white deposits (70%) due to scale at water entry points from inner and outer edges	Clean	Almost clean
Comparison	In crevice couples (6061/241 + 6061/237), both coupons were almost identical in appearance			
1100/228	Bright dull area (50%) and dark dull area (50%). Some bright spots without scale under washer	Unattacked bright area (30%), white scale deposits (70%)	Almost clean	Almost clean
1100/221	Fully covered with scale. Whole area uniformly dull in colour. Dark dull area under washer with signs of bright spots under washer	Unattacked bright area (30%), white scale deposits (70%)	Clean	Dull scale deposits
Comparison	In crevice couples (1100/228 + 1100/221), both coupons had almost identical surface conditions			

TABLE 10.6. MICROSCOPIC OBSERVATIONS MADE ON RACK 2 COUPONS AFTER EXPOSURE

Marking	Top, scratched surface (exposed to water)	Bottom (coupled surface)
Galvanic couple 316/112 + 6063/114		
316/112	No corrosion, no deposition. Only marks of insulating washer and scratches, which remained bright during exposure. Areas under washer in contact with specimen bright but with pits. All other exposed areas covered by scale. Under microscope, scale seemed crystalline	A few spots of scale, otherwise specimen is bright. No pits
6063/114	Pit depths: 4, 4, 4, 4, 4, 6, 6, 8, 8, 8, 10, 10, 14, 16, 16, 4–10, 6–12, 25 μm Range: 4–25 μm deep. Shape: mostly round, elliptical, shallow and a few undercut. Grain boundaries also etched in this region	Scale formed where water made channels. Contact areas bright. No pits
Galvanic couple 316/119 + 6061/143		
316/119	Insulating washer produced a thin boundary line without any pits. Other areas bright and unattacked. At a few sites on this line, some shallow pits 2 μm deep found. Under insulating washer, pits developed and grain boundaries were etched	Scale streaks 2 μm thick formed owing to seepage of water within crevice. No pits
6061/143	Pit depths: 6, 6, 6, 6, 8, 8, 10, 10, 10, 12, 12, 12, 14, 14, 16, 16, 20 μm. Pits mostly in the range 6–12 μm deep, with round openings. Pits of maximum depth 20 μm rarely found. Other exposed surfaces fully covered with scale of thickness 6–10 μm	Contact area unaffected. No pits. Some areas near the outer edge revealed grain boundaries while others remained unaffected. No pits

TABLE 10.6. (cont.)

Marking	Top, scratched surface (exposed to water)	Bottom (coupled surface)
Crevice couple 6063/167 + 6063/187		
6063/167	Pits under washer, with various types of opening, i.e. round and irregular. Most occurred at grain boundaries. Pit depths: 8, 10, 10, 10, 12, 12, 12, 14, 14, 14, 18 μm	Very shallow pits, 2 μm deep. Some contact areas bright. Most of the area unattacked. Water channels formed in crevice resulted in scale formation
6063/187	Surface exposed to water developed uniform scale. Very few bright areas observed under washer, and even these covered with thin scale. Thick scale formed probably because this coupon was below 6063/167	Scale formed at areas where water entered. Other areas remained bright and unattacked. No pits
Crevice couple 6061/241 + 6061/237		
6061/241	Under insulation washer, scale in small areas peeled off. Portions with and without scale showed very shallow pits. Scale thickness measured 10 μm	Contact area bright. Water channels formed scale. No pits
6061/237	Pitting under insulation washer. Pit depth: maximum 20 μm. Uniform scale formed on all exposed surfaces	Contact area bright. Thin scale at other areas of water entry into crevice. No pits
Crevice couple 1100/228 + 1100/221		
1100/228	Under insulation washer, small shining area left. Generally no pits observed; however, a few undercut-type pits found, 10–16 μm deep. Uniform and dense scale on exposed areas	Contact area bright. No pits
1100/221	Small bright area under washer. No pits. Thick and uniform scale developed on exposed surface	Scale developed in regions where water had entered. No pits
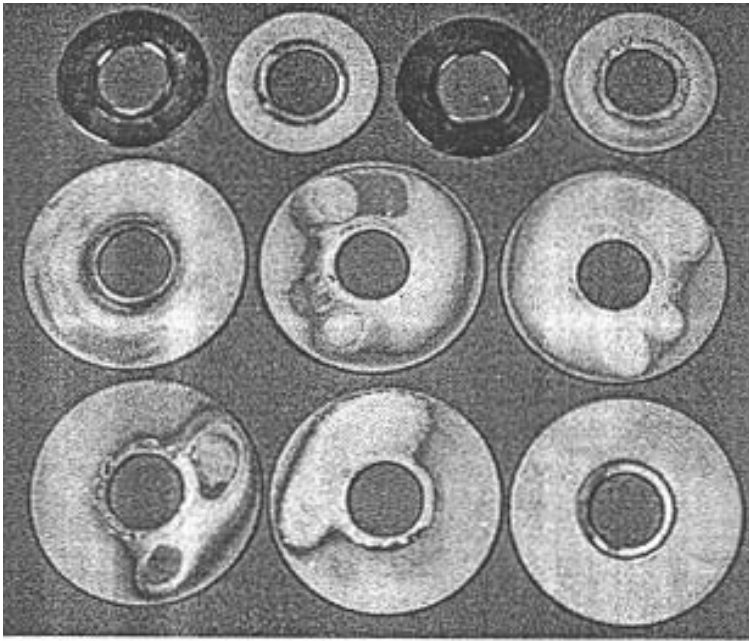
(a)
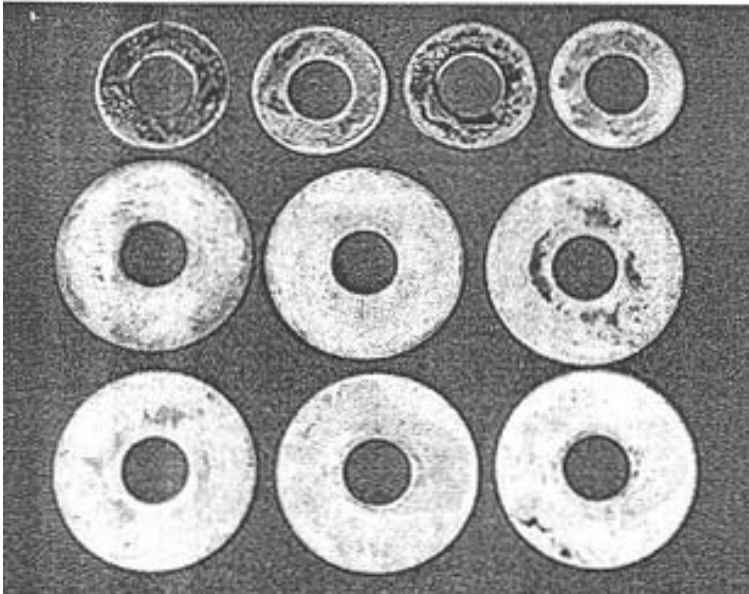
(b)

FIG. 10.1. Photographs of rack 3 coupons. (a) Fronts (exposed to water) and (b) backs (coupling side).

REFERENCES TO CHAPTER 10

[10.1] AMERICAN SOCIETY FOR METALS, Metals Handbook, 9th edn, Vol. 13, ASM, Metals Park, OH (1987) 18–44.

[10.2] HOWELL, J.P., "Al-clad spent fuel in reactor basin water storage", Corrosion/95, Natl Assoc. of Corrosion Engineers, Houston, TX (1995) paper 429.

[10.3] GODARD, H.P., et al., The Corrosion of Light Metals, Wiley, New York (1967) 3.

[10.4] FONTANA, M.G., Corrosion Engineering, 3rd edn, McGraw-Hill, New York (1986).

[10.5] HAMPEL, C.A., Encyclopedia of Electrochemistry, Reinhold, New York (1964) 925–929.

[10.6] HOWELL, J.P., "The durability of aluminium-clad spent nuclear fuels in wet basin storage", Corrosion/96, Natl Assoc. of Corrosion Engineers, Houston, TX (1996) paper 128.

[10.7] SZKLARSKA-SMIALOWSKA, Z., Pitting Corrosion of Metals, Natl Assoc. of Corrosion Engineers, Houston, TX (1986).

[10.8] SVEREPA, O., Werkst. Korros. **9** (1958) 533.

[10.9] MEARS, R.B., BROWN, R.H., Ind. Eng. Chem. **29** (1937) 1087.

Chapter 11

CORROSION RESISTANCE OF DIFFERENT ALUMINIUM ALLOY COUPONS IN THE SPENT FUEL POOL OF THE MIR REACTOR, DIMITROVGRAD, RUSSIAN FEDERATION

11.1. INTRODUCTION

The first batch of coupons was received in August 1996 at the first RCM, held in Budapest in 1996. The second batch of coupons was received at the second RCM, held in São Paulo in 1998. The investigation consisted of exposing the coupons to the aqueous conditions of research reactor spent fuel pools; periodic inspection of the coupons, both visually and with photographs; and the determination of corrosion product weight gains.

At the State Scientific Centre of the Russian Federation, Research Institute of Atomic Reactors, the investigations were carried out at the spent fuel pool of the MIR research reactor. This chapter presents the following:

(a) Description of the coupons and the experimental device;
(b) Coupon preparation procedure;
(c) Specific features of pool operation;
(d) Water quality maintenance parameters and technology;
(e) Results of four interim inspections.

11.2. COUPON PREPARATION

The coupons of the three racks were 3 mm thick discs with diameters of 100 or 70 mm and a 30 mm central hole. The coupons of rack 1 were assembled, either individually or as couples, and were separated with ceramic insulating discs. The coupons of racks 2 and 3 were similar in diameter. Unlike the coupons of rack 1, those of rack 2 appeared polished. The coupons in all the racks included small SS 316 discs. Prior to disassembly and coupon preparation, the racks were stored away from corrosive chemicals. Coupon preparation consisted of degreasing with ethyl alcohol followed by rinsing with deionized water. The coupons were then dried, weighed in a VLR-200 analytical balance (accuracy ±0.0005 g), assembled in the rack and placed in the spent fuel pool of the MIR reactor.

11.3. MAIN FEATURES OF SPENT FUEL POOL OPERATION
IN THE MIR REACTOR

The MIR reactor (commissioned in 1966) is a channel pool type apparatus with the core (immersed in the pool water) assembled from beryllium blocks pierced through by zirconium channels containing working fuel assemblies (FAs). The reactor power can reach 100 MW. The working FAs are cooled by water in a primary circuit with the following parameters:

Inlet temperature	40–50°C
Outlet temperature	Up to 100°C
Inlet pressure	1.4 MPa
Coolant rate	Up to 10.0 m/s

The reactor is designed for testing experimental assemblies and has 11 closed circuit loops to conduct these tests.

A working FA includes four cylindrical elements, one inserted inside another (six cylinders were used at first), with the outer cylinder 70 mm in diameter. Each fuel cylinder is 1484 mm in length and 2.0 mm thick, and the water gap between the cylinders is 2.5 mm.

Either UAl_x (in aluminium) or UO_2 (in aluminium) of 90% enrichment in ^{235}U is used as fuel. The core is 1 m high. The total amount of ^{235}U in the assembly is 350 g. The maximum power of such FAs is 4 MW. The average number of FAs in the core is 48. The cladding material is SZAV-6 aluminium alloy, 0.72 mm thick, with a maximum working temperature of 120°C. The average burnup of an unloaded working FA is about 40%.

Since the reactor operates at a power that is significantly less than the rated power (about 40–60%, and because the same power level enables loop tests to be conducted), the actual average operation time of the FAs in the core is about six months. The spent FAs are then extracted from the core and allowed to cool in the reactor's cooling pool. All refuelling operations are performed under water.

The total capacity of the MIR reactor cooling pool is such as to permit the storage of spent FAs unloaded from the reactor during three years of normal operation at the rated power level, plus an additional 20% reserve.

The spent fuel pool of the MIR reactor is a pit 11 m in diameter and filled with distilled water (about 2000 t). The pool walls are lined with stainless steel 1X18H10T. All the equipment and appliances for spent product storage are made of the same steel. Leaktight boxes can be used to store FAs with breached cladding. The refuelling tools are made of both stainless steel and SZAV-6 aluminium alloy.

Visual control of the pool elements is performed regularly during scheduled preventive maintenance. During 30 years of operation, there have been no problems related to pool equipment or FA cladding failure during FA storage in the cooling pool.

It is well known that corrosion processes are enhanced if there are high levels of impurities in the water. Therefore, to keep the level of impurities low, an ion exchange purification system has been employed since startup in the MIR reactor cooling pool. This system includes a heat exchanger, a pump, two filters with a total capacity of 800 L, a flowmeter, shut-off valves and other fittings. The filters are filled with Russian made nuclear grade ion exchange resins KU-2-8 (cationic) and AV-17-8 (anionic) in the ratio of 2:1. This system provides reduction of the specific β activity by more than a factor of 10. When this index drops to a factor of 2, the resin is replaced; otherwise, as a rule, it is replaced once a year.

The main feature of the spent fuel pool operation is that approximately once a month during refuelling it is linked via the lock space with the reactor pool, in which the water quality is identical but specific β activity is higher (by 1–2 orders of magnitude). While the pools are connected, the spent working FAs and the experimental FAs are transported using transport devices, and partial mixing of the waters from the two pools takes place during these operations (Fig. 11.1). The make-up of the pool system envisages the supply of fresh distillate to the spent fuel pool.

During operation of the spent fuel pool, coolant quality is periodically controlled (once a week) using modern analytical methods, including ion chromatography, potentiometry, photometry, γ spectrometry, etc. Table 11.1 presents the average values of spent fuel pool water parameters determined in the water before it passes through the ion exchange filter system. These are average values for the whole period of this investigation. Table 11.2 presents the typical γ spectrum of the coolant before it passes through the ion exchange filters. After purification, the coolant quality indices drop by about an order of magnitude.

11.4. RESULTS

Rack 1 was inspected four times, and racks 2 and 3 were inspected twice during the period they remained immersed in the spent fuel pool of the MIR reactor. During these inspections, the racks were removed from the pool and the coupons were disassembled, dried, weighed, photographed (macro- and microphotographs), reassembled in the rack in the same order and returned to the same position in the pool.
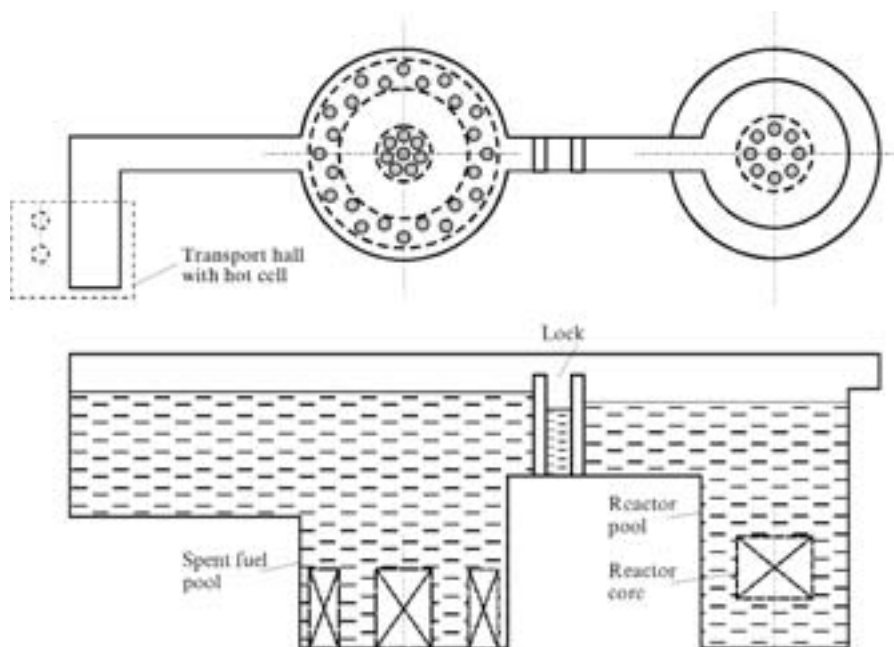
FIG. 11.1. Schematic diagram of the two MIR pools.

TABLE 11.1. PARAMETERS OF THE SPENT FUEL POOL COOLANT BEFORE IT PASSES THROUGH THE ION EXCHANGE PURIFICATION SYSTEM

pH at 25°C	5.7–6.0
Electrical conductivity	1.2–1.5 μS/cm
Total hardness	1–2 μg-eq/kg
Mass concentration of ion impurities	
Chlorides[a]	1–5 μg/kg
Nitrates[a]	30–60 μg/kg
Nitrites[a]	5–20 μg/kg
Iron	10–15 μg/kg
Aluminium	5–15 μg/kg
Copper	5–10 μg/kg
Sulphates[a]	5–20 μg/kg
Specific β activity	Up to 4×10^5 Bq/kg
Specific α activity	Up to 37 Bq/kg

[a] Data were obtained by ion chromatography.

TABLE 11.2. TYPICAL γ SPECTRUM OF THE MIR REACTOR SPENT FUEL POOL COOLANT BEFORE IT PASSES THROUGH THE ION EXCHANGE PURIFICATION SYSTEM

	Volumetric activity (Bg/kg)	Error (%)	Fraction of nuclide activity (%)
Ba-140	5.96×10^4	12.7	34.2
Xe-133	2.98×10^4	21.8	17.1
La-140	2.45×10^4	13.2	14.0
I-131	1.62×10^4	13.3	9.3
Cs-137	9.10×10^3	12.7	5.2
Np-239	9.00×10^3	16.5	5.2
Ce-141	5.18×10^3	13.2	3.0
Zr-95	4.37×10^3	19.0	2.5
Nb-95	2.80×10^3	17.7	1.6
Co-60	2.35×10^3	19.5	1.4
Ru-103	1.50×10^3	23.4	0.9
Mo-99	9.69×10^3	22.8	5.6
Total	1.74×10^5		

11.4.1. Investigation of coupon surfaces

The surfaces of the coupons of all three racks differ in appearance depending on whether the surface was exposed to the pool coolant, was in contact with another coupon or was in contact with the ceramic disc. A coupon surface exposed to the pool water is shown in Fig. 11.2. The top surface of this coupon showed red and brown spots (Figs 11.2(b) and 11.3(a)). Closer examination at $100 \times$ magnification revealed that on the polished coupons, pits formed at grain boundaries (Fig. 11.3(b)). This phenomenon was not observed on unpolished coupons (Fig. 11.3(c)).

The surface of a coupon that was in contact with another coupon is shown in Fig. 11.4. Regions of the surface with different degrees of damage and others covered with white film can be observed. Pits can be seen in the regions with different degrees of damage. The depth and area of the pits increase with time (Fig. 11.5). It is estimated that on all coupons, the pit depth after 1.5–2 years was 0.02 mm, and for the coupons of rack 1 after 3.5 years, it was 0.05 mm. On aluminium coupons in contact with the stainless steel coupons, a narrow stained region along the outer edge was observed, as shown in Fig. 11.4(b). The corrosion behaviour of this region differed from that of the rest of the surface.

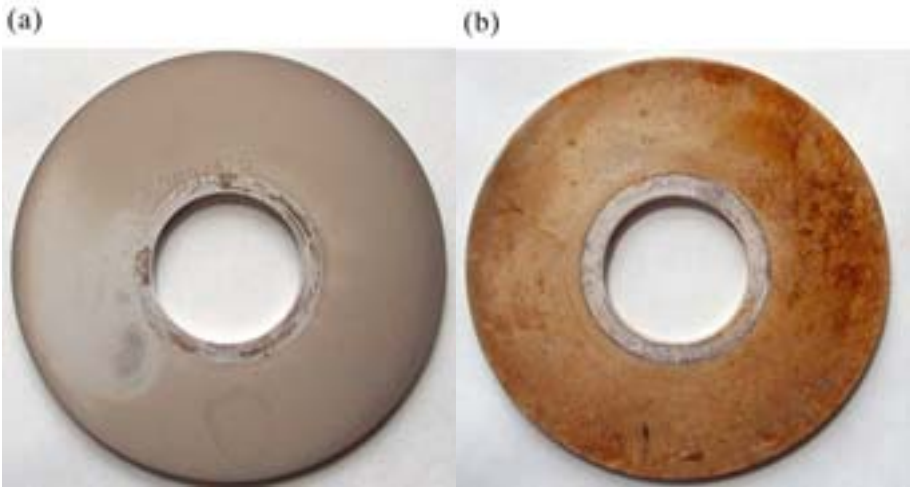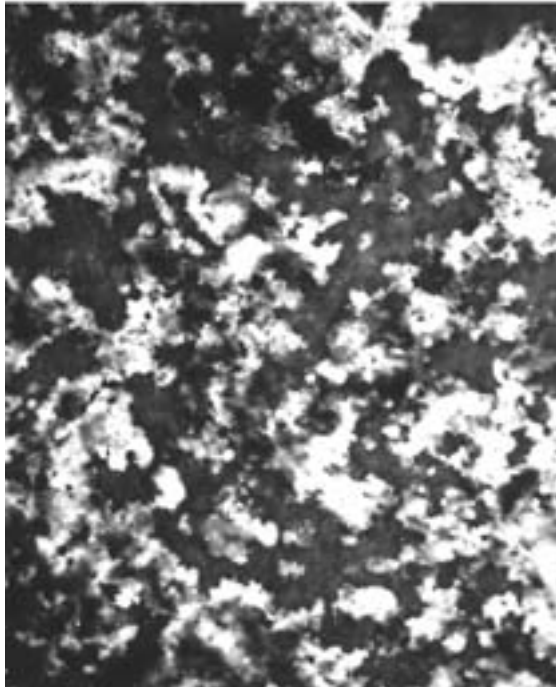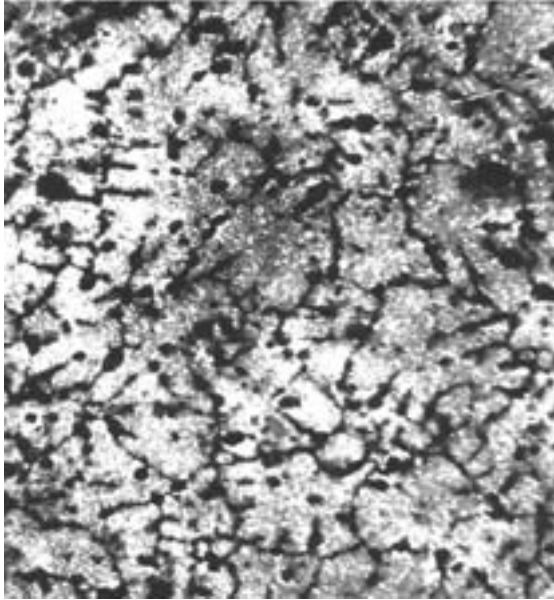*FIG. 11.2. Coupon surfaces (a) without film and (b) with red and brown film.*

(11.3(b))

(11.3(c))
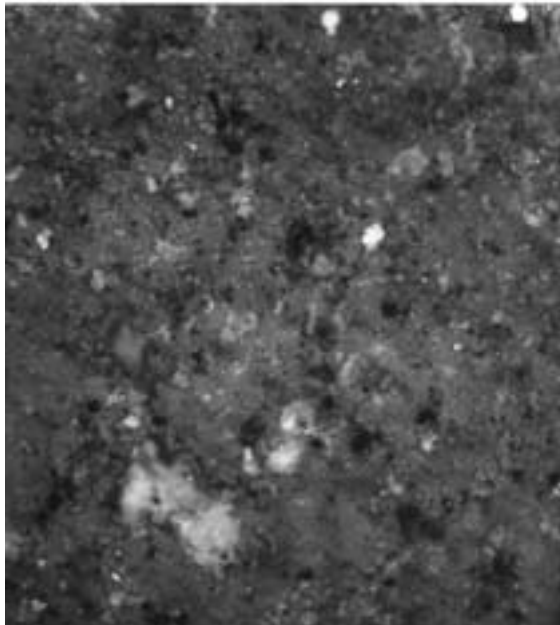
FIG. 11.3. Washed surfaces of coupons in racks 1, 2 and 3. (a) Region with red and brown particles (racks 2 and 3); (b) typical failure in racks 2 and 3; (c) unpolished coupon from rack 1. All photographs at 100 × magnification.

FIG. 11.4. Surface of coupons from racks 2 and 3 in contact with (a) an alloy of the same grade, and (b) SS 316.

FIG. 11.5. Contact surfaces on coupons with different degrees of damage: (a) one year of exposure, and(b) two years of exposure (100 × magnification).

FIG. 11.6. Coupon surface in contact with steel (100 × magnification).

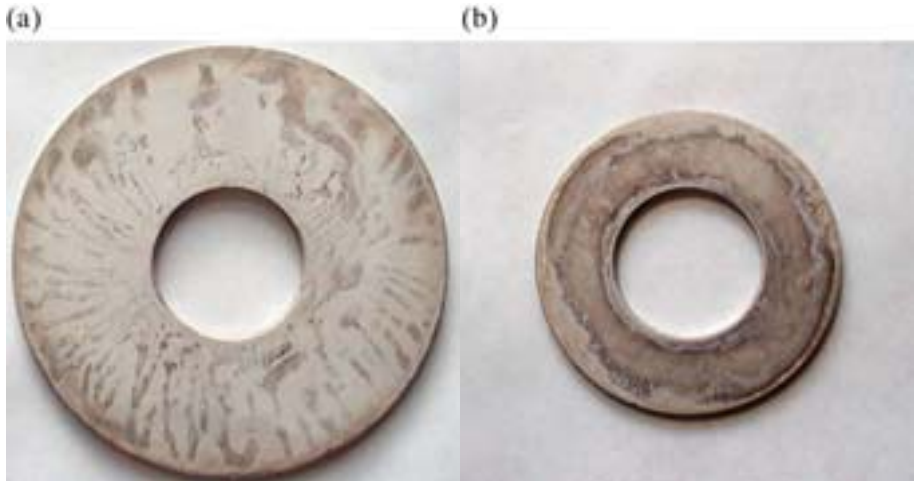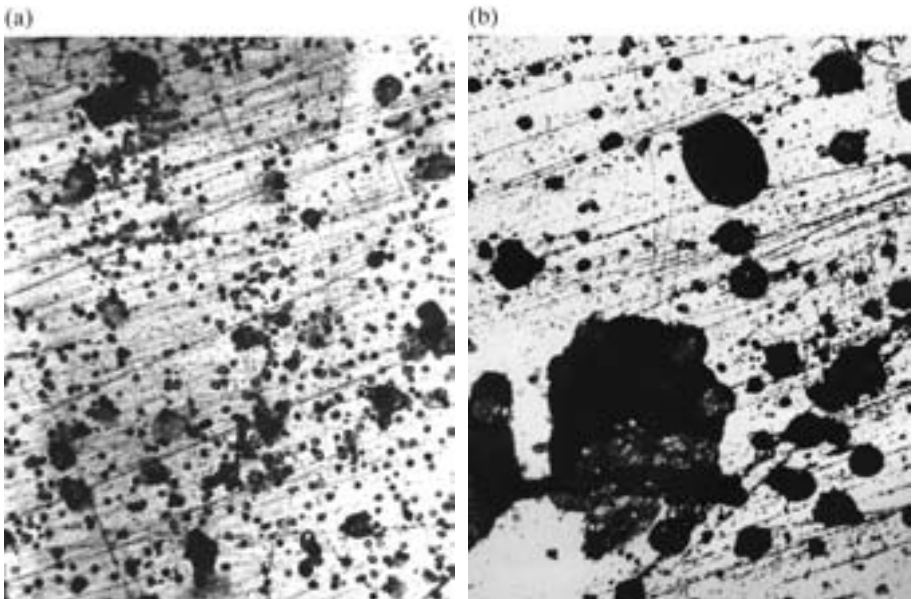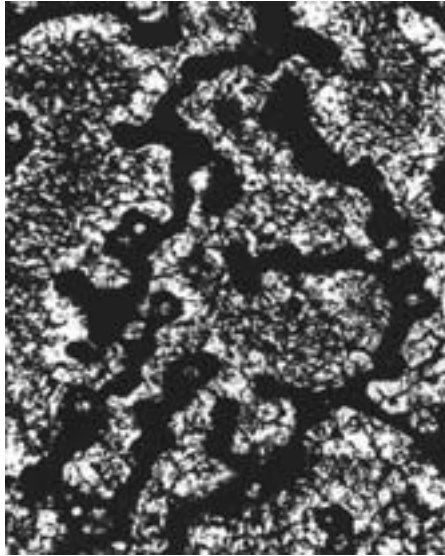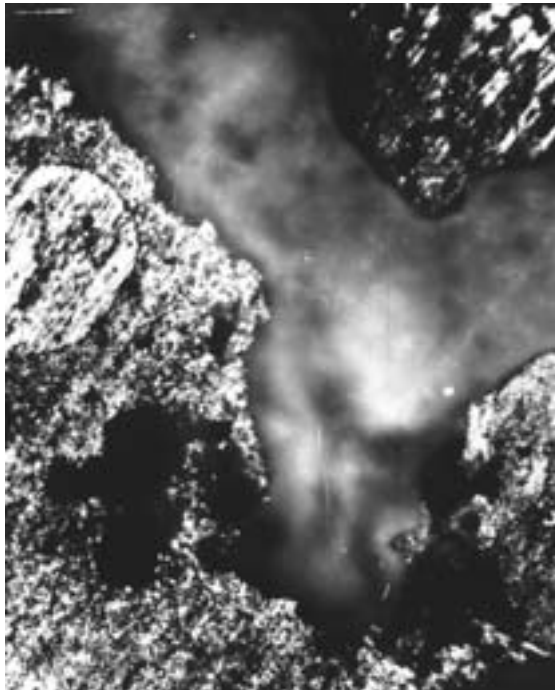*FIG. 11.7. White film region on coupon of rack 1 (100 × magnification).*

At a magnification of 100 ×, etching along grain boundaries was observed (Fig. 11.6), indicating the onset of intercrystalline corrosion. A white film was observed on the surface of all aluminium alloy coupons (Fig. 11.7). A significant amount of this oxide formed on contact surfaces of crevice and galvanic couples.

To obtain a more detailed understanding of the characteristics and mechanisms of aluminium coupon corrosion, it is necessary to determine pit depth, pit width, and the composition and structure of the different corrosion layers using destructive techniques (metallography, electron and Auger microscopy, etc.).

11.5. CONCLUSIONS

On the basis of the results obtained from exposing different aluminium alloy coupons to the cooling pool of the Russian research reactor MIR, the following conclusions can be drawn:

(a) The water quality maintenance programme, the use of very pure distillate and the use of ion exchange filters provide conditions that are adequate for the storage of spent fuel assemblies with no risk of cladding failure due to corrosion, within the normal cooling period.

(b) Under the present conditions, the alloys 6061, 6063, 1100 and SZAV-1, either on their own or in contact with other aluminium alloys or SS 316, showed satisfactory corrosion resistance over 3.5 years, the duration of this investigation.

(c) To study the characteristics and mechanisms of aluminium coupon corrosion, it is essential to conduct investigations using destructive techniques (metallography, electron and Auger microscopy, etc.).

Chapter 12

CORROSION OF ALUMINIUM ALLOY COUPONS IN THE IR-8 REACTOR SPENT FUEL STORAGE BASIN AT KURCHATOV INSTITUTE, MOSCOW, RUSSIAN FEDERATION

12.1. INTRODUCTION

The corrosion of aluminium alloy coupons in the light water fuel storage basin of the IR-8 reactor has been studied at the Russian Research Centre Kurchatov Institute [12.1]. This investigation was part of the IAEA CRP on Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water. The main objective of this project was to determine the environmental conditions that accelerate the corrosion of aluminium alloys in spent fuel storage conditions, and to control the corrosion.

The first rack (rack 1) with aluminium alloy coupons was suspended in the spent fuel storage basin on 1996-10-18. A description of the first rack of coupons, the main parameters of the storage basin water and the interim inspection results after exposure for 171 and 361 days have been presented in the progress reports of the CRP. Some of the results of this investigation were also reported in the November 1997 questionnaire circulated as part of the CRP. The interim inspections included visual examination, photography and weighing of the test coupons. Comparative evaluation of the data showed that the corrosion rates of both the galvanic and the crevice couple coupons were considerably higher during the first period (171 days) than during the second period (190 days). Visual observations of the test coupons after exposure for 171 and 361 days revealed that the surface oxide was uniformly distributed and that there were no pits. The third interim inspection of rack 1 coupons was carried out in April 1998 after an exposure of 529 days. On 1998-04-20, two new racks (racks 2 and 3) with aluminium alloy coupons were suspended in the spent fuel storage basin.

Further interim inspections of the three racks took place as follows. After 184 days of exposure, rack 2 was withdrawn from the basin and the corrosion of the coupons was evaluated by visual inspection and metallography. During this inspection, racks 1 and 3 continued to remain in the storage basin. In April 1999, the fourth inspection of rack 1 (after 896 days) and the first inspection of rack 2 (after 367 days) were carried out. These two racks were then returned to the basin water. In April 2000, the fifth inspection of rack 1 (after 1254 days) and the first inspection of rack 3 (after 725 days) were carried out. After the

inspections, these racks were suspended once again inside the storage basin. Thus at the time of writing, two racks (1 and 3) were still in the spent fuel basin. This chapter presents the results of visual examinations of the test coupons and other measurements carried out to investigate the effect of exposure to basin water, of radiation and of temperature on the corrosion behaviour of aluminium alloy coupons.

12.2. DESCRIPTION OF THE ALUMINIUM ALLOY COUPONS OF THE THREE RACKS

As mentioned above, the coupons of the three racks were exposed under identical conditions to the coolant of the IR-8 reactor spent fuel storage basin and were later examined.

12.2.1. Rack 1

The description of rack 1 and the corrosion coupons can be found in Chapter 4. All components of the rack assembly were carefully degreased with alcohol, rinsed in deionized water and dried at room temperature, prior to assembling the rack inside a vessel containing silica gel. All the coupons were marked for identification.

12.2.2. Racks 2 and 3

The coupons of the two new racks were made of the same materials as those of rack 1. The coupons of these racks were polished in the as-received condition. The alloy 6063 coupons were passivated at 95°C for 24 h in water. The passivated surface was scratched on the side without the identification mark. The polished coupons were washed in petrol and in alcohol and were dried in hot air. The coupons were handled with gloves.

Racks 2 and 3 were suspended in the IR-8 reactor spent fuel storage basin water without disassembly (in the as-received condition). The coupons were handled with clean gloves, as recommended.

12.3. REACTOR OPERATING CONDITIONS

The IR-8 reactor was built at Kurchatov Institute to replace the previous IRT reactor, constructed in 1957. The necessity to construct a new reactor arose from the fact that in late 1978 and early 1979, a leak was detected in the

aluminium (alloy AD-1) liner of the reactor pool, after 21 years of operation. In 1981, the IR-8 research reactor was put into operation. The core and beryllium reflectors are situated in a pool filled with water. The liner of the new pool, made of stainless steel, was placed inside the old aluminium tank of the former IRT reactor. The space between the old aluminium tank and the new steel pool was filled with ordinary concrete. The depth of the new tank is 11 m. The thickness of the wall of the lower section of the tank is 10 mm and the thickness of the rest is 6 mm.

The core of the reactor consists of 16 fuel assemblies. The reflector consists of two parts: an inner one composed of replacement beryllium blocks and an outer one composed of prismatic beryllium blocks with holes for vertical and horizontal channels. The reflector is fixed to the aluminium vessel from the outside.

The cooling system of the IR-8 reactor consists of a primary and a secondary circuit and a cooling circuit for biological shielding. The maximum water temperature of the reactor pool is 40–50°C. The volume of the reactor pool is about 100 m^3. The reactor basin contains the following parts of the primary circuit:

(a) A delay tank of ~5 m^3 volume.
(b) The ejector.
(c) A distribution duct with a vertical partition containing holes.
(d) A section with pressure and suction pipelines. All components are made of stainless steel.

A basin to store spent fuel assemblies is located near the reactor pool and is connected to the reactor pool via a sluice. The depth of this basin is 5.5 m. The basin liner is made of stainless steel. There are 120 cells in the basin to store fuel assemblies and spare blocks of the reactor's reflector. Each cell is made of the aluminium alloy AD-1, which has a minimum aluminium content of 99.3%. The maximum temperature of the storage basin water is 40°C. The IR-8 research reactor has operated for over 20 years. Its effective capacity is about 60%.

Presently there are approximately 42 spent fuel assemblies in the storage basin cells. They have been stored for 1–7 years. Visual observation of these spent fuel assemblies revealed that the fuel element surfaces had a uniform oxide film.

The test coupon racks were suspended in the IR-8 reactor spent fuel storage basin water. The reactor pool water was purified with a purification system consisting of mechanical and ion exchange filters. The volume of the storage basin water was approximately 30 m^3. The water was continuously circulated at a flow rate of about 10 L/min in the vicinity of the test racks. The

storage basin was connected to the reactor pool, where the water was continuously purified using a system consisting of mechanical and ion exchange filters (with mixed bed type resins).

Stainless steel wires were used to suspend the test racks. The location of the immersed racks was at 510 cm from the water surface, 40 cm from the bottom, and 20 cm from the wall of the basin, from the wall of the spent fuel rack and from the other test racks.

The water chemistry was analysed periodically during the test. The basin water parameters are shown in Table 12.1.

12.4. RESULTS AND DISCUSSION

The test coupons of rack 1 were inspected after 171, 361, 529, 896 and 1254 days of exposure to the basin water. The results of inspections after 171 and 361 days were presented in previous progress reports within the framework of this CRP. The test coupons of rack 2 were inspected after 367 and 551 days of exposure, and those of rack 3 after 725 days of exposure.

After withdrawal of each rack assembly from the basin and prior to weighing and decontamination, the pH of the water on the external surface of each coupon and on the inside faces of crevice coupons was determined using pH

TABLE 12.1. MAIN BASIN WATER PARAMETERS

Temperature	20–40°C
Flow rate (in the vicinity of the racks)	~50 L/min
pH	5.8–7.6
Conductivity	1.2–11 μS/cm[a]
Cl^-	<0.05–0.3 ppm[b]
NO_2	<0.01–0.03 ppm
NO_3	<0.02–0.08 ppm
Fe	<0.01–0.07 ppm
Al	<0.01–0.095 ppm
Cu	<0.01–0.029 ppm
Exposure dose power (from spent fuel assemblies)	15–20 rem/h
Water activity in storage basin (during reactor operation)	~200 Bq/mL

[a] Electrical conductivity increased to 7–11 μS/cm during the period 13–26 March 1997, to 6–6.4 μS/cm during the period 1–15 July 1998, to ~7.1 μS/cm during the period 12–22 April 2000 and to 10–11 μS/cm during the period since 20 August 2000.

[b] Chloride content during the period 13–26 March 1997 was ~0.3 ppm.

paper. These measurements did not show any noticeable difference from the pH of water in the vicinity of the test rack. The rack assembly was then dismantled, and the coupons were decontaminated by rinsing with clean deionized water and were dried at room temperature. The two surfaces of all the coupons after disassembly were photographed. The main features of the coupon surfaces can be described as follows:

(a) Crevice couple: coupon 1100/204–coupon 1100/208. The outer side of coupon 1100/204 (alloy 1100 coupon No. 204) in contact with the basin water was dull grey in colour and had a dense corrosion film. The identification number (204) was still visible. The inner side of coupon 1100/204 in contact with coupon 1100/208 retained its polish on ~30% of the contact area. The other ~70% of the contact area was covered with a white oxide film. The inner contact surface of coupon 1100/208 was similar to the inner contact surface of coupon 1100/204. The outer side of coupon 1100/208 in contact with the water was dull grey-white in colour and had a dense corrosion film. No pits were observed on the outer and inner sides of coupons 1100/204 and 1100/208.

(b) Crevice couple: coupon 6061/229–coupon 6061/240. The outer side of coupon 6061/229 in contact with the basin water was covered with a uniform grey-white film. The outer edge was grey in colour and retained the polish in some regions. The identification number was still visible and there were no pits. The inner contact surfaces of coupons 6061/229 and 6061/240 were similar and had a uniform grey-white oxide film. The identification numbers were barely visible and there were no pits. The outer side of coupon 6061/240 in contact with the water had a uniform grey-white film and retained its polish in some regions. Some pits were observed along the rim of both coupons. The pit densities along the rims of coupons 6061/229 and 6061/240 were ~2.1 and 3.4 pits/cm^2, respectively.

(c) Crevice couple: coupon 6063/184–coupon 6063/166. The outer side of coupon 6063/184 facing downward and in contact with the basin water was covered with a uniform dull grey-white film. Along the edge on the outer side of this coupon a grey film was observed. The identification number was visible and there were no pits. The inner contact surfaces of coupons 6063/184 and 6063/166 were almost identical. The inner surfaces were covered with a uniform grey-white oxide film. The identification numbers were visible and there were no pits. The outer surface of coupon 6063/166 facing upward and in contact with the water retained its polish. The region close to the central part of the surface was covered with a thin light-grey film and revealed no pits.

(d) Galvanic couple: coupon 6061/101–coupon SS 316/145. The outer side of coupon 6061/101 facing downward and in contact with the basin water had a uniform grey film. The identification number was barely visible. The inner

contact side had a light-grey film. Pits were observed along the rim of coupon 6061/101, and the pit density was ~7.6 pits/cm^2. A typical rim pit on coupon 6061/101 is shown in Fig. 12.1.

The depth of this pit is ~0.45 mm and the width ~1 mm. In order to carry out microscopic examination of coupon 6061/101, the oxide film over the pit and in the pit was first dissolved using a 10% phosphoric acid solution and then using a 50% phosphoric acid solution, until the initiation of bubble formation.

(e) Galvanic couple: coupon 6063/133–SS 316/136. The outer side of coupon 6063/133 facing downward and in contact with the basin water was covered with a dull dark-grey film. Along the outer rim of this coupon, polished regions free of film were seen. The diameter of the polished spots varied from 6 to 10 mm. The identification number was visible and there were no pits. The contact surface of coupon 6063/133 was covered with a white-grey film. Some parts of this surface retained their polish and there were no pits. There were pits along the rim of coupon 6063/133, and their density was ~1.5 pits/cm^2.

Oxide film removal with phosphoric acid was poor, except on the surfaces of coupons 6063/166 and 1100/204. The weights of these coupons after treatment with phosphoric acid were less than their initial weights.
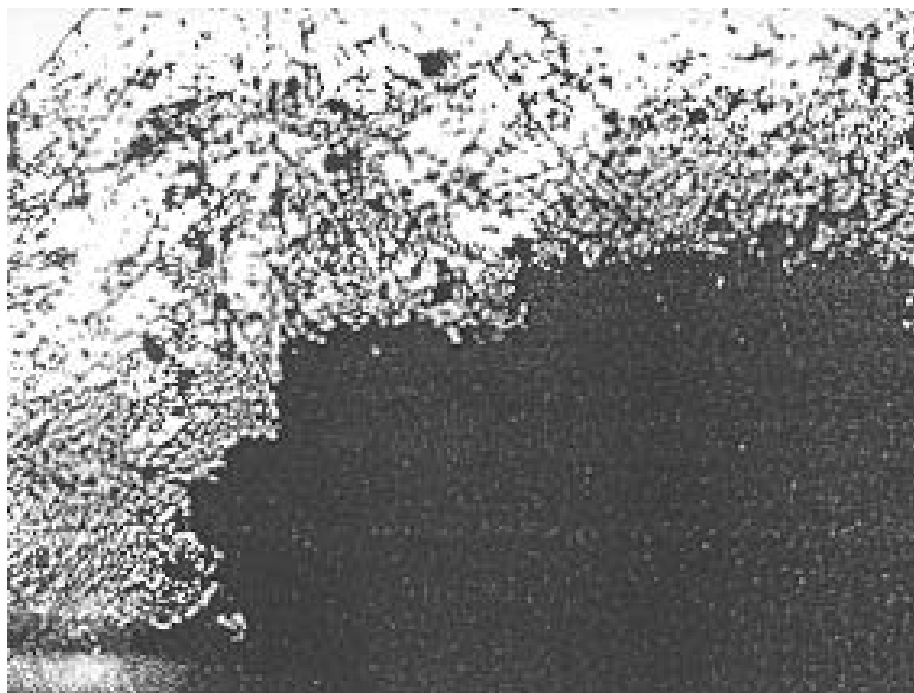

FIG. 12.1. Cross-section of a pit on the 6061/101 coupon (magnification 100 ×).

The following observations can be made concerning oxide film dissolution:

(1)   The oxide films on coupons 6063/166 and 1100/204 in contact with the basin water were more uniform, light and thin. These films dissolved easily until a polished surface was revealed. Nevertheless, the oxide film on the surface of coupon 6063/166 facing upward did not dissolve completely.

(2)   The outer surfaces of coupons in the assembly had a darker oxide film that dissolved poorly. However, the inner edge surfaces on the coupons were easily attacked by phosphoric acid.

(3)   The inner contact surfaces of crevice and galvanic coupons were quite similar. After treatment with phosphoric acid, the surfaces revealed a thin, light-grey film.

12.5. CONCLUSIONS

The corrosion monitoring programme of the IAEA CRP relating to typical aluminium alloys used for fuel cladding was carried out in the IR-8 research reactor storage basin of Kurchatov Institute.

Three aluminium alloy coupon racks were used in this investigation. Rack 1 was first suspended in the storage basin in October 1996. Further testing with two new racks (racks 2 and 3) was started in April 1998.

The main objectives of the programme were to provide comparative information about the corrosion behaviour of different types of aluminium alloy coupon in the IR-8 storage basin water. The following results were obtained:

(a)   The crevice and galvanic couples of rack 1 had insignificant variations in corrosion behaviour and in the condition of the coupon surfaces. The coupon surfaces in contact with water were covered with a uniform grey-white film. Moreover, the external appearances of all the coupon surfaces after exposure for 896 and 1254 days were almost identical. Visual examination of all the coupons did not reveal any pitting. The aluminium alloy coupons inside the glass ampoules (Nos 15 and 20) revealed no obvious change. The water inside the glass ampoules was transparent. The coupons of rack 1 (after exposure for 1254 days) and rack 3 (after 725 days) were disassembled, visually inspected, photographed, weighed, reassembled and immersed once again into the basin water for further exposure.

(b)   Visual observations and metallographic examinations of rack 2 coupons revealed pits on the rim of the crevice couple coupons (6061/229 to

6061/240) and galvanic couple coupons (6061/101 to SS 316/145 and 6063/133 to SS 316/136). A number of pits were observed on the rim of the crevice couple coupons (6061/240 to 6061/229). Alloy 1100 demonstrated satisfactory corrosion behaviour and revealed no pits.

On the basis of these results, the following activities can be recommended for the next stage of the IAEA programme on the corrosion of research reactor aluminium clad spent fuel in water:

(1) Kurchatov Institute is continuing to expose the coupons of racks 1 and 3 to the storage basin water in order to: (a) obtain more data about the low corrosion rates observed so far; (b) investigate further the pitting corrosion on 6061 and 6063 test coupons; and (c) clarify the reasons for the differences in corrosion behaviour between the coupons of racks 1 and 3.
(2) The corrosion research programme could usefully be extended to investigate the influence of various surface treatments, for instance anodizing and preliminary autoclaving, on the corrosion behaviour of aluminium alloys.
(3) It is well known that the corrosion resistance of aluminium alloys can be improved by adding inhibitors to the aqueous environment. Consequently it would be worth evaluating the corrosion behaviour of aluminium alloys in the presence of inhibitors such as phosphates and chromates.

ACKNOWLEDGEMENTS

REFERENCE TO CHAPTER 12

[12.1] GONCHAROV, V., et al., "Creation of the IR-8 reactor at the Kurchatov Institute of Atomic Energy (reconstruction of the IRT-M reactor)", Proc. Conf. of Specialists on Experience Exchange on Reconstruction of Research Reactors in COMECON Member Countries, Moscow, 1982, Moscow State Committee on Atomic Energy, Moscow (1984) 5–26.

Chapter 13

CORROSION OF ALUMINIUM ALLOY COUPONS IN THE SPENT FUEL BASIN AT THE OFFICE OF ATOMIC ENERGY FOR PEACE, BANGKOK, THAILAND

13.1. INTRODUCTION

The Thai Research Reactor 1 started operation in 1962 at a thermal power of 1 MW. It is a swimming pool type light water reactor. In the beginning, HEU MTR plate fuel with aluminium cladding was used. In 1967, after 15 years of operation, the reactor core was modified to a TRIGA type using stainless steel rod type fuel. Since then, the MTR plate fuel assemblies have been stored under water. In 1977, a basin was constructed in a separate building adjacent to the reactor building to store all the aluminium clad MTR type spent fuel elements. The basin is 3 m × 4 m and is 5 m deep. The basin pool was equipped with a mixed bed ion exchange cleanup system which was operated once a month at a flow rate of 12.5 L/min for about 6 h to maintain the conductivity of the water below 2 μS/cm. The water was slightly contaminated with ^{137}Cs before work related to this CRP was initiated. This contamination indicated some minor leak from the spent fuel assemblies. Thus the corrosion behaviour of aluminium in this environment is of interest. Later the pool was also used for interim storage of ^{60}Co sources.

The experiments carried out in Thailand related to the exposure of standard coupons to spent fuel basin water were based on instructions provided at the first RCM, held at KFKI in Budapest in August 1996, and the second RCM, held in São Paulo in March 1998. During the second RCM, a protocol was established to handle, prepare, expose and evaluate standard coupons.

13.2. EXPERIMENT

The following equipment was used:

(a) A portable conductivity/pH meter with a temperature probe;
(b) A titroprocessor with a dosing device capable of delivering 0.001 mL of titrant;
(c) A liquid chromatography system with dual pumps and with variable wavelength ultraviolet/visible and conductivity detectors;

(d)   A γ spectrometer with a germanium detector and a multichannel analyser card;

(e)   An optical microscope.

13.3. PROCEDURE

13.3.1.   Water basin chemistry

A submerged pump was used to collect spent fuel pool water samples from a depth of 3 m and from close to the coupon rack. The following parameters were measured without pretreatment:

(a)   Conductivity.

(b)   pH and temperature.

(c)   Chloride ions, detected by microtitration using silver nitrate solution as the titrant to react with the chlorides in the solution. A platinum electrode was used to monitor the change in the number of millivolts of the system. The end points were automatically detected and the chloride ion concentration was calculated.

(d)   Nitrate, sulphate and phosphate ions, detected by ion exchange chromatography. A reaction suitable for anion separation using salicyclate buffer as eluant was used.

(e)   γ activity. (Since no significant β activity was ever detected, this parameter was not monitored during the CRP investigations.)

13.3.2.   Radiation field

Periodically the Radiation Measurement Division of the Office of Atomic Energy for Peace (OAEP) measured the radiation field as 'absorbed dose in air' at three different locations close to the coupons. In March 1999, most of the MTR type spent fuel was shipped back to its origin in the USA, and the radiation field measurements were no longer carried out. Since February 2000, the spent fuel pool is also being used as interim storage for a ^{60}Co source. The activity of the source is estimated to be 425 Ci (1.57×10^{13} Bq).

13.3.3.   Coupon preparation

The coupons of rack 1, received at the first RCM, were ground using coarse and fine sandpaper, rinsed in high purity water and acetone, air-dried and re-examined until no pits were observed, then reweighed and assembled in

the rack. The rack was first immersed in the spent fuel basin on 1996-11-06 at 10.30 a.m. The rack was positioned to be at a depth of 3 m and 50 cm from the side wall of the basin, about 1 m above MTR spent fuel assembly No. 12. It was withdrawn in March 1988 and moved to the north-western corner. The positions of the coupons in the rack were as decided at the first RCM.

Racks 2 and 3 were received at the second RCM. Just before loading these racks into the spent fuel pool, the coupons were removed and photographed. The coupons were not given any surface treatment. Rack 2 was loaded on 1998-03-18 about 50 cm from the side and above MTR type spent fuel assembly No. 12. Rack 3 was immersed in a different location about 3 m below the pool surface and also 50 cm from the side wall. The coupon arrangement was as received.

13.3.4. Coupon monitoring

The coupon racks were visually observed every 30–40 days. Photographs were also taken periodically. Some coupon assemblies were periodically removed from the basin for pit measurements, i.e. of pitting density and pit depth. Pit measurements were performed using an optical metallurgical microscope at a magnification of 200–500 ×. The coupons from rack 1 were washed in 5% phosphoric acid to remove the oxide layer prior to carrying out the measurements. The coupons from rack 2 were taken for pit examination without removing the oxide layer.

13.4. RESULTS

13.4.1. Basin water chemistry

The γ activity and chemical parameters of the basin water are shown in Tables 13.1 and 13.2. The chemical composition of the water shows an increase in impurity content compared with that of a year earlier. The slight decrease in γ activity of ^{137}Cs since the removal of the MTR type spent fuel rods in March 1999 indicates that ^{137}Cs leaked from one or more of the fuel assemblies. Even after the source of the leak was removed, it was not possible to remove the ^{137}Cs using mixed bed ion exchangers. Additionally, the chemical composition of the water clearly indicates that the quality of the water had deteriorated as the ion exchanger was used at less frequent intervals.

13.4.2. Coupon monitoring

Rack 1 was withdrawn from the basin once every 30–40 days (during the first six months); the rack was disassembled and the coupons were photographed.

The crevice couples were stuck together at the first examination carried out after 40 days. Other coupons showed normal corrosion. The corrosion process was found to be much slower after the first visual examination. However, in February 1997, one crevice couple was removed, and the pH of the solution inside the crevice was determined and found to be 5.5. After about four months, a few nodules were visually detected on some coupons. After six months of exposure, three coupons were removed for destructive examination. They were rinsed in water and acetone, dried, reweighed and then cleaned with 50% phosphoric acid. They were again rinsed with water and acetone, dried and reweighed. Weight loss was insignificant even after removal of the oxide. Coupons were then taken for pit measurement. The whole rack was removed on 2000-10-12 and the coupons were photographed, as shown in Fig. 13.1.

Racks 2 and 3 were examined visually every month for any signs of corrosion, and photographs were taken at regular intervals. Figures 13.2–13.4 show photographs of rack 2. Some edge corrosion was observed on some of the coupons, but after this, no significant corrosion was observed during the periodic examination of the assembled rack. On 2000-10-12, rack 2 was removed and disassembled. The pH on the contact surface of crevice and galvanic couples was measured and found to be 5.5, equal to that of the pool water. Table 13.3 catalogues the observations made visually on the coupons of rack 2 after 33 months of exposure. The coupons were taken for pit measurement without removing any oxide film.

13.4.3. Pit measurements

The pitting data on the five coupons from rack 1 are presented in Table 13.4. The average pit depth was 10–40 μm. Higher pit densities were observed close to the edge of the coupons. In the case of the crevice couples, more pits were found on the crevice side (4–6 pits/cm^2) than on the non-crevice side (1 pit/cm^2). Pits were deeper on the non-crevice side. The 1100 coupons were more resistant to corrosion than the SZAV-1 coupons, and the 6061 alloy exhibited the highest corrosion among the three types of alloy in terms of both pit density and pit depth.

Table 13.5 presents pitting information obtained from metallographic investigations carried out on the coupons from rack 2. The data reveal that galvanic effects between SS 316 and 6063 or 6061 alloy caused more pits to form than the crevice effect. The pits on 6061 alloy were larger in size and deeper, the maximum size being about 3 mm with 0.4 mm depth. Figure 13.5 shows the connected pits on the contact side of alloy 6063 with SS 316. Several pits were close to each other and some even merged. The pits were large enough to be seen using a digital camera. Most of these pits were found close

(a)

(b)

FIG. 13.1. Coupons of rack 1. (a) Non-contact side; (b) contact side.
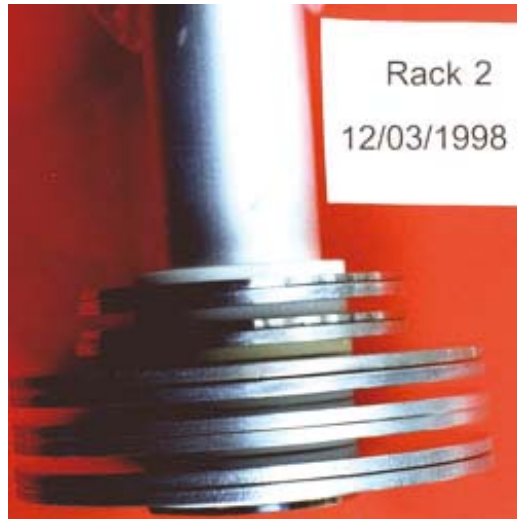
FIG. 13.2. Rack 2 before immersion.

FIG. 13.3. Rack 2 after six months of immersion.

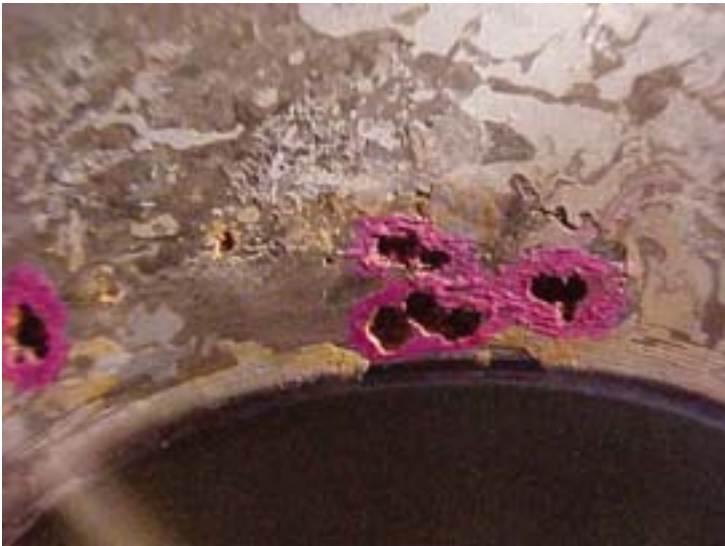FIG. 13.4. Rack 2. Scratch mark on the 6063 alloy after 24 months of immersion.

FIG. 13.5. Pits on the contact side of the crevice couple from rack 2.

TABLE 13.1. CHEMICAL PARAMETERS AND RADIOACTIVITY OF
THE SPENT FUEL BASIN WATER

	Conductivity (μS/cm)	Temperature (°C)	pH	Cs-137 activity (Bq/L)	Remarks
1993-07-05	<2	NA[a]	NA[a]	27	Surface
1995-09-27	<2	NA[a]	NA[a]	116	Surface
1996-03-13	1.46	28.9	6.53	66	Surface
1996-07-08	1.94	28.8	6.07	198	Surface
1996-12-19	3.74	26.4	6.82	80	3 m depth
1997-04-03	3.00	28.8	6.11	137	3 m depth
1997-08-07	2.22	29.1	6.38	115	3 m depth
1997-12-04	1.83	28.6	7.80	132	3 m depth
1998-04-01	2.75	29.4	5.04	187	3 m depth
1998-08-06	2.99	29.3	7.08	206	3 m depth
1998-12-15	2.34	27.8	6.23	158	3 m depth
1999-04-09	9.44	28.7	7.12	143	3 m depth
1999-08-05	4.38	28.0	6.35	169	3 m depth
1999-12-07	5.17	27.6	7.00	127	3 m depth
2000-05-25	5.15	28.4	6.78	109	3 m depth
2000-09-13	6.51	28.7	6.48	108	3 m depth

[a] NA: data not available.

TABLE 13.2. CONCENTRATION (ppm) OF CERTAIN IONS IN WATER
SAMPLES TAKEN FROM A DEPTH OF 3 m

	Cl^-	SO_4^{2-}	NO_3^-	PO_4^{3-}	Ag	Cu
1996-11-06	<1	<1	<1	<1	NA[a]	NA[a]
1997-04-03	0.21	<1	<1	<1	NA[a]	NA[a]
1997-07-07	0.14	<1	<1	<1	NA[a]	NA[a]
1998-02-05	<0.1	<1	<1	<1	<0.01	<0.01
1998-06-10	0.40	<1	<1	<1	<0.01	<0.01
1998-10-07	0.19	<1	<1	<1	<0.01	<0.01
1999-02-04	0.25	<1	<1	<1	<0.01	<0.01
1999-10-06	0.45	<1	<1	<1	<0.01	<0.01
2000-02-01	0.47	<1	<1	<1	<0.01	<0.01
2000-06-28	0.44	<1	<1	<1	<0.01	<0.01

[a] NA: data not available.

TABLE 13.3. CORROSION OBSERVATIONS ON COUPONS OF RACK 2
AFTER 33 MONTHS OF IMMERSION

Specimen/ configuration	Observations
6061/galvanic	General corrosion on non-contact side and some localized corrosion under the washer, depth not significant. Oxide stain and some pitting on contact surface. Pits easily located with the naked eye. Higher density of pits near inner edge of coupon. Some parts of coupon still shiny.
6061/crevice	General corrosion on non-contact side with dark grey to white oxide. Large spots of small and shallow pits. Significant edge corrosion. No significant pitting on contact side, and some shiny areas observed.
6061/crevice	General corrosion on non-contact side with dark grey to white oxide. Oxide layer thick enough to cover identification number. Significant edge corrosion No significant pitting on contact side, and some shiny areas observed.
6063/galvanic	General corrosion on non-contact side with dull grey colour. Few localized corrosion spots under the washer. Some pits on contact surface, easily located with the naked eye. Pits found close to inner edge of coupon. Most of the contact side shiny with stains of white oxide.
6063/crevice and scratched	General corrosion on non-contact side. Scratch mark still visible. No localized corrosion under the washer, and some shiny areas present. Surface light grey and with white oxide stains. Very few pits on contact side. Less shiny areas observed.
6063/crevice	General corrosion on non-contact side. Some large spots of small and shallow pits. Under the washer, some oxide patches and shiny areas. Surface light grey and with white oxide stains. Few pits on contact side, and some shiny areas observed.
1100/crevice	Normal corrosion on non-contact side, dark grey in colour. A few patches of white oxide under the washer. No significant local corrosion. Very few pits on contact side. Small shiny areas observed. Colour dull white, lighter than other alloys.
1100/crevice	Normal corrosion on non-contact side with white oxide. No significant local corrosion. Very few pits on contact side. Some shiny areas observed. Colour dull white.

TABLE 13.4. PITTING DATA FROM COUPONS OF
RACK 1

Coupon alloy	Exposure (months)	Max. pit depth (µm)	Pit density (pits/cm^2)
6063	4	9[a] and 16[b]	4[a] and 1[b]
6063	4	15[a] and 48[b]	6[a] and 1[b]
SZAV	6	56	3
6061	6	86	5
1100	6	28	2

[a] Contact side.
[b] Non-contact side.

TABLE 13.5. PITTING DATA FROM COUPONS OF RACK 2 AFTER
33 MONTHS OF IMMERSION

Coupon alloy	Diameter (mm)	Couple type	Pit size (mm)	Max. pit depth (µm)	Number of pits	Observations
6061	70	Galvanic	0.10–0.30	300	6	
			0.30–0.60	320	7	
			0.60–1.0	200	1	
			>1	480	1	Combination of 2–3 pits, size about 3 mm
6061	100	Crevice	0.10–0.30	100	7	
6061	100	Crevice	0.10–0.30	120	5	
6063	70	Galvanic	0.10–0.30	150	3	Combination of 3–4 pits close to each other
			0.30–0.60	440	4	
			0.6–1.0	260	1	
6063/165	100	Crevice/ scratched	0.10–0.30	120	5	
6063/191	100	Crevice	0.10–0.30	180	9	
			1.5	360	1	
1100/235	100	Crevice	0.10–0.30	100	1	
1100/227	100	Crevice	Nil	Nil	Nil	

to the inner rim of the coupons. Crevice corrosion under the washer seemed to have some effect, since some non-uniform white oxide stains were seen. Comparison of the corrosion resistance of the three aluminium alloys revealed that 1100 exhibited the highest corrosion resistance, and 6061 exhibited slightly higher corrosion resistance than 6063. Higher pit density was found in crevices with 6061, but the depth and size were less significant. The crevice couples of 1100 did not show significant pitting after 33 months of immersion in good quality water.

13.4.4. Glass ampoule coupons

Visual inspection of the coupons in the glass ampoule with high purity water revealed that these were in the same state as in August 1996.

13.5. CONCLUSIONS

The water quality was adequate for the safe storage of the spent fuel assemblies prior to their shipment to the USA. Subsequently the water quality control was less rigorous. Some debris was found on the specimen surfaces, but no corrosion was associated with it. Corrosion was observed only along the edges. The presence of ^{137}Cs activity indicated that, although the spent fuel had been removed, some ^{137}Cs still remained in the pool.

Since a limited number of coupon racks were distributed to the participants, the amount of data collected was also limited. Overall, the corrosion observations indicated that the spent fuel storage facilities at OAEP are adequate for mid-term storage.

REFERENCES TO CHAPTER 13

[13.1] SUPARIT, N., SUKHARN, S., BUSAMONGKOL, A., LAOHAROJANA-PHAND, S., "Water chemistry management of the spent-fuel pool in Thailand", Proc. 6th Asian Symp. on Research Reactors, Mito City, Japan, 1999, Japan Atomic Energy Research Soc. (1999).

[13.2] LAOHAROJANAPHAND, S., NILAPHRUK, A., BUSAMONGKOL, A., SUPARIT, N., "Corrosion of aluminium alloy in water", Proc. 1st Thailand Materials Science and Technology Conf., Bangkok, 2000, Science Soc. of Thailand (2000).

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