IAEA-TECDOC-1637

Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water

IAEA
International Atomic Energy Agency

CORROSION OF RESEARCH REACTOR ALUMINIUM CLAD SPENT FUEL IN WATER

The following States are Members of the International Atomic Energy Agency:

AFGHANISTAN
ALBANIA
ALGERIA
ANGOLA
ARGENTINA
ARMENIA
AUSTRALIA
AUSTRIA
AZERBAIJAN
BAHRAIN
BANGLADESH
BELARUS
BELGIUM
BELIZE
BENIN
BOLIVIA
BOSNIA AND HERZEGOVINA
BOTSWANA
BRAZIL
BULGARIA
BURKINA FASO
BURUNDI
CAMBODIA
CAMEROON
CANADA
CENTRAL AFRICAN REPUBLIC
CHAD
CHILE
CHINA
COLOMBIA
CONGO
COSTA RICA
CÔTE D'IVOIRE
CROATIA
CUBA
CYPRUS
CZECH REPUBLIC
DEMOCRATIC REPUBLIC OF THE CONGO
DENMARK
DOMINICAN REPUBLIC
ECUADOR
EGYPT
EL SALVADOR
ERITREA
ESTONIA
ETHIOPIA
FINLAND
FRANCE
GABON
GEORGIA
GERMANY
GHANA
GREECE
GUATEMALA
HAITI
HOLY SEE
HONDURAS
HUNGARY
ICELAND
INDIA
INDONESIA
IRAN, ISLAMIC REPUBLIC OF
IRAQ
IRELAND
ISRAEL
ITALY
JAMAICA
JAPAN
JORDAN
KAZAKHSTAN
KENYA
KOREA, REPUBLIC OF
KUWAIT
KYRGYZSTAN
LATVIA
LEBANON
LESOTHO
LIBERIA
LIBYAN ARAB JAMAHIRIYA
LIECHTENSTEIN
LITHUANIA
LUXEMBOURG
MADAGASCAR
MALAWI
MALAYSIA
MALI
MALTA
MARSHALL ISLANDS
MAURITANIA
MAURITIUS
MEXICO
MONACO
MONGOLIA
MONTENEGRO
MOROCCO
MOZAMBIQUE
MYANMAR
NAMIBIA
NEPAL
NETHERLANDS
NEW ZEALAND
NICARAGUA
NIGER
NIGERIA
NORWAY
OMAN
PAKISTAN
PALAU
PANAMA
PARAGUAY
PERU
PHILIPPINES
POLAND
PORTUGAL
QATAR
REPUBLIC OF MOLDOVA
ROMANIA
RUSSIAN FEDERATION
SAUDI ARABIA
SENEGAL
SERBIA
SEYCHELLES
SIERRA LEONE
SINGAPORE
SLOVAKIA
SLOVENIA
SOUTH AFRICA
SPAIN
SRI LANKA
SUDAN
SWEDEN
SWITZERLAND
SYRIAN ARAB REPUBLIC
TAJIKISTAN
THAILAND
THE FORMER YUGOSLAV REPUBLIC OF MACEDONIA
TUNISIA
TURKEY
UGANDA
UKRAINE
UNITED ARAB EMIRATES
UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND
UNITED REPUBLIC OF TANZANIA
UNITED STATES OF AMERICA
URUGUAY
UZBEKISTAN
VENEZUELA
VIETNAM
YEMEN
ZAMBIA
ZIMBABWE

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".

IAEA-TECDOC-1637

CORROSION OF RESEARCH REACTOR ALUMINIUM CLAD SPENT FUEL IN WATER

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 2009

Sales and Promotion, Publishing Section
International Atomic Energy Agency
Vienna International Centre
PO Box 100
1400 Vienna, Austria
fax: +43 1 2600 29302
tel.: +43 1 2600 22417
email: sales.publications@iaea.org
http://www.iaea.org/books

For further information on this publication, please contact:

Nuclear Fuel Cycle and Waste Technology Section
International Atomic Energy Agency
Vienna International Centre
PO Box 100
1400 Vienna, Austria
email: Official.Mail@iaea.org

CORROSION OF RESEARCH REACTOR ALUMINIUM CLAD SPENT FUEL IN WATER
IAEA, VIENNA, 2009
IAEA-TECDOC-1637
ISBN 978-92-0-113409-7
ISSN 1011-4289

Printed by the IAEA in Austria
December 2009

FOREWORD

A large variety of research reactor spent fuel with different fuel meats, different geometries and different enrichments in ^{235}U are presently stored underwater in basins located around the world. More than 90% of these fuels are clad in aluminium or aluminium based alloys that are notoriously susceptible to corrosion in water of less than optimum quality. Some fuel is stored in the reactor pools themselves, some in auxiliary pools (or basins) close to the reactor and some stored at away-from-reactor pools.

Since the early 1990s, when corrosion induced degradation of the fuel cladding was observed in many of the pools, corrosion of research reactor aluminium clad spent nuclear fuel stored in light water filled basins has become a major concern, and programmes were implemented at the sites to improve fuel storage conditions. The IAEA has since then established a number of programmatic activities to address corrosion of research reactor aluminium clad spent nuclear fuel in water. Of special relevance was the Coordinated Research Project (CRP) on Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water (Phase I) initiated in 1996, whose results were published in IAEA Technical Reports Series No. 418. At the end of this CRP it was considered necessary that a continuation of the CRP should concentrate on fuel storage basins that had demonstrated significant corrosion problems and would therefore provide additional insight into the fundamentals of localized corrosion of aluminium. As a consequence, the IAEA started a new CRP entitled Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water (Phase II), to carry out more comprehensive research in some specific areas of corrosion of aluminium clad spent nuclear fuel in water.

In addition to this CRP, one of the activities under IAEA's Technical Cooperation Regional Project for Latin America Management of Spent Fuel from Research Reactors (2001-2006) was corrosion monitoring and surveillance of research reactor aluminium clad spent fuel. These corrosion activities were quite similar to those carried out in the CRP.

Eight Member States participated in Phase-II of the CRP and five Member States in the Regional Project RLA/4/018. Two of the countries participating in the regional project were also participants in the CRP.

This report documents the work performed in the IAEA Coordinated Research Project (CRP) on Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water (Phase II) and in the IAEA's Technical Cooperation Regional Project for Latin America (RLA/4/018) entitled Management of Spent Fuel from Research Reactors. The key activity of both, the CRP and the Regional 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 and evaluation of sediments settling in the spent fuel pools. The report includes: a description of the standard corrosion racks, experimental protocols, test procedures and water quality monitoring; the specific contributions by each of the participating laboratories; a compilation of all experimental results obtained and the analysis and discussion of the results, along with conclusions.

The IAEA acknowledges the contributions of R. Haddad, Comisión Nacional de Energía Atómica, Argentina and L.V. Ramanathan, Instituto de Pesquisas Energeticas e Nucleares, Brazil in the preparation of this report. The IAEA technical officers responsible for this report were P. Adelfang and A.J. Soares of the Division of Nuclear Fuel Cycle and Waste Technology.

EDITORIAL NOTE

CONTENTS

CD ROM: COUNTRY REPORTS

Final Report of the work done in Argentina for an IAEA CRP and a Regional Project for Latin America on Corrosion of Research Rreactor Aluminium Clad Spent Fuel in Water
R. Haddad, R. Guasp

Corrosion of Aluminium Alloy Coupons in the Spent Fuel Storage Basin of IEA-R1 Research Reactor at IPEN, Brazil
L.V. Ramanathan

Corrosion of Aluminium Alloys in Triga Research Reactor IPR-R1 (Brazil)
C. F.C. Neves, W. R.C. Campos, J. E. Camos Filho, M. S. Moreira

Corrosion of research reactor aluminium clad spent fueil in water in Chile
C. Lamas et al.

Corrosion of aluminium alloy test coupons in the WWR-K reactor cooling pool and wet storage tank in Almaty, Kazakhstan
O. Mksimkin, M. Gusev

Corrosion of aluminium alloy test coupons in the Triga Mark III research reactor of Mexico
M. E. G. Méndez, C. R. A. Juárez F. A. Hernández

Corrosion of aluminium clad in the spent fuel basin of RP-10 research (Peru) reactor
C. O. L. Benitez, C. I. B. Fuentes, Á. D. R. Silva

Corrosion of research reactor aluminium clad spent fuel in water: report of the work done in Poland
S. Chwaszczewski et ali..

Final report of work done in Romania on corrosion of research reactor aluminium-clad spent fuel in water (phase II)
A. Zorliu et al.

Corrosion of aluminium-clad spent fuel in the RA research reactor storage pool (Serbia)
M. Pesic et al.

Thailand: Final report of work done in Thailand on corrosion or research reactor aluminium clad spent fuel in water
S. Laoharojanaphand, S. Ninlaphruk, B. Suanmamuang

1. INTRODUCTION

1.1. GENERAL BACKGROUND AND ORIGIN OF THE PROJECT

According to the IAEA database on Nuclear Research Reactors in the World, as of December 2008 there were 242 research reactors in operation, with 246 reactors shut down, plus 172 decommissioned, 7 under construction and 4 in the planning stages [1]. The age distribution of operating research reactors peaks around 45 years, with 70% 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. Russian designed research reactors utilize fuel assemblies of different geometrical types, which can be divided into two main groups — multi-tube assemblies and multi-rod assemblies.. The cladding alloys of Western fuel types are usually 6061 or 1100 grade aluminium ranging in thickness from 0.375 to 0.75 mm. For Russian fuel types usually the cladding is made of SZAV-1, a different type of aluminium alloy. For both types of reactors, Western and Russian, the fuel core can be low enriched (LEU) with contents of ^{235}U below 20%, or highly enriched (HEU), with contents of ^{235}U above 20%. Common enrichments for HEU are 36, 80 and 93%. For LEU it can be 4, 10 or 19.9%. However, it is possible to find research reactor with different levels of enrichment. As a consequence, a large variety of research reactor spent fuels with different fuel meats, different geometries and different enrichments in ^{235}U are presently stored underwater in basins located around the world. Some fuel is stored in the reactor pools themselves, some in auxiliary pools (or basins) close to the reactor, and some is stored at away-from-reactor pools. In some cases, corrosion induced degradation of the cladding has been observed, compromising the integrity of the fuel. More than 90% of these fuels are clad in aluminium or aluminium based alloys that are notoriously susceptible to generalized or localized corrosion in water of less than optimum quality. Generalized corrosion of aluminium and its alloys is reasonably well understood and actually it is not a problem for RR fuel. Contrarily to generalized corrosion, the much more insidious process of localized corrosion has led to serious safety issues at several RR spent fuel pools. As discussed in the following parts of this document, localized corrosion of aluminium-clad spent fuels is an extremely complex phenomenon, very difficult to predict, and has been a very serious issue, causing concerns in some RRSNF storage sites. In all cases the fuel clad degradation started with one of the three main forms of localized corrosion described in Section 2: pitting corrosion, crevice corrosion or galvanic corrosion.

The process of localized corrosion is highly dependent of the quality of the water in the fuel storage basins, which ranges from highly deionized water to untreated and uncirculated water. In the latter condition, the result is an extremely aggressive environment, in which the aluminium clad fuel is very susceptible to pitting corrosion. This kind of environment was not uncommon in the early 1990s, causing corrosion of aluminium clad fuel to be an issue at several storage basins. It was also observed on some pool structures and on materials test reactor (MTR) type research reactor fuels.

Considering the documented cases of corrosion in research reactors, in December 1994, a consultancy meeting was held at the IAEA in Vienna, Austria as part of an ongoing coordinated research project (CRP) entitled Irradiation Enhanced Degradation of Materials in Spent Fuel Storage Facilities, with the specific objective to discuss the problems related to research reactors. At this meeting, information was shared with the IAEA and participants from Europe and the USA on spent fuel corrosion issues at Savannah River Site (SRS) and other sites in the USA. At the SRS in the USA, long term corrosion surveillance tests were conducted to obtain information about the state of the fuel assemblies in the storage basins and also to control the water parameters to reduce, if not mitigate, corrosion of the fuels and other components. Based on this experience as well the major concerns of most RR operators, the IAEA initiated a CRP on the corrosion of Al- clad spent RR fuel in water (Phase-I). This CRP was designed to address several issues presented by vulnerability assessments conducted at some of the spent fuel storage sites. It had as its objectives: (a) establishing uniform practices for corrosion monitoring and surveillance, (b) providing a technical basis for continued wet storage of research reactor spent fuel, (c) collecting data to help in the prediction of lifetimes of fuel handling tools and storage racks, and (d) establishing a uniform basis for the characterization of water in fuel storage basins. Ten countries were invited by the IAEA to participate in the CRP. The participating countries were: the USA, Hungary, the Russian Federation, Serbia, Thailand, China, India, Brazil, Argentina, and Pakistan. Research agreements with institutes in these countries were put in place for the work to be performed and the IAEA furnished a detailed work package and standard corrosion test samples to each scientific group. The results of the CRP Phase-I were documented in the Technical Report Series Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water (TRS-418) [2].

At the end of this Phase I of the CRP it was deemed necessary that a continuation of the CRP should concentrate on fuel storage basins that had demonstrated significant corrosion problems and would therefore provide additional insight into the fundamentals of localized corrosion of aluminium. It was also considered that improved understanding of the fundamental mechanisms of Al corrosion would permit prediction of corrosion rates under different combinations of environmental parameters, enabling thereby storage pool operators to control these parameters and ensure safe and efficient interim storage of Al-clad spent fuel. More comprehensive research was recommended in the following specific areas:

1. Evaluation of the effect of dust sediments on the corrosion of coupons and its implication in terms of corrosion of fuel cladding.
2. Identification of the different Al alloys and other metals presently in use in spent fuel basins and design of experiments to evaluate the effect of specific bimetallic couples;
3. Evaluation of the effect of hydrodynamic conditions on coupon and fuel cladding corrosion;
4. Evaluation of the effects of water quality parameters on localized corrosion of Al fuel cladding in the wide range that exists between known poor water chemistry conditions and optimum conditions.

To address these issues, the IAEA started a new CRP in 2002 entitled Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water (Phase II). Argentina, Brazil, Czech Republic, Kazakhstan, Poland, Romania, Serbia and Thailand participated in Phase-II of the CRP. The reasons that were presented for the continuation of the CRP were:

1. To obtain information from facilities with localized corrosion problems.
2. To extend corrosion data base on the performance of Al alloys in wet storage to provide a sounder basis for extrapolation There are large differences in Al alloy durability that is still not well understood, including the protective properties of the oxide films, pitting factors as they apply to fuel storage pools, crevice corrosion and the synergistic effects of various impurities.
3. To correlate coupon corrosion with fuel cladding corrosion

The main objectives established for the new CRP were:

1. To collect information from participating laboratories from examination of existing fuels and from records of water quality to obtain correlations;
2. To continue collecting data from coupons that were provided during CRP-Phase I to some countries for long term exposition.
3. To establish and validate improved standard practices for corrosion monitoring and surveillance;
4. To expand the data base on the performance of and durability of Al alloy components in wet storage. to provide an improved technical basis for extended interim wet storage;
5. To improve the data base on the ranges of water chemistry parameters that allow safe, reliable and economical storage of Al clad RR fuel and provide a corrosion resistant environment;
6. To assess the improved resistance provided by various oxide films through corrosion coupon studies;
7. To examine in detail the correlation of coupon behaviour;

8. To provide a link between the studies proposed during the CRP with ongoing studies of the US national corrosion programme and studies underway in the Regional TC project RLA/4/018 in Latin America.

1.2. FIRST RCM

The first research coordination meeting (RCM) was 28 October-1 November 2002, in Buenos Aires, Argentina. At this meeting the participants established the detailed scope and agenda for the work to be done, with a common agreement that the work should emphasize experiments with aluminium coupons, immersed in the different water basins used to store research reactor spent fuel. The IAEA furnished the corrosion surveillance racks with coupons made of aluminium alloys generally used in research reactor nuclear fuel claddings, and recommendations for individual participants to supplement 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 early 2003 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 observations were reported after 16 months at the second RCM of the CRP.

1.3. SECOND RCM

The second RCM was held at the Institute of Nuclear Physics, National Nuclear Center, Almaty, Kazakhstan, 14-18 June 2004. At this meeting, progress reports from the different participants were scrutinized and general recommendations were prepared for all the participants. Details and procedures related to coupon evaluation were discussed, including a practical demonstration of withdrawal of racks and on site evaluation of coupons. During the meeting some participants made presentations describing experimental and technical studies, including “basic studies related to corrosion of aluminium alloys in pure water: behaviour of precipitates and effect of sediments”; “effect of coupon orientation on corrosion behaviour of aluminium alloy coupons and control of sediments in spent fuel storage facilities”; “sources of dust and settled solids in away-from-reactor and in-reactor basins”. More about these studies is described in Section 5.

At this meeting, new coupons were distributed to the participants, with specific instructions to assemble them using the rack withdrawn after one year of exposure in CRP-Phase II. It was recommended that the rack with the new coupons should be called **Rack-1-V** and immersed horizontally (with coupons in vertical position) in the spent fuel basins for a year. Most of these racks were immersed in the individual basins by end of 2004.

Also, the test protocol of the CRP was updated on the meeting, to include:

1. A clear and agreed list of definitions, to facilitate exchange of information and comparison of results;
2. Instruction for handling and characterization of coupons during the “pre-assembly” phase;
3. Instruction for assembling the racks;
4. Instructions to position the racks horizontally in the basins, with coupons vertically oriented;
5. Instructions for water monitoring and interim examination of racks during the test;
6. Instruction for removal and examination of coupons;
7. Recommended format for the final report.

Finally, a recommendation was made for participants to carry out sediments evaluation in their basins and to include the results in the final report In this case sediments should be filtered using a media with a maximum pore size of 0.5 μm and dried at 110 °C for 24 hours.

1.4. THIRD RCM

The third RCM was held at the IAEA in Vienna in December 2005. The main activities during this RCM were:

1. Presentations of individual reports describing the corrosion behaviour of coupons in spent fuel storage basins of the participating country;
2. Discussion and analysis of the questionnaires prepared during a consultancy meeting held in April 2005. The objective of this questionnaire was to verify if the participants had followed the instructions in the 'test protocol' of the CRP. The discussions during this activity were extremely useful, enabling an adequate explanation for deviations in overall corrosion behaviour of the coupons as a function of basin water parameters and/or other alloy related factors. These discussions also allowed clarification of some aspects of the 'test protocol' that was revised and updated. It is expected that this 'test protocol', as detailed in Section 4, can be used as a guide for any research Reactor spent fuel basin operator to conduct a corrosion surveillance programme.
3. Preparation and outline of a proposed IAEA TECDOC. The preparation of a TECDOC based on the results of the CRP and the results of the corrosion activities within IAEA-TC Regional Project for Latin America was discussed, with identification and assignment of responsibilities for the preparation of each specific section. The structure of the participating country's final reports and deadlines for submission were discussed and agreed upon.
4. Preparation of summaries of country status reports.

Two major points of discussion in the meeting were the effect of settled solids on the coupons and coupon orientation. According to the meeting participants, coupon orientation had a marked effect on the extent of pitting in most spent fuel basins. Horizontal coupons pitted to a greater extent than vertical coupons. Additionally, the top surfaces of horizontal coupons pitted more than bottom facing surfaces, demonstrating a clear evidence of the effect of settled solids on the dynamics of the pitting corrosion process.

The participants agreed on the benefits of establishing a corrosion surveillance programme with actions to monitor settled solids at the different sites, and all participants expressed the intention to continue with corrosion surveillance testing and the evaluation of settled solids in their facilities, with a common understanding that aspects related to the number of coupons, the alloys, coupon orientation as well as periodicity for removal and evaluation of coupons will be site specific. Settled solid determination and analysis at periodic intervals will be also site specific.

1.5. CORROSION ACTIVITIES IN THE TC REGIONAL PROJECT FOR LATIN AMERICA

In Latin America, many research reactors (RRs) have been in operation since the late fifties, and a significant amount of spent fuel has been accumulated. Most of the research reactor spent nuclear fuel (RRSNF) elements have been returned to the USA and some Latin American countries, aware of their responsibility of safely and securely manage the spent fuel from their research reactors, started the IAEA TC Regional Project RLA/4/018, entitled Management of Spent Fuel from Research Reactors. The countries with concerns related to spent fuel storage that participated in the project were Argentina, Brazil, Chile, Mexico and Peru. The concerns were based on the fact that in May 2006, the option to send the RRSNF to USA would cease, and national solutions in countries without major nuclear power programmes would be very difficult to implement. These concerns were the driving force for the initiation of the IAEA sponsored Regional Technical Cooperation Project for Latin America. The objectives of this Project were to provide the basic conditions to define a regional strategy for managing research reactor spent fuel and to provide solutions, taking into consideration the economic and technological realities of the countries involved. In particular, to determine the basic conditions for managing RR spent fuel during operation and interim storage as well as for final disposal, and to establish forms of regional cooperation for spent fuel characterization, safety, regulation and public communication.

The Project was divided into 4 subprojects: (1) spent fuel characterization; (2) safety and regulation; (3) options for spent fuel storage and disposal; (4) public information and communication. Corrosion monitoring and surveillance was one of the activities of the subproject 'Spent fuel characterization'.

The dominant fuel type used in the Latin American (LA) RRs is plate-type (MTR), clad in Al, and followed by TRIGA-type. Almost all the spent fuels from LA RRs are stored in racks within the reactor pool, in decay pools or in away-from-reactor wet basins. The in-reactor storage facilities consist of aluminium or stainless steel storage racks. Two of the countries participating in the regional project (Argentina and Brazil) were also participants of the IAEA sponsored Coordinated Research Project (CRP) on Corrosion of Research Rreactor Al-clad Spent Fuel in Water. The corrosion activities of the Regional Project initiated in 2002, when four test racks with aluminium coupons in different orientations were immersed in the spent fuel basins of the participating countries. The test protocol was based on the CRP and the main objective was to evaluate the effect of Latin American spent fuel basin parameters on the corrosion behaviour of research reactor fuel cladding. More information about the Regional Project can be found in reference [3].

Considering that the corrosion activities of the regional project were quite similar to those carried out in the CRP, it was decided to include results from both activities in the same report. Individual results of both activities, the CRP and the Regional Project, are presented in the country reports Section, at the end of this publication.

Argentina, Brazil, Chile, México and Peru participated in the IAEA TC Regional Project for Latin America (RLA4018).

1.6. OUTLINE OF THE REPORT

The detailed background and description of the CRP and TC regional project RLA/4/018 programmes are presented in this Section 1. A thorough state of the art literature review on the corrosion of aluminium alloys was compiled by the IAEA in 1998 (IAEA-TECDOC-1012) [4]. 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 report that apply to the aluminium alloys and fuels predominantly used in fuel for research and test reactors have been updated and are presented in IAEA Technical Reports Series No. 418 [2], consequently in Section 2 only a summary of the fundamentals of aluminium alloys corrosion is presented. Section 3 refers to materials and methods, and presents details of the corrosion coupons, racks and experimental protocols used in the CRP. Section 4 presents some recommended Guidelines for Conducting Corrosion Monitoring Programmes, based on the knowledge gained with the work performed in this CRP and in the equivalent activities of the regional project; and Section 5 presents the results of the CRP, including the findings of effect of settled solids on the corrosion of aluminium-clad research reactor spent fuel in water and three specific case studies with lessons learned during the CRP. The summary of the work done is described in Section 6, and the overall conclusions in Section 7. The country reports, prepared by the institutes participating in the CRP and TC regional project RLA/4/018 are presented at the end of the publication, in the form of individual contributions. The CD placed at the end of the publication, inside the back cover, contains the full digital images produced for EWA and MARIA reactors, as documented by S. Chwaszczewsk et al. in their country report. Instructions on how to access and use the images are given at the end of the respective report.

2. CORROSION OF ALUMINIUM ALLOYS

Given its low thermal neutron capture cross section, availability, convenient mechanical properties and corrosion resistance, aluminium and its alloys have been largely used in nuclear applications at temperatures below and around 100ºC in water. Many components of experimental and production reactors are manufactured with these materials: reactor vessels, nuclear fuel, thermal columns, irradiation channels, piping, etc. Being extremely reactive, aluminium owes its noble characteristics to the protective properties of the aluminium oxide layer that normally forms in contact with oxygen, even at room temperature. As long as this film remains stable, the aluminium or aluminium alloys components will not suffer of corrosion. The only concern with respect to oxidation is the nuclear fuel in-service performance. In this case, the oxide will present a parabolic growth, which will depend on the temperature, heat transfer, heat extraction and other variables. If the oxide thickness exceeds some value in the range of 25 to 50 μm, the "spalling" phenomenon is likely to appear, with oxide damage, blistering and intergranular attack. This behaviour is more probable at higher temperatures; for this reason, Al and its alloys are not suitable for use in power reactors. The maximum allowable temperature for aluminium alloys use in water is between 150 and 200ºC.

Depending on the conditions (mainly humidity and temperature) various kinds of aluminium oxides may be formed, from the anhydrous alumina (Al_2O_3) to the successively more hydrated bohemite ($Al_2O_3.H_2O$), Bayerite and Hydrargyllite (two crystalline forms of $Al_2O_3.3H_2O$) [5]. $Al(OH)_3$ (aluminium hydroxide) can also form. All these compounds are soluble in water, depending on the pH. The minimum solubility (maximum stability) is attained at pH=5.1, as seen in Fig. 1.

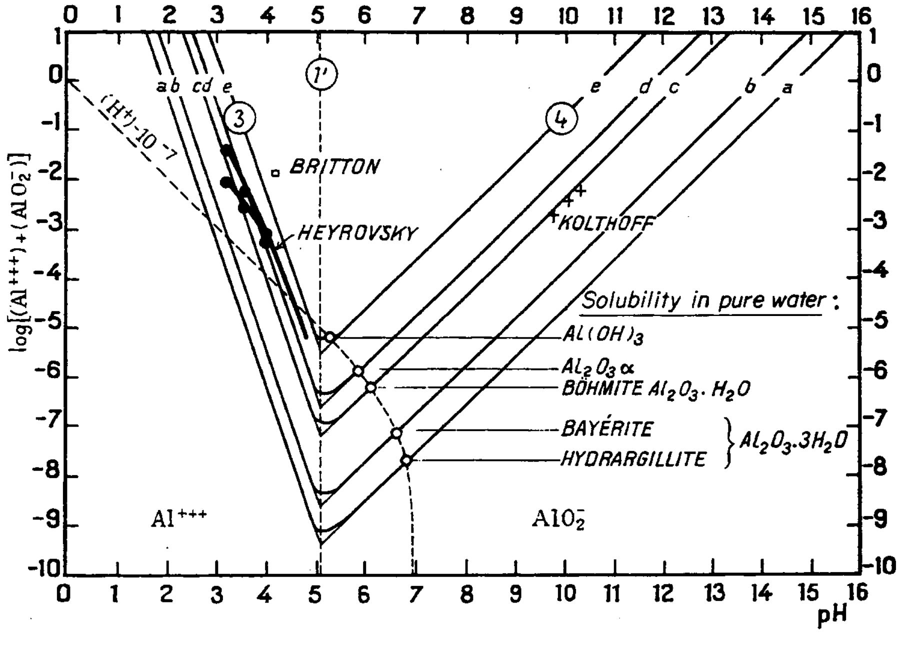


FIG. 1. Solubility of aluminium oxides in water [5].

Consistently, aluminium alloys are commonly resistant to corrosion in aqueous solutions when the pH is in the range from 4 to 8 approximately. The main exceptions are those environments containing aggressive species, mainly chloride ions. In these cases the oxide film could be attacked, losing its protective attributes.

2.1. FORMS OF ALUMINIUM CORROSION

The main types of aluminium corrosion concerning the nuclear fuel performance, especially during long term interim wet storage in water basins, are pitting, crevice, galvanic and intergranular corrosion. These are all different forms of localized corrosion, which may produce plate perforation with the consequent loss of containment of nuclear material and release of fission products. Generalized corrosion is not expected to take place, unless abnormal drifts of chemical conditions bring the pH to acid or alkaline extremes.

2.1.1. Pitting corrosion

The aluminium barrier oxide film can be unstabilised by specific dissolved ions, especially chlorides, which may attack the protective layer in localized regions, exposing the bare metal to the environment oxidising action. Being aluminium a highly reactive material, it will corrode at a high speed in those spots, producing deep pits. The solution inside these holes will have a high concentration of dissolved metal ions, which hydrolyse generating a strongly acid medium. Also, the dissolved anions will concentrate inside the pits, attracted by the accumulation of metal cations. In this strongly acid and saline solution aluminium oxides cannot be reformed, making the corrosion pitting process auto-catalytic.

One key variable with respect to pitting corrosion is the so called “pitting potential”, E_P. This parameter is specific of each metal-anion system. Each time the electrode potential (which essentially is the electrical potential drop across the metal-solution interface) is higher than E_P, pitting corrosion of the metal will take place in the presence of that particular aggressive anion. Electrode potential increases with cathodic reactions, as the oxygen reduction. The higher is the oxygen content, then, the higher is the probability of this form of corrosion. Aluminium oxides are not good cathodes; so, incrementing the cathodic area by electrically connecting aluminium with other metal (copper alloys, stainless steel, etc.) will tend to significantly increase the electrode potential, stimulating pitting attack.

Pitting potential increases when ion concentration decreases, tending to infinite in pure water (no pitting possible). Any reaction which alters the acidity in the interior of pits will tend to affect E_P, influencing pitting susceptibility. That is why the addition of alloying elements to aluminium may produce different results, as depicted in Fig. 2.

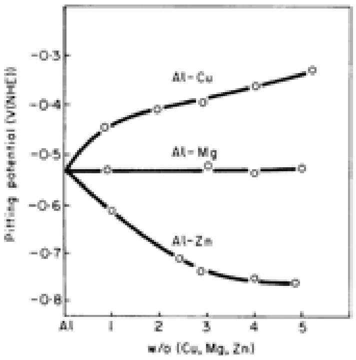


FIG. 2. Effect of different alloying elements on Al pitting potential in chlorides [6], [7].

The addition of copper increases the pitting potential because is a good cathode and enhances the hydrogen reaction, diminishing the acidity, thus hindering pitting. Instead, zinc acts as a poison for that reaction, with an opposite effect. In the case of magnesium, as this element is much more reactive than aluminium, it will tend to dissolve preferentially, leaving pure aluminium in contact with the environment; for this reason, the pitting potential of this alloy will be similar to that of pure aluminium.

Pitting susceptibility varies in environments with different anions. This is revealed by the distinct values of E_P measured in different solutions. As chlorides are the most aggressive anions, the E_P values in these solutions are the lowest. A compendium of E_P values for various solutions can be seen in Fig. 3.

As the pitting mechanism involves acidification of the solution inside the pit, increasing the pH of the water solution will tend to inhibit this process. The same effect will be obtained by adding some substances, as the case of nitrates, which form ammonium in a protons consuming reaction. However, the addition of species with high redox potentials will promote electrode potential increases; consequently, there will be a higher pitting probability.

2.1.2. Crevice corrosion

Gaps or other zones of a metallic component where the water or other liquid environment becomes retained and stagnant may have a different chemistry than the bulk. Corrosion in crevices can proceed, then, through a mechanism similar to that of pitting corrosion. It is triggered by the presence of the same dissolved aggressive species and is also autocatalytic in nature. The main difference is that it is much easier to attain a corrosive environment into these enclosed regions than on the bare surface. For this reason, this phenomenon takes place at lower electrode potentials than pitting. Crevice corrosion is affected by the same variables that pitting, but design factors also have to be taken into account, to reduce at a minimum the presence of crevices.

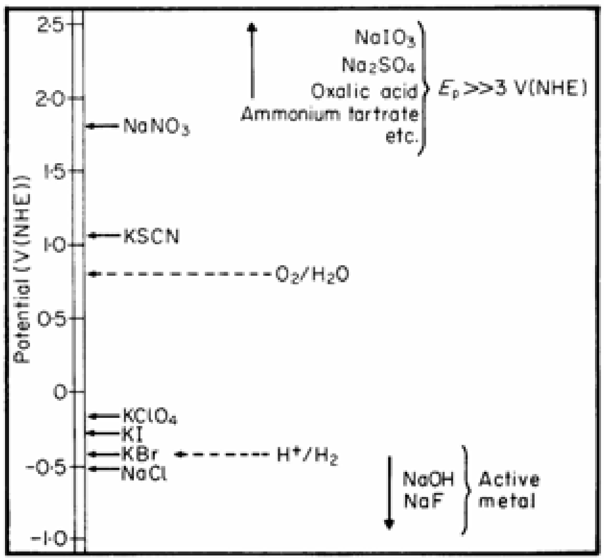


FIG. 3. Pure Al E_P values in solutions of various anions [8].

2.1.3. Galvanic corrosion

As pointed out previously, galvanic contact of aluminium with other metals will produce an increase in the electrode potential through intensification of cathodic reactions. This will tend to increment all the electrochemical corrosion processes. In the presence of corrosive species, such as chloride ions, the electrode potential can become higher than the pitting potential E_P and pitting corrosion will occur. Other forms of corrosion, as crevice corrosion, will also be enhanced. In highly pure water, instead, only some increment in the oxidation rate should be expected, which will depend on the temperature and should only affect the vicinity of the electrical contact region.

2.1.4. Intergranular corrosion

The grain boundaries are normally more active regions due to the disordered arrangement of atoms, what make them prone to their selective corrosion. When this happens, a small amount of intergranular material dissolution can produce material disintegration and catastrophic failure. In pure aluminium this event can take place only at temperatures of 200ºC and above, which are not likely in experimental reactors. However, aluminium alloys can be susceptible to this type of attack, depending on the mechanical and thermal treatments they are subjected to, along their fabrication route. Al-Cu, Al-Mg and Al-Mg-Si alloys can develop vulnerable structures during the ageing process, in which certain intermetallic particles can precipitate along the grain boundaries, leaving a continuous stripe of reactive material, as depicted in Fig. 4. This will preferentially dissolve in case corrosion conditions are present, giving place to intergranular corrosion.

The susceptibility to this phenomenon depends on the ageing time, as shown in Fig. 5. The worst microstructure is attained when the highest hardness is reached. The procedure to achieve the best mechanical properties is accomplished at the expense of corrosion resistance.

As all the phases present in the microstructure of aluminium alloys are passive in neutral environments, intergranular corrosion proceeds through pitting of the more reactive ones. Hence, all the considerations with respect to pitting corrosion are applicable to grain boundary attack. It will be promoted by the presence of aggressive anions like chloride, the existence of oxidant species, galvanic couples, etc. The incidence of this problem will be reduced by lowering the electrode potential, purifying the water or by adding inhibitors to pitting.

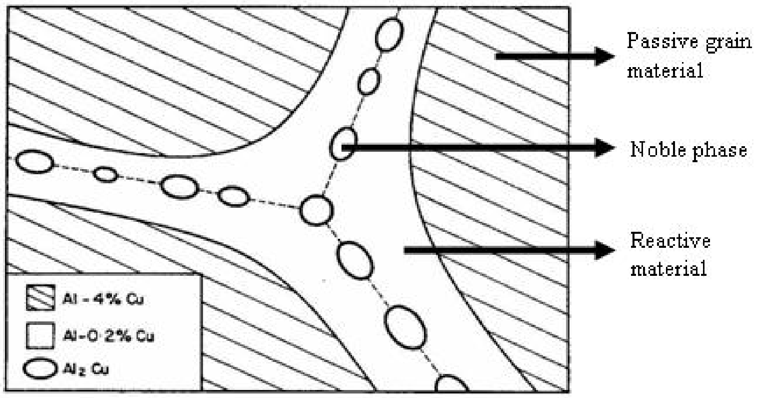


FIG. 4. Second phase precipitation in Al-Cu alloys [9].

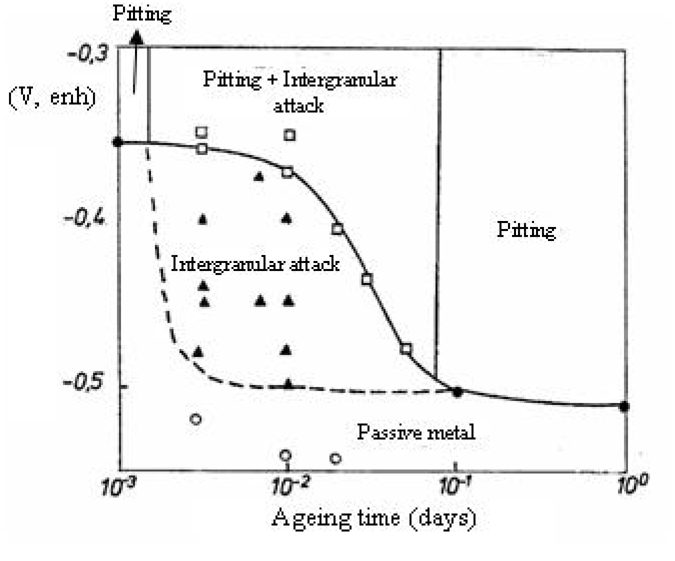


FIG. 5. Effect of ageing time in corrosion susceptibility of Al-Cu alloys in NaCl solutions [9].

2.2. EFFECT OF WATER QUALITY ON ALUMINIUM CORROSION

As pointed out in the previous Sections, aluminium corrosion processes in aqueous environments are of electrochemical nature, involving electrical charge transfer through the metal-solution interface. Therefore, the main environmental variable to be considered is water electrical conductivity. Keeping it at the lowest possible value will minimize the risk of degradation. This is attained through water purification, which removes all sorts of dissolved species from the water. Doing this not only reduces the electrical transfer rate, but also eliminates non desirable elements from the water: aggressive anions, oxidant species, etc. Getting rid of them impedes the occurrence of various forms of localised attack, like pitting and crevice corrosion. The aim would be to rule out their presence in the water; for this reason, the limits of concentration of dissolves species established for the operation of research reactors and spent fuel storage basins have always been set at the best detection threshold. This used to be 0.5 ppm for a long time, but in recent years it has been reduced to the ppb range, as in the case of receiving basins for offsite fuels (RBOF) basin in Savannah River National Laboratory and the one in Idaho National Laboratory, which operate at 10 and 50 ppb respectively.

Conductivity is normally kept in the range of a few micro-Siemens per centimetre (this unit, μS/cm, corresponds to a water electrical resistance of 1 MΩ/cm). After the experience obtained in the CRP on "Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water - Phase I" [2], the recommendation was to reduce this limit to around 1 μS/cm.

pH requirements are related to oxide stability. Taking into account the solubility dependence with pH displayed in Fig. 1, it is recommended that water pH be maintained between 4.5 and 7. In open pool research reactors and fuel storage basins, water pH is normally established by the solubility equilibrium of carbon dioxide (CO_2), which is set at a pH value of 5.7, to insure aluminium oxide stability.

One important factor which is not fully covered by standard purification methods is the presence of dust and other particles which may fall on the pools. These can be of diverse compositions, promoting various effects: crevice or galvanic corrosion, chemical attack, etc., which in many occasions take the appearance of pitting. This sort of under-deposit corrosion is also dependent of the water quality, but can even happen in highly purified water. More on the specific mechanisms applying in this case can be found in Section 5.2.

3. MATERIALS AND METHODS

3.1. INTRODUCTION

Essentially, a corrosion research programme consists in the immersion of aluminium coupons manufactured with aluminium alloys similar to those used to fabricate the nuclear fuel, in the vicinity of stored spent fuel or close to the operating fuel in nuclear reactors with long fuel residence.

For this CRP the coupons were stacked in stainless steel support structures called "racks". Provisions were made to avoid electrical contact between coupons, between coupons and racks and between coupons and any other structure, component, rack, etc.

Material to construct several racks was distributed to every participating country. The number of racks in each place depended on the number of sites to be monitored. Initially, two racks per site were provided in the CRP and three for the regional project [2], [3]. All of them were to be dipped at the start of the study and withdrawn one by one after each passing year. Later, more material was supplied to perform the same work with racks in horizontal position (coupons with their surfaces vertically oriented).

3.2. DESCRIPTION OF THE TEST RACKS

Various kinds of RR nuclear fuels are kept in the storage facilities of countries that participated in the CRP or in the RLA. Most of them are MTR (Material Test Reactor) type fuel, which is an array of fuel plates, but rod assemblies or concentric tubes arrangements can also be encountered. Table 1 lists the characteristics of the different types of fuel considered in these programmes.

As can be derived from Table 1, among the different aluminium alloys used to manufacture RR nuclear fuel, those most commonly employed are AA 6061 (so denominated by the American Aluminium Association), AA 1050 and the SZAV series, of Russian origin. Hence, these three materials were selected as the most representatives to be included in the surveillance programmes.

AA 6061 and SZAV-1 were selected for the CRP, whereas AA 1050 and AA 6061 for the regional project. Several countries decided to add coupons of their own alloys, in order to include them in the comparison. Therefore, some room was reserved for locally manufactured coupons. In Romania, coupons made of $AlMg_3$ alloy were added, AA 5251 in Chile, and local manufactured AA 6061 in Argentina, Brazil and Chile. Typical composition of the mentioned alloys can be found in Table 2.

The coupons were essentially 3 mm thick discs, with 100 mm in diameter and a 35 mm central hole, similar to those recommended by the American Society for Testing and Materials (ASTM). They were inserted in a stainless steel tube forming a stack. Provisions were made to avoid electrical contact between coupons and between coupons and the support tube, by means of ceramic rings which acted as separators. Fig. 6 shows a schematic representation of a typical rack used in the regional project. The uppermost positions, marked in white in Fig. 6, show the slots reserved for local coupons. A picture of an assembled rack is displayed in Fig. 7.

Table 1. Types of fuel and materials

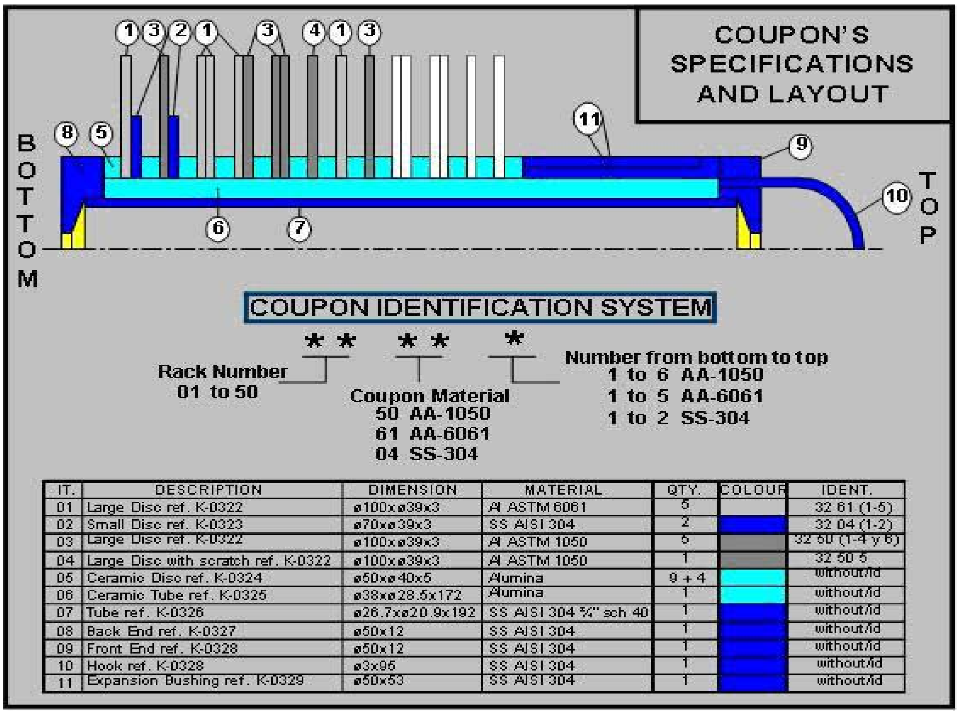
COUNTRY	*FUEL CONSTRUCTION TYPE*	*CLAD ALLOY*
POLAND	*EK 10 - 10 mm rod*	*SZAV Al alloy*
	WWR-SM/SM2 - 3 concentric tubes	*SZAV Al alloy*
	MR - 5 or 6 concentric tubes	*SZAV Al alloy*
ROMANIA	*EK-10 - rods*	*SZAV Al alloy*
	S-36 - rods	$AlMg_3$
THAILAND	*MTR, later TRIGA*	*AA 6061*
CHILE	*MTR*	*AA 5251 - AA 6061*
ARGENTINA	*MTR*	*AA 1050 - AA 6061*
PERU	*MTR*	*AA 6061*
CZECH REP.	*IRT-2M (tubes assembly) and EK-10*	*SZAV-1*
KAZAKHSTAN	*concentric hexahedral pipes*	*SZAV-1*
REP. of SERBIA.	*TVR-S cylindrical slug*	*SZAV-1*
BRAZIL (IPEN)	*MTR*	*AA 6061*
BRAZIL (CTDN)	*Rods*	*AA 1100*
MEXICO	***Rods***	***SS 304***

Table 2. Typical composition of alloys used in the programmes

Element	*Al 1050*	*Al 6061*	*Al 5251*	$AlMg_3$	*SZAV-1*
Al	***Min. 99.5***	***balance***	***balance***	***balance***	***balance***
C	**-**	**-**	**-**	**-**	**-**
Cr	**-**	***0.04 – 0.35***	***0.15***	***0.15***	***0.31***
Cu	***Max. 0.05***	***0.15 – 0.40***	***0.15***	***0.3***	***0.018***
Fe	***Max. 0.40***	***Max. 0.70***	***0.50***	***0.235***	***0.25***
Mg	***Max. 0.05***	***0.8 – 1.2***	***1.7 - 2.4***	***0.57***	***3.60***
Mn	***Max. 0.05***	***Max. 0.15***	***0.1 - 0.5***	***0.06***	***0.072***
Ni	**-**	**-**	**-**	***0.0043***	**-**
P	**-**	**-**	**-**	**-**	**-**
S	**-**	**-**	**-**	**-**	**-**
Si	***Max. 0.25***	***0.4 – 0.8***	***0.40***	***0.294***	***0.15***
Ti+Zr	***Max. 0.03***	***Max. 0.15***	***0.15***	**-**	***0.023***
V	***Max. 0.05***	**-**	**-**	**-**	**-**
Zn	***Max. 0.05***	***Max. 0.25***	***0.15***	***0.064***	***0.025***

Some coupons were positioned in pairs, either of two aluminium alloys or one aluminium alloy and one stainless steel. The purpose was, in the first case, to study the effect of the crevice formed between the two discs; in the second, the influence of galvanic contacts on aluminium corrosion. These types of conditions are sometimes encountered in RRSNF stored in water basins. Crevices are formed in several parts, as the joints between fuel plates and support structures. Galvanic couples may be formed if stainless steel screws are used to assemble aluminium fuel, or if this is stored in stainless steel racks, etc. 304 stainless steel was used both in the racks structure and to form the galvanic couples.

The coupons were manufactured from a common source, to permit a better comparison between results in different sites. For the CRP they were machined from a cast rod produced by a Hungarian company under contract with the Atomic Energy Research Institute (AEKI-KFKI) of Hungary. This had been previously used to cut discs for the IAEA CRP on Aluminium Corrosion Phase I. For the regional project all the coupons were fabricated in Brazil. As one of the findings of CRP Phase I was that pitting morphology seems to depend on the manufacturing history, these new batch of coupons were cut from a rolled plate, rather than from a cast rod, to have a metallic structure similar to that of nuclear fuel plates. Later on, for the last part of both the CRP and the regional project, discs cut from extruded (Ex) and rolled (R) plates were also included in those racks used to test the behaviour of the vertical oriented coupons.



IT.	DESCRIPTION	DIMENSION	MATERIAL	QTY.	COLOUR	IDENT.
01	Large Disc ref. K-0322	ø100xø39x3	Al ASTM 6061	5	⬜	32 61 (1-5)
02	Small Disc ref. K-0323	ø70xø39x3	SS AISI 304	2	🟦	32 04 (1-2)
03	Large Disc ref. K-0322	ø100xø39x3	Al ASTM 1050	5	▨	32 50 (1-4 y 6)
04	Large Disc with scratch ref. K-0322	ø100xø39x3	Al ASTM 1050	1	▨	32 50 5
05	Ceramic Disc ref. K-0324	ø50xø40x5	Alumina	9 + 4	🟦	without/id
06	Ceramic Tube ref. K-0325	ø38xø28.5x172	Alumina	1	🟦	without/id
07	Tube ref. K-0326	ø26.7xø20.9x192	SS AISI 304 ¾" sch 40	1	🟦	without/id
08	Back End ref. K-0327	ø50x12	SS AISI 304	1	🟦	without/id
09	Front End ref. K-0328	ø50x12	SS AISI 304	1	🟦	without/id
10	Hook ref. K-0328	ø3x95	SS AISI 304	1	🟦	without/id
11	Expansion Bushing ref. K-0329	ø50x53	SS AISI 304	1	🟦	without/id

FIG. 6. Schematic representation of a test rack used in the regional project.

FIG. 7. Example of test rack.

Another aspect that deserved attention was surface finishing, as in some stored fuel sites pitting occurred on scratches produced during handling of oxidised spent fuel. In order to study this type of phenomenology, some coupons were pre-treated to grow an oxide and a scratch was made on their surfaces. These coupons were named “PS” (pre-oxidised and scratched), whereas those that were tested without any surface treatment were named “AF” (as fabricated).

Altogether, four different types of test racks were prepared for the two programmes, with seventeen different kinds of coupons, as described in Table 3.

Table 4 contains the information about the stacking sequence of coupons in different racks, beginning with the one closest to the test rack hook hanger. As already mentioned, some room was available to add locally manufactured coupons on top of the pile supplied by the IAEA.

Table 3. Types of coupons used in the CRP and regional project programmes

PROGRAMME	HORIZONTAL COUPONS	VERTICAL COUPONS
CRP	CAST SZAV-1 AF	ROLLED (R) AA 6061
	CAST SZAV-1 PS	
	CAST AA 6061 AF	EXTRUDED (Ex) AA 6061
	CAST AA 6061 PS	
RLA	ROLLED (R) AA 1050	ROLLED (R) AA 1050 AF
		ROLLED (R) AA 1050 PS
	ROLLED (R) AA 6061	ROLLED (R) AA 6061 AF
		ROLLED (R) AA 6061 PS
	EXTRUDED (Ex) AA 1050	EXTRUDED (Ex) AA 1050 AF
		EXTRUDED (Ex) AA 1050 PS
	EXTRUDED (Ex) AA 6061	EXTRUDED (Ex) AA 6061 AF
		EXTRUDED (Ex) AA 6061 PS

Table 4. Coupon stacking sequence for the different test racks

CRP racks (Horiz. coupons)	RLA racks (Horiz. coupons)	CRP racks (Vertical coupons)	RLA racks (Vertical coupons)
SZAV-1	AA 1050	AA 6061(R)/AISI 304	AA 1050-Ex
SZAV-1 (PS)	AA 6061	AA 6061(R)/AA 6061	AA 1050-R
SZAV-1/SZAV-1	AA 1050 (PS)	AA 6061(Ex)/AISI 304	AA 1050-Ex(PS)
SZAV-1/AISI304	AA 1050/AA 1050	AA 6061(Ex)/AA 6061(Ex)	AA 1050-R(PS)
AA 6061	AA 6061/AA 1050		AA 1050-Ex/AISI 304
AA 6061 (PS)	AA 6061/AA 6061		AA 1050-R/AISI 304
AA 6061/AA 6061	SS 304/AA 1050		AA 6061-Ex
AA 6061/AISI 304	SS 304/AA 6061		AA 6061-R
			AA 6061-Ex(PS)
			AA 6061-R(PS)
			AA 6061-Ex/AISI 304
			AA 6061-R/AISI 304

3.3. TEST PROCEDURES

In order to make the results comparable, all the operations required to carry on the corrosion monitoring exercise were standardised. A document called "test protocol" was issued at the beginning of the programme and improved during its development, including the recommendation arising from the countries experience, presented during the successive research coordination meetings (RCM). These directives were to be strictly followed by all participating countries. It included from a glossary of specific programme terms to detailed instructions on how to handle the supplied coupons, how to prepare the site specific coupons, how to assemble the racks, how to perform the racks immersion in the basins or reactor pools, which complementary activities to complete during the programme period, how to do interim examinations, how to remove and assess the coupons corrosion state, etc.

What follows is the detailed set of guidelines, updated on December 2005, and using the following adopted terminology:

Corrosion coupon: (or coupon) is the circular disk of aluminium alloy or stainless steel. The word coupon was adopted to avoid the use of confusing words like specimen, sample, disk etc.

Rack: consists of the central support tube with a set of coupons and ceramic spacers assembled to be held in place with a nut that has a hook.

Basin: is the contained volume of water used for storing spent fuels.

3.3.1. Pre-assembly

- Unpack rack and disassemble it. Handle with surgical gloves, removing any talcum powder on the outside of the gloves. Weighing of individual coupons is optional. No further cleaning or surface treatment of coupons is necessary. Each rack has one coupon passivated at 95°C for 12 hours in water and scratched (on the side *without* the identification number).
- Add coupons of site specific materials:

The coupons should be 100 mm in diameter, 3 mm thick and the diameter of the central hole should be 35 mm. Remove the burr and grind/polish of the two surfaces to almost mirror finish. Identify the coupons either by laser scribing or by punching the identification number close to the inner edge. Use the following procedure to chemically prepare the coupons:

(a.) Pickle coupon by immersion in 10 wt% NaOH at 70-80º C for 30 seconds kept in Tank-I;
(b.) Remove the coupon and brush the two sides while washing it in flowing deionised water for 1 minute- Tank-II;
(c.) Wash coupon with flowing deionised water at room temperature for 1 minute – Tank-III;
(d.) Neutralize coupon by immersion in a 5% solution of HNO_3 (by volume) at room temperature for 1 minute to neutralize it – Tank-IV;
(e.) Wash coupon with flowing deionised water for 1 minute in Tank-III;
(f.) Again pickle coupon by immersion in tank-I for 30 seconds;
(g.) Repeat steps b, c, d and e;
(h.) Immerse coupon in Tank-III for 5 minutes;
(i.) Wash coupon in flowing deionised water for 1 minute;
(j.) Dry coupon in hot air (180ºC) for 1 minute.

- The site specific coupons should have identification numbers. The numbering system chosen should be logical and carefully recorded at the beginning of the test and adhered to throughout the programme.
- Photograph the front and back of each coupon.

3.3.2. Assembly

- Assemble coupons in a specified order. The coupon with the scratch should be assembled with the scratch side facing upwards. Site specific stainless steel coupons should be placed below or above, with all aluminium alloy coupons not interspersed.
- Note the position of site specific coupons in the rack.
- Tighten the top hanger-nut by hand until tight and then give a further 10° turn.
- Photograph the assembled rack.
- Attach a stainless steel rope to the hanger of the rack. (Do not use a rope made of any synthetic material, as they degrade under radiation).
- In the preparation of a rack to be immersed horizontally in the basin the following procedure and/or precaution should be observed:
    - Avoid contact between the steel cable and the coupons (use two or more ceramic spacers to prevent the contact);
    - Use clips (preferably stainless steel) to join the cable instead of attempting knots.
    - Test the horizontal assembly outside the pool to ensure that the rack remains horizontal;
    - Choose basin location to avoid contact of rack caused by its eventual swaying.

3.3.3. Immersion of racks in fuel storage basin

- As soon as possible suspend the racks in the spent fuel basin using a stainless steel wire or rope. Use stainless steel clips instead of tying a knot as these seldom hold, especially if the rope is ≥2 mm thick. Previous experience has shown that nylon ropes disintegrate in the presence of radiation.
- Lower/position the corrosion rack in the vicinity of spent fuel if possible.
- Position racks above basin floor. Do not allow the rack or any of the coupons to touch the walls or floor of the basin, sludge or other metallic components.
- Identify the test rack with a label containing adequate information about the rack and those responsible for carrying out the test (to prevent tampering or inadvertent removal or repositioning of the rack).
- Record the date of immersion.
- Record the location of the rack (depth, distance from walls etc.). Make a sketch of the spent fuel basin and the position of the test rack (a) as a reminder of the position of the rack and (b) for use in the final report.

3.3.4. During the test

- Measure the radiation field intensity near the rack at periodic intervals (Sv/h).
- The water chemistry should be periodically monitored.
- Determine all the impurities in the basin water, such as chlorides, sulphates, nitrates, nitrites, carbonates, bicarbonates, iron, copper, silver, mercury, aluminium and other cations or anions which may be considered to be specific to the site basin. This should be done once a month during the first six months in the water taken preferably from the vicinity of the immersed rack. After six months, the impurities whose levels have remained constant need not to be measured again. However, monthly determinations of certain impurities which influence aluminium alloy corrosion should continue, such as chlorides, sulphates, iron, copper and other heavy metal ions.
- The real values of the impurities in the basin waters should be reported along with the dates of measurement. Averaged values of several measurements should not be reported.
- Indicate flow conditions near the rack (flowing or stagnant), rate of or frequency of renewal of water in basin etc.
- Observe if loose particles are present on the pool surface and/or coupon surface, and if they appear to be causing any corrosion problems, please describe.

- Prepare and immerse a sediment collector in the vicinity of the test rack for a period of 4-6 months to determine the quantity and composition of solids that settle on the surfaces of the coupons. The sediment collector should have a lid and this lid should be in place primarily when the collector is being withdrawn from the basin to prevent collection of solids floating on the surface of the basin.
- Express the quantity of solids that settle in the basin in micrograms per square centimetre per month.

3.3.5. Interim examination of racks during the test

Interim examination of the rack should be carried out once every three months. This examination consists of studying the overall appearance of the rack with an underwater camera and recording the features. In order to do this, the rack can be raised to be close to the water surface, but still under water. Alternatively, the examination can be done visually with an ordinary camera. In this case the rack can be raised and brought out of the water for a very short period (not exceeding 2 minutes, to prevent the surfaces from drying).

NOTE: Remember to have all the necessary accessories for the examination ready, prior to removing the rack from the basin.

Results of this examination, along with water parameters and analysis, were required to be reported to the CRP coordinator every 3 months.

3.3.6. Removal and examination of coupons

- Withdraw the rack from basin.
- Measure pH of water on the external surface of coupons, and compare with pH of bulk water, registering all values.
- Photograph the rack prior to disassembly. Photograph all points of interest including any corrosion of the edges.
- Remove the coupons from the rack.
- Photograph front and back of each coupon. A small card with a note about the material, immersion time and coupon identity number should be photographed together with the coupon.
- Make observations of specific corrosion phenomena for each coupon, 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 or embedded particles (can be felt with a gloved finger), etc.
- Measure pH (with pH paper) on the contact surfaces of crevice and bimetallic coupons; compare with bulk water pH and with that on the outside surface of the coupon.
- Count the number and measure size of the pits.

3.3.7. Post storage detailed examination

- Decontaminate coupons with a chloride-free detergent and rinse with deionised water.
- Air dry/wipe.
- To evaluate pitted aluminium coupons: Use 10% phosphoric acid solution, if necessary, to clean/dissolve oxide from pits to conduct 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. In case of thicker surface oxide, up to 50% phosphoric acid can be considered, exercising caution not to etch the alloy.
- In the case of pits on pre-oxidized coupons, pit evaluation should be carried out.
- Ensure that there are no oxides in the pits before determining the true pit depth.
- Conduct metallographic evaluation on the deepest pit(s). Measure pit depths with a calibrated focusing technique or repeated polishing and optical microscopy.

3.3.8. Further notes for evaluating coupons after exposure

a. Pitting corrosion

- Pits should be photographed.
- Pit depths should be determined.
- 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.
- The sectioning should be through the deepest part of the pit.

b. Crevice corrosion

- Visual and photographic inspection, together with determination of pH using pH paper, preferably in the range 4-9 with measurement intervals of 0.1.
- Metallographic inspection should be carried out only if pits are observed on the contact area.
- Evaluation of pitting in the crevice should follow the above instructions for pitting.

c. Galvanic (bimetallic) corrosion

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

3.4. IMAGE ANALYSIS

A special system was set up by the IPEN Institute in Brazil, to be used by participant of the regional project, in order to perform a thorough assessment of pit size distribution in tested coupons. Fig. 8 shows the Leica Image Analysis Work Station, used for this purpose.

FIG. 8. The Leica Image Analysis Work Station (left) and detail of the motorised stage (right).

This device consists of a Leica inverted stage optical microscope supplied with a motorised stage and a video camera, capable of recording images of the coupons, transfer them to a computer, to be analysed by special software. The system is able to locate pits by colour contrast, isolate them, measure their widths and count them. One of the programme outputs is a histogram of the number of pits as a function of their apparent diameter.

The system can work in a fully automatic way, taking pictures of an area of approximately 2 by 2 mm, covering the full coupon area (some 1700 fields per coupon), or it can be operated manually, selecting a limited, pre-defined number of areas. Several controls help to adjust the colour thresholds in order to compensate for background intensity differences. As the pitting locating mechanism is based in colour differences between the points of interest and the matrix, the coupon surface state is crucial. Darker spots are considered pits, because normally their interior is in darkness, whereas the outer surface is illuminated. If the metal is covered with a thick oxide, this contrast is lost and the discriminating capability strongly diminished. Hence, it is a requirement to have clean surfaces. This can be accomplished by means of pickling. Care has to be exercised in finding a convenient compromise between surface cleaning and the alterations that can be produced on the surface features of interest.

To concentrate in significant points and reduce the amount of time consumed in each analysis, only details larger than 30 µm are taken into account. As a result, a graphical distribution of the type shown in Fig. 9 is obtained as an output.

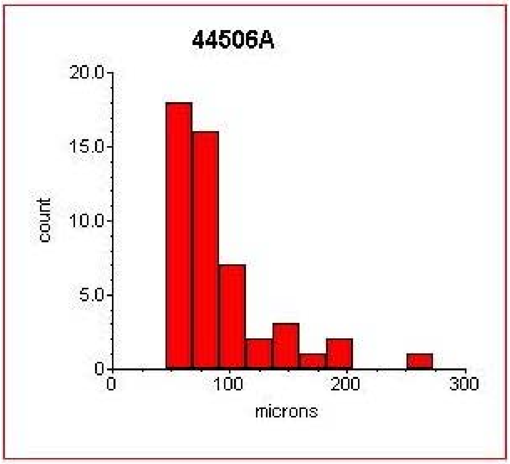


FIG. 9. Example of histogram obtained with the image analyser.

The example of Fig. 9 is interpreted as follows: in the examined coupon there are 18 pits with diameters between 40 and 65 µm, 16 between 65 and 90 µm, 7 between 90 and 115 µm, and so on. The behaviour of different samples can be easily compared through their histograms.

3.5. SEDIMENT COLLECTOR, COLLECTION AND IDENTIFICATION

Given the reported effect of settled particles on the corrosion of coupons of aluminium alloys, a procedure was set up in order to collect sediments in the vicinity of the racks location. Appropriated containers were constructed and installed with this purpose. The accumulated material was then recovered and analysed to establish its amount and chemical composition. More on the sediment collection, including procedures and results, is presented in Section 5.2.

4. GUIDELINES FOR CONDUCTING CORROSION MONITORING PROGRAMMES

The main reason for conducting a corrosion surveillance, or corrosion monitoring programme (CMP) at a RR facility, or at a spent fuel wet-storage facility, is to evaluate the effect of the prevailing water parameters on the corrosion of the spent fuel cladding, and/or other structural materials. A programme of this nature gives an insight into the extent of corrosion of the metallic materials. It is well known that good quality water is essential to prevent corrosion in a spent fuel basin. However, certain water parameters like conductivity, chloride ion content and some other ions, in quantities well below levels of concern, have a synergistic effect on the pitting corrosion behaviour of aluminium alloys. Hence, maintenance of water parameters within specified limits is not reason enough for complacency about corrosion of fuel cladding. A well-planned and executed CMP would give the RR or spent fuel basin manager an insight into the state of fuel cladding and/or metallic structural materials in terms of corrosion. A CMP involves the exposure of test coupons to the RR or basin water for a pre-determined period followed by its evaluation to detect for corrosion. The CMP also involves the determination of water parameters at periodic intervals. Thus, the RR or basin manager is informed of any transients in water parameters, (which often go unperceived in the absence of a CMP) and its effects, if any, on the corrosion of the coupons, and consequently on that of the fuel cladding and other structural materials. The CMP described in this Section is based on the experience gained during the work done for the CRP and for the regional project, and it is intended to be a guide for research reactor managers and operators in implementing similar programmes in their facilities.

4.1. STAGES OF A CMP

A CMP involves 3 stages, the planning stage, the execution stage and the action stage.

4.1.1. The planning stage

The **planning stage** includes: (1) identification and list of all materials that are exposed to the RR or spent fuel basin water; (2) specification of alloy composition, microstructure, heat treatment and surface condition; (3) selection of materials for the programme; (4) specification of the duration of the programme; (5) specification of frequency for corrosion analysis; (6) specification of frequency for monitoring water parameters; (7) selection of locations within the RR or spent fuel basin to place the coupons; (8) confirmation of sufficient materials in the desired states, and availability of a manufacturer or supplier adequately equipped to manufacture the test coupons and racks, all accessories required to identify, introduce, follow-up and withdraw the rack of test coupons; (9) preparation or selection of laboratory facilities for water analysis, sediment analysis, test coupon evaluation; (10) preparation of full specification for the coupons, the insulating separators and racks; (11) definition of coupons configurations with respect to nature of corrosion – crevice and bimetallic; (12) definition if settled solids need to be evaluated in terms of quantity and composition, and if so, aspects mentioned in sub-items 7 through 9.

4.1.2. Identification and listing all materials that are exposed to the RR or spent fuel basin water

A variety of metallic materials are often used in RR or in spent fuel basins. For the CMP, only alloys that are of major concern need be selected. This includes the fuel cladding and any other thin walled aluminium alloy component that if perforated would lead to concerns. Materials that are prone to corrosion and form voluminous corrosion products, which in turn could result in further corrosion of the fuel cladding should be included. Other metals that could form a bimetallic couple with the fuel cladding should be also included in the list of materials. Listing all materials exposed to the RR water helps to identify the eventual presence of materials that are not radiation resistant, and whose degradation can compromise the water quality.

4.1.3. Specification of alloy composition, microstructure, heat treatment and surface condition

Besides knowing the designation of the alloy and its nominal composition from standard tables, it is essential to know, if possible, the exact composition. Small deviations in composition result in formation of alloy phases or intermetallics. It is important to know the metallurgical state of the alloys. The microstructure, grain orientation, inclusions, intermetallic precipitates and other second phases influence corrosion and are often the points for initiation of corrosion, especially in Al alloys. The type of heat treatment given to an alloy alters its composition and its stress state. These also influence the corrosion behaviour of the alloy. One of the last stages in the manufacturing processes of RR fuel plates is surface treatment. Many surface defects are removed and a thicker surface oxide is grown. These in turn reduce the number of defects at which pits can initiate and the latter protects the Al surface. Hence, knowledge of the surface state is essential to produce a test coupon with alloy and surface characteristics similar to that of the fuel cladding.

4.1.4. Selection of materials for the programme

Following guidelines described above, the alloys to be tested for their corrosion resistance in the basin environment should be selected. Among the different Al alloys, the most important is that used as the fuel cladding. Many fuel storage racks are made of stainless steel. If such is the case, it is essential to select a stainless steel with composition as close to that of the storage rack. If the storage rack is made of an aluminium alloy, it is also important that this alloy be selected.

4.1.5. Specification of the duration of the programme

An ideal CMP is one that is carried out constantly. In a constant CMP, racks of test coupons are always awaiting withdrawal after specified durations. If a specific facility is unable to conduct a constant CMP, it is recommended that a 3-year programme be initiated, with yearly withdrawals of at least one rack with test coupons.

4.1.6. Specification of frequency for corrosion analysis

The frequency of corrosion analysis is the periodicity at which racks are withdrawn from the RR pool or spent fuel storage basin. For pools or basins with very good water quality management, yearly withdrawals of racks should be sufficient. Pools or basins with poor quality water or with significant amount of settled solids should adopt a six-monthly or even a three-monthly withdrawal, considering a time interval in which the water quality is well under control. It is important to emphasize that at the end of each interval a full rack is removed. It is **not recommended** that one or more coupons be removed from a rack and the rack with the remaining coupons returned to the pool or basin. Experience has shown that with only utmost care can coupons be prevented from drying before a withdrawn rack is partially disassembled for removal of some coupons, prior to its return to the pool. A partially dried coupon, if returned to the pool or basin does not represent or reproduce conditions similar to that of a fuel cladding or reactor component continuously exposed to the same environment. During this stage it is also necessary to define the procedures that will be used to analyse the coupons.

4.1.7. Specification of frequency for monitoring water parameters

Most RR facilities determine the temperature, pH, conductivity, chlorides, sulphates, iron, and a few heavy metal ions at regular intervals. The first 3 parameters are often monitored on-line and recorded at regular once or twice daily intervals. Water analysis at many RR facilities are carried out at twice or once monthly intervals. In away-from-reactor spent fuel storage sites, water analysis, if carried out, is often very infrequent. It is recommended that at the CMP site, water of less than desired quality be analyzed at least twice a month. If no marked variation in ion composition is noted after 3-6 months, monthly measurement is suggested.

4.1.8. Selection of locations to place the rack(s) within the RR or spent fuel basin

The location for immersing a rack with test coupons should be representative of the region where the spent fuel is stored. Often, this location is somewhere very close to the stored fuel. Other aspects to be borne in mind while selecting this location are: (a) the rack should not hinder regular fuel handling; (b) the rack should not be knocked about during regular reactor or basin operations; (c) the rack should not be exposed to excessive amounts of settled solids, unless of course it does reproduce conditions similar to that of stored fuels.

4.1.9. Confirmation of sufficient materials, and availability of supplier

Having decided upon the materials, the duration of the programme and the frequency of withdrawal of racks, it is essential to ensure that adequate material is available before embarking on the CMP. Ideally the Al alloys to be used for making coupons should have the requisites mentioned earlier. It is important that the manufacturer of the coupons and rack components be made aware of the requirements, especially in terms of final surface conditions of the coupons. Details about suggested coupon and rack designs, including dimensions, can be found in Section 3. It is also important to ensure that facilities are available to adequately identify racks and suspend them in the basin.

4.1.10. Preparation or selection of laboratory facilities for water analysis, sediment analysis, test coupon evaluation

Conducting periodic water analysis and final coupon evaluation are the two main parts of any CMP. Hence, facilities to conduct these are essential. Sediment analysis, although important, is a recommended complement to a CMP. Most RR facilities are equipped to determine certain water parameters. However, analyses for specific constituents in the water samples or in the settled solids are carried out at other in-house or near-by laboratories. A well equipped metallurgical laboratory is often sufficient to evaluate test coupons.

4.1.11. Preparation of full specification for the coupons

Most CMPs have used circular coupons, although of different diameters. The diameter of coupons used in the CRP was less than that specified in standards for conducting similar tests [2]. This was due to the restricted space in basins and for ease of transport of coupons and racks. Different types of racks have been used in the two phases of the CRP and in the regional project programme [3]. However, all the racks were made of stainless steel. The model of racks used in CRP-II and the regional project are recommended. These racks evolved from other designs. The insulating separator should be non-porous and resistant to radiation. It is recommended that dense alumina be used for manufacturing the insulating discs. Some guidelines with respect to coupon shape and size, rack designs and the insulating ceramic discs can be found in Section 3.

4.1.12. Definition of coupon configuration

Since the objective of a CMP is to determine the corrosion susceptibility of metal coupons in situations similar to, if not identical to, fuel cladding and/or other reactor/basin structural components, it is important that coupons be configured to simulate geometric conditions similar to that of fuel and components in the RR pool or storage basin. In this context, crevices existent between components in the RR or bimetallic contacts should be reproduced. Crevice-coupled coupons or bimetallic-coupled coupons should simulate crevices or bimetallic contacts mentioned above.

4.1.13. Specification if settled solids need to be evaluated

Most RR pool or storage basin water surfaces have dust, which if un-skimmed, become wetted and settle on surfaces inside the pool. It is therefore important, as part of a CMP, to determine the amount of settled solids as well as their composition. Details about the sources of settled solids, their effects on corrosion of coupons and components, procedures to collect and analyze the solids are in Section 5.2

4.2. THE EXECUTION STAGE

The **execution stage** involves all actions related to preparing the test coupons and racks, conducting the corrosion programme and evaluation of the coupons. Details of this stage can be found in the “Test Procedures” described in Section 3.3.

4.3. THE ACTION STAGE

The **action stage** involves: (1) correlation of the results of coupon corrosion evaluation and the water parameters; (2) correlation of the results of coupon corrosion with that of the spent fuel cladding and/or other structural components; (3) taking of appropriate actions, if necessary, to alter water parameters, reduce extent of settled solids and verify fuel cladding surface integrity.

5. RESULTS OF THE COORDINATED RESEARCH PROJECT AND REGIONAL PROJECT

5.1. MAIN RESULTS OF THE CRP AND REGIONAL PROJECT

Many of the observations in IAEA Technical Reports Series No. 418 (a comprehensive report on Phase I of the CRP) [2] have also been verified during the development of Phase II of the CRP and the Regional Project RLA/4/018. Main findings of the investigation carried out under these two activities may be summarized as follows:

- Coupon orientation has a marked effect on the corrosion behaviour of aluminium alloy coupons;
- Aluminium corrosion is directly dependent on the quality of the basin water. When the conductivity is higher, all corrosion effects are stronger;
- For longer exposure times the corrosion is more intense, as measured by the oxide thickness and depth of galvanic attack;
- Corrosion may be induced by particles settled on aluminium surfaces. Those coupons which are more exposed (upper surfaces of top coupons in vertical racks) have been the most affected by this phenomenon. If the aluminium surfaces are vertically oriented, so as to reduce the possibility of sedimentation, this effect is greatly diminished; and
- Pre-treating the aluminium surface to grow a protective oxide layer has demonstrated to be a significantly beneficial procedure. It inhibits the oxidation and also the particle effect.

The results obtained in laboratory tests, carried out in parallel to the surveillance programme in the basins, demonstrated the effect of settled particles on aluminium surfaces. This effect was more pronounced when the coupons were coupled to stainless steel. The next Section describes the study developed to correlate settled solids with corrosion on aluminium surfaces, followed by three case studies developed during the realization of the CRP.

5.2. EFFECT OF SETTLED SOLIDS ON THE CORROSION OF ALUMINIUM-CLAD RESEARCH REACTOR SPENT NUCLEAR FUEL

One of the main results of the CRP Phase II was the recognition that settled solids play an important role on the corrosion of aluminium-clad research reactor spent fuel when stored in water basins. To illustrate how settled solids affect the components of a reactor, Fig. 10 shows a test rack being immersed on a storage basin, and its withdrawal after 24 months. The quantity and nature of these solids vary. These solids settle on all surfaces inside pools or basins. Most of these solids eventually settle at the bottom of the pool or basin and are the main constituents of sludge. The origin or sources of these solids are mainly: (a) airborne dust; (b) corrosion products; (c) precipitated salts.

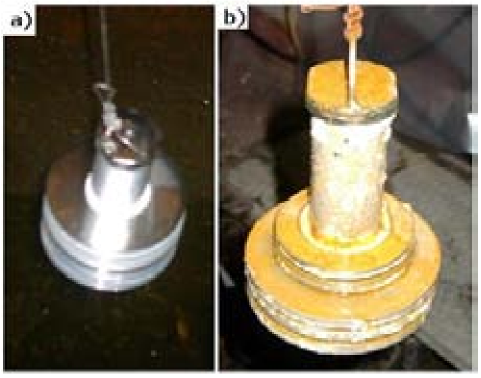


FIG. 10. (a) Test rack being immersed; (b) removed after 24 months from a spent fuel storage basin.

Airborne dust in the reactor hall or in the spent fuel basin hall settles on reactor pool or spent fuel basin (SFB) surfaces, as shown in Fig. 11. The amount and nature of this dust varies depending on the extent of control of the environment in the reactor or SFB hall and the nature of activities in the vicinity of the pool. The dust (fine solid particles) on the pool/basin surface floats until wetted by the water. Surface skimmers in reactor pools remove most of the floating dust. However, depending on properties of the solid, mainly density, it settles at the bottom of the pool or on any surface that it encounters as it descends through the pool or basin water. Solids settle faster in stagnant regions of the pool. Fine solid particles also have a tendency to agglomerate to form larger particles which settle faster. This tendency varies with the composition and density of the particles.

Corrosion products that form as a result of an electrochemical reaction between metallic surfaces in the reactor or SFB and dissolved oxygen in the water are another major source of solids. Depending on the metal, the extent and composition of the corrosion products vary. Corrosion products on metallic surfaces in contact with flowing water are easily detached and carried in the circulating water stream, often returning, depending on its size, to the reactor pool or basin.

FIG. 11. Spent fuel storage facilities with solids floating on water surface.

Another source for solids is when salts precipitate. Salts precipitate when their solubility limits in the solution are exceeded. Dissolved salts are often found in municipal waters or untreated waters from other sources. The water used in most RR installations and SFB is deionized and of good quality, and seldom presents salt precipitation.

In most research reactor installations, the pool water chemistry is monitored and the water circulated. The extent of circulation affects settling of the solids. Filters in the cooling circuit retain the solids that otherwise would have settled. Spent fuel storage facilities that are in a different parts of the RR hall, often share the same water as that of the main RR pool. However, in many such storage facilities the water is comparatively more stagnant and therefore, more solid particles settle. Withdrawal, or under water shifting, of immersed reactor components disturbs the normal pattern of water movement and results consequently in movement of settled solids or solids in suspension. Shifting of components near the pool bottom provokes a cloud of settled solids or sludge and these resettle on any surface in the vicinity.

Other sources of dust that settle on the reactor pool surface are: (a) movement of cranes in the reactor room to shift components, (b) opening of doors that lead to less controlled areas, (c) immersion of inadequately dusted components into reactor pool for experiments or other purposes.

In away-from-reactor fuel storage facilities the above mentioned scene plays out to a greater extent. This is due mainly to these facilities being less controlled in terms of its environment, infrequent circulation of water, and overall reduced level of housekeeping. These facilities also have just one door with access to more dusty environments, compared with reactor pools that are within a building that is more closely monitored. Some away-from-reactor spent fuel storage facilities are underground facilities with simple sliding steel doors. Also, depending on the geographical location of these facilities, condensation of moisture leads to corrosion of these doors and peeling of corrosion products that drop on the basin water surface and eventually on stored spent fuels.

Experimental work carried out in this CRP included the exposure of horizontally and vertically oriented coupons to spent fuel basins. Comparison of the corrosion behaviour of the coupons exposed vertically and horizontally revealed that horizontal coupons corroded considerably more than vertically oriented coupons. This lent clear proof to the role of settled solids on the corrosion of Al coupons. Further observations such as (a) increased corrosion of upward facing surfaces of coupons compared with downwards facing surfaces of the same coupon and (b) increased corrosion of upwards facing surfaces of coupons higher up in a vertical rack, compared with the upwards facing surfaces of other coupons further down in the rack, lent further proof to the dominant role of settled solids on the corrosion of Al coupons and, by extension, on the corrosion of spent fuel element surfaces.

Consequently, in this CRP further studies were undertaken to: (a) determine the amount of settled solids and the rate of settling of these solids at the various sites; (b) determine the composition of the solids and (c) role of specific settled solids on the nature and extent of corrosion of Al alloys.

5.2.1. Evaluation of settled particles on coupon surfaces

This study consisted of placing a collector in the vicinity of the corrosion coupon racks in the spent fuel basins of the participating countries for a predetermined time, followed by its withdrawal and determination of the amount of the solids and its composition.

5.2.1.1. The settled solids collector

A variety of collectors have been used by the participants of the CRP and regional project, and a few are shown in Figs 12 to 14. The main criterion in the design of the collector was to prevent the collection of solids floating on the pool/basin surface at the time of withdrawal of the collector. This criterion took into consideration that not all material floating on the pool surface is wetted and settles on surfaces. Regardless that some participant used acrylic, the recommended material for construction of the collector was stainless steel or aluminium.

FIG. 12. Collector used at CCHEN, Chile. Material: AISI 304 stainless steel; dimensions: diameter 24.9 cm, height: 10 cm, Area: 486.9 cm2.

FIG. 13. Collectors used in: (left) CDTN, Brazil. Material: Acrylic, Dimensions: diameter: 18.9 cm, height: 3.8 cm, Area: 280.6 cm2. (right) IPEN, Peru. Material: Aluminium, Dimensions: Diameter: 20 cm; Area: 314 cm2.

FIG. 14. Collector used in Romania. Made of Aluminium, with diameter equal to 20 cm (314 cm^2).

Details about the collectors such as material of construction, dimensions etc., used by the participants of the CRP and regional project can be found in the respective country reports, presented at the end of this publication.

Collectors were installed and removed after a specific duration (varied from 4-6 months) at the different sites. Figure 15 shows collectors in position at two different sites. The collectors were positioned close to the immersed corrosion racks. Prior to removal, the lids of the collectors were put in place. After removal from the reactor pool or the SFB, the water in the collector was stirred and then allowed to pass through a filter. The sediments were collected on a filter paper, dried in an oven at 100ºC for 24 hours, weighed, mixed and representative specimens examined in a scanning electron microscope (SEM). The appearances of solids retained on filters or in the collector are shown in Fig. 16. An extreme case of sediment or sludge accumulation at a spent fuel basin is shown in Fig. 17. The techniques used for analysis varied, depending on access to or availability at a specific site. The techniques used were: (a) energy dispersive spectroscopy (EDS), (b) X ray diffraction (XRD), (c) X ray fluorescence (XRF), (d) mass spectrometry.

FIG. 15. Photographs showing the position of the collectors in: the reactor pool in Thailand (left) and the spent fuel basin in Romania (right).

FIG. 16. Settled solids on a millipore filter (left) and the collector (right).

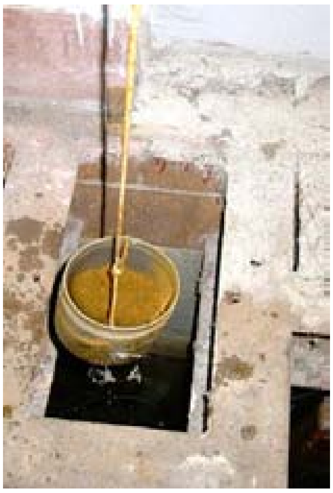


FIG. 17. A bucket of sludge being removed from the bottom of a spent fuel storage basin.

The rates of sedimentation of solids at different sites and their composition and/or constituents are shown in Table 5. Overall the solids consisted of oxides of aluminium, iron, silicon and calcium. This indicates that the main sources of solids are construction debris, atmospheric dust and corrosion products of aluminium alloy and steel components in the pool or basin. Other constituents in the settled solids are site specific, like plant tissue in Thailand and deionizer resin in Kazakhstan. At some sites more detailed examination of the morphology of the solids and determination of composition was carried out. Figure 18 shows the scanning electron micrograph and X ray diffractogram of solids collected in the storage section of IEA-R1 research reactor at IPEN, Brazil.

5.2.1.2. Research reactor settled solids and their effect on corrosion of aluminium alloys

Severe fuel deterioration has been verified during long interim aluminium clad spent fuel storage in some water basins [10]. In some cases, the occurrence of particle sedimentation on the fuel surface has been suspected to have had some influence. This effect has been verified during the various surveillance programmes organised by the IAEA, utilising test racks with aluminium coupons. Pits of about 50 µm in depth were produced in the Central Storage Facility (CSF) of Argentina [2], after 60 days of exposure to water with chloride content in the range of 10-20 ppm and conductivity near 70 µS/cm. More surprisingly, small pits were also encountered on coupons immersed in the RA6 Basin Pool, in Argentina, where the conductivity is less than 1µS/cm and there are no detectable amounts of chloride ions. In all these cases, the influence of particles of dust or other material settled on the coupon's surfaces was considered to be the main cause of the phenomenon. This suspicion was later confirmed by comparison with results obtained in coupons vertically oriented, in which the incidence of this type of defect is considerably lower [11].

Table 5. Rates of formation of settled solids and the composition and/or constituents of the solids

Participant	Rate of sedimentation ($\mu g/cm^2$/month)	Composition or constituent of settled solid
RECH-1, Chile.	58.6	Al; SiO_2 (quartz);SiO_2 (cristobalite) $(Ca,Na)(Si,Al)_4O_8$ (anortite)
RECH-2, Chile.	1.5	SiO_2 (quartz)
CDTN, Brazil.	18.1	Amorphous $CaCO_3$ (calcite); Fe_3O_4 (magnetite), SiO_2 (quartz); $CaMg(CO_3)_2$ (dolomite)α-$Al_2O_3.3H_2O$ (gibbsite), Fe_2O_3 (hematite) $Mg_3Si_4O_{10}.(OH)_2$ (talc)
ININ, México.	17.666	Iron oxides (hematite, magnetite), aluminosilicates, sodium and calcium carbonates
IPEN, Peru.	107.92	Sc, V, Cr, Mn, Fe, Ni, Cu, Mo, W
România.		Fe, Zn and Cd
SF pool, Thailand.	195	Fe, Al, SiO_2, Cu, Ba; Light particles of plant tissue, bio-mass floating in water with some fine dust. Main component is iron.
Reactor pool, Thailand.	141	Fine light brown dust. Main component is iron.
Cooling pool, Kazakhstan	36.000	Deionizing column resin
Storage pool, Kazakhstan	12.000	Deionizing column resin
RA3 Decay Pool, Argentina	19.5	Silicon oxide and combined Si, Al and Fe oxides
IPEN, Brazil	178.2	56.79 Al_2O_3, 21.04 SiO_2, 4.93Fe_2O_3, 2.35 CaO, 1.6 Cr_2O_3, 0.76 TiO_2, 0.6 NiO (wt%)

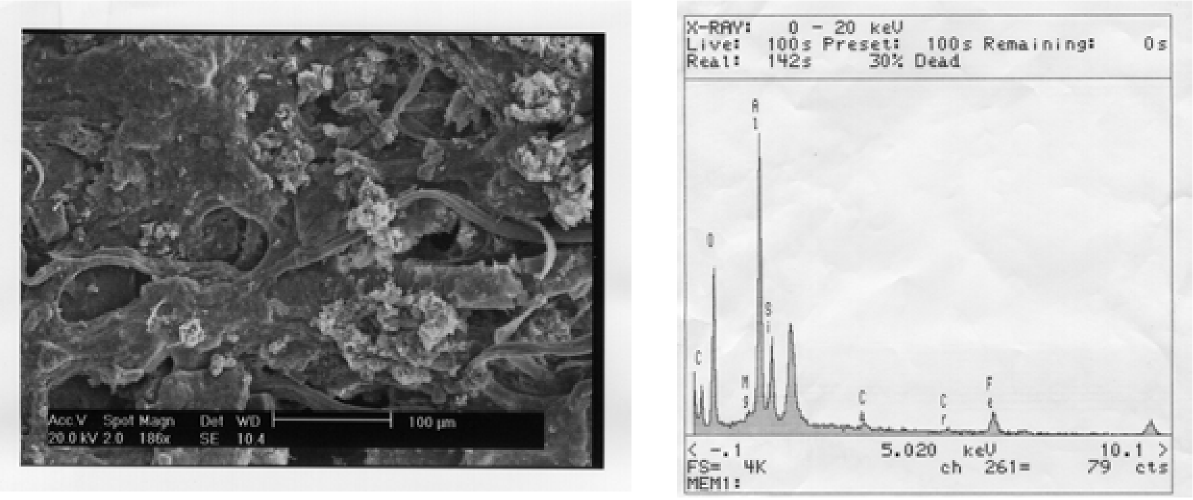


FIG. 18. Scanning electron micrograph(left) and X ray diffractogram (right) of solids collected from the spent fuel storage section of the IEA-R1 reactor in IPEN, Brazil.

Aluminium and its alloys present a good corrosion resistance in pure water due to the formation of a very protective oxide layer. This film is stable only in a certain pH interval, roughly from 4 to 8[1] (see Fig. 19). Any time the water pH is outside this range, metal dissolution will be produced, provided the electrode potential takes values above the equilibrium. In the presence of certain aggressive anions, mainly chloride, the passive layer will become unstable whenever the potential surpasses the pitting potential (E_P), and localised attack will occur. The lower E_P the more susceptible the aluminium is to pitting corrosion.

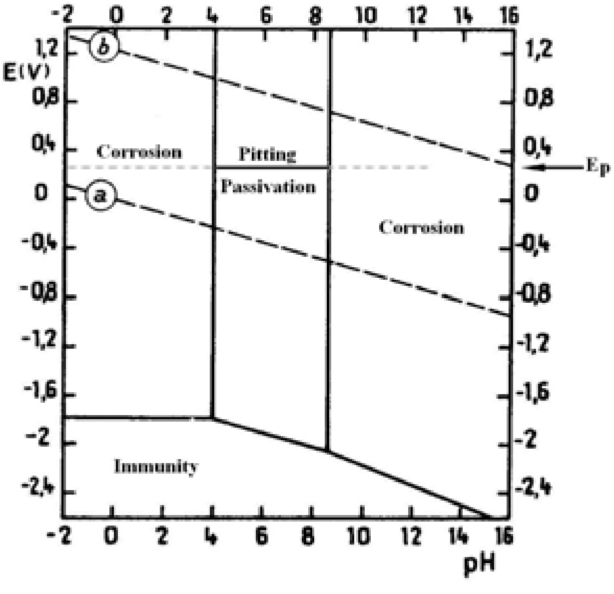


FIG. 19. Stability range of aluminium oxide.

Aluminium and its alloys are prone to suffer of pitting corrosion also in the presence of other anions, like sulphates and nitrates. E_P essentially depends on the aggressive anion concentrations, being lowest for chlorides. In the event of having a crevice, E_P values can go further down, making more probable the onset of corrosion.

---

[1] Note that, as described in Section 2.2, the recommended interval for pH is between 4.5 and 7.

Aluminium and its alloys are not expected to suffer of pitting corrosion in environments totally free of these species. Also, since most corrosion events involve electrochemical processes, the lack of conductivity strongly reduces the chance for their progress. Several different mechanisms could apply in the particle-induced corrosion of aluminium:

(1) The sediments could be of alkaline nature or lixiviate alkaline products, what will give place to chemical attack.
(2) A crevice could be formed under the sediments, which will promote corrosion in the presence of aggressive species.
(3) Conductive particles may serve as cathodes for the oxygen and hydrogen reactions, which in term will entail a local pH increment, causing metal dissolution.

The first option would apply when particles of materials like concrete are involved. Particles of this material have been shown to produce attack on the surrounding area when settled on aluminium surfaces [12]. Figure 20 shows an example of the result of this interaction after 40 days of exposure in nuclear grade demineralised water.

The crevice corrosion susceptibility of Aluminium alloys is very well known [13]; it would operate in case there are dangerous dissolved ions. In a pure water environment it is possible that these could be supplied by the sediments themselves. As for the local cathodic reaction effect this mechanism has been largely proven at microscopic level [12]. Figure 21 shows a cavity produced by enhanced cathodic reaction on a Fe containing intermetallic particle; the dissolved metal precipitates at some distance, forming an oxide rim.

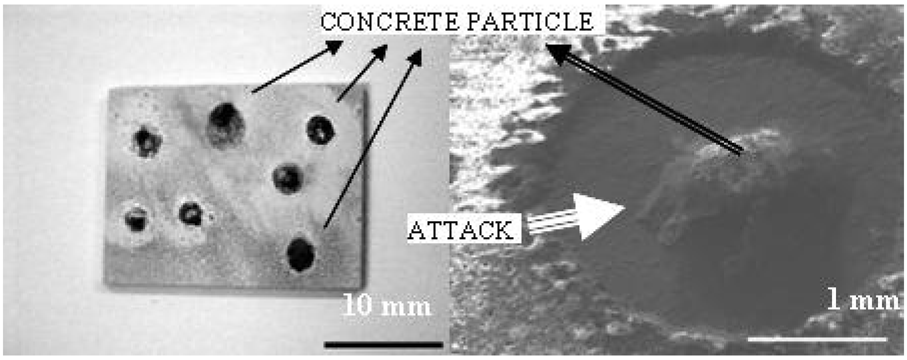


FIG. 20. Corrosion effect of concrete particles on 6061 alloy in pure water.

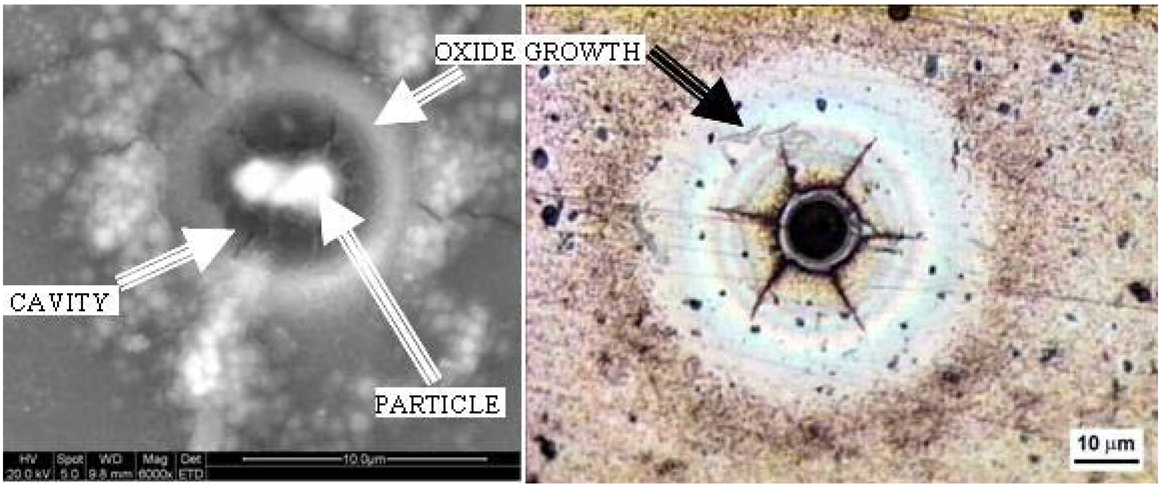


FIG. 21. Microscopic cathodic reaction effect. Left: SEM image. Right: optical microscope image.

There are indications that this mechanism could be feasible at a macroscopic level too [12]. Some attack can be generated around magnetite particles deposited on AA 6061 samples after 40 days under pure water, but not if the particles are made of magnetite, as seen in Fig. 22.

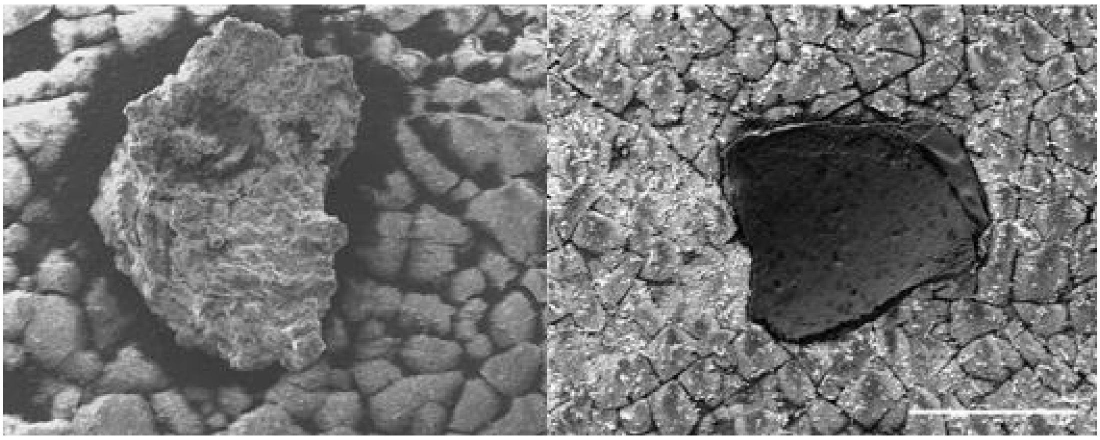


FIG. 22. Different behaviours of iron oxide particles. Left: hematite. Right: magnetite.

The conductivity under deposits could be higher than in the bulk due to various reasons: Mg_2Si second phase particles tend to dissolve easily even in pure water, releasing ions; also, there can be dissolution of some of the sediment's constituents. The characteristics of the solution inside the gap, then, could be particularly deleterious for aluminium alloys.

The sediment induced pitting produced in the laboratory resembles the effects observed in the basins to some extent, but not the penetrating corrosion observed on spent fuel stored for many years. In order to establish the influence of sediments in short term experiments, immersion tests were performed in waters simulating that of some of the surveyed basins. In some cases, the electrode potential was increased to help accelerating the process [14]. This was accomplished connecting aluminium 6061 samples to stainless steel wire cathodes, as depicted in Fig. 23. The anode-cathode area ratio was calculated so that the mixed potential is below but near 50 mV, the measured pitting potential of the aluminium alloy in the tested environment. The effect of hematite, magnetite and glass particles deposited on the aluminium surface was studied in Sodium Chloride solutions of various concentrations.

FIG. 23. Assembled galvanic couple in a cell (left). Sample detail, showing deposited oxide bits (right).

5.2.1.3. *Effect of hematite deposits*

No pitting was found in isolated samples after the full immersion 60 days period, in a solution containing 40 ppm of chloride, as seen in Fig. 24. Only stains remain in the zones that were covered by the oxide particles, but no signs of attack. On the contrary, in only 7 days pitting was produced in samples coupled with stainless steel cathodes. Figure 25 shows the different aspects encountered in the various environments used. There is an obvious effect of chloride concentration. The more concentrated is the solution stronger is the corrosion attack on the samples. Both pitting and crevice corrosion are visible in waters with higher chloride contents, but the second form was exclusively produced under the resin, in the border of the working area.

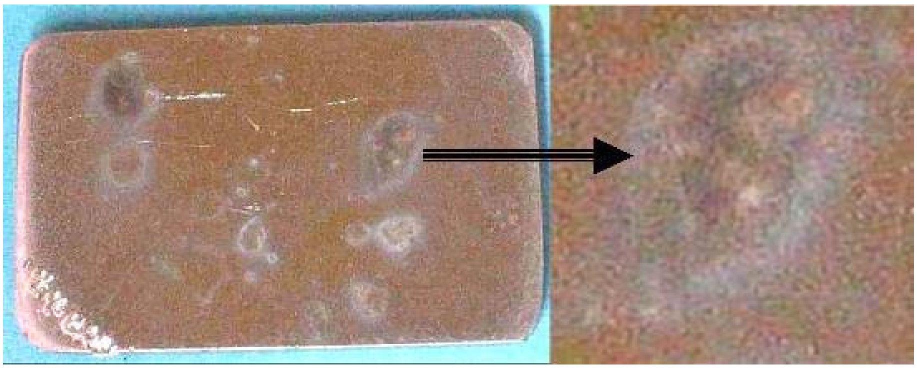


FIG. 24. Aspect of uncoupled sample immersed in NaCl 0.1N after 60 days. Stains were left by the sediments (left). No pitting is observed in the detailed view (right).

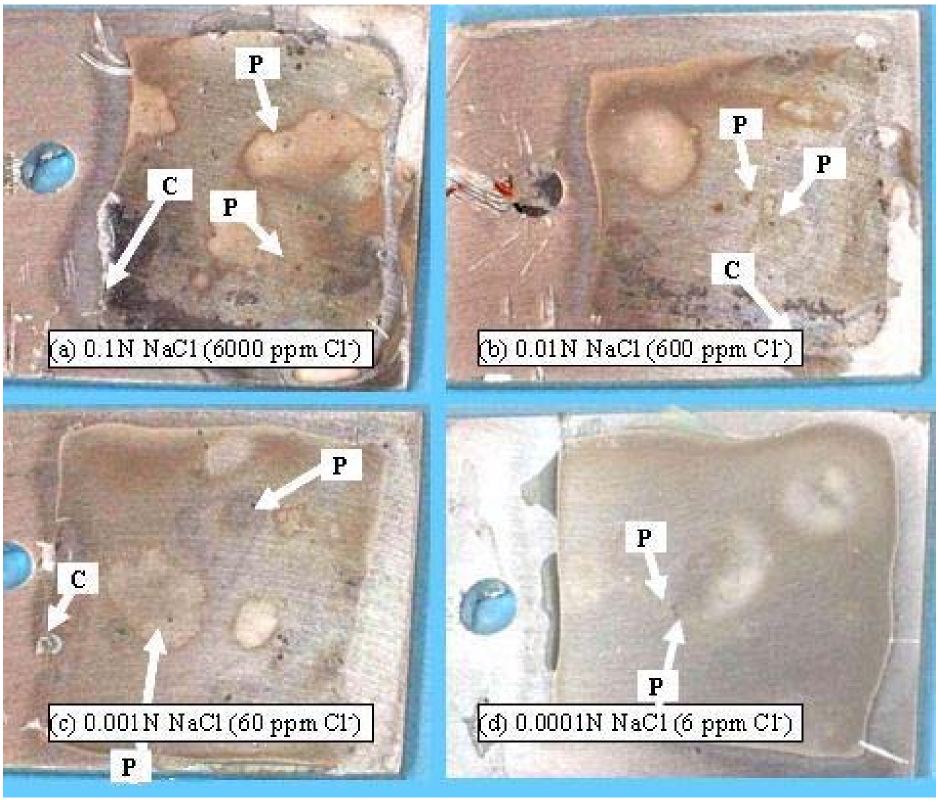


FIG. 25. Surface appearance of aluminium samples with hematite sediments after 7 days of exposure to NaCl solutions of different concentrations. Pitting is indicated with "P" and crevice corrosion with a "C". The stains produced by the sediments are still visible.

In the solutions with higher chloride concentration, pits are formed both under the deposits and on the free surface. However, in the 0.001N solution very few of them grew outside the sediments and in the 0.0001N one, all the encountered sites are located beneath the particles. Figure 26 shows one of these regions in detail. No attack is observed outside the zone covered by the sediment, but the entire portion that was coated presents signs of corrosion. The point where the pitting seems to be visible with the naked eye appears to be a composition of many tiny pits gathered in a cluster.

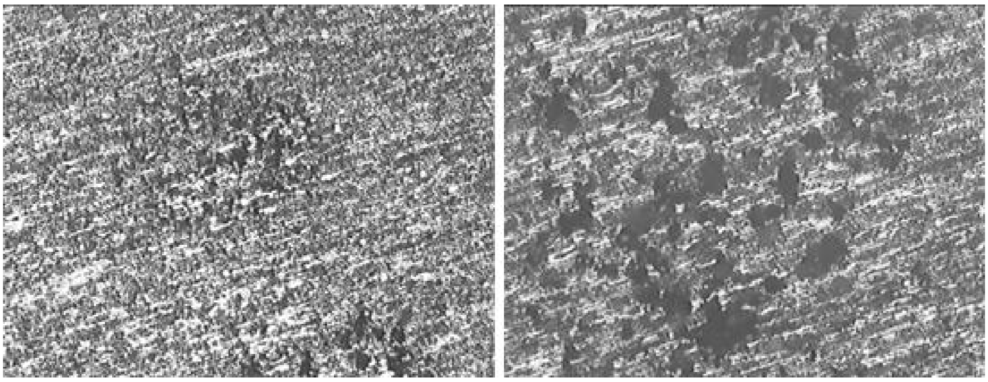


FIG. 26. Detail of surface under a deposit for a sample tested in 0.0001 N NaCl (FIG. 25). Left, region under deposit (200 μm). Right, detail of pitting attack (points marked with "P") (100 μm).

5.2.1.4. Effect of magnetite deposits

Figure 27 shows a sample tested with magnetite deposits during 7 days in a 0.001N NaCl (60 ppm chloride) solution, before and after removing the particles. Pitting corrosion is observed beneath and around sediments, but only associated with those fragments that transformed from magnetite to hematite, as indicated by the colour change. The easiness of non transformed particles removal, which did not leave any sign on the metal surface, indicates poor surface adherence, which in term may imply poor electric contact with the aluminium alloy.

FIG 27. Sample tested with magnetite deposits, before (left) and after (right) cleaning. "A": transformed particle, "B": non-transformed particle. Arrows indicate pitting attack.

5.2.1.5. Effect of glass deposits

The main objective of utilising this material is to study the effect of particles that may be inert from the electrochemical point of view. In Fig. 28 a sample immersed 7 days in a 0.001N NaCl solution can be seen, before the termination of the test, with the glass bits on. Pitting can be appreciated through the transparent sediments, as indicated by the arrows.

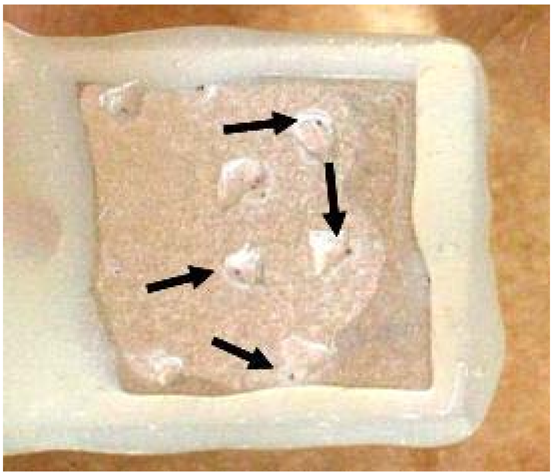


FIG. 28. Sample with glass particles. The pits can be seen through.

A magnified view of one of these sites can be appreciated in Fig. 29a. Two contiguous pits can be seen. The metallographic cross section is depicted in Fig. 29b, where the depth of the attack can be established: 66 and 104 µm for each pit.

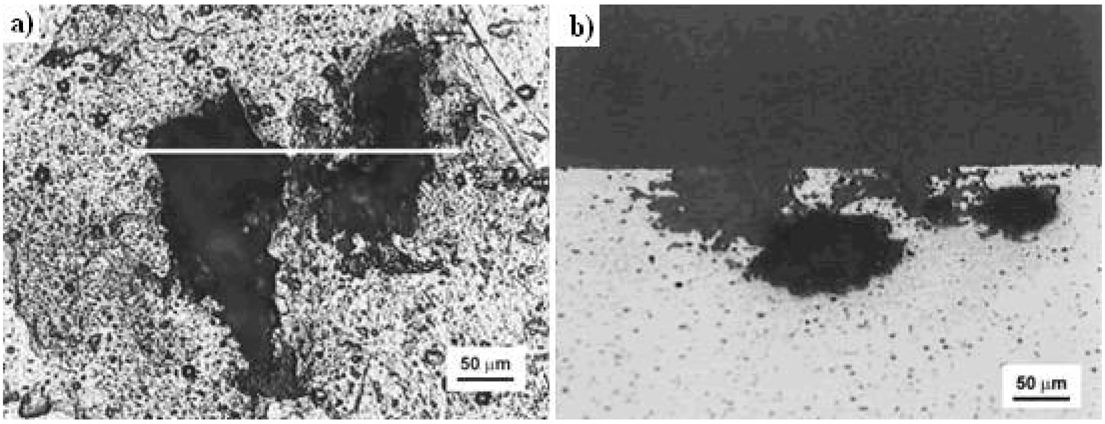


FIG. 29. (a): Pit formed under glass in a 0.001N NaCl. (b): Cross-cut of the same pit, along the marked white line.

5.2.2. Discussion on the effect of settled solids on the corrosion of aluminium-clad research reactor spent nuclear fuel

Given the relatively short experiment time, 7 days, it becomes quite clear that spent fuel elements that are stored for periods of decades can easily undergo this kind of environmental assisted degradation. It is quite probable that, with enough time, corrosion may proceed even in less corrosion inducing conditions.

In limit situations, the presence of sediments can trigger the onset of pitting, which would not otherwise occur. Taking into account the lack of corrosion signs in isolated samples immersed up to 60 days in solutions containing 40 ppm of chloride ions, these results clearly demonstrate the deleterious synergistic effect of galvanic contacts and sediments. This condition facilitates the start of the corrosion process, which in the most diluted environment, with chloride concentrations around 0.00001N, takes place only beneath the deposits. This exactly reproduces the situation in some spent fuel storage sites, in which the bundles are positioned inside steel structures, with no provision for electrical isolation [10]. Note that the chloride content of the 0.0001N solution is about 6 ppm, concentration that can easily be reached in some storage sites.

These results explain the occurrence of pitting in aluminium coupons immersed in some basins for periods of the order of 2 months [2], as well as the degradation of the fuel itself. In the particular case of the Central Storage Facility of CNEA in Ezeiza, Argentina [2], the fuel remains seated into steel tubes and the fall of iron oxide particles -produced by corrosion of carbon steel components that are present in the facility- on the stored fuel has been verified. In those conditions the oxide speckles would be mainly composed of hematite, which are shown to be capable to produce pitting in the most diluted solutions. For higher chloride concentrations, even inert particles are capable of starting the corrosion process by forming a crevice.

The following conclusions can be derived from this experience:

(1) Iron oxide particles that settle as sediments on spent fuel aluminium alloy surfaces, can produce pitting corrosion in waters with low amounts of chlorides, like 6 ppm, even when the corrosion potential is lower than the pitting potential in that environment.
(2) Other particles may also trigger the onset of pitting at higher concentrations, by a simple crevice effect.
(3) Galvanic contact with steel strongly influences corrosion susceptibility, by means of increasing the corrosion potential of aluminium to a point in which the pitting process is triggered under the sediments, what would not happen otherwise.

5.2.3. Recommendations to minimize effects of settled solids on stored aluminium-clad research reactor spent fuel

Settled solids in a research reactor pool or in a spent fuel basin consists of Al oxide and a variety of other oxides. Aluminium alloy fuel cladding and structural components are the main source of the Al oxide in the solids. Most of these oxides on an Al surface play the role of an inert solid and cause corrosion of the surface through formation of oxygen concentration cells. Some of the alkaline oxides, concrete, cement etc. found in the settled solids, result in corrosion of the Al surface through direct involvement. The composition of the settled solids at a specific site helps indicate the possible source. Knowing the source of dust, steps can and be taken to reduce or eliminate it. The actions are usually site specific. However, some general recommendations can be made to reduce or eliminate airborne dust from settling on the pool or spent fuel basin water surface. These include:

(1) Increase in efficiency and/or frequency of circulation of water through a filter.
(2) Use of a skimmer and filter system.
(3) Increased water flow in the vicinity of stored spent fuel.
(4) Use of stainless steel doors or lids for away-from-reactor storage basins.
(5) Use of corrosion protection schemes, if plain carbon steel doors or lids are used.
(6) Installation of double doors, in case of a dusty atmosphere just outside a spent fuel basin.
(7) Periodic vacuuming of all surfaces in the reactor hall and inside the pool, in the case of in-reactor basins.
(8) Improved air circulation and filtering of air pumped into the reactor hall.
(9) Reduction in water turbulence in the basin, to prevent resettling of solids on other surfaces.

5.3. CASE STUDY 1 - A COMPARISON OF WATER QUALITY IN CENTRAL STORAGE FACILITY (CSF) VERSUS WATER QUALITY IN REACTOR POOL OF RA6 RESEARCH REACTOR

During the development of the CRP, the influence of water quality on aluminium corrosion had become evident. In Argentine storage sites there was a wide range of water conditions, depending on whether the installations were active or passive, periodically surveyed or without maintenance, etc. The extreme conditions were found in RA6 reactor pool (included in the study due to the long fuel residence in the core, more than 20 years) and in some channels of the central storage facility (CSF). RA6 water is maintained according to reactor operation standards, with continuous on-line conductivity monitoring. Any time this parameter reaches a value of 0.8 μS/cm the purification process is started and only interrupted when the value goes down to about 0.4 µS/cm. If this level cannot be reached in a reasonable time, the purification resins maintenance procedure is performed. In CSF, instead, water upkeep activities were halted in the past, due to the increased water activity generated as a result of fission product leakage. Consequently, water conditions worsened as time passed.

5.3.1. The Central Storage Facility (CSF)

The first indication of fuel deterioration in CSF came to light in the early eighties, when a set of spent fuel elements was selected for use in the new RA6 reactor. In that occasion, a visual fuel inspection revealed that the elements were covered with a brown layer, mainly consistent of iron oxide coming from the corrosion of the carbon steel channel shielding caps [2]. Then, during the development of the IAEA CRP on Corrosion of Aluminium Clad Spent Fuel in Water (Phase I), it was demonstrated that 50-100 µm deep corrosion pits could be produced on aluminium coupons in periods as short as 60 days [2]. Finally, during the full inspection performed for the take back programme operations, the real corrosion state of the stored fuel was established [10]. Massive corrosion was found to have taken place in several fuel elements, which included in many cases fuel plate perforation, nuclear material loss of containment and fission products release. A few examples can be seen in Fig. 30.

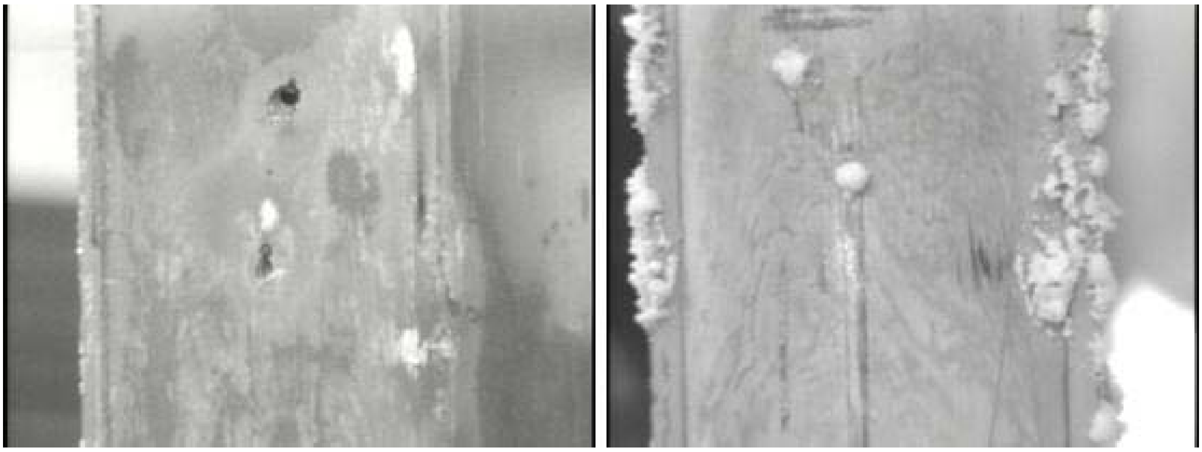


FIG. 30. Massive pitting (left) and crevice corrosion (right).

There were large holes (one centimetre of diameter or more) visible in side plates, which could be the consequence of the development of pits. Also, there were cases of big corrosion nodules arising from inside scratches and crevices (Fig. 30). Galvanic corrosion was ostensible as well (Fig. 31). The bottom part of a fuel element appeared to be massively corroded in a place that could be a contact point between the steel channel floor and the resting fuel. In other appreciable case, severe dissolution had taken place around stainless steel screws used to assemble the element. The screws appeared to have gone out.

RA6 fuel, on the other hand, was visually inspected in several occasions through the years. No signs of corrosion were found, nor the water activity showed any abnormal increases during the reactor lifetime.

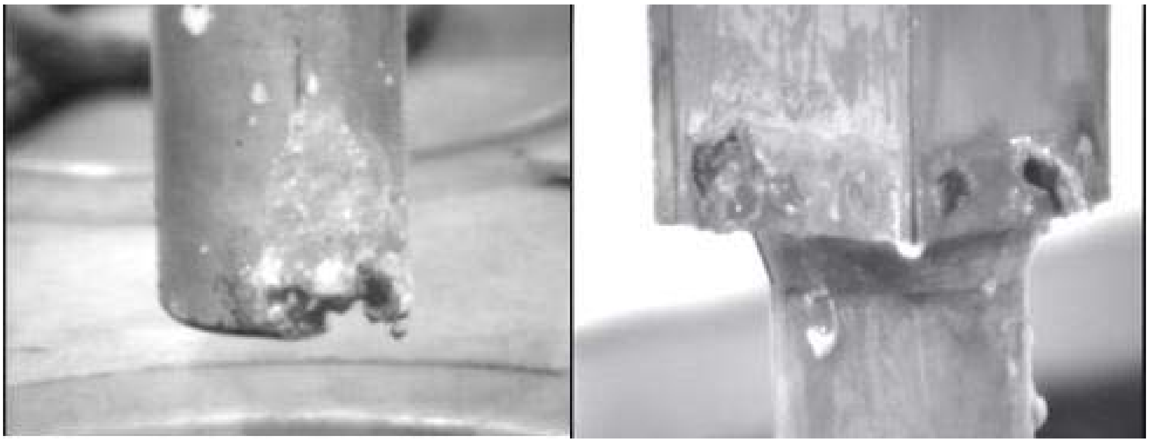


FIG. 31. Galvanic Corrosion in spent fuel. Left: contact with steel channel. Right: contact with steel screws.

As explained in Section 2, aluminium alloys are corrosion resistant in water, provided their protective oxide layer remains stable. They can withstand immersion in corrosive environments provided oxide aggressive species are not present. They can even tolerate to some extent exposure to some of these, as chlorides, with the condition that the electrode potential be below the pitting potential in that solution. For instance, pure aluminium will not corrode in sea water if is not electrically connected to a cathode. However, water in CSF reached so poor conditions, that all the elements responsible for corrosion were present: relatively high conductivity, high chloride content and contact with a cathodic electrode, because the fuel elements are placed inside steel channels, with close contact between the two metals. Given this dangerous configuration, the merging of falling particles on the aluminium alloy surfaces only serves to aggravate the situation, acting as corrosion triggers. Settled speckles are known to promote pitting in chloride containing solutions (see Section 5.2) mainly if the electrochemical potential is increased by galvanic contact. This must have been the mechanism by which the corrosion processes begun in CSF. Once started in an installation without maintenance, it will only generate increasing water conditions deterioration. Even so, the proportion of damaged fuel over all the installation was rather low [2].

The relation between the four mentioned detrimental elements (high conductivity, presence of chlorides, galvanic contact and sediments) and aluminium corrosion has been corroborated by two situations. In first place, after the water purification performed in the line corresponding to channel #97 of CSF, the monitoring programme revealed that coupon corrosion had been halted in that specific position, although there still was some particle sedimentation present. Corrosion nodules simply would not develop as fast in low conductivity water as they did in other channels.

5.3.2. The storage facilities at RA6

The second situation was produced in RA6 in 1999 and was reported in the Final Report of the first CRP [2]. At that time operations were being performed in the RA6 reactor in order to construct a BNCT facility. During this period a lot of dust was produced in the reactor room’s atmosphere, as a result of masonry work, etc. This circumstance became evident in the water chemical analysis of RA6 reactor pool water, which showed a peak of total soluble solids (TSS) corresponding to the building time, as shown in Fig. 32. The basin pool, located in the same building, was also affected; given the intermittent nature of the maintenance procedure in this facility, the parameters variation were more noticeable, as depicted in Fig. 33.

In Fig. 33, the withdrawal time of a corrosion test rack is marked. It was right after the peak in the water parameters excursion. Some special corrosion marks were encountered on the top coupon of the rack, on the surface pointing upwards. It consisted on a stained region of about 1 cm by 2 cm, in which the oxide had been removed. Tens of tiny pits were visible by eye. Some of them showed to be somewhat penetrating when viewed with a magnifier, as illustrated in Fig. 34.

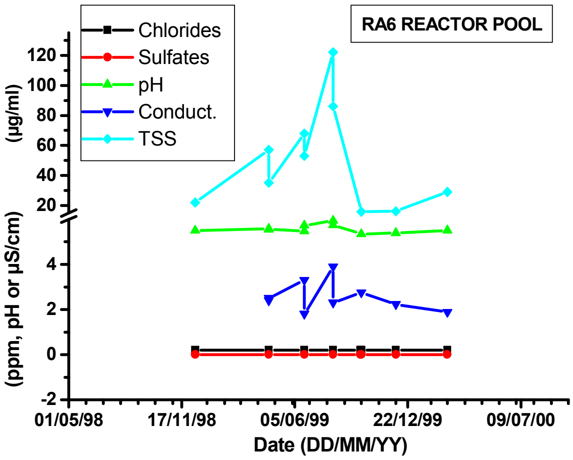


FIG. 32. Evolution of chemical variables in RA6 RP.

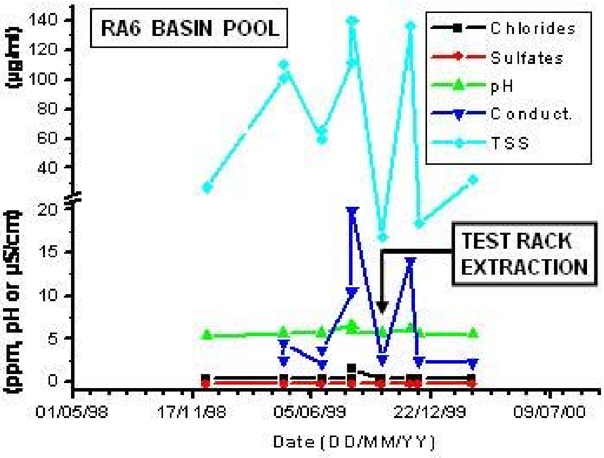


FIG. 33. Evolution of chemical variables in RA6 DP.

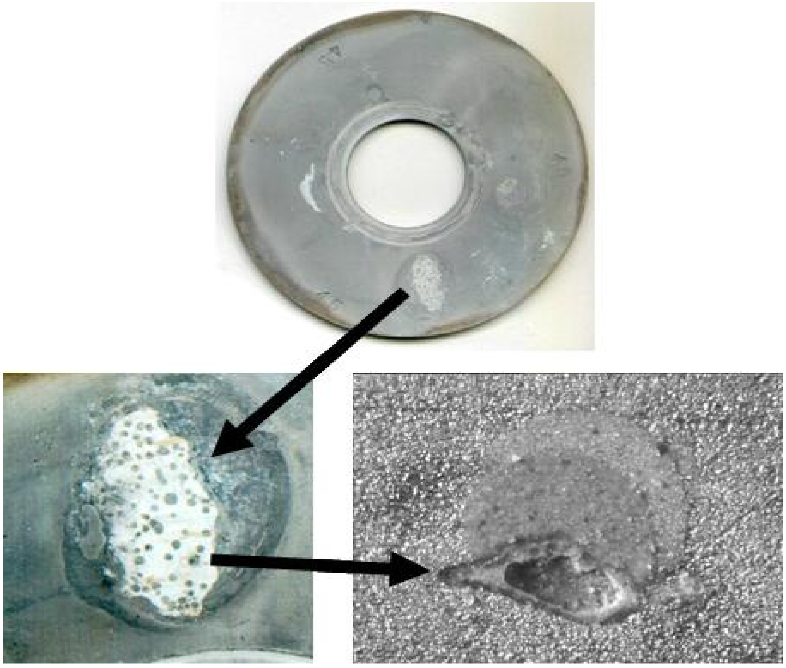


FIG. 34. Pitting observed on an AA 6061 coupon immersed in RA6 BP.

Never before had an aluminium coupon tested in this facility presented this sort of feature. Nor were they seen again after the problem was solved. The occurrence of this phenomenon demonstrated that pitting can be initiated by particle sedimentation even in very pure nuclear grade water. The fact that this event could be reported and explained is an excellent example of the advantage of having a continuous surveillance programme in places where nuclear fuel has to stay for long periods immersed in water.

As a conclusion, there are four main elements concurring to aluminium clad fuel corrosion. They are water conductivity, dissolved aggressive ions, galvanic couples and sediments. Each one separately does not seem to be able to produce significant damage. When two or more of these ingredients are simultaneously present the synergistic effect can jeopardise the integrity of the fuel elements, mainly the nuclear material and fission products containment capacity of the fuel plates.

5.4. CASE STUDY 2 - STAINING OF ALUMINIUM SURFACES IN THE IEA-R1 RESEARCH REACTOR

IEA-R1 is a pool type, light water moderated, beryllium and graphite reflected research reactor, at the “Instituto de Pesquisas Energéticas e Nucleares” IPEN, which is part of the Brazilian Nuclear Energy Commission. Although designed to operate at 5 MW, IEA-R1 has operated at 2 MW during most of its life. The reactor is used to perform research in nuclear and solid state physics, radiochemistry and radiobiology, production of radioisotopes and to offer irradiation services. The facility has a wet storage section located at one end of the reactor pool. The wet storage section contains racks to store spent fuel elements (FE) and also FE while loading and unloading the reactor core. The racks were originally made of aluminium sections bolted together and suspended from the walls of the pool at a depth of 6 meters. In 1977, when the reactor pool liner was changed from ceramic tiles to stainless steel, the aluminium racks were replaced with stainless steel racks. In 2003 the stainless steel racks were lined with an aluminium alloy to minimize bimetallic contact and thus galvanic corrosion between the fuel and the rack.

The typical basin water parameters, which are the same as that of the reactor pool, is shown in Table 6. These parameters are maintained with the help of two water purification systems. More details about the water purification systems can be found in the respective country report at the end of this publication.

Table 6. Typical values for basin water parameters

Parameters	Units	Typical Values
pH	-	5.5 to 6.5
Conductivity	µS/cm	< 2.0
Chloride ions	ppm	< 0.02
Iron ions	ppm	< 0.001
Sodium ion	ppm	< 0.4
Temperature	^{o}C	25 to 40
Total solids dissolved	ppm	< 2
^{99}Mo	Bq/L	< 310
^{131}I	Bq/L	< 90
^{133}I	Bq/L	< 430
^{132}Te	Bq/L	< 95
^{239}Np	Bq/L	< 750

5.4.1. The problem – Staining of aluminium surfaces

In May 2004, the IEA-R1 reactor manager expressed concerns that all aluminium alloy surfaces that are normally bright and light grey was staining and turning dark grey. This was first observed on structural components and later on fuel cladding surfaces. The reactor staff also reported that the reactor which had operated for almost 45 years at 2 MW was being operating at its rated capacity of 5 MW.

5.4.2. Utilization of coupons from the CRP and RLA regional project to identify the cause of the problem

During this period, activities related to this CRP as well as the RLA regional project, were in progress. The activities consisted of exposing coupons of various aluminium alloys in test racks in the spent fuel storage section of the reactor pool, followed by coupon evaluation to determine the extent of corrosion. Figure 35 shows the position of the test racks in relation to the reactor core and the fuel storage racks. Test racks were immersed for periods of up to 3 years starting July 2002, with programmed withdrawals of one rack a year in each of the projects. One set of racks was withdrawn in July 2003 and the second set of racks of the RLA project was scheduled for withdrawal in July 2004. These racks contained mainly AA 1100 and AA 6061 coupons with composition as shown in Table 7. To throw more light on the unforeseen staining of the aluminium surfaces in the IEA-R1 reactor, the Chief Scientific Investigator of the CRP and RLA project in IPEN decided to withdraw one test rack, (R2) of the RLA project, two months prior to its programmed withdrawal i.e. after 22 months of exposure instead of the scheduled 24 months. It was withdrawn in May 2004. The rack was disassembled and the coupons were prepared for examination as per procedures outlined in the test protocol.

The temperature, conductivity and pH of the reactor pool were monitored at regular intervals. Fig. 36 shows graphically the variations in these parameters during the period 2002-2004.

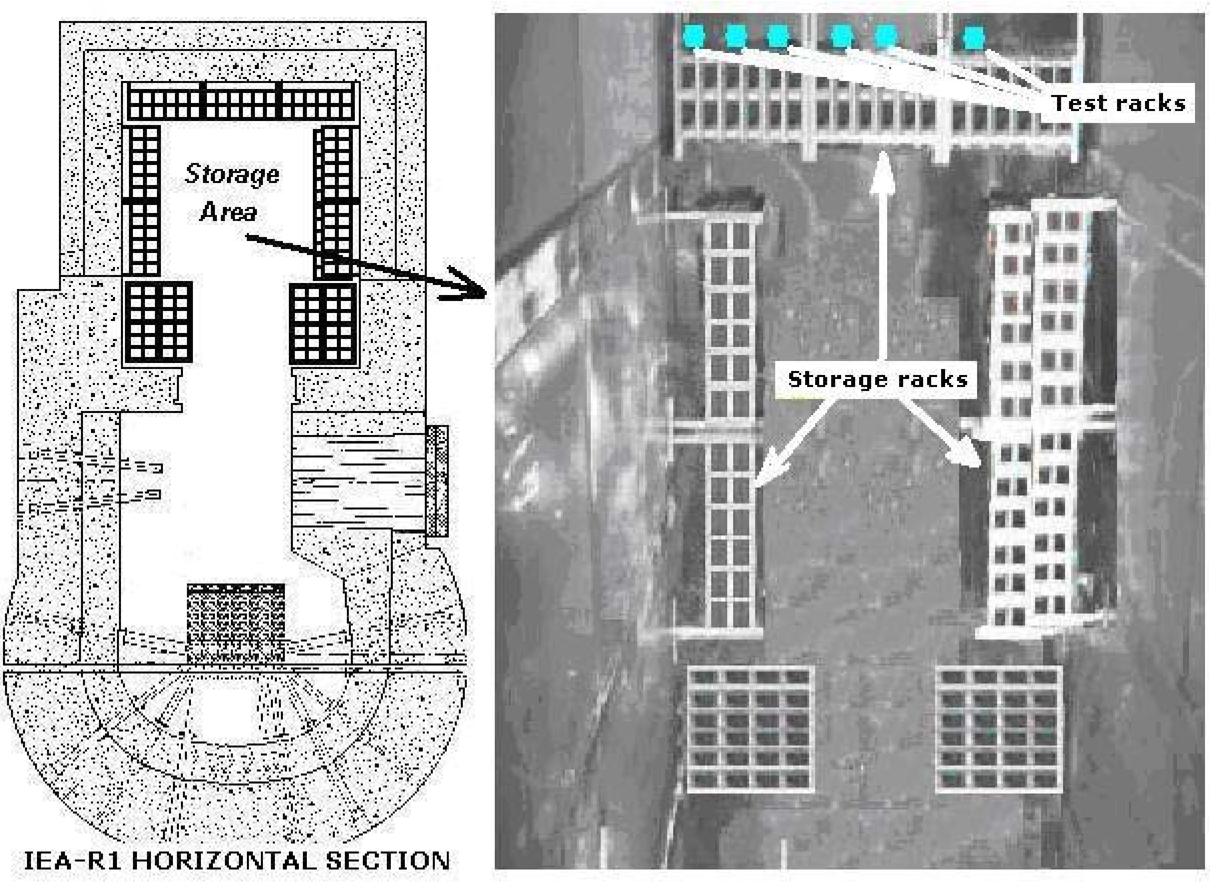


FIG. 35. Position of test racks in IEA-R1 reactor spent fuel storage section.

Table 7. Chemical composition of aluminium alloys (in %)

Alloy	Cu [%]	Mg [%]	Mn [%]	Si [%]	Fe [%]	Ti [%]	Zn [%]	Cr [%]
AA 1100	0.16	<0.1	0.05	0.16	0.48	0.005	0.03	0.005
AA 6061	0.25	0.94	0.12	0.65	0.24	0.04	0.03	0.04

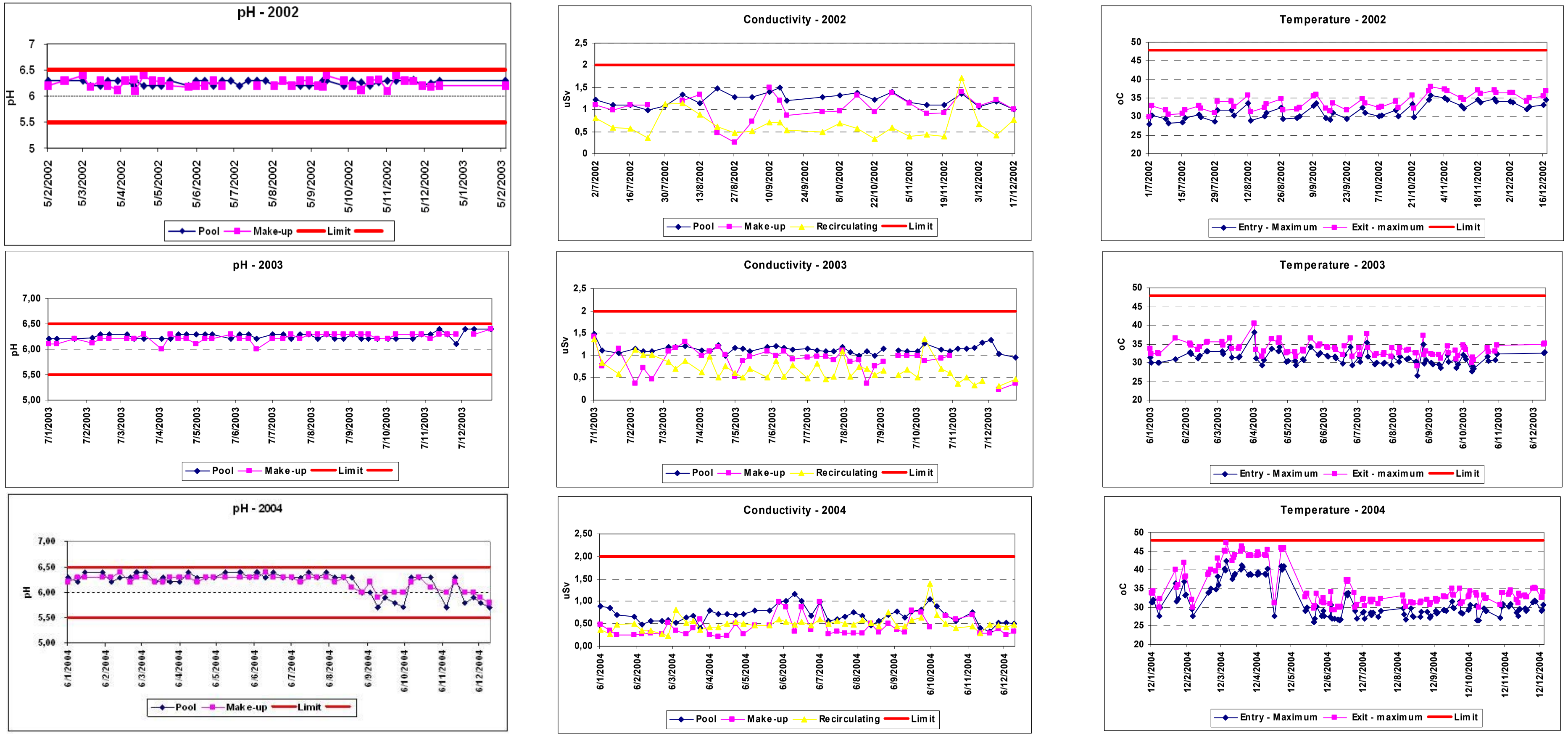


FIG. 36. pH, conductivity and temperature of the IEA-R1 reactor storage basin water in the period 2002-2004.

5.4.3. Coupon evaluation

The coupons of rack R2 were placed next to corresponding coupons from rack R1 withdrawn after 12 months of exposure for comparison and as shown in Fig. 37. It was evident that the surfaces of coupons of R2 were darker and stained. The extent of staining was similar to that observed on the other Al surfaces in the reactor.

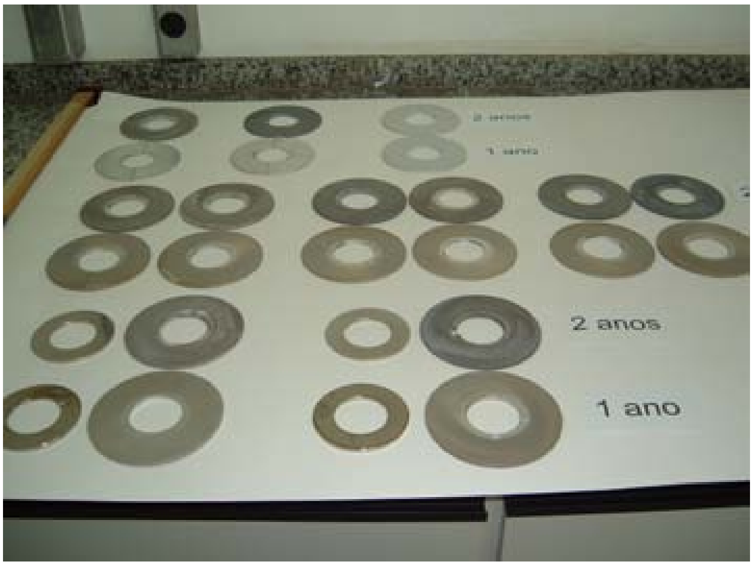


FIG. 37. Photograph of coupons exposed for 12 (1 year) and 22 months (2 years) to IEA-R1 SFSS.

The 3 water parameters shown in Fig. 36 during the period when the two test racks were exposed to the reactor coolant was scrutinized. These parameters were well within their prescribed limits. However, the only parameter that showed some deviation was temperature, which during the period July 2003 (when R1 was withdrawn) and May 2004 (when R2 was withdrawn) was in the range 22-50ºC compared to the range 25-38ºC. The latter was the temperature range during the period when R1 was exposed. Coincidentally, during the period January–May 2004, the reactor power had been raised from 2 MW to 5 MW. The main concern was that, this reactor was designed to operate at 5 MW and the pool temperature was within the specified limits, also shown in Fig. 36. The increased average pool water temperature during this above mentioned period was attributed to insufficient cooling of the primary water in the heat exchanger. Even though the pump was adequately dimensioned for the increased flow rate necessary for reactor operation at 5 MW, the flow valves were partially closed to prevent excessive vibration of the heat exchanger tubes. This in turn resulted in inadequate water flow through the reactor core and consequent gradual increase in pool water temperature. Although the reasons for the pool water temperature increase had been deciphered, there were still concerns about the staining of aluminium surfaces exposed to the pool water that had increased by just 10ºC.

5.4.3.1. Coupon surface analysis

To determine the cause of staining of Al surfaces in the reactor, specimens of the two alloys, AA 1050 and AA 6061, exposed for 12 and 22 months (nominal 2 years) were taken for examination in a scanning electron microscope (SEM) and for X ray diffraction (XRD) analysis. The SE micrographs of the surfaces of AA 1050 and AA 6061 exposed for 12 and 22 months are shown in Figs. 38 and 39. Energy dispersive spectroscopic analysis of these surfaces are shown in Figs. 40 and 41 revealing significantly higher oxygen peaks on surfaces of the two alloys exposed for 2 years compared with those exposed for 1 year.

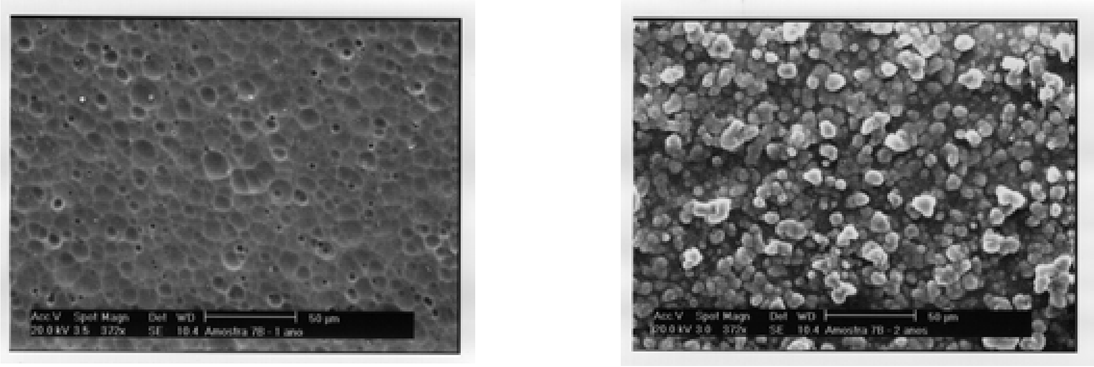


FIG. 38. Scanning electron micrographs of AA 1050 coupon exposed for 12 months (left) and 22 months (right) to IEA-R1 SFSS.

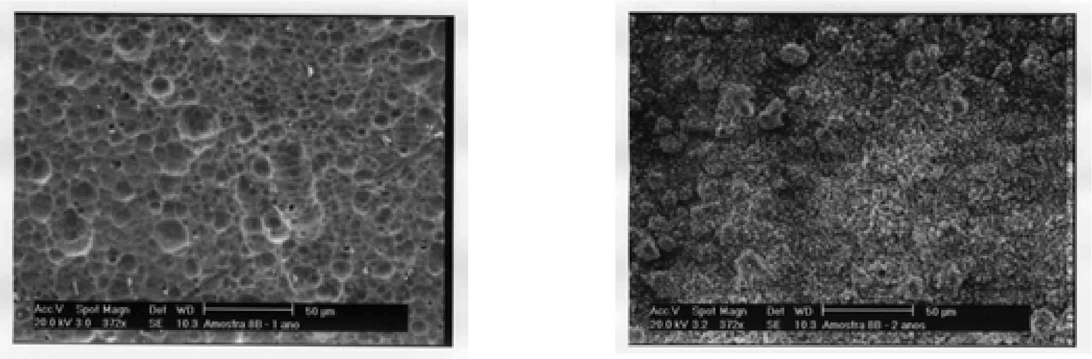


FIG. 39. Scanning electron micrographs of AA 6061 coupons exposed for 12 months (left) and 22 months (right) to IEA-R1 SFSS.

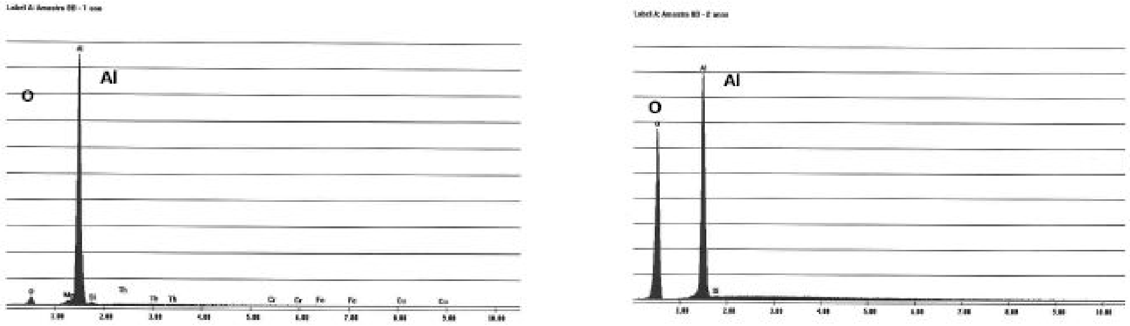


FIG. 40. EDS results of the surfaces of AA 6061 coupons exposed for 12 (left) and 22 months (right).

The X ray diffractorgrams of the surfaces of AA 1050 and AA 6061 exposed for 12 and 22 months are shown in Fig. 42. The surfaces exposed for 22 months (2 years-nominal) revealed peaks of the aluminium oxide ‘bayerite’ where as that exposed for 12 months did not. The SE micrographs in Figs. 38 and 39 also revealed marked differences in the morphology of the oxide formed on the coupon exposed for 2 years, compared with that formed on the coupon exposed for one year. Bayerite, a type of Al oxide, forms at temperatures below 70º C. The type of oxide formed on the AA 1050 surfaces exposed for 12 months was ‘boehmite’ were as that formed on the surface of the same alloy exposed for 22 months was bayerite.

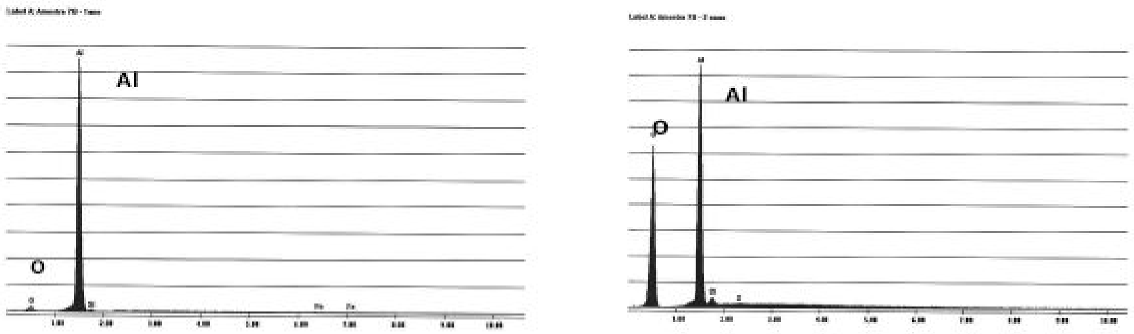


FIG. 41. EDS results of the surfaces of AA 1050 coupons exposed for 12 (left) and 22 months (right).

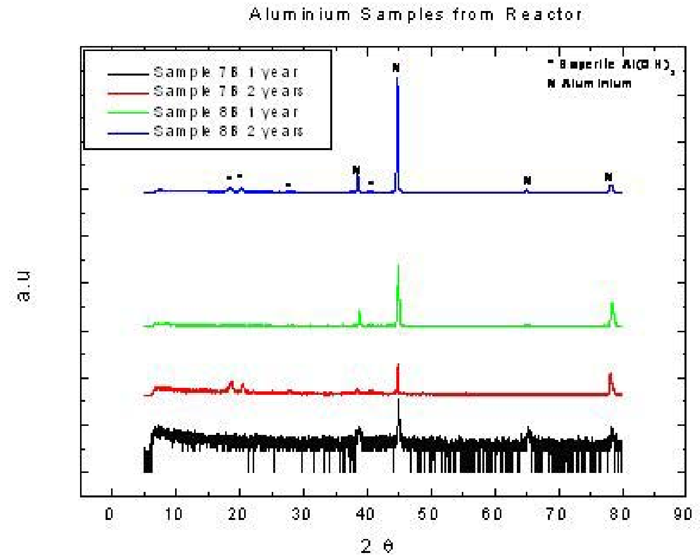


FIG. 42. X ray diffractograms of the surfaces of coupons exposed for one and two years to the reactor pool.

5.4.4. General discussion

The IAEA corrosion monitoring programme helped throw light on reasons that lead to staining of Al surfaces in the IEA-R1 reactor pool. The staining was attributed to formation of the Al oxide ‘Bayerite’ on surfaces exposed to the reactor pool water at higher temperature. Although the temperature difference was just 10ºC, this was sufficient for the nature of the Al oxide formed on Al alloy surfaces to change and display a different colour. Even though the reactor personnel were aware of the higher pool water temperature, it was not cause for alarm. However, when the surface colour of various aluminium components started changing, they started wondering if the increased reactor power was liberating products that lead to staining. The corrosion monitoring programme put to rest these concerns also.

The outcome of this overall exercise was that the primary coolant was not being adequately cooled, due to insufficient heat exchange capacity of the heat exchanger. This was eventually attributed to insufficient primary coolant flow rate. The coolant flow rate was reduced to prevent excessive vibrations of the heat exchanger tubes at high flow rates. This resulted in gradual increase in pool water temperature.

This study clearly highlights some of the unexpected advantages of an ongoing surveillance programme. Since a surveillance programme of this nature monitors not just the corrosion behaviour but also other environmental aspects that affect corrosion, it does have the advantage of aiding other reactor operations in unforeseen ways.

5.5. CASE STUDY 3 - THE CONJOINT EFFECT OF IMPROPER WATER CHEMISTRY, IMPROPER STRUCTURAL MATERIALS, INADEQUATE MAINTENANCE AND EXCESSIVE SEDIMENTS ON CORROSION IN SPENT FUEL POOL

5.5.1. The RA research reactor spent fuel storage pool

This Section describes the RA reactor spent fuel storage pool at the Vinča Institute in Rep. of Serbia and the events and practices, (or the lack of it) that led to the overall situation being a case worth studying. The pool is 6.5 m deep, with four inter-connected basins and an annex to the fourth basin. Each basin has a rectangular cross-section, with about 1.60 m wide (except basin no. 1 with width of 1.25 m) and 3.80 m long. Each basin can be separated from the underground transport channel in the storage room, i.e., closed (but not hermetically) by double doors lined with carbon steel plates. The concrete walls, with thicknesses between 0.60 m and 1.3 m, and the concrete bottom of the pool are lined with 1 cm thick stainless steel plates. Fig. 43 shows a schematic diagram of the storage pool. To increase spent fuel storage capacity, aluminium barrels (ALB) were made in the mid-1960s at the Vinča Institute to store fuel elements. Each ALB was filled with 150 to 180 (maximum) spent fuel elements distributed in aluminium tubes. Cadmium strips were inserted into the ALB to assure sub-criticality, and then the ALBs were filled with de-mineralised water and closed. In the period 1962 to 1984, about 4900 LEU fuel elements were repacked into 30 ALBs.

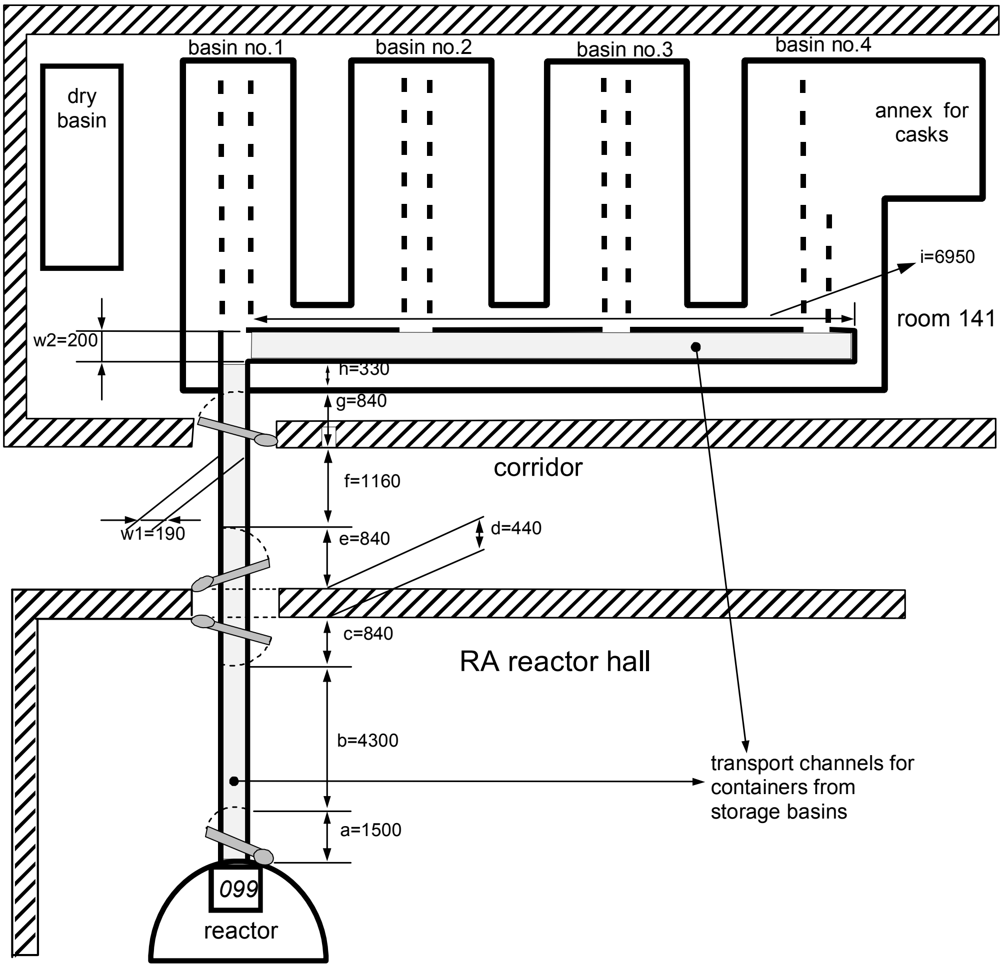


FIG. 43. Schematic diagram of the RA reactor spent fuel storage pool.

5.5.2. Condition of the water in the storage pool

Until 2000 or even later, the pool remained filled with about 200 m^3 of stagnant tap water. The pool is connected by a special underground water transport channel to the reactor block in the reactor room (hall). This channel permits transfer of spent fuel assemblies to the storage area. The water level in the pool and the transport channels is about 70 cm below ground level. Movable carbon steel plates cover the basins openings. In each basin, below the plates but above the water level, there is a carbon steel grid that was designed to position the stainless steel channel-holders (SSCH) with the fuel assemblies. There are also ventilation ducts in the concrete walls between the water surface and the carbon steel covers. Loss of water due to evaporation was compensated for, once a year, by adding tap water to the pool. A carbon steel structure (including two pairs of carbon steel coaxial tubes) that was designed for decontamination of fuel assemblies were in basin no. 4 at the edge of the annex, as shown in Fig. 44. This structure was heavily corroded and it was removed in 2006. For years, floating dust and other debris were observed on the stagnant pool surface, as pictured in Fig. 45.

FIG. 44. Corroded steel structure inside of spent fuel storage pool.

FIG. 45. Water surface of the spent fuel storage pool.

First reference to poor quality water in the basin, based on visual inspection, can be found in the 1962 Annual Report of RA Operation [15]. Water purification was recommended but no action was taken. In 1984, low levels of ^{137}Cs activity was detected in the storage pool water, and this was attributed to leaks from a spent TVR-S LEU fuel element (called the ‘lost slug’) that was at the bottom of the pool since 1976. Figure 46 shows the slug being removed. Subsequently, periodic monitoring of chemical and radiation parameters of the pool water, installation of a water purification system and use of appropriate norms were proposed [16], [17]. From the time the reactor went into operation until 1994, no actions were taken to improve water quality conditions. In 1994, visual inspection of the storage pool revealed thick deposits of sludge on the walls and at the bottom of the pool. Realizing a need for thorough inspection of the storage facilities, experts from the IAEA, USA and the Russian Federation were called upon to help.

FIG. 46. Lost fuel slug being lifted from the bottom of the storage pool.

In 1995, for the first time, water samples from the basins and the SSCH, as well as sludge samples from the bottom of the pool and transport channel, were analyzed. The pool water chemistry was found to be inadequate for spent fuel storage and the gamma-ray specific activity of the samples showed the presence of ^{137}Cs and ^{60}Co nuclides. The water analyses revealed that the pool water was quite corrosive with respect to aluminium alloys. The electrical conductivity and chloride content were very high, and specific activity was about 100 Bq/ cm^3 for ^{137}Cs nuclide. This parameter was fifteen times higher in the sludge samples.

The specific activities of wet and dry sludge samples were measured in 1996 and 1997 at the Vinča Institute and in the IAEA Seibersdorf Laboratories [18]. The chemical composition of a few sludge samples was also determined in the radiochemical laboratories of the IAEA [18]. Iron, about 83% by weight, was the main component in the sludge and contributed to the dark red–brown colour. Corrosion of carbon steel components in the basin was considered to be the main source of Fe_2O_3. The sludge also contained a few percent of Pb, Cr, Mn, Ca and Zn, besides traces of Cu and Ni.

Visual inspections of TVR-S fuel elements in some SSCH and in fuel assemblies stored in the RA reactor core revealed deposits (determined later to be mainly aluminium hydroxide) covering the aluminium cladding of the fuel slugs. Visual examinations carried out as part of core unloading procedures in the period 1979-1984 revealed stains and surface discoloration on many spent fuel elements. Formation of deposits, stains and surface discoloration were attributed to inappropriate chemical parameters and reduced flow rate of heavy water, the primary coolant and moderator in the RA reactor core.

The measured ^{137}Cs specific activity in the water sample taken from the SSCH (in 1996) with the failed fuel slug was 50 ± 5 MBq/cm^3. About 10 % of all water samples taken in 2003 from SSCH containing fuel assemblies presented very high ^{137}Cs specific activity, in the order of MBq/cm^3 [19]. This indicated that the Al cladding of some fuel elements had breached due to corrosion, resulting in probable leak of fission products from specific fuel elements into the SSCH.

Underwater drilling of ALBs was proposed in 1998 to check: (1) fuel cladding integrity, (2) activity of water inside the barrels and (3) for probable high pressure inside the barrels due to corrosion and/or fission gases. Sixteen ALBs were drilled and they did not reveal high gas pressure inside the barrels. However, gas bubbles were observed when the ALBs were shifted underwater. Very high total specific activity from ^{137}Cs nuclide (0.5 to 1.5 MBq/cm^3) was measured in water samples taken from most of the drilled ALBs. This lead to the conclusion that not only the first barrier against fission products release (the cladding), but also the second barrier (the ALB walls), had breached. It was also suspected that the cadmium strips, placed in the ALBs to assure sub-criticality, could have reacted with aluminium, from the barrel walls and fuel elements, and contributed to increase corrosion inside the ALBs. Fission product leaks (mainly ^{137}Cs nuclide) from failed (due to corrosion) fuel elements to the water in the spent fuel storage pool were confirmed.

Serious measures were taken since 1997, to improve overall conditions and water quality in the storage pool. Debris and most of the sludge (about 3 m^3) were removed from the pool. Sludge immobilization was done using a technique and with equipment that was developed at the Vinča Institute for sedimentation and cementing of sludge-water mixture. Approximately 90 L of sludge-cement mixture was packed in 200 L barrels shielded on the inside by a 7.5 cm thick concrete wall. About 40 such barrels are stored as low-level waste in an interim waste storage area at the Vinča Institute. Further actions related to storage pool remediation included; (a) removal of the steel structure from basin no. 4 (in 2006); (b) removal of the balance of the sludge (in 2006 and 2007); (c) continuous purification of the pool water in basin no. 4 and the annex; (d) regular monitoring of chemical parameters of the water and specific activity of ^{137}Cs nuclide in the pool.

The water was always kept at ambient temperature for the long period (20-40 years) in which the spent fuel remained in the pool. The concentration of Al, Cu, Fe and NO_3 ions were determined sporadically. The Al, Cu and NO_3 ions contents were generally below detection limits of the methods and techniques that were used. During the period 1995-2002, chemical parameters of water samples taken a few times a year from the basins of the storage pool were measured. Subsequently it became a monthly activity.

In 2003 the SSCH were thoroughly examined to ascertain the state of the fuel elements [19]. The ^{137}Cs and ^{60}Co specific activities, pH and electrical conductivity of water samples taken from about 200 SSCH were determined. The pH varied in the range 2.31 - 8.15. The electrical conductivity was in the range 13.5 - 21000 µS/cm (the latter value being that of the SSCH with pH = 2.31), but mostly, in the range 50 - 400 µS/cm. The concentration of specific ions in water samples taken from the SSCH was determined in only a few cases. This was due to the very high radioactivity level of the samples. The chloride ion content was found to be in the range 1 - 70 mg/L. The sulphate ions, in the range 29 - 35 mg/L, where as the Fe and Al ions were below detection limits of analytical techniques that were used.

Marked reductions in pH in 2000, 2001 and 2003 (shown in Fig. 47) was initially attributed to activities such as underwater drilling of ALB and SSCH, which were carried out in the pool. However the real reason for the decrease in pH is still a mystery. The respective country report at the end of this publication gives more information about the chemical parameters of the water in the storage pool.

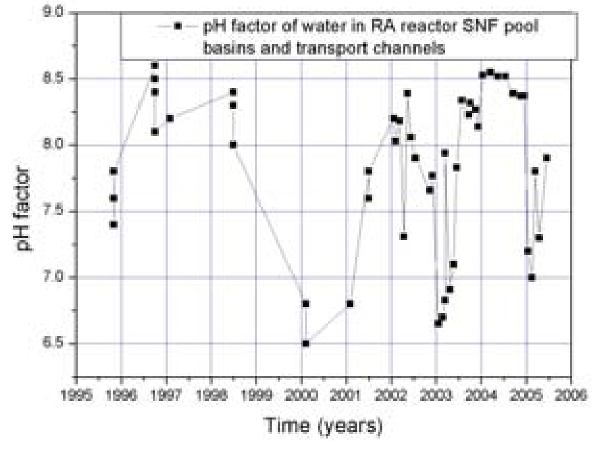


FIG. 47. Measured pH of water in SNF storage pool.

5.5.3. Sediments in the storage pool

One important activity carried out during the work of the CRP was the collection of sediments in the storage pool. The sediments were collected in basin no. 4 and the total mass of sediments was 5.038 ± 0.005 g. The sedimentation rate was reported to be 11.3 ± 0.5 mg/cm^2 per month. The consequence of high sedimentation rate associated with untreated water in the storage pool can be seen in Fig. 48, which shows CRP test racks being immersed and removed from the pool.

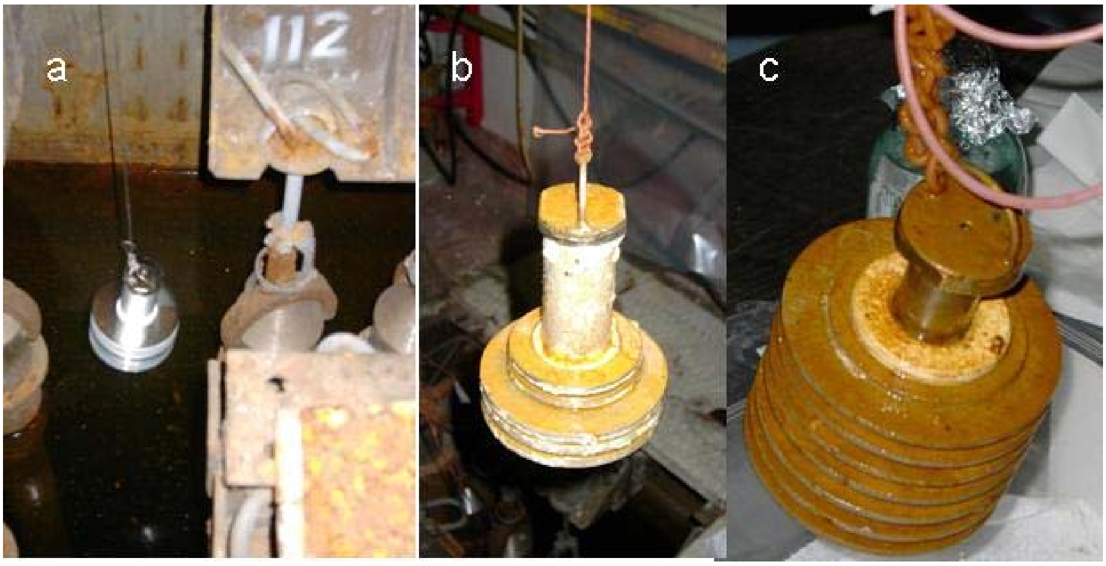


FIG. 48. CRP test rack being immersed in storage pool (a), removed after 24 month (b), and removed after 72 months (c).

5.5.4. General comments and conclusions

Prolonged use of water of improper quality, excessive amounts of floating debris on the pool surface, improper combination of metals and inadequate control of both water composition and settled solids lead to excessive corrosion of fuel cladding. This also leaded to cladding breach and contamination of the pool, stored fuels and test coupons. Figure 49 shows the appearance of some of the coupons withdrawn from the pool.

FIG. 49. Appearance of coupons after six years of exposure to the water on spent fuel basin showing White jelly-mushroom type sludge on front side of coupon AA 6061 of Rack#2.2 (left) and Dark-red sediments on front side of coupon SS 316 of Rack#2.2 (right).

The lessons learned from this exercise were: (1) use good quality water in spent fuel storage pools; (2) avoid the use of plain carbon steel as a material of construction of storage pools; (3) avoid the use of incompatible metals and alloys in the spent fuel storage pool; (4) prevent dust and debris from falling on pool surfaces; (5) avoid any accumulation of sludge in the pool; (6) conduct a corrosion monitoring programme.

6. SUMMARY

The overall objective of the CRP was to improve management, storage practices and storage procedures at facilities used for interim wet storage of research reactor spent fuel, through better understanding of the localized corrosion of aluminium cladding and the ranges of water chemistry parameters that provide resistance to corrosion.

The research work carried out during the CRP can be summarized as follows:

Aluminium alloy coupons (10 cm in diameter) made of different aluminium alloys were assembled in stainless steel racks with alumina separators. The separators prevented metallic contact between coupons and between the coupons and the rack. Site specific alloy coupons were added to the racks. Al alloy-Al alloy and Al alloy-stainless steel couples were included in the study to simulate crevices and bimetallic (galvanic) contacts. At many sites, racks were immersed both vertically (with its coupons horizontal) and horizontally (with its coupons vertical). The coupon racks were immersed in the spent fuel storage basins of the 11 participating countries for periods of up to 3 years. During this period, water parameters such as ph, conductivity, chloride content, temperature and other site specific ion contents were monitored. Overall, the quality of basin water at the different sites varied significantly, from very good to very bad. After pre-determined periods the racks were withdrawn from the basins, were photographed and the extent of corrosion of the coupons evaluated. The ph in the crevices of the crevice and bimetallic couples were also measured. The coupons were examined using an optical microscope. Pitting was the main form of corrosion and this was influenced by parameters such as water conductivity, chloride ion content, formation of galvanic couples with stainless steel and settled solid particles. Complementary tests were carried out to determine the composition of the settled solids and their effect on corrosion.

Many of the observations in IAEA Technical Reports Series No. 418 (a comprehensive report on Phase I of the CRP) were also verified during the development of Phase II of the CRP and regional project RLA/4/018. A summary of observations originated in Phase II of the CRP and RLA/4/018 are listed below:

(a) Pitting and galvanic corrosion are by far the most relevant degradation mechanisms observed;
(b) While galvanic corrosion in surveillance coupons can be clearly associated with coupling aluminium with other metals as stainless steel, a precise determination, based on experimental observations, of the conditions leading to pitting in coupons does not seem to be obvious;
(c) Pitting of coupons immersed in spent fuel basins seems to be caused by a number of different phenomena that may interact among them with synergistic or antagonistic effect, making very difficult to identify a clear cut cause-effect relation, for example in connection with alloy composition or water chemistry;
(d) Pitting extent is directly related to orientation of coupons. Pitting in horizontally oriented coupons occurs much more frequently than in vertically oriented coupons;
(e) All above mentioned observations point to a strong relation between pitting and occurrence of particle sedimentation on the metal surface.
(f) The relative amount of sediments collected in various surveyed sites is consistent with particle induced pitting mechanisms observed in spent fuel basins;
(g) It was possible to reproduce the particle induced pitting in the laboratory, in conditions similar to those existent in spent fuel wet storage; and
(h) Galvanic effects of unexpected intensity were observed in sites with good quality water. For these particular cases further investigation is necessary.

7. CONCLUSIONS

Eleven countries participating in the CRP and RLA/4/018 have improved the management and storage practices and procedures at facilities used for interim wet storage of research reactor spent fuel through better understanding of the localized corrosion of aluminium cladding and the ranges of water chemistry parameters that provide resistance to corrosion. Sustainable corrosion surveillance programmes have been implemented in all these Member States.

Conclusions of Phase I of the CRP have been verified by the results of CRP Phase II and RLA/4/018.

A number of general conclusions from both phases of the CRP and RLA/4/018 are summarized below:

(1) Water quality is by far the most important factor affecting aluminium clad spent fuel preservation during long term interim storage in water basins, because it influences all corrosion mechanisms. Recommended practices for the corrosion protection of aluminium cladding alloys are presented in [2] and in Section 2.2. Adequate control of dust and particles settling on aluminium clad spent fuel surfaces has to be added to the set of parameters that need to be monitored to ensure good water quality;

(2) Corrosion of aluminium clad spent fuel in water is also influenced to a certain extent by some design aspects of storage basins, for example:
   2. (a) Suitability of basin design in connection with water purification processes. In some basins with specific design constraints it is not possible to carry out efficient water purification, especially when a fast enough replenishment and mixing of water is not allowed.
   2. (b) Use of inappropriate materials can give place to water contamination due to corrosion (for example, basin parts made of carbon steel).
   2. (c) Contact of aluminium clad spent fuel with other metals should be avoided in the design, to prevent formation of galvanic couples, which promote aluminium corrosion.

(3) Implementation of corrosion surveillance programmes besides providing relevant information on the condition of the stored spent fuel may also be useful to encourage basin operators to improve water quality. For example, during implementation of the CRP and RLA/4/018 it was not unusual to note significant water quality improvement (as indicated by analysis of water chemical composition) in some sites, after corrosion surveillance programmes were initiated.

(4) The two phases of the CRP and RLA/4/018 have made evident long term aluminium corrosion mechanisms for which little previous reference existed. Basic research carried out by participating organizations to study these mechanisms succeeded in providing an improved interpretation of these phenomena. as a consequence, a better understanding of a number of issues associated to safe long term interim storage of research reactor aluminium clad spent fuel in water and a suitable methodology to tackle them has been achieved.

REFERENCES

[1] INTERNATIONAL ATOMIC ENERGY AGENCY, Research Reactor Database (RRDB), http://www.iaea.org/worldatom/rrdb/

[2] INTERNATIONAL ATOMIC ENERGY AGENCY, Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water, Technical Reports Series No. 418, IAEA, Vienna (2003).

[3] INTERNATIONAL ATOMIC ENERGY AGENCY, Spent Fuel Management Options for Research Reactors in Latin America, IAEA-TECDOC-1508, IAEA, Vienna (2006).

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

[5] POURBAIX, M., "Atlas of Electrochemical Equilibrium in Aqueous Solutions", NACE-CEBELCOR Ed., first ed. 1974.

[6] MULLER, I.L. AND GALVELE, J.R., Corros. Sci. 17, 179 (1977).

[7] MULLER, I.L. AND GALVELE, J.R., Corros. Sci. 17, 995 (1977).

[8] DE MICHELI, S.M., AND GALVELE, J.R., Metalurgia (ABM), 27, 589 (1971).

[9] GALVELE, J.R. and DE MICHELI, S.M., Corros. Sci., 10, 795 (1970).

[10] WESTINGHOUSE SAVANNAH RIVER COMPANY “Impact of Degraded RA3 Fuel Condition on Transportation to and Storage in SRS Basins”, WSRC-TR-2000-00152, July 2000.

[11] CORREA, O. V., et al., “Effect of coupon orientation on corrosion behaviour of aluminium alloy coupons in the spent fuel storage section of the IEA-R1 Research Reactor”, Proc of International Conference on Research Reactor Utilization, Safety, Decommissioning, Fuel and Waste Management, Nov. 2003, Santiago, Chile, IAEA, Vienna (2004), paper CN-100-44 http://www-pub.iaea.org/MTCD/publications/PDF/Pub1212/P1212_Papers_web.pdf

[12] RODRIGUEZ, S., et al.,"Study of the effect of sedimented particles on the corrosion behaviour of aluminium clad spent fuel during storage in water", Proc of International Conference on Research Reactor Utilization, Safety, Decommissioning, Fuel and Waste Management, Nov. 2003, Santiago, Chile, IAEA, Vienna (2004), paper CN-100-10 - http://www-pub.iaea.org/MTCD/publications/PDF/Pub1212/P1212_Papers_web.pdf

[13] RAMANATHAN, L.V., “Corrosão e seu controle” (In Portuguese), Hemus ed., São Paulo, Brazil (1988).

[14] HADDAD, R., LANZANI, L., and RODRIGUEZ, S., ”Mechanisms of cladding corrosion during long term interim storage of MTR spent nuclear fuel in water basins”, Proc. of 10th Intl Topical Meeting on Research Reactor Fuel Management (RRFM 2006), Sofia, Bulgaria, 30 April - 4 May 2006. - http://www.euronuclear.org/meetings/rrfm2006/transactions.htm

[15] THE “BORIS KIDRIČ” INSTITUTE OF NUCLEAR SCIENCES, “Annual Reports of the RA Reactor Operation,” (in Serbian) The Vinča Institute of Nuclear Sciences, Vinča, Yugoslavia (1960-1984).

[16] THE “BORIS KIDRIČ” INSTITUTE OF NUCLEAR SCIENCES, “Study on Spent Fuel Storage Pool of the Reactor RA,” Internal Report Z5.A1.4 (in Serbian) The Vinča Institute of Nuclear Sciences, Vinča, Yugoslavia (1984).

[17] ŠOTIĆ O., et. al., “Research Reactor RA – Operation and Maintenance Report in 1984,” Internal Report (in Serbian) The Institute of Nuclear Sciences "Boris Kidrič", Vinča, Yugoslavia (1984).

[18] INTERNATIONAL ATOMIC ENERGY AGENCY, “Appendix II to IAEA Mission Report to Vinča Institute in February 1997,” IAEA, Vienna (1997).

[19] ŠOTIĆ, O., PEŠIĆ, M., et. al., "Preliminary Analyses of the Feasibility of Spent Fuel Management (Phase 1)”, Vinca-NTI-114, Report on IAEA TCP Contract No. SCG/4/003-89102A ‘Safe Removal of Spent Fuel of the Vinca RA Research Reactor’, Vinca (2003).

ANNEX I. SYNOPSIS OF THE CRP (PHASE-I)

As explained in the Introduction to Section 1, in December 1994 a consultancy meeting was held at the IAEA in Vienna as part of an ongoing coordinated research project (CRP) entitled Irradiation Enhanced Degradation of Materials in Spent Fuel Storage Facilities, with the specific objective to discuss the problems related to research reactors. At this meeting, information was shared with the IAEA and participants from Europe and the USA on spent fuel corrosion issues at Savannah River Site (SRS) and other sites in the USA. At the SRS in the USA, long term corrosion surveillance tests were conducted to obtain information about the state of the fuel assemblies in the storage basins and also to control the water parameters to reduce, if not mitigate, corrosion of the fuels and other components. Based on this experience as well the major concerns of most RR operators the IAEA initiated a CRP on the corrosion of Al- clad spent RR fuel in water (Phase-I). This CRP was designed to address several issues presented by vulnerability assessments conducted at some of the spent fuel storage sites. The objectives set for the CRP were: (a) The establishment of uniform practices for corrosion monitoring and surveillance, (b) To provide a technical basis for continued wet storage of research reactor spent fuel, (c) To collect data to help in the prediction of lifetimes of fuel handling tools and storage racks, (d) The establishment of a uniform basis for the characterization of water in fuel storage basins, and (e) The development of an experimental programme with aluminium coupons, to study the influence of water conditions on the corrosion process of aluminium-clad research reactor spent fuel. Ten countries were invited by the IAEA to participate in the CRP, namely, USA, Hungary, the Russian Federation, Serbia, Thailand, China, India, Brazil, Argentina, and Pakistan. Research agreements with institutes in these countries were put in place for the work to be performed and the IAEA furnished a detailed work package and standard corrosion test samples to each scientific group.

For the experimental part of the work, the materials selected for testing were representative of typical aluminium cladding alloys used in foreign research reactor fuels, handling tools, and storage racks. Aluminium alloy types AA 5086, AA 1100, AA 6061, AA 6063, and SZAV-1 and AISI 321 stainless steel were produced by the KFKI Atomic Research Institute in Budapest, Hungary and supplied to the participants as round disk shaped coupons. These coupons were assembled in stainless steel racks with alumina disks as insulators between the individual coupons. In addition to the IAEA rack of corrosion coupons, many of the participants immersed an additional rack into their basin. This rack consisted of alloy coupons specific to the cladding alloys used on their research reactor fuel.

The corrosion coupon racks were immersed in late 1996 in the spent fuel storage pools of the different countries and these pools had a wide range of water chemistry. The environmental parameters were monitored periodically. The extent of corrosion of the first set of coupons were determined by the participants and reported after 18 months at an interim meeting held in Sao Paulo, Brazil. Pitting and crevice corrosion were reported to be the main forms of corrosion. Corrosion induced by iron deposits and other cathodic particles on the surface of the aluminium fuel was observed in a number of basins. The extent of pitting and crevice corrosion worsened when the Al coupons were galvanically coupled to stainless steel. Corrosion was generally not observed on coupons exposed to water with conductivity close to 1 µS /cm and with chloride ion concentration in the parts-per-billion range. However some sites reported pitting of the coupons even in high quality water.

A new set of corrosion racks were provided to the CRP participants in Sao Paulo in March 1998. Most of these racks were immersed in the different spent fuel basins by mid-1998. The coupons were examined visually for corrosion and at some sites when corrosion was detected the coupons were withdrawn from the basin for further examination. Also during the second round of tests, it was found that aluminium corrosion is strongly dependent of the water quality. Crevice corrosion was seen, as expected, in the crevices of some couples just because the pH was about 0.5-1.0 unit lower than that of the bulk water pH. In poorer quality water, more corrosion was observed. The bimetallic and crevice couples had to be forced apart because of oxide growth in the crevices. Results from both rounds of tests were presented by the participants at the final meeting held in Bangkok, Thailand, in October 2000.

In a parallel programme, corrosion of aluminium-clad spent fuel was studied extensively in the USA at the Savannah River Site in Aiken SC. Corrosion surveillance racks containing a large number of aluminium alloys were immersed in 4 different fuel storage basins under a wide variety of conditions and for long time exposures. Results similar to those obtained in the CRP were observed. Significant pitting and galvanic corrosion were observed in the early 1990's when water quality was poor. A concentrated basin management effort was then undertaken and the water quality improved quickly. Since 1994 with the new and improved storage basin conditions, no pitting corrosion was reported in any of the fuel storage basins at SRS. These results along with those of the CRP were reported in publication IAEA-TRS-418. [1]

A large amount of data about corrosion of aluminium-clad materials was generated from the CRP and the Savannah River Corrosion Surveillance Programs. This data indicated that the factors that contribute to corrosion of aluminium alloys in the spent fuel storage basins are:

- High water conductivity. (100-200µS/cm).
- High concentration of aggressive ions. (Cl^-).
- Deposition of particles that are cathodic with respect to aluminium. (Fe, etc.).
- Sludge (which contains Fe, Cl, and other ions in large concentrations)
- Galvanic coupling between dissimilar metals (such as stainless steel/aluminium).
- Scratches and imperfections in the surface oxide.
- Poor water circulation.

These factors influence corrosion of aluminium and its alloys and operate both independently and synergistically. Actually it is common knowledge that the most important key to prevent corrosion is to maintain good water chemistry. Water conductivity close to 1µS/cm generally ensures that the aggressive ions, like chlorides, are in the parts-per-billion range and significantly reduces the corrosion of aluminium alloys. Nevertheless, during the programmes it was found that good water chemistry did not always guarantee that corrosion will be prevented, as it was observed from the tests conducted in the RA6 decay pool in Argentina. In these tests iron oxide particles that deposited on the coupon surface caused pitting corrosion even in high purity water. This was also observed in tests carried out at other fuel storage basins. Pitting corrosion associated with deposited particles can be due to the setting up of galvanic and/or oxygen depletion cells.

Based on the information from the IAEA sponsored CRP and the corrosion surveillance programme at SRS, further understanding of the corrosion of aluminium-clad spent fuel was obtained. Guidelines for corrosion protection of cladding alloys were developed and are part of IAEA-TRS-418 [1]. A discussion of the fundamentals of aluminium alloy corrosion in wet storage of spent nuclear fuel is presented in Chapter 3 of IAEA-TRS-418 [1]. It examines the effects of various parameters in the storage environment on corrosion, presents the results of corrosion surveillance tests at SRS, and discusses fuel storage basins at other sites of the Department of Energy in USA.

A state of the art review of available literature on corrosion of aluminium alloys was compiled by Dr. A. B. Johnson in 1998. This review was published in IAEA-TECDOC-1012 entitled Durability of Spent Nuclear Fuels and Facility Components in Wet Storage [2]. This publication covered a wide range of quantitative and semi-quantitative data on cladding alloys used in nuclear fuel elements and assemblies. Separate sections on corrosion of aluminium, zirconium, stainless steel, carbon steels, and copper alloys in wet storage environments were discussed. Appropriate sections of this publication, which apply to aluminium alloys and fuels predominantly used in research and test reactors, have been updated and presented in IAEA-TRS-418 [1].

Details about the test matrix, the corrosion racks, and the test protocol used in the CRP are presented in Sections 3 and 4, and in Chapter 4 of IAEA-TRS-418 [1]. The individual country reports are presented at the end of this publication. The CRP was deemed to have been a great success, with the reactor managers of the participating countries becoming more aware that long term storage of aluminium-clad spent fuel strongly depends on maintenance of good water quality.

REFERENCES (to Annex I)

[1] INTERNATIONAL ATOMIC ENERGY AGENCY, Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water, Technical Reports Series No. 418, IAEA, Vienna (2003).

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

ANNEX II. SCIENTIFIC RESULTS BASED ON THE ACTIVITIES DEVELOPED IN THE CRP AND IN THE CORROSION STUDIES OF THE TC REGIONAL PROJECT RLA/4/018

II-1. PUBLICATIONS PRESENTED ON MEETINGS, CONFERENCES AND WORKSHOPS

[1] CORREA, O.V., LOBO, R. M., FERNANDES, S. M. C.,MARCONDES, G., RAMANATHAN, L. V. “Effect of coupon orientation on corrosion behaviour of aluminium alloy coupons in the spent fuel storage section of the IEA-R1 Research Reactor”, International Conference on Research Reactor (Utilization, Safety, Decommissioning, Fuel and Waste Management), Santiago (Chile) 10-14 November 2003, paper CN-100-10.

[2] RODRIGUEZ, S., LANZANI, L., QUIROGA, A., SILVA, E., HADDAD, R. "Study of the effect of sedimented particles on the corrosion behaviour of aluminium clad spent fuel during storage in water", RERTR Conference, Santiago (Chile) 10-14 November 2003, paper CN-100-10.

[3] HADDAD, R., LANZANI, L., RODRIGUEZ, S.“Mechanisms of cladding corrosion during long term interim storage of MTR spent nuclear fuel in water basins”, RRFM 2006, Sofia, Bulgaria, 30 April - 3 May 2006.

[4] PEŠIĆ, M., MAKSIN, T., DOBRIJEVIĆ, R., IDJAKOVIĆ, Z., “Corrosion of Aluminium-Clad Spent Fuel at RA Research Reactor,“ International Conference on ‘Research Reactor Utilization, Safety, Decommissioning, Fuel and Waste Management’, Paper No. IAEA-CN-100-136, Santiago, Chile (10-14 November 2003), Proceedings, pp. 677-686, IAEA, STI/PUB/1211, Vienna (June 2005).

[5] PEŠIĆ, M., MAKSIN, T., JORDANOV, G., DOBRIJEVIĆ, R., “Corrosion of Spent Nuclear Fuel Aluminium Cladding in Ordinary Water”, The 26th International Meeting on Reduced Enrichment for Research and Test Reactors “RERTR 2004”, Vienna, Austria (November 7-12, 2004), posted at the RERTR Program web page: http://www.rertr.anl.gov/RERTR26/pdf/P12-Pesic.pdf.

[6] PEŠIĆ, M., MAKSIN, T., DOBRIJEVIĆ, R., JORDANOV, G., IDJAKOVIĆ, Z., “Study of Corrosion of Aluminium Alloys of Nuclear Purity in Ordinary Water – Part I”, Nuclear Technology & Radiation Protection, Vol. XIX, No.2, pp. 77-93 (2004).

[7] PEŠIĆ, M., MAKSIN, T., DOBRIJEVIĆ, R., JORDANOV, G., IDJAKOVIĆ, Z., “Study of Corrosion of Aluminium Alloys of Nuclear Purity in Ordinary Water – Part II”, Nuclear Technology & Radiation Protection, Vol. XX, No.2, pp. 45-60 (2005).

[8] PEŠIĆ, M., MAKSIN, T., DOBRIJEVIĆ, R., “A Study on Aluminium Corrosion in Water using a Rack with Vertically and Horizontally Immersed Coupons in Spent Fuel Storage Pool”, the ENS 10th International Topical Meeting on 'Research Reactor Fuel Management - ENS RRFM 2006', Sofia, Bulgaria (April 30 - May 3, 2006).

[9] RAMANATHAN, L.V., HADDAD, R.A., ADELFANG, P., RITCHIE, I.E., “Corrosion of Aluminium-Clad Spent Research Reactor Fuel in Wet Storage”, the ENS 10th International Topical Meeting on 'Research Reactor Fuel Management - ENS RRFM 2006', Sofia, Bulgaria (April 30 - May 3, 2006).

[10] HADDAD, R., LANZANI, L., RODRIGUEZ, S.,“Mechanisms of Cladding Corrosion During Long Term Interim Storage of MTR Spent Nuclear Fuel in Water Basins”, the ENS 10th International Topical Meeting on 'Research Reactor Fuel Management - ENS RRFM 2006', Sofia, Bulgaria (April 30 - May 3, 2006).

[11] RAMANTAHAN, L. V., HADDAD, R., ADELFANG, P. “Corrosion of Spent Research Reactor Fuel: the Role of Settled Solids”, the ENS 11th International Topical Meeting on 'Research Reactor Fuel Management - ENS RRFM 2007', Lyon , France (March 11-15, 2007).

[12] RAMANTAHAN, L. V., HADDAD, R., ADELFANG, P. “A Corrosion monitoring programme for research reactor spent fuel basins”, the International Conference on Research Reactors: Safe Management and Effective Utilization, Sydney, Australia, (November 5-9, 2007)

[13] RAMANTAHAN, L. V., HADDAD, R., ADELFANG, P. , RITCHIE, I.G., “Corrosion of Spent Aluminium-Clad Research Reactor – Synergism in the Role of Storage Basin Water Parameters” the ENS 12th International Topical Meeting on 'Research Reactor Fuel Management’ - ENS RRFM 2008, Hamburg, Germany (March 2-5 2008)

II-2. OTHER SCIENTIFIC ACTIVITIES

Lectures on RR water quality management, based on the findings of the CRP, were delivered at the IAEA National Training Course on Water Chemistry of Research Reactors, Indonesia, September 2004. The course was attended by 35 participants, ranging from reactor operators/technicians to managers from the 3 Indonesian research reactors, and corrosion surveillance programmes were implemented as a course follow up activity.

IAEA Training Course on Water Quality Management for Research Reactors and Research Reactor Spent Fuel Facilities, Ljubljana, Slovenia, December 2007, attended by 43 participants from 26 Member States.

Assistance on water quality management, including corrosion surveillance based on the findings of the CRP, was delivered to Libya, under a technical cooperation project.

PARTICIPANTS IN THE CORROSION STUDIES OF TC REGIONAL PROJECT RLA/4/018

Haddad, R.E.
Materials Department (UAM)
Comisión Nacional de Energía Atómica (CNEA- CAC)
Av.Gral Paz 1499
1650 San Martin, Pcia de Buenos Aires, Argentina
E-mail: haddad@cnea.gov.ar

Ramanathan, L.V.
Centro de Ciencia e Tecnologia de Materials
Instituto de Pesquisas Energéticas e Nucleares
IPEN-CNEN/SP
Av. Lineu Prestes, 2242
CEP 05508-000 – São Paulo, Brazil
E-mail: lalgudi@ipen.br

Neves, C. F.C.
Centro de Desenvolvimento da Tecnologia Nuclear (CDTN)
Comissao Nacional de Energia Nuclear (CNEN)
Av. Antonio Carlos, 6627
Caixa Postal 941
30123-970 Belo Horizonte, Brazil
E-mail: caf@cdtn.br

Lamas, C. J.
Comisión Chilena de Energia Nuclear (CCHEN)
Amunategui No. 95
Casilla 188-D
650-0687 Santiago, Chile
E-mail: clamas@cchen.cl

Méndez, M. E. G.
Instituto Nacional de Investigaciones Nucleares (ININ)
Carretera Mexico – Toluca S/N
La Marquesa, Estado de Mexico,
52750 Ocoyoacac– Mexico
E-mail: miguel.gachuz@inin.gob.mx

Benitez, C. O. L.
Instituto Peruano de Energia Nuclear (IPEN)
Avenida Canada 1470
Apartado 1687
Lima 41, Peru
E-mail: cleon@ipen.gob.pe

PARTICIPANTS IN THE COORDINATED RESEARCH PROJECT

Chwaszczewski, S.
Institute of Atomic Energy
Department of Nuclear Energy
05-400 Otwock Swierk – Poland
E-mail: sch@cyf.gov.pl

Dragolici, C.A.
National Institute of Research and Development for Physics and Nuclear Engineering “Horia Hulubei” - IFIN-HH
Atomstomstr/ Nr. 407
P.O.Box MG-6
77125 Magurele, Bucarest, Romania
E-mail: adrag@ifin.nipne.ro

Haddad, R.E.
Materials Department (UAM)
Comisión Nacional de Energía Atómica (CNEA- CAC)
Av.Gral Paz 1499
1650 San Martin, Pcia de Buenos Aires, Argentina
E-mail: haddad@cnea.gov.ar

Laoharojanaphand, S.
Chemistry Division
Office of Atoms for Peace
Vibhavadi Rangsit Road, Chatuchak
Bangkok 10900, Thailand
E-mail: sirinart@tint.or.th

Maksimkin, O.
Institute of Nuclear Physics
National Nuclear Center
Ulitsa Ibragimova 1.
480082 Almaty, Kazakhstan
E-mail: maksimkin@inp.kz

Pešić, M.
VINČA Institute of Nuclear Sciences
P.O.Box 522
YU-11001 Belgrade, Rep. of Serbia
E-mail: mpesic@vinca.rs

Ramanathan, L.V.
Centro de Ciencia e Tecnologia de Materials
Instituto de Pesquisas Energéticas e Nucleares
IPEN-CNEN/SP
Av. Lineu Prestes, 2242
CEP 05508-000 – São Paulo, Brazil
E-mail: lalgudi@ipen.br

Splichal, K
Reactor Service Division
Nuclear Research Institute Rez plc
25068 REZ, Czech Republic
E-mail: spl@ujv.cz

Research Coordination Meetings

Buenos Aires, Argentina, October 2002,
Almaty, Kazakhstan, June 2004,
Vienna, Austria, December 2005

PARTICIPANTS IN THE CORROSION STUDIES OF TC REGIONAL PROJECT RLA/4/018

Benitez, C. O. L.	Instituto Peruano de Energia Nuclear (IPEN) Avenida Canada 1470 Apartado 1687 Lima 41, Peru E-mail: cleon@ipen.gob.pe
Haddad, R.E.	Materials Department (UAM) Comisión Nacional de Energía Atómica (CNEA- CAC) Av.Gral Paz 1499 1650 San Martin, Pcia de Buenos Aires, Argentina E-mail: haddad@cnea.gov.ar
Lamas, C. J.	Comisión Chilena de Energia Nuclear (CCHEN) Amunategui No. 95 Casilla 188-D 650-0687 Santiago, Chile E-mail: clamas@cchen.cl
Méndez, M. E. G.	Instituto Nacional de Investigaciones Nucleares (ININ) Carretera Mexico – Toluca S/N La Marquesa, Estado de Mexico, 52750 Ocoyoacac– Mexico E-mail: miguel.gachuz@inin.gob.mx
Neves, C. F.C.	Centro de Desenvolvimento da Tecnologia Nuclear (CDTN) Comissao Nacional de Energia Nuclear (CNEN) Av. Antonio Carlos, 6627 Caixa Postal 941 30123-970 Belo Horizonte, Brazil E-mail: caf@cdtn.br
Ramanathan, L.V.	Centro de Ciencia e Tecnologia de Materials Instituto de Pesquisas Energéticas e Nucleares IPEN-CNEN/SP Av. Lineu Prestes, 2242 CEP 05508-000 – São Paulo, Brazil E-mail: lalgudi@ipen.br

No. 21, July 2006

IAEA
International Atomic Energy Agency

Where to order IAEA publications

In the following countries IAEA publications may be purchased from the sources listed below, or from major local booksellers. Payment may be made in local currency or with UNESCO coupons.

Australia
DA Information Services, 648 Whitehorse Road, Mitcham Victoria 3132
Telephone: +61 3 9210 7777 • Fax: +61 3 9210 7788
Email: service@dadirect.com.au • Web site: http://www.dadirect.com.au

Belgium
Jean de Lannoy, avenue du Roi 202, B-1190 Brussels
Telephone: +32 2 538 43 08 • Fax: +32 2 538 08 41
Email: jean.de.lannoy@infoboard.be • Web site: http://www.jean-de-lannoy.be

Canada
Bernan Associates, 4611-F Assembly Drive, Lanham, MD 20706-4391, USA
Telephone: 1-800-865-3457 • Fax: 1-800-865-3450
Email: order@bernan.com • Web site: http://www.bernan.com

Renouf Publishing Company Ltd., 1-5369 Canotek Rd., Ottawa, Ontario, K1J 9J3
Telephone: +613 745 2665 • Fax: +613 745 7660
Email: order.dept@renoufbooks.com • Web site: http://www.renoufbooks.com

China
IAEA Publications in Chinese: China Nuclear Energy Industry Corporation, Translation Section, P.O. Box 2103, Beijing

Czech Republic
Suweco CZ, S.R.O. Klecakova 347, 180 21 Praha 9
Telephone: +420 26603 5364 • Fax: +420 28482 1646
Email: nakup@suweco.cz • Web site: http://www.suweco.cz

Finland
Akateeminen Kirjakauppa, PL 128 (Keskuskatu 1), FIN-00101 Helsinki
Telephone: +358 9 121 41 • Fax: +358 9 121 4450
Email: akatilaus@akateeminen.com • Web site: http://www.akateeminen.com

France
Form-Edit, 5, rue Janssen, P.O. Box 25, F-75921 Paris Cedex 19
Telephone: +33 1 42 01 49 49 • Fax: +33 1 42 01 90 90 • Email: formedit@formedit.fr

Lavoisier SAS, 14 rue de Provigny, 94236 Cachan Cedex
Telephone: + 33 1 47 40 67 00 • Fax +33 1 47 40 67 02
Email: livres@lavoisier.fr • Web site: http://www.lavoisier.fr

Germany
UNO-Verlag, Vertriebs- und Verlags GmbH, August-Bebel-Allee 6, D-53175 Bonn
Telephone: +49 02 28 949 02-0 • Fax: +49 02 28 949 02-22
Email: info@uno-verlag.de • Web site: http://www.uno-verlag.de

Hungary
Librotrade Ltd., Book Import, P.O. Box 126, H-1656 Budapest
Telephone: +36 1 257 7777 • Fax: +36 1 257 7472 • Email: books@librotrade.hu

India
Allied Publishers Group, 1st Floor, Dubash House, 15, J. N. Heredia Marg, Ballard Estate, Mumbai 400 001,
Telephone: +91 22 22617926/27 • Fax: +91 22 22617928
Email: alliedpl@vsnl.com • Web site: http://www.alliedpublishers.com

Bookwell, 24/4800, Ansari Road, Darya Ganj, New Delhi 110002
Telephone: +91 11 23268786, +91 11 23257264 • Fax: +91 11 23281315
Email: bookwell@vsnl.net • Web site: http://www.bookwellindia.com

Italy
Libreria Scientifica Dott. Lucio di Biasio “AEIOU”, Via Coronelli 6, I-20146 Milan
Telephone: +39 02 48 95 45 52 or 48 95 45 62 • Fax: +39 02 48 95 45 48

Japan
Maruzen Company, Ltd., 13-6 Nihonbashi, 3 chome, Chuo-ku, Tokyo 103-0027
Telephone: +81 3 3275 8582 • Fax: +81 3 3275 9072
Email: journal@maruzen.co.jp • Web site: http://www.maruzen.co.jp

Korea, Republic of
KINS Inc., Information Business Dept. Samho Bldg. 2nd Floor, 275-1 Yang Jae-dong SeoCho-G, Seoul 137-130
Telephone: +02 589 1740 • Fax: +02 589 1746
Email: sj8142@kins.co.kr • Web site: http://www.kins.co.kr

Netherlands
Martinus Nijhoff International, Koraalrood 50, P.O. Box 1853, 2700 CZ Zoetermeer
Telephone: +31 793 684 400 • Fax: +31 793 615 698 • Email: info@nijhoff.nl • Web site: http://www.nijhoff.nl

Swets and Zeitlinger b.v., P.O. Box 830, 2160 SZ Lisse
Telephone: +31 252 435 111 • Fax: +31 252 415 888 • Email: infoho@swets.nl • Web site: http://www.swets.nl

New Zealand
DA Information Services, 648 Whitehorse Road, MITCHAM 3132, Australia
Telephone: +61 3 9210 7777 • Fax: +61 3 9210 7788
Email: service@dadirect.com.au • Web site: http://www.dadirect.com.au

Slovenia
Cankarjeva Zalozba d.d., Kopitarjeva 2, SI-1512 Ljubljana
Telephone: +386 1 432 31 44 • Fax: +386 1 230 14 35
Email: import.books@cankarjeva-z.si • Web site: http://www.cankarjeva-z.si/uvoz

Spain
Díaz de Santos, S.A., c/ Juan Bravo, 3A, E-28006 Madrid
Telephone: +34 91 781 94 80 • Fax: +34 91 575 55 63 • Email: compras@diazdesantos.es
carmela@diazdesantos.es • barcelona@diazdesantos.es • julio@diazdesantos.es
Web site: http://www.diazdesantos.es

United Kingdom
The Stationery Office Ltd, International Sales Agency, PO Box 29, Norwich, NR3 1 GN
Telephone (orders): +44 870 600 5552 • (enquiries): +44 207 873 8372 • Fax: +44 207 873 8203
Email (orders): book.orders@tso.co.uk • (enquiries): book.enquiries@tso.co.uk • Web site: http://www.tso.co.uk

On-line orders:
DELTA Int. Book Wholesalers Ltd., 39 Alexandra Road, Addlestone, Surrey, KT15 2PQ
Email: info@profbooks.com • Web site: http://www.profbooks.com

Books on the Environment:
Earthprint Ltd., P.O. Box 119, Stevenage SG1 4TP
Telephone: +44 1438748111 • Fax: +44 1438748844
Email: orders@earthprint.com • Web site: http://www.earthprint.com

United Nations (UN)
Dept. I004, Room DC2-0853, First Avenue at 46th Street, New York, N.Y. 10017, USA
Telephone: +800 253-9646 or +212 963-8302 • Fax: +212 963-3489
Email: publications@un.org • Web site: http://www.un.org

United States of America
Bernan Associates, 4611-F Assembly Drive, Lanham, MD 20706-4391
Telephone: 1-800-865-3457 • Fax: 1-800-865-3450
Email: order@bernan.com • Web site: http://www.bernan.com

Renouf Publishing Company Ltd., 812 Proctor Ave., Ogdensburg, NY, 13669
Telephone: +888 551 7470 (toll-free) • Fax: +888 568 8546 (toll-free)
Email: order.dept@renoufbooks.com • Web site: http://www.renoufbooks.com

Orders and requests for information may also be addressed directly to:

Sales and Promotion Unit, International Atomic Energy Agency
Vienna International Centre, PO Box 100, 1400 Vienna, Austria
Telephone: +43 1 2600 22529 (or 22530) • Fax: +43 1 2600 29302
Email: sales.publications@iaea.org • Web site: http://www.iaea.org/books

09-48361