Durability of spent nuclear fuels and facility components in wet storage

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DURABILITY OF SPENT NUCLEAR FUELS AND FACILITY COMPONENTS
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FOREWORD

Wet storage facilities continue to be the most common technology used for the management of irradiated fuel assemblies from power reactors, research and test reactors, and defence reactors. Some of the most important decisions that must be faced by the operators of these facilities involve the ageing of materials in ageing facilities. A broad variety of fuel types, involving numerous combinations of fuel and cladding materials, are currently stored in these facilities, which in many instances are at or near their design capacities and at or approaching their design lifetimes. Extending the licences of such facilities as their regulatory periods expire is not a straightforward proposition, and answers to questions concerning the degradation and ageing of materials in spent fuel storage facilities, which may be posed by regulatory bodies, require a broadly based materials database. However, because examinations of radioactive materials are expensive, access to materials data and experience that provides an informed basis to analyse and extrapolate materials behaviour in wet storage environments, especially quantitative data, is sparse. Moreover, it is believed that the available data, both quantitative and qualitative, for all of the common types of fuel cladding, categories of fuel material and the components used in spent fuel storage pools, has never been gathered together in a single review.

In 1993, a Co-ordinated Research Programme (CRP) on Irradiation Enhanced Degradation of Materials in Spent Fuel Storage Facilities was initiated by the IAEA with the twin goals of filling in some of the gaps in the materials database and providing input data to model and extrapolate materials behaviour. However, as the reality and immediacy of "extended storage" began to emerge, the need was recognized for a broader treatment that included, but was not limited to, radiation effects. Therefore, it was decided to collect together the required materials database and integrating into it the data and results developed by the CRP as it progressed. This review, developed during the CRP, is the result. It addresses materials behaviour in wet storage on the basis of important degradation mechanisms that apply to irradiated and unirradiated materials commonly found in wet storage facilities.

The IAEA wishes to express its thanks to A.B. Johnson, Jr. for his major work on compiling and processing the data, and all of the participants in the CRP. The IAEA staff member responsible for this publication and scientific secretary of the CRP was I.G. Ritchie of the Division of Nuclear Fuel Cycle and Waste Technology.

EDITORIAL NOTE

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SUMMARY

Wet storage continues to be the dominant option for the management of irradiated fuel elements and assemblies (fuel units). Fuel types addressed in this study include those used in: power reactors, research and test reactors, and defence reactors. Important decisions must be made regarding acceptable storage modes for a broad variety of fuel types, involving numerous combinations of fuel and cladding materials. A broadly based materials database has the following important functions:

–   to facilitate solutions to immediate and pressing materials problems;

–   to facilitate decisions on the most effective long term interim storage methods for numerous fuel types;

–   to maintain and update a basis on which to extend the licenses of storage facilities as regulatory periods expire;

–   to facilitate cost-effective transfer of numerous fuel types to final disposal.

Because examinations of radioactive materials are expensive, access to materials data and experience that provide an informed basis to analyse and extrapolate materials behaviour in wet storage environments can facilitate identification of cost-effective approaches to develop and maintain a valuable materials database.

Fuel storage options include: leaving the fuel in wet storage, placing the fuel in canisters with cover gases, stored underwater, or transferring the fuel to one of several dry storage modes, involving a range of conditioning options. It is also important to anticipate the condition of the various materials as periods of wet storage are extended or as decisions to transfer to dry storage are implemented. A sound basis for extrapolation is needed to assess fuel and facility component integrity over the expected period of wet storage. A materials database also facilitates assessments of the current condition of specific fuel and facility materials, with minimal investments in direct examinations.

This report provides quantitative and semi-quantitative data on materials behaviour or references sources of data to address the wide range of materials issues that face today's decision makers and wet storage facility operators.

ZIRCONIUM ALLOY DATABASE

Zr alloys are highly durable cladding materials in wet storage, based on a series of hot cell examinations after wet storage periods from 5 to 27 years. Results of the examinations are supported by laboratory data, by specific observations during fuel shipments and other fuel handling operations, and by visual surveillance by storage pool operators for periods approaching forty years. Results of data and experience continue to support a conclusion that wet storage of fuel with Zr alloy cladding will be acceptable for periods in the range of 50 to 100 years, including exposures to relatively aggressive water chemistry. It is clear that cladding penetration by uniform corrosion is not an issue, and no localized failure mode has been observed in several hot cell examinations. However, it is necessary to place into perspective the advancing corrosion that has occurred on Zircaloy clad uranium metal fuel from the Hanford N Reactor. The otherwise durable Zircaloy was mechanically damaged during reactor discharge, exposing uranium metal, that is vulnerable to aqueous corrosion in the temperature range encountered in wet storage environments. An additional issue involves advancing corrosion and hydriding of zirconium alloy cladding subject to extended burnup. Diminished low temperature ductility imposes the need for additional care in spent fuel handling operations to avoid any mechanical impact that may cause cladding fracture.

STAINLESS STEEL DATABASE

Stainless steels are subject to a broad range of corrosion behaviours in wet storage environments. The range of SS corrosion properties can be understood in terms of: (a) sensitization

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level, (b) stress level, and (c) environmental contaminants. Cladding from LWRs has been examined after wet storage periods up to five years; results suggest high SS integrity. In contrast, SS cladding from some GCRs and LMRs has been penetrated by corrosion in both water and moist air at low temperatures over relatively short storage periods. However, some LMR and GCR fuels have been stored in water for extended periods. The principal failure mechanism is IGSCC promoted by sensitization from the relatively high temperatures during reactor service and by the effects of radiation on the microstructures. However, other factors are generally involved in the degradation of sensitized SS, including high stresses and aggressive environments. A few unirradiated SS storage pool components, principally piping, have been penetrated by IGSCC in weld heat-affected zones, promoted by sensitization during welding. The failures occurred in the range of 20 to 40°C.

Quantitative hot cell investigations of SSs after periods of wet storage, aqueous corrosion studies at temperatures in wet storage facilities, and observations on the successful storage of some SS clad fuels indicate that for fuels with favourable metallurgical, stress, and water chemistry conditions, SS durability in wet storage will be satisfactory for many decades. Uniform corrosion is not an issue. Localized mechanisms have been identified, but only for cladding materials or facility components that were subject to severe conditions.

ALUMINIUM ALLOY DATABASE

Aluminium alloys also exhibit a wide range of corrosion responses in wet storage environments. The range of corrosion behaviour observed can be understood in terms of FSP water chemistries. Metallurgical examinations of coupons and other materials with exposures of up to 16 yearsindicate less than 25 μm of penetration by uniform corrosion and pitting in a pool where high purity conditions are maintained. In contrast, in impure waters, pitting corrosion has penetrated Al alloy coupons in 45 d; Al alloy cladding also has been penetrated by pitting in a few months. However, Al clad test reactor fuel has been inspected after 24 years without observing evidence of degradation. Wet storage facility components constructed of Al alloys have functioned for periods up to 35 years without evidence of substantial degradation, but components exposed to contaminated waters have developed deep pits. Pitting has emerged as the principal degradation mechanism for Al alloys in wet storage. After pitting reaches an advanced stage, it appears difficult to mitigate, even with improved water chemistry. Crevice corrosion has been identified as potentially aggressive to Al alloys in FSP conditions, but has not yet emerged as an operational problem. Uniform corrosion appears to be minimal, even in relatively impure waters. Results of corrosion studies on Al alloy specimens exposed in FSPs are given in this report. There has been some progress in rationalizing the wide differences in aluminium alloy corrosion behaviour, in terms of water chemistry parameters. Water conductivity appears to offer the most broadly relevant index of satisfactory water purity.

In wet storage environments with conductivities generally maintained near 1 μS/cm (with only mild excursions), aluminium alloy fuel cladding and storage facility components have not been subject to substantial degradation. Data from coupon studies in wet storage pools span the range, from penetration in a few weeks to corrosion rates of a fraction of a μm/year, suggesting that with proper water chemistry control, storage of Al clad fuel can be satisfactory in wet storage for several decades. However, advanced corrosion is evident on aluminium clad fuel stored in aggressive water chemistries.

CARBON STEEL AND COPPER DATABASES

Carbon steel components in wet storage facilities generally corrode at substantial rates and release corrosion products into the water in the storage facility. Coatings extend the onset of corrosion on CS, but in some FSPs, coatings have degraded, exposing large areas of the coated steels to extensive corrosion. Results of corrosion studies on CS specimens exposed in FSPs are reported in this communication.

Copper alloy heat exchangers function in some facilities. Copper corrosion is generally low in high purity waters, but increases in aggressive waters, and can have adverse effects on pitting of

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aluminium materials in the same system, particularly in aggressive chemistries. Corrosion rates for Cu alloys were determined on coupons exposed in FSPs, including periods of aggressive and benign water chemistries.

FUEL MATERIALS DATABASE

Effects of aqueous conditions on fuel materials have been examined, prompted by the need to understand fuel durability when exposed to pool waters at cladding defects. Uranium oxide fuels have been observed to remain stable for periods of years while exposed to pool water. Leaching experiments at 25°C indicate that rates of elution of radioactive species (e.g., Cs-137) approach low values after 30 d. Based on these results, continued storage of LWR fuel with cladding defects without canning seems justified. On the other hand, metallic uranium corrodes at substantial rates when exposed to wet storage conditions, releasing troublesome inventories of fission products, transuranics, and uranium oxide corrosion products. The corroding uranium generates oxides and also UH_3. The hydride can become pyrophoric when exposed to air; however, the hydride reacts with water and oxygen and is not considered to be a pyrophoric risk for non-swollen uranium metal fuels corroding in open pools. Conditions that have promoted generation of troublesome inventories of uranium hydrides have involved isolation of uranium in inert atmospheres where presence of moisture has generated a moist hydrogen atmosphere that results in accelerated corrosion and hydriding. While even relatively low concentrations of oxygen are present, corrosion is mitigated and hydriding is precluded except in areas where hydrides are occluded. Extended use of wet storage for uranium metal fuels that have cladding failures or cladding that is subject to penetration by aqueous corrosion is not viable.

Test reactor fuel technology includes wide use of UAl_x fuels. There are few data regarding corrosion of the fuels when exposed to wet storage environments. However, the aluminide particles are embedded in an Al alloy matrix, so degradation will be controlled largely by corrosion of the Al alloy cladding and matrix. Durability of UAl_x fuel therefore can be largely understood from the Al alloy corrosion database. The situation is similar for fuels with uranium oxide particles embedded in aluminium.

BIOLOGICAL AND SLUDGE EFFECTS

Other issues specific to wet storage include control of biological species. Control of alga has sometimes been necessary to maintain satisfactory visibility in pool waters. However, biological counter measures have sometimes resulted in aggressive chemistry conditions that caused accelerated corrosion of fuel cladding and facility materials.

Sludges that build up on the floors of storage pools are a potential source of accelerated corrosion. They tend to occlude metal surface areas, thereby contributing to concentration cells in the oxygenated pool waters. Also, limited systematic characterizations suggest that sludges may concentrate aggressive species, such as chlorides. The sludges represent an accumulation of corrosion products of materials in the pool, spallation of crud from fuel assembly surfaces, and airborne dust, etc., particularly in facilities that are not isolated from wind-borne debris.

RADIATION EFFECTS

Radiation effects in FSPs arise from gamma radiation from irradiated fuel assemblies or from cobalt-60 or radiocesium sources. The gamma fluxes have little effect on the properties of metals in the FSPs. However, gamma fields have had significant effects in some wet storage facilities that include components with materials that are subject to radiolytic decomposition, notably, neutron absorbers that include organic materials, and rack configurations that trap water that subsequently forms gas pressures from radiolyic decomposition. On the other hand, gamma radiation fields have not seemed to promote substantial increases in corrosion of the metals in wet storage conditions.

There are materials issues from residual effects of reactor irradiations on fuel and cladding. Metallic uranium develops porosity when irradiated to moderate to high burnups. The porous

uranium is prone to accelerated corrosion and associated hydriding if exposed to aqueous media, liquid or vapour. Neutron irradiation does not appear to significantly affect uniform corrosion of aluminium and zirconium alloys when subsequently exposed to wet storage conditions. However, losses of ductility have been observed in cladding from high burnup fuels clad with zirconium alloys, interpreted to include effects from irradiation-induced and hydrogen-induced embrittlement. The SSs are susceptible to irradiation-assisted phenomena at grain boundaries (IASCC) that can result in intergranular attack in water at reactor operating thermal regimes. There have not been sufficient systematic studies of irradiated SSs under aqueous storage conditions to isolate specific effects of neutron irradiation on stainless steel corrosion in storage. Stainless steel cladding from LWR service did not show evidence of intergranular attack under wet storage conditions, but SSs exposed in LMRs and GCRs have been subject to intergranular corrosion effects in wet storage that could be due to thermal or radiation effects, or a combination.

Relatively mild conditions in wet storage facilities mitigate degradation from factors such as stress and fatigue.

FUEL CATEGORIES AS A BASIS FOR FUEL MANAGEMENT DECISIONS

There are perhaps 100 specific fuel types that must be managed in storage modes. Some are suitable for extended wet storage; some need to be transferred to dry storage. Within the regimes of Al alloys and stainless steels there is greatly contrasting behaviour in wet storage. Also, the degree of conditioning needed to place the fuels into safe states for dry storage has a range of needs, depending on the type and degree of fuel degradation and the inventory of moisture in corrosion products. A category approach is suggested to assist in decisions about the selection of both the storage mode and the degree of conditioning needed for fuels destined for dry storage.

CONCLUSIONS

1. A major incentive for this study of materials behaviour in wet storage is that storage of irradiated fuels in water has become the major mode of storage, unforeseen when reprocessing of commercial and defence fuels was the fuel management assumption. In the 1990s, reprocessing has not reached the status that was earlier expected. In fact, reprocessing of defence reactor fuels has almost terminated in some countries, particularly in the USA, where commercial reprocessing was terminated earlier. Another factor in the augmented importance of wet storage is the delay in implementing permanent disposal for spent fuel in numerous countries. This dictates that fuel will remain in storage for periods longer than expected. Assurances are needed that the extended storage periods will not compromise the integrity of the fuel or storage facility components.

2. Materials are essential barriers in the safe containment of radioactivity in fuel storage facilities. Materials behaviour must be analyzed on a systematic and comprehensive basis to provide an effective database for decisions regarding sound management of numerous fuel and facility component types over periods of interim storage and transfer to final disposal.

3. Materials durability has been notably satisfactory in most aspects of commercial fuel management. In contrast, serious materials degradation presents challenges in some sectors of defence and test reactor technologies.

4. Radiation presents an obstacle to in-depth investigation of materials conditions on a major cross-section of irradiated and contaminated materials. It is therefore necessary to supplement direct examinations with relevant data from other sources and to conduct and document systematic observations on the fuels and facility components as opportunities arise.

5. An effective materials database is valuable to facilitate solutions to materials problems as they emerge, to guide decisions regarding long term interim solutions to management of numerous fuel types, to anticipate the technical basis that will be needed to further extend regulatory

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authorization of storage facility operations, and to transfer the numerous fuel types to final disposal.

6. Summarizing durability of materials prominent in wet storage technology:

   (a) The zirconium alloys represent a class of materials that is highly resistant to degradation in wet storage, including some experience in aggressive waters. The only adverse experience involves Zircaloy clad metallic uranium where mechanical damage to the cladding was a prominent factor during reactor discharge, exposing the uranium metal fuel to aqueous corrosion. Otherwise, the database for the zirconium alloys supports a judgement of satisfactory wet storage in the time frame of 50 to 100 years or more.

   (b) Stainless steel components in wet storage facilities have an excellent history of performance, including service in aggressive waters. However, stainless steel components and claddings that have been substantially sensitized have sometimes been subject to degradation in wet storage. Specific examinations of LWR SS fuel claddings indicate no evidence of degradation after periods of wet storage, but some GCR and LMR fuel claddings have degraded in water and in moist air at temperatures in the range of 20 to 40° C. Satisfactory service of SS clad fuels and facility components can be expected for several decades if materials with favourable microstructures and low stress levels are involved.

   (c) The aluminium alloys also have a wide range of durability in wet storage. The key to long survival of aluminium alloy fuels and facility components is consistent control of water chemistry parameters. This includes need to control biological species. Aluminium has a history of satisfactory service for periods beyond 30years in facilities with well-managed water chemistries. By contrast, pitting corrosion has developed within a few months in facilities with high water conductivities.

   (d) Carbon steel is a prominent material in defence reactor and some test reactor storage facilities. Unless effective coatings are maintained, CS corrodes in the oxygenated FSP environments. Consequences include compromised operation of equipment, penetration of metal components, and loss of visibility, due to suspended corrosion products.

   (e) Copper and its alloys are sometimes used in heat exchangers in FSP facilities. The copper can facilitate corrosion on other materials in the facility, notably Al alloys. However, there is evidence that in high purity waters, copper has little effect on aluminium corrosion.

7. A major consideration in the corrosion of fuel cladding is the potential impact when the fuel is transferred to interim dry storage or to permanent disposal. The concern is not only for diminished cladding integrity but also for water inventories associated with corrosion products. The water is a potential source of future corrosion, pressure buildup due to radiolytic generation of gases, and a source of hydrogen/oxygen mixtures. Observations that crud layers tend to soak loose after a few years of wet storage also has implications when the fuel is shipped, transferred to dry storage, or to a repository. High hydrogen contents of high burnup fuel clad with zirconium alloys suggests care to avoid impacts during fuel handling.

8. There is a large inventory of different combinations of fuels, claddings, and fuel element and assembly designs. It is not practical to investigate each type in detail. However, the types can be identified into categories with sufficiently similar characteristics that information available on one fuel type can be the basis for decisions regarding other fuels in the same category. Therefore, it is proposed to approach the wide variety of fuel types on the basis of categories.

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1. INTRODUCTION

The IAEA Spent Fuel Storage Glossary [1] defines extended storage as "storage of fuel units beyond the period of time originally planned". This concept has now become an important reality for a large fraction of the world inventory of stored fuel. In several countries there have been delays in commissioning repositories for disposal of spent fuel. There have also been cancellations or deferrals of reprocessing capacity.

For some fuel types, storage beyond the period originally planned does not compromise the fuel integrity; for other fuel types, extended wet storage has already resulted in substantial degradation of fuel cladding and, for metallic fuels, of the fuel material. At some facilities, materials comprising certain storage system components have degraded in extended storage. However, predominantly, storage facility components have functioned without substantial degradation beyond two decades, and up to four decades at some facilities.

It is important to note that in 1995, the cumulative generation of spent fuel from nuclear power reactors has been approximately 165 000 t HM [2]. In 1996, 100 000 t of Zircaloy clad fuel were in wet storage [7]. All fuels have had periods of interim storage, predominantly in wet facilities; much fuel has been shipped, by both wet and dry methods; approximately 50 000 t HM has been reprocessed; many thousands of tonnes of research reactor and defence reactor fuels also have been stored, shipped, and reprocessed. This experience is marked by a high degree of safety; in fact, there is not a single event in commercial fuel storage experience that is remarkable as a serious impact on the public or facility staff. It is essential that this impressive record continue, based on informed decisions regarding safe management of numerous fuel types that now exist in extended storage and are subject to aqueous corrosion.

This assessment was developed to provide a basis to judge the impacts of extended wet storage on the integrity of the fuel (including cladding and fuel materials) and the components of wet storage facilities, which also must perform their intended functions to facilitate satisfactory storage and retrieval of the fuels. This assessment has been developed from a materials perspective, to provide a basis to make judgements that are as quantitative as possible regarding expected behaviour of cladding, fuels, and facility components. This is a challenging effort because there have been few quantitative studies that are specific to materials performance of irradiated fuels in wet storage. Therefore, it is necessary to draw data from several sources that have relevance to conditions in the full range of wet storage environments, including the following data sources:

- quantitative data on fuel and storage facility component materials after periods of wet storage, generally obtained in metallurgical examinations in hot cells or similar facilities;

- non-destructive testing of fuel rods or facility components in hot cells or wet storage facilities;

- data from coupon studies conducted in wet storage facilities;

- laboratory studies on similar materials under conditions relevant to wet storage;

- extrapolation of kinetic data from related thermal and/or chemistry regimes;

- qualitative or semi-quantitative observations on behaviour of materials in extended wet storage, providing corroboration of the quantitative predictions.

This study draws input from another IAEA Co-ordinated Research Programme (CRP). The BEFAST (*BE*haviour of Spent *F*uel *A*ssemblies During Extended *ST*orage) Programme was implemented in 1981 and has focused on fuel and facility performance in long term wet and dry storage. Predominantly, BEFAST studies concentrated on commercial fuels and facilities. Two formal publications were developed that address aspects of materials behaviour and operational experience [3, 4]. A final report addressing BEFAST Phase I initiatives also was published [5]. More recently, the BEFAST Phase II focus has been on updating operational experience, which is important to assure that fuel storage technology is continuing to provide a safe basis for spent fuel management [6, 7].

The CRP study addressed in this report builds on the BEFAST database, but adds a more quantitative basis for assessing materials behaviour in wet storage and also expands the scope to include research and test reactor fuel types, defence reactor fuel types and storage facility materials Storage of numerous research and test reactor, and defence reactor fuels has moved into the "extended" category, in general, the cladding and fuels include materials that are prone to deterioration unless the storage conditions are effectively controlled Some research, test and defence reactor operators that expected their fuel to be reprocessed after short cooling periods did not make provisions for satisfactory water chemistry control At some facilities, the consequences have evolved into major corrosion problems (e.g Refs [8–11])

In a climate of détente, information on defence reactor fuels has been declassified and is now available in the open literature [12–14] Storage problems have arisen for some defence fuel types which were not expected to be subject to extended wet storage Predominantly, the materials are similar to materials used in commercial or research reactor fuel storage technologies and therefore contribute to and benefit from assessments of materials behaviour in commercial wet storage facilities To include available data from defence fuels and storage facilities therefore provides important perspectives and expands the circle of those who can benefit from this assessment

This CRP first focused only on the radiation effects on materials However, as the reality of "extended storage" began to emerge, those formulating the CRP scope recognized the need for a broader treatment that included, but was not limited to, radiation effects Therefore, materials behaviour in wet storage is addressed on the basis of important degradation mechanisms that apply to irradiated and unirradiated materials in the range of wet storage environments addressed here In treating degradation mechanisms there is a need to maintain a concise format Some materials which are rarely used (e g , titanium heat exchangers) are omitted Also, mechanism assessments that have been previously published are referenced but are not revisited in detail

Concrete is an important material in wet storage facilities It is often lined with SS, Al alloys, organic materials, or is coated with paint. Resistance to seismic events is an important consideration that had to be considered when the facility was designed The material and structural issues with concrete are beyond the scope of this report but should be addressed in any future study of the degradation of materials in spent fuel storage facilities

The major goal of this study is to provide wet storage facility operators and other decision-makers a basis to judge the durability of a given fuel type or facility component in wet storage, to facilitate fuel management decisions, for example, electing for dry storage if wet storage will not be satisfactory through the expected period of interim fuel management If perforation of the cladding is indicated or expected, the fuel type (oxide or metal) then becomes an important consideration in judging the acceptability of further wet storage. Durability of both oxide and metallic fuel types will be treated

A key intent of this assessment is to motivate wet storage facility operators to manage their storage environments to minimize fuel and facility degradation, degradation that has created difficult and costly problems at some facilities

A further intent is to recommend that as opportunities arise in fuel examination and handling, data and observations should be documented to contribute to the materials database that will facilitate cost effective fuel management in interim storage and transfer to final disposal Opportunities that are taken to examine materials used in storage facility components should be documented also, in a format that can be widely distributed

Wet storage technology generally involves relatively low temperatures (<50° C), it includes a broad range of water chemistries that are summarized in the following section, it involves numerous fuel types and facility component materials For practical reasons, it will be necessary to focus the treatment on fuel categories rather than addressing the details of perhaps a hundred specific fuel configurations and numerous facility designs

This assessment will focus on wet storage A subsequent assessment is planned that will address materials aspects of dry storage and a set of criteria for the transfer

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2. OVERVIEW OF MATERIALS CONSIDERATIONS IN WET STORAGE

The durability of a particular material is determined by several factors, including composition and metallurgical condition, stress levels (both internal and applied), its thermo-mechanical history (fabrication route), and history of ageing in the environments it has been exposed to. A given fuel type will generally have been subject to a series of environments, including pre-service, reactor service, fuel handling, one or more interim storage pool environments, and possible shipping, wet or dry. A study of several fuel types has illuminated the problems in precisely defining all of the factors indicated above for fuels that have been subject to extended histories in multiple facilities [15]. To facilitate the development of a perspective of expected fuel behaviour, an approach that identifies categories for various fuels is suggested. This provides a practical basis to judge fuel durability and required actions when the details of fuel characteristics and histories may be of minimal significance. The approach draws from all accessible data regarding a specific fuel, including materials, design, reactor service conditions, post-service handling and storage, and surveillance data on the same or similar fuels. Selected fuel characterizations may be justified, but examination of irradiated fuels is expensive and can be minimized by effective application of the category concept. The categories are structured in terms of cladding durability in the storage environment, the fuel service history, the consequences of cladding perforation, i.e., how durable is the fuel material if exposed to water. Application of categories to fuel storage evaluations is treated in Section 11.

2.1. RANGE OF MATERIALS

Annex I summarizes the range of fuel and cladding materials after service in commercial, research and test, and defence reactors, respectively; Annex II addresses components and materials in wet storage facilities. The Annex includes alloy compositions. Some fuels and storage component materials have been durable over several decades, including aluminium alloys maintained in good water chemistries, stainless steels that are in satisfactory states of stress and sensitization, and zirconium alloy fuel cladding. Other materials have degraded in a few months, including aluminium alloys exposed in impure waters, SSs with substantially sensitized microstructures, and uranium metal fuels exposed at breaches in fuel cladding; breaches caused by corrosion or mechanical damage. In subsequent sections, both the durable and corrosion-prone materials are identified and are characterized in terms of corrosion rates where data are available.

In a given facility, several material types are normally represented. A consequence is that dissimilar metals will sometimes be in contact. Behaviour of the metal couples has generally been satisfactory in wet storage facilities where benign water chemistries are maintained, but galvanic phenomena have been observed in facilities with aggressive water chemistries and susceptible couples [15, 16]. Detrimental interactions can occur for materials not in direct contact. For example, copper components in a system containing Al alloys can promote pitting of the aluminium if copper ions formed by corrosion, are transported to and deposited on the aluminium surfaces. A similar effect occurs when iron ions are transported to and plate-out on aluminium surfaces. In high purity waters, where corrosion is low, the effect of copper on aluminium has been minor [9]. Cases of substantial crevice corrosion have occurred, particularly on aluminium alloys that are adjacent to a dissimilar metal and where aggressive species such as chlorides can concentrate [16]. An update on water chemistries in several wet storage facilities can be found in Ref. [7].

2.2. RANGE OF WATER CHEMISTRIES

In general, satisfactory control of the corrosion environment is the most important factor that determines the durability of materials in fuel storage facilities. Reference [3] provides a comprehensive summary of fuel storage facility water chemistries, based on a survey of worldwide wet storage experience.

The summary indicates several categories of water chemistries:

- AFR, ISFSI, BWR, RBMK, research and test reactor, and certain other pools, where water chemistries generally involve deionized water, but with a range of impurity monitoring and control;

- Special chemistries, e.g., high pH waters to control Magnox corrosion and mitigate IGSCC of AGR fuels;

- PWR and WWER, generally with borated water chemistries;

- Other, comprising unusual or otherwise generally aggressive water chemistries, including waters subject to chemical biocides or waters drawn directly from natural sources, e.g., rivers.

A consistent feature of water pools is absorption of oxygen and carbon dioxide from the atmosphere. The oxygen concentration is about 8 ppm at 25°C; carbon dioxide equilibrium results in dilute carbonic acid, resulting in mildly lowering of the pH e.g., pH5.5 to 6, in otherwise neutral waters [17], and limits the control of pH to about 11.5, maximum, i.e., in facilities that store Magnox fuels [18].

For the materials addressed in this assessment, durability is characterized in terms of corrosion rates in specific environments represented in the storage facility water chemistries indicated above. The quantitative data are supplemented with surveillance information that represents a less quantitative, but important corroboration of the quantitative data. Materials behaviour in specific water chemistries will be addressed in sections dealing with the individual materials.

2.3. RADIATION EFFECTS

The prominence of irradiated materials in wet storage facilities prompts a need to assess effects of radiation on both the radioactive cladding and fuels and the unirradiated storage facility components that they are adjacent to [19]. The first consideration is the extent to which radiation during reactor service has permanently altered the fuel and cladding materials. The materials have been subject to intense radiation fields (for example, neutron fluxes up to approximately 10^{15} n/cm^{2}s, >1 MeV and gamma fluxes of 1×10^9 R/h). Whether the irradiations have left residual effects that accelerate degradation of the materials in wet storage is an important consideration that is not fully understood for all materials. For metals, neutron irradiation generally increases strength and decreases ductility. The stainless steels are susceptible to radiation-induced segregation (RIS) that contributes to irradiation-assisted stress corrosion cracking (IASCC). However, detailed hot cell examinations are available for several fuel/cladding types after periods of wet storage; interpretation of the examination results provides a basis to assess whether residual effects of reactor service are causing discernible degradation during wet storage.

The irradiated fuels continue to emit substantial gamma fluxes in the storage pools: on the order of 10^6 R/h upon discharge, but decreasing exponentially with time to levels of 10^3 to 10 R/h after several years; the fields affect water chemistries around the fuels and also impinge on adjacent materials. In some cases, effects of the fields have degraded materials subject to the fields. Specifically, certain neutron absorbers enclosed in storage racks have been subject to radiation-induced degradation (addressed in Section 9). Also, radiolytic decomposition of moisture trapped between stainless steel plates in fuel storage racks resulted in expansion of the plates, causing binding of fuel assemblies. The fuels continue to emit neutrons (post-irradiation neutron fluxes vary depending on fuel type and burnup, but an order of magnitude may be 10^3 n/cm^2 s). The fluxes are too low to be of practical significance related to materials degradation. Fuels exposed at cladding breaches represent sources of alpha and beta radiation; while possible local effects of these radiation sources need to be considered, available evidence suggests that these sources are not a significant cause of materials degradation in wet storage facilities. Radiation effects are treated in Section 9.

2.4. MATERIALS CHARACTERIZATIONS IN WET STORAGE

The range of data sources for materials behaviour in wet storage were outlined in an earlier section. The need to minimize the expense of comprehensive hot cell examinations on a wide range of fuels and facility components is obvious. On the other hand, a sound basis is needed to make decisions about interim fuel management and the necessary actions to transfer the fuels to final disposal.

Materials characterizations summarized in this report provide important perspectives on expected behaviour of several fuel types and facility materials. In those cases where further fuel examinations are deemed necessary, they should proceed after clearly identifying the range of issues that need resolution. The results should be documented in sufficient detail that they can be applied to similar materials. Co-ordinated planning and sharing of information on an international basis can minimize the total investment that is necessary to resolve fuel management issues. For example, a spent fuel technology information exchange between the Federal Republic of Germany [20] and the USA [19] provided important data that were mutually beneficial in a time frame that was important to develop technical bases for licensing of spent fuel facilities. The exchange included information relevant to both wet storage and dry storage issues.

At individual facilities, insertion of specimens into the spent fuel pool waters can provide a valuable database that includes effects of water chemistry excursions and provides evidence to support extended operation of the facility, including reviews necessary for license extensions. However, the specimen arrays need to represent actual materials. Placement of the specimens also is important. At some pools, chemistry gradients have been detected at various levels in the water [21], while relatively uniform conditions exist at other facilities [16], depending on water circulation and chemistry control. Issues in designing a corrosion coupon programme for a wet storage facility include the following:

-   selection of representative materials and metallurgical conditions, including welds;

-   investigation of crevice and galvanic effects to the extent that these are represented in the fuel assemblies and/or the facility components to be assessed;

-   placement of specimens to assess radiation effects, if considered important to the goals of the programme;

-   placement of specimens to consider gradients in pool chemistry, if relevant to the facility;

-   placement of specimens to include effects of sludge, if relevant to the facility;

-   inclusion of specimens with relevant surface films, including typical damage to the films, if relevant to the materials being investigated;

-   consideration of the numbers of specimens needed to address the time frame and frequency of specimen removal that will assure that the investigation yields definitive results that will permit extrapolations over foreseeable facility operation and fuel residence periods;

-   consideration of the environmental parameters that must be effectively monitored to assure that there is a satisfactory basis to interpret the corrosion results;

-   implementation of sound corrosion measurement methods to evaluate the extent and types of corrosion that develop on the specimens, including dealing with deposits that form external to corrosion films.

For specimens that include degradable materials, e.g., neutron absorbers with organic additions, the specimens must be placed in prototypic radiation environments. Preparation and examination of the specimens should be conducted according to standard methods, e.g., see ASTM G1 standards [22].

During fuel handling operations and when facility components are replaced or refurbished there are opportunities for systematic observation and documentation of materials conditions. This contributes to the facility materials database that may later prove to be valuable. Sharing information among facilities broadens the database.

Spent fuel storage has emerged as an extended interim measure at many facilities. In many cases, this was not an expected outcome, and therefore the facility and its materials were not designed for time frames that have now been imposed. The mindset that regarding materials in fuel storage facilities as a mundane consideration needs to be replaced with proactive, systematic initiatives that provide an informed basis for fuel management decisions and effective facility maintenance and refurbishment.

3. CHARACTERISTICS OF ZIRCONIUM MATERIALS IN WET STORAGE

Fuels clad with zirconium alloys represent the dominant fuel type in wet storage. The fuel types with zirconium alloy cladding are summarized in Annex I, including power reactor, test reactor, and defence reactor types. The traditional fuel cladding alloys include Zircaloy 2 and Zircaloy 4 (see Annex I for compositions) in western-bloc reactors and Zr-1Nb in reactors of Russian design. In the 1990s there have been initiatives by several nuclear fuel vendors to implement zirconium-based alloys with improved resistance to corrosion and hydriding in reactor service. Storage characteristics of the alloys in water are expected to be similar. Zirconium alloys are not represented in wet storage facility components. A few facilities store lengths of Zr alloy pressure tubes that were removed from service; the tube durability is expected to be similar to that of fuel cladding.

3.1. CORROSION MECHANISMS

Potential corrosion mechanisms for irradiated fuel with zirconium alloy cladding in wet storage have been examined in several prior studies [5, 6, 15, 19, 20, 24]. Several studies provide specific evidence, from fuel post irradiation examinations [3, 6, 20, 23–27], coupon studies [9, 11, 16, 28, 29], and theoretical assessments [5, 19, 20], that irradiated fuels with zirconium alloy cladding have high integrity over periods of many decades in wet storage. Even in relatively aggressive waters (up to 760 ppm chloride) [11], Zircaloy clad fuel survived without evidence of degradation in video inspections after storage up to 27 years.

The corrosion mechanisms examined in the studies referenced above include: (1) uniform attack, (2) pitting, (3) galvanic attack, (4) intergranular attack, (5) stress corrosion cracking, (6) crevice attack, (7) microbially-influenced corrosion, and (8) hydrogen embrittlement and/or redistribution. Evidence that these mechanisms are not active on zirconium alloys in wet storage comes from three sources, summarized in Figure 1: direct results of non-destructive and metallurgical

*Corrosion undetectable (<0.01 μm/year) on Zircaloy coupons exposed in pool water; conductivity range, 1 to 70 μS/cm over a period of 3 years [9].
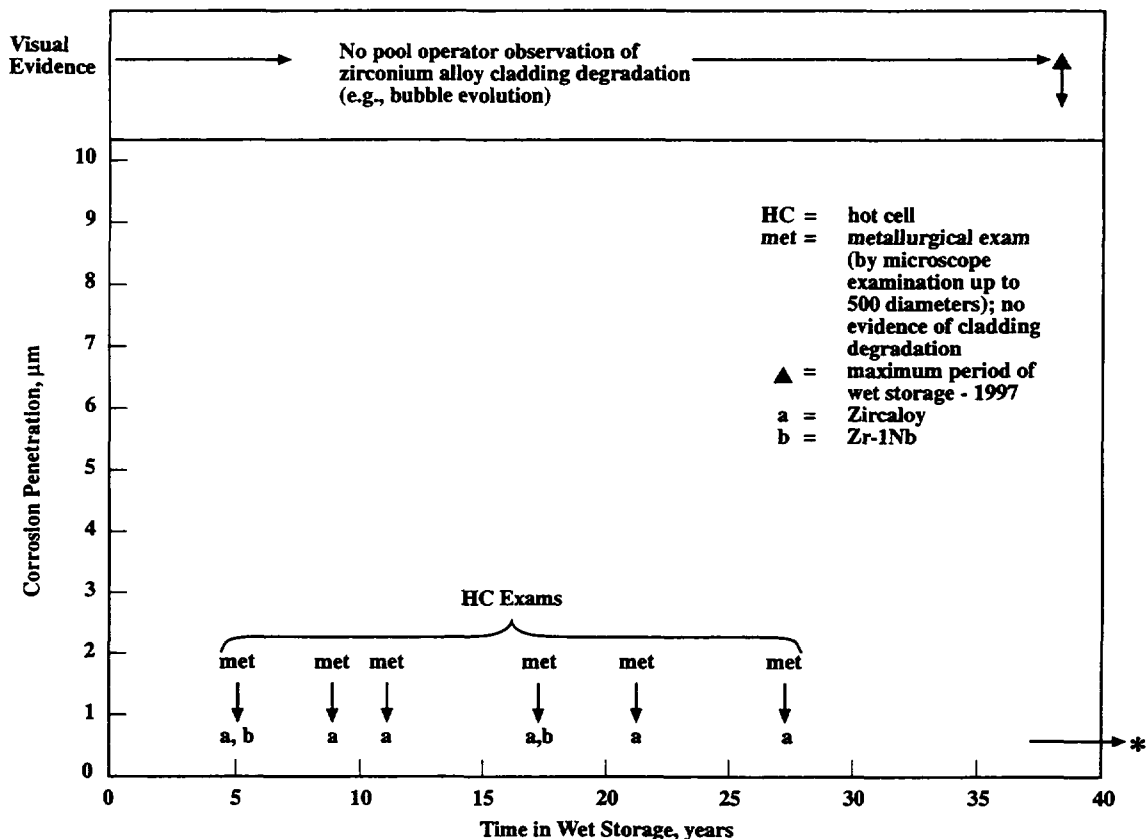
FIG. 1. Zr alloys: basis for cladding integrity assessment.

examinations in hot cells, indirect evidence from many routine fuel handling operations and observations on storage behaviour of several million fuel rods with zirconium alloy cladding that have been in wet storage (the oldest for periods approaching 40 years), and observations on coupons placed in storage pools (e.g., Ref. [9]).

3.1.1. Direct evidence from examinations of power reactor fuels

Examinations of nuclear fuel with zirconium alloy cladding are summarized in Figure 1, comprising non-destructive and metallurgical examination of irradiated fuel rods from power reactors, involving uranium oxide fuels. Detailed results of the examinations are provided in numerous publications and are summarized in IAEA reports [3, 4, 6]. The most recent fuel examination involves a Canadian study; the latest hot cell examination from that study was conducted on fuel with Zircaloy cladding after wet storage for up to 27 years [26]. The examination indicated that no significant cladding degradation has occurred (Figure 2). At a drilled hole, a small amount of UO_2 fuel, exposed to water for 21 years, had reacted to form a thin (<1 μm) deposit of $UO_3 \cdot 0.8H_2O$. The absence of any evidence of cladding degradation on ID or OD surfaces supports results of prior examinations to provide confidence that the cladding can be safely stored in water for periods of 50 to 100 years [26].

Zircaloy fuel from the Shippingport reactor was examined after wet storage for 20 years [23]. Results were compared with examination results on rods from the same assembly 20 years earlier. There was no significant change in the following:

- oxide thickness on the cladding;

- cladding hydrogen content or distribution;

- cladding mechanical strength and ductility;

- cladding ovality and dimensions;

- fission gas release fractions;

- rod appearance.

There was no evidence that localized corrosion mechanisms were active.

3.1.2. Indirect evidence from handling and observations on power reactor fuels

The longest storage of power reactor fuels with Zr alloy cladding in water is 38 years in 1997. Because many fuel rods have internal gas pressures, failure of a rod at a location accessible to the gas would result in bubble release from rods with pressures exceeding the hydrostatic pressure of the pool water. End-of-life gas pressures for BWR fuels at wet storage temperatures are typically in the range 30 to 300 psi (0.2 to 2 MPa). Corresponding pressures for PWR rods are 250 to 550 psi (17 to 37 MPa), typically, and 1200 psi (80 MPa), maximum. Internal gas pressures above 32 psi will exceed the combination of hydrostatic and atmospheric pressures at the bottom of a storage pool with a depth of 40 ft (12.2 m). There have been no reports by pool operators, including systematic world surveys through the BEFAST Programme, that any case of bubble emission or evidence of storage induced degradation from visual examinations of commercial power reactor fuel with zirconium alloy cladding has occurred.

There have been numerous opportunities to observe power reactor fuel rods during fuel handling campaigns, fuel assembly reconstitution, fuel shipments, rod consolidation campaigns, and in-pool non-destructive examinations. Examples of these activities are summarized in Table I.

The operations in Table I involved several campaigns where rods were handled and observed individually, including thousands of rods that were subject to NDE measurements and fuel assembly reconstitution [30]. To summarize the experience addressed in Table I:

◄ MOUNT

◄ OXIDE FILM

◄ CLADDING

20 μm
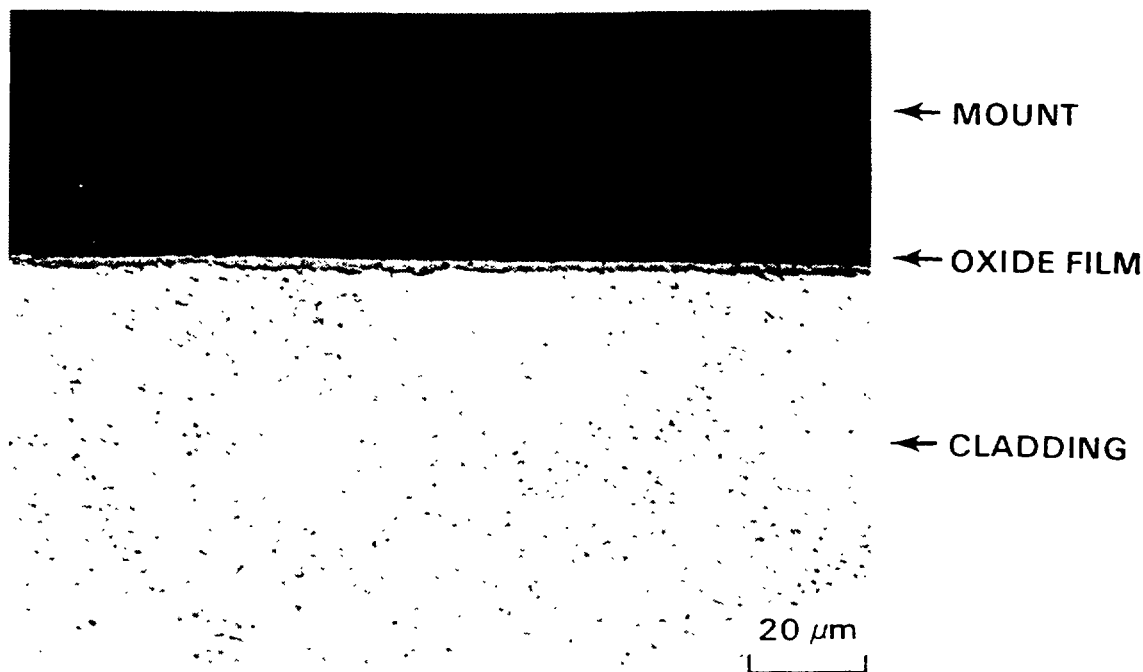
FIG. 2. Oxide film on Zircaloy clad Shippingport reactor fuel after 20 years in wet storage. No significant change in oxide thickness, hydrogen content, dimensions, mechanical properties, or onset of localized attack [23]. Similar result for CANDU fuel after 27 years in wet storage [26].

– Fuel shipments: there have been numerous shipments of power reactor fuels after periods of wet storage; the case addressed in Table I involves BWR and PWR fuel types with more than a decade of wet storage; the fuel assemblies were subject to video camera inspections prior to shipment; the fuel appeared to be in good condition; some assemblies had rods with reactor-induced cladding defects that were stored without special measures, and there was no indication that the defects had further degraded during storage; this and other fuel shipment campaigns provide evidence that cladding degradation has not advanced to stages that cause visual indications or that preclude the rigors of handling and shipping the fuel assemblies; another case involved shipment of Zircaloy clad fuel after up to 27 years of storage in an aggressive water chemistry (up to 760 ppm chloride from biocide treatments); W.J. Dirk of INEL indicated in a personal communication, 1995, that the assemblies were inspected with a video camera during preparations for shipment from the CPP-603 pool to the CPP-666 pool; video inspections and pool radiation monitoring suggested that the Zircaloy cladding had not degraded in the relatively aggressive environment, in contrast to aluminium materials that were visibly degraded.

– Assembly reconstitution: one category of in-pool operations involves replacement of rods that failed in reactor service with new rods or rods from other irradiated assemblies; generally, the operation occurs after relatively short periods of wet storage, but does offer opportunities to observe the condition of individual rods.

– Rod consolidation: in rod consolidation activities, rods with failed cladding were subjected to rod withdrawal forces from fuel assembly spacers; some rods with collapsed cladding were reformed to a more circular cross-section, indicating considerable residual ductility [25]; the operations involved observations of the conditions of individual rods; as in the shipping campaign, observations and fuel rod behaviour subject to stresses during consolidation suggested that there had not been substantial degradation of the rods in wet storage.

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TABLE I. EXAMPLES OF OBSERVATIONS ON POWER REACTOR FUEL RODS IN FUEL HANDLING CAMPAIGNS

Operation	Fuel type	Number of assemblies/rods	Time in wet storage	Observations
1.a. Return of FAs [a] from West Valley, NY to reactors [25]	BWR	430 FAs	12 to 18 years	No evidence of cladding degradation Crud loosening observed
1.b. Return of FAs [a] from West Valley, NY to reactors [25]	PWR	235 FAs	12 to 15 years	ditto
2. Fuel Assembly Reconstitution [b] [30]	BWR PWR	>50 000 rods[25]	up to 3 years	Only seven rods broken during handling operations involving rods with reactor-induced damage
3. Rod consolidations [c] See Ref. [25] for details	PWR [c]	106 FAs [>3100 rods]	up to ~15 years	Included fuel with cladding defects; no rods broken; rods found to be flexible No evidence of wet storage effects on cladding integrity Rods with collapsed cladding reformed to circular cross-section
4. In-pool NDE	BWR & PWR	>800 000 rods inspected [31]	up to 3 years	Identification of rods that failed in reactor service

[a] Fuel assemblies were inspected individually by underwater video camera prior to shipment from West Valley

[b] Failed rods were removed from assemblies and were replaced with intact rods

[c] Fuel rods were removed from assembly hardware and were close packed with rods from other assemblies to improve space utilization in storage facilities [25]

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–   *In-pool NDE:* large numbers of individual rods have been examined in storage pools to identify failed rods or to measure rod dimensions and/or oxide thicknesses [30]; as with reconstitution, the wet storage periods are relatively short, but information about individual rod condition is obtained.

In summary, Table I indicates fuel handling operations that have brought individual assemblies and rods into scrutiny, and have, in some cases (rod consolidation and fuel assembly reconstitution), subjected rods to withdrawal forces that would have likely forced breakage if they had been seriously degraded.

3.1.3. Coupon and laboratory studies

Aqueous corrosion rates of zirconium alloys are so low at wet storage temperatures that they are not measurable by techniques that are normally applied. However, some wet storage materials studies have included Zircaloy specimens. The results have indicated rates less than 0.01 μm/year [9], based on weight measurements. In fact, the absence of detectable interference colours on Zircaloy coupons after residence in the K Basins for three years suggests an oxidation rate less than 0.007 μm/year [9]. This result is based on the fact that development of a straw-coloured oxide on the Zircaloy coupons was not observed. The straw interference colour corresponds to an oxide thickness of about 200 angstroms. The coupons continued to appear silver after 3 years in pool waters, suggesting that oxide growth over this period was <200 angstroms. The Zircaloy coupons were in the basins during a period when water chemistry excursions occurred that markedly accelerated corrosion on Al alloy and carbon steel specimens [9]. Extrapolation of corrosion data from higher temperatures to 100°C indicated oxide growth of <1 mg/dm^2 (<0.07 μm) in 100 years [33]. The low "less than" values illustrate the difficulty of measuring zirconium alloy corrosion rates in wet storage environments.

3.1.4. Review of technical basis for wet storage of commercial power reactor fuels clad with zirconium alloys

The evidence cited above is consistent with prior perspectives suggesting that zirconium alloys are highly resistant to degradation in wet storage environments. However, it is important to continue to evaluate evidence regarding performance of zirconium alloys as wet storage periods increase and as design and service characteristics of the fuels change. This section briefly addresses basic understanding of zirconium alloy characteristics that relate to behaviour in wet storage.

3.1.4.1. Properties of zirconium alloys related to resistance to degradation in low temperature aqueous environments

–   *Oxides:* the bulk oxide that develops on zirconium alloys during aqueous corrosion is monoclinic ZrO_2; this observation has been confirmed for irradiated oxides on six alloys [34]; other oxides are observed, particularly in thin films, but the monoclinic form is the one of practical importance here; zirconium oxide is highly resistant to a wide range of aggressive chemicals; for example, if the oxide thickness is more than a few hundred angstroms, it is not dissolved in hydrofluoric/nitric acid solutions [35]; HF/HNO_3 solutions do rapidly attack unoxidized Zr alloys and can undercut oxide films at locations where the films are damaged; Griggs [36] attempted, without success, to identify an aqueous solution that would dissolve reactor-formed oxides on Zircaloy fuel rods at low temperatures.

The oxides that form on zirconium alloy fuel rods during reactor service vary in thickness from a few μm (3 to 5) for low burnup rods and at the ends of the rods to nearly 200 μm on high burnup rods [37]; in reactors with oxygenated coolants (BWRs and RBMKs), thick oxide nodules are observed that are separated by areas of thinner oxides; the oxides are generally tenacious, but some spallation occurs on thick oxides [38], sometimes involving loss of up to 50 μm of the oxide film formed in reactor service; the thick oxides are characterized by considerable porosity [39].

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In wet storage, the zirconium oxides have been stable over periods of nearly three decades, as indicated by the examinations summarized in Figure 1; even in aggressive pool chemistries, e.g., ICPP-603 at INEL [11], visual evidence suggested that the oxide films remained tenacious after periods up to 27 years in water with up to 760 ppm chloride, according to observations by Dirk of INEL, cited earlier. The oxides were also stable in accelerated tests under aggressive conditions [16].

- *Kinetics*: the kinetics of zirconium alloy corrosion in aqueous systems are well-characterized at elevated temperatures [33], related to investigations in unirradiated aqueous environments. The kinetic rate laws are generally cubic, but parabolic relationships sometimes apply, particularly in gas-phase environments at lower temperatures (e.g., 200°C) [40]. However, beyond "breakaway", kinetics become linear [39]. Linear relations of oxide growth with neutron fluence ($\phi \cdot t$) also occur in oxygenated reactor coolants. Kinetics in water-cooled nuclear reactors depend on numerous factors, including water chemistry, alloy composition, radiation level, and other factors discussed in a prior publication [39]. Due to excellent corrosion resistance at low temperatures, corrosion rates are difficult to measure, and no kinetic expressions are available; at intermediate temperatures (e.g., 200°C) the data seem to correlate with extrapolations from higher temperatures; extrapolation of the higher temperature data [33] to 100°C results in estimated oxide growth of less than 1 mg/dm^2 (<0.07 μm) in 50 years; while this extrapolation lacks specific precision, it provides general evidence of the excellent aqueous corrosion resistance of Zr alloys at low temperatures, in agreement with the data from a study at 90°C [19] and coupon studies in storage pools, indicating corrosion on Zircaloy 2 at less than detectable (i.e., <0.01 μm/year) [9]. Accelerated tests using crevice bent beam assemblies in spent fuel pools also showed no detectable corrosion on Zircaloy specimens [16].

- *Thermodynamics*: the Pourbaix diagram for zirconium [41] is similar to aluminium, with areas of corrosion in alkaline and acid solutions, but the area of oxide stability is much wider for zirconium, emphasizing the superior corrosion resistance. The thermodynamics of the Zr/O system favour dissolution of oxygen in the base metal, but at water reactor temperatures the fractional oxygen uptake is low [39], and is clearly not a source of oxide degradation at wet storage temperatures. The Gibbs free energy for the reaction of zirconium with water at 25°C is -135 kcal/mole [42], indicating a potentially energetic reaction, that proceeds with very slow kinetics, as indicated in the prior section.

3.1.4.2. Other damage mechanisms

- *Mechanical*: Prior summaries have addressed cases of mechanical damage to irradiated Zircaloy *clad* fuel assemblies when they are dropped during fuel handling operations [9,19,25]; for commercial power reactor fuel with lower burnups, the consequences of low temperature mechanical impacts have been minimal. However, some high burnup fuels are reported to have hydrogen contents above 600 ppm [43]. At this level, the hydrogen, combined with reduced ductility due to radiation, suggests low impact strength in the wet storage temperature regime. Therefore, impacts should be avoided when handling fuels in the higher burnup range. Zircaloy clad uranium metal fuel was mechanically damaged during discharge from the reactor, exposing uranium metal fuel to pool waters. This resulted in aqueous corrosion of the uranium exposed at breaches in the cladding [9]. Uranium metal corrosion is addressed in Section 8.

Oxide films on Zircaloy clad commercial power reactor fuel are typically scratched in fuel handling, particularly when fuel rods are withdrawn from the assembly spacers; however, the bare Zircaloy reforms a thin oxide that exhibits high resistance to aqueous corrosion at low temperatures, in contrast to Al alloys, that are susceptible to pitting at scratches in oxide films in high conductivity waters [10,28]. Mechanical damage that perforates cladding, exposing uranium oxide to pool water, generally results in minimal consequences (addressed in Section 8).

– *Hydriding*: Zirconium alloys absorb a fraction of the hydrogen released by the reaction:

$$Zr + 2\ H_2O = ZrO_2 + 4\ H\ (or\ 2H_2)$$
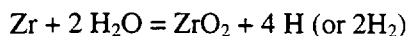
while corroding in reactor service; fuels with long reactor service have accumulated above 600 ppm of hydrogen in the cladding [43]; because corrosion rates are very low at wet storage temperatures, further hydrogen uptake by the reaction shown above is not expected. However, cladding with high hydrogen contents should be protected from low temperature impacts, as indicated in the prior section. Delayed hydrogen cracking is a phenomenon that has caused degradation of Zr alloys at relatively low temperatures [44]. Conditions in irradiated fuel rods at pool storage temperatures do not appear to apply to the delayed hydrogen cracking regime [19]. Hydrogen diffusivities are low in the wet storage temperature regime, estimated to be 4×10^{-13} cm^2/s at 25°C for α-zirconium [45]. So the principal concern for high burnup fuel with high hydrogen contents is to avoid impacts during fuel handling operations.

– *Galvanic*: Zirconium alloys (like titanium) are near the noble end of the galvanic series [41, p. 169], in contrast to Al alloys, which are near the active end of the series. Passivated stainless steels also are near the noble end. Metal-to-metal Al/Zr contacts would generate potentials possibly up to one volt, which is sufficient to promote accelerated corrosion of Al alloys and surface hydriding of Zr alloys at 90°C [46] in high conductivity waters; titanium alloys also were subject to hydriding when coupled to Al alloys at 65°C [46]. Al alloys are polarized anodically, promoting corrosion by water, forming hydrogen ions, which are attracted to the zirconium or titanium cathodes, where they react to form surface hydrides at temperatures (e.g., 65 to 90°C) where hydrogen diffusion rates are low. The low hydrogen diffusivity cited above suggests that hydrogen diffusion into the base metal will be slow. Oxide films inhibit formation of the couple.

At 25 to 85°C in high purity water, Al/Zr couples did not promote hydriding of the cathode [47]. Thus, in high purity water pools, chemistry and temperature conditions appear to be outside the regime where Zr alloys are prone to cathodic charging of hydrogen by coupling to Al. In high conductivity pool waters, the situation is not clear but would be mitigated by protective oxides on either or both of the metals and possibly by relatively low temperatures.

Noble potentials between Zr alloys and stainless steels or Inconels suggest that galvanic effects are not likely at low temperatures, though there are suggestions that they may occur in reactor service [39].

3.1.4.3. Water chemistry factors

Commercial power reactor fuel is generally stored either in deionized water pools or in water dosed with boric acid [3, 19]; fuel with zirconium alloy cladding has resided in both types of pool water chemistry for over two decades without evidence of degradation, based on indications cited in Sections 3.1.1. and 3.1.2. Some Zircaloy clad fuel resided in a pool with aggressive water chemistry, the CPP-603 pool at INEL [11], for times up to 27 years; about 470 fuel bundles have been moved to a high purity water pool; video inspections during fuel handling suggested that the Zircaloy cladding had not degraded significantly in the aggressive water (up to 760 ppm chloride ion).

3.1.4.4. Microbial attack

Microbial corrosion has occurred on most metals exposed to natural waters, for example in nuclear service water systems [48]; MIC attack on aluminium and stainless steels is addressed in those respective sections; titanium seems to be immune to MIC; we are not aware of studies specific to zirconium alloys, but the similarity to titanium suggests possible resistance; also, the series of detailed examinations (Figure 1) has not indicated phenomena that suggest MIC attack; at high radiation levels, some biological species may not survive, but some species are known to exist in relatively high radiation fields; what the radiation threshold level is for survival of MIC species that

participate in corrosion attack is not well defined. To this time, MIC has not been identified with detectable degradation of fuels with zirconium alloy cladding (biological phenomena are addressed in Section 10).

3.1.4.5. High burnup effects

Over the past decade, burnup trends for power reactor fuel with zirconium alloy cladding have increased. The current maximum burnup for Zircaloy clad power reactor fuel in wet storage is over 60 000 MW·d/MTU [43]. Fuel with burnups exceeding 50 000 MW·d/MTU has been in wet storage for more than a decade. Fuel in high burnup development programmes has been examined periodically by non-destructive techniques as the burnup increased, and by hot cell examinations at end-of-life [49]. Zircaloy clad Shippingport fuel with burnups up to 41 000 MW·d/MTU was examined after 17 years in reactor plus wet storage conditions (2131 days at reactor operating conditions) [50]. No evidence of wet storage impacts was observed. Characterizations of high burnup fuels indicate the following parameters:

- oxide thicknesses up to 200 μm [43] will have reduced typical PWR cladding thickness by approximately 20%; no additional significant loss of thickness is anticipated during wet storage; thick oxides (>60 μm) are sometimes observed to spall during reactor service; further spallation in wet storage is not likely unless impacts occur;

- the combination of high fluence (> 10^{22} n/cm^2) and elevated hydrogen contents (e.g., 600 ppm) results in low room temperature ductility [49]; the principal implication to wet storage is that the cladding will be susceptible to fracture by low temperature impacts, increasing the importance of avoiding impacts during fuel handling operations; (Note: rods with rod average burnups up to 65 MW·d/kg U have been withdrawn from assembly hardware, apparently without fracture [43]);

- Cs concentrations at the outer pellet surface were similar at burnups of 73 and 50 MW·d/kg U [43], but concentrations of other fission products at cladding surfaces at the highest burnups were not indicated;

- Iodine concentrations that promote stress corrosion cracking on internal fuel rod surfaces have been investigated [51]. In the absence of reactor service conditions, there is no evident mechanism to produce sufficiently high iodine concentrations to promote attack on the cladding inner surfaces under conditions in wet storage;

- hydrogen contents above 600 ppm are reported for PWR cladding, relating to prior comments about low ductility and impact strength at wet storage temperatures.

In summary, to date, performance of high burnup fuels with Zr alloy cladding has been generally successful, both in reactor service (although pressing hydrogen and oxide thickness limits in some cases) and particularly in wet storage. If the higher radiation levels and associated corrosion and hydriding are promoting degradation in wet storage, the phenomena have not become apparent. However, susceptibility to cladding fracture in lowtemperature impacts suggests need for special care in fuel handling operations for the high burnup fuels.

3.1.4.6. Storage behaviour of power reactor fuel with zirconium alloy cladding having reactor induced perforations

There are differences in philosophy regarding the storage of fuel with reactor-induced cladding defects; some pool operators place all power reactor fuel with known defects into cans to isolate it from the pool water. A worldwide survey of spent fuel storage experience [3] indicated that 70% of pool operators store failed LWR fuel on the same basis as intact fuel; the other 30% store failed fuel in canisters. Consequently, there are several thousand power reactor fuel rods that failed in reactor service that are stored in fuel storage pools without special measures. Such fuel has been the subject of assessments [52] and examinations [20, 52, 53]. The experience will be summarized in the format of case histories:

Case 1 Experience with Defective Fuel at an AFR Spent Fuel Pool [19]

Several hundred fuel assemblies with one or more Zircaloy clad rods with defects from reactor service are stored at the General Electric Co Morris Operation Gaseous radiation releases from the defective rods are not detectable The pool purification system maintains activity levels at about 4 10^{-4} µCi/ml

Case 2 Periodic Visual Observations on a Fuel Assembly with a Defective Rod–WAK Storage Pool, Karlsruhe, Germany [53]

In cases where uranium oxide fuel pellets are exposed to pool water, leaching of radioactivity has occurred very slowly There was no visually detectable dissolution of the pellets At the WAK pool, a fuel rod having a visible defect with exposed uranium oxide was removed from the pool and photographed annually Over a period of six years there was no visible dissolution of the pellet exposed to pool water

Case 3 Investigation of Durability of Zircaloy Cladding with Reactor-Induced Failures During Wet Storage [20]

Eighteen intact and ten defective fuel rods were investigated periodically during storage in a PWR pool, the rods were subject to the following tests visual inspection, profilometry, eddy current testing, and oxide thickness measurements, the rods were inspected four times in a seven-year period Even with loads imposed by handling during inspections, there was no detectable change in the rod parameters, including the size and shape of the rod defects The study has now been extended to 18 years without indication of changes in the defects [7]

Case 4 Comparison of a PWR Rod Defect on Discharge and after Eight Years in Wet Storage [54]

A PWR rod with a large cladding failure was photographed and gamma scanned soon after discharge Eight years later the same rod was re-photographed and gamma scanned There was no detectable difference in the size and shape of the cladding defect and no change in the exposed uranium oxide pellet interface, suggesting that the fuel material was stable in the storage pool environment (borated pool water)

Case 5 Examination of a Defective SGHWR Fuel Rod After Wet Storage [27]

An SGHWR fuel bundle, burnup, 1900 MW d/MTU, developed a cladding defect during reactor service After removal from the reactor, the rod was placed inside a closed canister in water The rod was investigated in detail after nine years in the canister There was no indication of metallurgical changes in the cladding There was a small increase in rod diameter near the defect, but no evidence that substantial oxidation of the exposed fuel pellet was taking place

Case 6 Examination of a CANDU Fuel Rod with a Drilled Hole After Wet Storage [26]

A Zircaloy clad CANDU rod with a drilled hole was examined after 21 years of wet storage Uranium oxide exposed at the hole had developed a thin surface phase that was identified as $UO_3 xH_2O$

The stability of uranium oxide pellets exposed to pool water is consistent with leaching studies on irradiated oxide pellets [55]

Two important results emerge from the cases cited above (1) defects in fuel clad with Zr alloys are not observed to enlarge during wet storage, (2) uranium oxides exposed at the cladding defects are not observed to dissolve detectably over periods of several years in contact with pool waters The

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latter result is supported by laboratory leaching studies on irradiated uranium oxide fuel [55] with burnups up to 54 MW·d/kg U at 25°C; the studies indicate leach rates for radioactive species in deionized water, so exposed fuel will contribute to the radioactive inventory in the pool water, but low temperatures and small exposed pellet areas limit releases to amounts that readily accommodated by pool cleanup systems.

There are cases where discharge of several fuel assemblies with reactor-induced cladding failures resulted in elevated concentrations of fission products in the pool water [52]. The pool cleanup systems were effective in reducing the radiation levels sufficiently that no operational problems resulted.

3.1.4.7. Tests on water-logged fuel rods

Tests were conducted on two BWR rods that failed in reactor service. The rods had absorbed water after the cladding failures. Tests were performed in a capsule in a hot cell to assess the characteristics of water removal. The water appeared to be largely removed (6 and 10 g) in 60 to 80 min. The remainder of the water came off within 320 min. Water intentionally injected was recovered. [See *Nucl. Tech.* 69, p. 186 (1985); also PNL-5987 (1986).]

3.1.4.8. Crud effects

Crud layers generally overlay the oxide films on fuel that has been in reactor service [31]. The crud layers comprise corrosion products from the reactor circuits that are carried by the reactor coolant and deposit on fuel rod surfaces. The composition of the layers differs depending on the reactor circuit materials and the water chemistries in the reactor coolant systems. In oxygenated coolants with iron-base alloy circuits, the crud layers are typically hematite, Fe_2O_3; there may be two layers: an inner tenacious layer and an outer loosely bound layer. In plants with more reducing chemistries and higher nickel alloys, nickel ferrites are typical, of the general composition, $Ni_xFe_yO_4$, where x + y is 3. Other species, such as Cr and Co also may be substituted. Crud thicknesses vary from approximately 50 μm to almost zero, with the thicker layers generally occurring in reactors with oxygenated coolants; recent improvements in water purity and chemistry control have minimized crud deposition.

When fuel assemblies are discharged after reactor service, the crud layers are carried into the wet storage facilities on the fuel rod surfaces. The important consideration here is behaviour of the crud layers during wet storage. In general, the crud layers have observable, but not serious impacts on wet storage technology; fuel from reactors where there have been cladding failures has been observed to desorb radioactive species (e.g., radiocesium isotopes) adsorbed from the reactor coolant; these species are removed from the pool water by the ion exchange system. Particulate species spall or desorb from crud layers and are observed both in the pool water and in the sludge on the pool floor; these species also are manageable with filtration and vacuuming, respectively. Of potential future significance is evidence that crud layers, originally tenacious upon reactor discharge, may soak loose from the fuel rods during long periods of wet storage. This phenomenon was observed during photographic definition of a PWR rod with a cladding failure [54]; the crud layer appeared to be flaking. Later, a poll of reactor pool staff that loaded and received the fuel shipped from the West Valley storage pool after periods of 12 to 18 years [56] indicated that both BWR and PWR fuels had shown evidence of crud loosening. The implication is that during future handling of fuels that have had long periods of wet storage, possible impacts of crud loosening should be anticipated and planned for, both in shipments and in transfers to dry storage.

3.2. SUMMARY OF ZIRCONIUM ALLOY BEHAVIOUR IN WET STORAGE

This summary updates prior studies that have indicated that zirconium alloys are highly resistant to degradation in wet storage environments. The latest survey of worldwide experience continues to support a position that fuel with zirconium alloy cladding would not have integrity problems in wet storage beyond 50 years [6]. The position presented here has the following elements:

- quantitative examination of fuel with zirconium alloy cladding after wet storage now up to 27 years, without indication of cladding degradation;

- visual observations on fuel stored up to 38 years, with no evidence of degradation, including fuel shipments and rod consolidation activities that involved close visual inspections of assemblies and rods; also, mechanical manipulation of failed rods, indicating high remaining ductility;

- reference to the high durability of zirconium oxide corrosion films in aqueous media;

- visual confirmation of Zircaloy fuel integrity after up to 27 years in aggressive pool chemistry (chloride concentrations up to 760 ppm);

- in-pool accelerated tests confirming high durability of zirconium alloys;

- in-pool coupon tests indicating absence of interference colour films over periods up to three years, suggesting oxidation rates less than 0.01 μm/year;

- kinetic extrapolations indicating very low rates of oxidation in wet storage environments;

- systematic evidence that reactor service defects in zirconium alloy cladding do not degrade detectably in periods approaching a decade;

- systematic evidence that uranium oxide exposed at cladding defects remains stable in contact with storage pool waters, involving both deionized water and borated water pools.

The evidence cited above provides a strong basis to support continued storage of fuels with zirconium alloy cladding and uranium oxide fuels in water. As a category, the commercial power reactor fuels with zirconium alloy cladding and oxide fuel are proposed to be the most durable fuel type in extended wet storage (see Section 11).

However, need to avoid mechanical impacts of Zircaloy clad fuel assemblies with higher burnups is suggested by the relatively high hydrogen contents that have been measured (>600 ppm). (Note: in 1997, the emerging evidence suggests that improvements in cladding metallurgy and reactor coolant control are resulting in lower hydrogen absorption on high burnup fuel [57].)

There are also indications that crud layers on Zircaloy clad fuel tend to soak loose during long periods of wet storage, suggesting that future fuel handling campaigns need to include assessment of impacts of loosened crud layers.

4. BEHAVIOUR OF STAINLESS STEELS IN WET STORAGE

Austenitic stainless steels (SSs) are prominent in spent fuel storage technology. The common formulation is Fe-18Cr-8Ni and the most common alloy is Type 304 SS and its companion alloy, Type 304L (see compositions, Annex I). The 304/304L materials have been used as cladding for LWR fuels (Annex I) and are the dominant materials for wet storage facility components (Annex II), including pool liners, fuel storage racks, piping, heat exchangers, etc. L grade denotes that the carbon content is low, maintained at ≤0.03 wt% to minimize thermal sensitization (Figure 3), an important phenomenon that will be addressed later in this section. The next most common material is the Type 316 or 316L grades (see Annex I for compositions). Type 316/316L materials are prominent in cladding for LMR fuels, but are seldom used for construction of fuel storage pool components. Type 348 SS has been used as cladding for some LWR fuels. AGR cladding is a 25Ni-20Cr material, stabilized with niobium. Early gas reactor test fuel was clad with Type 304 SS. Ferritic SSs have been used principally as duct materials for LMR fuel assemblies, but also as cladding on a limited basis.

As implied by the designation, the SSs are highly resistant to corrosion in many environments, including those in spent fuel storage pools. Stainless steel components have shown excellent corrosion resistance, even in some aggressive wet storage environments. However, they do have vulnerabilities that are relevant, even to the low temperature, often-benign environments in wet storage technology. Corrosion mechanisms for the SSs are addressed in Section 4.9.

Wet storage behaviour of fuel with SS cladding varies broadly, depending on the conditions during reactor service (Figure 2, Table II). Fuel irradiated at temperatures in the range 350 to 800°C has been prone to corrosion in water or moist air; by contrast, LWR SS clad fuel, irradiated in the range of 300 to 350°C, has not been susceptible to failure in wet storage environments (note that early BWR SS fuel cladding and small numbers of PWR cladding failed by IGSCC during reactor

LWR: 1 dpa ≅ 0.7 x 10^{21} n/cm^2, E >0.1M
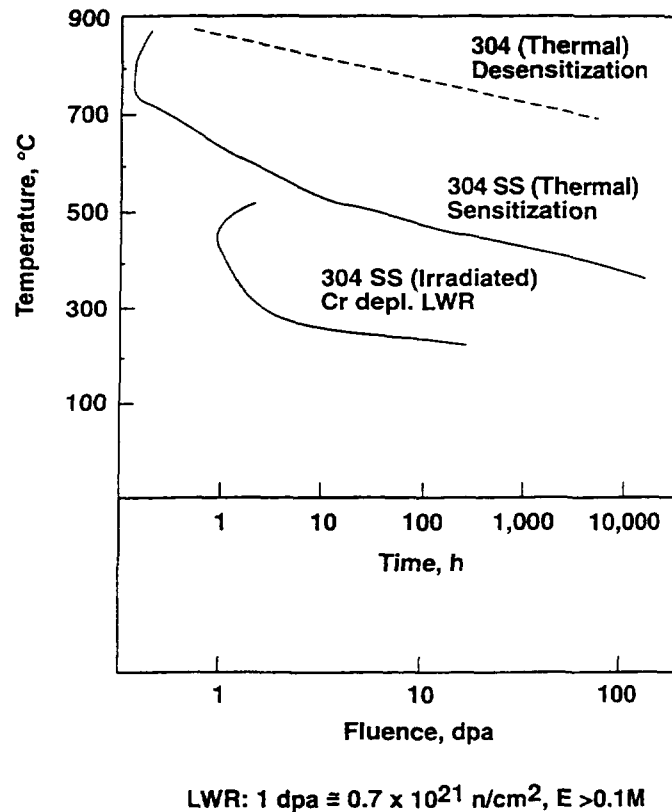
FIG. 3. Sensitization regimes for 304 SS: Thermal and irradiation-induced (Courtesy of S.M. Bruemmer, Pacific Northwest National Laboratory).

TABLE II SERVICE AND FAILURE CONDITIONS FOR SS CLAD FUELS AND COMPONENTS

Factor	LWR Fuel	LWR Fuel	LWR Comp	ORNL GCR	UK AGR	EBR II Fuel	FFTF Fuel	Other LMRs***
Alloy Designation (All Alloys Used)	304 304L	304	304	304	Fe25Ni 20Cr	316	316	
Component	Cladding	Guide Tubes	FSP pipes	Cladding	Cladding	Cladding	Cladding	
Service Temps, °C	340 max	300 max	35	815*	360-750	400-540	370-650	
Time at Temp In Service	1150 efpd	~1000 efpd	1300 d	50-100 d	to 5 y	250 d	~500 efpd	
Metallurgical Condition						Annealed	20% CW	
Range of Neutron Fluences, n/cm^2, >0 1 MeV			Zero			4-5 x 10^{22} > 1 MeV	>10^{23} max	
Welds (End Cap, Seam) & Weld Problems	End cap & long seam weld	Not significant	Yes	Not significant	Not significant	Not significant	Not significant	
Storage Condition(s). (Water, Gas)	Pool water	Pool water	Pool water	a)Moist N$_2$ b)Pool water	a)Moist air b)Pool water	a)Pool water b)Caisson air	a) Na b) Ar	
Storage Temps, °C	20-35	20-35	25-35	20	a)35 b)25	a)20-35 b)10-35	a)200 b)~35	
Storage Environment(s)	Borated	Borated	Borated	a)N$_2$ + H$_2$O b)H$_2$O	a)Moist air b)pH11 4 H$_2$O	a)Aggress, pool water b)Moist air	a)Sodium b)Argon c)Helium	
If Failures in Storage, Description	None	IGSCC at 16 tubes	Thru-wall IGSCC in HAZs of 9 pipes	IGSCC thru cladding wall	a)IGSCC b)IGSCC	a)IGSCC b)IGSCC	None observed	
Time to Failure	No failure	3 years	3 5 years	a)15-44 d b)?	a)35 d b)None	a)35 d b)?	N/A	
Cladding Exams Failed/Unfailed	Hot cell	Video	Hot cell	Hot cell	Hot cell	Hot cell	Visual	
Sensitization Estimate	**	High	High	High	High	High	High	

*Other components showed IGSCC in water after service at 427–650°C   ** Thermal – no, Irradiation – yes

***BN350, BN600, Phoenix, JOYO   316 SS cladding stored in water, up to 20 years

service). SS storage facility components have had excellent durability in low temperature aqueous environments, prompting the misconception that SS is immune to failure below 50°C. A few cases will be cited involving IGSCC failures at 20 to 30°C.

Examinations of irradiated fuels clad with SS have been conducted after periods of wet storage. Results of these examinations provide evidence regarding the wet storage characteristics of various fuel types with SS cladding. Also sections from spent fuel pool components have been examined by metallographic techniques after periods of wet storage.

4.1. OVERVIEW OF STAINLESS STEEL CORROSION IN WET STORAGE

Stainless steels are subject to some corrosion phenomena that do not have counterparts in other materials prominent in fuel storage technology. They are generally resistant to corrosion in wet storage environments. However, susceptibility to local attack can be induced when one or more of the following factors are not controlled:

- metallurgical condition (principally, degree of sensitization, involving denuding of chromium along grain boundaries) [58];

- stress level (stress levels that promote intergranular phenomena depend on the degree of sensitization and the aggressiveness of the environment [58]);

- environment (impurities, e.g., chloride, fluoride, thiosulfate [58, 59]; elevated pH was shown to be beneficial in suppressing IGSCC on sensitized AGR fuel in wet storage [60]).

Interactions of the three factors are sometimes represented schematically by three interlocking circles, each indicating one of the factors. Failure conditions are suggested by the situation where the three circles overlap. This suggests a synergistic dependence of the three factors. However, the relative importance of the three factors are not always evident, and there are cases where IGSCC attack has occurred on SS components in environments where aggressive species were not identified in the pool waters.

Specification of L (low carbon) grades (e.g., 304L, 316L) improves resistance to sensitization (L grades have carbon contents ≤0.03 wt%). However, if weld parameters, stress levels, and water chemistries are effectively controlled, regular grades of SS should be satisfactory for wet storage environments. Many stainless steel liners, fuel storage racks, piping, and other components are providing satisfactory service in wet storage facilities over periods approaching four decades. Stabilized SS grades involve additions of niobium or titanium to react with carbon in the grain boundaries, mitigating chromium depletion near the grain boundaries. However, the L grades are generally more expensive and have not been regarded as necessary for service in many wet storage facilities.

While SS generally has excellent durability in wet storage environments, some SS fuel cladding and components have been subject to degradation and failure in fuel storage pools and moist air or nitrogen (Table II). The positive and negative cases will be summarized in the following sections. Durability of LWR SS clad fuels will be differentiated from that of GCR and LMR fuels.

Corrosion mechanisms that are addressed in the following sections include uniform corrosion, pitting, galvanic attack, intergranular attack, stress corrosion cracking, crevice attack, microbial attack, and hydrogen effects. Most of these mechanisms have not been significant on SS cladding and components in wet storage. However, some mechanisms have been observed to degrade SSs even in the low temperature regimes in wet storage technology. Therefore, it is necessary to draw distinctions between the general high integrity of the SSs and the occasional vulnerabilities that have been observed.

4.2. THERMAL AND RADIATION SENSITIZATION OF STAINLESS STEELS

As indicated in Section 4.1, sensitization is a prominent phenomenon with the SSs, that does not have a counterpart with the Zircaloys, aluminium alloys, or mild steels. The phenomenon involves denuding of metal adjacent to grain boundaries of chromium, leaving zones of metal along the grain boundaries that are vulnerable to corrosion if exposed to aggressive species. Sensitization during thermal treatments at elevated temperatures is a phenomenon that has been recognized and characterized extensively [58]. Chromium depletion caused by radiation in nuclear reactors is a phenomenon that was recognized more recently, and the characterization is still underway, including determination of possible effects on SS integrity in wet storage.

4.2.1. Thermal sensitization of stainless steels

SSs are subject to chromium depletion in narrow zones adjacent to grain boundaries, caused by heating in a range of time/temperature regimes (e.g., 425 to 815°C for minutes to many days, depending on the temperature). A diagram outlining the thermal regime for sensitization of Type 304 SS is shown in Figure 3. Termed thermal sensitization, the process involves diffusion of chromium to the grain boundaries, where reaction with carbon forms chromium carbides (e.g., $Cr_{23}C_6$). The consequence is that a zone of metal along the grain boundaries is denuded of chromium, rendering it susceptible to corrosion when exposed to aggressive species. Aggressive corrosion environments result in intergranular attack (IGA) or intergranular stress corrosion cracking (IGSCC), if the attack is exacerbated by stress. Research to characterize degradation of SSs by these phenomena has been motivated by corrosion failures that have occurred at elevated temperatures, but IGSCC and IGA have been observed on cladding and components in thermal regimes in wet storage. The failures at low temperatures prompted some research to better understand the factors that contribute to attack in wet storage regimes [59 a,b,c].

Low carbon (≤0.03 wt%) alloys have higher resistance to sensitization because the carbon inventory available to react with chromium is smaller, but the L grades are not immune to sensitization. Another approach to mitigate sensitization, termed stabilization, involves adding niobium or titanium to the SS to react with the carbon in preference to chromium. However, both low carbon and stabilized alloys are sometimes subject to some degree of sensitization. Welding that involves excessive heat inputs is a common cause of thermal sensitization. Stress relief or other special heat treatments also have resulted in sensitization of SSs. For details regarding thermal sensitization regimes see Ref. [58].

As indicated in Figure 3, heating for sufficient times at required temperature conditions repopulates depleted zones with chromium. However, relatively high temperatures or extended times required for desensitization detract from practical implementation.

The thermal diagram for sensitization of Type 316 SS is similar to the one shown in Figure 3 for Type 304 SS, but the temperatures would be about 50°C higher for Type 316, based on discussion with S.M. Bruemmer, Pacific Northwest National Laboratory.

4.2.2. Radiation sensitization of stainless steels

Radiation damage effects during reactor service also can lead to chromium depletion at grain boundaries, termed radiation induced segregation (RIS). Radiation-induced vacancies promote chromium diffusion, resulting in depletion near grain boundaries. The slowest diffusing element, nickel, becomes enriched at sinks, while, chromium and iron in solution diffuse faster and become depleted. Therefore, radiation sensitization occurs by chromium diffusion away from the grain boundaries rather than diffusion to the grain boundaries and reaction with carbon to form carbides. As with thermal sensitization, chromium depletion leads to zones that are prone to intergranular attack and has been identified as irradiation-assisted stress corrosion cracking (IASCC). An ongoing study of IASCC is an element of this CRP [61]. The RIS becomes significant above neutron fluence

levels that differ somewhat for BWR and PWR environments (See Section 9). For details regarding RIS see Ref. [62].

Figure 3 also defines the regime for radiation-induced chromium depletion [63, BWR; 64, PWR]. Note that the radiation-induced sensitization thermal regime tends to lie below the regime for thermal sensitization, although there is some overlap. However, annealing of radiation damage precludes radiation sensitization above about 500°C. At 300 to 400°C, chromium depletion occurs at relatively low radiation-induced displacements per atom (dpa). As a comparison, for typical LWR neutron spectra, 1 dpa = 0.7×10^{21} n/cm^2. Beyond 20 dpa, Cr concentrations have decreased to about 10 wt% (Figure 4). At 500°C, Cr depletion is only slightly reduced, due to effects of radiation damage annealing.

The following sections summarize cases involving sensitization from one of the two mechanisms. It is important to recognize that sensitization alone does not assure that IGSCC or IGA will occur, but several cases will be summarized that have involved intergranular attack and some through-wall penetrations of cladding, tubing, or piping.

4.3. LWR STAINLESS STEEL CLADDING

LWR SS fuel cladding represents a class of irradiated SS that has not yet been observed to degrade in wet storage. Referring to Figure 3, the LWR cladding service conditions are in the range where radiation sensitization is active. However, the effect of sensitization seems to have been offset by mitigation of other synergistic factors, so that storage-induced degradation has not been observed on LWR fuel assemblies that have been examined after periods of wet storage.

As with zirconium alloys, there is both direct and indirect evidence regarding actual and expected performance of LWR SS cladding in wet storage. A comprehensive summary supports the perspective that LWR SS fuel behaved in a satisfactory manner in wet storage [65]. Results of metallurgical examinations of spent LWR fuel cladding have been published [3, 6, 27, 66]. Rods of Types 304 and 304L SS from three assemblies with two to five years in wet storage were examined in a hot cell, including examinations by high resolution metallography [66]. The assemblies had been stored in a borated water (PWR) storage pool. In a separate study, one assembly was examined after five years of wet storage in borated water followed by a period in a deionized water pool [3, 27]. One of the three assemblies examined after storage in the PWR pool had rods that failed during reactor

Calculated grain boundary Cr depletion for is shown based on a model calibrated to measured ion, proton and neutron irradiated austenitic stainless steels. The calculations indicate that irradiation induced Cr depletion for LMR (liquid metal reactor) end-of-life conditions are similar to that for LWR (light water reactor) end-of-life conditions. The calculated dose dependence for the LMR condition indicates that grain boundary Cr depletion is expected to saturate at a dose of about 20 displacements per atom (DPA).
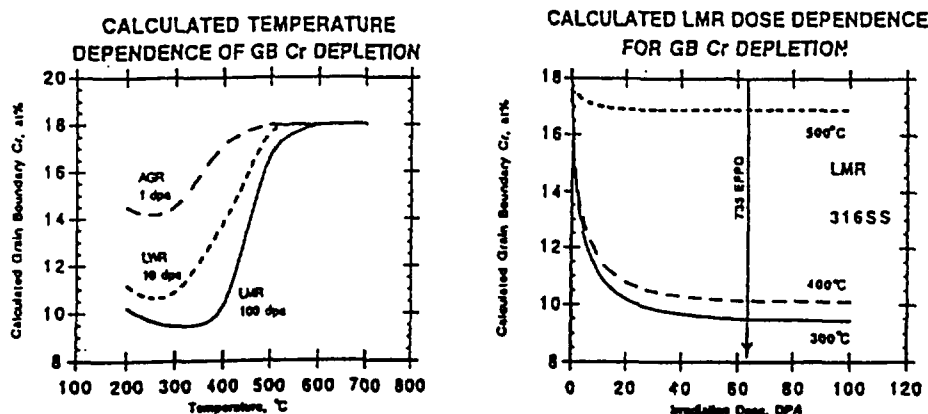
FIG. 4. Calculated chromium profiles at grain on boundaries of austenitic SSs in various reactors (left figure) and for an LMR case (right figure) [130].

service, which prompted its examination. The mechanism of cladding failure in reactor service involved IGSCC on exterior cladding locations that were subjected to high stresses by pellet chips wedged against interior surfaces. Cooling from reactor service temperatures would be expected to relieve the interfacial stresses between fuel and cladding, therefore mitigating the driving force for continued IGSCC at storage temperatures.

Detailed examination of the four assemblies suggested that the SS cladding was not degrading in wet storage. This is a significant result because IASCC has emerged as a prominent phenomenon on SSs during reactor service, and IASCC has been proposed as a factor in the degradation of GCR cladding in pool water and moist air [18, 67]. The maximum oxide thickness was about 6 µm on fuel cladding, which can be accounted for from reactor service and is consistent with results from reactor loop studies on SS [68]. The metallographic examination also indicated an absence of pitting and other localized phenomena on the LWR fuel cladding.

A preliminary study was performed to summarize the existing technical basis to transfer SS clad LWR fuel to dry storage [65]. The study takes into account the effects of reactor service and wet storage on SS cladding integrity.

Indirect evidence of satisfactory wet storage behaviour of LWR SS clad fuel includes 28 years (1997) of experience without visual indications of cladding degradation. The observations include 2000 LWR SS clad assemblies in US pools [65] and additional assemblies in European pools. However, maintaining pool purity is likely to be a more important requirement for continued satisfactory behaviour of SS clad fuel than for fuel clad with zirconium alloys.

There is a case involving IGSCC on SS guide tubes in a PWR fuel assembly [69]. The configuration involved 16 SS guide tubes above the fuelled section of the assembly. The tubes are connected to the in-core Zircaloy section by mechanical expansion joints. The tie plate, attached to the SS tubes, was heat treated to accommodate the mechanical property requirements of Inconel springs. When the fuel assembly was lifted after about three years of storage in the PWR pool, all 16 SS tubes failed, causing separation of the tie plate from the assembly. The key elements of the IGSCC appear to be a heat treatment that resulted in sensitization of the SS and residual stresses from the mechanical expansion. Whether there was also a chemical factor in the spent fuel pool water was speculated upon, but it was not indicated by analyses of the pool water. A few other fuel assemblies with the same configuration were judged by video inspection to be in some stage of degradation, though guide tube failures did not occur.

The minimal impact of uniform corrosion of the SS cladding on LWR fuel is illustrated by the calculation that wall thinning from aqueous corrosion of the cladding in reactor service represents only 2.5% of the wall thickness, even for the thinnest cladding (310 µm; the calculation assumes that 60% of the corrosion remained as oxide on the cladding surface [68]). Further corrosion during wet storage would be negligible, based on results from SS coupon exposures in pool waters [9], indicating uniform corrosion of 0.25 µm/year. Other data, obtained on SS at 105°C, in water with 7 ppm chloride ion, and a radiation level of 3×10^5 R/h indicated a corrosion rate of 0.3 µm/year [70]. Using the slightly higher rate, another 15 µm of cladding would be consumed in 50 years in wet storage (5% of the thinnest cladding).

4.4. GCR AND LMR SS FUEL CLADDING BEHAVIOUR

Certain classes of SS cladding have been susceptible to IGSCC in storage environments, both gas phase and aqueous phase. In contrast to LWR cladding, the fuel service conditions generally have spanned both thermal and radiation sensitization regimes (Figure 3, Table II). Cases of IGSCC that developed on the cladding exposed to relatively high service temperatures will be addressed in the following sections.

4.4.1. IGSCC failure of ORNL gas reactor stainless steel

Type 304 SS cladding exposed in a gas-cooled test reactor was in service at temperatures up to 815°C for periods of 50 to 100 d [71]. Subsequently fuel rods were placed in storage in both moist nitrogen and in deionized water at 20°C. Through-wall IGSCC failures occurred over periods of 15 to 45 d in both environments. Other components in the same test, exposed in the range 425–650°C, also were observed to have degraded by intergranular corrosion. A mechanism for the moist nitrogen failures will be proposed in the AGR section. Reference to Figure 3 suggests that that the cladding was heavily sensitized thermally, but radiation effects should have annealed out. Other factors that promoted the IGSCC failures in water are not clear. Oxygen dissolved in high purity waters facilitates IGSCC at elevated temperatures in reactor environments [72]. However, studies on sensitized Type 304 SS indicated that dissolved oxygen or H_2O_2 did not promote IGSCC below 120°C [72]. The studies indicated that chloride and sulfate were important in promoting IGSCC, including synergistic effects, in environments containing peroxide. The absence of a dissolved oxygen effect on IGSCC of SS below 100°C also has been reported [73]. Given that dissolved oxygen does not appear to be aggressive in promoting IGSCC at pool storage temperatures, there is no obvious aggressive factor reported to explain the failure of the GCR rods at ORNL in water at 20°C. Failures of similar rods in moist air could have involved a radiolytic nitric acid mechanism that is addressed in the following section.

4.4.2. Intergranular attack on AGR stainless steel cladding

The cladding alloy for the British AGR fuel has a composition that is nominally Fe-25Ni-20Cr, stabilized with Nb [67]. The AGR service temperature range that causes sensitization is 350 to 520°C. Maximum AGR service temperatures are up to 750°C, but healing (desensitization) occurs in the 5-year service period above 550°C. Peak sensitization occurs at about 420°C, due principally to RIS. The irradiated cladding has been exposed to both water and moist air environments [18, 67]. The indicated uniform corrosion rate of the irradiated cladding in pool water was less than 0.5 μm/year, and is suggested to be substantially lower than this limit of detection [67]. However, the cladding degradation was determined by metallography to be progressing intergranularly. It was concluded that even though the SS was niobium-stabilized, that it had become sensitized in AGR service conditions. To extend storage times in water, the pH is maintained at 11.4 [18].

Other irradiated AGR fuel has been exposed in moist air in a hot cell at about 35°C to 50°C. The cladding was subject to intergranular degradation [67]. The proposed mechanism was that nitric acid formed from radiolysis of nitrogen and moisture in the air, caused an aggressive environment on fuel rod surfaces that promoted the attack. Cracking was not observed at relative humidity below 14%. No attack occurred on SS in air without radiation. While this mechanism may apply to other cases of attack on GCR and LMR cladding exposed to moist nitrogen or air, there is no systematic confirmation.

4.5. INTERGRANULAR FAILURE ON LMR SS FUEL CLADDING

Fuel from several LMRs is or has been stored in water pools. The fuel cladding has generally been Type 316 SS or a similar alloy (See Table II). The reactors where irradiated fuel has been stored in water includes EBR II [74] in the USA, BN 350 and BN 600 in Kazakhstan and Russia, respectively [3], and Phoenix in France [75]. Spent fuel from the FFTF reactor has not been stored in water pools. Reference to Figure 3 suggests that the service temperature regime for EBR II fuel lies largely in the region that sustains RIS, but with some overlap with the thermal sensitization regime. Cladding temperatures in other LMRs also span the range of both radiation and thermal sensitization, but in some cases, lying largely in the thermal sensitization regime (Table II).

4.5.1. Intergranular attack on EBR II fuel cladding

Irradiated EBR II fuel cladding has failed by intergranular mechanisms in both wet storage [74] and when exposed to moist air [76].

4.5.1.1. EBR II cladding failures in wet storage

The fuel cladding on EBR II fuel is Alloy 316 in the annealed condition. The reactor service temperature range was 400 to 540°C. A typical reactor service period was 250 d, resulting in a neutron fluence of 4 to 5 × 10²² n/cm², >0.1 MeV. Until 1978, discharged assemblies where stored directly in the ICPP-603 storage pool at INEL for relatively short periods prior to reprocessing. Fission product releases were attributed to failure of the SS cladding. For example, an assembly placed in the pool in February 1976 showed no evidence of cladding failures in the transfer cask. However, about one month later radioiodine was detected near the storage rack [74]. Hot cell examinations on the assembly and a similar assembly revealed the cladding to be in advanced stages of degradation, including grain boundary precipitation, intergranular cracks, and loss of surface grains from the cladding. The cladding failures occurred during a period when the ICPP-603 storage pool had relatively aggressive conditions [11]. However, an unirradiated SS specimen, welded to carbon steel, did not degrade over a period of a decade in the 603 pool. The aggressive pool conditions included chloride concentrations up to 760 ppm. Stainless steel components exposed in the same pool have not appeared to degrade. Thus, the EBR II fuel failures represent additional examples of susceptibility of sensitized cladding to failure in water storage.

4.5.1.2. EBR II cladding failures in moist air

EBR II fuel rods were shipped in containers in air from INEL to Los Alamos National Laboratory. After the shipping tube was opened, one rod broke into several pieces during normal handling [76]. The intergranular degradation of irradiated fuel cladding in moist air has been given the pedestrian descriptor, "hot cell rot". The phenomena have not been investigated in depth, but the failures in moist air may have been promoted by the nitric acid mechanism proposed by British investigators [67], although it has not been confirmed.

4.5.2. Storage experience with other LMR fuels

Table II indicates several LMR facilities where irradiated fuel is stored in water, including BN-350 and BN-600 [3], the French Phoenix reactor [75], and a Japanese LMR. We are not aware of examinations of fuel assemblies from these reactors after periods of wet storage. While some degree of intergranular attack might be expected, based on British experience with sensitized AGR SS clad fuel, there have not been indications of substantial problems with radiation releases from the fuel after perhaps as long as two decades in wet storage. This result may be consistent with the apparent absence of accelerated corrosion on LWR fuel cladding that would be expected to have some degree of RIS effects. Adequate control of pool water chemistry may mitigate attack, even when the cladding is sensitized. Lack of adequate chemistry control in the ICPP-603 pool could be regarded as a major factor in the rapid degradation of the EBR II fuel cladding (Section 4.5.1.1).

Fuel from the FFTF reactor has been stored in sodium, in argon cover gases when examined in hot cells, or, more recently, in canisters in inert gas (helium). Therefore there has been no opportunity for water-induced degradation or "hot cell rot" on the FFTF fuel.

There is one study involving simulated LMR cladding that indicated no evidence of accelerated aqueous corrosion in water at 82°C [77]. The SS had been exposed in a sodium loop in the temperature range of 370 to 720°C for 2000 h. The explanation offered was that the resistance to intergranular attack depended on two factors: massive intragranular carbides, due to cold work, which prevented the alloy from sensitizing in the sodium tests, and the presence of a nickel-depleted layer with molybdenum-rich precipitates that promoted resistance to pitting attack.

4.6. STAINLESS STEEL FUEL STORAGE FACILITY COMPONENTS

As with fuel cladding, there evidence both general and specific in nature concerning the performance of SS components in wet storage. Thousands of components continue to perform

without apparent degradation, some with service times approaching forty years. However, a few SS components have degraded in spent fuel pool environments.

Detailed metallurgical examinations of sections from SS components were examined after periods of service in wet storage facilities [78]. Most of the areas examined, both visually and metallographically, were free of IGSCC and generally free of evidence of IGA; 21 weld sections were examined: only two, from the same component, had been subject to IGA, represented by mild attack, 75 μm, maximum after 1.4 years in a borated water storage pool. Another SS specimen had an area of mild pitting corrosion (15 μm) in a crevice region. In addition to the metallurgical examinations of weld regions, 79 welds were inspected visually; no evidence of degradation was observed.

At the TMI Unit I spent fuel pool, through-wall cracks developed at nine locations in weld heat-affected zones [79]. Laboratory examinations demonstrated that the metal in the failure locations was heavily sensitized, from metallographic evidence, and from electrochemical potentiokinetic reactivation (EPR) measurements that were > 20 μamp/cm^2, characteristic of sensitized SS. The welds were made in the field, where there may have been stresses imposed as pipe ends were matched for welding. While there was no evidence of significant impurities from water chemistry analyses, there were indications of chlorides on some of the failure surfaces. The failures occurred in a standby cooling loop for the fuel storage facility, where coolant remained stagnant for extended periods.

Data from laboratory studies were used to estimate the durability of 304L SS waste canisters in wet storage [70]. The assessment included consideration of both uniform and localized corrosion. The study suggested satisfactory durability of the canisters for times exceeding foreseeable periods of wet storage.

Visual inspection of a pool liner that had been wetted 8 years suggested that no degradation mechanisms had been active; the material was 304L SS, and the environment was deionized water [54]. Hundreds of storage pools worldwide utilize SS liners and other components; a few liners have developed small leaks; it has not always been practical to investigate reasons for the leaks, but the leakage is collected in channels and diverted to a waste processing system or is returned to the pool. A few fuel storage pool pipes have developed through-wall leaks (addressed under IGSCC), but predominantly, the performance of SS wet storage facility components has been excellent over periods approaching forty years.

4.7. ACCELERATED CREVICED BENT BEAM TESTS

Crevice bent beam (CBB) tests were conducted on three materials, including Type 304L SS specimens [16]. The SS specimens were tested in both unsensitized and sensitized conditions. Sensitization involved heating at 675°C for one hour. Specimen assemblies were lowered close to the bottom of two spent fuel pools in India, at Trombay and at Tarapur. Water chemistry conditions in the two pools were in the range of 2.5 to 13.5 μS/cm., representing good water chemistry control. The range represented measurements at different locations in the pools. There was no evidence of localized attack, including SCC in crevices on SS specimens, where pH values dropped to as low as 2 to 3 in less than six months. Tests proceeded for up to one year. The test series provided further specific evidence that SSs are resistant to attack in wet storage, even under relatively aggressive conditions.

4.8. SUMMARY OF STORAGE EXPERIENCE: STAINLESSS STEEL CLADDING AND FACILITY COMPONENTS

Some SS clad fuels have been susceptible to accelerated corrosion, even in what have seemed to be relatively benign wet storage environments. However, the thermal environment also must contribute because LWR SS cladding has not yet shown the degradation that has been obvious on GCR SS fuel claddings [67, 71]. The LMR cladding, exposed in a similar temperature regime, would also be expected to corrode in wet storage, although the LMR fuels are stored either in sodium or in

gas environments. However, the LMR fuels have been susceptible to a phenomenon described as "hot cell rot", involving irradiated assemblies that have been exposed to moist air [76]. AGR SS clad fuels are exposed in the temperature regime 350–750°C for periods up to 5 years. Cladding has developed through-wall cracks during exposures in moist air in hot cells; nitric acid formed by radiolysis in the moist air, was believed to be the aggressive species [67]. The AGR fuel cladding has also been susceptible to accelerated corrosion in wet storage [18]. The attack in water can be mitigated by dosing the water with NaOH to pH11.4.

The foregoing cases illustrate an aspect of SS corrosion in wet and moist environments that contrasts with the behaviour of LWR SS fuel cladding and with most SS storage facility components. The contrasting behaviour seems to relate to the high reactor service temperatures for the GCR and LMR fuels, that contribute to thermal sensitization of the microstructures. However, the relative contributions of thermal and radiation effects have not been systematically investigated. The GCR cladding irradiated at 800°C+ seemed to be more prone to intergranular failure than the AGR SS cladding irradiated at 500°C: the former failed at 20°C in moist air and in deionized water; the AGR cladding also failed in moist air, but seems to be less prone to failure in water. However, the SS cladding compositions differ in the two cases. The "hot cell rot" phenomenon has not been subject to substantial mechanistic investigation, but may be related to the moist air failures of the AGR fuel. The apparent immunity of the LWR fuel to intergranular attack in water seems to correlate with the lower reactor service temperatures. However, there has been no comprehensive correlation of SS service conditions and related susceptibilities to intergranular failure. It is also important to note that the sensitized EBR II fuel failed in highly impure water, while no attack was observed on LWR cladding that presumably had been subject to RIS, but was stored in waters of good quality.

It is relevant to acknowledge one case of a LWR fuel assembly SS component [69] and several cases of SS storage facility components [79] that have been subject to intergranular failures. These cases also are understood largely in terms of sensitizing heat treatments and the effects of stress. While the roles of stress level and environment were not clear for the cases cited, laboratory studies have been conducted to elucidate the failures that, somewhat unexpectedly, have occurred at low temperatures in what are regarded as benign environments [59 a,b,c].

The following sections address specific mechanisms that are potentially relevant to project the durability of SS cladding and components in wet storage environments.

4.9. STAINLESS STEEL CORROSION MECHANISMS

Stainless steels are considered to be highly corrosion resistant, particularly at low temperatures in relatively pure waters. However, the few cases that involve failure of SS wet storage components and cases of fuel cladding failures need to be exposed and understood to avoid future failures. The mechanisms discussed below largely reflect the durability of SSs in wet storage, but with exceptions introduced above. Most mechanisms have been studied in considerable detail, beyond the scope of this study to address, so the discussion will focus on aspects relevant to wet storage technology.

4.9.1. Pitting corrosion

Pitting corrosion of SS was reviewed and considered to be negligible for SSs at low impurity concentrations and temperatures [70], based on the work of Szklarska-Smialowska [80], including in the presence of gamma radiation. Detailed examinations of SS cladding and storage facility components have not indicated observable pitting attack in wet storage environments. Dirk [11] examined SS that had been in an aggressive pool chemistry (up to 760 ppm chloride, conductivity, 600 μS/cm) for more than a decade and found no evidence of corrosion attack. In contrast to advanced corrosion of Al alloy and CS components in this aggressive environment, SS buckets and cans seem to have survived relatively free of corrosion [11, 81]. The resistance to pitting, even in this relatively aggressive pool chemistry is consistent with the observation that pitting has been absent on SSs exposed to chloride ions up to 10^5 ppm below 50°C, even in highly acidic conditions (pH2); also, pitting was not observed on SSs up to 50°C at chloride contents up to 10^3 ppm [83]. In addition,

the FSP water was dosed with nitrate ions to inhibit pitting attack [11, 15; see also Uhlig and Revie, Corrosion and Corrosion Control, p. 313 (1985)].

4.9.2. Uniform corrosion

Austenitic stainless steels are notably resistant to uniform corrosion, even at LWR operating temperatures [65, 66, 68]. Under conditions in wet storage environments, corrosion rates on SS are difficult to measure [9], so kinetic data at 105°C [82] were used to assess SS corrosion in wet storage conditions because they had been quantified and represented a conservative basis for projection [70]. The uniform corrosion rate in water with 7.5 ppm chloride and 3×10^5 R/h radiation was 0.012 mil/year (0.3 μm/year) [82]. Therefore, the corrosion penetration will be negligible, even after 100 years in wet storage. This result is consistent with the absence of detectable corrosion on SS components examined metallographically after 15 years in wet storage [78].

Ferritic SSs are used as ducts and to a small extent as cladding for LMR fuel assemblies. In long exposures to water in wet storage, these materials may be susceptible to aqueous corrosion in oxygenated pool waters. Another phenomenon that may render austenitic LMR SS cladding susceptible to aqueous corrosion is formation of ferrite layers during service. The layers form on outer cladding surfaces by preferential diffusion of nickel that dissolves in the circulating liquid metal coolant. Wu observed formation of a ferrite layer 3 μm thick on stainless steel exposed 2000 h at 720°C in an unirradiated test loop [77]. Service of SS clad fuel in reactors has caused ferrite layer thicknesses of 5 to 25 μm [95]. On exposure of the ferrite layer to oxygenated water, it is possible that iron oxides will form. There are several iron oxide species, depending on oxygen concentrations, temperatures, etc. [83]. Two prominent candidates during aqueous corrosion in oxygenated pool water are Fe_2O_3, hematite, and FeOOH. The hematite my be hydrated or unhydrated [84]. In transfers from wet to dry storage, it will be important to consider possible effects of the corrosion products on the water inventory that must be dealt with. Insufficient drying leaves water molecules that can degrade by radiolysis if radiation fields are sufficiently high. The hydrated hematite releases water between 350 and 400°C [84]. However, if the principal corrosion product is FeOOH, the water (1/2 H_2O) is released at about 135°C [84]. Other water will be adsorbed on the corrosion products and may need to be expelled at elevated temperatures if the amount is sufficient to contribute to overpressurization of the dry storage container. FeOOH was the aqueous corrosion product from corrosion of CS components at one fuel storage site in specimens collected from floor sludge. However, the dominant iron oxides in sludge obtained from the canisters were Fe_2O_3 and Fe_3O_4 (see Section 6.2).

4.9.3. Galvanic corrosion

Stainless steels are expected to be noble compared to most materials they may contact in fuel storage pools, i.e., Al alloys and carbon steel [41]. Dirk investigated attack on a SS/CS weldment that had been in an aggressive pool chemistry for about a decade [11]. He found advanced attack on the CS but no observable attack on the SS. The potential difference of the SS/Zr alloy couple is expected to be small and has not shown detectable attack on either metal in casual observations. Large cathode-to-anode ratios will exacerbate corrosion of the less noble metal.

4.9.4. Intergranular attack

The IGA mechanism is active on SS that has been subject to sensitization at stress levels that do not promote IGSCC. A low incidence of IGA was indicated in a prior section, with maximum penetrations of 75 μm in a weld heat-affected zone (HAZ) after 1.4 years. No evidence of IGA was observed on SS LWR cladding after 5 years in wet storage [66]. However, IGA may be occurring on some sensitized SS claddings where stress is not a significant factor.

4.9.5. Stress corrosion cracking, including IGSCC

Stress corrosion cracking of SSs can involve both transgranular and intergranular mechanisms Transgranular cracking is often associated with chloride-induced degradation at relatively high chloride levels There has been no experimental evidence of chloride-induced SCC at chloride levels up to 10^5 ppm up to 75°C at neutral pH except at very high stress levels [59a] Also there has been no evidence of SCC in waters at low pH (pH2) or high pH (pH11) up to 60 and 90°C, respectively [85, 86] However, these test environments did not include another aggressive species (e g, thiosulfate/sulfide) that can promote SCC on austenitic SSs In relatively benign wet storage environments, the development of cracks has been intergranular, and has occurred on sensitized materials at temperatures near 30°C The factors include sensitization, there is usually reason to believe that high stresses were involved, but there has been minimal evidence of significant chemical impurities in the pool waters Therefore, the few cases of IGSCC that have occurred are not completely explicable in terms of the three classical factors understood to cause IGSCC

Several cases of IGSCC (some cases may involve IGA) were introduced in earlier sections

- GCR fuel cladding with reactor service at 800°C+, with IGSCC failures occurring at 20°C in moist air and water [71],

- GR fuel cladding with reactor service at up to 520°C, with failures at 35°C in moist air [67] and IGSCC in water (mitigated at pH11 4) [60],

- LMR fuel cladding with reactor service at up to 650°C, subject to "hot cell rot" in moist air at ambient temperatures [76], and corrosion in wet storage [74], but with some evidence that the LMR cladding can tolerate periods of wet storage [77] (elevated pH may by useful as it is with AGR fuel [18]) Fuels from French [75] and Russian LMRs [3] have been stored in water over extended periods without evidence of serious degradation, but with minimal detailed examination,

- fuel storage pool piping with through-wall failures at several locations in weld HAZs at 30°C after four years in borated (PWR) chemistry [79], microstructures were sensitized, but stress and water chemistry factors were not clear, there was speculation that thiosulphates could have leaked into the pool coolant system, several runs of pipe were replaced in the early 1980s, no additional leaks had been observed when plant staff was contacted in 1994,

- 6 SS guide tubes in a PWR Zircaloy clad assembly failed, allowing the upper tie plate to detach, considered to be promoted by a sensitizing heat treatment, stresses at a bulged joint, but with no clear evidence of a water impurity factor (again, thiosulphates were suspected but not confirmed) [69]

Laboratory studies conducted to investigate the factors in the failures indicated clear evidence of stress and sensitization effects, however, failures did not occur on moderately sensitized 304 SS in 15 ppm chloride solutions, below 180 % of the yield strength [59 a,b,c], the studies implicated a rough surface finish in the failure of TMI Unit 1 pipes [79] The laboratory studies confirmed that stainless steels are quite resistant to IGSCC, even with moderate sensitization, high stress levels, and 15 ppm chloride In tests at 32°C, furnace-sensitized 304 SS was subject to intergranular cracking in chloride, fluoride, and thiosulfate solutions However, at concentrations of 15 ppm, chloride solutions required higher stresses than fluoride solutions, and thiosulfate solutions caused failures at about one half the stress levels required for chloride solutions [59a]

Irradiation-assisted cracking (IASCC) will be addressed in Section 9 on radiation effects

4.9.6. Crevice corrosion

In the benign environments in most commercial storage pools, crevice corrosion of SS components was regarded to be a minor consideration [19], chloride ion concentrations of several

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thousand ppm are considered necessary to promote crevice corrosion of 304 SS at 50 to 100°C However, crevice corrosion that was promoted on Type 304L SS by gamma radiation in 3% NaCl solutions [87], but that chloride concentration is not relevant to storage environments Kain, et al has applied CBB studies to spent fuel environments The results indicate that even at high chloride concentrations and low pH values in the crevices, SS was not susceptible to crevice attack at storage pool thermal conditions [16]

Whether radiation-induced crevice effects are ongoing in fuel storage configurations is not clear, but their effects have not been evident

4.9.7. Microbially influenced corrosion

Biologically-based corrosion of SSs has been a leading problem in power plant service water systems, exposed to natural waters (river, sea, cooling pond waters) [48] In some cases, major MIC attack has occurred on SS in a few months at temperatures similar to the storage pool range [88] The common range for MIC to develop is pH4 to 9, 10 to 50°C, particularly in stagnant conditions, CS, SS, Al alloys, and Cu alloys, among other materials are susceptible [41, p 521] No cases of MIC attack on SS wet storage facility components have come to our attention [89], but local pitting of Al alloys in a high purity water pool is suspected to be due to MIC [81]

Of particular concern is transport of aggressive biological species from an infected pool to a previously clean pool Practical measures to mitigate transport of biological species between pools should be considered

Biological attack on irradiated fuel cladding may be mitigated by high radiation levels, but the threshold of radiation tolerance for various species is not clear (see Section 9 on radiation effects) As radiation levels decay, the prospect that microbial infestations may attack fuel cladding surfaces increases

Because there are many biological species in aqueous systems, it is difficult from monitoring biological counts to correlate corrosion observations with specific biological species Control of algae in fuel storage pools has been a problem at numerous facilities [89] At some facilities, the application of biocides has caused increases in corrosion of metals exposed to pool waters (e g Ref [9]) In the facilities cited in Ref [9], a coupon monitoring programme that was ongoing provided the basis to identify the impact of the biocide treatment on corrosion and also provided assurances that implementation of water chemistry control resulted in a return to relatively low corrosion rates

4.9.8. Hydrogen effects

Stainless steels are so-called endothermic occluders of hydrogen, indicating low solubilities and absence of distinct hydride phases However, hydrogen cracking is a recognized degradation mechanism for iron-based materials [90] For unirradiated austenitic SSs, the threshold, K_{th}, for hydrogen-induced crack growth is very high, so hydrogen-induced cracking is generally not expected to be a problem Radiation hardening facilitates hydrogen embrittlement phenomena, Jones observed hydrogen-induced crack growth in irradiated Type 316 SS at 100°C [90] However, for LWR fuel stored in pools at lower temperatures, a mechanism for ingress of sufficient hydrogen to promote cracking is not apparent

4 10 UNDERSTANDING STAINLESS STEEL CORROSION

The basis for the excellent corrosion resistance of stainless steels lies in their ability to form highly protective oxide films [91] Development of the passive films is facilitated by chromium contents The passive films can remain stable over periods of decades in relatively benign wet storage environments

4.10.1. Oxide types

Accurate assessments of oxide film compositions formed at low temperatures on SSs is difficult because the films are very thin Film compositions generally differ from the proportions in the alloy, but the compositions depend on the conditions of formation A review of SS corrosion film compositions is available [80] The oxides that form on stainless steels under wet storage conditions are too thin to be of practical significance and are therefore not addressed in detail here Berry [83] summarized the complex relationships of the various iron oxides In low oxygen coolants, typical of PWRs, the oxides that deposit on cladding are generally spinels of the Fe_3O_4 type (e g ,$Fe_xNi_yO_4$), with Cr, Ni, and other cations substituted for some irons These oxides are the principal species that form on SS cladding in PWRs Dark crud layers also deposit on PWR fuel rod surfaces, but the layers are generally very thin on SS clad fuel

In oxygenated coolants, the principal oxide species is Fe_2O_3 The alpha form of Fe_2O_3 that grows in oxygenated conditions is not adherent, appearing reddish brown This material is generally present in a loosely adherent layer on BWR fuel assemblies, but with an adherent crud layer of the same composition next to the fuel rod surface The crud layers form over the zirconium oxide on the fuel rod surfaces The source of crud in both BWRs and PWRs is corrosion products from reactor coolant system surfaces The corrosion products are transported to and deposit on the fuel rod surfaces Impacts of crud layers in wet storage operations were addressed in a prior section

The oxide films formed on fuel cladding have been observable in metallographic examinations, indicating thicknesses up to 6 μm [66] The oxide films are spinels of the magnetite type indicated above Evidence from the fuel examinations suggested that the films are stable in fuel storage pool waters Oxide films on SS fuel storage pool components were too thin to resolve by metallography after exposures up to 16 years at 20 to 30°C [78]

4.10.2. Kinetic bases

At fuel storage pool temperatures, SS corrosion rates are too low to justify defining kinetic relationships Estimated values for SS uniform corrosion rates were cited in Section 4 9 2 including data from coupon studies Parabolic corrosion rate constants have been published for SS at temperatures down to 150°C [92]

4.10.3. Thermodynamic bases

For the reaction

$$Fe + 4H_2O = Fe_3O_4 + 4 H_2$$
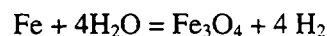
the Gibbs free energy is −16 kcal/mole at 25°C [42]

For the reaction

$$Fe + 4H_2O = 2Fe_2O_3 + 4H_2$$
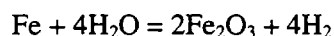
the Gibbs free energy is −128 kcal/mole at 25°C Therefore, both oxides are energetically possible in wet storage conditions, but the kinetics are very slow

4 11 OTHER DAMAGE FACTORS

Other factors that may influence SSs in FSPs are addressed in this section, including mechanical damage, effects of a range of water chemistries, burnup effects, attack on the inner cladding surface, and effects of ferrite layers on the outer cladding surfaces

4.11.1. Mechanical damage

Only a few cases of mechanical damage to SS clad fuel have come to our attention [93]. Specifically, top nozzles were broken from three PWR SS clad assemblies during refueling and cask loading. A few cases of twisting and bowing have been reported. Otherwise, mechanical damage to SS clad LWR fuel has been minor. We are not aware of mechanical damage to GCR and LMR fuel.

The oxide films formed on SS clad fuel are much thinner than the service films formed on Zircaloy clad fuel, e.g., 6 μm for SS compared to up to 200 μm for Zircaloy. The SS oxides do not appear to be susceptible to spallation, and the dissolution rate is very low at wet storage temperatures [66].

4.11.2. Water chemistry effects

Fuels with LWR SS cladding are stored in both borated (PWR) and deionized water (BWR, AFR) wet storage environments. Neither environment is expected to degrade the LWR fuel cladding provided that good water chemistry control is maintained. Fuel examinations were cited earlier that provide a basis for such an assessment. Susceptibility of other SS clad fuels (GCR, LMR) to failure in aqueous environments has been cited previously. The susceptibilities may be exacerbated by impurities in the pool waters, but failures can occur in relatively pure waters. The efficacy of high pH water to mitigate corrosion of AGR SS cladding was cited earlier.

4.11.3. Burnup effects

The highest fuel burnup for SS clad fuel discharged from US LWRs is 38 000 MW·d/MTU (Haddem Neck) [65]. Fuel from the same reactor was examined after 2.3 years in the reactor pool; the assembly had a burnup of 36 700 MW·d/MTU; absence of evidence of wet storage effects seems to address the burnup range of SS clad LWR fuels now in storage.

4.11.4. Storage of stainless steel clad fuel with reactor induced defects

Stainless clad LWR fuels have been susceptible to reactor-induced failures in both BWRs and PWRs. Because the fuel is uranium oxide, the storage characteristics in water are identical to failures in Zircaloy clad fuels, cited earlier. The fuels generally are stored without use of special containers to isolate the fuel from the pool water unless the cladding is seriously degraded.

4.11.5. Crud effects

Crud layers on SS LWR fuels are generally thin, and were not resolved in metallographic examination of irradiated cladding [66]. Superficial crud layers also appear to have been largely absent on LMR and gas reactor SS fuel cladding.

4.11.6. Fuel–cladding chemical interaction (FCCI)

During reactor service, fission products are generated that may attack the interior surface of the SS cladding. Similar phenomena were previously addressed for zirconium alloy cladding, identified as PCI. The attack on LMR cladding is termed FCCI. Correlations of FCCI with cladding temperature and oxygen-to-metal ratio have been published [94]. No FCCI is expected below 430°C for fuel irradiated at O/M greater than 1.9. Fuel adjacency is a term related to FCCI that refers to cladding interaction with fission products such that mechanical properties of the SS cladding are degraded. Fuel adjacency effects are activated at test temperatures as low as 370°C [65], but are not expected in the thermal range of wet storage. As the LMR fuel cools from service temperatures, the fuel is expected to shrink more than the cladding, thereby mitigating interfacial stresses at wet storage conditions.

4.11.7. Ferrite layer effects

The ferrite layer that forms during LMR fuel service was introduced in Section 4.9.2. The layer forms on the outer surface of the cladding due to nickel diffusion out of a narrow zone of the cladding surface. The nickel is then carried away by the circulating sodium. The layer thickness that developed on Type 304 SS in sodium at 720°C in an unirradiated test loop was 3 μm [77]. For irradiated LMR Type 316 fuel cladding, ferrite layer thicknesses in the range 5 to 25 μm have been reported [95].

4.12. SUMMARY OF BEHAVIOUR OF FUEL WITH STAINLESS STEEL CLADDING IN WET STORAGE

In contrast to the zirconium alloys, which have been consistently durable in wet storage, the SSs have a range of behaviours. Predominantly, the SSs have been highly durable over periods now approaching four decades. However, there are cases of failure of certain types of fuel cladding and a few SS wet storage facility components. There is a basis to understand the factors that contribute to SS failure in water at low temperatures. However, there is not, in every case, sufficient characterization of the specific stresses, metallurgical states, and environmental conditions to fully correlate with the factors that are understood to cause failures. The following observations characterize the behaviour of SS cladding and facility components in wet storage and low temperature air/nitrogen environments:

1. The predominant observation is that widely used SS wet storage facility components and LWR fuel with SS cladding have excellent histories of durability in FSPs in periods approaching 40 years for components and 30+ years for LWR fuel cladding. The fuel is expected to have radiation-induced sensitization; stress levels are not known, but are not expected to be particularly high. Indications are that pool water conditions have been consistently good. Stainless steel facility components have not been observed to degrade perceptibly in storage pool waters with chloride contents up to 760 ppm.

2. A few SS PWR fuel pool pipes have failed by IGSCC, but after application of appropriate welding procedures, no further failures have been observed in the same facilities. Sensitization at welds was confirmed; high stresses could be postulated, but there is not a basis to expect high impurity levels in the pool waters. Failure of an upper tie plate of a PWR fuel assembly is understood to have occurred from IGSCC promoted by pre-irradiation thermal sensitization and stressing, but a possible role of water impurities (thiosulphate) was based on speculation, and not on evidence from water analyses.

3. Fuel claddings in service at temperatures in the range 350 to 815°C in GCRs and LMRs have been subject to IGSCC/IGA, either from thermal or radiation sensitization or a combination. The LWR SS claddings, that would be expected to have some radiation-induced sensitization, have not been subject to observable degradation in detailed examination after up to five years in wet storage and in visual observations in storage facilities for up to 30+ years. Failure occurred in both water and moist air on cladding that would have been sensitized by reactor service in the thermal rather than radiation regime (ORNL case). Stress levels are not known and there was no evidence of substantial water impurities. LMR (EBR II) cladding, probably with a combination of radiation-induced and thermal sensitization, failed in about one month in high chloride water. Stress levels are suspected to have been relatively high, so all three factors seem to have been involved. However, several operators of LMRs store fuel in water. Despite expected sensitization, either from thermal or radiation sources, or a combination, there is currently no evidence that the fuel is seriously degrading after up to two decades. Details of water chemistry control are not known in all cases, but purities are generally thought to be good. In addition, stress levels in the cladding are not known. An LMR (FFTF), with fuel stored only in sodium or inert gas, has had only one post-discharge rod failure. It seems credible that for cases involving sensitized cladding, but no failures (LWR, some LMRs), maintaining a good water chemistry keeps the SS out of the failure regime. Relatively low stress levels could be a positive factor, but that has not been investigated systematically.

4   While stabilization with Nb and Ti tends to suppress thermal sensitization by removing carbon as a sink for Cr, at least one case has been cited (AGR cladding) where sensitization occurred despite stabilization with Nb The sensitization is suggested to be due to carburization at the outer cladding surface and by RIS through the cladding wall [18] The attack in water was not rapid and was mitigated by maintaining the pool water at pH11 4, with chloride at 0 05 ppm The attack in moist air was rapid and was hypothesized to be due to the aggressive effects of nitric acid formed by radiolysis of moisture and nitrogen

5   Comparing the cases of failed and unfailed SS, sensitization, either thermal or radiation-induced, has been a common factor for cases of failure

5. ALUMINIUM ALLOYS

Aluminium alloys are prominent in wet storage as FSP components [3, 78] and as fuel cladding, principally after service in research, test and defence reactors [3, 5–15]. Aluminium is an attractive material for fuel and target cladding because of low neutron absorption cross-section. Also, selected Al alloys have good corrosion resistance in high purity reactor coolants at cladding surface temperatures up to about 200°C. The performance of Al alloy fuel cladding in wet storage is a composite of effects of fabrication, reactor service, interim storage at reactor and AFR pools, handling, and shipping. Performance of the Al alloys in wet storage has a wide range of corrosion behaviours, from rapid penetration to minimal corrosion in more than two decades. Penetration of the cladding may release fission products, fuel particles, and transuranic species to the pool water, but the impact depends on the type of fuel that is exposed to the pool water through the cladding breaches. If the fuel involves metallic uranium, the exposed metal is subject to aqueous corrosion at pool temperatures (Section 8). If the fuel material is uranium oxide, it is relatively inert to pool water, as indicated in prior sections and Section 8. If the fuel comprises an aluminium alloy matrix with embedded fuel particles, release of fission products, transuranics, and particulates will depend on how readily the aluminium matrix corrodes.

Al clad fuels from test and defence reactors traditionally have had relatively short periods (9 to 18 months) of wet storage prior to reprocessing. However, with shutdown or mothballing of reprocessing capacity, particularly in the USA, Al clad defence and test reactor fuels are remaining in wet storage much longer than expected (8 to 35+ years). Fuels which are no longer candidates for reprocessing are now being evaluated for extended wet storage or transfer to dry storage.

It is important to diagnose fuel condition in wet storage as a basis to define conditioning that will be required if the fuel is transferred to dry storage [15]. On the other hand, there may be incentives to extend the period of wet storage, requiring a basis to predict fuel durability under the expected storage conditions.

As with the SSs, Al alloys have been exhibited a wide range of corrosion behaviours. This range must be defined and understood before the durability of specific fuels and components can be predicted with confidence. The database summarized here provides a substantial basis to identify parameters that, if systematically controlled, can extend satisfactory storage of aluminium fuels and facility components in water for several decades. However, failure to effectively control water chemistry parameters can lead to degradation of Al alloy cladding and components in periods less than one year. Once severe pitting of aluminium components has set in, there is evidence that the corrosion may proceed, even when the water is filtered, deionized and brought under excellent chemistry control [9]. In contrast, where water chemistry control has been systematically maintained, aluminium corrosion has been minimal, even over periods of more than a decade [9, 78] and, on visual evidence, over more than two decades [6].

5.1. RANGE OF ALUMINIUM ALLOY CORROSION BEHAVIOURS IN WET STORAGE

To illustrate the range of Al alloy corrosion behaviours, conditions and corrosion data are compared for four FSPs in Table III.

Conditions in Pool A have resulted in low corrosion rates. However, Pool B, with similar chemistry control, has a limited indication of high Al pitting rates; the role of microbially influenced corrosion (MIC) is being investigated. In Pool C, the environment resulted in relatively rapid pitting of aluminium. Pitting rates in Pool D, with higher Cl⁻ and conductivities, were no higher than in Pool C. However, nitrate was added to inhibit corrosion. A potentially significant difference between conditions at Pools A and B is that lighting has been minimal at Pool A and bright at Pool B, possibly contributing to the biological activity that may be occurring in Pool B. Nevertheless, it is important to note that pitting is the principal corrosion mechanism. Uniform corrosion was relatively low, even in the more aggressive pool waters.

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TABLE III. COMPARISON OF CONDITIONS AND Al ALLOY CORROSION IN FOUR FSPs

	Pool A	Pool B	Pool C	Pool D
Conductivity μS/cm	~1	~1	170–190	630
Chloride, ppm	<0.1	<0.01	6–20	760 to 50
pH	6.7–7.8	5.5 typ	5.5–8.5	7.8–8.4
Other	NO₃, SO₄⁻, ppb levels	MIC?	<17 ppm NO₃ <14 ppm SO₄	NO₃/Cl⁻: 3/1
Al corrosion behaviour: Pitting: Uniform:	<0.001 mm/year <0.001 mm/year	0.3 mm/year 2.5×10⁴ mm/year	0.75 mm/45–180 d(a) low	0.44 mm/year low
References	[78, 97]	[11]	[28, 96]	[11]

(a)Alloy-dependent 8001 >1100 and 6063.

Figure 5 illustrates the broad range of corrosion behaviours for Al alloys in spent fuel storage environments. At the extremes are: (a) severe pitting within a few months, indicated by the trend on the left, near the ordinate; (b) a trend of low corrosion rates, near the abscissa. (Note that the visual examination indicated at 24 years was conducted on fuel cladding [6]). Understanding the factors that contribute to aggressive and benign water conditions is the crux of a systematic, sustained basis to protect Al alloy fuel cladding and facility materials for the period that they need to remain in wet storage.

While water chemistry is the most important single factor in aluminium durability, other factors must be considered when they apply:

- alloy composition, particularly in more aggressive water conditions [96];

- characteristics of corrosion films that formed on fuel elements during reactor service; if formed below ~60 to 70°C the films will comprise principally the trihydrate $Al_2O_3 \cdot 3H_2O$; if formed above 80°C, the monohydrate will be the principal species [98]; unless damaged, both films will suppress further oxidation in fuel storage pools; however, some scratching and even mechanical distortions can be expected as fuel elements and components are handled, which can result in pit initiation sites, particularly in aggressive waters [28, 97];

- galvanic effects, shown to be important for aluminium alloys in wet storage environments, when combined with crevices [16] and in borated water [99], but with no indication of attack at contacts between aluminium canisters and a SS liner after seven years in a deionized water pool chemistry [19]; in impure waters, galvanic attack has been observed on aluminium in Al/SS couples [16, 96] and even between different aluminium alloys [11, 28, 96];

- crevice effects, demonstrated to be important for aluminium alloys in wet storage environments, even in deionized water chemistries [16]; however, as a practical consideration, Al alloy components that rest on SS liners are still functional in numerous FSPs now approaching four decades of storage;

– microbiological effects can develop, even in pools with high water purities (e.g., pool B); when the ultraviolet treatment equipment was out of service for more than one year; severe pitting of unirradiated Al alloy specimens has been observed (up to 2.5 mm in one year); slimes were observed, and MIC is suspected, though not fully confirmed [81]; there are plans to inspect fuel element surfaces to determine whether the attack is suppressed by radiation. Again, as a general observation, the most troublesome observable biological phenomenon in wet storage technology to date has been algae [89]. It is important to implement algae countermeasures that are not aggressive to fuel cladding and components in the wet storage facility [9].

Prediction of the durability of aluminium fuels and components must acknowledge the broad range of Al alloy corrosion behaviours represented quantitatively in Figure 5, and represented qualitatively by the following observations:

– Al clad fuel elements have survived up to 24 years in wet storage (>35 years for some assemblies in Brazil, while others show signs of corrosion) [6];

– aluminium-alloy racks and other components continue to function over periods approaching 40 years in FSPs [3, 78];

– Al alloy components have degraded rapidly in aggressive water chemistries [9, 11, 23, 28, 9], and in one high purity pool where MIC is suspected [81]. The water chemistries that promote rapid degradation of Al alloys are not fully understood; there is a pitting correlation that provides general guidance [100], but water conductivity appears to offer a useful, practical correlation with aluminium corrosion, in co-ordination with other factors outlined above. This study will include a summary of water chemistry factors that influence aluminium corrosion under wet storage conditions.
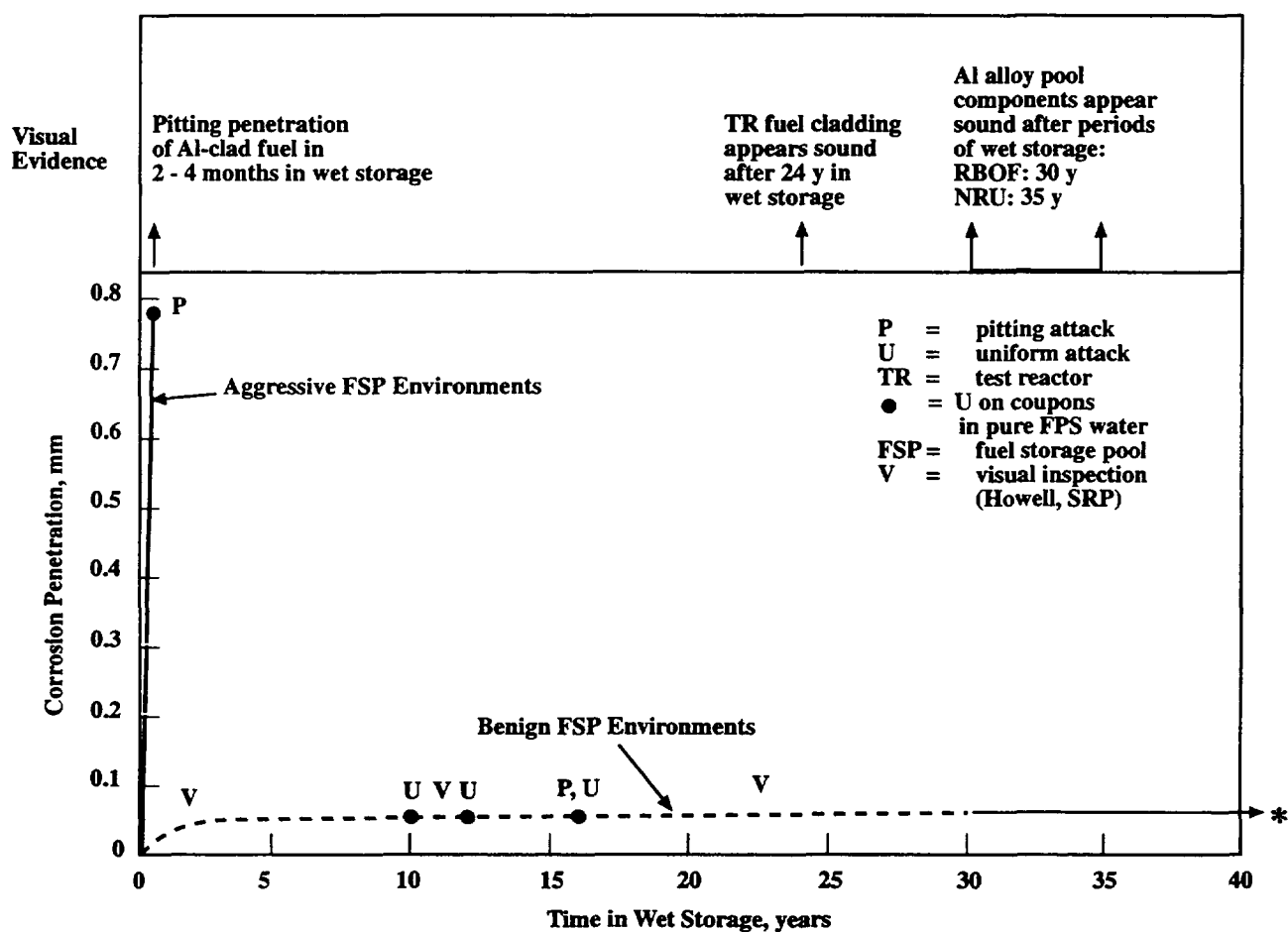
* Steady-state uniform corrosion rates on Al alloy coupons in fuel storage pool water: ~0.25μm/y, conductivity range of 1 to 10 μS/cm [9]

FIG. 5. Range of Al alloy corrosion rates in FSP environments.

42
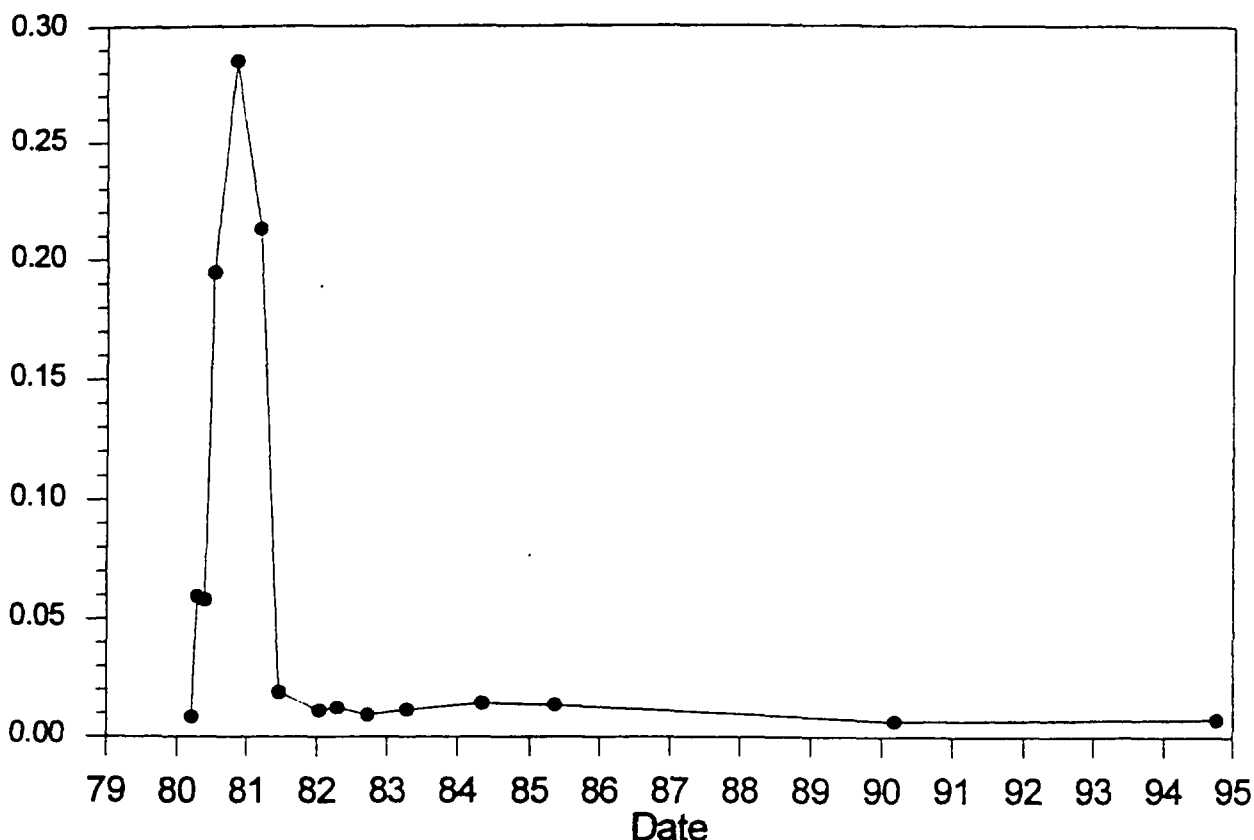
FIG. 6. Uniform corrosion rates on type 6061 aluminium in Hanford K-West FSP, based on coupon data*. Excursion due to biocide dosing of FSP water.

*Rates on type 6061 aluminium remained higher in K-East FSP until deionizers installed in 1986. Since 1990, rates nearly equal [9].

The impact of a water chemistry excursion on Al alloy corrosion in a wet storage facility is illustrated in Figure 6. Biocide treatments (commercial compounds; composition not indicated) were made to the pool water just prior to the time frame of the corrosion excursion [9]. Copper alloy heat exchangers in the system corroded, indicated by a blue colour in the water, probably contributing to the Al alloy corrosion. The time frame to return the water purity to a level that mitigated Al alloy corrosion is indicated in the figure. Note that Al alloy corrosion rates decreased to 0.01 mpy (0.25 μm/year).

5.2. CORROSION MECHANISMS

Potential corrosion mechanisms for aluminium alloys in wet storage environments have been examined [28] and are summarized in the following sections.

5.2.1. General corrosion

Aluminium is one of the most active metals, based on thermodynamic properties. It depends on formation of a protective barrier oxide for generally good durability in a variety of environments. General (uniform) corrosion rates of aluminium alloys in most waters at low temperatures are relatively low, as indicated in Table III. Aluminium forms a highly stable oxide that suppresses rapid thinning of the aluminium component, in contrast to mild steels exposed to oxygenated waters. In general, oxides on aluminium are stable in the pH range 4 to 8.5 [41]. Outside this pH range, the protective oxides are subject to dissolution and loss of protective character. Heavy metals, e.g., mercury, and copper and iron ions tend to destroy the passive character of the film. Aggressive species, such as chlorides, also degrade the passive film locally [28]. However, as indicated in Table III, uniform corrosion is generally not the limiting mechanism for aluminium degradation in wet storage.

Additions of hydrogen peroxide (e.g., $10^{-3}N$) reduce the aqueous corrosion rate of aluminium at elevated temperatures (see Uhlig and Revie, Corrosion and Corrosion Control, p. 344, 1985). Peroxide dosing was effective in eliminating bacterial colonies while maintaining tolerable corrosion on Al alloys [9]. Peroxide dosing was also applied effectively at two research reactors without significant impact on materials [89]. The implication is that dosing with peroxide to counter biological species will be beneficial rather than detrimental to aluminium durability.

5.2.2. Galvanic corrosion

Aluminium alloys lie at the active end of the galvanic series. Reference [28] includes illustrations of accelerated corrosion of Al alloys, promoted by coupling to SS. It also provides of review of factors that facilitate galvanic corrosion. Galvanic corrosion of aluminium alloys has been observed in fuel storage environments, when coupled to stainless steels [11, 16, 28], and even when different aluminium alloys are coupled in waters with high conductivities, e.g., >100 μS/cm. In galvanic couples, the less corrosion resistant material becomes anodic and corrodes, while the more corrosion resistant material becomes cathodic and relatively passive. The magnitude of the corrosion current is determined by the potential difference between the coupled metals. For example, in a copper/aluminium couple, the copper is cathodic with a standard potential of 0.52 volts at 25°C. The potential of the aluminium half cell is -1.66 volts, so the couple has a potential of 2.18 volts, suggesting a driving force for relatively large corrosion currents. The relative voltages change as a function of environment and can even reverse for certain combinations of couples and environments, so the standard EMF series can only be used as a general guide.

Factors affecting galvanic corrosion include area ratios, distance between electrically connected materials (throwing power), and geometric shapes. Galvanic corrosion of the anodic material may take the form of general or localized corrosion, depending on the configuration of the couple, the nature of protective films, and the metal characteristics. In fuel storage pools, SS/Al alloy couples are common. In highly pure waters, galvanic effects have not appeared to degrade the service capability of Al alloy components. In fact, examination of Al alloy containers that had been in contact in a BWR (DIW) pool for seven years resting on a SS liner indicated that the containers had not degraded significantly [19]. However, CBB tests in DIW pool waters indicated advanced attack on an Al alloy in crevices, where low pHs (pH2) and increased concentration of chlorides had occurred.

Galvanic attack has been observed on Al Alloy 8001 in contact with Alloy 1100 in high conductivity pool waters [28]. Galvanic factors are largely mitigated when water conductivities are maintained in the range of 1 to 3 μS/cm, except in dissimilar metal crevices that facilitate development of low pH and concentration of impurities [16].

5.2.3. Crevice corrosion

Crevice corrosion is a localized form of attack, occurring in closely fitted surfaces that are sufficiently offset to allow water entry. The attack was first attributed to oxygen concentration cells that develop between bulk water and the recesses of the crevice. Recent work indicates the action of a complex mechanism in which chloride ions are drawn into the crevice as metal dissolution proceeds and acidic conditions develop [16, 28]. Aluminium, which depends on passive oxides for protection, is particularly susceptible to crevice corrosion.

Crevices exist in many locations in storage pools, for example, where fuel is supported by hangers or is resting on storage racks, within the racks, and between racks and metal pool liners. Crevice corrosion can proceed in stagnant areas that are not swept by thermal plumes or other circulation and where oxygen concentration cells can develop. For example, storage of Mark 31A target elements in SS buckets promotes crevice corrosion [28]. The elements are stacked, in the past resided in relatively impure waters, and could have trapped sludge, which tends to concentrate species such as chloride ions. As with galvanic attack, crevice corrosion of aluminium materials is mitigated when water conductivities are maintained in the range of 1 to 3 μS/cm. However, advanced

corrosion has occurred on aluminium in CBB specimens exposed in DIW FSPs [16]. Advanced corrosion was observed on aluminium in the crevice areas after six months, amounting to 110 to 120 μm/year, overall corrosion rates, with local attack of 0.4 to 0.6 mm.

Crevice corrosion was observed on Type 6061 aluminium fuel storage canisters that were standing in direct contact with the SS FSP liner in borated (PWR) water [19]. To mitigate the crevice corrosion, alumina insulators were placed between the canisters and the liner.

5.2.4. Stress corrosion cracking

Stress corrosion cracking has not been a significant phenomenon in Al alloys in spent fuel storage facilities because the cladding and component alloys are not susceptible [28]. The leading alloys are 1100, 6061, 6063, and 8001 (see Annex I for compositions).

5.2.5. Pitting corrosion

Pitting corrosion is the leading degradation mechanism for Al alloy fuel cladding and FSP facility components. It has been carefully reviewed by Howell [28]. Pitting is a localized form of corrosion, with metal removed preferentially, resulting in cavities or pits. The attack is generally limited to small areas, while the larger areas remain passive. However, pits can start at small areas and spread or they may remain small in area and increase in depth.
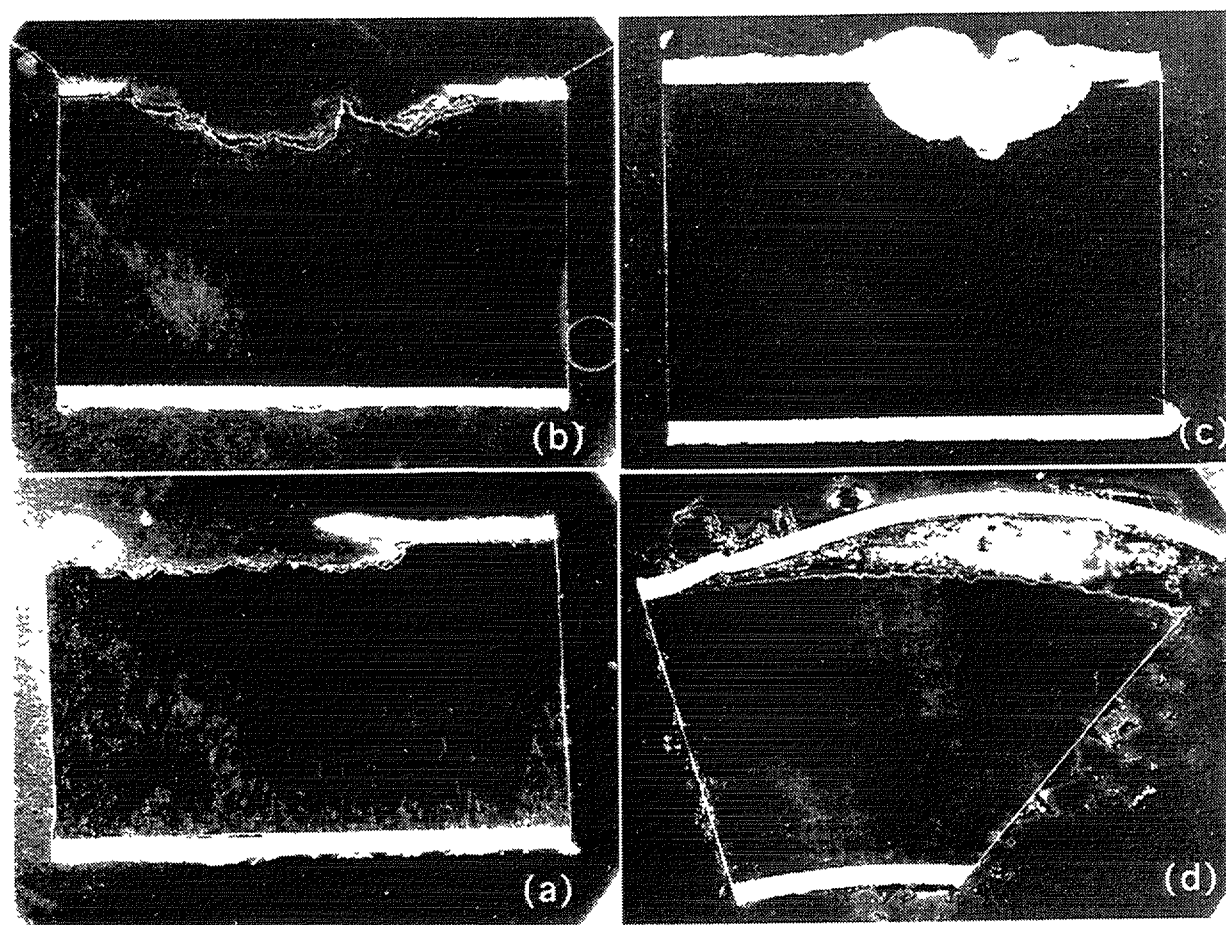
FIG. 7. Pitting of Al clad uranium metal. Four typical pit types on unirradiated target, after corrosion in a FSP over five years: (a) shallow corrosion penetration of uranium core, (b) deeper penetration of uranium core, (c) vertical penetration of uranium core, (d) bubble formed under aluminium cladding [10].

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FIG. 8. Al alloy fuel storage canister exposed 3 ½ years in Hanford K-East FSP in filtered Columbia River water. Some pits propagated through 2.3 mm wall after 19 years; 10 years in DIW [9].

5.2.5.1. Types of pits on aluminium cladding and components

Figure 7 illustrates cross-sections of typical pits on aluminium clad uranium metal [10]. Local chemistries develop in the pits; in some cases the chemistries are isolated from the bulk water by crusts that form over the pits. In this case, improving the water chemistry may have only a slow acting effect on the pitting attack. Pitting on an aluminium canister is shown in Figure 8; the canister was initially exposed to filtered Columbia River water, with a conductivity above 100 µS/cm. After the water chemistry improved, about ten years after initial corrosion, the pitting appeared to continue and fully penetrated a 0.09 in. (2.3 mm) canister wall in 19 years [9].

5.2.5.2. Pitting rates

Pitting rates on Al alloys in four FSPs are compared in Table III, varying from <1 µm/year to 5000 µm/year. Water conductivities in the extremes were approximately 1 µS/cm, corresponding to the low rates, to 600 µS/cm, corresponding to the highest rate. Estimated pitting rates on the Hanford canisters averaged about 120 µm/year [9]. Corrosion rate studies on Al alloy coupons in the same Hanford FSP were in place during a period of accelerated corrosion, due to biocide dosing (Figure 6). Eventually corrosion rates on the coupons returned to low values (0.25 µm/year). The data imply that pitted areas on the canisters corroded at rates nearly 500 times faster than uniform rates on the coupons.

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5.2.5.3. Pit initiation

The pit life cycle is: initiation, propagation, termination, and re-initiation [28]. Initiation involves a local cell that is anodic at the initiation site. Chloride ions promote local depassivation of a passive oxide. Chloride also stimulates metal dissolution, promoting growth of the pit. Pits tend to develop at defects in the passive film. For example, scratch marks in the reactor-formed oxide film are consistent sites for pit initiation [28]. On irradiated Al alloy elements with reactor-formed oxides, pitting did not appear to initiate, even though advanced pitting was evident on adjacent, unfilmed aluminium containers [9]. The fuel elements appeared to resist attack during the period of aggressive water chemistry that had caused accelerated corrosion on Al alloys (Figure 6).

5.2.5.4. Basis to predict pitting corrosion

The major challenge for fuel storage facility operators is to understand the importance of consistently maintaining water chemistry to mitigate corrosion of Al alloy fuel cladding and components.

Howell [28] has investigated the applicability of a pitting parameter developed by Patak and Godard [100] as a basis to rationalize the wide diversity of corrosion properties of Al alloys in wet storage facilities. The pitting rate index (PRI) includes effects of five water chemistry parameters: pH, resistivity, chloride, sulphate, and copper. The parameter is based on corrosion studies on aluminium exposed to natural waters. The PRI is defined as the number of weeks to achieve a maximum pit depth of 40 mils (0.040 in., 1 mm). The equation is shown below:

$$\log PRI = -0.28 \log(\text{sulfate}) + 0.18 \log(\text{chloride}) - 0.02 \log[(pH - 7)^2 \times 100] - 0.42 \log(30000/R) - 0.064 \log(\text{copper} \times 10^3)$$

where R = 1/C (conductivity, μS/cm)

Concentrations are in ppm by weight.

A PRI less than 25 weeks is taken to indicate aggressive water. Bicarbonate was not included because it did not increase the standard error of the result. Pathak and Goddard acknowledged that agreement of the relationship to actual pitting performance was only fair. The applicability to prediction of pitting in FSP waters is still being investigated. However, no relationship has been found that provides a satisfactory basis to interpolate between the extremes in corrosion that are indicated in Figure 5. The relationship provides a general perspective on important water chemistry parameters, but does not account for all of the species and factors known to affect aluminium corrosion. The equation has some problems, but it does predict the relative aggressiveness of waters. It is not valid at pH7 and the chloride ion effect is in the opposite sense to most observations reported in the literature.

In general, Howell found qualitative correlations in comparisons of PRIs, based on water chemistries in several storage pools. The parameter predicted full penetration of aluminium (40 mils,1 mm) in about 10 years under conditions in Pool A, Table I. However, metallography on an Al alloy specimen indicated pitting penetration less than 25 μm (1 mil) in 16 years [78]. Therefore, the parameter greatly over-predicted the pitting rate for Pool A. However, Howell has calculated PRIs for facilities with a range of water chemistries. The PRIs correlated reasonably with the water chemistries of the individual facilities [28]. When the water chemistry of a given facility was improved, the PRI reflected an improvement in pitting rate. The PRI was not fully concomitant with water conductivity, but as a practical approach, conductivity appears to offer a general basis for satisfactory control of water chemistry to minimize pitting corrosion of Al alloys that is based on chemical rather than biological factors.

5.3. REVIEW OF THE TECHNICAL BASIS TO ANALYSE WET STORAGE INTEGRITY OF Al CLAD FUELS AND STORAGE FACILITY COMPONENTS

The summary of experience cited above demonstrates the wide range of corrosion behaviours of Al alloys in wet storage technology. This section addresses properties of Al alloys that provide a basis to understand the range of corrosion behaviours.

5.3.1. Aluminium corrosion reactions

In most normal water environments, the overall reaction for aluminium corrosion results in formation of aluminium hydroxide and hydrogen:

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2$$
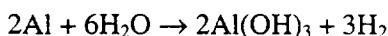
Aluminium corrosion is almost always electrochemical. The oxidation (anodic) reaction is:

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

The reduction (cathodic) reaction is:

$$2H^+ + 2e^- \rightarrow H_2.$$
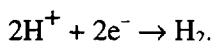
The corrosion product precipitates into Bayerite, $Al_2O_3 \cdot 3H_2O$ or Boehmite, $Al_2O_3 \cdot H_2O$, depending on the temperature (see next section). Formation of Bayerite in the wet storage thermal regime is expressed by the relationship:

$$2Al + 6H_2O = Al_2O_3 \cdot 3H_2O + 3H_2.$$
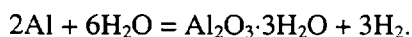
The corrosion products have very low solubilities in the passive region of the pH range [41]. Outside the passive range, aluminium corrodes in many acids and bases because the oxides become soluble.

5.3.2. Properties of aluminium alloys related to performance in low temperature aqueous environments

– *Oxides*: oxides that form on aluminium and its alloys in high purity waters depend on temperature; below a critical temperature (between 60 and 70°C [101]), film growth occurs in three stages: (a) amorphorous, (b) Boehmite (alpha $Al_2O_3 \cdot H_2O$), (c) Bayerite (beta $Al_2O_3 \cdot H_2O$). Above about 80°C, only Boehmite films form over the original amorphorous film. Therefore, the type of oxide that exists on Al clad fuel elements depends on reactor operating conditions. High performance reactors that sometimes operate with fuel temperatures above 200°C will discharge fuel with Boehmite films; reactors that operate at relatively mild conditions <60°C will have Bayerite films. Oxide film thicknesses on ATR fuel elements, operating at up to 225°C, were up to 50 μm (2 mils) [15]. The cladding oxides may be overlain with crud layers that comprise corrosion products from reactor coolant circuit materials, as indicated for other fuel types. There is evidence that the reactor-formed films are protective under wet storage conditions and seem to protect the metallic cladding, even in relatively aggressive pool waters [9]. Adjacent aluminium without reactor-formed films had advanced stages of pitting attack in the same waters. Howell observed that pitting initiated at scratches formed on Al clad fuels during discharge and post-discharge handling [28].

Even though aluminium oxide films are indicated to have significant solubilites in aqueous media [102], the films are sufficiently stable in the wet storage thermal regime that low corrosion rates have been maintained over more than a decade, as suggested by data in Figures 5 and 6. The key factors are: an oxide without damage sites (e.g., scratches), sustained maintenance of water purity, and absence of aggressive biological species.

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- *Kinetics*: because uniform corrosion is not the primary cause of Al alloy degradation, the kinetic concerns focus on pitting attack. Aziz and Godard reported that the pitting rate curve for Al alloys can be represented by a cubic equation [103]. However, the rapid pitting reported by Howell [28] (e.g., 40 mils in 45 d) seems to suggest that more aggressive rate laws (possibly linear) may apply for some pitting regimes. At higher temperatures, aluminium oxide formation is represented by parabolic kinetics [104].

- *Thermodynamics*: formation of aluminium oxide is a highly energetic reaction, with a Gibbs free energy at 25°C of −188 kcal/mole [42]. However, the film is generally protective and precludes rapid consumption of the metal. The metal lies in the active region of the galvanic series and therefore is often anodic in couples with other metals, as indicated in the zirconium alloy section. Howell's review includes the Pourbaix diagram for aluminium, indicating the stability regimes for the metal and its various oxides. As indicated elsewhere, the oxides are generally stable over a pH range of 4 to 8.5.

5.3.3. Other damage mechanisms

- *Mechanical*: the aluminium clad fuels are generally lighter than LWR assemblies, so the consequences of dropping elements during fuel handling are less. Some fuel handling operations cause mechanical distortions that may damage protective oxide films. As indicated earlier, it is the observed that scratches in protective oxides, caused during fuel handling, are sites for pit initiation [28].

- *Hydriding*: the solubility of hydrogen in Al alloys is very low, so hydrogen damage has been minimal, but sometimes involves blistering under oxides or surface coatings (e.g., nickel plates) because the hydrogen accumulates at the metal surface rather than diffusing into the base metal.

- *Galvanic*: the anodic character of Al alloys was indicated earlier. This tends to promote corrosion of aluminium coupled to more passive metals, such as SS or Zircaloy. Massive local corrosion occurred near SS/Al contacts on Al clad fuel in relatively high conductivity waters [28, 97]. Even couples between different Al alloys resulted in galvanic attack in the same waters. Coupling Al alloys to Zircaloy results in an aluminium anode and a Zircaloy cathode. This has resulted in major surface hydriding of the Zircaloy, as indicated in Section 3.1.4.2. In high purity waters and relatively low temperatures, the hydriding phenomenon is not observed [47].

5.3.4. Water chemistry factors

The importance of sustained, systematic water chemistry control to maintain the integrity of Al clad fuel and facility components has been a major theme in prior sections. Additional considerations are provided in this section.

- *Conductivity*: water conductivity appears to be the most significant single indicator of satisfactory conditions for Al alloys, although it is only one factor in the PRI discussed earlier. Maintaining water conductivity at ~1 μS/cm has been effective in limiting the corrosion on Al alloy fuel cladding [6], components [78], and coupons [9]. In contrast, when conductivities have been in the 100 to 200 μS/cm range, rapid corrosion has occurred on Al alloys [8, 9, 28], except on Al clad fuel with reactor-formed films, that seemed to survive exposure to aggressive waters that attacked unfilmed aluminium [9].

- *pH effects*: at low temperatures, aluminium has a relatively broad minimum in the corrosion/pH curves, over the range 4 to 8.5 [28, 41]. At 50°C corrosion rates are generally relatively low over a pH range of 4 to 8 in oxygen-saturated water, but the range depends on the specific ions present. Silicates have a beneficial effect, extending the favourable pH range to about 11.7. Chloride attack is mitigated in the range 5.5 to 8.5 [91]. Therefore, in pools with good water purity control, uniform corrosion does not substantially degrade Al alloys, as demonstrated in Table III.

- *Oxygen/carbon dioxide effects* because FSPs are in contact with the atmosphere, it is important to consider effects of species that enter pool water from the atmosphere Al alloy corrosion is relatively insensitive to dissolved oxygen in aqueous solutions [91, p 41] Carbon dioxide appears to have a slight inhibiting effect on Al alloy corrosion in waters

- *Aluminium ions* there is evidence that aluminium ions accelerate the corrosion of aluminium [21], however, Uhlig [91, p 42] indicates that distilled water is not contaminated by contact with most Al alloys

5 4 SUMMARY — Al CLAD FUEL AND FACILITY COMPONENT DURABILITY

It is evident that optimum management of aluminium alloys in FSP environments can result in satisfactory durability of irradiated fuel cladding and the functionality of pool components for more than two decades The ultimate limits of aluminium alloy durability have not been established, but extrapolations from Figure 3 and the continuing functionality of SFP components suggest that wet storage can be extended to more than 30 years if pool operating parameters are systematically controlled

In contrast, when requisite water quality is not maintained and MIC is not controlled, pitting corrosion can penetrate Al alloys in a few months

Key factors that promote aqueous corrosion of Al alloys are

- high water conductivity, e g , values reported in the range of 100 to 600 μS/cm, conductivities near 1 μS/cm have been shown to be effective in suppressing aqueous corrosion if MIC is not a factor,

- aggressive ions e g , chloride concentrations of several tens of ppm Chloride concentration specifications for FSPs vary from <10 ppm to <0 05 ppm,

- sludge contains Fe oxides, Cl⁻, Al oxide hydrates, dust, and other airborne debris, crud spalled from fuel assembly surfaces, depending on corroding materials in the pool and whether the facility is subject to ingress of wind-borne species,

- galvanic couples dissimilar metals generally exist in wet storage facilities, whether galvanic attack occurs depends on the galvanic potentials and the water chemistry, particularly the conductivity,

- crevices CBB tests have indicated that even in relatively pure pool waters, low pHs and concentration of chloride ions can develop, causing high corrosion rates on Al alloys in crevice areas,

- damage to protective oxides these sites serve as locations for pit initiation, particularly in aggressive waters,

- relatively stagnant waters circulating waters carry impurities to filters and ion exchange columns and may sweep impurities from otherwise stagnant areas,

- biological species include alga, slimes, biofilms, yeasts, bacteria and fungi, several measures to deal with biological species have been identified However, there are cases where biological counter measures have been applied without adequate attention to impacts on materials, causing accelerated corrosion of Al alloys, among other materials

As with other fuel cladding and facility component materials, there is a major need to seize opportunities to inspect or investigate metal condition when cost-effective opportunities are presented It is also very useful to document the results of the evaluations, including important details, such as water chemistry history, time in service, alloy, etc

For more comprehensive reviews of Al alloy performance in wet storage facilities, see Howell [28, 29, 97]

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6. CARBON STEELS IN WET STORAGE

Carbon steels are rarely used in contact with storage pool waters in power reactor wet storage facilities. However, CS canisters were used to store Magnox power reactor fuel at a reprocessing site [105] and have been used in defence reactor storage pools, as fuel canisters, buckets, canister handling equipment, fuel storage racks, piping, supports, tools, etc. [8, 9, 11, 15]. Canisters have, in some cases, been galvanized or coated with nickel. A coupon study of corrosion in two storage pools at a defence reactor facility included CS specimens [9]. The data are illustrated in Figure 9. The same chemical excursion that accelerated Al alloy corrosion (Figure 6), due to biocide treatments, also accelerated CS corrosion rates. Continuing relatively high corrosion rates after the 1980–1981 excursion were due to the use of filtered Columbia River water for K East FSP water until 1986, when ion exchange capacity was installed.

6.1. CORROSION MECHANISMS

Carbon steels are alloys of iron with 0.05 to 1% carbon. They have relatively poor corrosion resistance in oxygenated waters at low temperatures. In fact, dissolved oxygen is necessary for iron to corrode significantly at low temperatures. A typical corrosion rate in water with dissolved oxygen is about 0.01 in./year (250 μm) at 25°C (see Uhlig and Revie, Corrosion and Corrosion Control, p. 95, 1985). After effects of the biocide excursion abated, corrosion rates in the Hanford K East FSP were only about one fifth of this value and were considerably less in the K West FSP. Iron corrosion is insensitive to pH in the range 4 to 10 (Uhlig, p. 96). Coatings are often applied to mitigate corrosion. However, holes in the coatings promote pitting. In one facility [9], the coating on fuel racks failed in large areas, perhaps facilitated by damage from fuel handling operations. The Halden (Norway) reactor fuel storage pool has a unique liner: coated carbon steel [19].
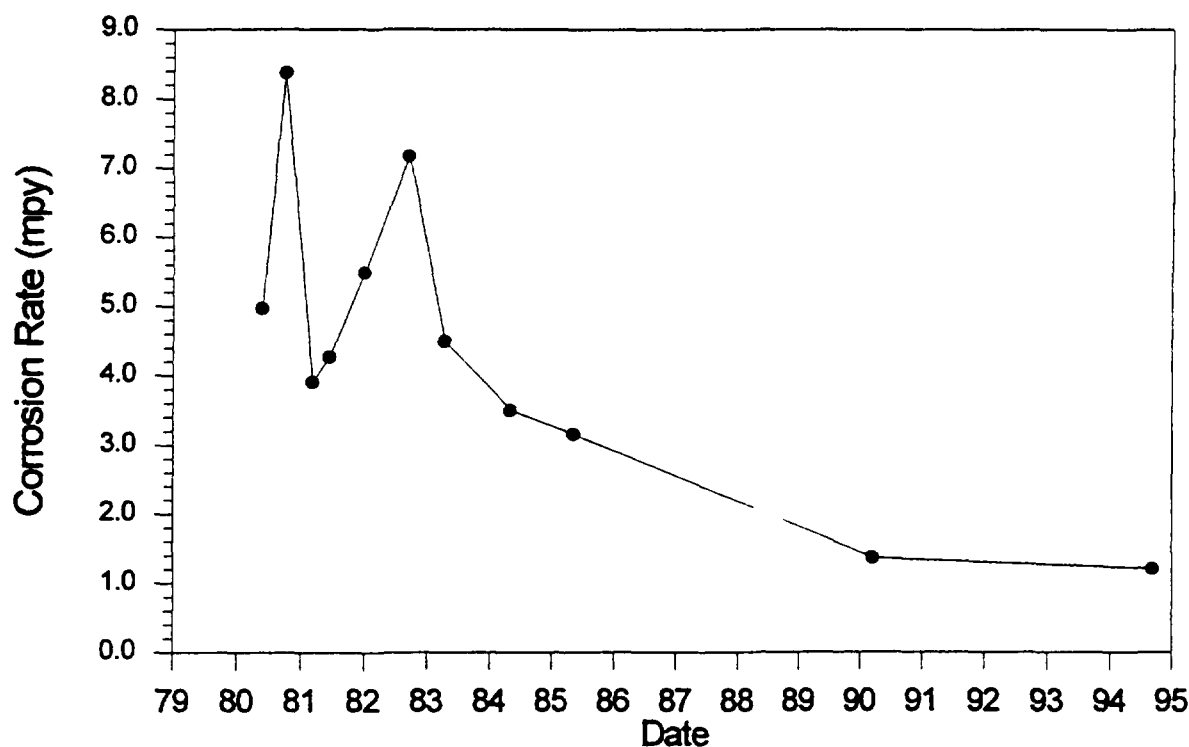

FIG. 9. Uniform corrosion rates on type 1018 carbon steel in Hanford K-East FSP*, based on coupon data. First excursion due to biocide dosing. Second excursion correlates with major fuel handling campaign. Water deionized since 1986. [9]
*Rates on type 1018 CS were lower in K-West FSP [9].

Carbon steels exposed in fuel storage pools have been subject to the following corrosion mechanisms

- **uniform corrosion** a CS bar on a fuel hanger had corroded 0 1 in (0 25 cm) after exposure to an aggressive pool water (up to 760 ppm chloride) for 24 years [11], zinc-coated carbon steel corroded at the rate of 4 mils/year (100 μm/year) in a 40 years exposure [11] Data from the coupon study cited above [9] are shown in Figure 8 An early excursion in corrosion rates was caused by dosing the pool with a biocide, paralleling the excursion shown for Al alloy coupons (Figure 6), the water conductivity increased from 2 to 23 μS/cm, there were pH excursions from a base of 5 5 to 6 2 to as low as 4 1 The CS corrosion increased to 8 mpy (200 μm/year), then decreased to 1 mpy (25 μm/year) as water purity was restored In a companion pool, with somewhat better water chemistry control, CS corrosion rates decreased to 0 2 mpy (5 μm/year) [9]

- **pitting corrosion:** large shallow pits developed on zinc-coated CS in a 40 years exposure [11],

- **galvanic corrosion:** CS welded to SS was subject to accelerated corrosion in the aggressive pool chemistry cited earlier [11]

Corroding carbon steel components in wet storage facilities release reddish brown corrosion products to the water that interfere with visibility and contribute to the sludge inventory [9] Even when the CS components were initially painted, the paint often degrades over time and exposes the steel substrate to corrosion

6 2 CARBON STEEL CORROSION PRODUCT SPECIES

The notable appearance of carbon steel corrosion products is reddish brown The corrosion products are often suspended, especially when fuel handling or other operations are underway Berry summarized the relatively complex array of iron corrosion products [83] In oxygenated conditions at elevated temperatures, the principal corrosion product is hematite, Fe_2O_3 The gamma form is generated in degassed water at high temperatures and is protective The alpha form is a common product in water and steam containing oxygen and is non-adherent However, the reddish brown product that formed by corrosion of carbon steel pipes and racks in the Hanford K East FSP was analyzed by X ray diffraction of sludge samples taken from the pool floor The only iron oxide species detected in the floor sludge was FeOOH (lepidocrocite form) [106], which is indicated in the International Centre for Diffraction Data files as reddish brown The goethite form, listed in the Handbook or Chemistry and Physics [84], is indicated to be brown or blackish Therefore, at least in the Hanford floor sludge, the iron aqueous corrosion product is indicated to be FeOOH, rather than hydrated hematite, also indicated to be reddish brown [84] However, analyses of sludge in the fuel storage canisters indicated that Fe_2O_3 and Fe_3O_4 were the detectable iron oxide species [see HNF-SP-1201, 1997] Reasons for the different compositions of canister and floor sludge have not been investigated

6 3 IMPACTS OF CARBON STEEL CORROSION

Corrosion products on mild steel in oxygenated water are generally loose and easily become suspended Particularly while work is going on in a FSP, the suspended iron oxides can interfere with visibility The corrosion products also form sludges on the bottom of the pools The sludges can become aggressive by concentrating species such as chlorides Over decade-long service periods, carbon steel corrosion products can become quite massive The cross-section of the corroding components will be reduced, so it is important to assess the condition of equipment or components that may be compromised by corrosion Carbon steel fuel canisters developed leaks, but it is not clear that corrosion was a factor [105]

The iron oxide corrosion products are readily transported throughout the pool and deposit on fuel and component surfaces If fuel is to be transferred to dry storage, iron oxides that deposit may become significant sources of water unless action is taken to remove the iron oxides before the fuel is

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placed in dry storage containers. Water can be adsorbed and absorbed on the iron oxides. However, potentially more important are waters of hydration. Hematite can bond with up to three water molecules, which are released at 350 to 400°C [84]. As indicated in the prior section, analyses of Hanford K East floor sludge indicates that the iron oxide species is FeOOH [106] or Fe_2O_3 and Fe_3O_4 in canister sludge [HNF-SP-1201, 1997]. The goethite form of FeOOH is indicated to release water (1/2 H_2O) at about 135°C [84]. If iron oxides are a factor on the surfaces of fuel elements destined for dry storage, removal by washing may be feasible, with or without brushing. Otherwise, it seems important to determine the oxide species and inventory that is involved if the associated water is considered to be significant in developing pressures and hydrogen/oxygen gases inside the container.

If fuel elements have been in service in reactors with aqueous coolants and steel or SS circuits, there is likely to be an iron oxide crud layer overlaying the oxide layer formed on cladding in reactor service. The crud layer may be thin and not contribute significantly to the water inventory on the element, but that may be judged from the amount of crud that is on the fuel element surfaces. If the crud layer is substantial, then the iron oxide species becomes an issue in estimating the water inventory, as indicated above.

7. COPPER ALLOYS IN WET STORAGE

Copper alloys are seldom used in spent fuel pools. Their principal application has been as heat exchangers. In some cases, copper has functioned concomitant with aluminium alloy components. In benign waters, the Al alloys do not appear to be affected, based on coupon data [9]. Addition of an aggressive industrial biocide caused corrosion of the copper (the pool water turned blue), coinciding with an excursion in Al alloy corrosion rates and in copper alloy corrosion rates (Figure 10). When the water purity was restored, the Al alloy corrosion rates returned to the normal range, even though the copper alloy heat exchangers remained in the systems. The copper alloy corrosion rates also returned to a range of 0.02 to .1 mpy (0.5 to 2.5 µm/year). The corrosion rates were determined on coupons that were removed periodically from coupon assemblies that were maintained in the two K Reactor FSPs.

Copper alloy heat exchangers were installed to maintain the water temperatures at about 10°C to minimize corrosion of uranium metal fuels exposed at breaches in the Zircaloy cladding caused by mechanical damage during discharge from the reactor [9]. The low temperatures also mitigated development of algae in the pools. Algae was again observed when water temperatures rose to about 20°C.
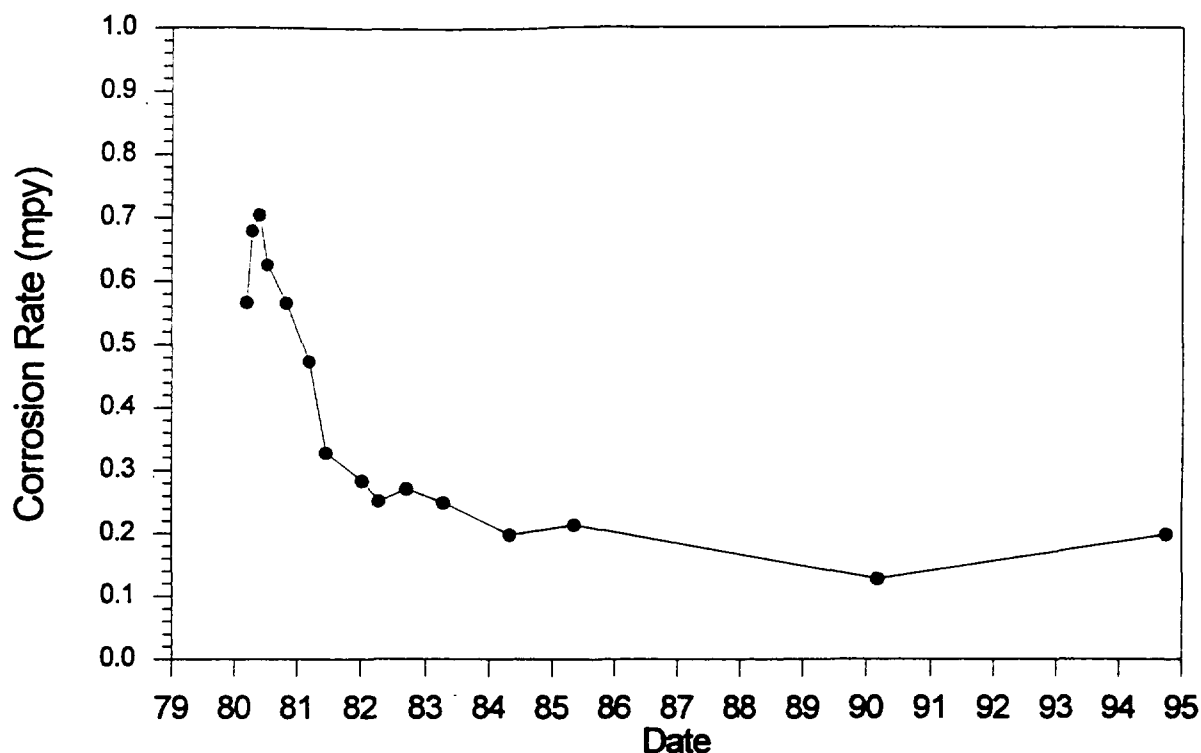
FIG. 10. Uniform corrosion rates on 2410 Cu-Ni alloy in Hanford K-West FSP*, based on coupon data. Excursion due to biocide dosing. Water deionized since 1978 [9].
* Rates on 2410 Cu-Ni lower in K-East FSP [9].

8. FUEL MATERIALS IN WET STORAGE

The behaviour of fuel materials in contact with pool waters becomes important when cladding breaches occur, in reactor service, in discharge from reactors, or from corrosion penetration of the fuel cladding by corrosion or mechanical damage during wet storage. Numerous fuel types have been developed and irradiated. It is not practical to address all fuel types here, so this assessment will focus on oxide fuels, uranium metal, uranium aluminide, UAl_x/Al, and UO_2/Al.

8.1. URANIUM OXIDE FUELS

Uranium oxide pellet-type fuel is utilized in AGR, PHWR, LWR, and LMR reactors. Some test reactors also use uranium oxide fuels. Evidence for durability of the oxide fuel when exposed to water through cladding defects was discussed in Section 3.1.4.6. Laboratory studies on leaching of irradiated oxide fuel in water have been summarized [55, 107–109]. Rates of leaching of fission products (e.g., ^{137}Cs) decrease and become essentially asymptotic after 20 to 30 days at 25°C. The leaching studies did not address dissolution of the uranium oxide, but the observations cited in Section 3.1.4.6 suggest high stability of the irradiated oxide fuel in contact with pool water. This result is the basis for storing several thousand commercial water reactor fuel rods with breached cladding without isolation from the pool waters. As mentioned earlier, a survey conducted through IAEA indicated that approximately 70% of pool operators store oxide fuel with reactor-induced cladding defects without canning [3]. If oxide fuel with cladding defects is transferred to dry storage, the entrained, absorbed, and chemically bound waters will need to be removed if judged to be troublesome. Water was recovered from water-logged BWR rods at 325°C [see Nucl. Tech. **69**, p. 186 (1985); also PNL-5987 (1986)].

8.2. URANIUM METAL FUELS

Uranium metal has been utilized in defence reactor fuels, in Magnox power reactor fuels, and in some test reactor fuels. The fuel compositions are predominantly uranium with several hundred ppm each of aluminium, carbon, and iron (100 ppm silicon). Some test reactor fuels have included uranium alloys, e.g., U-10 Mo [119]. Wet storage of the uranium metal fuels includes the requirement to deal with elements that have failed cladding, because the exposed uranium metal is subject to significant rates of aqueous corrosion at pool water temperatures, that release fission products, transuranics, and particulates to the pool water.

8.2.1. Corrosion reactions

Aqueous corrosion of uranium metal occurs by the reactions:

$$U + 2H_2O = UO_2 + 2H_2 \tag{1}$$

$$2U + 3H_2 = 2UH_3 \tag{2}$$

The hydride reacts by the reactions:

$$2UH_3 + 4\,H_2O = 2UO_2 + 7H_2 \tag{3}$$

$$2UH_3 + 2O_2 = 3H_2 + 2UO_2 \tag{4}$$
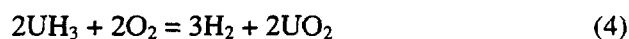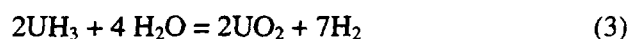
Reaction 4 is rapid at low temperatures. Thus, if aqueous corrosion proceeds in the presence of oxygen, accumulations of uranium hydride that could be troublesome tend to be precluded by Reaction 4. It is when the corrosion occurs in oxygen-depleted environments that hydride inventories may reach amounts that can release substantial heat if suddenly exposed to oxygen. The concept of a "match head" phenomenon has been proposed to denote accumulation of sufficient hydride to release heat that can ignite adjacent uranium [110] (several grams of UH_3). However, when uranium corrodes in an open pool, reactions 3 and 4 minimize the inventory of hydride. Only occluded hydrides will remain, either hidden under films or in crevices where oxygen and water are unable to penetrate in

sufficient quantities to react with the hydrides after they form The amount of hydride remaining when reactions 3 and 4 are active is 1 to 10% [112] Addisson [112] indicates that "It is generally considered that corrosion of non-swollen uranium with free access to water and oxygen, although producing some hydride, does not represent a significant pyrophoric risk"

8.2.2. Burnup effects on swelling of uranium metal

Uranium develops porosity in the metal fuel at burnups that cause swelling and porosity near the outer surfaces of metallic uranium fuel elements Swelling up to about 50% has been observed on British Magnox fuel [111] Burnups for the British fuel range up to about 9800 MW d/t The porosity greatly accelerates uranium metal corrosion, up to three orders of magnitude [115]

Several factors, including metal composition, reactor service temperatures and pressures influence the fuel swelling A detailed summary is beyond the scope of this study, but several references provide a basis for further understanding [113–115] British data indicate a marked upturn in Magnox fuel swelling above about 4000 MW d/t Swelling of Hanford N Reactor uranium metal fuel was measured, indicating 3 6% on fuel with a burnup of 3100 MW d/t Swelling of the Hanford fuel may be mitigated by the relatively high system pressures (11 MPa, 1600 psi) compared to only 1 to 2 7 MPa for Magnox fuel British data indicate maximum void growth in the temperature range 390–430°C The British specification for aluminium in the uranium was increased from 1,200, max to 1500 max to retard "breakaway" swelling The aluminium specification for N Reactor fuel was 700 to 900 ppm

French fuel was reported to have significant swelling in the range 2500 to 5800 MW d/t [116] How this rationalizes with British and Hanford N Reactor data is not clear

8.2.3. Effects of excluding oxygen on corrosion and hydriding of uranium metal

When oxygen is excluded from the corrosion environment, the uranium corrosion rates increase, up to 2 orders of magnitude [117] (a factor of 30 on average) British and French Magnox reactor operators have placed elements that fail in service into canisters with inert cover gases and stored them in FSPs If water leaks into the canisters, the exposed uranium corrodes, forming hydrogen, resulting in a moist hydrogen atmosphere that accelerates both corrosion and hydriding When canisters with the hydrided fuel were opened to air in hot cells, pyrophoric phenomena occurred, that were suppressed with inert gas injection or other methods [110] The important perspective here is that exclusion of oxygen allows hydride inventories to accumulate, that otherwise are limited when oxygen is present, due both to lower corrosion rates and to immediate reaction with the hydride as it forms

8.2.4. Ignitions and absence of ignitions of corroded uranium metal while stored in water

Irradiated uranium metal fuel from Magnox, defence reactors, and research and test reactors is handled under water, including elements that have reactor-induced cladding defects or that have been declad prior to reprocessing

French experience has been reported involving flashes from irradiated Magnox fuel elements as they were being declad mechanically [116] However, the most common cases, in the 1970s, were vigorous reactions on elements that had been chemically declad (dilute nitric acid) This occurred on fuels with burnups from 2500 to 5800 MW·d/t, one to two years after reactor discharge The flashes appeared under water during impact or friction They were characterized by an intense light and the evolution of bubbles rising to the surface of the FSP Variable quantities of residual metal were left after the ignitions However, the ignitions did not propagate to adjacent elements The flashes were interpreted to be initiated at porous areas on the uranium surfaces, caused by radiation-induced swelling, resulting in larger specific surface areas, hence higher chemical reactivity and lower peripheral thermal conductivity, promoting local overheating Several mechanisms were invoked, including uranium hydride formation, interaction of Cs or sub-stoichiometric UO_2 with water

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Hydride formation was regarded as the most plausible explanation. At the lower end of the burnup range, swelling would be only 2 to 3%, based on British data on Magnox fuel [115] and swelling effects on uranium corrosion [111]. That the chemical decladding rendered the uranium surface chemically active seems reasonable, but it is not clear that substantial swelling was involved, particularly at a burnup of 2500 MW·d/t.

An important case involving complete lack of pyrophoricity under water involves the Hanford N Reactor fuel. The fuel is Zircaloy clad uranium metal. A fraction of the elements were mechanically damaged as the fuel dropped up to 15 meters and fell onto a metal trampoline or impacted other elements (Figure 11) [9]. Uranium metal exposed at the cladding breaches corroded in the pool water. Often the corrosion involved formation of observable oxide masses on the ends of the elements (Figure 12), but in other cases, a large fraction of the fuel corroded out of the cladding. In 1983–1984, approximately 65 000 fuel elements were emptied from about 5000 canisters onto a metal sorting table. In some cases, elements were stuck in the canisters, due to expansion of corrosion products, and had to be expelled by vigorous mechanical action. Each element comprised an annular outer element with an annular inner element resting inside (Figure 12). In the campaign, inner elements were pressed out of outer elements, again involving mechanical force. In this extensive campaign, involving uranium that had corroded up to a decade, there was no case where a pyrophoric event was observed. Corroding fuel has continued to reside in the K East basin in uncapped canisters for up to nearly 25 years, with no indication of pyrophoricity.

Similar corroding N Reactor fuel has been stored in the K West FPS in closed, water-filled canisters for more than 15 years. Hydrogen had displaced the original nitrogen cover gas, indicating that corrosion was ongoing inside the canisters. When the canisters were decapped under water, no pyrophoric events were observed.

These two cases represent contrasting behaviour: pyrophoricity of declad, swelled uranium under water in the French case; complete lack of pyrophoricity for N Reactor fuel that corroded in an open pool, consistent with the position stated by Addison [112].

8.2.5. Treatment of corroded/hydrided uranium metal fuel

There are initiatives underway to transfer corroded uranium metal fuel to dry storage, for example, over two thousand tonnes of fuel stored in two water pools at Hanford [9]. Plans are also in motion to transfer fuel to dry storage at other sites, e.g., [23] (see also WSRC-TR-95-0347, Acceptance Criteria for Interim Dry Storage of Aluminium-Alloy Clad Spent Nuclear Fuels). It is important to understand the impacts of wet storage on the fuel and how these dictate operations that will be required to prepare the fuel for dry storage. The principal considerations are: a) the type and degree of degradation that the fuel has undergone in wet storage, and b) the water inventories that are associated with corrosion products and deposits that have formed on the fuel. It is also necessary to understand residual effects of reactor service, shipping, and handling.

In France, corroded Magnox fuel from destructive and non-destructive tests at Cadarache has been stored in canisters in water pools since the 1960s and 1970s. In the 1980s, fuel re-handling indicated that some of the canisters had leaked water, causing corrosion and hydriding that rendered the fuel unsuitable for long term storage or reprocessing [116]. Consequently, a facility designated STAR was built at Cadarache to condition 17 t U of the corroded, irradiated fuel. The conditioning process involves:

— fuel drying at 100°C under argon;

— progressive temperature increases up to 430°C to decompose hydrides and to remove bound water; hydrogen evolution stops when hydride decomposition is complete;

— controlled oxidation of uranium to stabilize metal particles formed by decomposition of hydrides, taking place at 250°C in argon, then with progressive additions of oxygen, up to 21%.
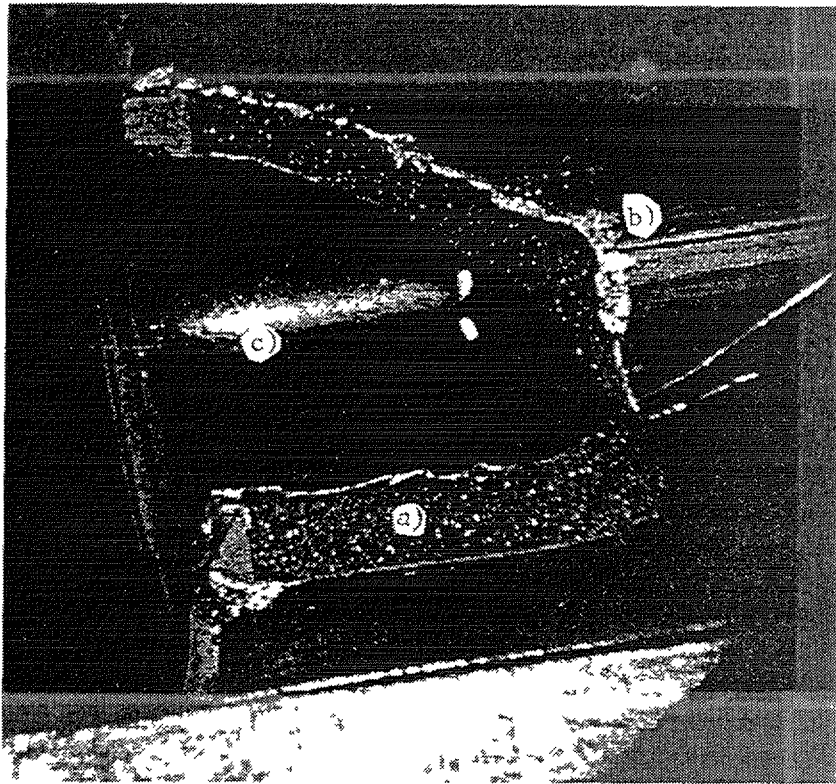
FIG 11. Hanford N Reactor fuel assembly damaged during reactor discharge, (a) exposed uranium metal fuel, (b) outer Zircaloy 2 cladding on outer element, (c) outer Zircaloy 2 cladding on inner element [9]. See FIG. 12 for end view of outer/inner configuration.
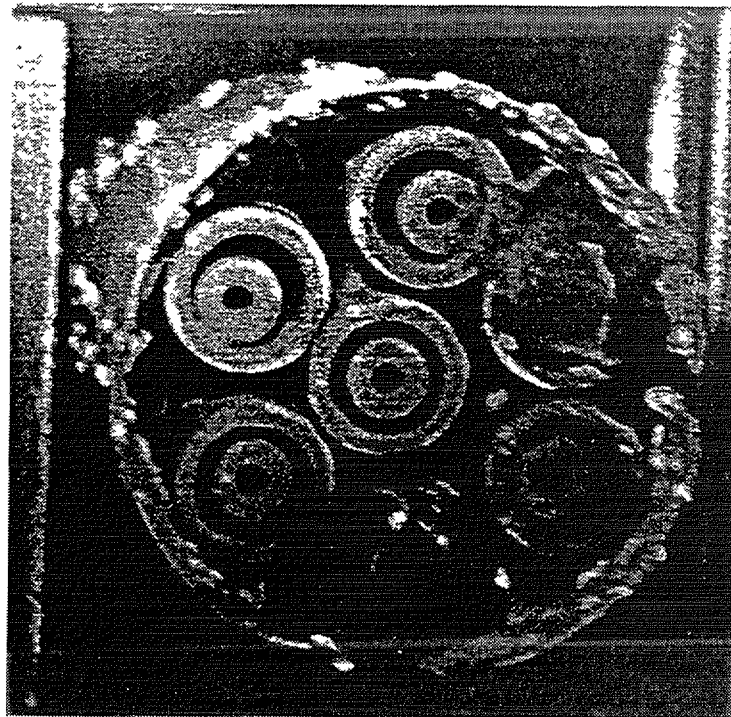
FIG. 12. End view of Hanford N reactor fuel assemblies showing inner/outer configuration. Note areas where uranium metal is corroding in FSP water at sites of cladding mechanical damage [9] Oxide nodules are also evident on the aluminium alloy canister (see Figure 8)

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The stabilized fuel is then placed in aluminium canisters with welded lids. The STAR facility began operation in 1994 and was in continuous operation starting in early 1996. A similar conditioning process, with somewhat different parameters, is foreseen for treatment of the N Reactor fuel as it is transferred to dry storage.

8.2.6. Kinetics and thermodynamics of uranium metal corrosion

Kinetic [117] and thermodynamic [42] data for corroding uranium metal have been summarized [118]. The rate for Reaction 1 in oxygenated water at 25°C is 1×10^{-4} mg/cm^2 h. The rate in deoxygenated water is about a factor of 30 faster. Comparative rates for corrosion of uranium alloys have been published [119]. For example, a Ur-10%Mo alloy corrodes at rates several orders of magnitude lower than corresponding rates for pure uranium metal. Reaction 4 can occur rapidly at ambient temperatures. All four reactions have negative free energies at 25°C.

8.2.7. Case histories: Storage and handling of corroded uranium metal fuel

The following case histories illustrate the methods and problems of managing uranium metal fuels in wet storage.

8.2.7.1. Magnox fuel

Magnox power reactors operate or have operated in several countries, principally in France and the United Kingdom. The fuel is magnesium clad metallic uranium. The magnesium alloy has less than 1% of either Al or Zr. The reactor coolant is carbon dioxide. After reactor service, the fuel is discharged to water pools with special water chemistries: pH11.5, dosed with sodium hydroxide, and chloride + sulphate controlled to <1 ppm [120]. The elevated pH limits uniform corrosion of the cladding, and the low impurity levels limit pitting corrosion. Aqueous corrosion of Magnox cladding involves the reaction:

$$Mg + H_2O = Mg(OH)_2 + H_2.$$
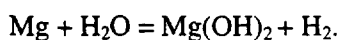
The hydroxide forms a partially protective layer that is preserved at elevated pH. In impure waters, pitting can penetrate the cladding in 30 to 50 days. In contact with the atmosphere, carbon dioxide absorption limits the pH to 11.5. To further reduce Magnox corrosion, elements are sometimes stored in closed (vented) containers, where pH13 is maintained. Under these conditions, the Magnox corrosion rate is 0.05 mg/dm^2 d (0.06 μm/d) and the fuel can be stored in water for several years without breaching the cladding. Otherwise, the fuel is generally reprocessed within several months to avoid cladding penetration.

Once the cladding is breached, corrosion of the uranium metal proceeds and contributes radioactive species to the pool water. The most prominent isotope is Cs-137, but tritium, strontium, transuranics and numerous other species must be dealt with.

A variation on pool (pond) storage occurs when elements fail during reactor service. Failed elements are placed in cans with an inert cover gas that are stored underwater. If water leaks into the cans, accelerated corrosion of the uranium can occur if a moist hydrogen environment develops. Even though hydrides form during corrosion inside the canisters, the fuel does not present a pyrophoric risk until it is opened to air. The following case indicates that the corroded fuel can be managed safely if the condition is properly anticipated.

8.2.7.2. Magnox fuel stored at Sallugia

Magnox fuel from the Latina power reactor (Italy) was placed in carbon steel canisters and stored in a FSP at Sallugia [105]. The original cover gas was air; however, monitoring indicated that corrosion and radiolysis were generating hydrogen, so the cover gas was switched to nitrogen.

Continued monitoring indicated that uranium fuel was corroding in some canisters, signalled by release of Kr-85. After storage for 19 years, some of the fuel elements were almost completely consumed by corrosion and were assumed to contain substantial inventories of uranium hydride. British Nuclear Fuels staff back-filled the canisters with water, which, from Reactions 3 and 4, would react with exposed hydrides. The fuel was then shipped to Sellafield in the UK for reprocessing.

This case demonstrates that (a) the corroded/hydrided fuel was not a significant safety hazard while stored underwater in the canisters, and (b) that the corroded fuel could be safely managed during shipping and reprocessing.

8.2.7.3. Magnox fuel stored in the United Kingdom

Magnox reactors have been a substantial source of electric power in the United Kingdom. In general, the fuel is discharged to reactor pools where it is held for up to 120 d. Special water chemistry control to minimize Magnox cladding corrosion was outlined in Section 8.2.7.1. In general, the strategy of limited wet storage/reprocessing has been satisfactory. However, fuel which failed in reactor service was placed in canisters with an inert cover gas, and the canisters were stored in the bottoms of the pools (ponds) [110]. Some canisters developed leaks which allowed pool water to enter and corrode the uranium exposed at cladding defects. Because the atmosphere is inert, oxygen is not present to suppress corrosion and hydriding. Over time, inventories of potentially pyrophoric uranium hydrides have accumulated. While the canisters were stored underwater there were no pyropyhoric events. When canisters were removed from wet storage and opened in hot cells, pyrophoric events occurred as air entered the canisters [110]. The events were suppressed by introduction of argon into the canister or covering the canister with a fire blanket. In contrast, Addison indicates that non-swollen, failed Magnox fuel with exposed uranium, corroding in an open (oxygenated) pool does not present a pyrophoric risk, as indicated earlier.

The exception to the British Magnox fuel management strategy outlined above is the approach used at the Wylfa power station in Wales. Here the Magnox fuel is discharged directly to dry storage, first in carbon dioxide, then in air after the fuel cools below 150°C [121]. A situation developed where water leaked into the dry store and filled several cans containing Magnox fuel [122]. It was assumed that the fuel corroded completely while exposed to the water and that hydrides were formed, even though the water ingress occurred in a vault with an air cover gas. At this writing, recovery of the fuel has not been reported. The approach was indicated to involve using an argon cover gas to assure that ignitions of possible hydrides did not occur.

8.2.7.4. Magnox fuel stored in France

As in the UK, Magnox fuel has been stored in water pools in France prior to reprocessing. Also similar to UK experience, some fuel with failed cladding has been stored underwater in sealed canisters with inert cover gases. The consequences and recovery strategy for this corroded and hydrided fuel were addressed in Sections 8.2.4 and 8.2.5.

8.2.7.5. Hanford N reactor fuel

The Hanford N Reactor produced power and also defence materials. The fuel for the reactor was Zircaloy clad uranium metal. The Zircaloy is highly durable in water storage, as indicated in Section 3. However, during reactor discharge, the fuel was pushed from horizontal tubes and fell up to about 15 m (50 ft) onto a metal trampoline, causing mechanical damage that breached the cladding on a fraction of the elements. Figure 11 illustrates damage caused by impacts of the fuel assemblies. A section of Zircaloy clad uranium metal is missing from the end of the outer element (see Figure 12 for an end view of the fuel assemblies, comprising inner and outer elements). The cladding breaches exposed metallic uranium to pool water, allowing corrosion to proceed. This was not a substantial problem while reprocessing was available because storage times in the pool were generally only a few months. Once reprocessing was precluded, wet storage became the only fuel management option, and corrosion took on importance [9]. Consequences of the corrosion included leakage of tritiated

water from the pool in soil adjacent to the pool, loading of resins with transuranics, and elevated radiation levels in work areas.

The N Reactor fuel was placed in stainless steel and aluminium canisters and was stored in two pools at the Hanford K Area. The fuel was placed in open cans in the K East pool (Figure 12) and in closed (vented) cans in the K West pool. In all, 2000 t of fuel is stored in the two pools. The water in the pools is now deionized and the temperatures are controlled to 10°C to minimize corrosion. Corrosion product is visible on failed rods in the K East pool (Figure 12), and monitoring of Cs-137 activity provides a rough measure of the corrosion rate [9]. The Cs-137 evolution rate responded to the temperature decrease. The closed canisters were dosed with 500 ppm of potassium nitrite to mitigate uranium corrosion. Fuel examinations are underway (1997) to evaluate the uranium corrosion characteristics. Plans are underway to transfer the N Reactor fuel to dry storage.

8.3. URANIUM ALUMINIDE/ALUMINIUM ALLOY FUELS

The uranium aluminide fuels are prominently used in research and test reactors [15]. The fuel composition is UAl_x/Al, where x can be 1, 2, or 3, and Al denotes that particles of the aluminide are embedded in an Al alloy matrix. The fuels generally are clad with an Al alloy. Examples include the ATR fuel (Annex I, Table I.2). Performance of the fuels has been summarized [15, 81]. While corrosion rates for UAl_x fuels exposed to pool waters are lacking, the data for Al alloy corrosion (Section 5) suggests that uniform corrosion rates are low in storage pools, and pitting rates are highly dependent on pool water chemistry. Exposure of the UAl_x particles by corrosion of the Al alloy matrix seems unlikely to produce concentrated inventories of uranium hydride because the particles are dispersed [15]. In aggressive waters, the cladding may be penetrated after relatively short exposures in wet storage, as suggested in Figure 5. Breached cladding results in release of small amounts of radioactive species, but the consequences will be far less than for breached cladding on uranium metal fuels. Corrosion of the aluminium matrix will largely influence the rate of degradation of the fuel, so fuel durability depends on water quality.

9. RADIATION EFFECTS IN WET STORAGE

The important considerations involving radiation were introduced in prior sections but are addressed in this section in more detail The following radiation effects are considered

- radiation effects on fuel assembly (element) materials during reactor service,
- effects of radiation on materials adjacent to fuel assemblies during storage,
- effects of radiation on local water chemistries

In reactor service, fuel assembly materials are exposed to numerous radiation species, including neutrons with a range of energies (thermal to >1 MeV), the neutron energy distribution depends on the spectrum of the specific reactor The principal changes in metal properties are the result of neutron radiation The reactor radiation includes large gamma fluxes that can cause major degradation to organic materials, but have minimal effects on metal microstructures Certain local corrosion effects occurring during reactor service are attributed to beta fluxes [123], but have no significant consequence on metal degradation during storage

An important consequence of reactor service for fuel assembly materials is the residual radiation resulting from transmutations and fission products However, the radioisotopes are predominantly short-lived and decay to inconsequential levels within days or weeks After decay through ten half-lives, the residual radiation is only 0 1% of the original Isotopes with long half-lives (e g , I-129, 10^7 y) have low activities Therefore, the significant gamma sources in wet storage facilities involve isotopes with half-lives in the range of several years, e g , Cs-134, 2 1 years, Cs-137, 30 years, Co-60, 5 6 years Other isotopes are present, for example, tritium, with a half-life of 12 3 years, but the isotope only emits a weak beta particle and therefore has no significant effect on materials degradation in wet storage However, if tritium is released to pool waters by corrosion of fuels, it may constitute a significant airborne contaminant and may be a concern for ground water contamination if pool water leaks into the surrounding soil The gaseous fission product Kr-85, has a half-live of 10 76 years It is released when cladding failures occur Its detection offers one method of monitoring for cladding failures (e g Ref [124])

9 1 RADIATION EFFECTS DURING REACTOR SERVICE

Reactor radiation causes changes in materials that do not have counter parts in unirradiated environments Detailed treatments of the fundamentals underlying changes in materials properties under irradiation are available (e g Ref [125]) and will not be repeated here Neutron bombardment causes displacement of atoms, creates vacancies, interstitial atoms, and dislocations that contribute to property changes Radiation may cause accelerated corrosion, for example, on zirconium alloys, and can contribute to enhanced absorption of hydrogen Radiation-induced materials properties changes are briefly reviewed here, emphasizing those that have potential impacts in wet storage

9.1.1. Changes in strength and ductility

Reactor neutron fluxes generally increase the strength and decrease the ductility of metals The consequences during post-irradiation handling and storage are generally not evident However, for fuel assemblies that have been subject to high burnups, the decrease in ductility may be sufficient to markedly reduce low temperature impact strength For the zirconium alloys, the radiation-induced loss of ductility is exacerbated by addition of hydrogen due to corrosion Some high burnup Zircaloy clad fuels are reported to have hydrogen contents above 600 ppm (Section 2) The high hydrogen contents are facilitated by accelerated corrosion that has been shown to involve radiation enhancements [39, 123] A phenomenon, referred to as the "Thick Film Effect" [123, 126] has markedly increased in-reactor corrosion rates on non-fuelled Zircaloy components in low oxygen coolants, after a threshold oxide thickness had developed The effect also would be expected to occur on PWR fuel cladding, and there is some evidence, but the interpretation is complicated by heat flux effects Marked decreases in Zircaloy cladding ductility have been measured for high burnup

assemblies [127, 128]. The ductility loss will not have adverse impacts in storage unless the fuel assemblies are subject to impacts that are sufficient to fracture the cladding. Cases involving dropping of fuel assemblies during post-irradiation handling have occurred, that had minimal effects [19], but the assemblies had low or moderate burnups. Similar events with high burnup assemblies may result in more significant consequences, due to decreases in low temperature impact strength. While SS and Al alloy cladding have also been subject to radiation-induced decreases in ductility, they have low hydrogen solubilities and do not absorb large hydrogen inventories. That does not fully absolve hydrogen as a source of hydrogen embrittlement, particularly for the SSs [90]. However, there is no evidence from more than two decades of handling LWR SS clad fuel that ductility is a problem.

9.1.2. Changes in microstructures

Reactor radiation has discernible effects on metal microstructures. Second phase particles in the Zircaloys dissolve [39]. Radiation-induced ageing occurs on Zr-2.5Nb alloys [129], to illustrate two consequences of neutron radiation on microstructures. However, neither effect seems to have practical impact on storage behaviour of fuel with zirconium alloy cladding. Similarly, there are no radiation-induced microstructural effects that seem to influence aluminium alloys in storage. However, the SSs are susceptible to RIS that needs to be considered in assessing storage behaviour of SS clad fuels (see following section).

9.1.3. Radiation induced segregation (RIS) in stainless steels

Neutron irradiation of stainless steels results in a phenomenon that parallels the thermally-induced sensitization. The phenomenon is referred to as radiation-induced segregation (RIS), which can promote irradiation assisted stress corrosion cracking (IASCC) when stress levels and aggressive species are significant synergistic factors. Figure 3 indicates the thermal regime where radiation-induced sensitization is active. The phenomena involve radiation-enhanced diffusion of species, including chromium. Because chromium diffuses faster than nickel, the grain boundary zone becomes depleted in chromium, paralleling thermal sensitization, but involving a different mechanism. Effects are limited to about 500°C because annealing of radiation damage precludes radiation effects on chromium transport at higher temperatures. Figure 4 indicates a chromium depletion profile that occurs at SS grain boundaries as a function of the level of radiation damage, based on a modelling approach [130]. The model only accounts for RIS effects. Therefore, Figure 4 does not indicate possible effects of thermal sensitization on SS cladding irradiated in the range where RIS is not a factor. The combined effects of thermal and RIS effects may be augmentative, but modelling is not yet available to account for the combined effects.

The threshold for development of microstructures that promote IASCC at reactor service temperatures is about 0.5×10^{21} n/cm^2 >1 MeV in BWRs and 3×10^{21} n/cm^2 in PWRs [62–64]. These fluence levels are below fluences on much of the SS clad LWR fuel now in storage. For example, PWR fuel at a burnup level of 35 000 MW·d/t corresponds to a neutron fluence of 6.6×10^{21}, >1 MeV (see NUREG/CR-6534), Vol. 2), which is above the threshold for RIS. Cases of cladding degradation for GCR and LMR fuel cladding during storage were discussed in Section 4. The SS clad LWR fuel would be expected to be subject to RIS, but detailed examinations [3, 27, 66] have not indicated evidence of cladding degradation during periods of wet storage. This suggests either that cladding stresses are relatively low or that the water environment was sufficiently pure to preclude a synergistic interaction that would degrade the cladding.

Studies included under this CRP involve investigation of RIS phenomena and interpretation of them in the context of spent fuel storage [61]. The fact that SS LWR cladding is expected to be subject to significant RIS suggests that there is a major incentive to maintain good water chemistry control in pools where the fuel is stored, and to take measures to preclude the so-called "hot cell rot" phenomenon when the fuel is transferred to dry storage or permanent disposal (see Section 4). Similar considerations apply to GCR and LMR SS clad fuel.

9.1.4. Fission product effects on interior cladding surfaces

Fission product attack on the inside surfaces of fuel rods has been observed for the zirconium alloys [131, 132] and for SSs [94, 133] A pellet clad interaction (PCI) phenomenon has caused cladding failures of zirconium alloys in reactor service It involves combined effects of aggressive fission products and high local stresses imposed by fuel pellets on the cladding ID surface In wet storage, fission product decay, lower temperatures, and diminished stresses seem to be sufficient to preclude PCI failures in storage for the zirconium alloys [19]

From US and foreign correlations of FCCI estimates for SS clad LMR fuel during service, the depth of FCCI to 125 µm, maximum, depending on fuel operating conditions, is expected to be 50 µm [133] FCCI attack does not seem likely to propagate at the mild conditions in FSPs Examination of LWR SS clad fuel, cited in Section 4, did not indicate evidence of damage from fission product attack on cladding inner surfaces Eddy current scans on several rods did not indicate any large incipient cracks on LWR SS cladding While incipient cracks have been observed on Zircaloy cladding after reactor service, relaxed stresses and low fission product concentrations are not expected to propagate cracking in wet storage The active species is indicated to be radioiodine [132] The iodine is in the form of CsI While laboratory studies have shown that CsI dissociates under gamma radiation (10^9 R/h over several hours), and can cause cracks to propagate at 300 to 400°C, these conditions do not exist in wet storage [133] A crack did propagate through PWR cladding on one rod during a dry storage demonstration [124], evidenced by release of ^{85}Kr to the test chamber However, the cause was not considered to involve SCC

9 2 EFFECTS OF RADIATION ON MATERIALS IN WET STORAGE FACILITIES

Gamma radiation is emitted from irradiated fuel assemblies at levels near 10^6 R/h when the fuel is first discharged Smaller elements, a decade after discharge, have radiation levels near 5 R/h In some storage pools, irradiated cobalt targets and radiocesium are stored metal capsules, radiation levels are up to about 10^6 R/h The high radiation levels result in doses to adjacent materials The materials include metals in facility components, such as fuel storage racks, pool liners, canisters, etc Organic materials are sometimes enclosed in fuel storage racks to act as neutron absorbers These materials degrade as they accumulate dose from gamma fields

9.2.1. Effects of gamma radiation on metal corrosion in FSPs

Available evidence suggests that gamma fluxes do not accelerate aqueous corrosion of the zirconium alloys [39] In fact, detailed investigations of LWR Zircaloy and SS fuel cladding and aluminium and SS FSP components that have been subject to gamma radiation from self irradiation or adjacent fuel elements have not indicated detectable effects on aqueous corrosion mechanisms However, laboratory data were reported to indicate a factor of three (average) increase in aqueous corrosion rate for SSs exposed to gamma radiation [134–136] However, the accelerated rate was reported to be 10 µm/year, more than an order of magnitude higher than results reported elsewhere for SS corrosion under irradiation [82] In reality, SS corrosion rates in wet storage conditions are so low (e g Ref [9]) that the radiation enhancement has no practical consequence, consistent with the prior indication that examination of SS component specimens did not show detectable corrosion in detailed investigations, even when exposed to gamma radiation from adjacent fuel assemblies (e g Ref [78]) Metallographic examination of an Al spacer that had been adjacent to an irradiated fuel assembly for 16 years provided evidence that radiation had not affected either pitting attack or uniform corrosion significantly

9.2.2. Implications of thick-film phenomena to gamma effects in FSPs

A "thick film effect" was observed to accelerate Zircaloy corrosion in reactor fluxes in low oxygen environments after the oxide films reached a threshold thickness [123, 126] The associated hypothesis is that water permeates cracks and pores in the oxide Radiolysis within the porous oxide creates local environments that control the corrosion environment While the radiation levels in the

FSPs may be too low to promote the thick-film oxidation phenomena, there is evidence that gamma radiation promotes crevice corrosion of SSs in chloride solutions [87]. The study was carried out in solutions with 3% sodium chloride. Results of the experiment are summarized in Section 9.3.2.

9.2.3. Radiation effects on fuel storage racks

Radiation effects on storage racks have taken several forms. In some pools, water leaked inside storage rack panels. When the leakage sites resealed, radiolysis generated hydrogen and oxygen inside the rack panels, causing them to swell, resulting in binding of the fuel assemblies. The problem was solved by drilling holes in the panels to relieve the hydrogen pressure. A permanent solution was facilitated by venting to allow gases formed by radiolysis to escape.

A more serious effect of gamma radiation on storage rack materials has involved neutron absorbers with organic carriers, most prominently, a material referred to as Boraflex (silicone base). Exposure of storage racks containing these materials to gamma radiation in wet storage facilities has resulted in degradation of the neutron absorber [137]. This has resulted in considerable technical and regulatory attention to assure that criticality margins for fuels stored in the racks are not compromised [see American Nuclear Society, Trans. Vol. 74, pp. 322–328 (1996) for updates on solutions to the Boraflex problem].

9.2.4. Radiation effects on biological species

The effect of radiation on biological materials is a significant consideration in fuel storage facilities. Because there has been little systematic study of radiation thresholds that various biological species tolerate under wet storage conditions, there is little basis to predict how much pasteurization occurs in the waters adjacent to irradiated materials. However, two data points suggest that certain microbe species can tolerate relatively high radiation doses. The first case involves bacterial spores that required 3–4 kGy (3 to 4×10^5 rads) to effect a 90% kill [138]. The other case involves Micrococus radiodurans; in the vegetative state, the organism requires 10 kGy (1.3×10^6 rads) for 90% kill. In the perspective of FSP radiation levels, at the upper end of about 10^6 rads/h, the species could be largely eradicated in dwell times of 0.4 to 1.3 h. However, in a pool under brisk circulation, considerably more time would be required to accumulate the required dose. How much the organisms can repair non-lethal damage as they cycle in and out of the radiation fields is not clear. As radiation levels decrease with fuel residence times, the pool radiation fields will become less damaging to the organisms. An important consideration is to investigate thresholds that organisms can begin to infest surfaces of fuel cladding, with the prospect that corrosion damage to the cladding could ensue. On one hand, no evidence of corrosion attributable to MIC has been reported on fuel cladding. On the other hand, there are few opportunities to examine fuel cladding in sufficient detail to judge whether there is evidence of MIC.

A useful insight is provided by an observation in a pool at the Savannah River Site. A gamma field from a radiocesium source impinged on a pool wall that was infested with algae. Radiation killed algae in a circular pattern on the wall. The radiation threshold for algae survival was about 25 R/h [89].

9.3. EFFECTS OF RADIATION ON WATER CHEMISTRIES IN WET STORAGE FACILITIES

Effects of radiation on water chemistries is a complex subject that involves formation and reaction of short-lived ions and radicals and longer lived relatively stable species. The species formed include both oxidizing and reducing types. There are a few systematic studies that relate to effects of radiation effects on water chemistries in FSPs, but results have been somewhat contradictory. So, on one hand, there are uncertainties regarding what effects radiation may be causing in the remote reaches of FSPs, where examination is difficult. On the other hand, aside from obvious phenomena that were described in Section 9.2.3, there is minimal evidence that radiation is causing substantial degradation of materials due to effects on water chemistry.

9.3.1. Radiation chemistry effects

It is not practical here to recount in detail the complex subject of radiolytic processes in water Burns has addressed radiation effects on water chemistries in detail (e g , summary in Ref [39]) Many potentially aggressive ions and radicals are formed by radiation that have lifetimes much less than one second Long lived species, principally hydrogen peroxide are also generated While hydrogen is a reducing product, it is relatively mobile, leaving behind the hydrogen peroxide This oxidizing species may supplement local oxidizing potentials additional to that provided by oxygen in the pool water from equilibrium with the atmosphere (about 8 ppm at 25°C) In some cases the oxidizing conditions may be beneficial in maintaining protective oxides It is observed elsewhere in the report that aqueous corrosion of Al alloys seems to be largely unaffected by dissolved oxygen This is also true of zirconium alloys under wet storage conditions For the SSs, the situation is less clear Dissolved oxygen promotes IGSCC of SSs at BWR operating temperatures, but in the wet storage temperature regime, dissolved oxygen is generally regarded as relatively benign toward SSs (e g Ref [72]) However, as suggested in Section 9 2 2, radiation effects may be promoted in crevices, as indicated in the following section

Corrosion of SSs in moist air in gamma radiation fields has been observed [67, 136] The accelerating factor was proposed to be nitric acid generated by radiolysis [67]

9.3.2. Radiation effects in crevices

There is conflicting evidence regarding radiation effects in crevices, summarized in Ref [87] Some results were interpreted to indicate beneficial effects of oxidizing species in counteracting detrimental effects of de-aeration and acidification Another study suggested that gamma radiation may shift the potential in a crack to more reducing conditions, mitigating subcritical crack growth in Type 316 SS at 100°C (see Jones and Henager, J Nucl Mat 191, 1012, 1992) Another study indicated that radiation increased the rest potentials of SSs by 200 to 300 mV, and had little effect on pitting breakdown or re-passivation potentials The observations implied that radiation will increase the propagation rate of established pits A study conducted in 3% sodium chloride solutions involved Type 304L SS in fields of 10 to 10^3 Gy/h If radiation fields are sufficient, generation of peroxide in the crevice will provide oxidizing conditions that raise the free corrosion potential on low alloy steels The shift in corrosion potential may be sufficient to promote crevice corrosion The corrosion may also propagate if there is ample cathodic area The propagation rate should increase with radiation dose, related to production of peroxide

The effect of radiation on pit initiation on austenitic SSs is negligible because the free corrosion potential of the SSs remains about 300 mV less than the pitting potential However, gamma radiation was observed to promote initiation and propagation of crevice corrosion in austenitic SS in chloride solutions, which would not occur in the absence of radiation [87] The effects were proposed to be related to generation of hydrogen peroxide, but the influence of short lived radiolytic species was not ruled out The absence of crevice corrosion on SS was indicated in CBB tests on SS in FSPs [16]

10. WATER CHEMISTRY FACTORS

Water chemistry effects specific to certain metals have been addressed in the individual sections. This section provides an overview, because many pools include multiple materials that may not all be mutually compatible in water chemistries adjusted to accommodate a specific material. Biological phenomena are closely coupled to water chemistries, and some biological counter measures require water treatments that cause aggressive conditions in the FSP water. Algae foul surfaces and interfere with visibility. Microbial species have caused degradation of numerous metals in some aqueous systems. The prospect of MIC in FSPs is an important consideration.

10.1. WATER CHEMISTRY CONTROL IN WET STORAGE FACILITIES

Methods to control water chemistries in storage pools include: ion exchange, filtration, skimmers (to remove floating species) and periodic vacuuming (to remove sludges from the floor of the facility). Ion exchange and filtration remove radioactive and non-radioactive species. However, in some cases, it is necessary to impose special measures to address control of radioactive species. One of the most troublesome species is Cs-137 because it is a prevalent fission product, is highly soluble, and therefore is readily released to the pool water, and has a 30 years half-life . Special ion exchange media are available to remove the cesium, generally involving zeolites. Water chemistries in a wide range of wet storage facilities are summarized elsewhere [3, 19].

When the water chemistry control methods indicated above are effectively and systematically applied, environmental conditions in the pools are in the benign range, e.g., conductivities near 1 μS/cm, chloride concentrations <1 ppm, and pHs in the range of 4.5 to 8.0, depending on whether boric acid additions are made, principally in PWR pools.

10.1.1. Water chemistry excursions, recovery, mitigation, and monitoring

Some water pools have been subject to extended periods of poor chemistry control. When effective measures to control the water chemistry were instituted, major improvements in chemistry were accomplished in a relatively short time. For example, the L Basin at the Savannah River Site has a volume of over 3 million gallons (over 11×10^6 litres). When effective ion exchange was instituted, the water conductivity decreased from over 100 μS/cm to less than 10 μS/cm in three months. Similar experience involves a water chemistry excursion in the Hanford K basins, where a biocide addition raised corrosion rates of several materials [9] (see sections on Al alloys, CS, and Cu). Within six months the water chemistry had been improved, and low corrosion rates had been re-established. A comprehensive corrosion monitoring programme was underway in the FSPs prior to the chemistry excursion. Effects of the excursion and subsequent water cleanup measures on corrosion were monitored by periodic removal and evaluation of coupons [9].

In another FSP, water chemistry control was compromised by addition of aggressive biocides for algae control [11, 15, 81]. Chloride concentrations ranged up to 760 ppm and were above 50 ppm for more than two decades. Nitrates were added to mitigate the corrosion effects on fuel cladding and FSP facility materials. However, corrosion was a prominent problem on Al alloys and CS. Early failure of reactor-sensitized SS clad LMR fuel assemblies prompted canning of similar assemblies to isolate them from the aggressive water [76]. Otherwise, SS facility components seemed to weather the aggressive chemistry, also suggested by absence of corrosion on SS specimens that were periodically inspected [11]. Zircaloy clad fuel that resided in the aggressive pool for up to 27 years showed no evidence that it had degraded in video inspections as it was removed from the facility.

10.1.2. Range of routine FSP chemistries

In contrast to the aggressive chemistries cited above, predominantly, FSP water chemistry control is good [3, 19]. Power reactors operate to regulatory guidelines for FSP waters. Water chemistry control in test reactor storage pools is less uniform, and serious corrosion problems have developed at some facilities (e.g. Ref. [8]). Water chemistry control has generally not been a priority

at defence reactor FSPs because the expectation of reprocessing after short periods of wet storage seemed to minimize the prospect of serious fuel cladding corrosion In some countries reprocessing is continuing In some cases, FSP waters are drawn directly from rivers or other water bodies and are given minimal chemistry control The short storage periods seem to be consistent with the expectation of minimal corrosion In other cases, e g, at US defence sites, when reprocessing capacities were shut down, the traditional reliance on short storage periods was no longer a protection from cladding corrosion Because pools were not equipped to maintain good water quality, corrosion has emerged as a major problem at several sites [9, 11, 28] Initiatives are underway to transfer the fuel to dry storage At all sites, actions have been taken to improve water chemistry control

10 1 3 Special FSP water chemistries

Special water chemistries have been specified for certain fuel cladding types, to mitigate cladding corrosion [18] For fuels with Magnox (Mg alloy) cladding, the FSP pH is maintained at 11 5, which is the limit for waters in contact with atmospheric CO_2 Impurities, chloride and sulphate, are maintained at <1 ppm, total, and preferably less than 0 5 ppm When storage for longer than a few months is needed, fuel elements are placed in canisters with pH maintained at 13 The high pH mitigates uniform corrosion and impurity control mitigates pitting attack on the Magnox

As indicated in prior sections, the AGR fuel SS fuel cladding sensitizes during reactor service Storage in the reactor FSPs involves water dosed with boric acid (for criticality control), with sodium hydroxide added to maintain the pH at about 7 [18] Chloride and sulphate levels are maintained below 1 ppm, and the water temperature is kept below 27°C This phase of the storage is limited to about 100 d before the fuel is transported to the reprocessing plant Because of difficulty in maintaining satisfactory chloride and sulphate levels in open FSPs near the sea, water chemistry was adjusted to pH11 4, with chloride and sulphate at <0 5 ppm The environment has proved satisfactory in mitigating IGSCC on the sensitized cladding for more than a decade

10 2 WATER TEMPERATURE EFFECTS

Temperatures in FSPs are in a range generally considered benign Many FSPs have heat exchangers to remove decay heat when the level is high enough to raise water temperatures beyond specified or desired levels However, in some wet storage facilities, sufficient cooling capacity has been installed to maintain temperatures below ambient to minimize corrosion rates [9] In the Hanford K Area FSPs, when there was minimal cooling capacity, water temperatures varied from about 25°C to 10°C annually, following ambient temperature trends In 1993, refrigerated cooling capacity was installed in the two FSPs, each with a volume of about 5 10^6 litres (1 3 x 10^6 gal) The coolers controlled water temperatures to about 10°C year round The benefits included lower corrosion rates on exposed uranium metal fuel The lower corrosion rates were reflected in lower rates of Cs-137 release to the pool water [9] Corrosion rates on other metals, including Al alloys, CS, and Cu alloys, were undoubtedly also lower A further effect was suppression of algae The algae returned in a section of one pool that was isolated from the cooled water by a barrier The temperature in the isolated water volume was about 20°C

10 3 BIOLOGICAL SPECIES AND THEIR CONTROL

A 1997 publication summarizes papers from a conference held in Budapest, Hungary, that focused on microbial degradation processes in fuel storage and repository environments [138]

Biological species that may invade fuel storage facilities include algae and slimes, including fungi, yeasts, and bacteria that are sessile However, the species present are also water-borne Bacteria include *Sporovibrio desulfurican* (sulfate reducing bacteria), which generate H_2S by metabolizing sulfates, and Crenothrix ("iron-eating" bacteria), which metabolize soluble iron and manganese while excreting the oxides Various bacteria have been know to attack a wide range of materials in low temperature aqueous systems Weld metals on SSs are areas vulnerable to MIC attack Titanium is notably resistant to MIC While biological species that attack metals have been

observed in spent fuel pool waters, there is relatively little specific evidence of serious MIC attack [89, 139], including metallographic examinations of SS and Al alloy specimens that had resided in wet storage facilities (e g Ref. [78]) However, there is some evidence of MIC attack on an Al alloy exposed in a FSP with good water chemistry control [81]

Table IV provides a summary of biological countermeasures Some measures involve addition of aggressive species that have resulted in aggressive water chemistry conditions that markedly accelerated corrosion of some materials in the storage facilities [9, 11, 28] Controlled additions of peroxides have seemed to provide satisfactory algae control, while maintaining acceptable rates of corrosion of FSP metals [9, 89]

A major consideration for wet storage facilities that accept fuels from other facilities is to minimize transport of biological species into the receiving pool This requires co-ordination with the shipping pool operators to impose measures to minimize the transport of biological species between facilities

TABLE IV CHARACTERISTICS OF CANDIDATE METHODS FOR BIOLOGICAL COUNTER-MEASURES

Method	Problems	Effectiveness
Hyprochlorites	Non-penetration of biomasses Promotes corrosion	Suppresses algae, microbes
Chlorine	Non-penetration of biomasses Promotes corrosion	Suppresses algae, microbes
Hydrogen peroxide	Non-penetration of biomass, safety, cost	Suppresses algae, microbes
Ozone	Non-penetration of biomass, capital cost Attacks inhibitors Attacks organics (e.g., gaskets)	Suppresses algae, microbes
Ultraviolet light	Limited efficacy Interference by suspended solids	Only effective for suspended species
Organics	Degraded by radiation, sometimes hazardous to handle	Can target certain species Can have long half-lives
Mechanical removal	Sometimes limited access	Only where colonies are accessible
Lower temperature	Often costly to implement	Effective for algae at $<\sim15°$ C
Radiation	Threshold for effective control not well defined	Algae not observed in high dose areas, but do occur in low dose areas, certain microbes tolerate high doses
Lighting	Some lighting usually necessary Microbe activity occurs without light	Algae growth seems minimal where lighting is minimized, some microbes affected by light
Water purity	Operating costs	high purity pools not immune
Infection	Casks used to ship fuels not always treated to minimize biological species	Could be an important source of biological species

Notes   Macroporous resin beads, sand filters contribute to microbial infection, mitigated by enzymes/biocides,
Consider biofouling coupons to monitor fuel storage facilities,
Algae species sensitive to pH and temperature

10.4. DISSOLVED OXYGEN

Waters in wet storage facilities are in equilibrium with the atmosphere and there are subject to oxygen saturation. At 25°C the saturation concentration is about 8 ppm. The solubility increases with decreasing temperatures and decreases with increasing temperatures. Oxygen can be expelled by boiling, by sparging with inert gas, and by reaction with oxygen scavengers, e.g., hydrazine. Sulphite resins are used to deoxygenate waters. However, none of these measures has been considered practical or necessary to maintain satisfactory corrosion control at wet storage facilities.

11. BASES FOR FUEL CATEGORIES

Minimizing and controlling radiation releases to the pool water and to the environment is a central consideration in wet storage technology. Two considerations are key determinants of radiation releases from the fission product and transuranic inventories in the irradiated fuels:

- durability of the fuel cladding to degradation by water;
- durability of the fuel material to degradation by water.

If the cladding is highly durable, as with zirconium alloys and LWR SS, and is not mechanically damaged, then the corrosion resistance of the underlying fuel material is not an issue because it is not exposed to water. If the cladding is subject to damage in reactor service, during discharge from the reactor, or can become perforated by corrosion in wet storage, then the durability of the fuel material becomes a determining factor in the viability of further wet storage. From cases cited in preceding sections, we can illustrate the cases. A small fraction of the LWR Zircaloy clad fuel has developed cladding breaches during reactor service, exposing the underlying uranium oxide fuel. Most of the readily leachable radioactive species washed from the fuel before reactor discharge. Therefore, further leaching while the fuel is exposed to pool water occurs at relatively low rates. Consequently, the majority of FSP operators (70% according to a worldwide survey [3]) store failed LWR fuel on the same basis as intact fuel, i.e., without canning to isolate it from the pool water. Studies indicate that the exposed fuel pellets are stable in pool waters over extended periods (Sections 3.1.4.6, 8.1).

Contrasting behaviour is represented by Zircaloy clad fuel from the Hanford N Reactor. The Zircaloy cladding has the same high degree of integrity in wet storage as it does with LWR fuel, if the cladding remains intact. However, as indicated in a prior section, a fraction of the fuel cladding was mechanically damaged during fuel discharge operations. In contrast to the oxide fuel exposed at cladding defects, the uranium metal fuel is subject to aqueous corrosion that releases troublesome inventories of fission products and transuranics. Both cases involve the same cladding, that resists degradation in wet storage environments. In one case, cladding defects are tolerable because the fuel material is durable when exposed to water. In the other case, corrosion of the susceptible fuel material precludes wet storage as an acceptable long term fuel management option.

Other cases involve cladding which is susceptible to aqueous corrosion, e.g., Al alloys in aggressive waters. When the underlying fuel is also subject to aqueous attack, wet storage is marginal or unacceptable, depending on release rates of radioactive species. When the underlying fuel resists attack, wet storage may be viable for prolonged periods.

There are perhaps more than 100 fuel types worldwide, accounting for fuel, cladding, and configurational differences. Considering the various fuel types in terms of categories seems to offer a basis to simplify decisions regarding future fuel management, including choice of wet or dry storage and selection of an appropriate level of conditioning. Table V illustrates categories, based on durability of both cladding and fuel to aqueous corrosion. Aluminium alloy cladding has a range of integrities in wet storage, depending on the aggressiveness of the environment. At best, aluminium is considered to be less resistant to aqueous environments than zirconium alloys or LWR SS; therefore, it is assigned Category B for extended wet storage and Category C for fuel more appropriate for dry storage (note that some Al clad fuels have remained in wet storage for more than two decades without evidence of substantial degradation).

When the underlying fuel material is corrosion-prone and the cladding is either damaged (Zircaloy clad N Reactor Fuel), or subject to penetration of the cladding by corrosion in the foreseeable environments and time frames, the assigned category is D.

Table V can be expanded to include other fuel types, based on judgements or data relevant to the two criteria: durability of cladding and durability of fuel. The table can also be expanded to consider levels of conditioning needed for fuels destined for dry storage. For example, Al clad fuels with minimal corrosion film were only dried in a hot cell at 40°C [141]. Uranium metal fuels that

TABLE V CLASSIFICATION OF IRRADIATED FUELS BASED ON DURABILITIES OF CLADDING AND FUEL MATERIALS IN WATER [140]

Category	Cladding Material	Durability in Water	Fuel Material	Durability in Water
A	Zircaloy	High	UO_2	High
A	LWR SS	High	UO_2	High
B/C[1]	Al Alloys	High to Low	UAl_x/Al	Intermediate
The Committe e	LMR SS	Low	UO_2	High
D	Al Alloys	High to Low	U Metal	Low
D[2]	Zr Alloys	High	U Metal	Low

[1]The range of Al alloy durability depends on the aggressiveness of the wet storage environment
[2]Category D applies to Zr alloy cladding that is subject to mechanical damage, otherwise Category A could apply for undamaged Zr alloy cladding

have been subject to aqueous corrosion are assumed to have some inventory of uranium hydride, and have been subject to more stringent conditioning [116]

Albert Einstein advised us that "Everything should be made as simple as possible — but no simpler" In the complex world of spent fuel, categories seem to offer a simplification in our deliberations regarding management of the fuel, while avoiding oversimplification if properly interpreted

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Annex I

SUMMARIES OF NUCLEAR FUEL AND CLADDING MATERIALS

TABLE I.1. POWER REACTOR FUEL AND CLADDING MATERIALS [3]

Entries listed comprise traditional materials and do not include test or other alternate materials that may have been in service.

Characteristics	LWR		HWR			GCR		FBR*
	PWR	BWR	CANDU	MZFR	Atucha	AGR	Magnox	Phoenix/ BR300
Cladding mat'l	Zry 4	Zry 2	Zry 4	Zry 4	Zry 4	SS 25Ni-20Cr	Mg Alloy	316 SS
Fuel type	UO_2	UO_2	UO_2	UO_2	UO_2	UO_2	U Metal	UO_2/PuO_2

*Representative of other LMR fuels

Alloy compositions

A. Zircaloy:

Element	Zircaloy-2	Zircaloy-4
Sn	1.2 to 1.7	1.2 to 1.7
FE	0.07 to 0.20	0.18 to 0.24
Cr	0.05 to 0.15	0.07 to 0.13
Ni	0.03 to 0.08	...
O	0.12 typical	0.12 typical

Zr - 1 Nb cladding and Zr-2.5 Nb pressure tubes used in reactors of Soviet design

B Stainless steel

Alloy	%C	%Mn	%Si	%Cr	%Ni	%P	%S	% Other*
304	0 08	2	1	18-20	8-10 5	0 045	0 03	
304L	0 03	2	1	18-20	8-12	0 045	0 03	
316	0 08	2	1	16-18	10-14	0 045	0 03	2-3 Mo
316L	0 03	2	1	16-18	10-14	0 045	0 03	2-3 Mo
347	0 08	2	1	17-19	9-13	0 045	0 03	10 X %C min Nb + Ta
348	0 08	2	1	12-19	9-13	0 045	0 03	Nb + Ta 0 8

*Balance is Fe

C Magnox fuel cladding

British   Mg - 0 8 Al - 0 6 Mn (Several variations)
French   Mg - 0 5 Zr

D Uranium metal fuel

British Magnox
    Al   600 to 1200 ppm (increased to 1000 to 1500 ppm)
    Fe   250 to 400 ppm

US (Hanford N Reactor)
    Al   700 to 900 ppm
    C   365 to 735 ppm
    Fe   300 to 400 ppm
    Si   100 ppm

TABLE I 2 EXAMPLES OF TEST REACTOR FUEL CLADDING AND FUEL MATERIAL[a]

Entries in Table I.2 represent a significant cross-section of research and test reactor fuel materials

Fuel	Abbreviation	Fuel Matrix/Cladding
Atomics International (a SNAP fuel)	AI	UZrH/declad
Army Package Power Reactor	APPR	UO_2 SS cermet/SS
Advanced Reactivity Measurement Facility	ARMF	UAl/Al
Advanced Test Reactor	ATR	UAl/Al
BMI, Battelle Thermal Reactor	BMI	UO_2 SS cermet/SS
Boiling Reactor Experiment V	BORAX V	UO_2 SS cermet/SS
Swiss Test Reactor	DIORIT	Zry/UO_2
Experimental Breeder Reactor II	EBR II	U-5% Fissium/SS
EBR II Scrap	EBR II, ANL-6	U-5% Fissium/SS
Enrico Fermi Atomic Power Plant (SS clad only)	Fermi I Blanket	UMo/SS
High Flux Beam Reactor	HFBR	UAl Al cermet/Al U_3O_8 Al cermet/Al
University of Missouri Research Reactor	MURR	UAl/Al
Oak Ridge Reactor	ORR	UAl/Al
Pathfinder	Pathfinder	UO_2 SS cermet/SS
SM-1A Army Reactor	SM-1A	UO_2 SS cermet/SS
Systems for Nuclear Auxiliary Power	SNAP	UZrH/declad
Organic Moderated Reactor Experiment	SPEC (OMRE)	UMo/SS
Special Power Excursion Reactor	SPSS (SPERT)	UO_2 SS cermet/SS
Kansas State, Cornell, Texas, Hanford, MSU, and GA TRIGA SNF with Al cladding	TRIGA Al	UZrH/Al
Berliner Experimenter Reactor II	TRIGA Ber II	UZrH/SS
Neutron Radiography Reactor	TRIGA FLIP	UErZrH/SS
MSU, GA, and Berkeley TRIGA SNF w/SS cladding	TRIGA SST	UZrH/SS
University of Washington Argonaut Reactor	UW	UAl/Al
Vallecitos Boiling Water Reactor	VBWR (GENEVA)	UO_2 SS cermet/SS

[a]Based principally on information in Reference [15]

TABLE I 3 DEFENCE REACTOR FUELS

Entries are general, not specified by reactor type, and may not include all materials that have been in service

Cladding	Fuel material
Al alloys	Metallic uranium
Magnesium alloys	Metallic uranium
Zirconium alloys	Metallic uranium

Aluminium alloys

Alloy	Al	Fe	Ni	Si	Mg	other
1100	99(a)	(b)	–	(b)	–	0 05 to 0 2 Cu
6061	97 9	–	–	0 6	1 0	0 25 Cr, 0 25 Cu
6063	98 9	–	–	0 4	0 7	0 1 max Cu
8001	(c)	0 6	1 1	(c)	–	0 05 to 0 25 Cr
5086	94 6	–	–	0 4	3 5 to 4 5	0 1 Cu 0 2 to 0 7 Mn

(a)Minimum
(b)Si + Fe = 1% max
(c)1100 Al with Fe & Ni additions

Annex II

TYPICAL WET STORAGE FACILITY COMPONENTS: COMMERCIAL AND DEFENCE FACILITIES

TABLE II.1. TYPICAL FACILITY COMPONENT MATERIALS IN COMMERCIAL LWR STORAGE POOLS [19]

Component	Sub-Components	Material[a]	Alloy
Wall	--	Reinforced Concrete	--
Pool Liner	--	Stainless Steel Epoxy, Fiberglass	304
Heat Exchanger[b]	--	Stainless Steel	304/316
Filter·	Vessel	Stainless Steel	304L
	Filter Elements:	Stainless Steel Diatom, Earth, Fiber	304L
Recirculating Pumps:	Casing, Shaft	Stainless Steel	316
	Impeller	Bronze	
Demin Water Return Pump	Casing, Impeller, Shaft	Stainless Steel	316
Deionization Unit	Tank	Stainless Steel	304L
Cask Head Support Racks	--	Stainless Steel	304L
Gates and Guides	--	Stainless Steel	304L
Canister Storage Racks	Racks:	Stainless Steel Aluminium	304L 6061-T6
	Embedded Supports	Stainless Steel	304L
Fuel Storage Canisters·[c]	--	Stainless Steel Aluminium	304L 5083/5086/6063
Leaker Can Support Racks	--	Stainless Steel Carbon Steel, Epoxy-Coated	--
Control Rod Cluster Storage Racks	--	Stainless Steel	--
Portable Offgas Hoods:	--	Stainless Steel Aluminium	--
Cask Handling Crane	Cable & Grapple	Stainless Steel	--
Canister Crane	Cable & Grapple	Stainless Steel	--
Fuel Transfer Conveyer	--	Stainless Steel	304L
Insulators	--	Tygon, Neoprene	
Cask Impact Pad	Cladding Pad (not exposed to H_2O) Honeycomb (not exposed to H_2O)	Stainless Steel Carbon Steel (3 ½ in. thick) Aluminium	

[a]Types identified in survey, other types may be used in some pools

[b]Carbon steel tubes were originally installed in heat exchangers at one pool, severe rusting caused a visibility problem in he pool water, resulting in retubing with stainless steel Copper alloy tubes are used at one R&D facility pool

[c]Some canister walls contain boron-impregnated aluminium for reactivity control, clad with stainless steel or aluminium

TABLE II 2 RANGE OF MATERIALS IN DEFENCE REACTOR STORAGE FACILITIES* [9]

Material Type	First Installed		Application
	KE	KW	
1020 carbon steel	1973	1978	Cubicle Racks
Various carbon steels	1973	1978	Piping, structural components, fuel handling equipment
90-10 copper-nickel alloy	1973–1983	1978-83	Heat exchanger tubing (no longer in service)
Copper	1983	1983	Chiller tubing (currently in service)
195086, 6061-T6 aluminium	1975	1981	Mark 0 and Mark 1 storage canister barrels
6061-T6 aluminium		1981	Mark 1 canister lids
316 stainless steel		1981	Valves on Mark 1 and Mark 2 canister lids
304-L stainless steel	1981	1981	Mark 1 and Mark 2 storage canister barrels, Mark 2 canister lids, fuel handling equipment
416 stainless steel		1982	Mark 2 canister lid locking bars (original
Inconel 718			Mark 2 canister lid locking bars (new)

*Illustrated by materials in the Hanford K East and K west FSPs, used to store Hanford N Reactor fuel

Alloy compositions (see also Table I 1)

Carbon steel (typical)
    Fe-0 3C-1 2 Mn

Inconel 718
    50 to 55 Ni-17 to 21 Cr-5 (Nb + Ta)-3 Mo, bal Fe

Ferritic stainless steel (typical)
    Fe-11 5 to 13 5 Cr-1 Mn-1 Si-0 08 Cr

90-10 Copper nickel
    Cu -9 to 11 Ni-1 to 1 8 Fe-1 Zn

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ABBREVIATIONS

Al	aluminium
ASTM	American Society for Testing and Materials
AGR	advanced gas cooled reactor
AFR	away from reactor (storage facility not associated with a reactor)
BEFAST	*BE*haviour of *F*uel *A*ssemblies during extended *ST*orage
BWR	boiling water reactor
CBB	crevice bent beam
CS	carbon steel
DIW	deionized water
FCCI	fuel–cladding chemical interaction
FA	fuel assembly
FSP	fuel storage pool
GCR	gas cooled reactor
HAZ	heat affected zone
HM	heavy metal
ASCC	irradiation assisted stress corrosion cracking
ICPP	Idaho Chemical Processing Plant (603 is a FSP at ICPP)
IGA	intergranular attack
IGSCC	intergranular stress corrosion cracking
INEL	Idaho National Engineering Laboratory
ISFSI	independent spent fuel storage installation (may be close to a reactor or power station but in a separate facility)
LMR	liquid metal reactor
MAGNOX	*MAG*nesium-*No* *OX*idation (CO_2 cooled GCR; Mg alloy cladding)
MIC	microbially influenced corrosion
mpy	mils per year (1 mil = 0.001 inch or 0.00254 cm)
NEA	Nuclear Energy Agency (of the OECD)
NDE	non-destructive evaluation
PCI	pellet–cladding interaction
ppm	parts per million (by weight)
PRI	pitting rate index
PWR	pressurized water reactor
RBMK	graphite moderated pressure tube reactor of Russian design
RIS	radiation induced segregation; also, radiation induced sensitization
SS	stainless steel
SGHWR	steam generating heavy water reactor
t	tonne (1000 kg, 2200 pounds)
WWER	PWR of Russian design
μm	micrometre
μS	micro-Siemens

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