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Coolant Chemistry Control and Effects on Fuel Reliability in Pressurized Heavy Water Reactors

Report of a Technical Meeting

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COOLANT CHEMISTRY CONTROL AND EFFECTS ON FUEL RELIABILITY IN PRESSURIZED HEAVY WATER REACTORS

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REPORT OF A TECHNICAL MEETING

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FOREWORD

The structural materials of the primary circuit of pressurized heavy water reactors (PHWRs) experience corrosion as they are exposed to the coolant. Passive oxide layers formed on the structural materials are dissolved to some extent in the coolant and transported as corrosion products throughout the primary circuit. These soluble and insoluble corrosion products can be deposited on fuel cladding surfaces. For PHWRs with natural uranium fuel and with specific coolant chemistry control, it has been accepted that corrosion deposits on the fuel cladding are relatively harmless for the fuel integrity, unlike for light water reactors. This may be dependent on the physical form and location of the deposits and their possible influence on the heat transfer.

However, in 2008, a power reactor operator in Canada discovered black deposits on the fuel cladding, which increased interest in the significance of corrosion deposits. These observations of deposits on fuel bundles discharged from the reactor have raised concerns regarding operational safety (e.g. an increase of local cladding temperature, leading to a reduction of margin to dryout) in operating PHWRs. To minimize the impact of fuel deposits on fuel fitness for service, coolant chemistry control may need to be reoptimized.

In PHWRs, coolant chemistry control is achieved mainly through dosing and control of the ‘apparent pH’ of the primary coolant pH_a and the deuterium concentration by adjusting the concentration of lithium and hydrogen, as appropriate. It also needs to be noted that concentration of lithium under fuel bundle bearing pads could lead to crevice corrosion, localized over relatively small regions such as areas of low flow or stagnation, and potentially cause fuel failures and pressure tube damage.

The present publication is based on the presentations and discussions from the Technical Meeting on the Control and Monitoring of Coolant Chemistry and Related Issues on Fuel Reliability in Pressurized Heavy Water Reactors, organized by the IAEA and held in Toronto, Canada, on 25–28 November 2019. The publication provides information on national practices to control the coolant chemistry under various operating conditions and R&D programmes to understand the corrosion phenomena and their influence on fuel fitness for service in the primary heat transport system of PHWRs.

The IAEA wishes to thank all the participants in the technical meeting for their active involvement and presentations, as well as the subject matter experts, including J.G. Roberts (Canada), D. Lister (Canada), R. Srinivasan (India) and P. Chan (Canada), for their valuable contributions to the drafting of this publication. Special acknowledgement is given to the Canadian Nuclear Safety Commission for hosting the technical meeting and the CANDU Owners Group for providing the venue. The IAEA officer responsible for this publication was K. Sim of the Division of Nuclear Fuel Cycle and Waste Technology.

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CONTENTS

1. INTRODUCTION

1.1. BACKGROUND

Since the early 1980s, the IAEA has supported Member States to exchange information on interactions of the primary circuit and fuel cladding materials with the coolant in the framework of coordinated research projects, technical reports and technical meetings. (Examples are shown in [1–10].) These activities provided an overview of the results of investigations into the water chemistry practices and concerns in the primary circuit of water-cooled power reactors; however, they were mainly based on light water reactor (LWR) experience and contained only piecemeal information on pressurized heavy water reactor (PHWR) experience. Actually, there exist many differences between LWRs and PHWRs in terms of primary circuit and fuel designs, and in terms of reactor operating and coolant conditions, which can affect the coolant chemistry.

In 2008, a power reactor operator in Canada discovered black deposits on the fuel cladding, which increased the interest of utilities' community in corrosion deposits. Observations of large and thick deposits on fuel bundles discharged from the reactors have raised a concern on the operational safety (via an increase of local cladding temperature and a reduction of margin to dryout) of ageing PHWRs. About four years later an event occurred at another Canadian plant following a commissioning activity after plant refurbishment resulting in observed magnetite deposits on fuel.

In response to request from Member States with operating PHWRs, the IAEA organized a technical meeting held in Toronto Canada from 25th to 28th of November 2019 to provide a forum where participants can share the national practices and prospects on the control and monitoring of coolant chemistry and share the research and development (R&D) activities on crud formation and transport in the primary circuit of a PHWR. At the technical meeting, participants were requested to develop a state-of-the art review related to chemistry control to confirm and warrant no impact on fuel fitness for services due to either ageing and/or various operating states.

1.2. OBJECTIVE

The purpose of this publication is to share the up-to-date knowledge on coolant chemistry control, corrosion phenomena observed in the primary heat transport system and consequent effects on fuel reliability in PHWRs[1], based on the results of the technical meeting in Toronto from 25th to 28th of November 2019.

1.3. SCOPE

This publication covers the following scope items:

- Feedback from national and international R&D programmes on coolant chemistry;
- Some operational experience (OPEX) of PHWR power plants;
- Technological opinion and corresponding observations regarding corrosion, oxidation, changes in material properties, radioactivity buildup etc.;
- Corrosion modelling;
- Technical basis for remedial actions to ensure reliable fuel performance.

1.4. STRUCTURE

Section 1 describes the rationale for developing this publication and also describes the purpose, the scope and the structure of this publication.

Section 2 describes the issues faced or the current focus on the coolant chemistry control in PHWRs by the participating States including their R&D works to understand the corrosion phenomena in the primary heat transport system (PHTS) of ageing PHWRs.

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[1] PHWRs can be distinguished into two groups depending on channel direction: vertical channel-type PHWRs and horizontal channel-type PHWRs. The latter includes Canadian PHWRs (CANDUs) and Indian PHWRs, whilst the former includes Argentina's Atucha-1 and Atucha-2. In the context of this publication, PHWRs imply horizontal channel-type PHWRs unless otherwise specified, and sometimes used interchangeably with CANDUs.

Since sharing knowledge and OPEX on coolant chemistry control was identified as an important issue, a floor discussion on knowledge retention and management was arranged during the technical meeting. Section 3 summarizes key results from the discussion.

Section 4 describes some recent advances in chemistry and corrosion R&D related to PHWRs based on papers presented at the technical meeting. Section 4 also describes a review of their significance within the overall subject of fuel reliability.

Section 5 describes the impact of the coolant chemistry control on the fitness for service of fuel, and also describes technical basis for remedial actions taken to ensure the reliable fuel performance.

Section 6 provides conclusions and overall recommendations for future work on the coolant chemistry.

Annex contains papers presented at the technical meeting in Toronto, in November 2019.

2. NATIONAL PRACTICE ON COOLANT CHEMISTRY CONTROL

Five States with operating PHWRs (Argentina, Canada, China, India, Romania) participated in the technical meeting (25-28 November 2019, Toronto, Canada). This Section provides a summary of national practice and related R&D activities on coolant chemistry control in the PHTS of PHWRs, based on presentations and discussions made at the technical meeting.

2.1. R&D ACTIVITIES

Various R&D programmes are underway. Some establishments presented materials of interest to the technical meeting in Toronto. This Section introduces an overview of these R&D programmes, whilst detailed information on the R&D programmes can be found in Sections 3 and 4.

The presentation entitled "Chemical Modelling Studies of Magnetite Solubility Effects during CANDU Reactor Startup and Hot Conditioning" was provided by Tremaine of University of Guelph, Canada (see Session II of Annex). The paper presented by Tremaine reports calculated values for the dependence of magnetite solubility on pH, dissolved hydrogen and temperature, and their applicability in reviewing strategies for controlling iron transport during normal operation and under conditions encountered during startup after lay-ups and hot conditioning. This data is important for current plant operators and those whose plants are undergoing refurbishment after which some form of heat transport hot conditioning would be performed.

Magnetite properties have been studied extensively by Tremaine: one early paper by Tremaine and Leblanc in 1980 [11] quoted magnetite solubility data at different concentrations from that quoted in the 1970 paper by Sweeton and Baes [12]. Whilst these differences did not present problems for plant operators, issues arose for researchers and those investigating plant performance observations, for example, explain activity transport phenomena at one plant circa 1989 [13].

The presentation entitled "Recent Research Developments in Primary Heat Transport System Chemistry" was delivered by Yakabuskie of Canadian Nuclear Laboratories (CNL), Canada (see Session II of Annex). CNL is continuing work over the past approximately 70 years researching and supporting PHWR primary chemistry control. Yakabuskie identified that there are limited options for chemistry control advances and changes including narrow band pH_a control, dissolved deuterium concentration range, purification system media (filters, resins), outage chemistry control, hot conditioning, oxidant control, decontamination, also that plant upsets often drive re-evaluations and advances.

Knowledge gaps were identified as being in radiation chemistry, pure water radiolysis and significant gaps in high temperature metal ion radiolysis. Overall system integration can help to advance understanding. Areas currently being studied at CNL include advanced critical hydrogen concentration tests and modelling, high temperature metal ion radiolysis and interpretation of plant data from online sources. This information is also important to plant operators, especially for those plants that are extending life.

The presentation entitled "Effect of Oxide Dissolution on Material Transport in Reactor Coolant Systems" was delivered by Lister of University of New Brunswick, Canada (see Session II of Annex). The paper presents how the corrosion of system materials forms the basis of material transport and how it varies around the primary circuit. It is important to know that a reliable model of system fouling, including deposition in-core, can be formulated by considering material transport and variations in corrosion. Such mechanistic model for CANDU reactors is under development at University of New Brunswick.

Whilst not a research facility, Ontario Power Generation (OPG) independently has supported research into fuel cladding deposits that can be formed during hot conditioning of the primary heat transport system. The presentation entitled "Insights on Fuel Sheath Deposit Formation during primary Heat Transport Hot Conditioning" was delivered by Scrannage of OPG, Canada (see Session IV of Annex). The experimental work was performed at Stern Laboratories in Hamilton, Ontario.

OPG's Darlington Unit 2 has recently been refurbished. Part of the startup evolution included hot conditioning of the heat transport system. Two other Canadian CANDU plants had also returned to service following refurbishment. One utility had reported black deposits on the fuel cladding following their conditioning process.

OPG had concerns pertaining to these deposits and their potential impacts on heat transfer, fuel cladding integrity and safety analysis margins. The research investigations have demonstrated that the planned PHTS hot conditioning evolution for Darlington Unit 2 did not represent a risk to fuel fitness for service, performance or safety analysis margins.

The presentation entitled “Investigations on Surface Oxide Films Formed on Primary Circuit Materials (PHWR) in presence of Externally Added Metal Ions” was delivered by Srinivasan of Bhabha Atomic Research Centre (BARC), India (see Session II of Annex). The BARC R&D group focused on the extra corrosion protection afforded to the major materials in the PHTS by growing their oxide films in the presence of cationic additives in the coolant.

Some research work had been performed on irradiated coupons removed from the heat transport autoclaves of the Cernavoda Unit 1 reactor to investigate the corrosion process. Examination of the Zircaloy-4, the alloy used for fuel cladding, coupons was described by Lucan of Romania’s Institute for Nuclear Research at Pitesti, Romania (see Session I of Annex). Morphology and composition of the deposits were described. No mention was made of any radionuclides found. The report concluded that the coupons were covered with iron compounds, primarily magnetite, but had not suffered any apparent attack. Of note is that within the Cernavoda Unit 1 autoclaves the sole heat source is that of the coolant.

2.2. OPERATION

2.2.1. Argentina

The Embalse nuclear power plant in Argentina has a CANDU 6 reactor that was supplied by Atomic Energy of Canada Limited and entered commercial operation in 1984. The plant was shut down at the end of 2015 for the modernization work, which included reactor retubing and replacement of the steam generators. It also included a 6% increase of the plant’s capacity to 683 MW(e). The plant has now returned to service for another 30 years of operation. For the modernization work, an integral overhaul of the entire plant was necessary with a service outage for a considerable time (approximately 36 months).

A paper was presented by Sampierto on the hot conditioning of the recently refurbished Embalse CANDU unit (see Session I of Annex). Canadian utilities have showed much interest on the OPEX related to the hot conditioning process, by OPG staff looking toward the hot conditioning of, initially, Darlington Unit 2, and by Bruce Power staff for unit restart following refurbishment of Unit 6.

2.2.2. Canada

The paper presented by Liao described recent OPEX at OPG’s Pickering and Darlington plants with respect to dissolved deuterium control, focusing on the heat transport chemistry specifications (see Session I of Annex). Additional focus was placed on the Darlington units for which in-situ deuterium generation was creating an operational issue regarding deployment of operating staff to vent the heat transport heavy water storage tank. As a result, an engineering evaluation was performed, coupled with an independent review, leading to changing the deuterium specification range to a maximum of 17cc/kg from 10 cc/kg. This specification change has been adopted.

OPEX from both Point Lepreau and Embalse stated that with the new higher chromium content feeder material (A106C as opposed to A106B) the deuterium generation rate is lower, consistent with a lower corrosion rate. This makes deuterium control and venting much more manageable and the original specification can be maintained. OPG is considering their path forward following restart after refurbishment (see the paper presented by Scrannage and co-authors, Session IV of Annex).

Point Lepreau station has returned to service following completion of refurbishment then hot conditioned, using a modified process.

2.2.3. China

The Qinshan Phase Ш NPP contains two CANDU 6 units with capacity of 2×728 MWI. The two units have been in commercial service since early the 2000’s. Since then, the PHTS components and equipment have been modified or optimized to reduce operating costs, increase component life, and minimize environmental releases and occupational exposure.

In Qinshan units there were three modifications made to purify the PHTS coolant: optimization of pH ranges for normal operation and outages, replacement of 5μm filter cartridges with 0.1 μm filter cartridges in the PHTS purification circuit and change of the exchange columns resin and volume. The paper presented by Lu and co-authors (see Session I of Annex) reports that no deposit has been found on the fuel bundles so far.

The paper presented by Lu and co-authors (see Session I of Annex) identified a novel problem not reportedly experienced by any other CANDU utility. The plants face some challenges with release of silica, believed to be from the new purification filter media fabricated of fibreglass. It was unknown if other utilities have the same issue or if even the same filter manufacturer was used. This important issue continues to be investigated.

There was no discussion of either PHTS activity transport or radiation fields. Activity transport can be detected by gamma analysis of water samples and often can be used to identify potential problems.

2.2.4. India

The paper presented by Rangarajan and co-authors (see Session II of Annex) mentioned that, of late, there were few chemistry issues in Indian PHWRs; the corrosion related issues have not increased, except for the pressure tube issues at one of its utilities. However, the Indian utilities have been trying to improve the water chemistry conditions and also modify the surface oxide films on the structural materials to further reduce the corrosion rates and minimize the activity transport problems. Similarly, the Indian utilities have been trying to minimize the corrosion release and the transport and deposition of corrosion products in the steam generator circuits by using film forming amines and by injecting dispersants like polyacrylic acid and its derivatives. The above developments would soon be tested under pilot plant scales. Further, efforts would be made to revise the technical specifications which satisfy both the regulators as well as the plant operators.

2.2.5. Romania

Two operating CANDU 6 units are located at the Cernavoda nuclear power plant (NPP) with the capacity of 2×706 MW(e). Unit 1 started commercial operation in 1996. A refurbishment outage at Unit 1 is expected from December 2026 and December 2028. Unit 2 started commercial operation in 2007. No deposits on fuel bundles have been observed.

Note that Romanian utility continues keeping autoclaves in service, while Canadian utilities have given up the use of autoclaves. Autoclaves provided excellent data for defect fuel investigation during which significant activity transport issues were experienced at a Canadian plant, whilst autoclaves were also a problem at some plants due to valves leaking into the reactor vault.

3. KNOWLEDGE RETENTION & MANAGEMENT

3.1. OVERVIEW

Since the inception of nuclear power, there has been much R&D performed to support coolant chemistry in operating nuclear power plants. Astonishingly, problems, occasionally including new issues, are still encountered. It is important, therefore, that utility staff are aware of the R&D programmes performed and operating experience (OPEX). Such awareness and knowledge can reduce the necessity of spending scarce funds available to utilities ‘to reinvent the wheel’. To this end, shared knowledge and OPEX is crucial to both avoidance of plant problems and minimization of operating costs.

During the technical meeting, sharing knowledge and OPEX was identified as an important issue at the session of national practice on coolant chemistry control. This section summarizes key results from the discussion.

3.2. PROBLEM DESCRIPTION ON SHARING KNOWLEDGE AND OPEX

The presentation by Roberts (see Session I of Annex) discussed the history behind CANDU heat transport chemistry and specifications, i.e. the development of CANDU reactor heat transport pH control from prior to the first CANDU plant (i.e. NPD) to today. Indeed, this history is unknown to many, especially the younger generation. Parts of this history are important in that they make up the basis for the heat transport chemistry specifications. In addition, if individuals are aware of the history, the costs for ‘reinventing the wheel’, which are huge, will be saved.

Knowledge transfer is an important facet of sharing OPEX, some of which can be achieved through training programmes. An equally important opinion is mentoring of staff by knowledgeable peers, supervisors and others. This interaction leads to improved understanding of issues which can be of great importance when considering not only the specifics of the corrosion mechanism but also how plant operating conditions impact on that mechanism.

3.3. PROBLEM RESOLUTION

A number of avenues exist for sharing OPEX including, but not limited to, personal contacts, attending conferences, reviewing available databases. Several databases exist internationally including those of the CANDU Owner’s Group (COG), Institute of Nuclear Power Operations INPO) and World Association of Nuclear Operators (WANO). The International Reporting System for Operating Experience (IRS) database, jointly operated by the IAEA and the Organisation for Economic Co-operation and Development/Nuclear Energy Agency (OECD-NEA), is another example to OPEX database.

Today, utilities have central filing systems that can be useful in capturing OPEX. The difficulty lies in having the OPEX filed and named in such a manner that the interested party can (two or more years) later successfully retrieve the OPEX. One of the strengths of mentoring is the ability of the mentor to introduce the mentee to historical OPEX. Actually, there are examples in which significant chemistry issues resulted in significant cost to the utility due to unavailability of historical OPEX.

An excellent knowledge management programme[2] will have allowed staff to benefit from transfer of knowledge from station staff and/or mentors. This activity takes time to perform effectively – it is most useful when an issue arises.

Knowledge transfer is best managed in small bites so that the recipient(s) have an opportunity to absorb the OPEX and later ask questions, for instance, during the following day(s). Such an approach will allow reinforcement of the knowledge transferred. This approach does consume time but is time well spent.

In summary, knowledge transfer is a process that needs to start soon after an individual staff joins, in this case, the chemistry department, then continue throughout the individual’s career.

The OPEX feedback process needs to contain all of the components that close the feedback loop: collection, review and quality control, analysis, conclusions, dissemination, follow-up and feedback.

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[2] This publication is discussing chemistry, but the knowledge management issue applies equally to all disciplines.

A knowledge management component needs to be built into the system with efficient search functions – for example, semantic searches – to ensure the maintenance of relevant information and its transfer to future generations.

4. TECHNICAL OPINION AND CORRESPONDING OBSERVATIONS ON CORROSION PHENOMENA

In this section, four papers on recent advances in chemistry and corrosion R&D related to PHWRs are summarized and their significance within the overall subject of fuel reliability is reviewed. These papers were presented in the corresponding section at the IAEA technical meeting on the Control and Monitoring of Coolant Chemistry and Related Issues on Fuel Reliability in Pressurized Heavy Water Reactors (at the CANDU Owners Group Offices, Toronto, Canada, 25–28 November 2019).

The first paper concerns the phenomena underlying the production and transport of corrosion products in the primary coolant and demonstrates how deposits around the circuit can be successfully modelled; the second shows how the corrosion of circuit materials may be mitigated by the addition of extraneous cations to the system to 'dope' the oxide films and make them more protective; the third points out the latest chemistry control parameters for CANDU reactors and describes radiolysis research aimed at defining more precisely the oxidizing-reducing condition of the coolant during reactor operation; and, the fourth details recent measurements of the solubility of corrosion products under coolant operating conditions – seen as the driving force for material transport.

4.1. MECHANISMS AND MODELLING OF CORROSION AND OXIDE FORMATION IN PHWRS

Section 4.1 shows how the corrosion of system materials is the basis of material transport and how it varies around the primary circuit; it is based on the paper presented by Lister and co-authors (see Session II of Annex). Only by considering these variations in corrosion can a reliable model of system fouling, including deposition in-core, be formulated. The latest such mechanistic model for CANDU reactors is described in the paper presented by Lister and co-authors (see Session II of Annex) and this section shows how it developed from early phenomenological attempts in the industry internationally and notes areas for improvement.

4.1.1. Basic corrosion mechanisms

The main aim of coolant chemistry control is to protect the pressure boundary from excessive corrosion; minimizing material transport has been a secondary consideration. Nevertheless, mechanistic modelling of corrosion-product transport recognizes the corrosion process itself as the main driver. This applies to activity transport, whereby radiation fields grow around out-core components, as well as to crud formation and system fouling. For ^{60}Co contamination of a steel surface, for example, the incorporation of the cobalt ions into the growing oxide film could be described in terms of their concentration in the coolant, their diffusion through the liquid boundary layer and their incorporation into the oxide crystal lattice [14]. The oxide is a double layer of fine-grained particles overlaid with precipitated octahedral crystallites about 1 μm in size and reflects the type of oxide that forms on primary heat transport system (PHTS) inlet feeders. The extensive surface area of carbon steel feeders in the PHTS of PHWRs makes iron the major metallic dissolved species in the primary coolant and magnetite the dominant corrosion product in the system.

The relatively high solubility of magnetite under the constant chemistry conditions of the coolant at operating temperature, coupled with the increasing solubility as the coolant is heated in traversing the core, lead to the carbon steel outlet feeders' being immersed in coolant that is undersaturated in dissolved iron; the outer-layer magnetite cannot form and in the high-velocity coolant the steel corrodes more rapidly (by flow accelerated corrosion, FAC) than was allowed for at the reactor design stage. The resulting corrosion products are transported around the circuit and cause fouling problems, particularly in the steam generators, and lead to issues such as inlet header temperature rise [15].

Modelling corrosion product transport and the subsequent activity transport and system fouling in PHWRs therefore involves modelling feeder FAC (see the paper presented by Lister and co-authors (see Session II of Annex). This has been done quite successfully in terms of the processes acting on the oxide film. These involve the dissolution of the metal at the metal-oxide interface (M-O), the precipitation there of about half the resulting iron ions as magnetite, the diffusion of the other half through the oxide to the oxide-solution interface (S-O) and their transport across the fluid boundary layer to the bulk coolant. Even as the magnetite is precipitated at the M-O it is dissolved at the S-O until eventually a steady-state occurs when the oxide film achieves a constant thickness and the FAC rate becomes constant. The fundamental processes of metal dissolution (corrosion), oxide precipitation, oxide dissolution and hydrogen production involve electron transfer and depend upon the local electrochemical potential, which needs to also be modelled for a realistic outcome.

The kinetics of magnetite dissolution and the underlying mechanism in the overall process, have been determined under appropriate coolant conditions [16]. When incorporated in the model, they indicate that the processes of oxide particle spalling, or erosion needs to be included to achieve realistic results [17].

The original mechanistic model [18] accurately described the corrosion of outlet feeders at the Point Lepreau NPP, predicting the local variations of FAC rate around bends and along the length of selected feeders as well as the overall trend of feeder thinning with time (see the paper presented by Lister and co-authors, Session II of Annex). Along with the corrosion rates, the oxide thicknesses and particle releases by spalling/erosion were predicted realistically. The model was extended to the inlet feeders, which are exposed to coolant saturated in dissolved iron after leaving the steam generators and gave realistic predictions of corrosion rate and oxide growth.

The corrosion of the carbon steel headers and piping between the feeders and the steam generators may be modelled in similar fashion to the inlet or outlet feeders, depending on the iron concentration in the coolant at the location to be modelled. It is important to note that the bulk concentration is not in equilibrium with the surface; thus, the undersaturation effect in the outlet feeders may extend into the outlet header and even into the hot leg of the steam generator. Likewise, the saturation from cooling and decreasing solubility leading to precipitation in the steam generator cold leg may extend into the inlet header. These effects are revealed by the convergence of the system transport model as described in the next section (4.1.2 below).

The corrosion of the remainder of the circuit evolves differently from that of the carbon steel components. The zirconium alloys in the core produce very insoluble oxides, and the corrosion contributes little to the transported corrosion products. Depending on the coolant chemistry, however, in-core surfaces develop electric charges that affect the deposition of corrosion-product particles transported from elsewhere in the circuit. It is also possible that excessive wear or localized corrosion of in-core components, by contact of fuel appendages with Zr-2½%Nb pressure tubes, for example, can release zirconium or niobium species to the coolant. The CANDU 6 steam generator tubes are an austenitic alloy, typically Alloy 800, which develops a protective and virtually insoluble oxide based on iron chromite ($FeCr_2O_4$) at the M-O and an overlying film of precipitated crystallites based on nickel ferrite ($NiFe_2O_4$) at the O-S. The general corrosion rate is very low, so the oxide accumulating in the steam generators is dominated by the transported/precipitated magnetite. The dissolution behaviour of the constituents of the alloy account for traces of elements other than iron such as nickel and chromium appearing in the corrosion-product inventory. Their transmutation in the core give rise to troublesome radionuclides such as ^{58}Co and ^{51}Cr, which contribute to activity transport and radiation field build-up around components. They are supplemented by ^{60}Co from impurity levels of cobalt in the carbon steel and other alloys in the circuit and from the wear of cobalt-bearing alloys such as Stellite, which are employed as hard-facing materials; however, the main driver of material transport in the PHWR primary circuit remains the carbon steel corrosion and its product magnetite.

4.1.2. Corrosion product transport

Modelling of material transport in water-cooled reactors began with a phenomenological approach. For the primary coolant of a PWR for example [19], the circuit was divided into nodes such as the fuel assemblies and the steam generators and the coolant acted as the transport vehicle between them. Thus, the deposition of a species on a surface could be written as an exchange process:

$$\frac{dCw}{dt} = k_d C_b - k_r C_w \qquad (1)$$

where C_w is its concentration on the wall, C_b its concentration in the bulk coolant, and k_d and k_r are the deposition and release constants, respectively. The description of a complete system then became a set of equations to be solved simultaneously, with measurements of deposit thickness and coolant concentration, for example, provided as inputs and the coefficients adjusted to achieve convergence. Before the widespread availability of digital computers, the solutions to complex systems could entail ingenious mathematical manipulation [20].

As more reactors came on-line, radiation fields around components were seen to increase with time after start-up and fuel surfaces became fouled with corrosion products. Early innovations in modelling involved the introduction of physical and chemical mechanisms to replace phenomenological descriptions, and it became clear that corrosion and the development of corrosion-product films on circuit materials were key processes [14]. System models based on differences in solubility of oxides around the circuit and dependent corrosion rates produced reasonable values of average corrosion-product loading [21] while more detailed modelling resulted in complex codes; for PWRs, for example, the French PACTOLE and PROFIP merged into the extant OSCAR code [22] and Westinghouse with support from the Electric Power Research Institute developed BOA [23] to account for crud-induced power shifts (CIPS – formerly known as AOA or axial-offset anomaly).

Progress has been made recently in modelling transport in CANDUs by incorporating the basic corrosion mechanisms described above [16]. Briefly, iron as dissolved species and as corrosion-product particles constitutes the bulk of the transported material. Solubility differences and dissolution and precipitation kinetics drive the movement of dissolved species [11] and spalling/erosion produces particles that interact with surfaces as described with existing empirical relations [24]. Other elements such as nickel are treated similarly, depending upon their species and concentration and their solubility, and important radionuclides like ^{60}Co are carried along with them.

The distribution of dissolved iron as the major transported material in the coolant around the primary circuit of the Point Lepreau NPP at the end of the first operating year following refurbishment has been predicted [25]. In the inlet feeders, in-situ corrosion precipitates the relatively thick magnetite layer, in the core there is precipitation at the inlet and dissolution of deposited particles at the outlet, in the outlet feeders the oxide dissolves rapidly via the FAC process and in the steam generators precipitation occurs only after some distance into the hot leg. It is interesting to note that the bulk iron concentration is predicted to vary between 1.6 and 3.1 μg/kg around the circuit, driven by the feeder corrosion and production of magnetite. In PWRs, with surfaces of austenitic alloy that corrode much more slowly and produce different oxides, the bulk concentrations of corrosion product are predicted to be almost constant around the circuit [21].

Material transport as particulate oxide depends upon the concentration in the coolant (the so-called crud level) and the deposition on surfaces as modelled with empirical relations determined elsewhere (see the paper presented by Lister and co-authors, Session II of Annex). After one operating year there is predicted to be a thin layer of particulate oxide amounting to about 0.1 g/m^2 (equivalent to 0.02 μm thick for maximum oxide density) on out-core surfaces but roughly doubling in-core because of the heat transfer and possibly the surface-charge effects. Notably, in-core boiling is predicted to have a large effect on the deposition towards the fuel channel outlet because of the enhanced deposition mechanism induced by steam-bubble nucleation [25]. These predictions, in conjunction with those for the distribution of radionuclides around the primary coolant system for periods up to thirty years, are in reasonable agreement with observations from operating plants [26]. However, the coolant crud level leading to realistic deposit values around the circuit is optimized at 40 μg/kg, a value considered excessive since the rather sparse plant measurements suggest values more like 1 μg/kg or less for particles greater than 0.45 μm, while the original modelling of feeder FAC indicated 0.05 μg/kg for such particles [18].

4.1.3. Summary

The corrosion product magnetite from the large surface area of the carbon steel feeders and headers in CANDUs and similar PHWRs dominates the inventory in the primary coolant circuit. The distribution of crud both in-core and out-core can be predicted quite well on the basis of mechanistic models for corrosion, especially flow-accelerated corrosion of the outlet feeders, and dissolution/precipitation of iron species coupled with empirical models for particle transport. The kinetics of the dissolution/precipitation processes as well as the thermodynamics are important. Fouling of the steam generator tubes is shown to begin at some distance into the hot leg and to continue along the cold leg, while deposition on fuel towards the fuel channel outlet is enhanced by boiling. The magnetite acts as the vehicle for the transport of radionuclides, allowing activity transport and radiation field build-up to be estimated.

The major uncertainty is the treatment of particle transport. The empiricism in the modelling involves unrealistically high concentrations of particulates in the coolant (40 μg/kg), whereas the few measurements of reactor coolant concentrations that are available from operating systems indicate values of the order of 1 μg/kg [27, 28]. Moreover, the empirical expressions are mostly derived from experimental systems rather than operating reactors and are mostly formulated at low temperature. A recommendation would therefore be to refine the particle transport model, especially with regard to particles smaller than 0.45 μm, and to incorporate surface phenomena associated with colloids [15] – recognizing that little colloid chemistry has been studied at reactor temperatures.

4.2. MODIFICATION OF OXIDE FILMS ON SYSTEM MATERIALS BY CATION DOPING

Section 4.2 is a discussion of the paper presented by Rangarajan and co-authors (see Session II of Annex) that describes laboratory studies of the extra corrosion protection afforded to the major materials in the PHTS by growing their oxide films in the presence of cationic additives in the coolant. Magnesium is seen as a likely alternative to zinc, the additive now used widely in LWRs but which, unless depleted in the isotope ^{64}Zn, produces an undesirable radionuclide as it passes through the reactor core. This Section provides background information and comments on the mechanism by which an additive is incorporated in the oxide film on metals. Measures that need to be taken before an additive may be applied in an operating reactor are noted.

4.2.1. Cation doping to influence corrosion

The incorporation of extraneous cations into developing oxide films on corroding materials in reactor coolant systems has been suggested for some time as a means of controlling corrosion and, subsequently, corrosion-product transport. After all, the low corrosion rate of austenitic alloys and stainless steels is known to be due to the protective nature of the chromium-rich oxide film that develops rapidly next to the metal, while the extra corrosion protection afforded by the added elements in low-alloy steel is similarly ascribed to the modification of the oxide film. If metal constituents can produce protective oxides, cannot extraneous cations added to the coolant have the same effect?

In the 1980s, the presence of zinc in the feedwater of boiling water reactors (BWRs) with brass condensers was shown to reduce activity transport below levels found in BWRs with stainless steel condensers, essentially by incorporating in the oxides on stainless steel to make them more protective [29]. An oxide layer based on zinc chromite, $ZnCr_2O_4$, next to the metal is more protective than the indigenous iron chromite, $FeCr_2O_4$. The extra stability imparted to the oxide by the zinc can be explained in terms of the lattice energies of the ions in the spinel crystal structure [30]. The overall effect of zinc on the system is even more pronounced on the large surface areas of austenitic alloys in pressurized water reactors (PWRs) [31], where the coolant is constantly reducing and leads to all oxides being of the spinel type rather than mixtures with ferric oxides of the corundum type as found in the more oxidizing coolant systems of BWRs. Zinc is now employed extensively in LWRs, although to reduce the radiation problems from the ^{65}Zn radioisotope 'depleted zinc' with reduced levels of ^{64}Zn is often employed. Other metal additives that have been suggested for reducing activity transport in LWRs have included magnesium [32] and manganese [33].

For the PHTS of CANDUs, one of the early ideas to mitigate feeder FAC after the discovery of excessive wall thinning at the Point Lepreau NPP was to add chromium ions to the coolant during shutdowns, since it was well known that the chromium content of the carbon steel has a strong influence on FAC rate; indeed, specifying a minimum chromium content of the steel in CANDU feeder materials has improved the corrosion resistance by 50% or more. However, adding soluble Cr^{6+} to the coolant to 'soak' the magnetite films for limited periods only during shutdown had a limited effect and was not seen as a viable option. Another additive that had shown promise in the laboratory is the titanium ion, Ti^{4+}. In spite of its low solubility, its release from titanium components and its modification of oxide films on carbon steel, reducing the corrosion rate, had been demonstrated in a high-temperature water loop [34] (it is notable that at the lower temperatures of feedwater systems, the even lower solubility of titanium reduced its transport and it proved ineffective for mitigating FAC [35]). A trial in which a soluble titanium compound was injected into a primary coolant feeder at the Darlington NPP during operation, however, created unacceptable deposits on the fuel, so the technique was abandoned [36].

4.2.2. Cation doping and oxide type

The predominance of carbon steel as a material of construction in CANDUs produces magnetite as the major oxide in the primary coolant, forming the circulating crud and the protective film on the steel, although the indigenous films on the austenitic-alloy steam generator tubes and the zirconium alloy in-core surfaces are similar to those in the PWRs. It will be recalled that the PWRs have mainly austenitic alloys that produce nickel-ferrite-type circulating crud and rely on compact chromite-type oxides for corrosion protection – as noted in Section 4.1 above. The mechanisms of cation incorporation into the protective oxide films on alloys and on carbon steel are therefore different. Thus, the protective chromites on the stainless steel and nickel alloys of the LWRs are normal spinel oxides of the type $A.B_2.O_4$, in which all the divalent ions A such as Fe^{2+} reside in sites in the crystal lattice that have tetrahedral symmetry and all the trivalent Cr^{3+} ions B reside in octahedral sites. Doping with zinc replaces Fe^{2+} with the cation Zn^{2+}, which has a higher preference energy for tetrahedral sites and stabilises the crystal lattice [30]. On the other hand, magnetite, which is the protective oxide on carbon steel, is an inverse spinel also of the type $A.B_2.O_4$ but in which the divalent ions A, here Fe^{2+}, are in octahedral sites while half of the trivalent ions, Fe^{3+}, are in the tetrahedral sites and the other half are in octahedral sites. Replacing Fe^{2+} with Zn^{2+} in the octahedral sites in magnetite is much less favourable energetically, so zinc as an additive for corrosion reduction is expected to be much less effective in PHWRs than in LWRs.

4.2.3. Additive effectiveness under PHWR conditions

It is useful to bear in mind that the incorporation of divalent transition-metal cations into oxide growing on steel under primary coolant conditions had been evaluated as early as the 1970s, when ^{60}Co contamination of steels was modelled in terms of the corrosion rate of the metal (see Section 4.1 above). In that case, the Co^{2+} was in trace quantities in the coolant and was assumed to have little influence on the oxide properties. To improve the protection afforded by the oxides on PHWR system surfaces, possible additives need to be evaluated at higher concentrations. Thus, the paper presented by Rangarajan and co-authors (see Session II of Annex) summarised here describes how the cations Zn^{2+}, Mg^{2+} and Ni^{2+} in the mg/kg (ppm) range were evaluated for improving the corrosion resistance of materials under Indian PHWR primary coolant conditions. The effects of all three on carbon steel and just Mg^{2+} on Zircaloy-2 and Alloy-800 were studied (see the paper presented by Rangarajan and co-authors, Session II of Annex). The experiments involved exposing samples of carbon steel in a static autoclave to simulated primary coolant at 250°C and $pH_{25°C}$ 10.3 (controlled with LiOH) for periods of 96 and 240 h in the presence of 1 ppm of the sulphate salt of each cation as the additive. By contrast, samples of Zircaloy-2 and Alloy-800 were exposed in a dynamic autoclave at 294°C and $pH_{25°C}$ 10.3 for 7, 21 and 42 days with and without 1 ppm of $MgSO_4$ as the additive. After exposure, all specimens were tested electrochemically, and the oxide films developed on all surfaces were examined with grazing-incidence x-ray diffraction. Oxides grown on the carbon steel were evaluated with gravimetric analysis and those on the Zircaloy-2 and Alloy-800 were characterized with laser-Raman spectrometry.

The oxide films on the carbon steel attained different thicknesses, depending on the dopant. Zinc doping produced the thinnest films followed by magnesium, both producing films that tended towards a constant thickness with time in similar fashion to the growth of the undoped magnetite; by contrast, nickel conferred no improved protection over the undoped magnetite.

The x-ray diffraction indicated that all oxides on the carbon steel were of the cubic spinel type like magnetite and furnished the sizes of particles or crystallites making up the films. Magnesium and zinc had the greatest effect, producing the smallest particles of size ~7–14 nm, especially after the longer exposure. Nickel produced particles of similar size to those in the non-doped oxide throughout the exposure, i.e., ~16-20 nm. As described in Section 4.1 above, the behaviour of the particles constituting the magnetite films on outlet feeders is important for the flow-accelerated corrosion; interestingly, they are of the order of 10-20 nm – similar to the sizes measured here [17].

Although performed at room temperature and in a deaerated aqueous solution of LiOH (1.5 ppm Li & pH_{RT}: 10.3), the electrochemical studies of the exposed carbon steel specimens and a baseline, unexposed, polished specimen generally indicated that the additives led to more protective films. The effects of zinc and magnesium were similar and somewhat more beneficial than those of nickel, which conferred little improvement over the exposures with no dopant. The electrochemical experiments therefore support the idea that the doped films are more compact and protective than the undoped magnetite and, if generated in an operating PHWR, might reduce the general corrosion rate of carbon steel components (see the paper presented by Rangarajan and co-authors, Session II of Annex).

Since magnesium looks promising as an additive to mitigate the corrosion of carbon steel, its effects on the Zircaloy and Alloy-800 components of the PHWR primary circuit were evaluated. According to the Raman analyses of the exposed Zircaloy-2, the 1 ppm magnesium additive in the autoclave coolant did not change the structure of the oxide film from the monoclinic phase of ZrO_2; however, the room-temperature electrochemical studies indicated that the additive made the film more protective, decreasing the passivating current density which became a minimum for the 21-day exposure. This was verified by the electrochemical impedance measurements. Calculations of concentrations of n- and p-type defects in the oxide, which control the metal corrosion, from Mott-

Schottky analyses of the measured electrochemical capacitances also indicated significant reductions due to exposure to magnesium, again with a minimum registered for the 21-day exposure.

Diffraction studies of the exposed Alloy-800 specimens indicated the development of nickel ferrite films that were modified progressively by the replacement of Ni^{2+} cations with the larger radius Mg^{2+} ions (see the paper presented by Rangarajan and co-authors, Session II of Annex). The most intense Raman-shift peak, ascribed to the spinel oxide, also shifted significantly as magnesium was incorporated. The electrochemical polarization studies of the doped specimens showed little consistent effect of magnesium incorporation, although impedances were generally greater for the specimens with doped oxide. Only n-type vacancies were indicated by the capacitance analysis of the passive film; their density was decreased by the magnesium incorporation with the maximum effect's occurring at 21 days.

4.2.4. Summary

As reported in the paper presented by Rangarajan and co-authors (see Session II of Annex), the incorporation of the divalent cations of zinc, magnesium and nickel into the magnetite that normally forms on carbon steel under static PHWR primary conditions was studied in static autoclave experiments. Improvements in the corrosion resistance of the steel were inferred from the post-exposure properties of the oxides measured at low temperature. Zinc and magnesium demonstrated the most consistent effects, and since magnesium produces fewer troublesome radionuclides than zinc during exposure in-core it would be the more promising additive for deployment in a reactor. Also as reported in the paper presented by Rangarajan and co-authors (see Session II of Annex), post-exposure tests on two other important circuit materials, Zircaloy-2 and Alloy 800, indicated that magnesium generally improved the corrosion-resistant properties of their oxide films. It was interesting that the maximum effects on those alloys apparently occurred after 21 days' exposure and not the total exposure of 42 days.

Since the flow-accelerated corrosion of the carbon steel outlet feeders is critical for material transport and system fouling in the primary circuit of PHWRs, it would be enlightening to test the effectiveness of the additives – especially magnesium – under operating FAC conditions. The mechanism of FAC involves rapid turnover of the magnetite film, and this would affect the ability of the cation to access the metal-oxide interface, where the incorporation into the magnetite would occur. In this respect, the durability of a film conditioned by an addition of the dopant to the coolant for a limited time would be useful to know. Moreover, it would be particularly useful to evaluate the effects of additives on all pertinent materials with pre-formed oxide films to see if extra protection could be given to materials already aged in the system.

The effect of any significant concentration of a magnesium additive on the primary coolant chemistry would be a serious consideration before any reactor application were envisaged. The effects on fuel and ion-exchange resin performance will also need to be considered carefully.

Recommendations would therefore be to investigate the effectiveness of magnesium as an additive in mitigating flow-accelerated corrosion of carbon steel under primary coolant conditions, and to determine the minimum concentration of Mg^{2+} which could be applied with worthwhile effect. The effects of a plausible magnesium additive on overall system chemistry would then be evaluated.

4.3. DEVELOPMENTS IN PRIMARY HEAT TRANSPORT SYSTEM CHEMISTRY

Section 4.3 outlines the basis for chemistry control in the PHTS and indicates how it influences material transport. Chemistry is controlled principally for protecting the pressure boundary (Section 4.1 above), which involves setting the major parameters pH and reducing conditions. Recent research presented at the IAEA technical meeting preceding this document has explored limits to the parameters (see the paper presented by Yakabuskie and co-authors, Session II of Annex).

4.3.1. Chemistry control – general

The evolution of chemistry control in high-temperature water systems stemmed from the original experience with fossil-fuelled boilers, where it was well-established that corrosion of carbon-steel components was minimised by imposing alkaline conditions via the addition of a strong base such as sodium hydroxide to $pH_{25^\circ C}$ ~11 [37]. Early research into water reactor chemistry in high-temperature loop experiments established that high pH also minimises corrosion-product transport [20], and this was true in carbon steel as well as stainless steel systems. The dual-cycle reactors PWRs and PHWRs of the CANDU type add lithium as the strong base to the PHTS, although the changing boron content during a fuel cycle of the former complicates the addition sequence in order to achieve as near a constant high-temperature pH (pH_T) as possible; CANDUs with their on-power fuelling, and separate moderator circuit, need no boron in the primary coolant for reactivity control and maintain nominally constant lithium conditions. As indicated in Section 4.1, the transport of the dominant corrosion product magnetite is governed by its changing dissolution behaviour around the circuit, and since its solubility increases with temperature under operating conditions [11] a high pH_T is deemed necessary to minimise deposition in-core. This minimises activity transport and radiation field build-up as well as fuel fouling. Traditionally, a pH_a (see footnote [3]) of 10.6 – 10.8 had been specified for CANDU reactors, but since the flow-accelerated corrosion of the carbon-steel feeders is exacerbated by high pH under operating conditions [17] a lower value of 10.2 – 10.4 is now recommended (see the paper presented by Yakabuskie and co-authors, Session II of Annex).

The other major chemistry control parameter is the reducing condition of the coolant, achieved by the addition of hydrogen to the system (although hydrogen as H_2 gas is added to the heavy water, the proportion of H:D is very small and atomic exchange processes induced by irradiation in the core produce essentially dissolved D_2). Water normally forms aggressive species by radiolysis as it undergoes irradiation in the reactor core; oxidising species such as the transient hydrogen peroxide and the ultimate product oxygen are to be avoided in order to minimise the degradation of PHTS materials – especially cracking of the nickel alloy steam generator tubes. Maintaining dissolved hydrogen in excess over that formed radiolytically with the oxygen ensures that the radiolytic species are recombined back to water. Applying high concentrations of hydrogen, however, runs the risk of degrading the zirconium alloy pressure tubes in the core by forming hydrides within the matrix of the metal crystal structure. An optimum concentration is required.

A thorough understanding of water radiolysis is clearly of benefit to the nuclear industry, which has traditionally relied on empirical evidence to specify hydrogen additions to CANDUs to concentrations of 3-10 mL/kg or 3-15 mL/kg (quantified at laboratory conditions), depending on the reactor (see the paper presented by Yakabuskie and co-authors, Session II of Annex). Although radiolysis has been studied since before the wholesale advent of nuclear reactors, there are gaps in knowledge of the detailed chemical processes involved in the formation of the transient species, their reactions and the final products, especially under the harsh conditions of an operating power reactor.

4.3.2. Latest insight into PHTS radiolysis

The paper presented by Yakabuskie and co-authors (see Session II of Annex) summarised here describes in-pile loop experiments in the now defunct NRU reactor at the Canadian Nuclear Laboratories. The objective was to determine the critical hydrogen concentration (CHC), defined as the minimum concentration of hydrogen required to prevent the net radiolytic production of oxygen, which occurs along with the stoichiometric production of hydrogen, in the system as a whole (note that transient species may be present in the core or near the core outlet even at the CHC). The experiments were also intended to determine the effect of in-core boiling up to 3% quality on the measured CHC.

The loop operated under PHTS conditions and had two legs passing through the reactor core in series, each containing six CANDU fuel bundles. The coolant could be sampled before and after the fuel in the downstream leg and the core outlet was equipped with an electrode assembly for measuring on-line the ECP – the electrochemical corrosion potential – of carbon steel and the oxidizing potential of the coolant via a platinum electrode, both relative to a reference electrode. The sample system allowed bulk oxygen and hydrogen concentrations to be measured and the electrode system indicated any transient oxidizing species such as hydrogen peroxide that left the core before decomposing or being recombined. An experiment proceeded by first establishing the normal operating condition with zero oxygen concentration and the normal hydrogen concentration of 3 – 15 mL/kg and then slowly adding oxygen (as air) to the inlet, all the while sampling the inlet and outlet for dissolved oxygen and hydrogen and measuring the potentials at the outlet for oxidizing conditions. An experiment was performed with no in-core boiling and repeated with boiling.

During oxygen addition, the sampled hydrogen concentrations diminished at the inlet and outlet and the potentials stayed low until at the CHC the potentials increased sharply. As shown in the paper presented by Yakabuskie and co-authors (see Session II of Annex), the measured CHC is reported as being similar in both the

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[3] pH_a is the “apparent” $pH_{25°C}$ of a solution in heavy water measured with a pH meter calibrated in light water.

non-boiling and boiling case at 0.25 mL/kg and 0.2 mL/kg respectively; however, to rationalise the apparently contradictory statement that the CHC in boiling is higher than that in non-boiling, the latter value needs to be considered in the context of gas stripping to the vapour in accordance with the general understanding that boiling requires more added hydrogen to complete the recombination reactions, which occur in the liquid phase [38]. These measurements may be compared with the CHC determined in a previous experiment as 0.5 mL/kg [39]. It is a significant finding of these experiments that in both the non-boiling and boiling case the potentials began to increase slightly at hydrogen levels higher than the CHC (0.5 mL/kg and 0.4 mL/kg, respectively), indicating that oxidizing species were surviving and leaving the core even though there was no indication in the samples.

The paper goes on to point out that radiolytic species may react with metal ions in the core and affect the oxidation state and therefore the dissolution/precipitation behaviour of metals such as iron, nickel or chromium (see the paper presented by Yakabuskie and co-authors, Session II of Annex). Models for corrosion-product transport as described in Section 4.1 above could then be affected. Since only the reaction between the ferrous ion and the hydroxyl radical [40] has been studied over a range of temperatures — with poor agreement among the results of six studies, especially at high temperature — it would seem appropriate to investigate the radiolysis reactions of the important metals under PHTS conditions.

4.3.3. On-line monitoring

Recent reviews have discussed the advantages of on-line monitoring in the control of chemistry and corrosion in the coolant systems of fossil-fuelled [41] and nuclear [28] power plants. The latter paper mentions the HePro, a non-intrusive instrument that has proved useful in monitoring on-line the corrosion of carbon steel piping in chemically reducing environments [42]. It measures the nascent hydrogen (or deuterium) from the corrosion that effuses through the pipe wall, which at PHTS conditions is the stoichiometric amount from the steel-water reaction. It consists essentially of a silver cup, sealed to the outside of the pipe to be monitored, connected to a pressure sensor and a vacuum pump. The influx of gas is monitored via the increase in pressure, and at intervals the cup is evacuated to restart the monitoring sequence.

The sensitivity of an HePro on an outlet feeder at the Point Lepreau CANDU for some time after the plant was refurbished and hot-conditioned is described in the paper presented by Yakabuskie and co-authors (see Session II of Annex). As the PHTS conditions changed because of the replacement of ion-exchange resin, for example, the corrosion rate of the feeder jumped from ~20 µm/year to ~40 µm/year immediately then slowly decreased. When the pH_a was later increased gradually by extra lithium additions prior to a shutdown the corrosion rate began to increase again. The HePro had earlier proved useful in indicating the successful hot conditioning of the plant [43] and one has recently been employed during the hot conditioning of the Darlington Unit 2 CANDU after refurbishment.

4.3.4. Summary

Now that the NRU (National Research Universal) reactor in Canada has been shut down there is no possibility of further in-situ chemical tests involving full-size PHWR channels fuelled with CANDU bundles. The experiments reported here (see the paper presented by Yakabuskie and co-authors, Session II of Annex) are apparently the last such tests and have found that the defined CHC for the coolant system is not the concentration that will prevent all transient radiolytic species from being formed or leaving the reactor core; however, the specified lower limits for hydrogen addition to the PHTS in an operating plant, which are multiples of the CHC at least in the non-boiling case, are enough to guarantee suppression. The information will be useful in improving the modelling of high-temperature radiolysis and will help future studies of the effects of radiolysis on metal ions under PHTS conditions. The effect of in-core boiling, which occurs in operating CANDUs, on the CHC was not fully quantified in the paper. It would be useful to assess the partitioning of hydrogen gas to the vapour and its effect on the coolant sampling and in-core chemistry in order to arrive at even an approximate value for the system CHC in boiling.

An on-line, non-intrusive probe for monitoring the FAC of carbon steel piping has proved useful in showing how the corrosion of the outlet feeders responds to changes in PHTS chemistry.

4.4. MODELLING THE CHEMISTRY OF MAGNETITE DISSOLUTION

Section 4.4 discusses the latest information on the thermodynamic modelling for the equilibrium reactions of magnetite in water, as presented in the recent IAEA technical meeting (see the paper presented by Tremaine and co-authors, Session II of Annex). The solubilities calculated by the MULTEQ V8 code [44] reflect the earlier values of Tremaine and LeBlanc [11] that have been used extensively for modelling corrosion and corrosion product transport in high temperature coolants (see Section 4.1 above). The application of the data to PHTS chemistry during normal operation, transient conditions and lay-up is noted and the isotope effects in D_2O versus H_2O are discussed.

4.4.1. Role of solubility in modelling corrosion product transport

As explained in Section 4.1 above, the dominance of magnetite in the CANDU PHTS stems from the high corrosion rate of the carbon steel outlet feeders relative to that of the alloy components in the system. The formation of the protective film of magnetite on the steel can be visualised as the balance between its formation at the metal-oxide interface and its dissolution at the oxide-coolant interface [17]. It is the under-saturation in dissolved iron at the reactor outlet, arising from the increasing solubility with increasing temperature in the iron-free core, that promotes the film dissolution. By contrast, the inlet feeders are in coolant that is saturated in iron, having been cooled in the steam generators, and have more-protective magnetite films with a precipitated outer layer. The iron solubility is a controlling factor in the corrosion and provides the driving force for the transport; along with the dissolution and precipitation kinetics it forms the basic modelling equations.

The solubility equations themselves are for hydrolysis and redox equilibria involving magnetite, Fe_3O_4. Under reducing conditions at low pH (as equivalent to low pD in D_2O), the predominant dissolved species is the ferrous ion Fe^{2+} and at progressively higher pH the ion is hydrolysed to $FeOH^+$, $Fe(OH)_2$ and then at high pH the ferric ion Fe^{3+} as $Fe(OH)_4^-$ becomes stable. However, under PHTS operating conditions the species $Fe(OH)_2$ is often taken to be predominant for modelling purposes. The redox nature of the corrosion process itself, as iron is oxidised, creates differences in electrical potential within the oxide films and the corroding surface itself acquires a characteristic corrosion potential. Dissolution and precipitation of magnetite on corroding steel are therefore affected by the corrosion process itself. These factors are taken into account when modelling corrosion and transport, since dissolution kinetics [16] and solubilities are measured on bulk magnetite, not in-situ corrosion-product films.

The Tremaine and LeBlanc [11] measurements of magnetite solubility have been utilized extensively in transport studies, but the point is made that the measurements are very difficult to carry out, particularly at high temperature where the actual dissolved iron concentration is of the order of 1 µg/kg. The solubility data from several major studies have been compiled and reviewed for the EPRI (Electric Power Research Institute) database MULTEQ V8, which provides details of species and thermodynamic information for a range of chemical elements under PHTS conditions [44]. The most comprehensive solubilities for magnetite are presented (see the paper presented by Tremaine and co-authors, Session II of Annex), showing good agreement with the original Tremaine and LeBlanc data, for example, the minimum solubility at 300°C in [11] occurs at $pH_{25°C}$ ~9.8 and is 2.0×10^{-8} mol/kg, corresponding to 1.8 µg/kg for the species $Fe(OH)_2$; the MULTEQ model gives 2.0 µg/kg (see the paper presented by Tremaine and co-authors, Session II of Annex). Importantly, the latest data confirm the positive solubility gradient across the core during operation, which minimises in-core deposition, but also show tendencies to precipitate as the temperature is increased above 25°C during normal start-up and hot conditioning – depending on the lithium concentration.

It is noted that solubility measurements are traditionally made in light water and that accurate measurements of the isotope effect in heavy water would be very difficult (ss the paper presented by Tremaine and co-authors, Session II of Annex). Still, the ionization constants for heavy water and light water are available, with the latest measurements in this paper indicating that ΔpK_W (characterising the difference in ionization constant between D_2O and H_2O) is 0.958 ± 0.010 at 25 °C and 0.727 ± 0.120 at 250°C; in other words, there could be a significant effect on the hydrolysis/deuterolysis of iron species.

4.4.2. Summary

The most up-to-date information on the dissolution equilibria of magnetite is compiled in the EPRI database MULTEQ V8. The original data of Tremaine and LeBlanc [11], which have been used extensively for modelling corrosion and transport in coolant systems for forty years or so, are generally confirmed. It is pointed out that normal CANDU operation minimises precipitation on the fuel because of the positive solubility gradient with increasing coolant temperature through the core, but the opposite occurs during start-up or hot conditioning as temperature increases from 25 °C to 250 °C. The isotope effect, on iron solubilities, of deuterium in heavy water vis à vis hydrogen in light water would be difficult to measure, but measurements of the effect on the water ionization constant suggest that the iron hydrolysis values may be significantly altered.

5. IMPACT OF PHTS CORROSION ON THE FUEL FITNESS-FOR-SERVICE AND TECHNICAL BASIS FOR REMEDIAL ACTIONS TO ENSURE RELIABLE FUEL PERFORMANCE

5.1. OVERVIEW

Various type of deposits has been sporadically observed on fuel bundles discharged from operating PHWRs in Canada. In one specific case, oxygen ingress due to outage work combined with a pH change led to deposits on fuel bundles. In this specific case, the deposits (the crud levels) were typically limited in area (e.g. downstream of bearing and spacer pads) and thickness (e.g. on the order of <20 µm); and they are porous. Thermal conductivity of a typical crud's composition was measured and its effects on fuel temperature was modelled; hence the impact on fuel cooling was assessed under normal operating conditions.

Deposits are of concern as they may lead to the degradation of Zircaloy cladding due to localized corrosion or impacts on heat transfer. Therefore, the interaction with the coolant becomes significant as it may limit the design life of the nuclear fuels under demanding operating conditions (e.g. extended fuel residence time in the reactor core, increased temperature of the coolant, increased heat flux). Water-side corrosion of the cladding material is primarily related to the oxidation of the zirconium by the heavy-water coolant. Oxygen, dissolved or produced by radiolysis of water, can contribute to cladding corrosion, but not significantly under conditions when the primary-side dissolved hydrogen concentration remains within specification. Cladding oxidation that could lead to hydriding is limited, as an impermeable zirconium oxide (ZrO_2) is formed at the metal/oxide interface.

Any damage mechanism, if excessive, will render the fuel unable to fulfil its design requirements or fitness for service (FFS). The impact of corrosion/deposits on fuel, related to FSS, is discussed in this section by summarizing the contributions from participants including the:

- impact and modelling of magnetite layers;
- perspectives from the Canadian Nuclear Safety Commission (CNSC);
- results obtained from post-irradiation examination;
- corrective actions implementated at Canadian utilities;
- assessment of fuel reliability.

5.2. CORROSION MODELLING AND FUEL PERFORMANCE ASSESSMENT

The PHTS chemistry impacts fuel cladding in-reactor performance if not controlled. PHWR fuel bundles use Zircaloy-4 as the cladding material. This cladding had proven satisfactory performance against corrosion, with an impermeable tetragonal ZrO_2 that is stabilized by the compressive stress at the metal/oxide interface [45]. Coolant chemistries are hydrogenated to further suppress radiolytic oxygen species. This has been posted as a challenge to manage oxygen ingress during outages. Fuel damage mechanisms related to corrosion, as illustrated below, are controlled through combination of steps during manufacturing, operations and design:

- Deuteride/hydride damage: This is currently avoided by limiting the total amount of initial hydrogen within a fuel element and by controlling the pH of the coolant;
- Crud deposition: Raising the cladding surface temperature above saturation in a crevice could concentrate lithium hydroxide (LiOH) enough to lead to crevice corrosion at the clad. Chemistry control is an integral part of operations. Adequate chemistry control has minimized corrosion and reduce deposits on fuel;
- Bundle deformation: Contact between fuel elements and the pressure tube is avoided by strategically locating the spacer and bearing pads, and by controlling other dimensions and clearances.

The paper presented by Syrewicz (see Session III of Annex) described modelling on these corrosion phenomena and impact on fuel performance for Atucha 1 and 2 in Argentina. Atucha 1 and 2 are vertical channel-type PHWRs with a relatively low discharge burnup (7800 MW·d/tU and 11000 MW·d/tU, respectively). In normal operation, the oxide thickness of discharged fuels is very far below the limit set in the fuel design acceptance criteria. The water chemistry parameters are carefully controlled in order to assure the formation of a passivating oxide layer to minimize the corrosion velocity, the dose rate and the corrosion products release. Nonetheless, in abnormal situations some corrosion related issues may jeopardize the fuel integrity, such as high temperature oxidation in loss-of-coolant accident scenarios and pellet-cladding interaction/stress corrosion cracking in power ramps. Some analyses were performed to test the fuel reliability in the above-mentioned conditions with TRANSURANUS code. The paper provides a description of these phenomena, the methodology used for Atucha I and II final safety analysis report (FSAR) calculations.

The paper presented by Syrewicz (see Session III of Annex) concluded that there remained significant safety margins. The paper leads to a discussion on the impact of corrosion on the safety case, if oxidation needed to be included in typical safety analysis or if it could be ignored. The discussion then can be expanded into a follow-up discussion on the need for inclusion of corrosion in the safety assessments. The paper implied based on the analysis results that the impacts were seen as minor to insignificant and covered by the existing limited operating envelope (LOE) safety methodology. This preliminary result needs to be further investigated whether it is applicable to all PHWRs.

To date, cladding deposits on CANDU fuel in Canadian reactors have not resulted in any fuel cladding failure [46] under LOE. CNSC, however, raised a comment [58] that thermalhydraulic accident analysis codes do not account for thermal insulation due to deposits nor the impact of fuel subchannel restrictions for safety case analysis. With the formation of crud and in-reactor bundle deformation, the margin to avoid dryout at power during normal operation may be eroded. This led to a regulatory action to conservatively derate a CANDU unit by 3%, although the derate has since been removed (see the paper presented by Grant, Session IV of Annex).

5.3. REGULATORY PRACTICE AND PERSPECTIVES

Crud deposit on fuel bundles is one of the many key drivers to develop fuel safety criteria [59]. The application of defence-in-depth, throughout the design process and operation of the plant, is a cornerstone of the Canadian regulatory philosophy.

As stated by the CNSC (see the paper presented by Grant, Session IV of Annex), "Fuel performance and reliability need to be assured with a robust chemistry control and fuel inspection regime. This is to ensure, among other things, that chemical damage to the sheaths and deposits on the fuel are precluded and that the safety case is maintained."

The chemistry control for PHWRs follow stringent chemistry technical specifications. For example, the PHTS chemistry limits are partially illustrated in [47]. Indeed, the compliance verification activities performed by the regulator in the area of chemistry control at the PHWR units are effective in mitigating crud deposits. In this aspect, it is important to clarify regulator's role in the chemistry control program of the licensees and in the oversight of the fuel performance and fuel reliability.

The paper presented by Gingras and Holvey (see Session IV of Annex) provides a regulatory perspective on the verification of licensees' activities related to chemistry control. Chemistry monitoring parameters are classified as Control and Diagnostic. Control parameters are reported to the CNSC's Chemistry Compliance Index as performance indicators. Verification activities include analysing chemistry data provided by plant licensees, performing inspections and monitoring recent reportable events. The scope of these verification activities can be influenced by recent research in reactor chemistry. Despite these verification activities, chemistry-related incidents occasionally occur. A brief summary of a sample of events related to chemistry control is provided, along with the follow-up action taken by the Canadian regulator. Examples of the regulatory oversight of licensees' reactor chemistry-related licensee activities are also provided.

The paper presented by Grant (see Session IV of Annex) provides regulator's position on the oversight of the fuel performance and fuel reliability. As regards to the impact of chemistry on fuel reliability, the regulator seems to focus on:

- Cladding embrittlement (taking into account diminished tensile strain resistance);
- Crevice corrosion;
- Cladding insulation (resulting in higher cladding temperatures).

Fuel acceptance criteria for PHWRs have been established [48], which can be used to facilitate the prevention of cladding embrittlement. A comment was raised that some acceptance criteria are based upon tests using "as received" materials with an engineering safety factor applied, for example, the 5% cladding strain criterion for LOCAs came from burst tests with unirradiated cladding with no oxide.

The impacts of crud (the deposits) on fuel are related to a) thermal integrity, b) structural integrity and c) compatibility with surroundings. With the formation of crud and in-reactor fuel bundle deformation, the margin to avoid dryout at power under normal operating conditions may be eroded. The safety case for operating CANDUs assumes that all bundles are fit for service at the start of an accident with:

- Minor wear;
- Average burnup;
- No deposits;
- No damage or geometry changes;
- No residual strain.

The Canadian regulator considers that any deviation, e.g. due to crud formation, from these assumptions falls into Generic Action Item 94G02 that states “The condition of certain fuel bundles irradiated in CANDU reactors has been observed to differ from that predicted and accounted for in design, operation, and safety analysis documentation”. The regulator expects that “Licensees should establish a formal process to ensure that the condition of the fuel and fuel channels is identified and accounted for, to determine the extent of fuel degradation and, in general, to determine whether fuel remains within the analyzed condition. The process should include in situ surveillance inspections, laboratory examinations, and statements of the potential impact of the “as found” condition on safety. Analysis, research, design changes, and operational measures may be needed” (see the paper presented by Grant, Session IV of Annex).

For fuel reliability to account for deposits with the added uncertainties on fuel embrittlement, crevice corrosion and thermal conductance, CNSC has conservatively used cladding temperature of < 450°C and cladding strain of <0.5% as the derived acceptance criteria for FFS limits [49].

The Canadian regulator has instructed the licensees that (see the paper presented by Grant and the paper presented by Scrannage and co-authors, Session IV of Annex):

- Further hot conditioning of units with fuel in the core is not to be done;
- A more comprehensive safety case is required if fuel cooling is impacted.

Insights on fuel cladding deposit formation during PHTS hot conditioning are further discussed in Section 5.5. There are several potential concerns with the crud deposits, although it may not impact fuel performance during normal operating conditions. However, the formation of an extensive crud deposit may increase the potential of the following that could impact the existing safe analysis report and the Level I defence-in-depth:

- Decrease in critical heat flux resulting in a reduction in margin to dryout;
- Increase in impedance to heat transfer and flow, especially for aged reactors;
- Release of activated crud back to the coolant and increase radiation dose rate around the circuit.

5.4. POST-IRRADIATION EXAMINATION

Extensive studies have been done on the nature of deposits in PHWRs and the mechanism is well understood as discussed in Section 4. The crud deposits are considered to be acceptable during normal operation because of their nature (being permeable to water) and limited in extent with no discernible depth during in-bay visual inspection.

The porous iron oxide deposits observed are magnetite or hematite. The deposit acts as a thermal insulator, increasing the local temperature underneath the cladding. The porous nature of the deposits may allow water to still reach the cladding through channels. This phenomenon, known as wick boiling, is common in BWRs. This could be a concern if the pores get blocked, creating a trapped steam bubble against the cladding. Post irradiation examination (PIE), however, indicated that there was no discoloration or evidence of corrosion of the fuel cladding underneath these black deposits [47].

Post irradiation examination (PIE) of fuel elements from Bruce Power Units 1 and 4 confirmed that (see the paper presented by Gingras and co-author, Session IV of Annex):

- All elements appeared to be intact;
- Cladding was covered in a dark coating, with the exception of the endcap regions;
- UO_2 pellets and Zr-4 cladding, and hence the fuel performance, appeared unaffected by the deposits;
- Spacer pads and bearing pads wear was typical of normal operating conditions;
- No indications of incipient cracking in the endcap-to-endplate welds;
- Observed deposits appeared to be porous and were present in non-continuous patches;
- Deposit thickness on samples did not exceed 20 μm;
- ZrO_2 thickness underneath the deposits were typical of normally operated fuel;

- Deposits did not appear to result in preferentially oriented hydrides/deuterides or elevated hydriding/deuteriding;
- Activation analysis results suggested that the iron deposition could have resulted from hot conditioning,

All fuel claddings experience some level of oxidation (ZrO_2) during their operational life. At the normal operating temperatures for CANDU fuel, the oxidation rate is very slow and result in typical cladding oxide thicknesses of < 10µm. This is compliant with the design specification for maximum permitted fuel cladding oxidation. Crevice corrosion due to crud was not reported from PIE.

5.5. IMPLEMENTATION OF CORRECTIVE ACTIONS

PHWRs have maintained excellent control of coolant chemistry. Chemistry control of PHTS in CANDUs is achieved by maintaining optimal pH through addition of LiOH and controlling lithium within an optimal range by use of a lithiated mixed-bed ion-exchanged resin. In the event lithium is too high, a neutral mixed-bed resin is used to remove lithium. Dissolved oxygen is maintained with a low level of dissolved hydrogen to avoid hydrogen ingress to the pressure tube. Radionuclide inventory is controlled through continual purification. Potential for stress corrosion cracking is controlled by removal of chloride and fluoride ions through ion exchange (see the paper presented by Grant, Session IV of Annex).

An atypical incident did occur in the Pickering reactor during 2008 – 2012: coolant chemistry was affected for a short period, which led to significant deposits of crud on the fuel [47]. Licensee corrective actions have gradually reduced the magnitude of the deposits. The derating, which was ordered by the regulator, was subsequently removed [47]. Fuel performance at Pickering has remained acceptable since 2013, the deposit surface coverage has trended downwards. Ontario Power Generation (OPG) continues to submit quarterly reports on fuel inspections to the regulator.

Utility management has established a multi-functional working group consisting of chemistry, engineering, maintenance and fuel handling staff to prioritize and manage purification system equipment. The working group has implemented corrective actions to:

- Maintain the coolant chemistry specifications;
- Improve ion exchange column operation and the filtering system to remove particles of > 0.45µm;
- Institute tighter chemistry controls and mitigate oxygen ingress into the PHT during outages;
- Enhance coolant chemistry monitoring;
- Implement the Chemistry Control Program.

These corrective measures have resulted in decreasing the number and size of the fuel deposits [60]. The average discharge burnup (of <180 MW·h/kgU) and an average element linear power (of < 45 kW/m) are relatively low for CANDU natural uranium fuel design. These conditions further avoid unacceptable cladding oxidation and crud deposits, as observed in light water reactors.

The implementation of the chemistry control program (see the paper presented by Gingras and co-author, Session IV of Annex) also requires the utility to submit updates on the findings of the fuel inspections, heat transport purification system performance, PHTS chemistry and radiation fields. A decreasing trend in the average deposit coverage on the fuel bundles is evident since 2013 [47]. A summary of compliance activities related to chemistry control, the chemistry compliance index, as well as examples of how these activities are performed, during normal operations or accident conditions are provided in the paper presented by Gingras and co-author (see Session IV of Annex).

The paper presented by Scrannage and co-authors (see Session IV of Annex) describes the R&D activities undertaken by the licensee to ensure that the post-refurbishment hot conditioning of PHTS will not result in fuel deposits. CANDU OPEX provides evidence that performing post-refurbishment PHTS hot conditioning with fuel in core presents a risk that the fuel bundles may become coated with iron-based, primarily magnetite and hematite, deposits during the evolution. This OPEX also provide evidence that these deposits remain on the fuel cladding for a period of approximately three to six months into the subsequent operation of the plant before the deposit material is redistributed into the PHTS coolant and removed from the system through the PHTS purification system. Such deposits, while present on the cladding, are thought to contribute to fuel cladding corrosion and impact fuel element heat transfer properties.

OPG commissioned a series of laboratory testing to investigate the factors that contribute to the phenomena of fuel cladding deposit formation. These tests included comparative studies of hot conditioning evolutions, which emulated recent CANDU post-refurbishment OPEX in a laboratory setting. The hot conditioning evolution planned for return to service of Darlington Unit 2 will differ from strategies employed for both the Point Lepreau and Bruce Power Units 1 & 2 refurbishments (see the paper presented by Scrannage and co-authors, Session IV of Annex). Ontario Power Generation (OPG) out-reactor tests provide confidence that the 'conventional' hot conditioning evolution planned for Darlington Unit 2 poses minimal risk of causing deposition on fuel bundle surfaces [50].

Table 1 provides an overview of this testing program and key results. The OPG out-reactor testing programme has corroborated the expectations and professional judgement of industry experts [51]. Reference [51] has provided a pH versus cladding temperature control diagram which is a useful guide for return to service at Darlington to avoid deposition. The PHTS main pump will be the heat source to achieve hot conditioning temperatures for Darlington return-to-service.

TABLE 1. AN OVERVIEW OF TEST PROGRAMMES AND IMPORTANT RESULTS (REPRODUCED COURTESY OF R. SCRANNAGE, SESSION IV OF ANNEX)

	Trial Number				
Test parameter	Trial # 1	Trial # 2	Trial # 3		
	DNGS	Industry 1	Stages 1 & 2	Stage 3	Stage 4
Process	Conventional	Li EDTA	Conventional	Conventional	Conventional
Fuel Power (W/m)	No Power (0)	Low (500)	Low (500)	Low (500)	High (9000)
Chemistry Control	Poor	Poor	Poor	Good	Good
PHT Temperature	250	262	60	250	250
Observation (deposit thickness)	Low < 5 µm (measurement limit)	High ~8 – 10 µm	High ~10 µm	No deposit	No deposit

Measurements of fuel cladding inside temperatures as functions of deposit thickness and at element heat generation rates of 55 kW/m are provided in Fig. 1. This data demonstrates a small degradation in fuel to coolant heat transfer below a deposit thickness of ~30 µm. Even with thicker deposits and some degradation of heat transfer, cladding temperatures will not increase by 12ºC (an approximate threshold identified in the operational and safety assessments), until a deposit thickness of 66 µm is achieved. This experimentally derived limiting thickness is greater than the limiting thickness defined by analysis (40 µm).

These investigations provided clarity on the parameters relevant to this adverse condition and on controls that can be implemented to minimize deposition on fuel bundle cladding surfaces. OPEX observations suggested that the surface condition of fuel cladding may also be a contributing factor related to the probability of deposition. This indicates that fuel cladding that has been polished following tube production may be less susceptible to deposition of magnetite on cladding surfaces during hot conditioning.

There are many factors that determine cladding strain and temperature. A primary driver is the element linear power rating. One needs to note that to avoid excessive amount of oxidation and fission gas accumulated in the fuel gap, the average linear element rating for CANDU reactors is operated at < 45 kW/m. Furthermore, the crud deposit thickness from previous industry hot conditioning deposit examples, as examined by PIE (Section 5.4) did not exceed 20 µm.

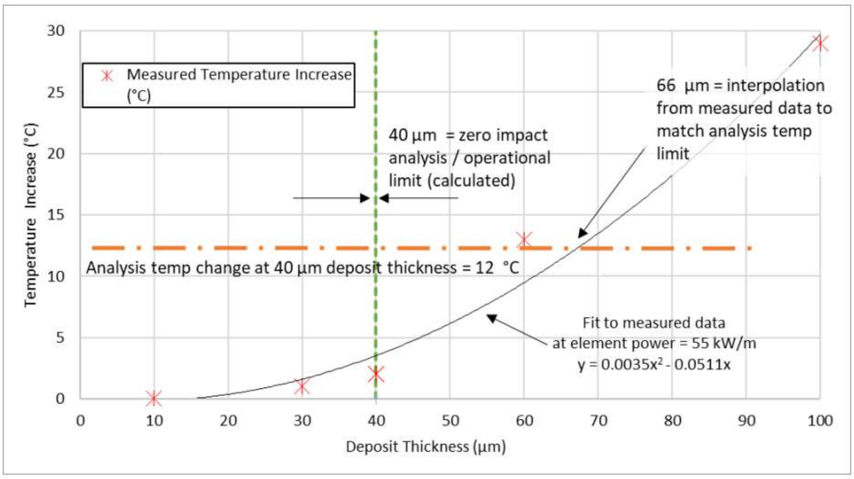

FIG. 1 Comparison of test and analysis data performed by OPG, reproduced courtesy of Ontario Power Generation (the paper presented by Scrannage and co-authors, Session IV of Annex).

5.6. FUEL RELIABILITY ASSESSMENT IN CANDU

As discussed earlier, any deposit that might occur in PHWR fuel are expected to be thin and heat transfer will not be compromised. It is not expected that margins to the neutron overpower protection trip set-point will be degraded due to deposition on fuel bundles. This ‘qualitative’ conclusion needs to be supported, as appropriate, by ‘quantification’ of margins via safety case analyses using computer codes to ensure that a sufficient operation margin exists in ageing PHWRs in operation. Several initiatives have already been made by academia [52 – 55] and industry. Preliminary results indicated that the CANDU fuel bundle design is robust and the probability of blocking the sub-channel areas due to crud deposits is not likely.

It was not discussed during the technical meeting in Toronto; however, further studies are recommended to:

- Determine the effects of pressure tube creep on bundle deformation under anticipated operational occurrence (AOO) and design basis accident (DBA) conditions. It is recommended that a 3D finite element model of a complete CANDU 37-element fuel bundle with contacts be developed;
- Provide the reassurance that crud deposits, if any, would have little additional risk on fuel failure by demonstrating the existence of significant margins to limits for all performance parameters. It is recommended that a “best-estimate plus uncertainty” approach be adopted where a probabilistic treatment of manufacturing and operating inputs is used to predict fuel performance. Probability distributions of manufacturing input variables need to be from real data provided by a Canadian fuel manufacturer. The inputs for fuel burnup and power need to be simulated and compared against fuelling data received from an operating station.

5.7. SUMMARY

Fuel deposits have only been only sporadically observed on the CANDU fuel bundles. Extensive studies to characterize the nature and the mechanism of forming these deposits have been performed, as reported in Section 4.

There has been no evidence of local cladding temperature increases due to the crud deposits under normal operating conditions. The UO_2 fuel pellets also exhibited characteristics that are well within acceptable temperature variations, as inferred from grain growth and cladding oxide thickness as reported by PIE.

The compliance verification activities performed by CNSC in the area of chemistry control at the CANDU stations have been shown to be effective in mitigating crud deposits.

The impact of deposits on a deformed (aged) bundle at various pressure tube diametrical creeps, in particular under accident conditions, needs to be further studied.

6. CONCLUSIONS AND RECOMMENDATIONS

Historically, it had been recognized that, for PHWRs using natural uranium fuel, corrosion deposits (crud) on fuel cladding surfaces were relatively harmless for the fuel integrity as compared to LWRs, although this may be dependent on their physical form, location and the influence they can have on the heat transfer. Since 2008, however, Canadian utilities have reported their observations of black deposits on the fuel cladding, which increases the interest of PHWR operators on the significance of corrosion deposits and their impact on the operational safety of ageing PHWRs. This publication is intended to provide a review of the up-to-date knowledge on coolant chemistry control to confirm and warrant no impact on fuel fitness for services due to ageing and various operating states, based on the results of the technical meeting in Toronto, 25–28 November 2019. Conclusions and recommendations made through such review are summarized below:

a) The PHWR utilities have modified, as appropriate, the technical specifications to ensure the fitness for services of PHTS components and fuel after various operating conditions including hot conditioning, refurbishment, outage, operation in hot channels (due to ageing and sub-cooling at the outlet ends), normal design-life-extension, etc. As a result of such remedial actions, overall there seem to be no significant issues raised related to the coolant chemistry in operating PHWRs.
b) The modification of the technical specifications has been largely supported by operational experience (OPEX), understanding corrosion phenomena and R&D activities.
c) As regards OPEX,

   - Additional OPEX is available from historical data of other NPPs, to support hot conditioning after plant refurbishment. It is recommended that the PHWR community amass the collective OPEX of hot conditioning;
   - It is also recommended that the knowledge management system within an organization be well established including staff training on available OPEX;
   - There is a concern on the apparent lack of awareness of activity transport. This is troublesome as heat transport system radiation fields can present serious operational challenges to unit maintenance. In addition, often the first indication of trouble is a change in heat transport water sample gamma signature. Whilst this data does not indicate specifics of the problem it allows the questions of what component might be damaged or what foreign material might have entered the system.

d) As regards the understanding of corrosion phenomena,

   - Flow-accelerated corrosion (FAC) of the outlet feeders is the main driver of corrosion-product transport and can be modelled mechanistically from the basic electrochemistry of aqueous corrosion coupled with the dynamics of fluid flow. The transport models incorporate the corrosion mechanisms, but the concomitant particle transport modelling remains essentially empirical and lacks certain features, notably the behaviour of colloids;
   - Feeder FAC is minimized by material selection (e.g., choosing a steel containing mitigating elements such chromium) and by chemistry control. The former is limited to component replacement, but the effect of the mitigating elements that work by improving the protectiveness of the magnetite film on the steel could perhaps be simulated by additions to the coolant. Magnesium has shown promise at the µg/kg level in laboratory experiments in improving the properties of the oxides on system alloys as well as on carbon steel, but more studies would be needed for it be accepted as an additive in an operating plant;
   - Imposing alkaline conditions in the coolant with lithium has long been understood as the primary method of controlling corrosion product transport in high-temperature coolant. To reduce feeder FAC, however, the recommended pHa of the PHTS in CANDU plants has recently been reduced from a range of 10.4 – 10.8 to 10.2 – 10.4. The effects on feeder FAC of changing lithium contents have been measured directly with an on-line probe at an operating CANDU station. Meanwhile, the critical hydrogen concentration (CHC) for maintaining chemically reducing conditions in the PHTS was re-evaluated with experiments in an in-reactor loop. The findings of previous radiolysis experiments with no in-core boiling were refined and it was shown how the defined CHC still allowed some transient oxidizing species to be formed and to leave the core. For application to operating CANDUs it would be useful to evaluate the CHC for in-core boiling conditions, although the recommended operating concentration of 2 – 15 mL/kg of dissolved hydrogen needs to be high enough to ensure adequate radiolysis suppression. It was pointed out that the effects of radiolysis on the dissolution properties of corrosion products in the coolant are largely unknown;
   - The solubility of magnetite, which is fundamental to the mechanisms of steel corrosion and to corrosion product transport, has been reassessed in a recent review of the existing measurements. The importance

of solubility gradients in moving iron species around the PHTS is reaffirmed, supporting the data that have been used in the industry for many years. High alkalinity induces positive gradients with temperature and keeps the fuel clean of corrosion products during normal operation; in the lower-temperature regimes during start-up and during the hot-conditioning of new and refurbished plants, however, the gradients are opposite and tend to promote deposition. It is pointed out that the solubility data are obtained for H2O systems and there is no pertinent information on the isotope effects for D2O systems. Recent measurements of the ionisation constant of water and heavy water over a range of temperatures suggest that the effects could be significant for metal ion hydrolyses.

e) As regards the impact of PHTS corrosion on fuel fitness-for-service,

- A preliminary analysis was done to address a discussion on whether the inclusion of crud corrosion is needed in the safety assessments. The preliminary result indicated that its impact would be minor to insignificant and covered by the existing limited operating envelope (LOE) safety methodology. This preliminary result needs to be further investigated by accounting for corrosion deposits on the deformation of the bundle in the reactor and associated erosion of margin to dryout;
- The compliance verification activities performed by the regulator in the area of chemistry control at the PHWR units appear effective in mitigating crud deposits.

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ANNEX: PROCEEDINGS OF THE TECHNICAL MEETING

OPERATIONAL EXPERIENCE (Session I)

TECHNOLOGICAL OPINION AND CORRESPONDING OBSERVATIONS ON CORROSION PHENOMENA (Session II)

CORROSION MODELLING AND FUEL BEHAVIOURS ASSESSMENTS (Session III)

REMEDIAL ACTIONS TO ENSURE RELIABLE FUEL PERFORMANCE (Session IV)

OPERATIONAL EXPERIENCE

(Session I)

Chairperson

J. ROBERTS
Canada

A BRIEF HISTORY OF CANDU REACTOR HEAT TRANSPORT PH CONTROL

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Abstract

The history behind CANDU heat transport pH control is briefly discussed along with the rationale. The journey progresses from early 1950s into the new millennium. pH specifications, where possible, are identified along with the rationale for changes. Equipment malfunctions are discussed along with challenges presented by unit outages.

1. INTRODUCTION

Heat transport chemistry is roughly based on testing performed on fuel for the nuclear submarine USS Nautilus, circa 1952. Initial tests at Chalk River Nuclear Laboratories (CRNL, now Canadian Nuclear Laboratories – CNL) were conducted using neutral light water by Lorne McConnell – then a second or sub-Lieutenant in His Majesty's Royal Canadian Navy, under supervision of Paul Cohen [1]. A visual inspection of the fuel was requested during which McConnell observed deposits. Neither Cohen nor McConnell could decide whether the deposits resembled mud or crap – so they settled on the word CRUD!

Cohen relayed the observation to his superiors who shortly arrived at CRNL to see for themselves. Sub-Lieutenant McConnell was surprised to meet then Captain, later Admiral, Hyman Rickover (now known as the Father of the US Nuclear Navy) and his aide de camp, Lieutenant (later US President) Jimmy Carter [1].

Following discussion, the pH was changed to alkaline and the deposits disappeared [1]. Thus, heat transport chemistry is designed to keep the fuel free of deposits. Dr. McConnell later participated in the design of the Nuclear Power Demonstration CANDU reactor NDP-2 becoming the first Station (Superintendent) Manager. He retired as Vice President of Ontario Hydro's Nuclear Generation Division. Some NPD-2 (known now as NPD) history can be found in reference [2].

2. NPD

It their 1962 paper [3], Rae and Yatabe state, in the first sentence, "An important consideration in the use of carbon steel as a construction material in the primary coolant system of a water-cooled reactor is the release of corrosion products to the water and their deposition on the fuel. Control of the pH of the water at about 10 with an alkali has long been known to minimize corrosion-product release and subsequent deposition. However, the beneficial effects of pH control are only fully obtained after an adherent, tenacious layer of corrosion product has been formed on the steel. This conditioning of the surface to produce an adherent layer of magnetite (corrosion product) is the subject of this paper.". This author neither came across Rae and Yatabe's paper nor recalls discussion with respect to fuel deposits when at Ontario Hydro. Interestingly, late in 2001 the issue arose during the author's time as Design Authority for Chemistry at Bruce Power.

Prior to commissioning of NPD Atomic Energy of Canada Limited (AECL) experimented with various chemistries in coolant loops of the NRX and NRU reactors. Tests were conducted using neutral, alkaline (lithium hydroxide, ammonia) under various conditions – a summary of the results are contained in [4]. Experiments were also conducted to determine how to approach the bare carbon steel to be used for feeders and headers at NPD. Concern had been expressed about minimising iron oxide deposits on the fuel. Following tests at NPD using ammonia and tests using anhydrous lithium hydroxide, the latter was selected as the pH adjusting agent [3,5]. Reference [5] also summarizes fuel deposit experience.

The NPD heat transport system was conditioned (now known as "hot conditioning) during February 1962 [6]. This conditioning was conducted using pump heat alone – the reactor had not been fuelled. A statement is made about crud concentration which the conditioning was meant to minimise "…it is important to control this material to prevent excessive amounts of it from depositing on the fuel" suggesting that some (i.e. not excessive) crud deposition on the fuel is to be expected. The paper discusses chemistry monitoring including pD (pH of heavy water), lithium and conductivity, an excellent practice.

The reactor was fuelled, then criticality followed during May 1962 [7].

An event occurred when a leak resulted in water collecting in the building sump; this water was recovered to maintain fuel cooling. Various contaminants were consequently introduced into the primary circuit including “a polymerized acrylamide (grout) and gallon quantities of oil” [6]. The reactor had been shut down and clean-up of the coolant performed. Following start-up, a crud burst occurred which disappeared after two days. The oil had disappeared during the first day at power. The statements “In spite of the large amount of impurities added to the primary system there is little concern that the fuel has suffered. Several bundles were removed following the equivalent of 50 full-power days after the incident which showed surface deposits that were very thin (0.5 mg/dm^2)”. A further statement reads “From this and earlier information it is clear that the crud release in the NPD carbon-steel system is low enough to be of no concern to the formation of worrisome deposits on the fuel…”[6].

The NPD event of having to recover water from a sump to cool the fuel is not unique (Pickering Unit 2 G16 event, 1983) but it may be the only such event after which the reactor was returned to power without component replacement work.

3. 1980 AND BEYOND

Moving to the 1980s the AECL specification for heat transport pH control, as pH_a[4] was 10.2 – 10.8, and was used by all CANDU reactors until Ontario Hydro introduced its own pH_a range specification of 10.3 – 0.7 circa 1980. The AECL specification remained in force for CANDU-6 reactors the first of which were commissioned during the early 1980s. At this time the author joined Bruce B, then under construction, as Station Chemist.

Primary circuit pH_a control at Bruce B continued using the approach at NPD – that is measurement and correlation of pH_a, lithium and conductivity. During 1989 Bruce B alone chose to tighten the primary side pH_a control range (to 10.3 – 10.5) following the Alliston Fuel Channel Seminar [8]. This was because there was indication of a correlation between lithium incorporation in the zirconium oxide of fuel channels and deuterium uptake. Heat transport system pH_a at Bruce B had been well controlled within the Ontario Hydro specification (and thus the AECL specification); hence adopting the tighter control range was not deemed a challenge [9]. An external review confirmed that the approach used at NPD for pH_a measurement and control was effective at Bruce B.

3.1. Equipment performance issues

Issues were encountered related to equipment performance. For example, passing valves on ion exchange (IX) columns containing D^+/OD^- resins could lead to pH_a depression as a result of lithium removal. If this issue were not identified and should lithium removal be required then placing the now exhausted D^+/OD^- IX column would have little, or no, effect until the IX resin was replaced. Unfortunately, such equipment problems continue today.

Pressurizer steam bleed valves that were incorrectly set up would allow steam to leave the pressurizer leading, in theory, to a reduction in pressurizer water level. The pressurizer water level would remain constant as a result of make-up from the heat transport system for which the pressurizer was maintaining pressure. The result was a continuous loss of water vapour (steam) containing no lithium but the water makeup contained lithium. Consequently, lithium concentration increased within the pressurizer. Should reactor power decrease then pressurizer level would lower resulting in an injection of concentrated lithium hydroxide into the heat transport system and a consequential increase in pH_a. Upsets to heat transport systems have occurred with, in some cases, consequential redistribution of magnetite following such events. Pressurizer level change is instantaneous whereas removal of lithium by purification takes many hours.

An example of this phenomenon occurred circa 1977/8 at Bruce Unit 2. The then Bruce A Station Chemist identified that his practice was, surprisingly, to not initiate corrective chemistry action after the lithium concentration and pH_a increased following a pressurizer level reduction, rather await the unit’s return to high power and return of lithium to the pressurizer [10]. At this point crevice corrosion had already been identified in Pickering

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[4] pH_a refers to the pH of heavy water when measured with a pH meter that has been buffered using light water buffers. The relationship between pH and pH_a is $pH_a = pH + 0.457$.

Fuel channels [11]. The lithium concentration within the Pressurizer was of concern so an evaluation was conducted which concluded that the vessel was not in any danger [12].

Passing steam bleed valves were encountered at Bruce B. Once staff had received training and been provided with the correct set-up equipment passing of steam bleed valves at Bruce B was infrequently encountered. It is important that these valves are not ignored during outage maintenance work.

Crevice corrosion of fuel channels is the name given to the consequence of lithium concentrating in the crevices formed between fuel bundle bearing pads and the fuel channel. Localised boiling is known to occur under some bundle bearing pads hence control of lithium concentration is important.

Interestingly, fuel bundles employed in the Pickering reactors produce the same power as those employed in the Bruce reactors. The difference is that the Pickering fuel bundles were designed with 28 pencils whereas those of Bruce were designed with 37 pencils. The Pickering pencils are fatter and contain more fuel than those of Bruce, hence more heat is available for transfer through the bearing pads of each Pickering pencil as compared with a Bruce fuel pencil.

Crevice corrosion was first detected in Pickering fuel channels about five years following initial power operation (circa 1976) [11]. It was ~18 years post initial power, when crevice corrosion was first identified in a Bruce B unit [13]. For Bruce B the specific channel was a surprise to some people in that it was an outer zone channel. (Bruce reactor heat transport systems have one circuit, two zones, as opposed to other units which have two loops). This was not a high-power channel and one for which the influent coolant was not sub-cooled, thus it would be one of the first channels to enter boiling under the bearing pad. The Bruce units were designed with external preheaters and for the primary coolant to have a degree of boiling with some steam quality in reactor outlet headers.

Feeder thinning was first identified in 1995 at Point Lepreau [14] and is the consequence of magnetite dissolution and transport. Magnetite solubility is related to pH_a and temperature – the higher the pH_a the greater the solubility. The industry's response was to adjust the pH_a control range lower to lower the magnetite mass being transported from the outlet feeders – the hotter coolant exiting the fuel channel was not saturated in magnetite, it has deposited in cooler parts of the circuit.

Heat transport pH_a control was designed to keep the fuel free of deposits and at pH_a ~9.6 the temperature solubility relationship flips from increasing with temperature to decreasing with increasing temperature. The challenge is to lower pH_a to a value that is sufficiently high to give confidence that an upset will not result in too low a pH_a. Another associated issue is the lower the pH_a then the greater the probability of magnetite deposition in crevices of, and on, fuel with a greater probability of activation of such elements as cobalt-59. At Bruce B the pH_a control range became 10.1 – 10.4.

4. HEAT TRANSPORT HOT CONDITIONING

Following on from NPD experience the heat transport system of each CANDU unit has, during commissioning, been "hot conditioned". Heat input was provided by running the main pumps (pump heat). Until Bruce Unit 4, what is became known as the 'conventional' process was used – alkaline pH and reducing conditions via hydrazine. These are, in effect, the same conditions as exist when the unit operates at zero power hot, sometimes for many hours.

Bruce Unit 4 hot conditioning (~1978) used a process, pioneered by the Russians, perfected by AECL and Ontario Hydro Research (now Kinectrics) which used the salt of a complexing agent, ethylamine diamine tetra-acetic acid (EDTA). Whereas pH_a control for conventional hot conditioning is, in effect, constant that for the EDTA process does change. It is important to use the di-lithium salt. The process involves removing all lithium, and other ions, prior to salt addition – so pH_a initially approaches 7 at 150°C. The pH_a again approaches 7 twice again – once prior to the second salt injection and again following completion of 24 hours at zero power hot. This process allows for a low concentration chemical clean which offers an opportunity to remove potentially detrimental contaminants.

The four Bruce B units were hot conditioned using Li_2EDTA. Unit 6 without fuel; Unit 5 had ten channels fuelled to demonstrate if loose-fitting garter springs (spacers) could be prevented from moving; for Units 7 and 8 each channel had 12 bundles and a strainer in position 13 – the channel inlet [9,17].

Two fuel bundles were removed from Unit 7 following completion of 'hot conditioning' and descaled in the station laboratory then the magnetite thickness was calculated [8]. The results, reported to Ontario Hydro's Design and Development Division, did not give cause for concern; unfortunately, the report and data appear irretrievable.

The magnetite deposited on fuel during hot conditioning dissolved following operation at high power. Each of the four Bruce B units experienced some fuel defects – in each case due to foreign material; no failures due to deposits.

Design differences exist between Bruce A and Bruce B. One difference is that Bruce A has two large steam drums, each having four tube bundles attached whereas Bruce B has eight steam drums, each with its own tube bundle. The Bruce A steam drums have to avoid stressing certain welds – this was not recognised when Unit 4 was originally hot conditioned. This weld stress issue can be avoided by transitioning rapidly from 90ºC to 120ºC. Such rapid temperature transitions cannot be achieved by pump heat alone, nuclear heat is required.

Both Bruce Units 4 and 3 were "hot conditioned" prior to restart (2003 and 2004) using the "conventional" process. Use of Li_2EDTA was considered unwise due to the requirement to maintain temperature at 150°C which existing fuel channels could not tolerate due to their hydrogen equivalent concentration [15,16]. No fuel performance issues were experienced from magnetite deposition.

One difference between operation of Units 3 and 4 prior to, and following, restart was that both cores were set to allow fuelling with, as opposed to against, the flow. Fuelling with the flow meant that fuel in channel position 13, which is half magnetite coated, would be pushed into the core as opposed to being discharged. No fuel performance issues were reported related to magnetite.

Units 5–8 cores were reordered to allow fuelling with flow during mid 2000s; no magnetite issues related to fuel were reported.

Units 2 and 1, following refurbishment, were hot conditioned using Li_2EDTA. The reason for the change in approach from Units 4 and 3 was that new components had been installed – pressure tubes, end fittings, liners and feeders. Information was lacking with respect to potentially deleterious contaminants hence the Li_2EDTA process.

5. HEAT TRANSPORT SYSTEM PHA CONTROL DURING OUTAGES

Maintenance of the asset is crucial to safe and reliable operation. Designs of the Pickering units do not allow for heat transport system purification during outages; however, designs of the Bruce, Darlington and CANDU-6 reactors do allow such.

Component inspection (fuel channels, steam generator tubes) during outages became usual during the 1980s and outage durations lengthened. Component inspections often require lowering of heat transport water level to allow person entry; thus, air displaces water. Air contains carbon dioxide which easily dissolves into alkaline water, hence without the benefit of purification pH_a will reduce. Under the effect of low pH_a and oxygen deposited magnetite can become detached. Under such situations, even after pH_a has been corrected, circulating crud levels will initially increase. If airflow into the heat transport system can be controlled the chemistry impact will be reduced.

Some strategies have been adopted that allow for control of heat transport chemistry during outages [18] thus minimising oxide release.

6. CONCLUSIONS

CANDU heat transport chemistry is designed to minimise magnetite deposits on fuel. Major impacts on the ability to control pH_a and magnetite transport can result from either equipment malfunction and/or outage maintenance activity. These impacts can be minimised by proactive maintenance and excellence in outage planning and execution.

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HOT CONDITIONING CARRIED OUT AT THE START OF THE REFURBISHED EMBALSE NUCLEAR POWER PLANT

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Abstract

The objective of hot conditioning is to achieve a passivating oxide layer that, even when very thin, protects structural materials and limits the transport of corrosion products and potential activity throughout the use of the plant. Therefore, the compact and homogeneous protective layer formed by hot conditioning limits the future deposition of the internal side of the steam generator tubes, which is produced by transporting iron from the components of the Primary Heat Transportation System (PHTS) without such protection. These deposits promote changes in thermal conductivity, in the friction factor, possible changes in the flow of the primary refrigerant and an increase in its temperature. The conditioning has two stages: cold conditioning stage and hot conditioning stage. The first stage is for the purification of the system and the second for the formation of passive oxide on the metallic surfaces of the PHTS and thus protect the structural materials of the system from corrosion during the second cycle of operation of the plant. Monitoring and control of physical-chemical parameters was carried out, determining the operational actions necessary to keep them within the specified ranges. From the beginning of the procedure, the CRUD values were reduced approximately 160 times. The target values of the diagnostic parameters and chemical control (concentration of lithium, soluble iron, deuterium, oxygen, anions, etc.) were satisfactorily achieved.

1. INTRODUCTION

The conditioning of the Primary Heat Transport System (PHTS) aims to achieve the physical-chemical conditions of the heavy water to establish a protective oxide layer on the materials, in order to achieve a proper subsequent operation limiting the corrosion, transport and activation of the species released to the primary coolant.

2. DESCRIPTION

The Embalse Nuclear Power Plant (CNE) has a CANDU 600 reactor from the designer Atomic Energy of Canada Limited (AECL). After preliminary feasibility studies, the possibility of prolonging the useful life of the CNE for a period of 30 years was evaluated. To achieve this objective, an integral overhaul of the entire plant was necessary with a service outage for a considerable time (approximately 36 months). The most relevant activities within the Reactor Building were the change of the Fuel Channels (reactor retubing) and the change of the Steam Generators.

As background, during the first period of life of the CNE hot conditioning was carried out:

- During commissioning of the plant, the procedure indicated in [1] with an EDTA solution. This was not done on this occasion because since there are surfaces of components that were not replaced and therefore have an appreciable oxide layer, it would be possible to release and mobilize high iron from these surfaces;
- After the resin entry event into the PHTS (1988) a passivation procedure was performed using Hydrazine indicated in [1]. During the resin entry event the structural materials, mainly carbon steel, underwent significant corrosion due to the acidification of the medium, which was not in any way the present situation.

In this recent hot conditioning, the PHTS was first cleaned and the temperature gradually increased to 250°C, always maintaining an alkaline and reducing medium by adding LiOH, removing the oxygen before reaching 100°C and avoiding the subsequent addition of Hydrazine or other chemical to the system. The conditions were very similar to a normal start after a scheduled outage and to the chemistry of the plant in normal operation.

Unlike the previous hot conditioning and given that a good part of the exposed surface of the materials, feeders, were new, a greater quantity of iron in solution and in the form of particles was expected that had to be gradually removed during the hot conditioning.

The conditioning of the PHTS was done in two stages:

- Cold conditioning;
- Hot conditioning.

The cold conditioning was carried out to reach the PHTS water chemistry conditions according to the Plant's Chemical Design Manual [2] and the hot conditioning was performed to achieve a passivating oxide layer on the PHTS metal surfaces.

Prior to conditioning, a theoretical and laboratory study was carried out to define the appropriate methodology for carrying out the PHTS conditioning with an interdisciplinary team.

2.1. PHTS conditioning pre-requisites

Before beginning the conditioning tasks, it was necessary to complete the following prerequisites:

- System filled with chemically approved heavy water according to the technical specification indicated in [2];
- PHTS Purification System filters (3335-FR1 / FR2) with 10 µm filter medium;
- Ion exchange columns of the PHTS Purification System: 3335-IX1 prepared with a fraction of mixed lithium resin (Brand: IRN150 Rohm & Hass) and 3335-IX2 prepared with lithium mixed resin (Brand: Purolite NRWLi).

2.2. Cold conditioning

It is considered that cold conditioning is carried out from storage temperature to 80°C, after which hot conditioning would be performed.

2.2.1. Heavy water cleaning

The cleaning process was carried out to remove impurities generated during the Scheduled Refurbishment Outage and those incorporated in the D_2O from the transfer stages from the PHTS and storage in the Exhausted Resin Handling System (7914-TK2 – Temporary Repository during Scheduled Refurbishment Outage). These are mainly soluble species and particulate: strong acid cations and anions that are potential promoters of localized corrosion phenomena. The cleaning was done using 10 µm filters and ion exchange resins of the PHTS Purification System (BSI 3335) and the 5 µm mechanical filters of the Main Pump Seals Water System (BSI 3334). During this stage the PHTS heavy water chemistry was constantly followed to ensure the required degree of cleanliness. The frequency of analysis was every 2 hours.

2.2.2. Alkaline conditions of heavy water

To achieve the passivation of the base metal, the alkaline conditions were maintained ($pH_a = 10.2 – 10.4$, 10.35 on average). These conditions were achieved by the addition of LiOH. Lithium dosing and concentration control was performed through the ion exchange columns of the PHTS Purification System according to those established in Section 2.1. The expected lithium concentration value for this treatment was set to [Li+] = 500 ppb. Maintaining the alkaline medium ensures that it is located within the passivity zone within the Pourbaix diagram, where the protective oxides are stable, its chemical activity and, therefore, its corrosion rate are reduced. This is important in order to maintain passive oxide in those materials that were not replaced during the scheduled overhaul outage.

2.2.3. Reduction medium maintenance

In the PHTS the predominant material is carbon steel, therefore, it was necessary to work in alkaline and reducing medium (absence of free oxygen). At the temperature that the system operates, the protective oxide is predominantly magnetite. During the entire passivation process the dissolved oxygen had to be kept less than 10 ppb to decrease both the uniform corrosion and the localized corrosion in the system.

One of the actions to decrease the concentration of oxygen was the addition of hydrazine, which reacts with oxygen as follows:

$$N_2H_4 + O_2 \leftrightarrow H_2O + N_2 \quad [80°C < T < 100\,°C] \tag{1}$$

Hydrazine is a reducing agent, with some corrosion inhibitory power and Fe^{+++} reduction to Fe^{++}. In practice, hydrazine can be added whenever there is free oxygen; if there is no oxygen the hydrazine decomposes forming

NH_3, which displaces the resin lithium. This is the reason why hydrazine was added proportionally to the oxygen present maintaining the working temperature for the removal of oxygen between 80-100°C because above that temperature the hydrazine decomposes into NH_3 raising the pH of the system, favouring dissolution of the protective oxide, formation of CRUD and not removing dissolved O_2.

The generated residual NH_3 was removed by the PHTS Purification System. Hydrazine solution was added and the reaction time between O_2 and hydrazine depended on the hydrazine volume. More hydrazine solution was added after the hydrazine in the system had been consumed. In this way, high concentrations were avoided which ensured a decrease in CRUD and guarantee that NH_3 was not produced. For the hydrazine solution, the procedure in [3] was used, maintaining the alkaline and reducing medium and the concentration less than $[N_2H_4] < 5$ ppm. In this process, both ion exchange columns were taken out of the PHTS Purification System (isolated columns and open bypass), to avoid the removal of hydrazine, and the depletion of resins in the columns.

2.3. Hot conditioning

It is considered that hot conditioning is carried out from 80ºC to 250ºC.

2.3.1. Temperature rise from 80ºC to 120ºC

The PHTS was heated to 120°C by means of the four main pumps, at that time 3335-IX2 was aligned to retain soluble Fe in the system. Twice per shift the analyses of the physical-chemical parameters were enhanced. Based on the results, it was decided whether to isolate 3335-IX2 and align 3335-IX1 periodically to retain excess Fe and Li (released by Fe retention) and bring back the $[Li^+] = 500$ ppb and pH working pH = 10 at 25°C.

2.3.2. Temperature rise from 120ºC to 150ºC

The temperature was increased whilst maintaining purification of the system with the 3335-IX2 ion exchange column and maintaining the filtrate through the Purification System verifying the physical-chemical parameters. If the concentration values of $[Li^+]$ did not comply with the specification, the ion exchange column 3335-IX1 was aligned and 3335-IX2 was isolated until the specified values were met.

2.3.3. Temperature rise from 150ºC to 250ºC

After aligning 3335-IX2, the SPTC temperature was slowly heated to 250°C at a temperature rate of 10°C/h, constantly monitoring the physical-chemical parameters. At this stage the oxide protective layer was formed. Surface passivation is formed by constantly maintaining the purification of the system with 3335-IX2 and filtering. It was expected that if the concentration of H_2 increased to > 2ml / kg in the PHTS it would necessary to put the Degasifier (3332-TK2) into service to control the concentration of H_2 but it was not necessary.

This temperature (250ºC) was maintained for 5 days to achieve the formation of the oxide layer, maintaining filtration and purifying with 3335-IX2 and, if necessary, 3335-IX1 was aligned to retain excess Li^+ and maintain the pH.

In this way the passivating magnetite layer was formed, and part of the Fe was released in solution in the form of particles and ions.

1) Magnetite formation

In passivation, a protective oxide is formed that limits the progress of corrosion by delaying the passage, entry and egress of species through it. For this purpose, it is well characterized that two layers of oxide, an inner layer and an outer layer are formed in the alkaline and reducing medium steels.

Forming reactions:

$$\begin{cases} Fe \rightarrow Fe^{2+} + 2e^- \\ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \end{cases}$$

$$\begin{cases} Fe^{2+} + H_2O \rightarrow Fe(OH)^+ + H^+ \\ Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ \end{cases} \qquad (2)$$

Below 100°C, the reaction of dehydration of hydroxides (Fe $(OH)_2$) and formation of magnetite (Fe_3O_4) requires the presence of O_2 in the medium:

$$3Fe(OH)_2 + \frac{1}{2}O_2 = Fe_3O_4 + 3H_2O \tag{3}$$

When the temperature exceeds 100°C and the hydroxide is in a medium without the presence of oxygen, it is dehydrated to form magnetite according to the Schikorr reaction:

$$3Fe(OH)_2 = Fe_3O_4 + H_2 + 2H_2O \tag{4}$$

At 260°C the magnetite formation is ensured

2) Pourbaix diagram (thermodynamic stability)

In the Pourbaix diagram can be seen the zone of formation of iron oxides that are thermodynamically stable comparing the potentials and pH, the oxides are:

- Magnetite: Fe_3O_4, mixed oxide of Fe^{+2} and Fe^{+3};
- Hematite: Fe_3O_4, oxide of Fe^{+3}.

In this diagram, 3 zones can be distinguished:

a) Passivity zone and Fe_3O_4: Iron oxides form a protective layer on the surface of the metal, which reduces its chemical activity and, therefore, its corrosion rate, which is why it is called a passivity zone. This will be the work area to be fixed by means of the pH and potential relationship.

b) Fe immunity zone: In this area of the diagram the thermodynamically stable species is metallic iron, therefore, the metal is immune and does not suffer corrosion.

c) Corrosion zone FeO_3: at very alkaline pH, stable iron species are found as ions, therefore it is a favourable condition for the dissolution of the metal. The dashed lines represent the reactions of water reduction (B) H_2O with dissolved O_2 and (A) oxygen-free water. At any pH the reduction potential of H_2O is above iron, so Fe versus H_2O always oxidizes. In the passive zone the oxides limit the corrosion of the base metal. It is emphasized that the pH-Potential ratios and the stability zones are temperature dependent. Therefore, Pourbaix diagrams calculated at different values from ambient temperature to operating temperature are available.

3) Variation of the solubility and corrosion of magnetite as a function of pH

It is convenient to work at a slightly alkaline pH and reducing medium, to ensure minimum corrosion rate of the base material and minimum solubility of the protective oxide.

4) Solubility of magnetite as a function of pH at 25ºC for different temperatures

There is a relationship between the solubility of magnetite oxide as a function of pH, expressed at ambient temperature, and operating temperature. There the minimum solubility is observed for each pH and temperature. It shows the convenience of operating at 250°C at a pH at 25°C around 9.6 (in light water) so that the oxide is at the minimum of solubility.

2.3.4. Cooling

The cooling was carried out gradually, without exceeding a rate of 0.6°C/min to avoid detachment of the magnetite layer.

2.4. Global evolution of the process

Figure 1 shows the evolution of the times and temperatures of the whole process.

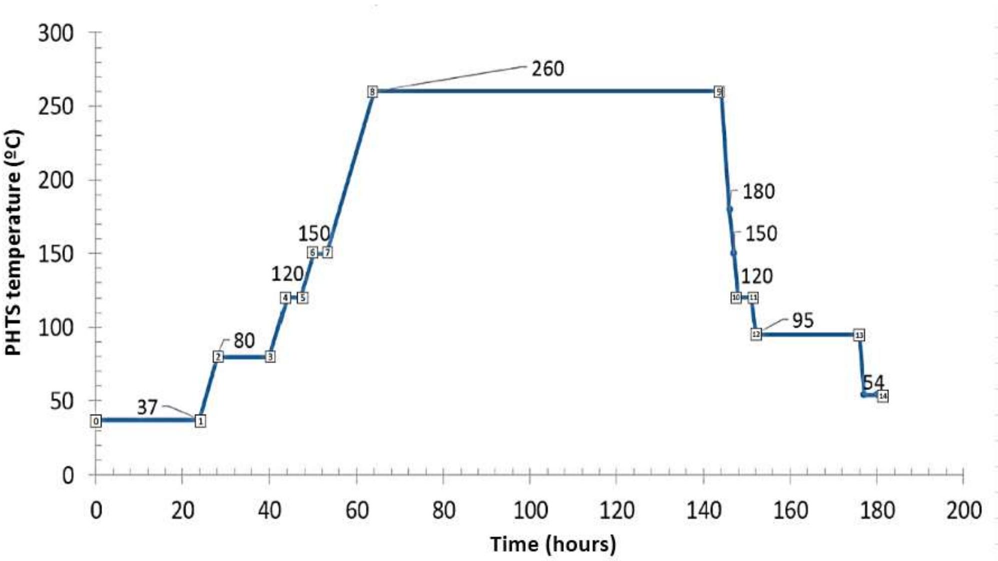

FIG.1. Temperature evolution during PHTS conditioning.

2.5. Evolution of chemical parameters

Figures 2 and 3 show the evolution of the chemical parameters during the process.

2.6. Study conducted on feeder materials

A generalized corrosion comparison study was conducted between the materials used during the first cycle of operation (A106 B) and those used during the second cycle of operation (A106 C). The coupons were tested under conditions similar to those of hot conditioning, but in a static autoclave.

The new A106 C material has improved specifications that make it more resistant to flow-assisted corrosion (FAC). The material of the feeders was selected because it is the most representative considering the exposed surface and the release of iron that needs to be controlled until passivation. The test was conducted by the National Atomic Energy Commission (CNEA).

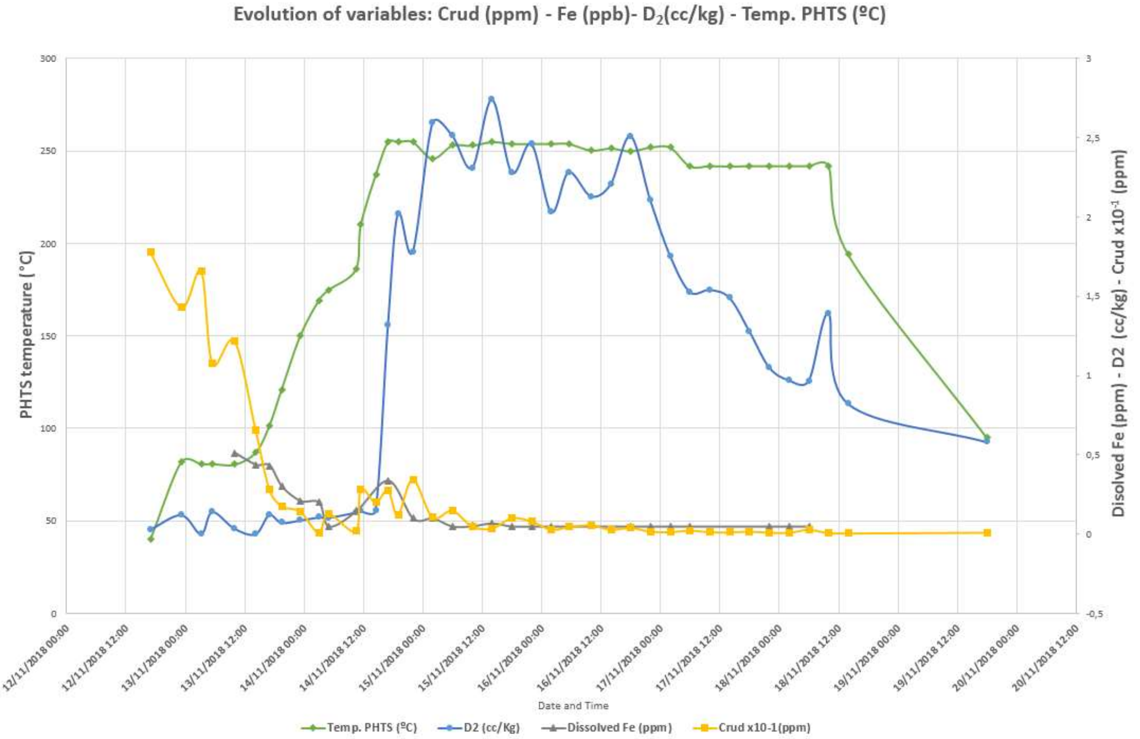

FIG. 2. Evolution of CRUD, Fe, D_2 and Temperature of PHTS.

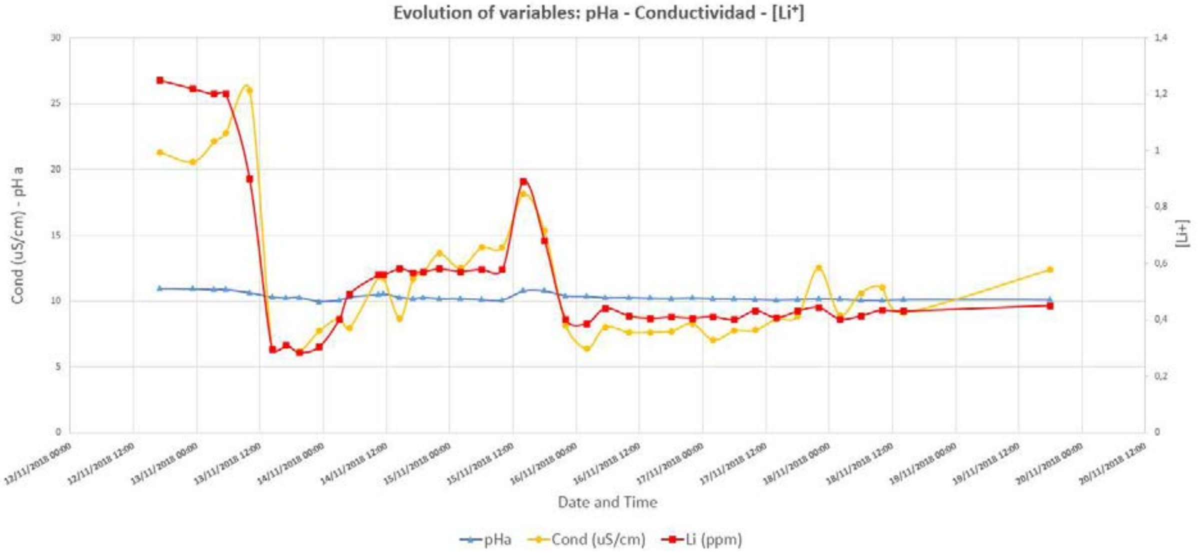

FIG. 3. Evolution of pHa, Conductivity and [Li⁺].

The comparison in Fig.4, between the evolution of the A106 B and A106 C steels under conditions similar to those of hot conditioning in CNE and for a given time, indicates that it is possible to achieve a greater thickness of adherent oxide with the material of the new feeders.

Figure 5 shows the surface of the A106 B and A106 C steel coupons, observed by SEM (Scanning Electron Microscopy) after 19 hours of hydrothermal treatment of the A106 B and A106 C steel coupons. Subsequently, the oxides were characterized by X-ray diffraction ensuring the formation of Magnetite.

The characterization of the surfaces by means of optical microscopy, allows to affirm that after 5 days a more uniform coverage is obtained in the case of A106 C steel, which also has advantages by reducing the probability of localized corrosion phenomena.

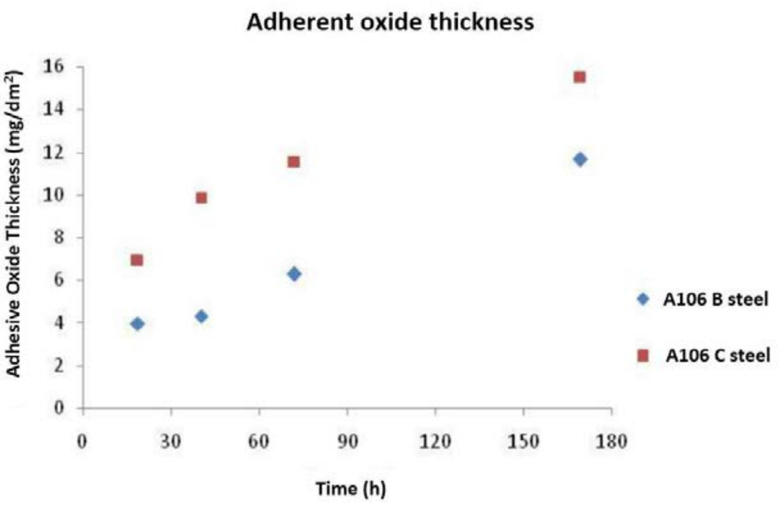

FIG. 4. Passivation test performed in autoclave. Adhesive oxide thickness vs. time in conditions similar to hot conditioning.

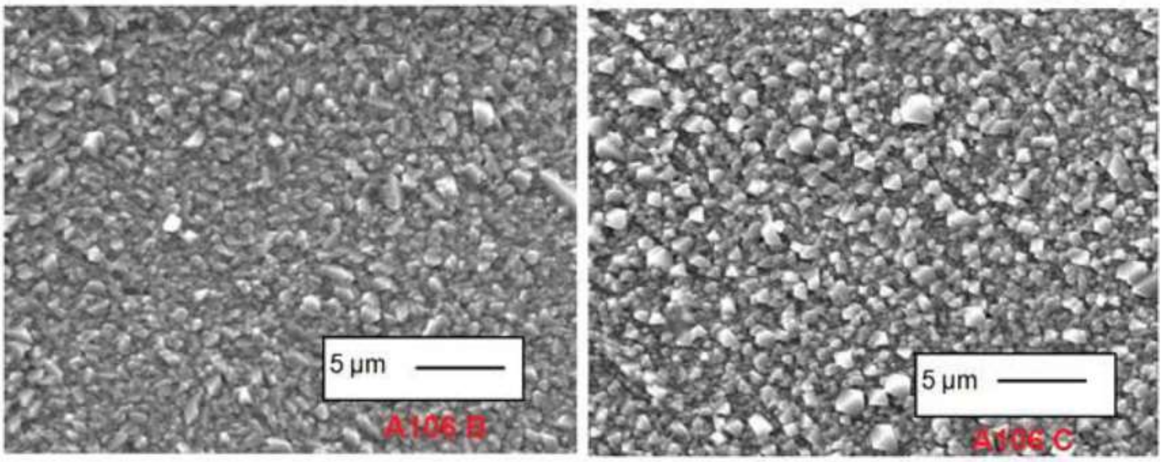

FIG. 5. Photo by electron microscope after the autoclave test after 19 hours of treatment.

3. CONCLUSIONS

From the theoretical concepts, antecedents in the CNE, autoclave experiences and international experience, it is possible to establish a protective oxide layer on the PHTS materials that is the basis for an adequate subsequent operation limiting the corrosion, transport and activation of the species released to the PHTS.

The target values of the diagnostic parameters and chemical control (concentration of lithium, soluble iron, deuterium, oxygen, anions, etc.) were satisfactorily achieved.

NOMENCLATURES

CNE	Embalse Nuclear Power Plant
EDTA	Ethylenediaminetetraacetic acid
FAC	Flow Accelerated Corrosion
SEM	Scanning Electron Microscopy
PHTS	Primary Heat Transport System

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THE CHEMISTRY CONTROL OF PHTS AT CANDUS IN CHINA

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Abstract

Qinshan Phase Ш NPP is the only PHWR NPP in China which installed two CANDU-6 heavy water reactors each with a capacity of 728 MW(e), which were put into commercial service in 2002 and 2003 respectively. In order to promote low operating costs, longevity of component life and minimize environmental releases and occupational exposure, many modifications and optimizations of the primary heat transport system (PHTS) have been done in these more than 16 years. These included optimizing pH control during normal operation and outages changing 5 micron paper filter cartridges to 0.1 micron glass fibre filter cartridges in the PHTS purification circuit and changing the exchange columns type and volume. Until now, no deposit has been found on the fuel bundles.

1. INTRODUCTION

1.1. CNNO Brief Introduction

CNNC Nuclear Power Operations Management Co., Ltd (CNNO), a subordinate company of China National Nuclear Corporation (CNNC), is a large-scale state-owned management company specialized in nuclear power operation. CNNO was established on September 19, 2010.

The company consists of Qinshan NPP 1, 2 and 3, and is responsible for the operation & management of nine nuclear power units at Qinshan as well as the production preparation, designed equipment management. The total installed capacity of the nine units is 6.5 GW(e).

Qinshan Ph. Ш NPP is the only PHWR NPP in China comprised of two CANDU-6 heavy water reactors each with capacity of 728Mwe, which were put into commercial service in 2002 and 2003 respectively. These two pressurized heavy water reactors of Qinshan Ph. III have achieved good operating performance.

Qinshan Nuclear Power has been committed to management improvement in safety, operations, outage, quality, etc. With nine units in the more than 400 units of the World Nuclear Operators Association (WANO) always at a good level and are in the first quartile. In 2018, a total of three units of the WANO comprehensive performance index reached 100 points, ranking first in the world.

In the past five years, the average capacity factor of Qinshan nuclear power WANO units has remained at around 90%, reaching 91.69% in 2018, which is at the advanced level in the world.

1.2. The chemistry control of PHTs in Qinshan Ph. III NPP

In the past 16 years, optimizing pH control during normal operation and outages, changing 5 micron paper filter cartridges to 0.1 micron glass fibre filter cartridges in the PHTS purification circuit, and changing the exchange columns type and volume are the three measures which have been done to improve coolant quality. Until now, no deposit has been found on the fuel bundles.

2. CHEMISTRY OPTIMIZATION

2.1. PH control during normal operation and outages

The pH of heavy water in the primary heat transport system (PHTS) of CANDU-6 heavy water reactor is an important chemical control parameter. The purpose of pH control mainly includes the following two points.

- Reduce the corrosion rate of system materials, prevent corrosion and cracking of system materials, and extend the service life of system materials;
- Reduce loss of heat transfer rate caused by the deposition of corrosion products on the fuel bundles and in the steam generator tubes.

The main corrosion of the primary heat transport system is flow accelerated corrosion (FAC) in all operating modes of which flow accelerated corrosion of the core outlet heat feeder pipes is the most serious.

Operational experience and research have shown that the FAC of the PHT system has a direct relationship with the pH of heavy water in the primary heat transport system.

In operating modes 1, 2, 3, it is appropriate to maintain the pH_a value at 10.0–10.2. At present, the Qinshan Phase III CANDU reactor chemical operating manual still uses the specifications of the previous design manual of the Canadian Atomic Energy Co., Ltd., and the desired value of pH_a is 10.2–10.4, which is also acceptable. However, the parameter specification is specified as 10.2–10.8, which is obviously high, and is not conducive to corrosion control and distribution of corrosion product deposits.

In operating modes 4, 5, reactor power is less than 0.1%FP, and all corrosion products are uniformly distributed throughout the pipelines. At $pH_a = 9.5$, the corrosion rate is 100 um/yh, which is the same as the corrosion rate at $pH_a = 10.4$ during power operation; at $pH_a = 8.5$, the corrosion rate = 120 um / yh, which is the 1.2 times of the corrosion rate at $pH_a = 10.2$ during power operation. In operating mode 5c large amounts of oxygen and carbon dioxide enter the system due to open access. In the aerobic state, an oxide film is formed on the surface of the carbon steel, and the FAC is rapidly lowered. So, the actual corrosion rate of the carbon steel is lower than the above data. Therefore, during an outage of the unit, even if the pH_a value of the heavy water of the primary heat transport system is lowered to 8.5, the corrosion rate is equivalent to or lower than the corrosion rate at pH_a is 10.2 during the power operation.

So, in the Operating Manual of Qinshan Phase III Heavy Water Reactor Nuclear Power Plant, the parameter specification of pH_a is 10.2–10.8 in operating modes 1. 2, 3, 4, 5a and 9.0–10.8 in operating modes 5b, 5c.

2.2. Filter cartridges change

Canada's 3L 5µ paper filters had been used in the two heavy water reactors of Qinshan Ph. III since they were put into commercial service in 2002 and 2003. Operational review showed that small radioactive particles in the coolant loop cannot be effectively intercepted, and the coolant radioactivity level is maintained at a high radioactivity level of 10^{-2} µCi/ml.

By comparison, the radioactivity level of the coolant of the advanced pressurized water reactor can be maintained at 10^{-7} Ci/ml by using high-precision glass fibre filter. More and more heavy water reactors use glass fibre filter cartridges which have been proven to improve the water quality of the primary circuit and reducing the radioactivity level.

During May 2017, Unit One of Qinshan Phase.3 NNP changed the filter cartridge of primary heat transport purification system from paper filter (5µ) to glass filter (0.1µ) during the outage (OT-109) and was put it into operation in July 2017. In January 2109, the concentration of silicon dioxide (SiO_2) of the primary heat transport system rose quickly and reached 1.5ppm in March 2019 before the outage (OT-110) (Fig.1).

After the filter cartridges were replaced during the outage (OT-110), the concentration of SiO2 of the main system decreased to 0.044 ppm, but began to rise again in August, to 0.18ppm by the beginning of November (Fig.2).

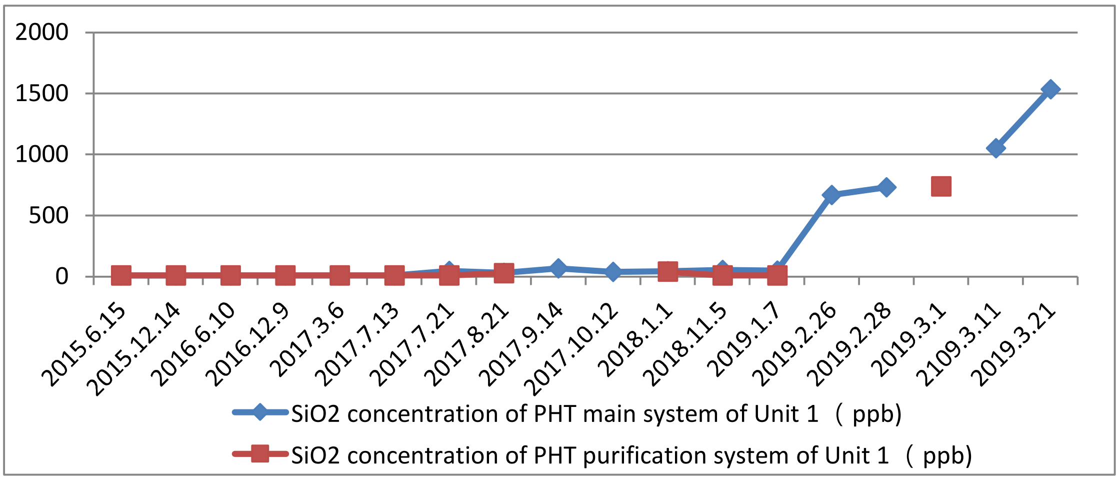

FIG. 1. SiO_2 concentration of PHT main system and purification system.

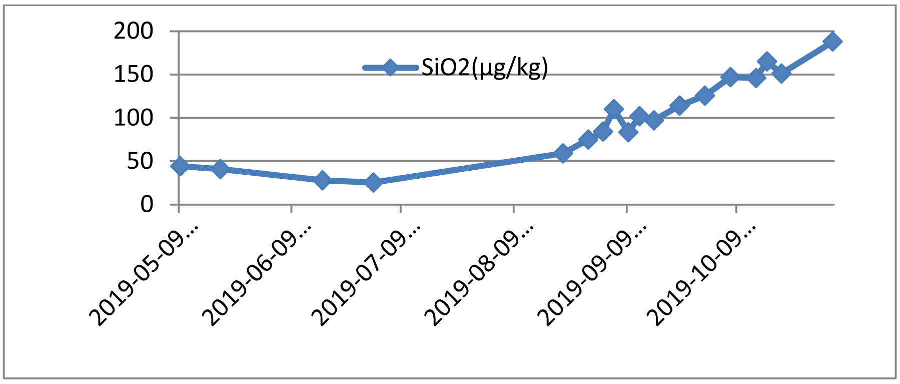

FIG.2. SiO_2 concentration of PHT main system in 2019 after the outage.

Unit 2 of Qinshan Phase 3 NNP changed the filter cartridges which were placed in service in May 2018, the concentration of SiO_2 was still below 0.01ppm.

The following five points are about the parameter specification of SiO_2:

— There is no silica-containing material in the CANDU power station design, so there are no silica parameters and indicators in the chemical design manual;

— There is no experience about silica parameters in other CANDU power stations;

— EPRI guidelines for silica in the primary circuit of light water reactors: the upper limit of silica can be relaxed by 3 ppm;

— Fuel supplier's recommendation: the upper limit of the power station without zinc can be set to 3ppm and the zinc power station is 1.5ppm;

— GE company's silica parameter for CANDU primary heat transport system: if the concentration of calcium, magnesium and anoeuvre in water is as shown in Table 1, the silica needs to be less than 1ppm, after being evaluated according to the actual situation, the silica parameter can be relaxed to 3ppm.

2.3. Exchange Columns Type and Volume Change

The primary heat transport system of CANDU-6 heavy water reactor has two ion exchange columns to remove hazardous and detrimental impurities. The initially and currently installed resins types and volumes of Qinshan Phase III are shown in the Table 2 and Table 3, respectively:

TABLE 1. CANDU HTS-SOLUBLE DATA

Reactor	Al undigested (ppb)	Al digested (ppb)	Ca undigested (ppb)	Ca undigested (ppb)	Mg undigested (ppb)	Mg undigested (ppb)
Pickering (avg. Feb & Mar 2003)	5.10	11.11	<10	14.08	2.93	3.82
Darlington U1 (avg. Sept &Oct 2003)	NA	8.98	NA	6.23	NA	2.05
Darlington U2 (avg. Sept &Oct 2003)	NA	8.55	NA	7.28	NA	2.67
Darlington U3 (avg. Sept &Oct 2003)	NA	11.96	NA	4.69	NA	2.80
Darlington U4 (avg. Sept &Oct 2003)	NA	13.50	NA	5.11	NA	2.80
Bruce Power U5 (avg.)	NA	10.02	NA	<1	NA	4.15
Bruce Power U6 (avg.)	NA	13.12	NA	<1	NA	6.96
Bruce Power U7 (avg.)	NA	10.79	NA	<1	NA	5.66

Note: Undigested – values are for soluble material.
Digested – values are for soluble and particulate material.

TABLE 2. INITIAL RESIN TYPES AND VOLUMES OF QINSHAN PH. III

Ion exchangers	Initially installed resins types and volumes
3335-IX1 or IX2	1080L Purolite NRW37LiLC
3335-IX2 or IX1	550L Purolite NRW37LC

TABLE 3. CURRENT RESIN TYPES AND VOLUMES OF QINSHAN PH. III

Ion exchangers	currently installed resins types and volumes
3335-IX1	1080L Amberlite IRN-217*
3335-IX2	550L Amberlite IRN160

3. OUT FEEDER MATERIAL CHANGE

Low chromium CS (0.019 wt% Cr) was used as the material of the feeder pipes in the early CANDUs. In light of the fact that increasing the Cr content to 0.2-0.4 wt% reduces the FAC rate of CS, Qinshan Phase III NPP used ASME SA-106 Grade B which was made by Sumitomo as the material of feeders, and the content of Cr is 0.32-0.33 wt%.

4. CONCLUSIONS

Thanks to material improvement and good operating chemistry control, no deposits or corrosion of nickel ferrite have been observed on the fuel surface of Qinshan Phase III CANDU units (see Fig.3 for illustration). Since the units have been in operation for more than ten years, the core inlet and outlet temperature has hardly changed, and the core outlet temperature has been maintained at around 308°C; the core inlet temperature is currently around 262°C (about 261°C at the beginning of the commercial period).

FIG. 3. The Bottom of Bundle Discharged in 2018.

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IN-SITU MONITORING OF PHWR WATER CHEMISTRY EFFECT ON FUEL CLADDING CORROSION

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Abstract

The water chemistry control in Nuclear Power Plants (NPPs) is important at least for the next reasons: structural materials integrity, plant radiation levels, deposits build-up and safety. One of the most important NPP systems is Primary Heat Transport System (PHTS) having in view its role in active zone cooling and heat transfer to steam generators. In PHTS the chemical control is directed to keep chemical parameters within specified limits in order to mitigate the corrosion of the key equipment and related piping, to control the corrosion rate and impurities concentration, such as corrosion and fission products and to minimize activity transport and heat transfer surfaces fouling. By operation in aqueous environment at high temperature and pressure, the structural materials from PHTS are covered with protective oxide films, which maintain the corrosion rate in admissible limits. A lot of potential factors exist, which can degrade the protective films and consequently intensify the corrosion processes. In order to minimize these adverse effects, an optimal water chemistry control and corrosion monitoring program were established. The understanding of the corrosion degradation phenomena that result in failure of some components from PHTS of CANDU NPP necessitates investigation of the structural materials corrosion processes in different conditions of water chemistry and temperature. Water chemistry management in Nuclear Power Plants can then be applied to mitigate the corrosive environments inherent in plant operation.

The basis of chemistry control process consists of operational experience, laboratory tests, structural materials corrosion behaviour and the transport and deposition of impurities and corrosion products under operating conditions. To investigate the corrosion process of some structural materials from PHTS (Zr alloys) of CANDU 6 reactor corrosion experiments were performed in autoclaves assembled in by-pass loops of CANDU 6 reactor PHTS Cernavoda Unit#1 This paper presents the results obtained by in-situ monitoring of PHWR water chemistry effect on fuel cladding corrosion, Zircaloy-4.

The optical metallographic and scanning electron microscopies, as well as XRD analysis have been used to evaluate the corrosion behaviour of the fuel cladding material, Zircaloy-4 coupons exposed in PHTS autoclaves system. The obtained results allowed us to establish the contribution of the water chemistry on the Zircaloy-4 corrosion behaviour.

1. INTRODUCTION

Precipitation of crud deposits in the core has to be avoided as far as possible, as it can lead to fouling of the fuel, loss of heat transfer efficiency, fuel failures, increased radiation fields and to neutronic disturbances in the core, [1–4]. The deposition rate on surfaces is controlled by the concentration of impurities in the coolant, the pH of the water and the surface temperature. In order to prevent cladding failures, the coolant chemistry has to be monitored and controlled in order to reduce the amount of deposited crud and oxygen potential [5].

The PHT System from Cernavoda Unit#1 NPP is arranged in two separate loops, which are normally tied together each loop serving 190 fuel channels, and comprises two boilers, two circulating pumps, two reactor inlet headers, two reactor outlet headers and necessary interconnecting piping. Chemical Control and Diagnostic Parameters for steady state operation are summarized in Table 1.

Chemistry control of the PHT System and Auxiliaries is required to:

- minimize the corrosion of system components;
- limit the production rate of radioactive corrosion products;
- minimize the fouling of the heat transfer surfaces by controlling the crud movement and removal;
- maintain heat transport storage tank cover gas deuterium and oxygen concentration below explosive limits.

TABLE 1. CHEMICAL CONTROL AND DIAGNOSTIC PARAMETERS SPECIFICATION

Parameter	Sample Origin	Specification	Desired Value
pH	Main System	10.2-10.8	10.2-10.4
	IX* Outlet	NIA	IX inlet
Dissolved D_2 (ml/kg)	Main System	3-10	7
Chloride (mg/kg)	Main System	≤ 0.2	ALARA **
	IX* Outlet	< IX inlet	ALARA
I-131	Main System	< 500	ALARA
MBq/kg	IX* Outlet	< IX inlet	ALARA
D_2 (%by vol.)	Storage tank cover gas	≤ 2	ALARA
O_2 (% by vol.)	Storage tank cover gas	≤ 1	ALARA
N_2 (% by vol.)	Storage tank cover gas	≤ 6	ALARA
Lithium (mg/kg)	Main System	0.4-1.1	0.5
Conductivity (µS/cm)	Main System	8-25	8-20
Fluoride (mg/kg)	Main System	< 0.1	ALARA
	IX* Outlet	< IX inlet	ALARA
Suspended Solids (mg/kg)	Main System	< 0.1	ALARA
	Gland Seal	< 0.010	ALARA
Total Organic Carbon (mg/kg)	Main System	≤ 1.0	ALARA
Radionuclide Gama Scan MBq/l	Main System	0.1	ALARA
	IX* Outlet	< IX inlet	ALARA

Note: Reproduced courtesy of Cernavoda [6].
* - IX – ions exchanger;
** - ALARA – As Low As Reasonable Achievable.

The above objectives are achieved by:

- controlling pH in the range of 10.1 to 10.4;
- maintaining excess dissolved deuterium in the range of 3^{-10} mL/kg to scavenge oxygen;
- maintaining purity of the PHT heavy water via the purification loop which contains Li^+/OD^- form ion exchange resin;
- purging the heat transport storage tank cover gas when required.

2. EXPERIMENTAL

The process of corrosion products formation on Zircaloy-4 fuel cladding surface and their consequences were evidenced by performing of some experiments in autoclaves circuits assembled in a by-pass loop of a CANDU-6 Reactor at NPP Cernavoda and in laboratory static autoclaves. The corrosion products formation on fuel cladding surface during steady state operation was followed by exposition of Zircaloy-4 coupons in autoclaves circuits assembled in a by-pass loop of CANDU-6 Reactor at NPP Cernavoda. The chemistry conditions for autoclaves circuits were standard conditions for the reactor, which comply with the chemical control and diagnostic parameters for steady state operation of CANDU-6 Reactor, [6]. The corrosion products formation on fuel cladding surface during steady state operation was followed by removal of Zircaloy-4 coupons from autoclaves circuits assembled in a by-pass loop of CANDU-6 Reactor at NPP Cernavoda. The chemistry conditions for autoclaves circuits were standard conditions for the reactor, which comply with the chemical control and diagnostic parameters for steady state operation of CANDU-6 Reactor.

To assist in monitoring and optimization of chemistry control and give warning of serious corrosion and/or activity transport conditions, one Autoclave System flow diagram is provided. The Autoclave System consists of four autoclave circuits, one from the reactor outlet header to the boilers and one from the circulating pump to the reactor inlet header, on each of the two PHT loops, Figure 1 [6].

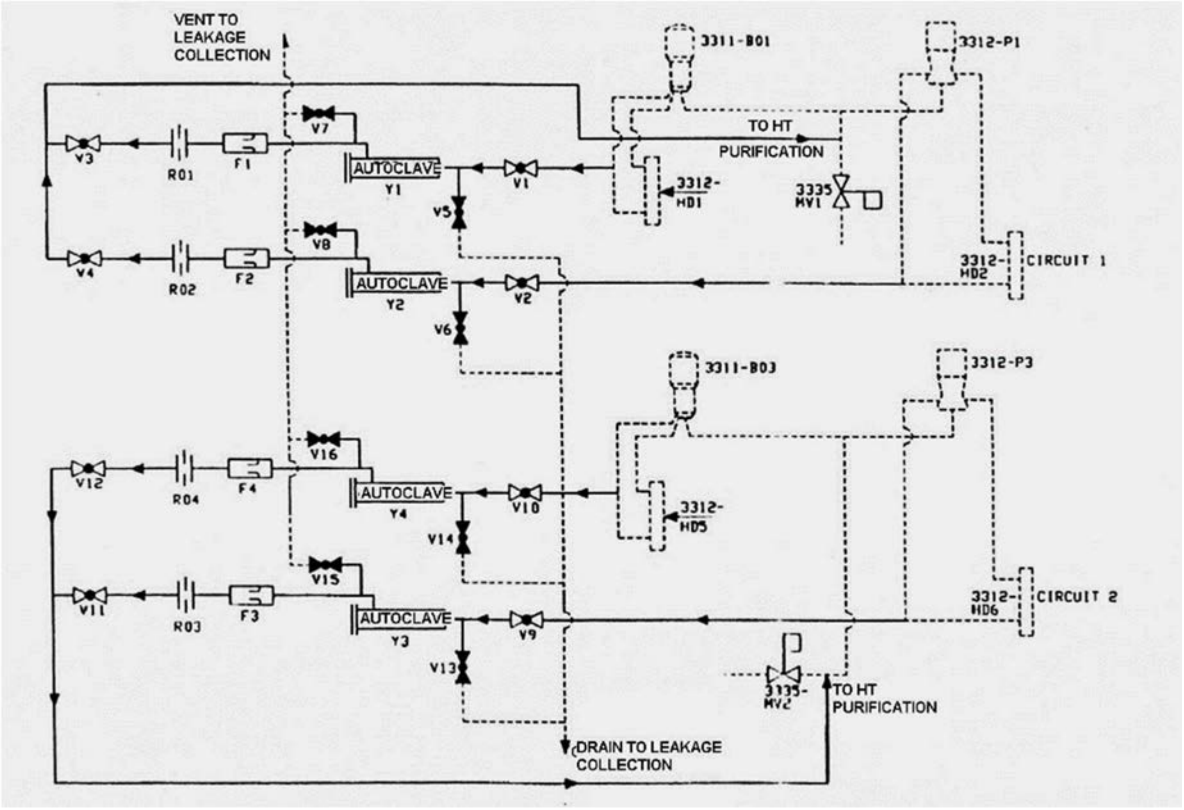

FIG. 1. PHTS autoclave system diagram (Reproduced courtesy of Cernavoda NPP [6]).

In normal operation the restriction orifices need to maintain a flow of approximately 250g*s^{-1} to achieve a flowrate of approximately 4.7 m*s^{-1}. Each autoclave contains six hanger bars, number 1 to 6 (S1-S6).

Standard coupons are 30 mm by 15 mm with a thickness between 1 and 1.5 mm. Coupons are mounted in pairs, with a maximum of 6 pairs or 12 coupons per hanger bar (Fig.2), 72 coupons in all. Each hanger bar (S1 to S6) from the four autoclaves (Y1 to Y4) holds Heat Transport System (HTS) materials as follows: carbon steel ASTM A 106 grade B and ASTM A 516 piping, headers, feeders, heat exchanger shell, stainless steel 403 m (end fittings) and 304 L (tubing of heat exchangers), Zr-2.5% Nb (pressure tube), Incoloy 800 (tubing of steam generators) and Zircaloy-4 (fuel cladding).

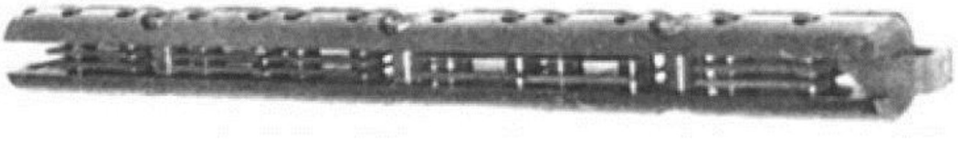

FIG. 2. The coupons hanger bar.

The chemical composition of the coupons from Zircaloy-4 has to meet the ASME chemical composition requirements presented in Table 2.

The corrosion coupons, from Zircaloy-4, used in this work are parallelepiped with dimensions 15 x 10 x 2 mm. The coupons investigated were: Y2 – 77 – exposure time <5 years (approximately 1440 days) and Y3-259 – exposure time> 5 years (approximately 2520 days).Initially, the coupons were passivized in LiOH solution with Na$_2$EDTA (142 hours at 150°C and 47 hours at 260°C) in static autoclaves or during commissioning of the primary circuit of CANDU 6 reactor.

TABLE 2. CHEMICAL COMPOSITION (% MASSIC) OF ZIRCALOY-4 CLADDING (ASME)

Alloy	UNS#	Sn	Fe	Cr	Ni	O [ppm]	Hf [ppm]
Zy-4	R60804	1.2-1.7	0.18-0.24	0.07-0.13	0.03-0.08	1200-1400	100

The destructive examinations included cutting transverse cross-sections of the cladding for metallographic examinations. These examinations were performed to measure the thickness of crud and to evidence the effect of these deposits on fuel rod material corrosion. The quantity of the adherent corrosion products was dependent on thickness and especially physical – chemical characteristics of the initial zirconium oxide films. To evidence this fact, as well as the impact of corrosive deposit on Zircaloy-4 alloy oxidation and hydriding, many laboratory experiments were performed in static autoclaves at different temperature on Zircaloy-4 coupons, used in PHWR systems [7].

Analysis of the corrosive deposits, oxidation and hydriding of Zircaloy-4 alloy were performed using gravimetric analysis, metallographic and electronic microscopy examinations and X-Ray Diffraction analysis.

3. RESULTS AND DISCUSSION

Corrosive deposits formed on fuel claddings during steady state operation of CANDU reactor is presented in Figure 3.

FIG. 3. The aspect of coupons observed by visual examination.

The surfaces of the coupons were examined visually at low magnification or with a magnifying glass with 12X magnification to identify any defects due to corrosion. This analysis makes a first estimate on the state of the surfaces of the different components in the boiler.

At the visual examination of the coupons in Zy-4, no differences were found between the two coupons in terms of the surfaces of the formed oxides. The coupons have no visible pores or cracks on the surface.

Both coupons have the surface completely covered with a glossy black oxide. The oxide that forms on the zirconium alloys has a white colour if the oxide is stoichiometric ZrO2, and the colour black or grey is specific to a non-stoichiometric oxide ZrO2-x, adherent, protective. It is expected that the oxide layer will have a small thickness, be uniform. The values of crud thus obtained are in agreement with the theories that explain the mechanism of generation of corrosion products in CANDU reactors with carbon steel feeders. The coupons from inlet reactor autoclaves (2600oC) have larger deposits since the coolant is probably still supersaturated in iron respect the solubility value and present a larger percentage (60%) of adherent crud deposited on the surface. The coupons inserted in outlet reactor autoclaves (3100) show smaller values of total deposits and a smaller percentage of adherent crud (30%), this difference can be attributed to the presence of particulate matter that is formed by erosion of crystals recently precipitated.

3.1. Morphology of Zircaloy-4 coupons

- Coupon Y2-77, <5 years, Figure 4 (x200): adherent, glossy, black film with pink irises;
- Coupon Y3-259, >5 years, Figure 5 (x200): film adherent, glossy, black with dark grey.

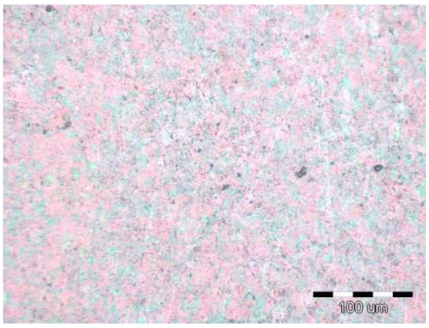

FIG.4. Zy-4_Y2-77_<5 years_x200.

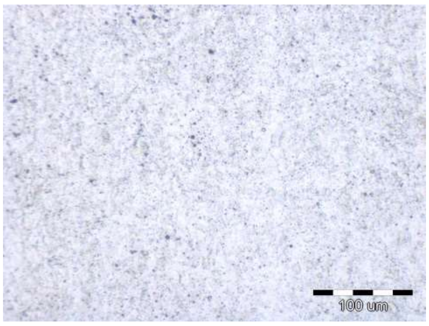

FIG.5. Zy-4_Y3-259_>5 years_x200.

3.2. Thickness layer

The layer thickness measurement was performed automatically, at various magnifications (x200 – x1000), using the "autoSYS auto" analysis program of the OLYMPUS GX71 microscope. In Table 3 the thickness of the oxide layer is presented, and in Figure 6 and Figure 7 the aspect of oxide layer for each coupon analyzed.

TABLE 3. THE THICKNESS OF THE OXIDE LAYER

Zy-4	Y2-77	< 5 years	1.4-2.4µm	1.8µm
	Y3-259	> 5 years	2.3-3.3µm	2.6µm

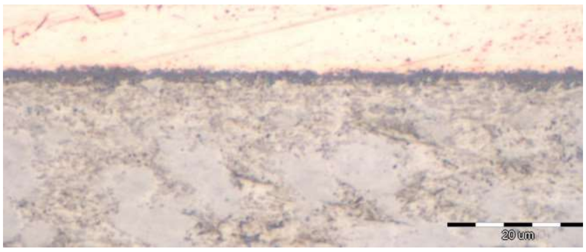

FIG.6. Zy-4 Y2-77 1.4-2.4 µm.

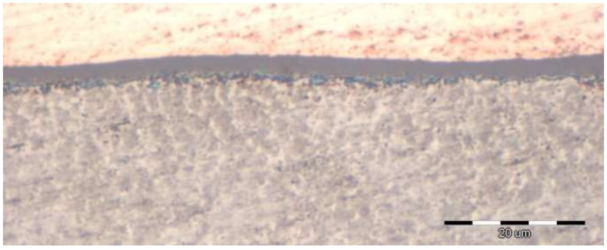

FIG.7. Zy-4 Y3-259 2.6 µm.

Zy-4: the oxide layer on the Y3-259 coupon (autoclaved over 5 years, Figure 7) is about 1.5 times thicker than the one on the Y2-77 coupon (autoclaved under 5 years, Figure 6). The microstructure survey was performed with the aid of specific reagents for each material, as follows: chemical attack 45% nitric acid, 45% water, 10% hydrofluoric acid; 7-12 seconds.

3.3. Microstructure of Zy-4 coupons

Control sample (as received) and Zy-4 coupons: Zirconium alpha hydrides (αZr):

- Figure 8 (x100) and Figure 9 (x200) – control of Zy-4 (sheath): hydrides;
- Figure 10 (x100) and Figure 11 (x200) – coupon Y2-77, <5 years: hydrides;
- Figure 12 (x100) and Figure 13 (x200) – coupon Y3-259, > 5 years: hydrides.

FIG.8. Zy-4 as-received: hydrides, x100.

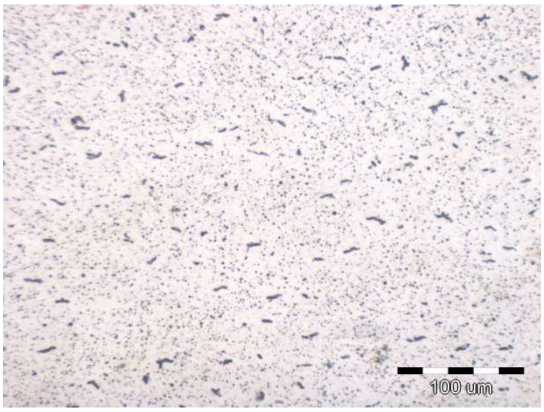

FIG.9. Zy-4 as-received: hydrides, x200.

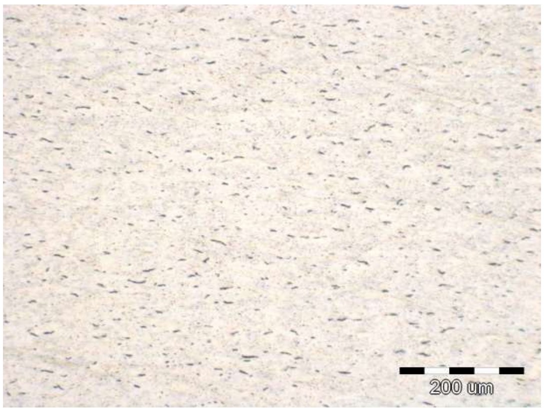

FIG.10. Zy-4_Y2-77: hydrides, x100.

FIG.11. Zy-4_Y2-77: hydrides, x200.

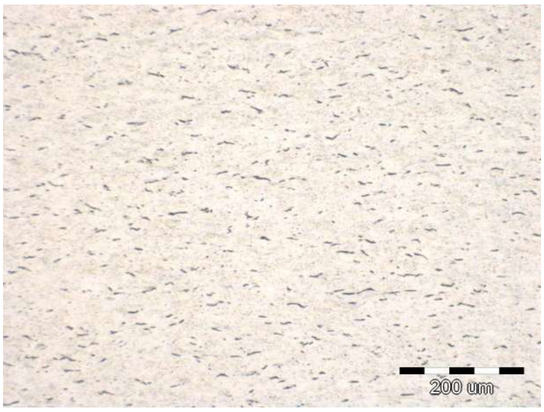

FIG.12. Zy-4 Y3-259: hydrides, x100.

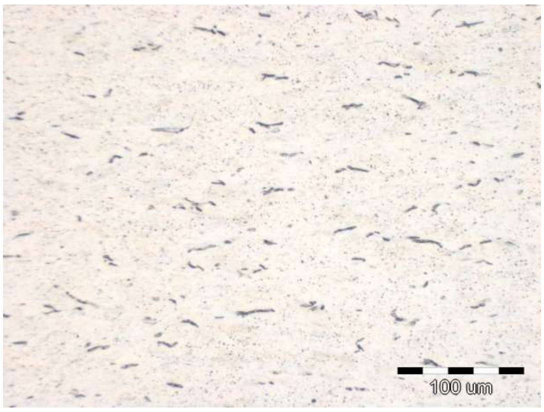

FIG.13. Zy-4 Y3-259: hydrides, x200.

3.4. X-Rays diffraction

In the case of the Zircaloy-4 alloy, only the coupon Y3-259 was investigated, on the S6 support, exposed over 5 years in the Y3 autoclave (circuit 2 – from the circulation pump to the reactor entrance). The compounds identified on coupon Y3-259 of Zircaloy-4, in the sample volume analyzed, are given in Table 4.

It was observed that the highest weight (65%) has the monoclinic form of zirconium dioxide. The tetragonal and cubic forms of zirconium dioxide appear with very little weight in the sample volume analyzed (4% and 3% respectively). In contrast, the cubic form of zirconium oxide is present in an amount of about 11%. Also, the hexagonal and rhombohedral forms of Zr_3O oxide were highlighted.

TABLE 4. COMPOUNDS IDENTIFIED ON ZY-4 COUPONS

Chemical formula	Crystallization system	Semi Quant [%]
Zr	hexagonal	7
ZrO_2	monoclinic	17
ZrO_2	cubic	3
ZrO	cubic	11
Zr_3O	hexagonal	6
ZrO_2	monoclinic	24
$Zr_{0.936}O_2$	monoclinic	24
$ZrO_{1.98}$	tetragonal	4
Zr_3O	rhomboedral	5

On the surface of the Zircaloy-4 coupon, the highest weight is given by the monoclinic form of zirconium dioxide. The tetragonal and cubic forms of zirconium dioxide appear with very little weight in the sample volume analyzed (3-4%). Also, the hexagonal and rhombohedral forms of Zr_3O oxide and the cubic form of zirconium oxide (ZrO) were highlighted, Figure 14.

3.5. Scanning electron microscopy surface oxide analysis

In the case of oxidized samples in the autoclaves of the primary circuit, the analyses were performed on the topographic images, of secondary electrons obtained at a scanning electron microscope of the TESCAN VEGA II LMU type. On scanning electron microscopy the surface of the coupons in Zy-4 – the filler material of the fuel elements, coupon Y2-77 (subject to the corrosion conditions specific to the cooling agent in one of the loops and whose exposure period was less than 5 years) by scanning electron microscopy at x1000 magnification, Figure 15, showed that the formed oxide is protective, does not show cracks, exfoliation or other surface defects. Throughout the surface of the coupon, pores smaller than 1 micron are observed that form in or under the thin layer of oxide.

In Figure 15 and Figure 16, dark – coloured deposits are observed on the surface of the oxide – identified – by X-ray spectroscopy methods with energy dispersion – as carbon) and very fine crystallites, nanometric present on the surface. The small crystallites present on the surface are atypical for zirconium oxides, they can come from the primary circuit by washing the oxides of other materials and subsequently fixing them on this coupon. Figure 16 shows pores open on the surface, but there are also many pores of very small, nanometric dimensions, formed under the internal oxide substrate which is thin.

3.6. Analysis of oxide layers

The images of scattered electrons taken in cross section on the Y2-77 coupon from Zircaloy-4, Figure 17, show the presence of a very small oxide layer and the metal oxide interface is slightly corrugated, [8].

In the case of coupon Y3-259 from Zircaloy-4, Figure 18 it was also noted that the oxide has a small thickness and the metal-oxide interface is slightly wavy. Very rarely, on the surface of zirconium oxide, there are deposited oxide particles brought by the cooling agent on the investigated coupon from other regions.

3.7. X-ray spectroscopy with energy dispersion (EDS)

Regarding the Zy-4 zirconium alloy, the surface deposits were examined and from the cartographic images it was found that the dark coloured deposits, Figure 19 and Figure 20, are carbon, and the crystallites present on the surface are iron oxides transported by the primary agent and brought on the zirconium alloy coupons.

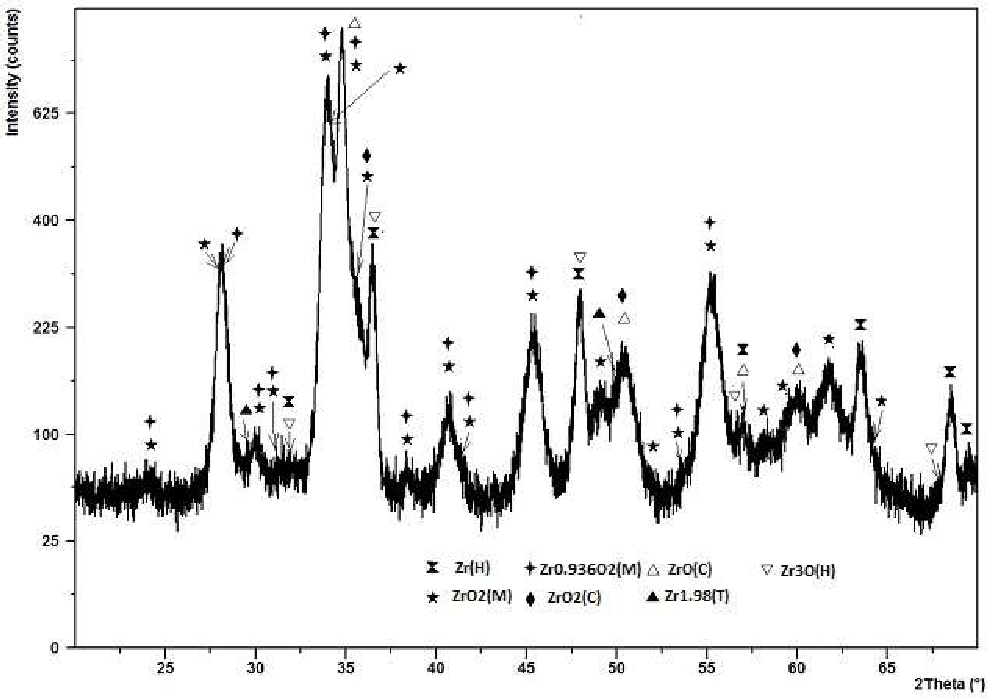

FIG. 14. Diffraction spectrum corresponding to coupon 259, exposed on the support S6 of autoclave Y3 – circuit 2 (from circulation pump to reactor inlet).

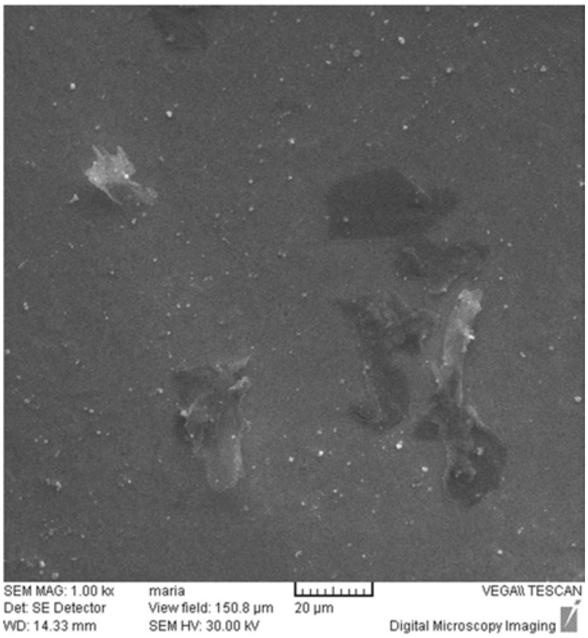

FIG.15. Surface of Zy-4 formed oxides (Y2-77).

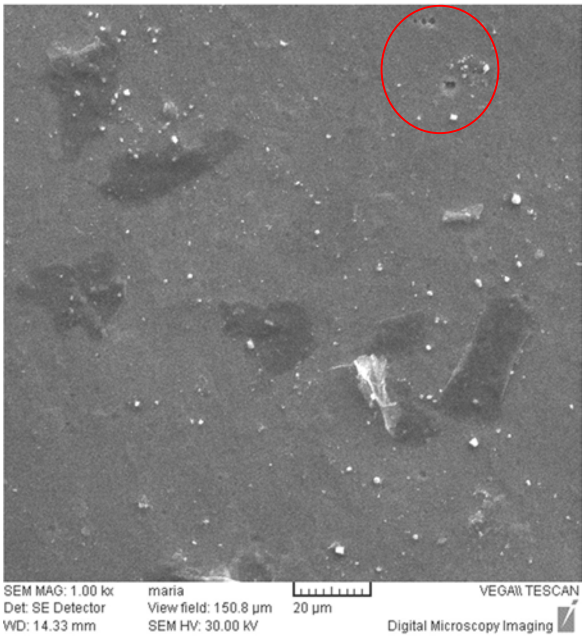

FIG.16. Pores present on Zy-4 (Y2-77).

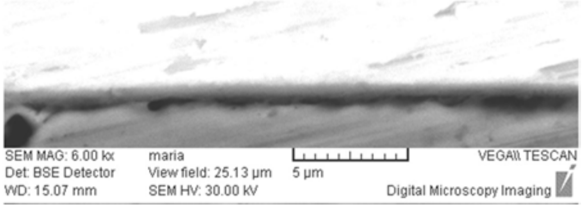

FIG. 17. Oxide layer on Zy-4 sample Y2-77.

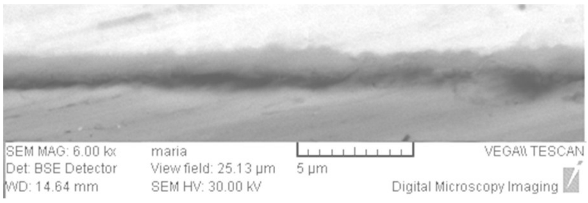

FIG. 18. Oxide layer on Zy-4 sample Y3-259.

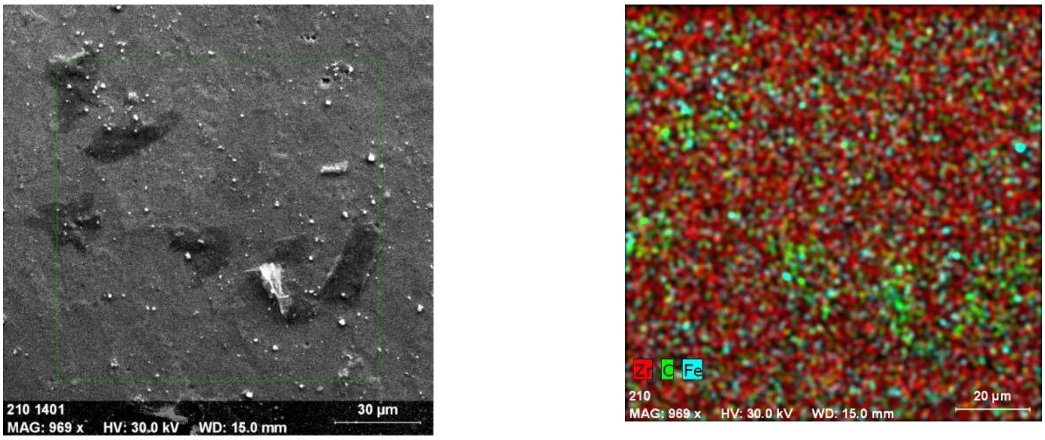

FIG. 19. SEM image and EDS mapping of Fe, Zr, C on Zircaloy-4 sample – Y2-77.

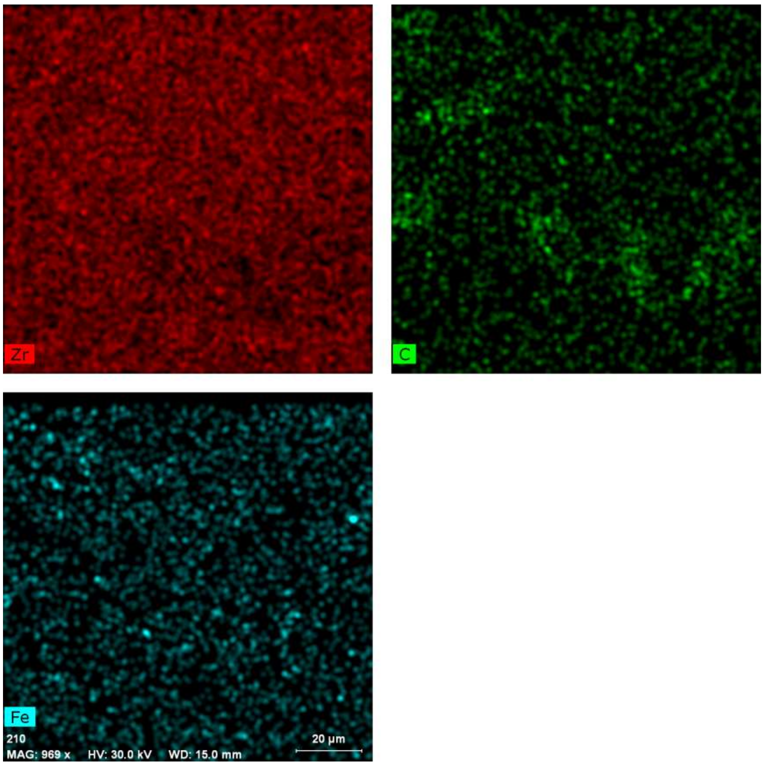

FIG. 20. Elemental cartographies Fe, Zr, C on Zircaloy-4 sample Y2-77.

4. CONCLUSIONS

During steady state operation of CANDU reactor with chemistry standard conditions, black and adherent magnetite crystallites, produced by carbon steel feeder's corrosion, have precipitated from primary coolant on Zircaloy-4 coupons surface. Presence of these corrosion deposits on surface did not influence oxidation and hydriding of Zircaloy-4 alloy.

The oxide layer on the coupon exposed over 5 years is about 1.5 times thicker than the coupon exposed under 5 years.

Microstructure of Zy-4 coupons: the control sample (tube) and the tested have numerous hydrides per zirconium alpha structure (αZr).

Coupon exposed over 5 years the highest weight is monoclinic form of zirconium dioxide (65%). The tetragonal and cubic forms of zirconium dioxide appear with a very small weight in the sample volume analyzed (4% and 3% respectively). The cubic form of zirconium oxide is present in about 11%. Also, the hexagonal and rhombohedral forms of Zr_3O oxide were highlighted.

The oxides formed on Zy-4 are in the form of adhesive and protective film both after an operating time of less than 5 years. At longer exposure times (over 5 years), the coupons contain slightly thicker oxides and at the metal oxide interface very fine pores are formed. This was observed on the available coupons that were observed and that there are deep traces on which iron and nickel oxides were fixed, which were transported in the autoclave. EDS analysis showed the presence of nickel and silica iron among the crystallites present on the surface, but also the presence of carbon deposits.

Corrosive deposits formed in normal water chemistry conditions did not influence oxidation and hydriding of cladding material. The corrosion rate was about $0.276 \div 0.313 \mu m/dm^2 day$ and metallographic examination evidenced presence of uniform zirconium oxide, having a thickness of 2-3μm and accelerated hydriding did not happen after approximately 2160 operation days. Morphology of hydrides was similarly with that of coupons tested in identical conditions from out reactor experiments.

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DISSOLVED DEUTERIUM CONTROL IN THE PRIMARY COOLANT IN ONTARIO POWER GENERATION CANDU UNITS

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Abstract

The heavy water coolant in the CANDU Heat Transport System (HTS) can undergo radiolysis to produce deuterium and oxygen. The presence of dissolved oxygen in the HTS is undesirable as one of the major materials of construction in the CANDU HTS is carbon steel. In order to suppress water radiolysis and minimize the dissolved oxygen concentration controlled amounts of H_2 gas are added to the coolant. This added H_2 undergoes rapid isotopic exchange in the D_2O coolant, so the as-measured species is dissolved D_2. It is important to implement a specification range for the dissolve deuterium concentration in the HTS to minimize adverse impact on the system needs to the dissolved deuterium be too high or too low.

The rationale for the dissolved deuterium specification regime applied in the Heat Transport System in Ontario Power Generation (OPG) CANDU units is presented. There is discussion on the revision to the dissolved deuterium specification based on information from operating experience and technical assessments. Trending of operational dissolved deuterium data from OPG CANDU units is used to validate the suitability of the implemented specification regime.

1. INTRODUCTION

The Heat Transport System (HTS) in a CANDU reactor is the primary circuit of the reactor, using heavy water as the coolant. This system consists of the fuel channels, the inlet and outlet headers and feeders and the steam generator tubes. While the materials for the fuel channels (zirconium alloy) and inlet and outlet headers and feeders (carbon steel) are the same for all Ontario Power Generation nuclear units, the steam generator tubing materials are not. The steam generators in Pickering Nuclear Generating Station (NGS) have Monel-400 tubing, while the steam generators in the Darlington NGS have Incoloy-800 tubing.

In the HTS, the heavy water can undergo radiolysis to form deuterium, oxygen and deuterium peroxide through the following overall reactions [1]:

$$\begin{aligned} D_2O &\rightsquigarrow D_2 + ½\, O_2 \\ D_2O &\rightsquigarrow ½\, D_2 + ½\, D_2O_2 \end{aligned} \tag{1}$$

D_2O_2 is very short-lived at coolant operating temperatures (249 to 310°C), with a half-life of about 0.2 seconds [2]. Any influence of the radiogenic deuterium peroxide is therefore largely confined to the in-core portion of the fuel channels and a short length of the carbon steel outlet feeders.

The radiolytic oxygen is of course more stable and can contribute to corrosion of the carbon steel components in the system. Corrosion product transport in the CANDU coolant is dominated by iron (magnetite), so chemistry control in the CANDU Primary Heat Transport Systems aims to minimize carbon steel corrosion and magnetite transport and deposition. Cobalt (Co-59) is present in trace amounts in carbon steels and steam generator tubing and at high levels, in the form of Stellite, in some valve hard-facing alloys and fuelling machine ram balls. Hence, in CANDU units Co-60 is a large contributor to radiation fields and occupational dose. In the HTS that Co-60 is associated with and incorporated into the magnetite, so control of carbon steel corrosion is largely synonymous with Co-60 control.

Owing to the design of the CANDU HTS and sampling systems it is difficult to directly measure dissolved oxygen concentrations in the coolant. Thus, the common approach in the CANDU community is to limit dissolved oxygen levels in the coolant by ensuring sufficient dissolved D_2 is present to suppress the formation of radiolytic O_2. This is done through gaseous hydrogen addition to the HTS. That added H_2 undergoes rapid isotopic exchange with the D_2O coolant, so the as-analyzed species is dissolved D_2. The introduction of protium through H_2 addition results in some low, manageable downgrading of the D_2O coolant. By increasing the concentration of dissolved deuterium in the HTS, the radiolytic formation of deuterium peroxide and oxygen is suppressed and there is no net decomposition of water [1].

The concentration at which radiolytic O_2 production is suppressed is denoted the Critical Hydrogen or Critical Deuterium Concentration (CHC/CDC) and is illustrated above and discussed in more detail below. This maintains reducing conditions in the HTS and suppresses water radiolysis.

2. DISSOLVED DEUTERIUM SPECIFICATION IN THE HEAT TRANSPORT SYSTEM

Control of the dissolved deuterium concentration in the CANDU primary coolant is aimed at limiting degradation of the major components: Zr-2.5%Nb pressure tubes, carbon steel feeders and headers and the steam generator tubing.

The lower dissolved deuterium specification limit is set based on the CDC [3]. The CDC is the minimum amount of dissolved deuterium required to suppress the radiolytic formation of oxygen and deuterium peroxide, as illustrated schematically in Figure 1.

Operation with dissolved D2 concentrations above the CDC maintains reducing conditions in the bulk coolant and suppresses water radiolysis. At dissolved D_2 concentrations below the CDC the risk of pressure tube hydriding and carbon steel corrosion increases. The CDC can vary from unit-to-unit and for CANDU plants varies from about 0.7 to 1.3 mL/kg for non-boiling fuel channels. To account for the potential for some localized in-core boiling the lower dissolved D_2 limit was set to 3 mL/kg.

The higher dissolved deuterium specification is set based on the concerns for cracking of the dissimilar metal welds present in the HTS system [3]. There is also the concern that high dissolved deuterium concentrations in the coolant could contribute to increased potential of hydriding of the Zr-Nb pressure tubes due to hydrogen/deuterium uptake.

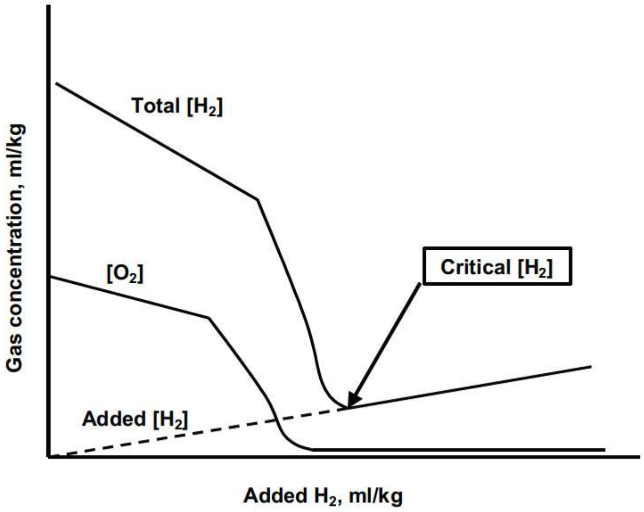

FIG. 1. Stylized Representation of the Critical Hydrogen or Critical Deuterium Concentration Concept.

Based on the above rationale, the HTS dissolved deuterium specification range of 3 to 10 mL/kg was implemented at Pickering and Darlington NGS; the lower specification range set to address CDC concerns and while the higher specification range set to address hydriding concerns. However, additional operational experience and research and development findings have resulted in the revision and refinement of the dissolved deuterium specification range that is more tailored to each station’s needs. This is reflected in the change in the upper dissolved deuterium specification at Darlington from 2015 onwards, which was revised to 17 mL/kg. These changes are summarized in Table 1.

As mentioned previously, the steam generator tubing materials are different in the OPG nuclear stations. This difference in materials can have a significant impact on the dissolved deuterium behaviour in the HTS. Monel-400 steam generator tubing is very permeable to hydrogen. It was assessed that as much as 80% of the hydrogen added to the HTS can be lost via permeation through the steam generator tubes in the Pickering HTS, and that high rates of hydrogen addition are needed to maintain the dissolved deuterium specification [4]. Incidentally, tritium permeation through the steam generator tubing accounts for the inevitable presence of low levels of tritium in the secondary (light water) system, even in the absence of steam generator tube leaks.

TABLE 1. HEAT TRANSPORT SYSTEM DISSOLVED DEUTERIUM SPECIFICATION FOR ONTARIO POWER GENERATION NUCLEAR UNITS

Period	Dissolved Deuterium (mL/kg @STP)*	
	Pickering Units	Darlington Units
In-service to 2015	3 to 10	3 to 10
2015 to 2019	3 to 10	3 to 17

* reference to standard temperature and pressure

The Incoloy-800 steam generator tubes at Darlington are about an order of magnitude less permeable to H_2/D_2 than Monel-400. Thus, the Darlington HTS, unlike the Pickering HTS, do not require continuous hydrogen addition during normal operation to maintain dissolved deuterium within specification. In practice, during normal operation, dissolved deuterium has a tendency to increase in the Darlington coolant, requiring periodic degassing to prevent deuterium build-up to undesirable levels; this has the undesirable effects of increasing helium consumption (used as the purge gas), thermal penalties (incurred since an increased fraction of the coolant is cooled and degassed through the inventory control system) and increased demand on station operational resources. Operating experience at other CANDU stations that have Incoloy-800 steam generator tubes indicate that a natural steady state concentration of dissolved deuterium in the coolant may be achievable, whereby hydrogen additions and degassing of the HTS may be required only infrequently [5].

The lower permeability of the Incoloy-800 steam generator tubing compared to Monel-400 is reflected in the difference between main steam tritium activities at the two sites; the average main steam H^{-3} at Darlington (Incoloy-800) is 0.14 μCi/kg for a primary coolant tritium level averaging 0.84 Ci/kg, while at Pickering (Monel-400) the main steam tritium averages about 6 μCi/kg for a primary coolant tritium level averaging 1.3 Ci/kg.

As a result of the field operating experience, a trial was implemented in a Darlington unit to optimize HTS dissolved deuterium control in 2013. During the trial, the dissolved deuterium upper specification limit was increased from 10 mL/kg to 17 mL/kg for a period of nine months to assess the impact of this change. The dissolved deuterium lower specification limit remains unchanged at 3 mL/kg. Prior to the trial, technical assessments were performed to ensure that an increase in the dissolved deuterium upper specification limit would have no adverse impact on the HTS materials, e.g. no negative impact on the hydrogen/deuterium uptake by the pressure tubes [6,7]. Research results have shown that the principal cause of hydrogen/deuterium uptake in zirconium alloys under CANDU conditions is due to atomic H/D from corrosion, and not from dissolved molecular deuterium in the coolant [3].

During the 2013 trial, the dissolved deuterium concentration in the coolant was, as expected, higher than the historical average concentration, but well within the specification range. The dissolved deuterium concentration in the coolant also appeared to approach a natural steady-state level with a four-fold reduction in the degassing frequency [8].

After the trial, an independent third party review was performed to assess the impact of long-term operation with higher dissolved deuterium concentrations. The report confirmed that there was no increased propensity for cracking of dissimilar metal welds or H/D pick-up when operating at the higher dissolved deuterium specification regime [9]. This conclusion, combined with the successful results from the field trial, lead to the revision in the dissolved deuterium upper specification limit for the Darlington HTS in 2015 [8]. The dissolved deuterium specification range for the Pickering HTS remain unchanged, due to the high permeability of hydrogen through the Monel-400 steam generator tubes.

3. DISSOLVED DEUTERIUM BEHAVIOUR IN THE PICKERING CANDU UNITS

From Table 1, the HTS dissolved deuterium specification range for the Pickering units is from 3 to 10 mL/kg. Table 2 shows the trending of the dissolved deuterium measurements for the six operating Pickering units from 2005 to 2019.

TABLE 2. HEAT TRANSPORT SYSTEM DISSOLVED D2 RESULTS FOR PICKERING NUCLEAR GENERATING STATION NUCLEAR UNITS: 2005 TO 2019

Heat Transport Dissolved D_2 (mL/kg) 2005 to 2019						
Parameter	Unit 1	Unit 4	Unit 5	Unit 6	Unit 7	Unit 8
Average	6.5	6.7	6.7	6.6	6.9	6.6
Median	6.3	6.5	6.5	6.4	6.6	6.4
σ	2.0	1.8	1.8	1.7	2.2	2.1

From the data presented in Table 2, it can be seen that there is good control of the HTS dissolved deuterium in the Pickering units. All operating units at Pickering NGS show similar average and median concentrations, and similar standard deviation. The average dissolved deuterium concentration for the six units ranged from 6.5 to 6.9 mL/kg over this period and is comparable with the median concentration for the six units, which range from 6.3 to 6.6 mL/kg. Both the average and the median concentration falls well within the specification range of 3 to 10 mL/kg.

4. DISSOLVED DEUTERIUM BEHAVIOUR IN THE DARLINGTON CANDU UNITS

The HTS dissolved deuterium specification range for the Darlington units was set at 3 to 10 mL/kg from 2005 to 2015. The specification range for the dissolved deuterium in the Darlington HTS was revised to 3 to 17 mL/kg from 2015 onwards (see Section 2.0). Table 3 shows the trending of the dissolved deuterium measurements for all the Darlington units from 2005 to 2015 while Table 4 shows the trending from 2015 to 2019.

TABLE 3. HEAT TRANSPORT SYSTEM DISSOLVED D_2 RESULTS FOR DARLINGTON NUCLEAR GENERATING STATION NUCLEAR UNITS: 2005 TO 2015 (I.E. 3 TO 10 ML/KG CONTROL RANGE)

Heat Transport Dissolved D_2 (mL/kg) 2005 to 2015				
Parameter	Unit 1	Unit 2	Unit 3	Unit 4
Average	5.7	6.4	6.4	6.5
Median	5.6	6.4	6.4	6.6
σ	1.2	1.1	1.1	1.3

Table 3 shows that when the Darlington units operated under the specification regime of 3 to 10 mL/kg, the behaviour of the Darlington HTS dissolve deuterium is similar to that of the Pickering units. The average and median dissolved deuterium measurements in Darlington Units 2 to 4 range from 6.4 to 6.5 mL/kg and 6.4 to 6.6 mL/kg, respectively. The dissolved deuterium concentrations are lower in Unit 1 compared to the other three units, with the average concentration at 5.7 mL/kg and the median concentration at 5.6 mL/kg. The standard deviation for the Darlington data is lower than that of the Pickering data. This is likely due to the much lower hydrogen permeation rate through the steam generator tubes, and thus results in better dissolved deuterium control in the Darlington HTS.

Table 4 summarizes the HTS dissolved deuterium behaviour at Darlington NGS from 2015 onwards, with the revised dissolved deuterium specification regime of 3 to 17 mL/kg. From Table 4, it can be seen that with the increase in the upper specification limit, the Darlington units achieved steady state dissolved deuterium concentration with a reduction in the need for active hydrogen control (i.e. decrease in the number of hydrogen addition and HTS degassing events), as hypothesized and supported by operating experience at other CANDU stations with Incoloy-800 steam generator tubes. The steady state concentration appears to be unit specific.

TABLE 4. HEAT TRANSPORT SYSTEM DISSOLVED D2 RESULTS FOR DARLINGTON NUCLEAR GENERATING STATION NUCLEAR UNITS: 2015 TO 2019 (I.E. 3 TO 17 ML/KG CONTROL RANGE)

	Heat Transport Dissolved D_2 (mL/kg) 2015 to 2019			
Parameter	Unit 1	Unit 2	Unit 3	Unit 4
Average	9.1	10.7	8.8	11.0
Median	9.1	10.9	8.7	11.3
σ	2.3	2.1	2.6	2.3

*Data for Darlington Unit 2 is only available up to October 2016 due to refurbishment work.

The average (i.e. steady state) concentration achieved (from 8.8 to 11 mL/kg) under the revised specification regime is higher than the average concentration achieved (from 5.7 to 6.5 mL/kg) under the previous specification regime. The difference in the steady state values between the different units also indicate that the steady state dissolved deuterium concentration might be unit specific. The median concentration is comparable to the average concentration for the Darlington units. The standard deviation for the revised specification regime are higher compared to that seen under the previous specification regime; however, this is expected as the specification range has increased by 70%, which allow for larger variation in the operating dissolved deuterium concentration. It is noted that the standard deviation in the Darlington HTS under the revised specification regime is comparable to the standard deviation seen in the Pickering HTS.

5. CONCLUSIONS

The rationale for dissolved deuterium control in the CANDU reactor Heat Transport System was presented. Data trending was performed for dissolved deuterium control at Ontario Power Generation nuclear stations: Pickering NGS and Darlington NGS. The presented data shows that there is successful control of the HTS dissolve deuterium concentration within the designated control range.

For HTS with Incoloy-800 steam generator tubes, which have low deuterium permeability, a steady state dissolved deuterium concentration can be achieved without the need for frequent hydrogen addition and HTS degassing. This is not the case for the HTS with Monel-400 steam generator tubes. It is not possible to obtain a steady state dissolved deuterium concentration in this type of system due to high hydrogen permeability through the Monel-400 material; for this system, frequent hydrogen addition has to be performed to maintain the dissolved deuterium specification range.

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TECHNOLOGICAL OPINION AND CORRESPONDING OBSERVATIONS ON CORROSION PHENOMENA

(Session II)

Chairperson

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EFFECTS OF OXIDE DISSOLUTION ON MATERIAL TRANSPORT IN REACTOR COOLANT SYSTEMS

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Abstract

The transport of corrosion products around primary coolants continues to hamper reactor operation and maintenance. The deposition on fuel of oxides and their distribution around the circuit can create fouling and radiation problems, depending on the variety of materials and the chemistry control of the coolant. The material distribution is often modelled on the basis of oxide production from corrosion, the differences in its solubility around the circuit caused by temperature gradients, and the coupled transport of particles. While reasonable agreement with observation is often achieved, the inclusion of subtler mechanisms can lead to more precise predictions. In particular, for PHWRs, the relatively high corrosion rate of the large surface area of carbon steel in the primary coolant circuit makes magnetite the predominant corrosion product; this inverse spinel oxide has dissolution kinetics that control its movement. The mechanism is similar to that which has been shown to control flow-accelerated corrosion at the lower temperatures in power plant feed-water systems. This paper describes laboratory experiments designed to measure the dissolution of corrosion product oxides at system conditions and shows how the results form the basis of models for activity transport.

1. INTRODUCTION

Early attempts to model the transport of material in reactor coolant systems were aimed at predicting radiation-field build-up ("activity transport") and relied upon phenomenological descriptions of the individual processes between nodes in the circuit. The expressions were coupled with mass balances to create a series of equations with coefficients and concentration driving forces [1] which were solved simultaneously after several assumptions about quantities such as "corrosion product release rate" were made. Before digital computers, complex systems required ingenious mathematical routines for solution [2]. As more reactors came on-line and as radiation fields around components increased with time after start-up, utilities instituted programs to address increasing occupational doses and the industry in general began to research the problem in earnest. Early innovations in modelling involved the introduction of physical and chemical mechanisms to replace phenomenological descriptions, and it became clear that corrosion and the development of corrosion-product films on circuit materials were key processes [3]. System models based on differences in solubility of oxides around the circuit and dependent corrosion rates produced reasonable values of average corrosion-product loading [4] while more detailed modelling resulted in complex codes; for PWRs, for example, the French PACTOLE and PROFIP merged into the extant OSCAR code [5] and Westinghouse with support from the Electric Power Research Institute developed BOA [6] to account for crud-induced power shifts (CIPS – formerly known as AOA or axial-offset anomaly).

For PHWRs such as CANDUs, the constant chemistry of the primary coolant during reactor operation, with $pH_{apparent}$ (the reading in D_2O solutions of a light-water-calibrated pH meter) kept high at 10.6 or so with dissolved lithium and reducing conditions maintained with dissolved hydrogen at about 6 cm3/kg, has made modelling material transport relatively straightforward. Major input terms to the coolant system are from the corrosion of the carbon steel feeders and headers and the nickel-alloy steam generator tubes, while major output terms are the deposition on surfaces and the removal by the purification system. Other, but intermittent, terms to be taken into account for detailed modelling are input of species such as cobalt from the fuelling machines and wear surfaces, which gives rise to Co-60, and output of corrosion products deposited on discharged fuel bundles [7].

This paper considers the formation of magnetite as the predominant corrosion product in CANDU and its input from the feeders and headers to the primary coolant. That input is controlled by the basic mechanism of flow-accelerated corrosion (FAC) of carbon steel, which involves the dissolution of its corrosion product, magnetite, under the coolant chemistry and high-flow conditions at the core outlet.

2. FEEDER CORROSION

During PHWR operation the inlet and outlet feeders experience very high flow rates with Reynolds numbers of the order of 106. The core inlet temperature of the CANDU-6 is nominally 265°C and the outlet is 310°C and under the chemistry of the coolant the corrosion product on the carbon steel is magnetite, Fe_3O_4. This is formed at the metal-oxide interface, M-O, by (using the analogous reactions in H_2O in place of D_2O):

The anodic reaction:

$$Fe = Fe^{2+} + 2e^- \tag{1}$$

and the balancing cathodic reaction:

$$e^- + H_2O = OH^- + H \tag{2}$$

The hydrogen atoms diffuse into the metal and are discharged as H2 molecules at the outside of the pressure boundary while half of the formed $Fe(OH)_2$ from reactions …1 and …2 precipitates as magnetite via the Schikorr reaction:

$$3Fe(OH)_2 = Fe_3O_4 + 2H_2O + H_2 \tag{3}$$

These hydrogen molecules and the other half of the $Fe(OH)_2$ (which is dissolved) diffuse to the solution/oxide interface, S/O, where the Schikorr reaction normally precipitates magnetite and forms more H_2, which escapes to the coolant. The magnetite film is then the well-known "Potter-Mann" double layer, with fine-grained crystallites of tens of nanometre size overlaid with octahedral crystallites of size up to ten micrometres or so [8]. This is the magnetite morphology at the core inlet, where the coolant is saturated in dissolved iron after its temperature drop in the steam generators. At the core outlet, however, the coolant is undersaturated in iron after its heating in the core, so the outer magnetite layer does not form and the otherwise inner layer dissolves at the S/O by the reverse of Equation 3. The removal of dissolved iron from the surface is promoted by mass transfer and at the same time loosened crystallites or particles of magnetite are removed by fluid forces at the surface, so turbulence is a major factor in thinning the film and making it less protective. These are the basic processes of flow-accelerated corrosion. Figure 1 shows the surfaces of carbon steel specimens exposed to iron-saturated and to iron-undersaturated coolant, the former showing typical Potter-Mann magnetite and the latter showing the oxide resulting from FAC as found under power-plant feedwater conditions. The oxide formed by FAC is thin enough to reveal the grain structure of the underlying steel, with the magnetite over the pearlite grains being coarser and more porous than that over the ferrite grains. Flow-accelerated corrosion under

CANDU primary coolant conditions also generates a single magnetite layer composed of crystallites/particles of size 20-50 nm (at least under laboratory conditions – see Figure 2). The general appearance of an outlet feeder from the Point Lepreau CANDU is shown in Figure 3, which illustrates the typical scalloping or sculpting of the surface produced by FAC. The mechanism of formation of scallops is not fully understood, but it apparently depends on the characteristics of the fluid turbulence with some influence of the grain structure of the metal [12].

3. MAGNETITE DISSOLUTION AND FAC OF OUTLET FEEDERS

FAC is controlled by the protectiveness of the oxide film. As shown in Figure 4, the film grows at the M-O and dissolves and degrades at the S-O, reaching a steady state when the release of iron from the magnetite equals the FAC rate and the oxide thickness (more precisely, the oxide protectiveness) is constant. The concept has been modelled in terms of the magnetite film developing and dissolving, as mass transfer removes the dissolved material to the bulk flow and magnetite particles at the S-O are loosened by dissolution and removed to the bulk flow at intervals determined by their size and fluid forces at the surface. Of the processes shown in Figure 4, those numbered 1, 2, 4 and 5 depend on electrochemical potential, and this is evaluated at every step of the computation along with effects of dissolved hydrogen. Fluid forces and mass transfer affecting processes 3, 4 5 and 6 are estimated according to the coolant flow and the local geometry with a computational fluid dynamics (CFD) code.

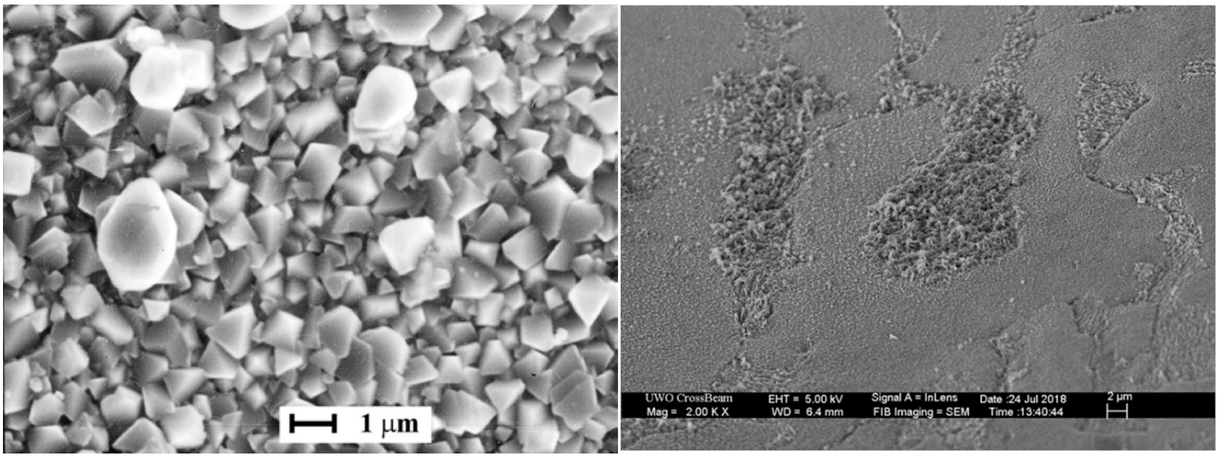

FIG. 1. Carbon steel exposed to: (left) static iron-saturated coolant at ~300°C, pH 10 (LiOH) and 18cm^3/kg dissolved H_2; (right) flowing (Re 53,000) iron-undersaturated coolant at 140°C and pH 9.2 (NH_4OH) – as in feedwater systems (reproduced courtesy of D. Lister [9]).

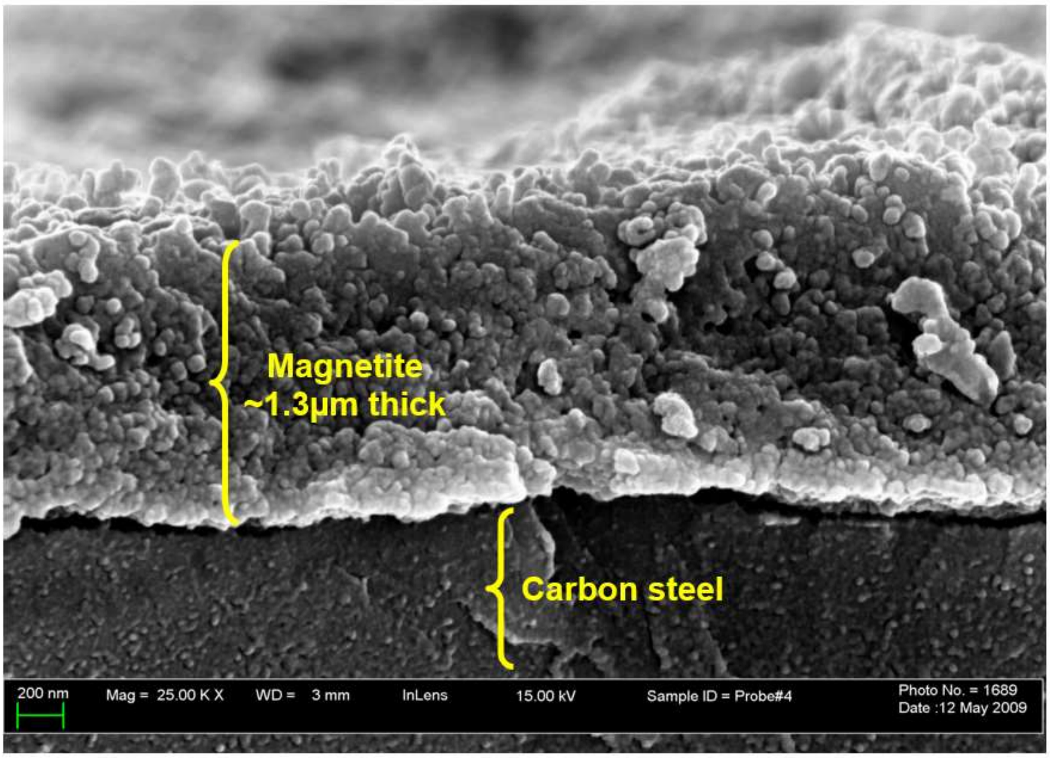

FIG. 2. Scanning-electron image of oxide film on carbon steel exposed under CANDU primary coolant conditions; specimen fractured under liquid nitrogen (reproduced courtesy of Canadian Nuclear Laboratories [10]).

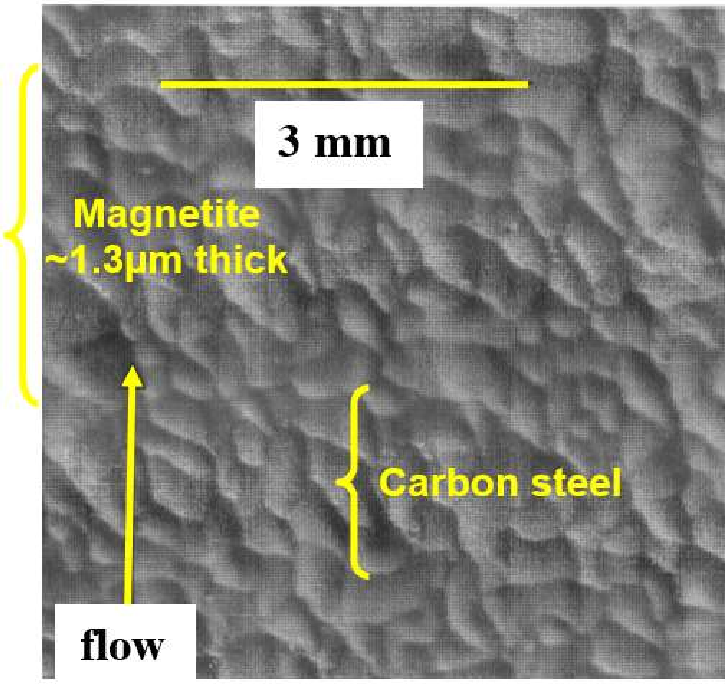

FIG. 3. The inside surface of an outlet feeder from the Point Lepreau CANDU reactor removed after ~14 years operation: pipe nominal ID 6.4cm, 0.019%-Cr steel, coolant heavy water at 310°C, pH$_{apparent}$ *~10.6, velocity 16.2 m/s (reproduced courtesy of D. Lister [11]).*

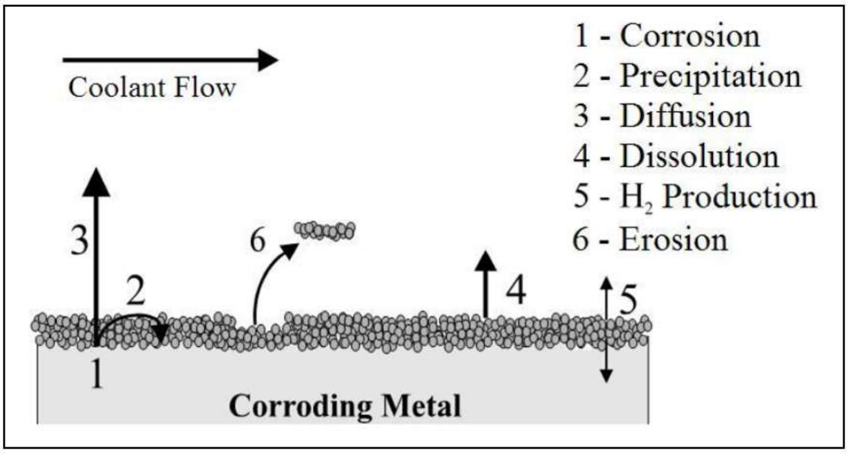

FIG. 4. Fundamental processes in FAC.

The model was first applied to the outlet feeders at the Point Lepreau CANDU before the reactor was refurbished [13]. The feeder steel was a low-chromium (0.019%) version of ASTM A106 Grade B, which had corroded much faster than the design allowance had anticipated (the replacement feeders after the refurbishment were of A106 Grade C steel, with 0.33% chromium, and corrode at about half the rate of the original). With one feeder measurement to bench-mark the computation, the FAC rate at the extrados of the bends of several feeders was predicted very well (see Table 1). The film thickness predictions were also realistic (there were no measurements from the modelled feeders available for comparison, but values from other specimens, including those in laboratory tests, were generally in the range 0.5-5 μm).

TABLE 1. PREDICTED STEADY-STATE CORROSION RATE AND OXIDE FILM THICKNESS AT THE EXTRADOS OF THE FIRST BEND OF OUTLET FEEDERS AT POINT LEPREAU WITH VARIOUS COOLANT VELOCITIES

Feeder	Diameter (mm)	Bend Angle (°)	Coolant Velocity (m/s)	Film Thickness (μm)	Corrosion Rate (μm/a)
R03	64	42	10.5	5.0	50.2
T05	64	73	10.4	3.2	59.0
K02	64	73	12.3	1.7	75.6
F06	64	73	15.6	0.85	105.9
S08	64	73	16.2	0.80*	110.0*
O06	64	73	17.5	0.67	123.1
B08	50	42	15.8	1.1	94.9
B06	50	73	11.9	1.7	74.8

* measured values for removed feeder S08 – used to bench-mark model.

When the predictions were superimposed on a plot from the Point Lepreau plant of feeder corrosion rates, estimated from ultrasonic measurements of wall thickness, against coolant velocity, good agreement with the simple empirical fit was obtained (Figure 5). It is significant that the fit shows the FAC rate depending on (velocity) 1.52 – a much higher power dependence than predicted by a model based solely on standard mass-transfer correlations.

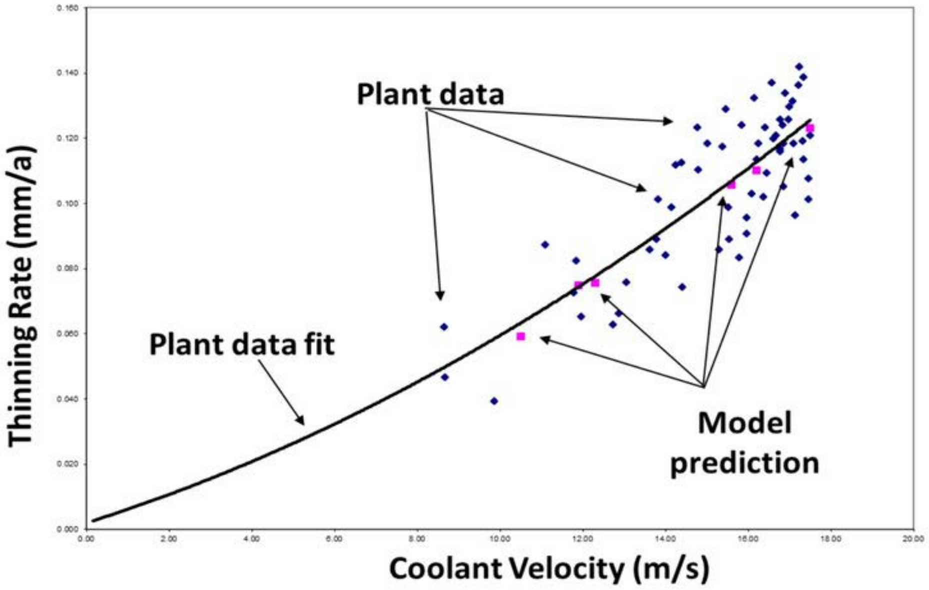

FIG. 5. Thinning rate of outlet feeders at Point Lepreau plotted against coolant velocity (pre-refurbishment) (reproduced courtesy of D. Lister [13]).

The corrosion of inlet feeders, which in iron-saturated coolant developed Potter-Mann-type oxide films, was also predicted realistically by the model after dissolution terms were replaced with precipitation terms (Figure 6). Little diametric variation across the core was expected. It will be noted that the outer oxide layer had occasional spalling events, as had been suggested from the results of the original laboratory testing [14].

The computation kept track of the particle erosion/spalling events and the corresponding particle sizes, leading to a steady-state source term of 240 ppb/operating-year for particles greater than 0.45 μm (the usual criterion for suspended "crud" in operating reactors). Along with a purification half-life of one hour for CANDU-6 primary coolant, this led to a predicted crud level of 0.05 ppb (μg/kg). While this is a reasonable value for PWR coolant during reactor operation, even considering the uncertainties introduced by having long sample lines and by operating sample systems intermittently [15], it would seem to be too low for CANDUs with their relatively abundant source of iron from the feeders.

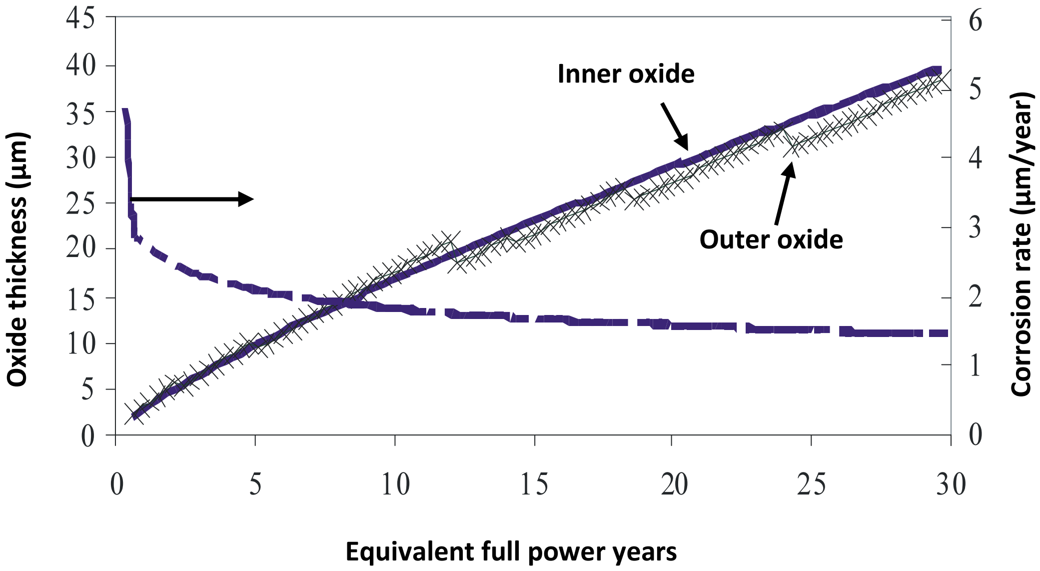

FIG. 6. Predicted corrosion of inlet feeders at Point Lepreau (reproduced courtesy of D. Lister [13]).

4. INFLUENCE OF MAGNETITE DISSOLUTION KINETICS

The mechanism of FAC depends upon two processes in series – dissolution of the oxide and mass transfer of the dissolved iron species (Fe(OH)2 under CANDU conditions) to the bulk coolant; the intermittent erosion/spalling of particles is a contributing factor. Both release processes account for most of the iron input to the CANDU primary circuit, which has caused fouling problems in the steam generators and the consequent rise in temperature of the coolant at the reactor inlet headers [7]. For two processes in series, the slower one controls, hence it was traditionally assumed that, because FAC obviously depends on flow, mass transfer has to be slower than dissolution. Dissolution was therefore assumed to be inconsequential in the original modelling attempts [16] and continues to be in many current formulations for FAC. Reference 13 refuted that assumption for CANDU feeders by pointing out that the only dissolution kinetic data at the time for magnetite at high temperature [17] were orders of magnitude lower than the appropriate range of mass transfer coefficients. Now, after several preliminary experiments [18], we have measured the dissolution rate of magnetite under a range of conditions pertinent to FAC in power plants and confirmed that, indeed, dissolution cannot be ignored in most coolant situations – including feedwater systems in all types of steam-raising plant [19].

5. DISSOLUTION EXPERIMENTS

Magnetite was synthesized via a solid-state reaction between haematite and iron:

$$4Fe_2O_3 + Fe = 3Fe_3O_4 \tag{4}$$

Stoichiometric amounts of powdered haematite and iron were heated for 12 h under vacuum at 600°C with a heating and cooling rate of 0.5°C/min. The resulting magnetite was hydraulically compressed into cylindrical pellets, 7.5 mm diameter x 7.5 mm long, which were sintered at 1300°C for 5 hours under an argon atmosphere [19]. In a typical dissolution experiment, the bottom face and curved surface of a pellet were sheathed in Teflon and mounted in the lower leg of a sideways-oriented Swagelok tee for installation in a recirculating high-temperature water loop. The upper leg contained a 0.5-mm orifice for directing a jet of incoming coolant from the loop onto the face of the pellet and the side arm of the tee exhausted the coolant back to the loop. Figure 7 is a schematic diagram of the pellet installation in the tee, with ports downstream for suitable instrumentation. The loop is made mostly of Type 316L stainless steel and can deliver up to 0.6 L/min of coolant at a maximum pressure of 12.5 MPa and temperature 320°C. The coolant is conditioned in a reservoir tank by sparging with a cover gas and dosing with pH additives such as LiOH to simulate reactor conditions. An experiment consisted of exposing a pellet to a submerged jet of coolant at constant conditions for a prescribed period and at the end of the run by-passing and cooling the test section before removing the pellet and examining the exposed face with scanning-electron microscopy (SEM) and measuring the volume of magnetite removed with a surface profilometer. This provided the average rate of removal over the exposure period (note that the mass transfer coefficient over the pellet face as determined by standard correlations was kept very high in order to ensure that dissolution always controlled; this principle was confirmed when the dissolution was measured after exposure). SEM pictures of a typical crater formed under conditions of rapid dissolution (neutral chemistry and 140°C) are shown in Figure 8.

The experiments revealed an interesting phenomenon. Occasionally, a newly-sintered pellet that was apparently of good quality with smooth surfaces would give anomalously high dissolution rates. When it was broken open and its interior examined microscopically it would indicate poor sintering – the original magnetite particles could be seen, although apparently bonded together quite strongly (the surface of the break was still hard and coherent). Figure 9 compares the surface of a poorly-sintered pellet with that of a well-sintered pellet; the former apparently arose from poor control of the temperature of the sintering furnace.

The rapid dissolution (apparently) of the poorly-sintered magnetite could be explained in the same way as the degradation of magnetite films during FAC of carbon steel, i.e., as described above, by dissolution enhanced by intermittent particle removal [9]. Note that the concept does not involve the breaking of the strong atomic bonds between sintered particles; instead,

dissolution loosens particles before they are swept away by the fluid. The total removal is then the sum of the dissolved iron and the particulate iron. The overall removal rate of the poorly-sintered specimen in Figure 9 was about 100 x that of the well-sintered one. To ensure that well-sintered pellets dissolved appropriately, experiments were repeated with single-crystal magnetite and gave confirmatory results.

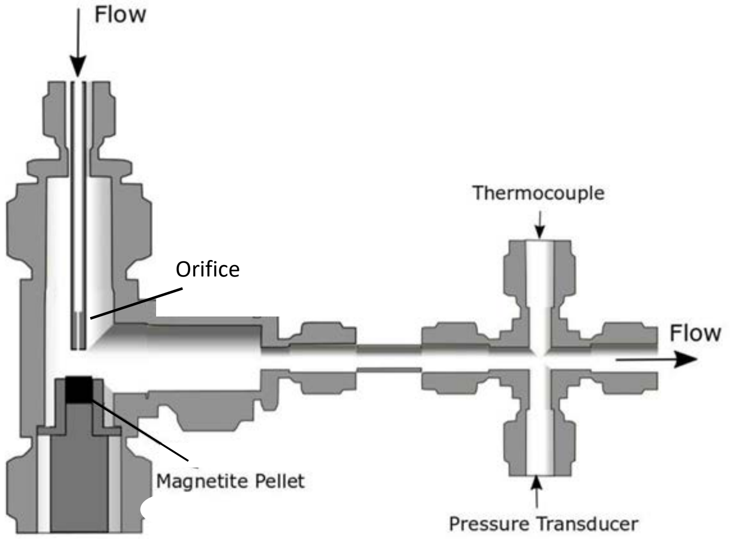

FIG. 7. Magnetite pellet mounted for dissolution experiment (reproduced courtesy of A. Turner [19]).

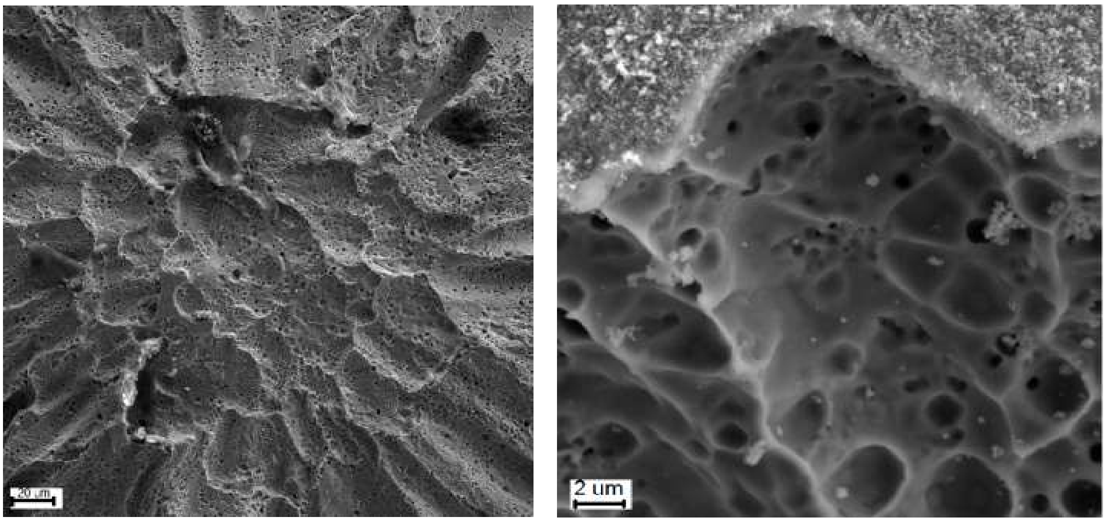

FIG. 8. Centre and rim of crater dissolved from magnetite pellet by impinging submerged jet of water at neutral chemistry and 140°C.

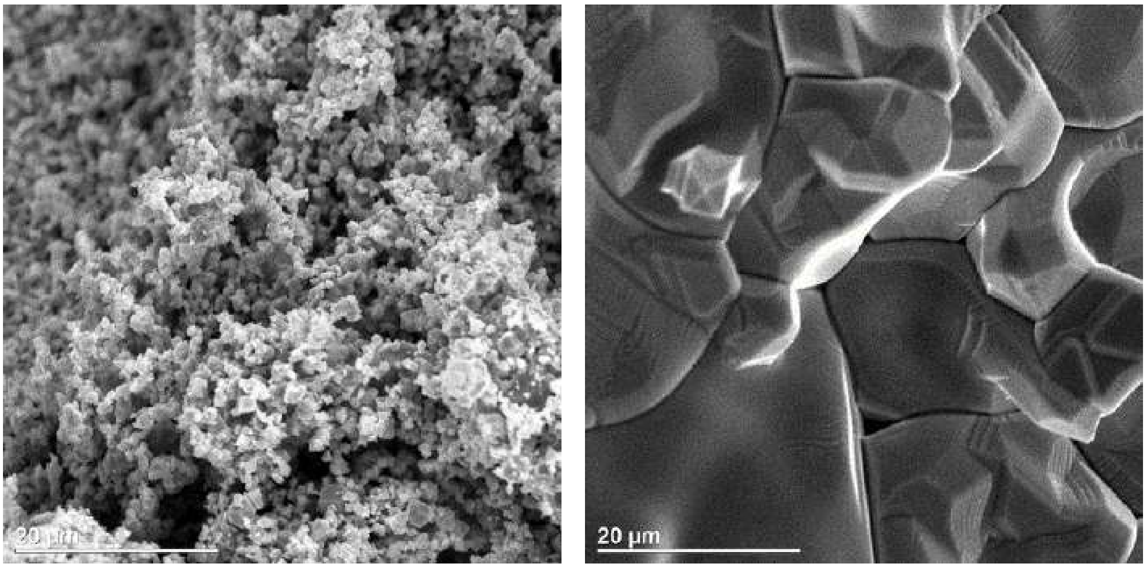

FIG. 9. Poorly-sintered (left) and well-sintered (right) magnetite.

Using the jet-impingement technique on well-sintered pellets, the dissolution rate constant for magnetite in light water under simulated CANDU primary coolant conditions of 310°C, 18 cm3/kg of dissolved H_2 and pH25°C of 10.5 (LiOH) was measured as 0.33±0.2 mm/s [18]. Note that the mass transfer coefficient during the measurements was ~50 mm/s, indicating that dissolution was always controlling; similarly, typical mass transfer coefficients for power plant coolant systems range from 2 to 20 mm/s, although there is considerable uncertainty in the estimates [12]. Such dissolution measurements allow FAC of the feeders to be modelled accurately, serving as corrosion-product source terms for estimating material and activity transport in CANDU coolant [7].

6. RECENT CANDU SYSTEM MODELLING

Utilising the mechanisms of FAC developed earlier and incorporating the latest data for magnetite dissolution properties, the primary coolant system of a CANDU 6 has been simulated [7,20]. Soluble and particulate iron are the vehicles for transporting other metals such as nickel and chromium as well as radioactive species such as Co-60 and Fe-59; the distribution around the circuit depends on solubility differences [21], dissolution and precipitation kinetics (the latter assumed from values of the former) and particle movement from established empirical relations [22].

Figure 10 presents the distribution of dissolved iron around the primary circuit of the Point Lepreau CANDU as predicted at the end of the first operating year [20]. The equilibrium or solubility values [21] follow the temperature as it increases through the core and decreases in the steam generators. For the feeders, the modelling takes account of the corrosion potential of the carbon steel, which has an obvious effect on the equilibrium concentration in the outlet feeders. The driving force for dissolution or precipitation at any point is the difference between the concentration at the surface (S/O interface) and the solubility. Dissolution occurs in the downstream part of the core, the outlet feeders (undergoing FAC) and the entrance to the steam generators (i.e., the hot leg) while precipitation occurs in the inlet feeders, the entrance to the core and the exit from steam generators (i.e., the cold leg). From the kinetic processes combined with the high coolant velocities and mass transfer, the predicted bulk concentration of dissolved iron varies from 1.6 ppb in the inlet feeders to 3.1 ppb in the steam generators. By contrast, the low corrosion rates of the alloys in PWR primary circuits produce virtually constant bulk concentrations around the circuit [4].

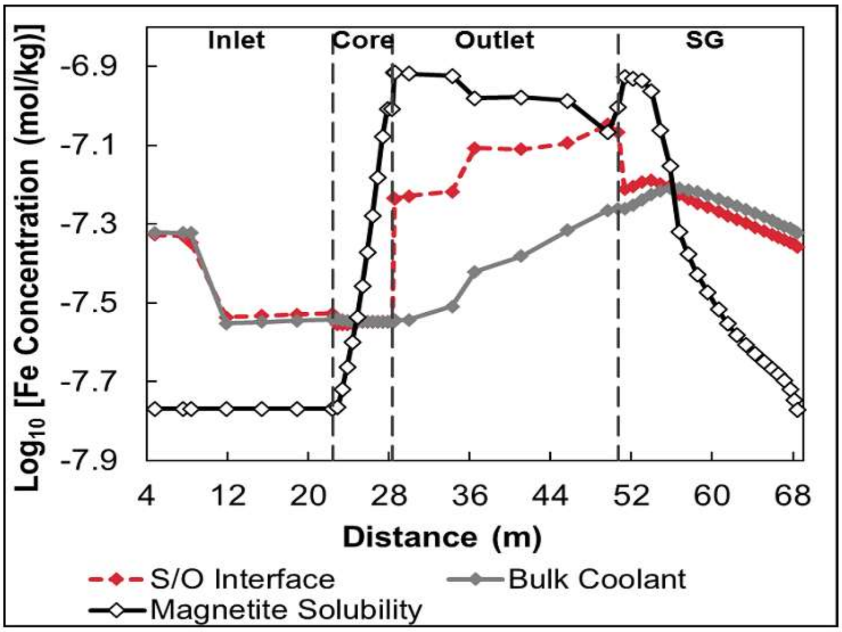

FIG. 10. Predicted distribution of soluble iron around the primary circuit of a CANDU 6 after one EFPY (S/O = solution/oxide interface).

The predictions of the deposition resulting from magnetite particle (crud) transport around the primary circuit of a CANDU 6 after one EFPY are presented in Figure 11 [20]. The deposits are thin, varying from about 0.02 μm on the inlet feeders (i.e., on top of the indigenous magnetite film) to about 0.05 μm in the core unless there is sub-cooled boiling on the fuel, in which case the extra deposition mechanism induced by steam bubble nucleation increases the deposit thickness to about 0.23 μm towards the core exit. The predictions have been run to 30 years to include other element distributions and activity transport and have resulted in generally good agreement with whatever plant data are available [7].

The rather low crud levels in CANDU coolant predicted by the early modelling (0.05 ppb – as described earlier) are contrasted with the values predicted by the later, more comprehensive modelling. Thus, in order to get good fits to the rather sparse data on deposit loading and activity transport throughout the primary coolant system, a crud level of 40 ppb was needed. This, in turn, looks high. Reviewing the assumptions and parameters in the models would seem to be in order; e.g., particles smaller than 0.45 μm and the special surface properties of colloids and small particles could be considered.

7. SUMMARY AND CONCLUSIONS

The corrosion of the large surface areas of the carbon steel feeders dominates material transport effects in the primary coolant systems of CANDUs and similar PHWRs. Measurement of the dissolution kinetics of magnetite, the predominant corrosion product, leads to realistic predictions of flow-accelerated corrosion, a major source term for the input of corrosion products from CANDU outlet feeders to the system and the basis of fouling and activity transport models. Extending the model to the inlet feeders also leads to realistic predictions of oxide film thickness and corrosion rate. The FAC predictions serve as source terms for particle input to the system and therefore crud levels in the coolant. Considered alone in early models, these particle inputs from FAC led to crud levels that seem too low for comprehensively modelling deposits and activity transport around the complete CANDU primary coolant circuit, while the necessary crud level for modelling realistic deposit loadings and activity transport seems high. It is recognised that accurate measurement of corrosion product concentrations in power system coolants is notoriously difficult [23], and nuclear systems with their necessarily long and usually tortuous sample lines have added complications. The real value of crud level as a transport source term remains an elusive quantity.

The experimental technique of impacting a submerged jet of coolant onto a sintered pellet of corrosion-product oxide and measuring the amount of material removed provides appropriate values of dissolution rate. Observations of the dissolution behaviour of poorly-sintered pellets, which release particles as well as dissolved material, support the concept of particle release from magnetite corrosion films as a component of the mechanism of FAC.

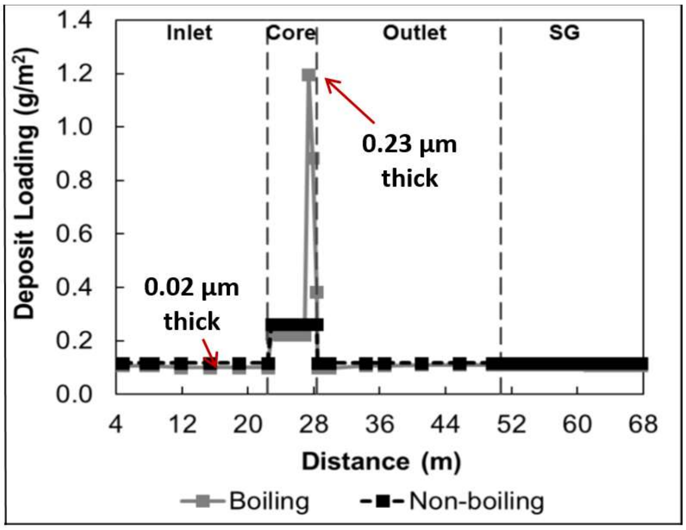

FIG. 11. Predicted crud deposits (from transported particles) around the primary circuit of a CANDY 6 after one EFPY.

ACKNOWLEDGEMENTS

The Natural Sciences and Engineering Research Council (NSERC) and the CANDU Owners Group (COG) are thanked for financial support. Staff and students of the UNB Nuclear research group are thanked for contributing to the underlying laboratory programs.

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INVESTIGATIONS ON SURFACE OXIDE FILMS FORMED ON PRIMARY CIRCUIT MATERIALS (PHWR) IN PRESENCE OF EXTERNALLY ADDED METAL IONS

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Abstract

The out of core structural material in the primary heat transport system of Indian Pressurized Heavy Water Reactor is Carbon Steel (CS). Prolonged operation of these reactors at high temperature and high pressure leads to the formation of activated corrosion products which get deposited on out-of-core surfaces causing radiation field build up and man-rem problems. Though the corrosion rate of CS is reduced by passive magnetite (Fe_3O_4) film, the radioactivity transport problem necessitates further reduction in the metal ion release. Metal ion passivation method is used to modify the oxide films to control the base metal corrosion. In this context, experiments were carried out to know the extent of improvement in corrosion resistance of CS with the addition of external metal ions such as Ni^{2+}, Zn^{2+} and Mg^{2+} compared to Fe_3O_4. In addition, the effect of Mg^{2+} on the surface oxide films formed on Zircaloy-2 and Incoloy-800 were also studied. For CS, all the experiments were carried out in a static autoclave with lithium hydroxide in presence of Ni^{2+}, Zn^{2+} and Mg^{2+} ions respectively at 250ºC exposed for 96 and 240 hours by hydrothermal method. For Incoloy-800 and Zircaloy-2, experiments were done in a dynamic loop for duration of 7, 21 and 42 days only with magnesium ion. The films were characterized both by surface analytical techniques like Raman and GI-XRD for compositional analysis and also by electrochemical techniques for evaluating corrosion resistance properties. On CS, the films grown in presence of metal ions exhibited a higher polarization resistance compared to its absence by impedance studies. Potentiodynamic anodic polarization studies showed a similarity in corrosion current densities for the films obtained in the absence and presence of metal ions. The calculated thickness of these modified films using Clarke's method was lower in presence of Zn^{2+} and Mg^{2+} ions compared to Ni^{2+} ions and Fe_3O_4. From the results, it was inferred that the zinc and magnesium ferrites form a more adherent and compact film compared to Fe_3O_4 and nickel ferrite. On both Incoloy and Zircaloy, a restructuring of oxide was indicated as a function of time and the corrosion rates and defect densities were found to be significantly lower on Mg^{2+} incorporated oxides.

1. INTRODUCTION

The out of core structural material in the primary heat transport (PHT) system of Indian Pressurized Heavy Water Reactor is Carbon Steel. Corrosion products are generated due to the prolonged operation of these reactors at high temperature and high pressure. Some of these corrosion products get neutron activated in the core and subsequently get re-dispersed on out of core locations causing man-rem problems. ^{60}Co, a major source of radioactivity significantly contributes to the radiation build-up. Though the corrosion rate of CS is reduced by Fe_3O_4 film, the radioactivity transport problem necessitates further reduction in the metal ion release. Measures like removal of corrosion products by chemical treatment and replacement of ^{60}Co source with low Co content materials have been implemented to reduce the activity build-up. Metal ion passivation (MIP), an alternative method to improve the protectiveness of the oxide and also to reduce the activity build-up over the structural materials, modifies the surface oxide films to control base metal corrosion by the addition of metal ions like Zn^{2+} and Mg^{2+} in very low concentration to the coolant system [1-2]. In boiling water reactor (BWR), the addition of Zn^{2+} at ppb level reduced the release of corrosion products and ^{60}Co pickup [3-4]. But ^{64}Zn has a high cross section for neutron absorption to produce γ-emitting ^{65}Zn, which partially offsets the reduction in radiation level and hence Mg^{2+} was studied as an alternative for Zn^{2+} and has been shown to reduce the corrosion as well as the deposition and release of cobalt under PHWR coolant chemistry conditions [5]. Previous studies indicated that Mg^{2+} ion modified water chemistry significantly reduced the CS corrosion [6]. Similar studies have been reported for BWR structural materials [7]. Hence, to know whether the addition of external metal ions (Ni^{2+}, Zn^{2+} and Mg^{2+}) would modify the existing oxide films and improve the protectiveness of CS interfacial film, this study was carried out. These metal ions also interact with other heat transfer materials in the PHT system and the modified oxide film can influence their corrosion behaviour. As the Indian PHWRs use Zircaloy-2 as clad and Incoloy-800 as steam generator tubes, the oxide modification on them by these inorganic additives is of important concern. Therefore, this study was carried out to modify the films on Zircaloy-2 and Incoloy-800 in simulated PHT water chemistry environment in presence of Mg^{2+} ions to understand the phase, structure, protectiveness and semiconducting properties of the oxide films.

2. EXPERIMENTS & RESULTS

2.1. Materials & methods

2.1.1. High temperature exposure experiments

Polished CS specimens were exposed in a preconditioned static autoclave for 96 and 240 hours in deaerated Lithium hydroxide (LiOH) (pHRT 10.3, conductivity 44-48 µS/cm) at 250°C. For the incorporation of Mg^{2+}, Ni^{2+} and Zn^{2+} ions into the Fe_3O4 lattice during its formation on CS, 1 ppm of the corresponding metal ions in the form of sulphate salts were added to the LiOH solution. Polished Zircaloy-2 and Incoloy-800 specimens were exposed to LiOH (pHRT 10.3, DO < 10 ppb) at 294°C for 7, 21 and 42 days in absence and presence of Mg^{2+} ions in a dynamic autoclave where constant chemistry conditions were maintained throughout the experiment by pumping fresh LiOH at a flow rate of 1.0 ml/min.

2.1.2. Surface characterization

The films developed on CS, Zircaloy-2 and Incoloy-800 were characterized by GI-XRD using M/S STOE, X-ray diffractometer with Cu Kα as the incident radiation (λ= 1.541 Å) in the range of 2θ=10o–90o with a step size of 0.05o. Raman spectra was recorded on Zircaloy-2 and Incoloy-800 using HORIBA Jobin Yvon HR 800 spectrometer, with 514.5 nm Ar+ ion laser from 100 to 1500 cm-1. Laser power was optimized to 0.5 mW on the sample surface and acquisition was carried out for 60s using a 100x objective lens and 1800 grooves/mm grating.

2.1.3. Electrochemical measurements

Electrochemical measurements were carried out using an Eco Chemie Autolab (PG STAT 30) in a three-electrode cell with platinum foil as counter electrode and saturated calomel as reference electrode. The uncoated CS was stripped cathodically at -1.0V potential for 3 minutes to remove any air formed film whereas this process was not carried out for coated specimen. The open circuit potential (OCP) was monitored for 30 minutes and then the impedance spectra was obtained with a perturbation of single sinusoidal voltage of ±10mV in the frequency range of 105-0.005Hz. The PDAP scans were obtained by polarizing the working electrode from -0.5V to +1.2V with respect to OCP at a scan rate of 0.5mV/s. Mott–Schottky (MS) measurements were carried out to understand the semiconducting properties of films formed on Zircaloy-2 and Incoloy-800 and to estimate the defect density of the films. The working electrodes were polarized in the cathodic direction in successive steps of 50mV from + 0.8V to -1.2V Vs. SCE.

2.2. Results and discussion

2.2.1. Carbon steel

Table 1 gives the thickness values calculated by Clarke's method. The thicknesses of the films slightly increased with increase in exposure time. The thickness obtained in presence of Zn^{2+} and Mg^{2+} ions were less compared to that obtained in presence of Ni^{2+} ions and Fe_3O_4.

TABLE 1. CALCULATED FILM THICKNESS

Exposure	Thickness (µm)			
Time (hours)	Fe3O4	NiFe2O4	ZnFe2O4	MgFe2O4
96	0.4801	0.3624	0.161	0.176
240	0.5485	0.6336	0.167	0.214

Figure 1 shows the GI-XRD patterns for films formed in absence (only Fe_3O^4) and presence of Ni^{2+}, Zn^{2+} and Mg^{2+} ions at 96 and 240 hours. The GI-XRD patterns showed cubic spinel ferrite peaks. An additional base metal peak was observed at ~ 45°.

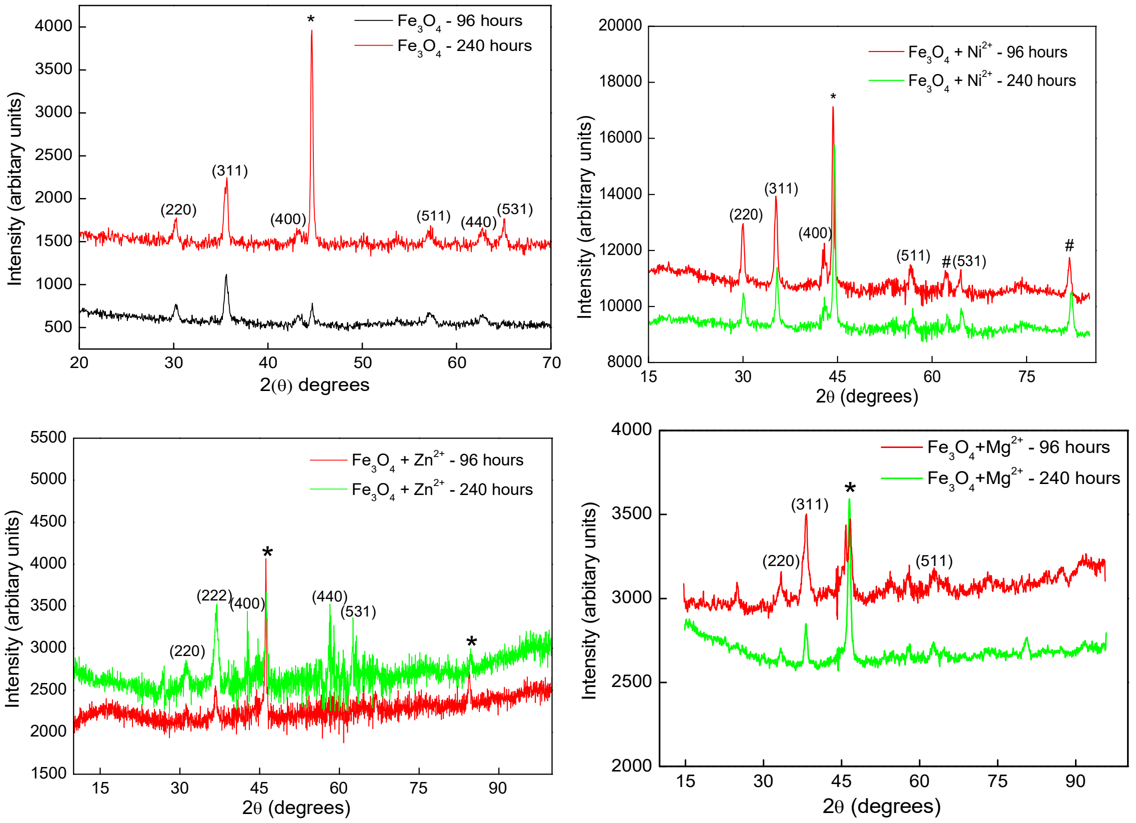

FIG. 1. GI-XRD patterns for films formed in absence (only Fe_3O_4) and presence of Ni^{2+}, Zn^{2+} and Mg^{2+} ions at 96 and 240 hours.

Table 2 gives the crystallite sizes of the films formed on CS estimated from the most intense peak using Scherrer's equation. Smaller sized crystallites were observed in presence of Zn^{2+} and Mg^{2+} ions compared to crystallites in presence of Ni^{2+} ions and Fe_3O_4.

TABLE 2. CALCULATED CRYSTALLITE SIZE (nm)

Exposure Time (hours)	Fe_3O_4	$Fe_3O_4 + Ni^{2+}$	$Fe_3O_4 + Zn^{2+}$	$Fe_3O_4 + Mg^{2+}$
96	15.9	16.98	13.7	11.5
240	19.24	19.83	9.4	7.0

Figure 2 shows the Nyquist plot for films formed in absence and presence of Ni^{2+}, Zn^{2+} and Mg^{2+} ions at (a) 96 and (b) 240 hours. An increasing trend in the Rp values was observed at 96 and 240 hours indicating a better corrosion resistance in presence of each metal ion. Longer exposure time (240 hours) showed similar Rp values in presence of metal ions, but higher than the value obtained for Fe_3O_4, indicating that the corrosion protection offered for CS is better in presence of metal ions.

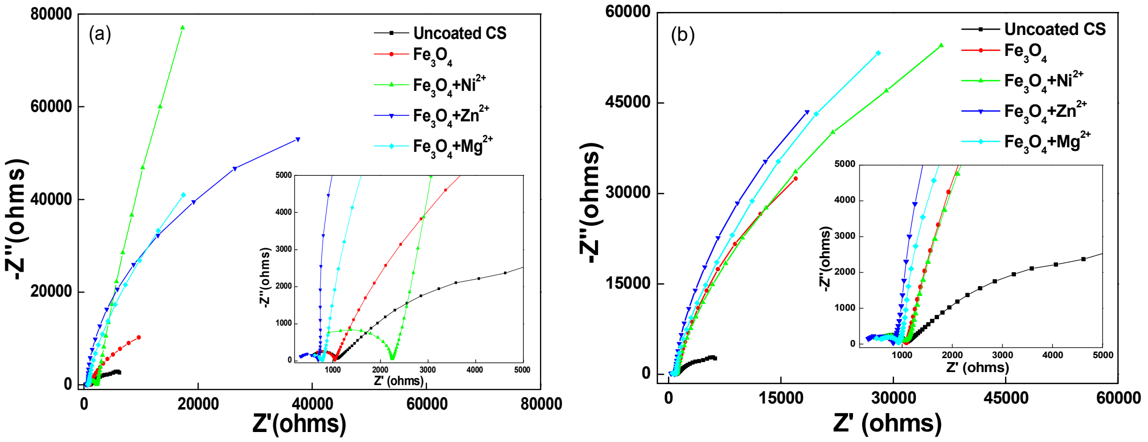

FIG. 2. Nyquist plot of films formed at (a) 96 and (b) 240 hours.

Figure 3 shows the PDAP plot for films formed in absence and presence of Ni^{2+}, Zn^{2+} and Mg^{2+} ions at (a) 96 and (b) 240 hours. The corrosion resistance for Fe_3O_4 film followed the order: 96 hours ≅ 240 hours > CS (uncoated). The current densities for the films formed in presence of Ni^{2+}, Zn^{2+} and Mg^{2+} ions exposed to 96 and 240 hours had magnitudes lower than that observed for Fe3O4 and uncoated CS and the corrosion resistance of CS in presence of Ni^{2+}, Zn^{2+} and Mg^{2+} ions followed the order: Fe_3O_4 < 96 hours < 240 hours. Though the film formed in presence of Mg2+ ions in case of 96 and 240 hours duration showed a lower passive current density compared to Fe_3O_4 and uncoated CS, the film was unstable at higher anodic potentials. Initially, though the corrosion rates were different for different films, longer exposure time showed similar corrosion rate values.

2.2.2. Zircaloy-2

Fig.4 shows the Raman spectra for Zircaloy-2 exposed for 7 days with and without Mg2+. Raman analysis for films formed in 21 and 42 days showed similar observation. Raman shift was observed at 180, 192, 335, 384, 479, 555 and 640 cm^{-1} and the values indicated the existence of ZrO_2 oxide phase mainly in monoclinic phase.

Figure 5 shows the EIS spectra and the fitted equivalent circuit typical of porous oxide film for passivated Zircaloy-2. Roxide and Rct represent the oxide resistance and the charge transfer resistance respectively. Higher absolute value of these parameters for Mg^{2+} modified oxides shows the better corrosion resistance property. The passive oxide film obtained after 21 days of exposure showed a maximum resistance value indicating the presence of a maximum protecting oxide film.

Figure 6 represents the PDAP curves for passivated Zircaloy-2 surfaces in deaerated borate buffer medium at RT. Passive current density values were obtained @ 0.5V and was found to be lower for Mg^{2+} modified oxides for all the exposed durations but the oxide formed in 21 days exposure showed a minimum value. These results again proved better corrosion resistance property for Mg^{2+} modified oxide.

The Mott-Schottky plots were generated for the passivated surfaces in inert/borate buffer medium at 28°C. From the positive and negative slopes at 1 kHz, the respective "n" and "p" type defect concentrations were calculated. Figure 7 shows the variation of defect density values with the exposure duration. Both the type of defect densities were generally lower for modified film by Mg^{2+} ions and the 21 days passivated oxide film showed the minimum defect density values.

2.2.3. Incoloy-800

Table 3 shows GI-XRD parameters for Incoloy-800 passivated for different durations. Presence of crystalline nickel ferrite was observed on all the specimens. The parameters computed from the most intense peak showed an increase in lattice parameter with Mg^{2+} incorporation and the % change increased from 0.05% to 0.3% with increase in exposure duration from 7 to 42 days. This can be due to the replacement of smaller ionic radii Ni^{2+} (0.69A°) with bigger ionic radii Mg^{2+} (0.72A°).

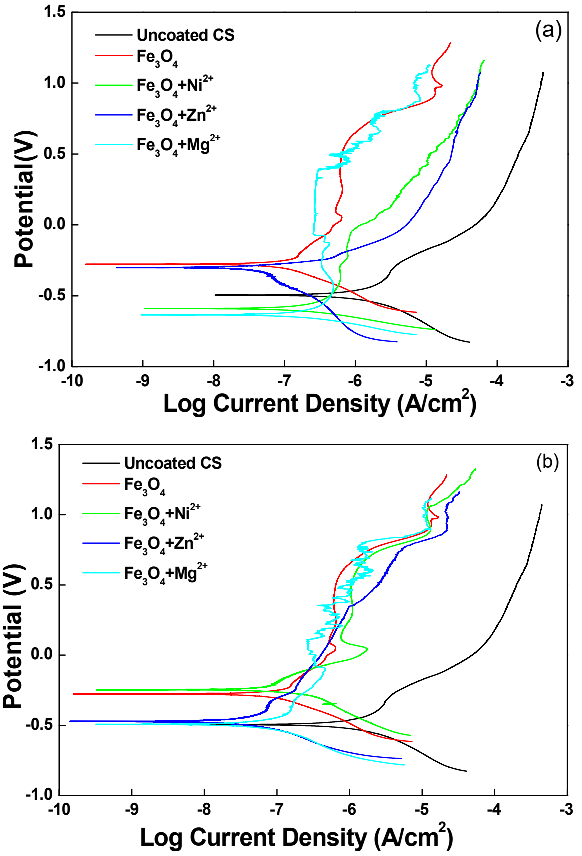

FIG.3. PDAP plot of films formed at (a) 96 and (b) 240 hours.

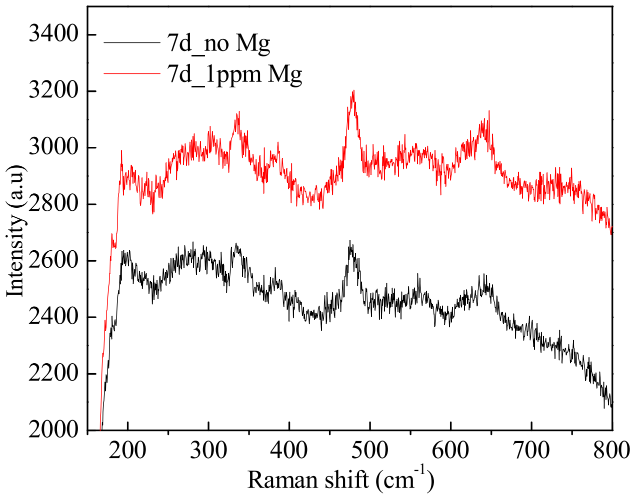

FIG. 4. Raman spectra of exposed Zircaloy-2 for 7 days with and without Mg^{2+}.

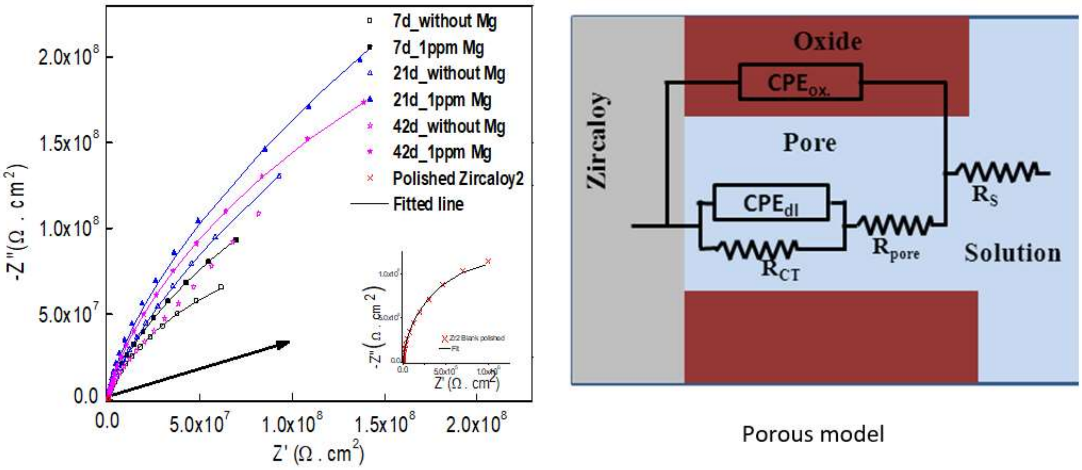

FIG. 5. EIS Spectra and fitted equivalent circuit for passivated Zircaloy-2.

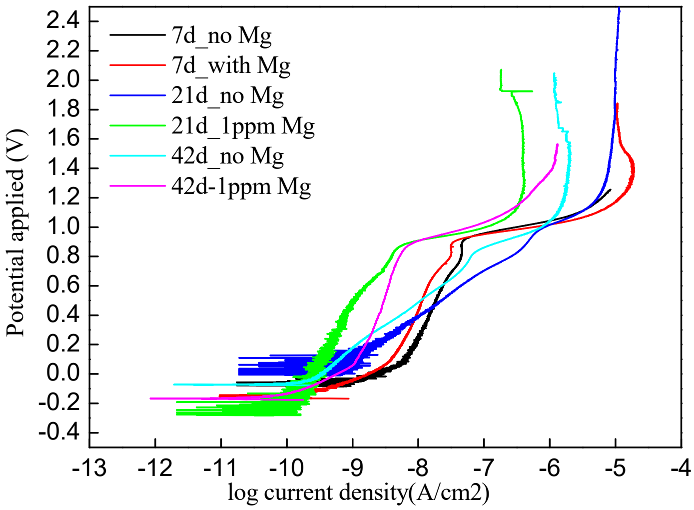

FIG. 6. PDAP curves for passivated Zircaloy-2.

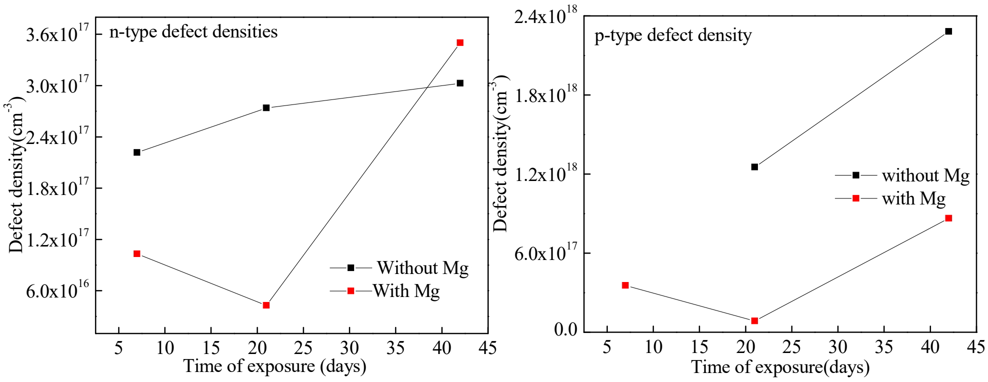

FIG. 7. Variation in n-type and p-type defect density values for passivated Zircaloy-2.

TABLE 3. GI-XRD PARAMETERS FOR INCOLOY-800 FOR DIFFERENT DURATIONS

Experiment	2 θ	FWHM	θ (radians)	d (A°)	a (A°)	% change in 'a'
42d No Mg	35.775	0.4053	0.312035	2.5082	8.3187	0
7d with Mg	35.757	0.3602	0.311878	2.5094	8.3227	0.049
21d with Mg	35.755	0.3533	0.311865	2.5095	8.3231	0.053
42d with Mg	35.655	0.3619	0.310991	2.5163	8.3457	0.325

Figure 8 shows the fitted Raman spectrum for Incoloy-800 surfaces passivated for 21 days of exposure in the presence of Mg^{2+}. The most intense peak at ~703 cm^{-1} indicated the presence of spinel oxide structure on Incoloy-800 surface. Comparison of Incoloy-800 specimens exposed to high temperature water in presence/absence of Mg^{2+} ions showed significant differences in Raman shift values for the main peak.

Figure 9 shows the EIS spectra for Incoloy-800 surfaces passivated for different durations. The Bode plots suggested the presence of at least two relaxation processes, one due to the oxide film and the other due to the charge transfer processes. The shape of the impedance plots indicated a non-ideal diffusion process controlling the rate of reaction across the interface.

The total impedance of the system was observed to be of MΩ order and was always higher for the oxides in presence of Mg^{2+} as compared to those in absence of Mg^{2+}. Log Z value for the film formed at 42 days was highest followed by film formed at 7 and 21 days.

Figure 10 shows the PDAP curves for Incoloy-800 surfaces passivated for different durations. The films formed showed stability till ~ 0.2V and dissolved slowly on further application of potential. The passive current density was found to be the least for 42 days exposed specimen and maximum for 21 days exposed specimen in both the presence and absence of Mg^{2+} in the oxide.

In Incoloy-800, only n-type defects were observed to be present in all the cases. Fig.11 shows the variation of n-type defect density values with the exposure duration. The defect densities were generally lower for the passive oxide film modified by Mg^{2+} ions. The defect densities calculated from the slopes corroborated the observation in PDAP studies and the defects in Mg^{2+} containing oxides were order of magnitude less.

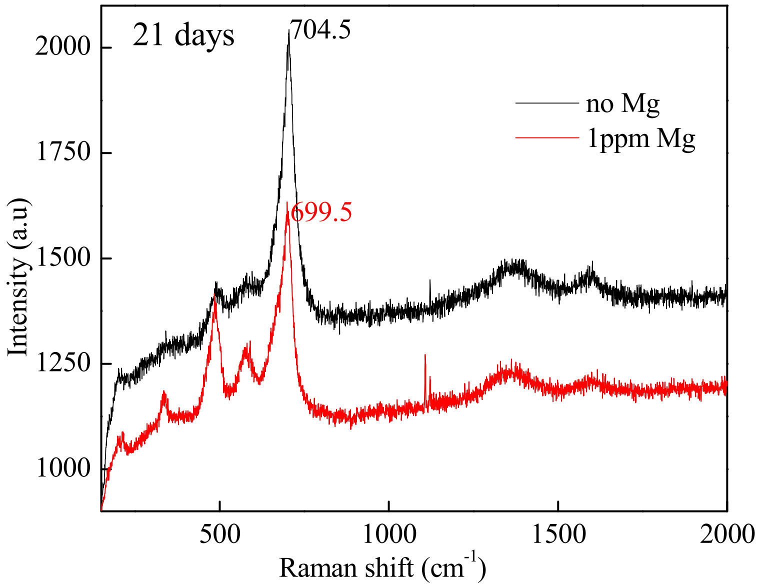

FIG. 8. Raman spectra for 21 days exposed Incoloy-800.

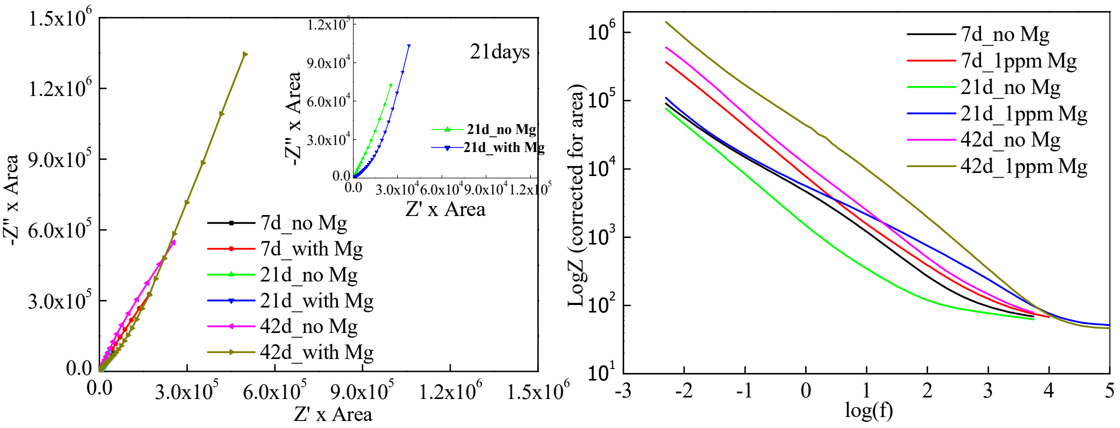

FIG. 9. EIS spectra for Incoloy-800 passivated for different durations.

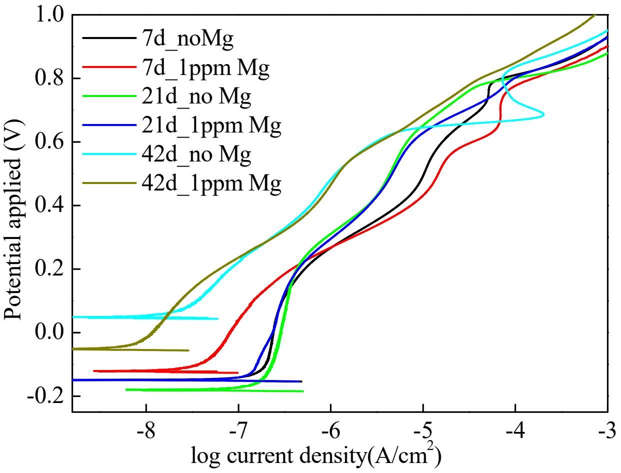

FIG.10. PDAP curves for Incoloy-800 passivated for different durations.

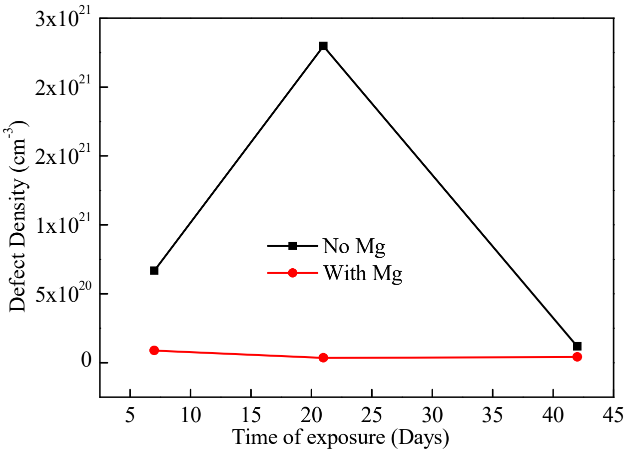

FIG. 11. n-type defect density values of the oxides calculated from Mott Schottky analysis.

3. CONCLUSIONS

Metal ion passivation studies were carried out to modify the oxide films formed on the structural materials used in the primary heat transport system of Indian PHWRs under the primary water chemistry conditions. Experiments were conducted with the addition of external metal ions such as Ni^{2+}, Zn^{2+} and Mg^{2+} for carbon steel and only Mg^{2+} for Zircaloy-2 and Incoloy-800. The thickness of the oxide film formed in 240 hours followed the order: $ZnFe_2O_4 < MgFe_2O_4 < Fe_3O_4 < NiFe_2O_4$. GI-XRD confirmed the formation of spinel phase $NiFe_2O_4$, $ZnFe_2O_4$ and $MgFe_2O_4$ films on CS in presence of nickel, zinc and magnesium ions respectively. At 240 hours, electrochemical measurements showed that the corrosion protection offered by these oxide films on carbon steel followed the order: $ZnFe_2O_4 \cong MgFe_2O_4 \geq NiFe_2O_4 \cong Fe_3O_4$. It was inferred that the zinc and magnesium ferrites form a more adherent and compact films compared to magnetite and nickel ferrite. On both Incoloy-800 and Zircaloy-2, a restructuring of oxide was indicated as a function of time and the corrosion rates and defect densities were found to be significantly lower on magnesium incorporated oxides. The study showed that metal ion passivation with Zn^{2+} and Mg^{2+} ions could improve the overall corrosion resistance of the structural materials by modifying the nature and composition of the oxide films formed on the structural materials in the primary coolant circuits of nuclear power plants.

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RECENT RESEARCH DEVELOPMENTS IN PRIMARY HEAT TRANSPORT SYSTEM CHEMISTRY

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Abstract

In general, Primary Heat Transport System (PHTS) chemistry for pressurized heavy water reactors (PHWRs) is stable and believed to be well understood. The current narrow-band pHa control to minimize feeder wall thinning and hydrogen addition to maintain reducing conditions are effective chemistry control strategies to maximize component lifetimes and minimize degradation and activity transport processes in the PHTS circuit. However, recent laboratory-scale investigations, ongoing evaluations of available reactor chemistry data and the increased availability of on-line analyses are providing more detailed insights into PHTS chemistry in operating plants that may allow future refinements to operating practices. This paper will provide an overview of recent work related to PHTS chemistry from CNL.

1. INTRODUCTION

Research towards improving the chemistry control of the primary coolant in PHWRs has been ongoing for more than 50 years. Across the industry, chemistry control of the primary coolant is guided by a few key principles which seek to:

- Minimize corrosion of materials;
- Minimize activation of materials and the transport of activity in the circuit;
- Avoid depositing corrosion products in-core and on the fuel.

Several generally accepted chemistry control practices have been adopted by the industry to achieve the chemistry control principles described above. These are:

- To maintain an alkaline pH_a in the coolant using LiOH addition;
- To maintain reducing conditions in the coolant by addition of sufficiently high concentrations of dissolved D_2;
- To maintain low impurity concentrations in the coolant through effective purification.

Advances in coolant chemistry control have historically been driven by operational experience. One such example was the discovery of outlet feeder wall thinning (and cracking) from flow accelerated corrosion (FAC). However, because of the inherent purity of primary D_2O coolant in PHWRs, there are few parameters available with which to modify chemistry control practices for continued improvement. Based on the aforementioned practices, modification of the recommended pH range, changes to the dissolved D_2 concentration range, or improvements in purification media efficiency appear to be the only chemistry-related parameters that can be adjusted for PHWR primary coolant. Furthermore, the impact of a chemistry control change has to be balanced across the system needs; alteration of one chemistry parameter may benefit one of the key principles but could lead to degraded control of another. Returning to the example of outlet feeder wall thinning, focused research on the chemistry at the core outlet demonstrated that a more narrow-band pH_a range was needed in the PHTS, and the upper pH_a specification was generally recommended to be reduced from 10.8 to about 10.4 across the PHWR fleet to reduce FAC rates [1,2]. The revised pH_a range (10.2 – 10.4) is in itself a compromise as the relative rate of feeder corrosion and the rate of in-core corrosion product deposition show opposite dependencies on pH_a; operating at the lower end of the pH_a range reduces the relative rate of FAC (owing to a reduction in the Fe solubility), but is associated with an increased risk for in-core corrosion product deposition as there is reduced margin above the pH_a where in-core deposition is predicted to begin.

While the chemistry control in PHWRs has proven effective over the last several decades, not all aspects of primary water chemistry are completely understood. Gaps remain in our understanding of the radiation chemistry of high temperature water, and particularly with respect to the behaviour of metal ions in such chemical systems. Increased availability of online chemistry monitoring is also providing new sources of data for interpretation. This paper will highlight recent work at Canadian Nuclear Laboratories (CNL) related to advancing our understanding of PHTS chemistry. The outcomes of advanced critical hydrogen concentration tests and modelling, high temperature metal ion radiolysis experiments, and applications of online chemistry data will be briefly discussed.

2. CRITICAL HYDROGEN CONCENTRATION TESTS AND MODELLING

2.1. Water radiolysis and the critical hydrogen concentration

A primary challenge for chemistry control in irradiated systems is to control the effects of water radiolysis. When exposed to ionizing radiation, water breaks down to form both reactive oxidizing and reducing species (Equation 1)[5] [3]. The short-lived radical products will recombine such that the net stable products of water radiolysis are hydrogen, oxygen, and hydrogen peroxide (Equation 2). Once produced, these products can persist outside of the radiation field and the oxidizing products can impact on the degradation of downstream materials.

$$H_2O \xrightarrow{\text{n and } \gamma \text{ irradiation}} \bullet e_{aq}^-, \bullet OH, \bullet H, H_2O_2, \bullet HO_2/\bullet O_2^-, H^+ \qquad (1)$$

$$H_2O \xrightarrow{\text{n and } \gamma \text{ irradiation}} \tfrac{1}{2}(1+n)\ H_2 + \tfrac{1}{2}\ n\ O_2 + \tfrac{1}{2}(1-n)\ H_2O_2 \qquad (2)$$

In order to minimize the corrosion of materials, net radiolytic generation of oxidants in the primary coolant has to be suppressed. This is achieved by adding sufficient concentrations of dissolved hydrogen to the system such that the recombination of radical products proceeds to regenerate water (Equation 3).

$$H_2O + H_2 \xrightarrow{\text{n and } \gamma \text{ irradiation}} H_2O + H_2 \qquad (3)$$

As a result, the dissolved hydrogen (or deuterium) concentration is one of the key chemistry control parameters for the primary coolant of nuclear reactors. Currently, CANDU reactors operate with a dissolved hydrogen (deuterium) concentration of between 3 and 15 mL/kg (plant specific).

The minimum concentration of hydrogen required to prevent the net radiolytic production[6] of oxygen (and hydrogen) is defined as the Critical Hydrogen Concentration (CHC). Experimental determinations of the CHC were previously completed in the National Research Universal (NRU) reactor U-2 loop, with CHC values of 0.5 mL/kg (STP) measured in these tests [4,5]. The data have been used to benchmark reactor radiolysis models, such as that presented in [6]. However, radiolysis modelling of coolant passing through the core shows that non-negligible quantities of oxidizing species are predicted to be formed in-core, even at dissolved hydrogen concentrations above the CHC, and lifetimes of some oxidants (e.g., H_2O_2) were predicted to be sufficiently long to allow for their transport to out-of-core surfaces [7]..

It is important to note that the CHC does not necessarily describe the hydrogen concentration at which the net radiolytic production of all oxidizing species is completely suppressed for regions close to the core. Oxygen is not a primary product of water radiolysis (see Equation 1). However, while other oxidants such as H_2O_2 and $\bullet HO_2$ are primary radiolysis products, these oxidants cannot be reliably monitored using sample lines due to their short lifetimes under reactor operating conditions. Past experience with boiling water reactors (BWRs) has demonstrated that all oxidizing species need to be considered in order to determine the likelihood of material degradation, and the risk for materials degradation can be predicted well by in-situ determination of the electrochemical corrosion potential (ECP) of reactor materials [8]. This paper describes measurements of the ECP of reactor materials in the NRU reactor U-2 loop close to the core outlet under CANDU PHTS conditions to provide an in-situ measurement of all oxidizing species produced in-core, and to more accurately determine the dissolved hydrogen concentration needed to minimize their production.

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[5] While the chemical reactions are shown and discussed for light water (H_2O), similar breakdown processes would occur in heavy water (D_2O), with deuterium replacing hydrogen in the reactions as shown.

[6] Net production is considered to occur once the concentrations are above detection limits.

2.2. Overview of advanced critical hydrogen concentration and ECP tests recently performed at CNL

The NRU reactor U-2 loop was a fuelled, light water loop that was designed to mimic the operating conditions for the PHTS of a CANDU reactor. The U-2 loop consisted of two test sections in series, each being half the length of a CANDU reactor fuel channel and containing 6 CANDU fuel bundles. Normal loop operating conditions included a core inlet temperature of around 270 °C, an outlet temperature up to 310 °C, and outlet pressure of 10 MPa. Alkaline coolant chemistry was maintained using LiOH, and sidestream purification and chemical addition systems were available. Sample lines optimized for short residence time were available at the test section inlet and outlet with online O_2 and H_2 measurements available using Orbispheres (Figure 1). Generic chemistry specifications for the loop are provided in Table 1. Dispensation was given to lower the dissolved hydrogen concentration below the specified range in order to perform the experiments. Hydrogen was added to the loop immediately following detection of oxygen after the CHC was reached to restore normal operating chemistry conditions.

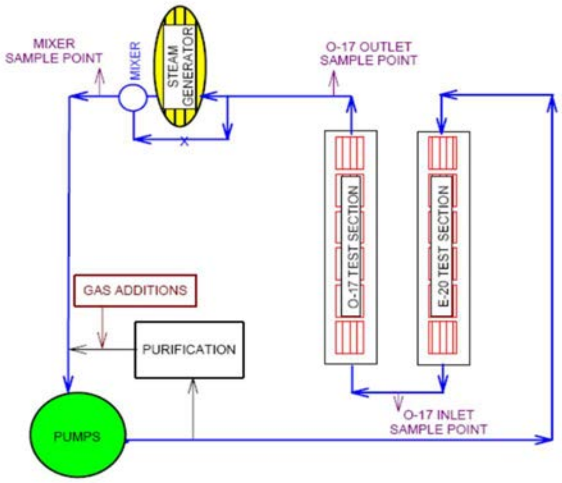

FIG. 1. Schematic of the core region of the NRU reactor U-2 loop with sample line positions.

TABLE 1. SELECTED NRU REACTOR U-2 LOOP CHEMISTRY SPECIFICATIONS

Parameter	Specification	Control Parameter
pH (25ºC)	9.9 – 10.1	
Lithium	0.56 – 0.88 mg/kg	Yes
Conductivity	2 – 3 mS/m	
Dissolved Hydrogen	3.0 – 15.0 mL/kg	Yes
Dissolved Oxygen	< 0.005 mg/kg	Yes
Chloride	< 0.1 mg/kg	Yes
Anions (NO_3^-, NO_2^-, $SO_4^=$)	< 0.1 mg/kg	

In the current tests, the potentials of platinum (Pt) and carbon steel (CS) electrodes were measured against an iron/iron oxide filled zirconia membrane electrode (ZME) at the core outlet of the NRU reactor U-2 loop under simulated CANDU reactor HTS chemistry conditions. The electrodes were supplied by General Electric/Reuter Stokes and were designed for use in-core for BWR environments. In the current tests, the ZME had an iron-magnetite (Fe/Fe_3O_4) internal couple and was used as a reference electrode for the potential measurements. Before installation into the U-2 loop, the electrodes were tested at CNL to verify their response at reactor temperatures and pressures. The experimental electrochemical corrosion potentials were seen to be only between 20 and 30 mV higher than the calculated values and this range served as a guideline for acceptance criteria during the reactor tests. However, due to reactor loop availability issues, there was an extended delay to commence the reactor loop experiments, hence, at the commencement of the reactor tests the potential difference between the Pt electrode and

ZME at a particular hydrogen concentration and pH was again compared against calculated values. The potential of the ZME was found to be slightly more offset at 65 mV greater than theoretical values, possibly due to oxidation of the electrode internals during storage. This offset was taken into account when expressing the Pt and CS electrode potentials on the SHE scale.

The electrode assembly was inserted into the lattice position O-17, as illustrated in Figure 2. At this position, the coolant transit time from the fuel to the electrode position was ~0.5 s, similar to the transit time from the core to the feeder pipes in a CANDU reactor. The flux profile at the core outlet was also similar to a CANDU reactor. The electrodes were securely attached to a modified upper fuel hangar bar with custom-built metal fasteners (Figure 3a) and enclosed within a cylindrical stainless steel cage with perforated ends Figure 3b) to contain any loose parts in the unlikely event of a mechanical failure. In order to route signal cables from the electrodes to the monitoring equipment outside the U-2 loop, a modified seal block was constructed, which included a socket welded Conax fitting to allow the three mineral-insulated signal cables to cross the pressure boundary (Figure 4). The instrumented hangar bar was then connected to the fuel string and inserted into the NRU reactor (Figure 5).

The conditions for these tests, and the strategy followed, were similar to those used for the CHC measurements in 1995 [4]. The dissolved hydrogen concentration was initially established to between 3 and 15 mL/kg with the addition of gaseous hydrogen and was lowered throughout the test by the admission of oxygen into the loop. During the hydrogen removal step, the dissolved oxygen and hydrogen concentrations and the electrode potentials were monitored constantly, and the rate of oxygen addition was adjusted accordingly. In these CHC determinations, hydrogen was removed more slowly than in the earlier tests owing to the use of air, rather than pure oxygen gas, for oxygen addition into the loop. Sample line residence times were carefully assessed through trial chemical manipulations prior to the test sequence and all data have been adjusted to account for delays for samples to reach the online analyzers. Tests were performed under both non-boiling and boiling conditions up to 3 wt % steam quality.

2.3. Advanced critical hydrogen concentration and ECP test results

A CHC determination was performed under non-boiling conditions using an oxygen mixture (air) addition rate of 50 mL/min during the approach to the CHC. The hydrogen and oxygen concentrations, ECP measurements, and oxygen addition rate for this test are plotted in Figure 6. The potentials of the Pt and CS electrodes both begin to increase at 0.5 mL/kg dissolved hydrogen, which indicates that oxidizing species are being detected near the electrodes. However, the chemical detection of stable radiolytic products and the achievement of the CHC occurred later in the test at 0.25 mL/kg dissolved hydrogen. At the CHC, the electrode potentials were around 50 mV higher than the initial values and increased significantly in accordance with the increase in dissolved oxygen in the coolant. This observation suggests that oxidizing species are being transported to the core outlet at dissolved hydrogen concentrations above the CHC.

A CHC determination was also performed under boiling conditions (Figure 7). The oxygen mixture addition rate was initially lowered to 100 and then to 50 mL/min during the approach to the CHC. Once again, the potentials of both the Pt and CS electrodes were observed to increase prior to the CHC, with oxidizing species being detected electrochemically at around 0.4 mL/kg dissolved hydrogen. At this stage, the hydrogen concentration remained somewhat constant, suggesting that the oxygen addition rate was insufficient to continue the approach to CHC under boiling conditions. As a result, the oxygen mixture addition rate was increased to 200 mL/min for the remainder of the test and the CHC was reached at a dissolved hydrogen concentration of 0.2 mL/kg. The electrode potential readings at the onset of the CHC were approximately 100 mV higher than the initial values and increased significantly when oxygen was detected. The CHC under boiling conditions is higher due to the stripping of hydrogen and other gases to the steam phase, however, as with non-boiling conditions, this test demonstrates that oxidizing species are being transported to the core outlet at hydrogen concentrations above the CHC.

The electrochemical observation of oxidizing species near the core outlet at dissolved hydrogen concentrations above the CHC is consistent with previous radiolysis model simulations [7] and helps to inform our understanding of the impacts of core chemistry on overall system behaviour, including material degradation processes. These new data will allow for further refinements of radiolysis models for reactor core chemistry conditions.

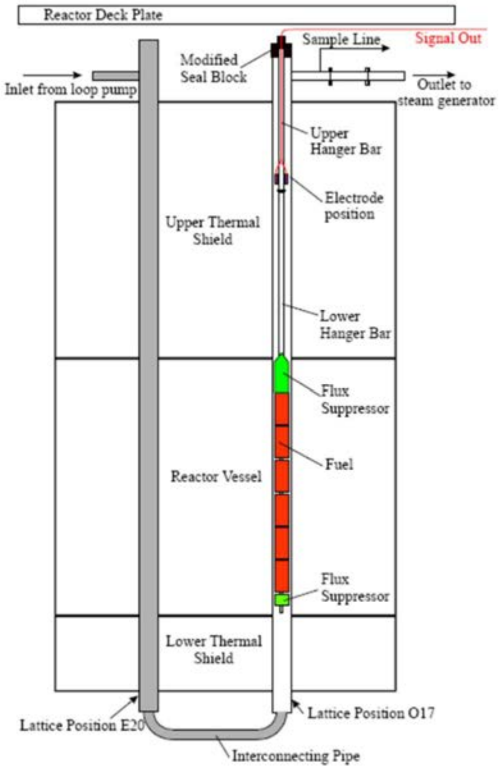

FIG. 2. Schematic of the core region of the NRU reactor U-2 loop, showing the position for electrode installation.

FIG. 3. (a) Installation of ZME (lower) and Pt (upper) electrodes on the upper hangar bar. The Cs electrode installation is located at the rear of the hangar bar. (b) Electrode enclosure during installation.

FIG. 4. The Conax seal with cable pass through on the modified seal block.

FIG. 5. Reinstallation of the main reactor deck plate, showing the instrumented hangar bar in place (circled in red).

3. HIGH TEMPERATURE METAL ION RADIOLYSIS

Current iron and activity transport models for CANDU reactors are based around magnetite solubility as a function of pH and temperature, as derived from equilibrium thermodynamics [9]. These hydrothermal models do not include any consideration of radiolytically-driven reactions that could occur in-core between dissolved iron species and water radiolysis products. Such interactions have been demonstrated at room temperature and can lead to changes in the oxidation state of dissolved iron species and, hence, can influence the overall solubility of iron that might be predicted in the solution, as well as the nature of iron in solution (e.g., dissolved or particulate species) [10,11]. The recent ECP tests have also shown that, even at dissolved H_2 concentrations above the CHC, oxidant species are radiolytically-produced in-core and can be detected at the core outlet. As a result, modelling of in-core iron behaviour may be better represented by a comprehensive kinetic model.

Recent efforts at CNL have focused on the development of a high temperature iron radiolysis model, which requires knowledge of the temperature dependence of the reaction rate constants up to 300 °C. Unfortunately, a literature survey revealed that only one iron reaction (Equation 4) has been studied at elevated temperatures, and few details pertaining to the experimental methodology and data treatment are described [12]:

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^{-} \quad (4)$$

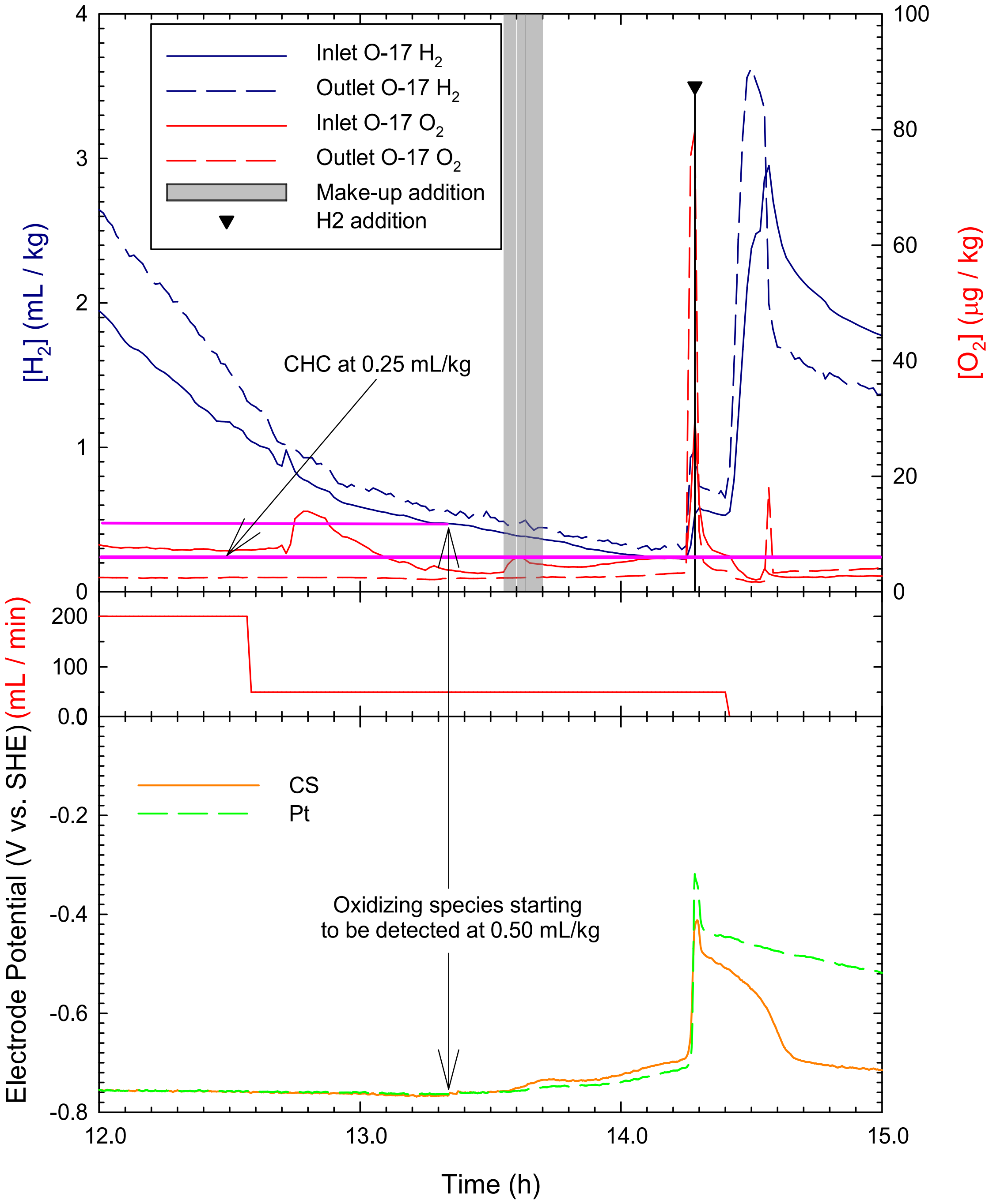

FIG. 6. The hydrogen and oxygen concentrations and ECP values measured for a CHC determination performed under non-boiling coolant conditions.

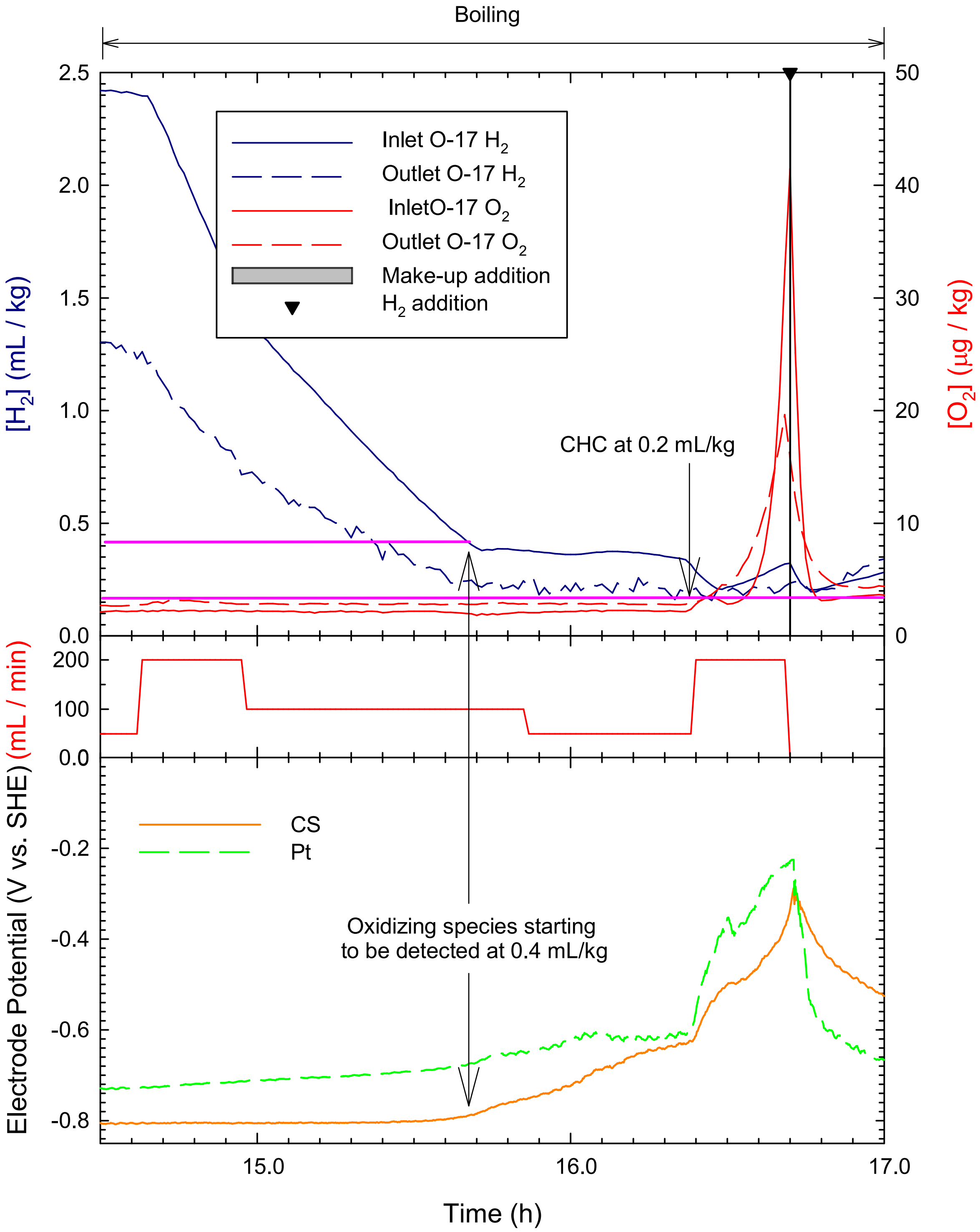

FIG. 7. The hydrogen and oxygen concentrations and ECP values measured for a CHC determination performed under boiling coolant conditions (3 wt%).

High temperature rate constants for this reaction were also recently measured at CNL, however, poor agreement was observed among the datasets at intermediate temperatures (25<T<200 °C), see Figure 8. It is noted that, compared to [12], the CNL data shows better agreement with other rate constant measurements performed at room temperature [13–15].

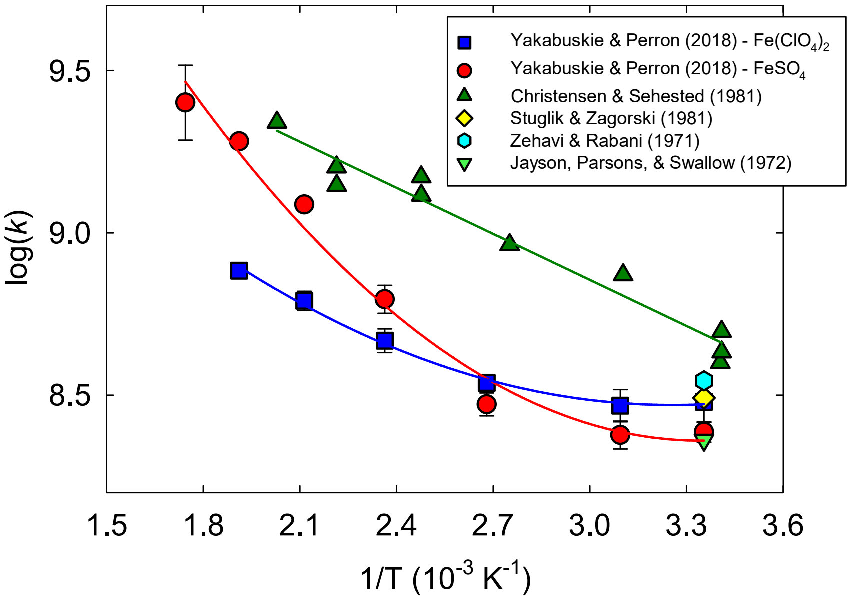

FIG. 8. Comparison of the CNL-derived temperature dependence of the second order rate constant for the reaction Fe^{2+} + *•OH with the results of other literature studies.*

In order to address this gap, CNL has initiated an experimental program on metal ion radiolysis intended to gather data on the high temperature kinetics of dissolved metals relevant to reactor primary systems (e.g., Fe, Cr, Ni) with water radiolysis products generated through Equation 1. There are significant challenges in studying the radiation chemistry of these systems, in particular due to the low metal ion solubilities under CANDU coolant conditions. CNL is investing in the development of irradiated, flowing high temperature loops to complement existing static radiolysis techniques in order to expand work in this area.

4. APPLICATIONS FOR ONLINE CHEMISTRY MONITORING DATA

Recently, there has been a drive across the nuclear industry to increase the availability of instrumentation that can perform online chemistry monitoring. In addition to reducing the sampling burden on chemistry staff, increased availability of online chemistry monitoring can also provide new sources of data for interpretation and new learning opportunities.

An HEProTM hydrogen effusion probe was installed at Point Lepreau Nuclear Generating Station (PLNGS) in 2012 to monitor the FAC rate of new feeders during hot conditioning following refurbishment. The chemistry data collected by the probe confirmed a significant decrease in the FAC rate with the new feeder material. However, since its installation, data from the HEProTM unit has also provided an opportunity to directly monitor the influence of other chemistry factors on feeder corrosion rates, including oxygen ingress from fuelling activities, pH_a changes, and IX resin changes. Figure 9 shows selected chemistry data measured at PLNGS, along with online corrosion rate measurements from the HEProTM unit over the same time period. From the Figure, a step change can be observed in the corrosion rate with the installation of a fresh IX resin column. Additionally, as the pH_a was allowed to increase in preparation for an outage, a gradual increase in the corrosion rate can also be observed.

The data being collected by the HEPro^{TM} unit is currently being leveraged by CNL in conjunction with the Centre for Nuclear Energy Research at the University of New Brunswick in support of ongoing CANDU Owners Group research projects relating to resin performance. Continued development and application of online monitoring techniques will provide opportunities to observe new correlations with respect to the influence of different parameters or events on overall system chemistry.

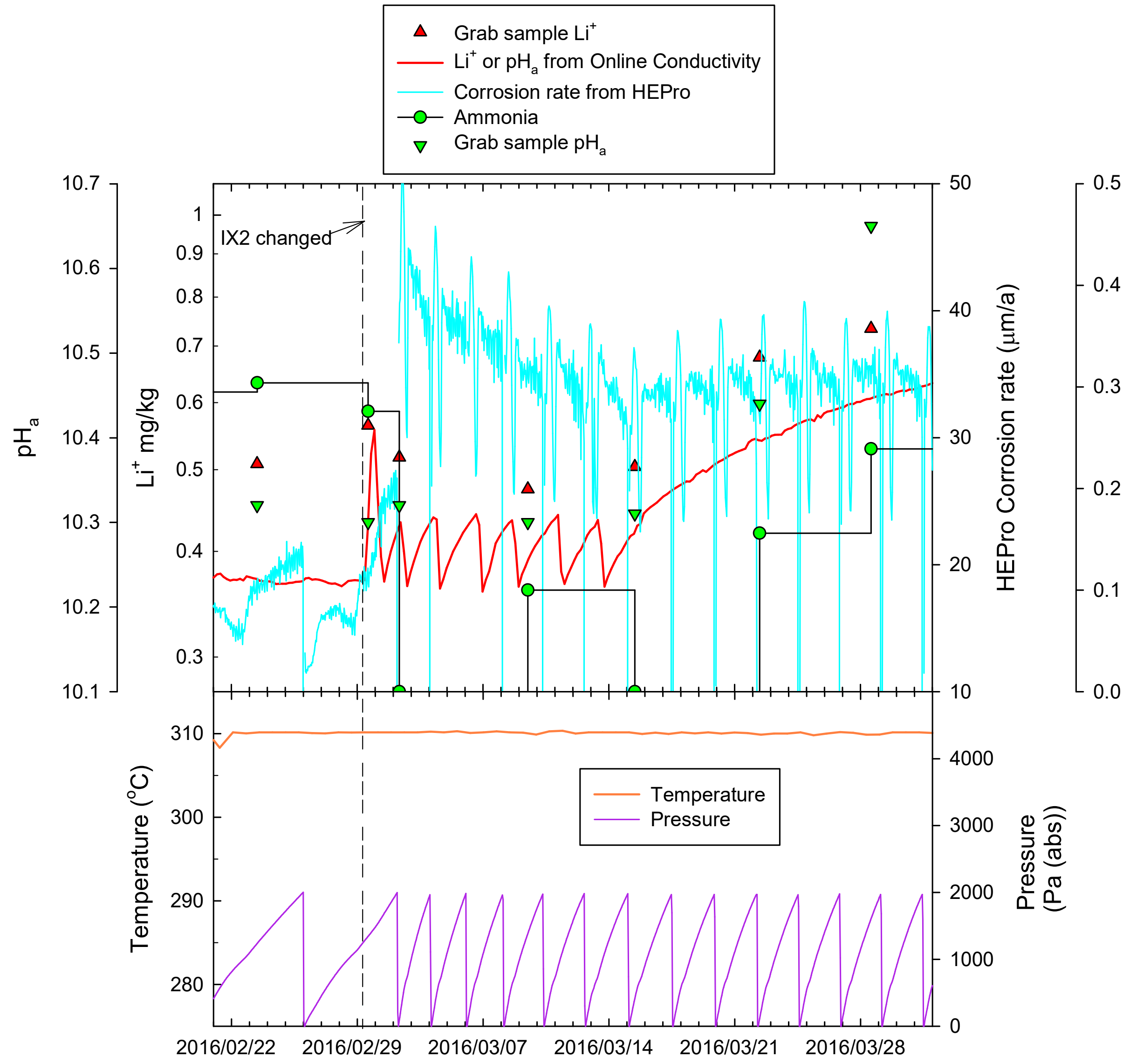

FIG. 9. Online corrosion rate measurements from the HEPro^{TM} probe are shown along with associated chemistry parameters. Figure used with permission from NB Power.

5. CONCLUSIONS

This paper has described a collection of recent work relating to PHTS chemistry that has been performed at CNL. Recent tests using ECP probes installed at the core outlet of the NRU reactor U-2 loop have demonstrated that oxidizing species can be transported out of the core, even when the dissolved hydrogen concentration is above the CHC. The temperature dependence of the reaction of ferrous iron with the hydroxyl radical was also measured at CNL by pulse radiolysis. High temperature kinetic data for the radiolytic reactions of dissolved metal ions is not widely available in the literature and represents a gap in our understanding of coolant chemistry in-core. A test program is underway at CNL to gather this information. The increasing availability of online reactor data was also shown to provide new opportunities to probe the chemistry of reactor systems.

The outcomes from these experimental programs and the increased availability of reactor data will assist in the further development of radiolysis chemistry models.

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CHEMICAL MODELLING STUDIES OF MAGNETITE SOLUBILITY EFFECTS DURING CANDU REACTOR START-UP AND HOT CONDITIONING

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Abstract

The recently published database for the EPRI chemical equilibrium model MULTEQ V.8 includes critically reviewed literature on the hydrothermal chemistry of magnetite and other transition metal oxides and ferrites under primary and secondary coolant conditions. This paper reports calculated values for the dependence of magnetite solubility on pH, dissolved hydrogen, and temperature, and their applicability in reviewing strategies for controlling iron transport during normal operation and under conditions encountered during start-up after lay-ups and hot conditioning.

1. INTRODUCTION

The primary coolant chemistry of CANDU nuclear reactors is largely controlled by the solubility of magnetite. Over the past several years, new databases for the solubility of magnetite, nickel and cobalt ferrites have been developed for the EPRI chemical equilibrium modelling code MULTEQ [1,2]. The purpose of this paper is to review the published literature on the hydrothermal chemistry of magnetite and other transition metal oxides and ferrites under primary coolant conditions, and to make use of the new database to examine strategies for controlling iron transport under conditions encountered in CANDU primary coolant circuits during normal operation and under conditions encountered during start-up after lay-ups and hot conditioning. The status of ongoing experimental projects to develop a heavy-water database is briefly reviewed.

2. CANDU PRIMARY COOLANT CIRCUIT OPERATING CHEMISTRY

2.1. The effect of temperature on solubility and mass transport of magnetite

Radioactive corrosion product transport in CANDU primary coolant circuits is largely controlled by the solubility of magnetite, which undergoes a reversal in its temperature dependence from negative to positive upon increasing the pH above pH 9.8 (0.45 ppm, $6\cdot10^{-5}$ mol·kg^{-1} LiOD). The operation of primary circuits at lower pH results in heavy fuel deposits and an unacceptable level of radioactivity transport, because magnetite deposits containing ^{60}Co are deposited in-core. However, carbon-steel feeder tube lifetimes in aging reactors are limited by flow accelerated corrosion (FAC) which is controlled by magnetite dissolution mechanisms and surface absorption effects, both of which require accurate data for the hydrolysis of iron (II) and iron (III). Among other options, a modest reduction in operating pH, to achieve lower levels of FAC at the cost of a reduced margin with respect to the formation of fuel deposits, could be a practical solution to this problem. There is also a need to model the solubility and transport of other transition metal ions such as ^{60}Co and ^{65}Zn. These are present as non-stoichiometric ferrites, $M_xFe_{(1-x)}Fe_2O_4$ (where M = Co^{2+} or Zn^{2+}), whose solubility is also dominated by hydrolysis [3].

Magnetite solubility is governed by both hydrolysis and redox equilibria of the type

$$Fe^{II}Fe_2^{III}O_4(s) \xrightleftharpoons{H_2,H^+} Fe^{2+} \xrightleftharpoons{OH^-} FeOH^+ \xrightleftharpoons{OH^-} Fe(OH)_2^0 \xrightleftharpoons[H_2]{OH^-} Fe(OH)_4^- \tag{1}$$

Accurate determinations of the solubility of magnetite are extremely difficult because they have to measure iron concentrations at levels of a few ppb as a function of pH, temperature and redox potential (hydrogen concentration). These measurements have to be carried out with meaningful checks to prove that equilibrium has been established and to characterize the surface saturating phase [3–7]. In the absence of radically new experimental approaches, solubility measurements cannot be sufficiently accurate to determine the minimum LiOH concentration required to avoid in-core precipitation in H_2O systems to better than approximately ±30% (±0.5 pH units). There is a larger uncertainty in pH_a because of the lack of experimental data measured in D_2O.

Activity transport models in the nuclear industry based on Sweeton and Baes' data[7] predict higher solubility and dissolution rates out of core at high pH than models based on the data of Tremaine and LeBlanc[4], Ziemniak et al.[5], and Palmer et al.[6] . Over the past several years, new databases for the solubility of magnetite, nickel and cobalt ferrites have been developed for the EPRI chemical equilibrium models MULTEQ and CHEMWORKS. The most recent model, developed by Dickinson et al.[1], is based on fits to critically-evaluated experimental data from the literature (1970 to 2010). The calculated magnetite solubilities from MULTEQ V.8 are more consistent with the results from Tremaine and LeBlanc, Ziemniak et al., and Palmer et al., than with Sweeton and Baes. They are also consistent with hematite solubilities reported by Diakanov et al.[8]. Diakanov's study confirmed the finding by Tremaine and LeBlanc that iron (III) species are significant at high pH, such that the effect of dissolved hydrogen is much less than if only Fe(II) was present.

The effect of LiOH concentration on magnetite solubility from 25 to 320 °C is plotted in Figure 1. Figure 1b expands the temperature range of the coolant as it passes through the core. It is necessary that the solubility remains unchanged or rises slightly as the water traverses the core, to minimize the formation of deposits on the fuel.

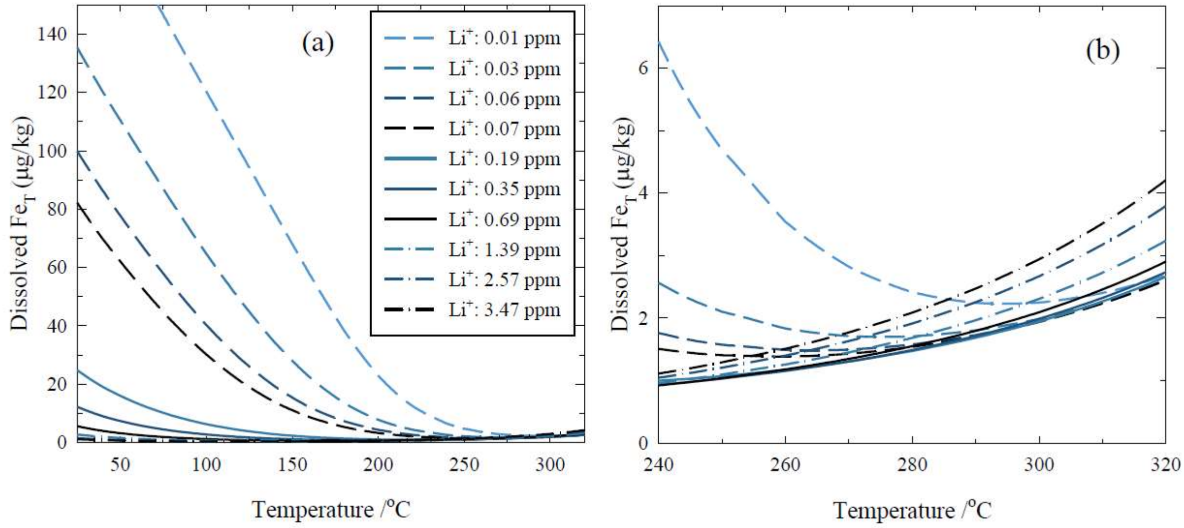

FIG. 1. The effect of LiOH on the solubility of magnetite from 25 to 300 °C and P_{sat} at a concentration of H_2 = 12 mL(STP)/kg. Typical CANDU reactor operating conditions are shown by solid curves.

2.2. Deuterium isotope effects on ionization and solubility constants

The experimental challenges make it unlikely that the deuterium isotope effect on magnetite solubilities can be measured directly. The effects of isotopic substitution on ionization constants at room temperature have been described by Arnett and McKelvey [9] and Laughton and Robertson [10]. At 25°C, typical deuterium isotope effects, ΔpK = pKD2O -pKH2O, range from approximately 0.2 to 0.7 pK units. The ionization constant of heavy water has been determined at elevated temperatures by Shoesmith and Lee [11] and by Mesmer and Herting [12]. We are aware of only two other experimental studies of acid/base ionization constants in D2O at temperatures above 100°C, prior to 2010. Work at Oak Ridge National Laboratories by Leitzke and Stoughton [13] and Mesmer and Herting [12] determined the ionization constants of DSO^{4-} and D_2PO^{4-} up to 200 and 300°C, respectively. Lietzke and Stoughton's values were determined by solubility methods which are less accurate than EMF or conductivity.

Recent UNENE-funded work at the University of Guelph has now measured values for the ΔpK of several simple acid ionization reactions at temperatures up to 325 °C (e.g., Conrad et al. [14]). The deuterium isotope effect on the ionization constant of water is (ΔpKw, = 0.958 ± 0.010 at 25°C; 0.727 ± 0.120 at 250°C). The deuterium isotope effect for most acid ionization reactions at 25oC fall in the range 1.0 ≥ ΔpK ≥ 0.1, and generally decrease with increasing temperatures. Preliminary computational results suggest that larger or smaller deviations of ΔpK may be possible for the individual stepwise hydrolysis constants of $Fe^{II}(OH)_2^0(aq)$ and $Fe^{III}(OH)_3^0(aq)$ in the magnetite solubility reaction.

2.3. The effect of lithium concentrations (pH_a) on magnetite dissolution and precipitation during reactor operations

The original practice in the industry for monitoring pH in heavy water, pD, was to measure the quantity called ‘apparent pH’ or ‘pH_a’, which is the pH of heavy water solutions taken from reactor sampling loops, then measured at 25°C with glass electrodes calibrated in light water buffers. This pH_a is used to calculate heavy water pD values by the relationship, $pD = pH_a + 0.41$, which is based only on the value of ΔpKw at 25°C. There has been little research to determine the validity of this relationship, and under what conditions it begins to break down. This practice was revised so that pD is now calculated from the concentration of dissolved lithium. Typical CANDU primary coolant specifications [15] are $0.22 < Li < 1.35$ ppm (3.2×10^{-5} to 2.0×10^{-4} $mol\cdot kg^{-1}$).

As shown in Figure 1, MULTEQ V.8 predicts that at lithium concentrations above 0.19 ppm (2.5×10^{-5} $mol\cdot kg^{-1}$) there is a positive magnetite solubility gradient between the inlet (260°C) and outlet (310°C) of the reactor core. If deuterium isotope effects are ignored, these correspond to a modest increase in the equilibrium solubility of magnetite from ~ 1 $\mu g\ kg^{-1}$ to 2 $\mu g\ kg^{-1}$ from 250 to 320°C, consistent with the absence of fuel deposits during normal operation. This is less than the solubility gradient assumed in some empirical activity transport models, which are based on Sweeton and Baes’ data, presumably reflecting the effects of disequilibrium and radiolysis in core. The effect of dissolved hydrogen is predicted to be negligible, suggesting that its major role is to suppress radiolysis effects. In-core precipitation is predicted to occur at lithium concentrations below ~0.10 ppm.

The lithium concentrations used under normal operating conditions are associated with a large negative magnetite solubility gradient during start-up and hot conditioning conditions in which the temperature is increased from 25 to 250°C.

3. HOT CONDITIONING CHEMISTRY

3.1. The effect of hydrazine on the solubility and mass transport of magnetite

Hot conditioning is typically carried out by increasing the temperature of the primary coolant circuit from 25 to 250°C using pump heat, and the temperature gradient between the in-core and out-core sections of the circuit is negligible (<1°C). The coolant chemistry consists of LiOH solutions (pH = 10.0 to 10.5) with hydrazine additions (30 to 100 mg/kg, 1×10^{-3} to 3×10^{-3} $mol\cdot kg^{-1}$) to maintain reducing conditions [16]. In the absence of hydrazine, the solubility of magnetite is low, <10 µg/kg at lithium concentrations above 0.69 ppm (1×10^{-4} $mol\cdot kg^{-1}$), and largely independent of temperature. At lower lithium concentrations there is a much higher solubility gradient. For example, for 0.07 ppm Li (1×10^{-5} $mol\cdot kg^{-1}$) the solubility was calculated to be 60 µg/kg at 60 °C dropping to 5 µg/kg at 250°C.

The effect of the addition of hydrazine was calculated on the assumption that 30 or 100 mg/kg of hydrazine (1 and 3×10^{-3} $mol\ kg^{-1}$) is initially at equilibrium, then thermally decomposes to form its decomposition products. Three scenarios were used: (i) The initial hydrazine equilibrium concentrations before decomposition were taken to be $N_2H_4 \rightleftharpoons N2 + 2H_2$ and $N_2H_4 \rightleftharpoons N2H^{5+}$. (ii) The thermal decomposition products of N_2H_4, as measured by Lucien [17] for ~ 230°C, were taken to be 3.9 mol NH_3 and 0.15 mol H_2 for every 3 mol of N_2H_4 for all temperatures. (iii) Hydrazine was assumed to form quantitative concentrations of ammonia and hydrogen so that 2 mol N_2H_4 gives 2 mol NH_3 and 1 mol H_2. The results for 30 or 100 mg/kg hydrazine additions to the 3.5 ppm (5×10^{-4} $mol\cdot kg^{-1}$) Li and 0.35 ppm (5×10^{-5} $mol\cdot kg^{-1}$) Li solutions using the first and third models are shown in Figure 2. At the higher lithium concentration, the results are similar. At 0.35 ppm (5×10^{-5} $mol\cdot kg^{-1}$) Li, the effect of the NH_3 as a decomposition product is to dramatically lower the low-temperature solubility of magnetite, leading to much smaller level of precipitated deposits as the temperature is increased.

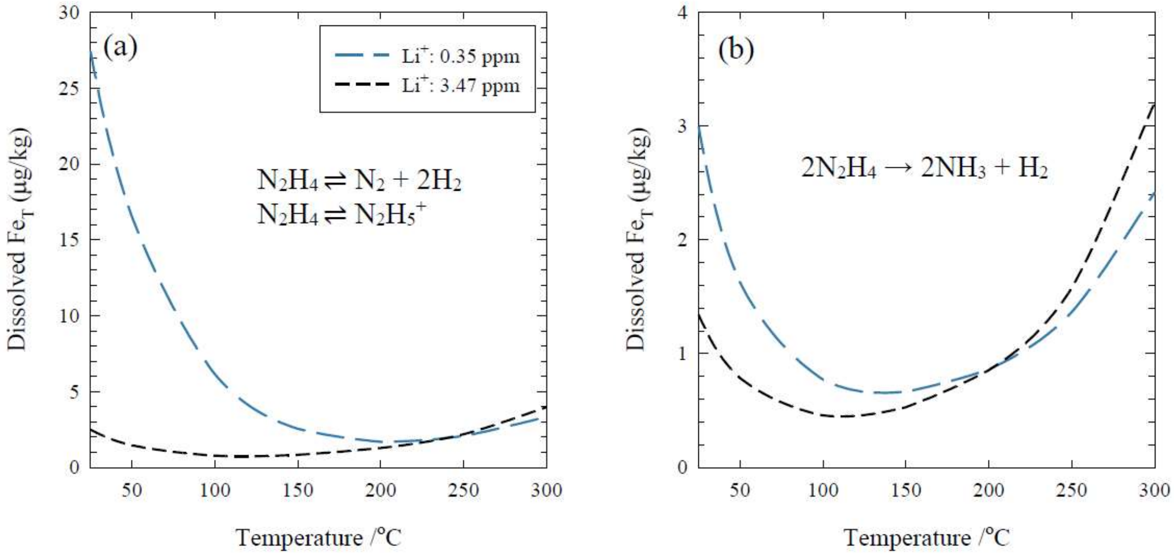

FIG. 2. The effect of temperature on the solubility of magnetite from 25 to 300°C at p_{sat} in the presence of 100 ppm hydrazine (a) Hydrazine equilibrium model in MULTEQ V.8, $N_2H_4 \rightleftharpoons N_2 + {}_2H_2$ and $N_2H_4 \rightleftharpoons N_2H_5^+$) or (b) Complete thermal decomposition of hydrazine according to $2N_2H_4 \rightarrow 2NH_3 + H_2$.

The effect of low lithium concentrations (Li < 0.35 ppm, 5×10^{-5} mol·kg^{-1}) without ammonia is to enhance the concentrations of iron at low temperatures during the heating cycle, possibly leading to the formation of heavier deposits of crystalline or polycrystalline magnetite at temperatures up to ~ 150°C during the hot conditioning process. We speculate that the higher alkalinity may favour enhanced epitaxial growth of passivating oxide film, rather than loose, non-adherent deposits, as the temperature is slowly and uniformly increased from 25 to 200°C. This is consistent with the experience during hot start-up at a particular CANDU plant [16] which used lithium concentrations above ~0.9 ppm (1.3×10^{-4} mol·kg^{-1}).

4. CONCLUSIONS

The iron database in MULTEQ V.8 is based on critically-evaluated literature data, including thermodynamic equilibrium solubility studies on both magnetite and hematite in light water at temperatures up to 300°C. Although they were not optimized to calculate the reversal in the magnetite solubility gradient with pH between 250 and 300°C, a preliminary assessment suggests that the results appear to be consistent with typical CANDU reactor operating conditions, based on LiOH concentrations. Because both iron (II) and iron (III) hydrolysed species are present, the effect of dissolved hydrogen on the equilibrium solubility is minimal. The database is therefore a useful tool in assessing the effects of equilibrium magnetite solubility on activity transport and FAC. It is important to note that the deuterium isotope effects on hydrolysis and the effects of radiolysis on redox chemistry under primary coolant conditions may be large. These are topics of ongoing studies.

One of the interesting findings from our initial studies is that that there are two distinct pH ranges for start-up and hot conditioning. At 'high' pH, Li ≥ 0.35 ppm (5×10^{-5} mol·kg^{-1}), the solubility of magnetite is low, < ~5 µg/kg, and almost independent of temperature. At 'low' pH, Li ≤ 0.07 ppm (1×10^{-5} mol·kg^{-1}) the low temperature solubility is much higher, >40 µg/kg at 100°C, and there is a sharp drop in the solubility of iron with increasing temperature. Under 'low pH' primary coolant chemistry conditions, there may be increased dissolution at low temperatures, followed by precipitation from solution as the primary coolant circuit is heated up to 250°C. There may be merit in exploring strategies based on different Li concentrations during start-up or hot conditioning that differ from those used in normal operation to minimize fuel deposits or optimize the growth of optimum passivating oxide films.

ACKNOWLEDGEMENTS

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CORRESION MODELLING AND FUEL BEHAVIOURS ASSESSMENTS

(Session III)

Chairperson

W. GRANT
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MODELLING OF CORROSION PHENOMENA IN ATUCHA I AND II NPP IN ACCIDENT ANALYSIS

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Abstract[7]

Atucha I and II are vertical PHWRs of German design with a relatively low average fuel extraction burnup (11000 MWd/tU and 7800 MWd/tU, respectively). In normal operation, the oxide thickness of the fuels to be extracted is very far from the limit set in the fuel design acceptance criteria. The water chemistry parameters are carefully controlled in order to assure the formation of a passivating oxide layer to minimize the corrosion velocity, the dose rate and the corrosion products release. Nonetheless, in abnormal situations some corrosion related issues may jeopardize the fuel integrity, such as high temperature oxidation in LOCA scenarios and PCI/SCC in power ramps. Some analysis were performed to test the fuel reliability in the above mentioned conditions with TRANSURANUS code. The present paper provides a description of those phenomena, the methodology used for Atucha I and II FSAR calculations and as an example some results obtained for Atucha I.

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[7] Only abstract is available.

REMEDIAL ACTIONS TO ENSURE RELIABLE FUEL PERFORMANCE

(Session IV)

Chairperson

R. KAMESWARAN
Canada

REGULATORY PERSPECTIVE ON CHEMISTRY CONTROL AT CANADIAN NUCLEAR POWER PLANTS

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Abstract

This paper/presentation provides a regulatory perspective on the verification of licensees' activities related to chemistry control. Verification activities include analyzing chemistry data provided by NPP licensees, performing inspections, and monitoring recent reportable events. The scope of these verification activities can be influenced by recent research in reactor chemistry.

Despite these verification activities, chemistry-related incidents do occasionally occur. A brief summary of a sample of events related to chemistry control is provided, along with the follow-up action taken by the CNSC. Examples of the regulatory oversight of licensees' reactor chemistry-related licensee activities are also provided.

1. INTRODUCTION

Chemistry control is an essential part of operations at a nuclear power plant (NPP). Adequate chemistry control will: minimize corrosion within the systems, reduce deposition on fuel, minimize worker radiation exposure caused by the activation of impurities in the core, and reduce the impact on the environment by lowering radioactive and chemical releases.

From a regulatory perspective, verification of the adequacy of the chemistry control programs in NPPs is therefore important to fulfilling the Canadian Nuclear Safety Commission's (CNSC's) mission, which includes regulating the use of nuclear energy and materials to protect health, safety, security and the environment8. This paper describes the compliance verification activities performed by the CNSC in the area of chemistry control. It also includes a description of the verification and analysis of safety performance indicators, information on how chemistry inspections are performed, and details on the sources of information needed to perform efficient compliance verification. Additionally, examples of the application of compliance verification are provided, either during planned or normal operations, unplanned or non-routine licensee activities, or after incidents at an NPP.

2. CHEMISTRY CONTROL BASIS

In Canada, the Commission Tribunal (currently called the Commission) is the regulatory body that issues licences to facilities using nuclear materials for several purposes, including generating electricity. When a licence is issued, this licence refers to a licence conditions handbook (LCH) that identifies the compliance verification criteria to be applied to the facility. Within this LCH, other legislations can be referred to as needed (such as those related to fire safety or environmental releases), as well as standards from the Canadian Standards Association (CSA) or International Atomic Energy Agency (IAEA) technical documents. These documents serve as the basis for verifying compliance.

In particular, CSA standard N286, Management System Requirements for Nuclear Facilities, provides general requirements for chemistry control, including requirements for a chemistry control program, chemical surveillance, chemistry specifications for systems, and storage and handling.

CNSC staff considers four main aspects in order to assess a licensee's ability to manage and execute an effective chemistry control program:

- understanding of chemical behaviour;
- aging management;
- chemistry monitoring;
- Research and development response.

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[8] From the Canadian Nuclear Safety Commission website.

The licensees are required to demonstrate that they are competent to operate the facility and perform activities as indicated in the licence and the Canadian Nuclear Safety and Control Act (NSCA). As part of that requirement, the chemistry control program needs to demonstrate that the operator understands the chemistry behaviour of various systems. That can be done through the proper identification of specifications and adequate justification. Additionally, the licensee needs to demonstrate the safe operating limits of these specifications, and the appropriate response when the facility is operating outside its chemistry specifications.

One of the main reasons chemistry control programs are important for the safe operation of a CANDU plant is that these programs control the degradation of systems and components, which rely on appropriate chemistry control to maintain their function throughout the design life. The chemistry control programs needs to demonstrate that adequate considerations are being made in relation to the aging management of these components.

Effective chemistry monitoring is essential to show that licensees can demonstrate an adequate understanding of the facility chemistry, and that they are able to minimize degradation to ensure components are able to maintain their effectiveness over their design life. The program will ensure that monitoring techniques remain effective and that calibration of equipment is done properly. Good chemistry monitoring programs also make use of online monitoring techniques to provide a greater ability to identify negative trends and out-of-specification results (in real time) to minimize the impact of degradation and plant operation.

During the lifetime of an NPP, unknown degradation mechanisms and phenomena are encountered. A robust research and development (R&D) program is required to understand and respond to any new chemistry or degradation mechanisms and to maintain the plant chemistry knowledge. While these R&D programs focus on any changes that may negatively affect the current safe operating envelope of the plant or its design basis, additional effort on mechanisms that accelerate degradation or compound the magnitude of any failure scenarios would need to be investigated.

3. COMPLIANCE VERIFICATION

At the CNSC, several activities are performed to verify compliance. These activities include the analysis of safety performance indicators (SPIs), and the review of documentation and inspections. These activities were previously explained by R. Kameswaran9, and an updated version is provided here.

3.1. Safety performance indicators

Licensees are required to report a set of twenty-five SPIs to the CNSC; two of which are chemistry-related. These are detailed in a Canadian regulatory document, REGDOC 3.1.1, Reporting Requirements for Nuclear Power Plants. These SPIs are different from other performance indicators used in the nuclear industry, and include two chemistry-related SPIs, the chemistry index (CI) and chemistry compliance index (CCI). The CI is the percentage of time that the selected chemical parameters are within specification. It quantifies the long-term control of important chemical parameters. The CI is used to determine long-term risks on safety-related systems, including corrosion. The CCI is the percentage of time that the selected chemical parameters are within the licensees' specifications for guaranteed shutdown state (GSS) and non- GSS conditions. The CCI parameters are selected based on potential immediate risks to safety, if these parameters are out of specification. These parameters are provided in the table below.

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[9] Ram Kameswaran, *Regulatory Oversight Strategy for Chemistry Program at Canadian Nuclear Power Plants,* conference paper, Nuclear Power Chemistry Conference, Paris, 2012.

TABLE 1. CHEMISTRY PARAMETERS MONITORED FOR THE SAFETY PERFORMANCE INDICATORS

Chemistry Index	Chemistry Compliance Index (non-GSS and GSS)
Primary heat transport system pH_a	Non-GSS
Primary heat transport system dissolved D_2	[Gd] in liquid injection safety system poison injection tanks
Primary heat transport system chloride	[Gd] in moderator (unit in poison outage, SDS2 actuated)
Primary heat transport system fluoride	Moderator D_2O isotopic
Primary heat transport system conductivity	Moderator H_3
Annulus gas [O2]	Moderator cover gas D_2
Steam generators chloride	Moderator conductivity
Steam generators sulphate	Primary heat transport system D_2O isotopic
Steam generators sodium	Primary heat transport system H_3
Feedwater dissolved O_2	Primary heat transport system I_{131}
Feedwater total iron	Primary heat transport system D_2O storage tank cover gas D_2
Feedwater hydrazine	Moderator to primary heat transport system D_2O isotopic purity difference check
Condensate extraction pump dissolved O_2	Annulus gas system dewpoint
Condensate extraction pump pH	End shield cooling water pH
	End shield cooling cover gas H_2 (for Point Lepreau, Gentilly-2, Pickering 5-8)
	ECI high-pressure water tank(s) pH
	ECI high-pressure water tank(s) hydrazine concentration
	Liquid zone control cover gas [H_2]
	Liquid zone control conductivity
	GSS
	Liquid injection safety system poison injection tanks pH_a (when SDS2 is available)
	[Gd] in moderator
	Moderator D_2O conductivity (except for Gentilly-2)
	Moderator D_2O pH_a
	Supplementary parameter(s) sampled

3.2. Review of documentation

One compliance activity is the review of documentation submitted by the licensee relating to potential changes to the operation of an NPP. Depending on what is indicated in the LCH, the licensee may simply be required to notify the CNSC of changes in documentation or may need to make a formal request to the CNSC for any major change(s) that might affect the licensing basis.

3.3. Inspections

Performing inspections is another important CNSC compliance activity. Currently, there are two types of inspections related to chemistry as part of the baseline at NPPs performed by the CNSC: type II inspections and field inspections. Type I inspections (audits) look at the entire program. This type of inspection is triggered only if the CNSC suspects a licensee chemistry program is ineffective. Type II inspections may be planned or reactive, announced or unannounced, and are conducted by one CNSC inspector or a team that includes a chemistry specialist. Field inspections are conducted by onsite inspectors. These inspectors use a guide prepared by specialists, typically without the specialist present; however, the specialist is available for support as needed.

3.3.1. Type II inspections

Currently in Canada, Type II chemistry inspections are performed at each NPP every five years and are performed over the course of approximately one week. They verify the results of licensee processes and include routine inspections/rounds to check equipment, systems, records, and products. During these inspections, the following verifications are made:

- licensee chemistry procedures, work instructions;
- training of the employees responsible for performing activities related to chemistry;
- records of chemistry-related activities such as results of chemistry analyses;
- visits of chemistry laboratories to verify the presence and proper functioning (i.e.: calibration, maintenance) of appropriate equipment;
- verification of proper chemical storage;
- observance of an employee performing chemistry-related activities.

The focus of these inspections will vary according to the information gathered prior to the inspection. The performance from previous years, events at the plant or elsewhere, or any change(s) in practices at the station or in the industry are also taken into account.

3.3.2. Field inspections

The nature of Type II inspections provides a very in-depth, but infrequent, overall view of a licensee's chemistry control program. Chemistry-related field inspections have recently been developed to improve the regulator's evaluation of chemistry control program performance by providing a more frequent assessment of this program. This will complement the quarterly SPIs. Field inspections are performed by on-site CNSC inspectors using a field inspection guide developed by chemistry specialists at CNSC headquarters. One advantage of developing field inspections is that it makes more time available during Type II inspections, which then allows for a more thorough review or for a shorter Type II inspection. The areas covered by these inspections have been selected to remove the necessity of involving a CNSC chemistry specialist on site. However, the chemistry specialist is available to respond to inquiries as needed (either before, during or after) and is sent a copy of the report. Follow-ups with the licensees are performed, also as needed. The areas currently covered by field inspections are chemical storage and online analyzers. Another field inspection being developed is related to chemistry control of the spent fuel storage bay.

4. SOURCES OF INFORMATION USED TO DETERMINE COMPLIANCE

In order to perform effective compliance verification activities in the area of chemistry, reliance on information from several sources is required. This information is invaluable, for example, to determine the scope of an upcoming chemistry inspection, or to assess when a compliance action is required (and which one), or to determine if a licensee's request is acceptable.

The chemistry specialists have to keep themselves apprised of information from the reactor chemistry research field. Information is gathered from reading research publications, attending chemistry conferences, and being a member of the NSERC/UNENE Senior Industrial Research Chair in High Temperature Aqueous Chemistry Technical Advisory Committee at Guelph University. This allows the chemistry specialist(s) to gain the latest knowledge in reactor chemistry. Additional information can also be accessed through chemistry-related events reported under the requirements stated in REGDOC 3.1.1, or via a CNSC database called Central Event Reporting and Tracking System (CERTS) (including international incidents at a CANDU NPP), as well as the IAEA International Reporting System for Operating Experience (IRS).

5. REGULATORY OVERSIGHT ACTIVITIES – UNEXPECTED EVENTS

In cases where a licensee experiences a previously unknown phenomenon during reactor manoeuvres or refurbishment processes, the CNSC provides regulatory oversight to confirm that these phenomena are well analyzed and do not inhibit the safe operation of the reactor or its safety systems. CNSC staff has recently provided regulatory oversight where the evidence of fuel deposits had been observed during post-refurbishment start-up activities at one of the Canadian NPP facilities. CNSC staff was invited on several occasions to take part in meetings where results from research were presented. CNSC staff also took part in discussions, that analyzed the implications of results on the reactor safe operating envelope. In addition, CNSC staff provide oversight for any proposed changes or modification(s) to the safety envelope or safety analysis that resulted from research findings.

The NSCA and other associated regulations provide strict requirements for reporting to the CNSC in the case of events. Examples can include unexpected fuel deposits during normal operations, or an unexpected release of a radioactive substance to the environment. Should the licensee become aware of an incident, an immediate preliminary report needs to then be made to the CNSC. This is followed-up later with a full report. CNSC staff then determines, according to criteria set in internal procedures, if the event is reportable to the Commission. If this is indeed the case, the incident is then discussed at the next meeting of the Commission. Chemistry specialists are involved (when needed) in the assessment of the event and the eventual follow-up. Should the event involve a Canadian licensee, the chemistry specialist will help present of the information to the Commission.

6. CONCLUSIONS

This paper provided a summary of compliance activities related to chemistry control, as well as examples of how those activities are performed, either during normal operations or accident conditions.

The CNSC's mandate is to regulate the use of nuclear energy and materials to protect health, safety, security and the environment in order to implement Canada's international commitments on the peaceful use of nuclear energy, and to disseminate objective scientific, technical and regulatory information to the public. The CNSC therefore verifies the compliance of facilities such as NPPs and ensures that any new information is taken into account by the licensee in performing its activities. Additionally, CNSC specialists keep abreast of research in the area of reactor chemistry and stay informed about incidents at NPPs worldwide, while verifying that appropriate actions are being taken by licensees to ensure safety.

INSIGHTS ON FUEL SHEATH DEPOSIT FORMATION DURING PRIMARY HEAT TRANSPORT HOT CONDITIONING

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Abstract

Pressurized Heavy Water Reactor (PHWR), CANadian Deuterium-Uranium (CANDU), Operating Experience (OPEX) provides evidence that performing post-refurbishment Primary Heat Transport System (PHTS) Hot Conditioning (HC) with fuel in core presents a risk that the fuel bundles may become coated with iron-based, primarily magnetite and hematite, deposits during the evolution. This OPEX also provide evidence that these deposits remain on the fuel sheath for a period of approximately three to six months into the subsequent operation of the plant before the deposit material is redistributed into the PHTS coolant and removed from the system through the PHTS purification system. Such deposits, while present on the sheath, are thought to contribute to fuel sheath corrosion and impact fuel element heat transfer properties. OPG commissioned a series of laboratory testing to investigate the factors that contribute to the phenomena of fuel sheath deposit formation. These tests included comparative studies of HC evolutions, which emulated recent CANDU post-refurbishment OPEX in a laboratory setting. These investigations provided clarity on the parameters relevant to this adverse condition and on controls that can be implemented to minimize deposition on fuel bundle sheath surfaces. Sensitive parameters and associated controls include; (1) use of a "conventional" HC process as compared to a chelating-agent type HC, that use forms of Ethylenediaminetetraacetic Acid (e.g. Li2EDTA), (2) HC prior to reactor first approach-to-critical (i.e. no fuel heat), (3) maintenance of PHTS pH per current industry expert recommendations, and (4) careful control of other dissolved materials in the PHTS during PHT cold flush. OPEX observations suggest that the surface condition of fuel sheathing may also be a contributing factor related to the probability of deposition. This indicates that fuel sheaths that have been "polished" following tube production may be less susceptible to deposition of magnetite on sheath surfaces during HC. While OPG has considered this observation to be interesting, it was not further investigated, and thus requires validation.

1. SUMMARY

The Return-to-Service (RTS) plan of the Ontario Power Generation (OPG) Darlington Refurbishment reactors schedules the Primary Heat Transport System (PHTS) Hot Conditioning evolution following fuel load. The purpose of this document is to provide the results of extensive investigations and assessments, which provide an improved understanding of the impact of this process on fuel condition and fuel fitness for service (FFS).

The Hot Conditioning (HC) evolution planned for return to service (RTS) of Darlington Unit 2 will differ from strategies employed for both the Point Lepreau and Bruce Power Units 1 & 2 refurbishments. Reactors at Point Lepreau, Bruce Unit 1 then Bruce Unit 2 were returned to service between July and October 2012. While Pt. Lepreau did not report adverse impacts on fuel condition due to HC (no deposits on fuel sheaths), Bruce Power has reported that fuel bundle surfaces became coated with magnetite and other depositing or precipitating materials. The concerns pertaining to these deposits were related to impacts on heat transfer, fuel sheath integrity and safety analysis margins.

Our out-reactor program initially tested the impact of the 'Conventional' HC process on fuel condition. Additional tests were then performed to study the impact of the alternate chelating agent (Li-EDTA) based HC evolution on deposit formation and fuel condition. The final phase of the out-reactor test program focused on assessment of the impact of fuel surface deposits on heat transfer and on fuel FFS.

These investigations have demonstrated that the planned PHTS Hot Conditioning evolution for Darlington Unit 2 RTS does not represent a risk to fuel fitness-for-service, performance or safety analysis margins. The following factors are most important:

- Application of the "Conventional" hot-conditioning process;
- Control of PHTS chemistry as specified in the recent COG State-Of-The-Art-Report (SOTAR) on fuel deposits;

- Reliance on PHTS main pump heat only to achieve hot-conditioning temperatures (i.e. HC prior to Approach-To-Critical (ATC); no fuel heat).

The Darlington Hot Conditioning evolution will be unlike the evolution that resulted in fuel sheath deposits. These alternate evolutions using the Li-EDTA hot-conditioning process, utilized fuel heat to achieve the required temperatures and suffered from excursions in PHTS chemistry.

The results of the OPG out-reactor tests provide confidence that the "conventional" HC evolution planned for Darlington Unit 2 poses minimal risk of causing deposition on fuel bundle surfaces. The OPG out-reactor testing program corroborates the expectations and professional judgement of industry experts.

2. INTRODUCTION

The refurbishment of the Darlington units involves replacing major components of the PHTS, including the fuel channels and the upper & lower feeder pipes. The rebuilt PHTS will be hot-conditioned in order to protect the new components from corrosion and pitting. The HC process will ensure PHTS FFS for subsequent unit operation.

The RTS OPEX of Point Lepreau and Bruce Power Unit 1 & 2 Restart (between July and October 2012) provides contrasting fuel performance OPEX. Fresh fuel bundles were in-core during HC in all 3 cases. Post-discharge inspections at Point Lepreau did not indicate fuel performance concerns, however, fuel bundles discharged from Bruce Units 1 & 2 were observed to have iron-deposits on the fuel bundle exterior surfaces [1]. This adverse OPEX was of concern to OPG as it represented a risk that HC of the Unit 2 PHTS after fuel load could degrade fuel FFS via. Reduction of fuel to coolant heat transfer, degradation of fuel sheath integrity, and overall decrease of performance and safety margins.

In response to these concerns, OPG has conducted extensive investigations of these evolutions and related issues.

3. ASSESSMENT STRATEGY

OPG has completed fuel performance studies, safety analysis assessments and out-reactor testing of the impact of the planned Darlington HC process. Further, OPG has attempted to replicate available OPEX to understand the mechanisms/phenomena that resulted in deposit formation. The focus of these efforts has been to provide a reliable assessment of the risks and benefits of the planned Darlington evolution and to understand the key factors, allowing mitigation of any adverse impacts.

OPG has undertaken the following initiatives:

- Formation of a high impact team (HIT) to assess the risks of PHT RTS after fuel loading and to review industry OPEX;
- Fuel fitness-for-service assessments and calculations (both internal and contracted);
- Safety analysis (SA) assessments;
- Execution of an extensive out-reactor testing program at the Stern Laboratories;
- Consultation and deliberations with a team of industry-recognized CANDU-Chemistry experts to provide insights, assessments and recommendations.

The following discussion provides the results of these initiatives.

3.1. Assessment of industry hot conditioning OPEX

3.1.1. Refurbishment Bruce Units 1 and 2

PHTS HC after refurbishment of the Bruce reactors were conducted using a chelating agent (Li_2 EDTA) and after the initial ATC.

Fuel sheath deposits were observed on almost the entire exposed surfaces of fuel bundles discharged after restart of the two Bruce reactors. Some of these bundles had been discharged prematurely, in response to fuel defects due to debris-fretting. Description of the deposits following Post Irradiation Examination (PIE) indicated that they were "fine and light, mainly grey/black in colour, non-adherent and easily brushed away". It is believed that the deposits were mainly magnetite (Fe_3O_4), in agreement with expert expectations. Examination of the inspection photos indicate that the deposits formed uniformly over sheath surfaces, but that deposition did not occur at the ends of fuel elements that were 'cleaned-back' for weld preparation during manufacturing.[10]

Bruce Power has published results of the hot-cell post-irradiation examinations (PIE) of fuel elements containing deposits and discharged from Bruce Units 1 and 2 [1]. The following information relevant to this discussion are provided:

— Deposits on some elements were up to 20 µm thick.
— Deposits were not present on the endcap regions of the fuel sheath.
— Deposits appeared to be porous.
— Fuel sheath oxidation beneath deposits were measured to be < 10 µm in thickness. This is compliant with the design specification for maximum permitted fuel sheath oxidation.
— Metallurgical examinations of fuel sheath material under the deposits did not reveal any indications of adverse fuel sheath behaviour such as changes in cladding metallurgical structure or elevated Hydrogen / Deuterium pick-up.

3.1.2. Refurbishment of Pt. Lepreau

PHTS HC after refurbishment of the Pt. Lepreau reactor was conducted using the 'conventional' process and after the initial ATC. PHTS chemistry was well controlled and pH remained above 10. Industry expert judgment precluded deposition on fuel sheaths at these pH and temperatures.

Inspections of fuel bundles discharged after return to service revealed that fuel bundle surfaces appeared to be free of deposits.

3.2. Deliberations of industry chemistry experts on hot conditioning

OPG organized an external team of respected experts in CANDU chemistry. Their assessments and recommendations are summarized below.

The deposition of magnetite, the major corrosion product found on CANDU fuel, is largely determined by the pH_a and temperature of the primary coolant. Magnetite deposition is mainly by heterogeneous precipitation on the cladding surface, with a small amount being deposited as particles from the coolant. Since the core of a CANDU reactor contains no iron-based alloys, only dissolved iron in the coolant entering the core would be available for deposition. For normal operation, the pH_a has to be maintained above the solubility minimum of magnetite to ensure that the solubility increases with increasing temperature, and therefore any dissolved magnetite would not deposit in-core.

The Expert Team provided clarity on the benefits of a discrete HC evolution prior to first criticality. Prior to the deliberations, choice of this sequence was largely supported by historical bias dating from the first commissioning of the Darlington reactors.

The chemistry deliberations also revealed that these initial HC evolutions prior to first commissioning at Darlington had been designed to protect PHTS steel components during the dry period between initial H_2O fill, flush and drain and subsequent refill with D_2O. It followed that if H_2O fill was not to be used for the first filling of the PHTS, then it might be acceptable to allow the relevant PHTS steel surfaces to become conditioned during the initial period of reactor operation after the required PHTS temperatures have been achieved. The possibility of a Hot Conditioning evolution after fuel loading was beneficial to the refurbishment timeline. The planned HC evolution was deemed appropriate to mitigate any risk of having high iron levels in the system during on-power operation, as not having a discrete HC evolution would introduce uncertainty and potential higher risk of deposits.

3.3. COG SOTAR on corrosion product deposition on CANDU fuel cladding

The CANDU Owners Group (COG) has produced a State-Of-The-Art-Report (SOTAR) on "Corrosion Product Deposition on CANDU Fuel Cladding" [2]. This report has reviewed a wide range of magnetite and crud

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[10] All CANDU fuel manufacturers "clean back" the ends of fuel sheaths to ensure the good quality of the endcap to sheath weld. In addition, the OPG fuel manufacturer polishes the entire fuel sheath as a required part of the production process. Our tests and observations of OPEX indicate that either sheath polishing or "clean-back" for weld preparation might reduce the possibility of deposition of fuel sheaths.

deposition data in nuclear PHTS. The scope of the document includes experimental results and both CANDU and non-CANDU OPEX.

This document provides the following insights relevant to this discussion:

- Magnetite is the main deposition material.
- Precipitation is an important part of the mechanism for creation of deposits.
- Deposits are expected to be porous. These porous deposits to depth of up to 40 µm result in enhanced cooling of sheath surfaces. There were no associated degradations of either the fuel sheath to coolant heat transfer, or of the sheath material.
- Coolant pH and temperatures are main factors in determining the probability and rates of deposition. The SOTAR has provided a pH vs. sheath temperature control diagram which will be a useful guide for RTS at Darlington (to avoid deposition).

The SOTAR also suggests that in the early Bruce OPEX, fuel bundles manufactured by one of the two primary fuel manufacturers were observed to be coated by magnetite whereas fuel bundles manufactured by the other manufacturer appeared to resist this phenomenon. The reason for this observed discrepancy was not discussed further in the SOTAR although, the lack of deposition on the ‘cleaned-off’ ends of elements (Bruce refurbishment OPEX) suggests that fuel sheath polishing might be a relevant factor. OPG did no studies in this area to further explore or validate this as a relevant factor.

4. OUT-REACTOR TEST PROGRAM

OPG has conducted a comprehensive out-reactor testing program to investigate issues related to hot conditioning after fuel loading [3]. The intent of the out-reactor testing was to assess the impacts on fuel bundles of the both the conventional and Li-EDTA Hot Conditioning processes, and to determine the optimal methodology, conditions and duration of Hot Conditioning to preclude fuel deposits. This constituted Phase 1 of the testing program. Phase 2 investigations were dependant on the result of the first phase of this program, and studied the extent of deposition on fuel, and the impact of any deposition on heat transfer and fuel sheath integrity.

For Phase 1, five (5) Trials were completed testing the three types of Hot Conditioning methodologies to investigate the formation/creation of deposits on the fuel sheath, as follows:

- Trial #1: Conventional, prior to first ATC (planned Darlington approach)
- Trial #2: Chelating agent (Li-EDTA), post ATC (Bruce Units 1 & 2 approach)
- Trials #3a, #3b and #3c: Conventional, post ATC (Point Lepreau approach)

The results of these tests are summarized as follows:

- Trial #1 – This conventional HC trial was performed first and resulted in minimal deposition (non-adherent and in the form of “stream-lines” and “spots” rather than layers) on fuel. Deposit thickness was inconsistent and below the measurable tolerance of the available “Optical Scanning” measurement equipment (± 5 µm). Test results contrasted to the heavier uniform deposits observed after Bruce Power refurbishment. Regarding this trial:
  - The trial was concluded after 48 hours. This trial might provide an overestimation of the quantity of deposit that might be observed after the planned Darlington evolution, as chemistry correction was not performed prior to shutdown (for reduction of Total Suspended Solids (TSS), including Iron).
  - Industry expertise recommend that the ideal range of coolant pH_a to prevent fuel sheath deposition and minimize feeder corrosion is 10.2 to 10.4 (equivalent to a pH of ~9.8 to 10.0). However, pH during the out-reactor trial dropped as low as ~ 9.0. Therefore, the test result is expected to represent a worst-case for the evolution planned for Darlington.
- Trial #2 – The Li-EDTA based Hot Conditioning trial, intended to replicate/emulate the Bruce Power Hot Conditioning conditions, resulted in greater deposit thickness than the previous trial. Fuel heat / reactor power was simulated during this test, as Bruce Units 1 & 2 Hot Conditioning evolutions were performed with the reactor at power.
  - A particular challenge with the EDTA methodology is the maintenance of pH while removing Li in preparation of Li2EDTA injections. As Li is removed the coolant pH drops dramatically and falls below the recommended range.

- Trials #3 – This trial was repeated 3 times. Chemistry control OPEX from the Point Lepreau HC informed that it was possible to maintain a high pH_a (10.5- 10.8) for the duration of the evolution. Stern improved their understanding of how to manage pH with each trial. During both the low-power and high-power stages of Trial #3, coolant pH was held > 9.7 and no deposition was observed on the fuel. The high-power trial included simulation of 20% Full Power operation.
- An additional observation made during these trials was that significantly more deposits were observed on the test loop's heater surface than on the test specimens. The heater element was simply a Zircaloy specimen fitted over an electrical heater in a similar configuration as the test specimen. The element power varied up to ~20 kW during the tests. The deposits were in the form of thick layers and were adherent to the sheath surface, an observation which supports the conclusion that a hot element surface temperature promotes deposit formation [SOTAR].

Table 1 provides an overview of this testing program and key results.

TABLE 1. SCOPE OF THE HOT-CONDITIONING TESTING PROGRAM

	Trial Number				
Test	Trial #1	Trial #2	Trial #3a	Trial #3b	Trial #3c
Parameter	DNGS	BP	PLGS	PLGS	PLGS
Process	Conventional	Li EDTA	Conventional	Conventional	Conventional
Fuel Power	Pre-ATC	Low (~500 W/m)	Low (~500 W/m)	Low (~500 W/m)	High (~9 kW/m)
Chemistry Control	Poor	Poor	Poor	Good	Good
PHT Temperature	250	262	60	250	250
Observation	Low deposits Less than measurable limit (< 5 µm)	High deposits ~10-15 µm	High deposits ~10 µm	No deposit	No deposits

Figure 1 provides the assessment of the Stern test evolutions based on the SOTAR pH guidance. Here, the accepted conversion from pH to pD (pH for heavy water) is provided in Chapter 15 of the "Essential CANDU Textbook", ISBN 0-9730040, as $pH_a = pD - 0.41$, where in the alkaline CANDU PHTS $pH_a = pH + 0.456$.

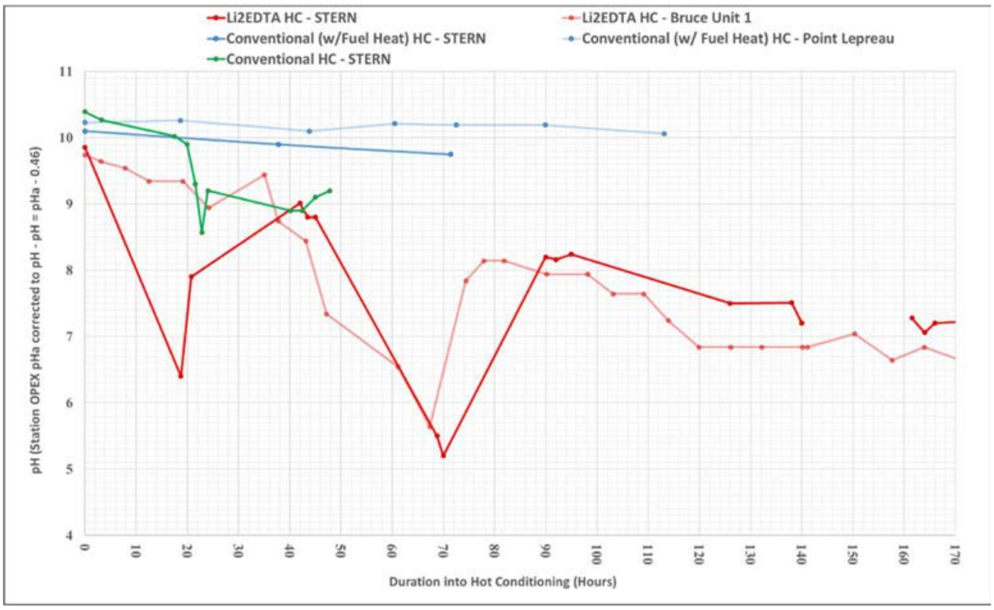

FIG. 1. Comparison of coolant pH trends; Stern tests and OPEX.

Legend: Trial #1 – GREEN; Trial #2 – RED; versus Bruce Power OPEX (LIGHT RED); Trial #3 (high power trial) – BLUE; versus Point Lepreau OPEX (LIGHT BLUE)

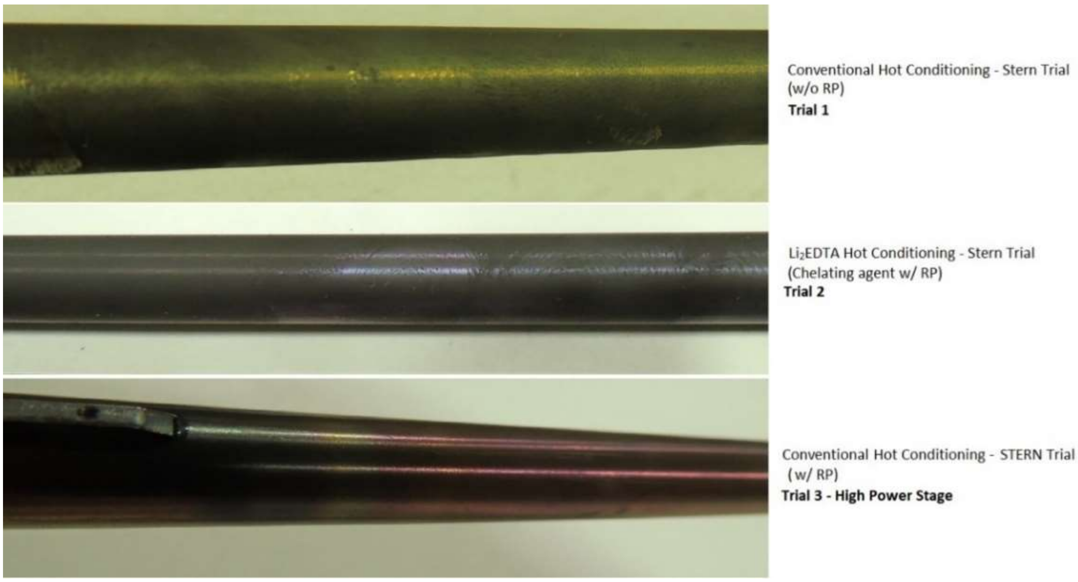

FIG. 2. Examples of deposition observed during testing at Stern for evolutions shown in Figure 1.

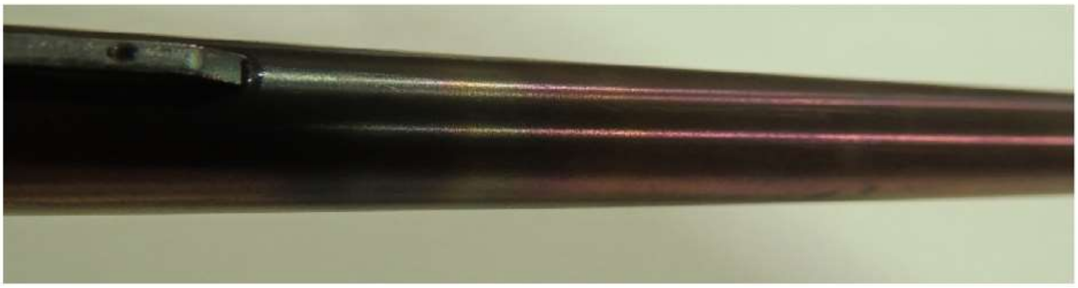

FIG. 3. Results of testing at Stern for Trial 3b (after low power stage).

The observed deposition on test elements for these evolutions are provided in Figures 2 and 3.

The Phase 2 tests have provided measurements of the impact of fuel sheath surface deposits, on heat transfer and sheath integrity for operating fuel elements. It is noteworthy that it was not possible to create deposits of measurable thickness if test conditions were kept consistent with the Conventional HC evolution planned for Darlington. Significant and non-representative reductions in coolant pH were required to promote deposit formation. Results of these tests are discussed in [3]. Assessments of these tests demonstrate that there will be no operational or safety impacts until deposit thicknesses exceed at least 40 µm. This is in agreement with the SOTAR which discusses that porous deposits with thicknesses of up to 40 µm will not adversely affect heat transfer. The assessment of the fuel condition against relevant Safety Analysis for Abnormal Operational Occurrences (AOOs) and Design Basis Accidents (DBAs) indicates that there will be sufficient margin to the respective acceptance criteria for fuel sheath dryout and fuel sheath temperature.

5. CONCLUSIONS

The results of out-reactor testing, Point Lepreau OPEX and expert assessments provide evidence that good chemistry control is effective in addressing the risk of deposition on fuel sheaths during HC. The adverse Bruce Power refurbishment OPEX (heavy and uniform deposits) is not relevant to the planned Darlington evolution.

For the hot-conditioning evolution, our investigations have identified three primary factors necessary to promote fuel fitness-for-service:

- Careful control of coolant chemistry and temperature as specified by Darlington procedures and the COG SOTAR;
- Use of the Conventional HC process as compared to the Li-EDTA process used at Bruce;
- HC before initial Approach-To-Critical.

In addition, fuel sheath surface finish (polishing) is possibly a relevant factor. This observation was not further investigated and thus requires validation.

The opportunity for formation of fuel sheath deposits is largely dependent on coolant chemistry. Deposition on fuel bundles, as experienced at Bruce Power, is not anticipated after HC at Darlington where the “conventional” method of Hot Conditioning is to be employed. Adherence to well controlled PHTS chemistry regimes, as have now been defined by industry experts and verified by our out-reactor tests, will minimize deposition.

The planned Darlington PHTS Hot Conditioning evolution will not compromise fuel FFS. In the worst case some light spotty deposits might be observed on fuel element surfaces, if chemistry control is challenged. Out-reactor testing has demonstrated that even this worst-case deposit would be of low and inconsistent thickness, and lightly adherent to fuel sheath surfaces. It will not be of sufficient thickness or quality to compromise fuel operations or reactor safety. The safe operating envelope as defined in the Safety Analyses will not be impaired.

The planned Darlington HC evolution will be unlike the HC evolution for the Bruce A RTS, and these differences have been shown to be relevant to the likelihood and extent of deposition during HC for return-to-service of Darlington reactors.

Finally, while Chemistry experts agree that a discrete PHTS HC evolution is not necessary if the system is to remain full after refurbishment, the impact associated with having a potentially iron rich environment on-power may introduce additional risks. These risks will be mitigated by the discrete conventional HC evolution that is planned for Unit 2 at Darlington.

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REGULATORY PERSPECTIVE ON FUEL RELIABILITY CHALLENGES

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Abstract[11]

This paper/presentation discusses the Canadian Nuclear Safety Commission (CNSC) staff's regulatory perspective on fuel performance, the impact of PHT chemistry control on fuel reliability and recent CANDU OPEX. Specifically, that fuel performance and reliability need to be assured with a robust chemistry control and fuel inspection regime. This is to ensure, among other things, that chemical damage to the sheaths and deposits on the fuel are precluded. In this context, recent experience with regulating CANDU reactors where coolant chemistry created fuel deposits is presented.

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[11] Only abstract is available.

ABBREVIATIONS

AOO	anticipated operational occurrence
BWR	coiling water reactor
CANDU	Canada Deuterium Uranium
CHC	critical hydrogen concentration
CNL	Canadian Nuclear Laboratories, former Chalk River Nuclear Laboratories (CRNL) of Atomic Energy of Canada Limited (AECL)
CNSC	Canadian Nuclear Safety Commission
COG	CANDU Owner's Group
DBA	design basis accident
ECP	electrochemical corrosion potential
EPRI	Electric Power Research Institute
FAC	flow accelerated corrosion
FFS	fitness for service
INPO	Institute of Nuclear Operations
LOE	limited operating envelope
LWR	light water reactor
M-O	metal-oxide interface
NPP	nuclear power plant
OPEX	operational experience
OPG	Ontario Power Generation
PHTS	primary heat transport system
PHWR	pressurized heavy water reactor
PIE	post irradiation examination
PWR	pressurized water reactor
R&D	research and development
S-O	oxide-solution interface
WANO	World Association of Nuclear Operators

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