LCC9 ANNUAL REPORT

Operational Issues, Practices and Remedies

Operational Issues, Practices and Remedies

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Contents

1 Introduction and summary (Francis Nordmann)

1.1 Objective of the document

This LCC9 Annual Report on Operational Issues, Practices and Remedies (AR) has been established selecting various subjects of particularly high interest for ANT-International customers, either from Utilities or Research laboratories or vendors/designers or Regulators.

These covered issues should allow understanding some plant issues and remedies, to improve plant operation in a safe, economical, environmentally sustainable way.

This report combines the following subjects of limited extent but potentially important consequences.

- Mitigation of various types of corrosion encountered in the second containment barrier of PWRs;

- Enriched Boric Acid (EBA);

- The behaviour of Co-58 and nickel in a high duty core;

- Degradation of concrete structures in NPPs

- Colloids, Zeta potential and activity transport in PWRs and BWRs

- Electrochemical Potential (ECP) measurements in PWR and BWR

- Key points, "lessons learned" and "best practices" of two recent conferences

  – Review of 2013 Source Term and Radiation Field Reduction Workshop – BWRs and PWRs"

  – "Summary of the important BWR items from the 16th International Conference on Environmental Degradation of Materials in Nuclear Power Systems".

Since these various subjects, selected based upon customers proposals and available knowledge may be very independent one from each other, this Introduction and summary section is covering each item separately.

1.2 Mitigation of various types of corrosion encountered in the second containment barrier of PWRs

So far, PWSCC has been the prevalent type of materials failures in PWRs NSSSs. Despite extended programs of components replacements (SGs, RPV upper head, pressuriser), there are still a lot of Alloy 600 components in operating plants. Replacing all Alloy 600 components may not be realistic, from various standpoints: practical, technical and economical. This is the reason why PWSCC mitigation techniques have been developed. In order to dramatically decrease the PWSCC risk, more and more PWRs operators throughout the world have or will successfully apply one or more of the mitigation techniques reviewed in this study.

Regarding Alloy 182, although the situation is somewhat better due to Alloy 182 stress relieving of welds during manufacturing, this treatment only delays PWSCC initiation. This is the reason why applying PWSCC mitigation techniques to Alloy 182 welds is highly recommended.

For Alloy 82, the situation is much more comfortable. The field experience shows that PWSCC had typically initiated in an area where the Alloy 82 original material has been diluted by the underlying material (generally Alloy 600 or Alloy 182). As a consequence, the Alloy 82 chromium content typically dropped from about 20% to about 17%, thus significantly impairing the deposited material PWSCC resistance as chromium content is one of the most influent parameters regarding this PWSCC resistance.

If stainless steels are rather PWSCC resistant, they are not immune to this type of failure. Moreover, stainless steels are present almost everywhere in a NSSS. Consequently, consideration should also be taken regarding applying PWSCC mitigation techniques to some specific stainless steels areas or components such as canopy seals, safe ends.

Table 1-1 compares all the PWSCC mitigation techniques reviewed in this report. For comparison purposes, the techniques related to environmental changes or adjustments (hydrogen optimization, zinc injection and RCS temperature drop) have been added. All the techniques introducing a surface deformation or surface cold work such as MSIP™, USP, LPB, WJP, LP and to a lesser extent ReNew™ may also have adverse effects. After applying one of these techniques, any subsequent deformation of the treated surface will dramatically increase the PWSCC risk. Anyway, this table shows that, besides some cost consideration, operators should consider implementing an efficient mitigation technique, whatever the component to be protected against PWSCC initiation. In conclusion, according to the rather recent development of several mitigation techniques, the trend should be a decrease of PWSCC failures events in the future.

Table 1-1:   Comparison of 19 PWSCC mitigation techniques, after [Cattant, 2009].

Mitigation technique	Easiness of implementation	Immediate efficiency	Long term efficiency	Industrial experience (PWSCC)	Implementation cost	Difficulties, specific pros and cons of the technique
[H₂] optimization	☺ Water	😐	😐	☹	☺☺	Operating PWRs are not designed to operate at very high or very low [H₂].
Zinc injection	☺☺ Water	☹	☺	☺☺	☺	
Temperature drop (RCS)	☺☺ Water	☺☺	☺☺	☺☺	☺☺	Real cost for the plant : ☹☹
Thermal treatment	😐 Air	☺☺	☺	☺☺	😐	Danger if the [C] too high or cold work too severe. Field TT is often not practical or feasible.
MSIP™	☹ Air	☺☺	☺	☺☺	😐 to ☹*	★ prior NDE recommended
UltraSonic Peening	☹ Air	☺☺	?	☺☺	😐 to ☹*	★ prior NDE recommended.
Low Plasticity Burnishing	☹ Air	☺☺	?	☹	😐 to ☹*	★ prior NDE recommended. No experience in nuclear industry.
Water Jet (cavitation) Peening	☹ Water	☺☺	☺☺	☺☺	😐 to ☹*	★ prior NDE and vibrations study recommended.
(Fibre) Laser Peening	😐 Water	☺☺	☺☺	☺☺	😐 to ☹*	★ prior NDE recommended
Laser Stress Improvement Process	☹ Air	☺	?	☺	😐 to ☹*	★ prior NDE recommended
ReNew™.	😐 Air/ ?	☺	?	☹	😐 to ☹*	★ Technique not yet mature but promising.
Material replacement	☹ to ☺	☺☺	☺☺	☺☺	😐 to ☹*	The replacement of all the BMIs of one bottom head is not realistic.
Weld OverLay	😐 Air	☺☺	☺☺	☺☺	☺	The cost assessment is for an implementation out of the critical path.
Weld InLay /Onlay	☹ Air	☺☺	☺☺	☺	☹	Cost : difficult not to impact the critical path.
Underwater Laser Beam Welding	☹ Water	☺☺	☺☺	☹	😐 to ☹*	Technique not yet mature but promising.
Cold Spray	😐 Air	☺☺	☺☺	☹	😐 to ☹*	No experience in nuclear industry but promising technique.
Ni plating	☹ Air	☺☺	☺	☺	☹	Implementation difficult and long.
SCrP™	☹ Air	☺	😐	☹	☹	Technique not yet ready for PWSCC mitigation.

| ☹* | if the mitigation treatment is on the critical path |
| ★ | any subsequent plastic deformation will dramatically increase the PWSCC initiation risk |

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1.3 Enriched Boric Acid (EBA)

A key issue of chemistry in the primary coolant is operating at sufficient pH_T for minimizing dose rates; however, this means that a sufficiently high lithium concentration has to be selected. This may require too high Li or K values. Increasingly higher fuel performance factors also necessitate higher B-10 concentrations at BOC, and thus even more incompatible lithium concentrations for the behaviour of various components of the Reactor Coolant System.

Thus, EBA, which typically decreases the boric acid concentration by a factor of 2 (with an enrichment about twice the one of natural boron, i.e. close to 20 %) will also allow to decrease Li (or K) concentration by a factor of 2, much more compatible with the various constraints.

The use of EBA, instead of natural boron, provides many important advantages with a direct impact on safety, material behaviour with plant life, dose rates and volume of safety tank, as highlighted in Figure 1-1 in addition to practical aspects; i.e. wastes releases, and compensation for B-10 depletion.
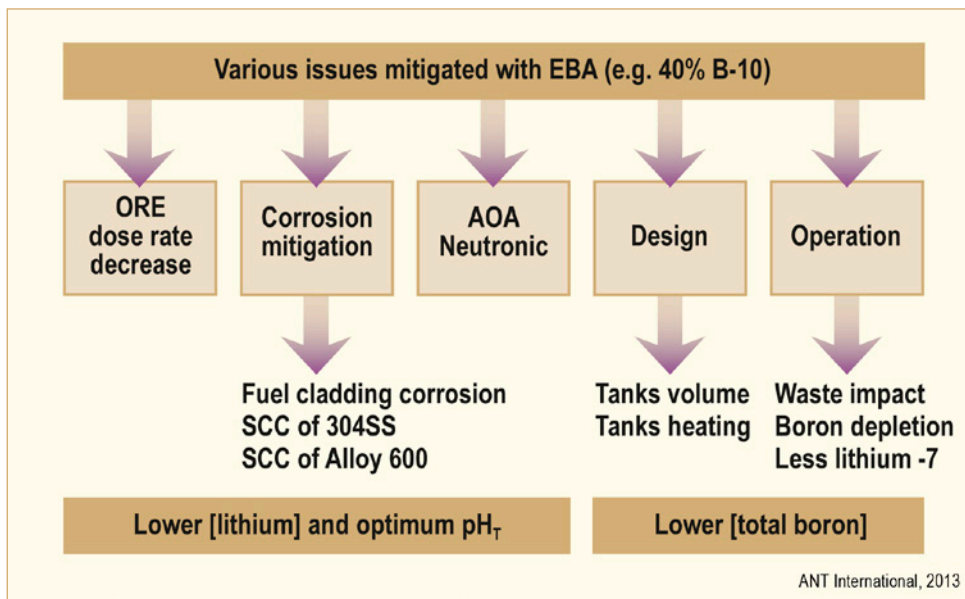
Figure 1-1: Various issues that may be solved by the use of EBA, after [Wiedenmann & Nordmann, 2012].

Although there is a cost impact of adopting EBA, with a typical enriched of about 40 % B-10, this option deserves to be considered when one or more of the issues listed in Figure 1-1 are of some concern. The rationale for evaluating the potential application of EBA is listed on Table 1-3. This explains why application of EBA in Ukrainian NPPs is being considered for new fuel loads (high burn up and MOX) while EBA has also been selected for new EPR reactors (37% B-10) under construction, and other advanced designs (Chinese ACPR1000+) bringing a higher safety margin to this new Generation III Nuclear Power Plant.

In addition, for compensation B-10 depletion, either in plants with EBA or natural boron, the use of small quantities of much higher enrichment is a very clever solution which drastically decreases the need to replace a large quantity of coolant to recover the target B-10 value.

Finally, it may be of high interest when Safety regulations require increased content of B-10 in safety injection tanks to ensure a safe shutdown, without putting reliance in control rods. EBA has been used in some German units for this last reason.

Table 1-2: Rationale for evaluation of EBA use

PWR VVER	Objective	Operating Units	New Units	Comments
Benefits	Dose rates mitigation, with optimum pH_T	If boric acid at BOC implies a too high Li or K content	As a precaution for any future fuel option	More frequently an important issue with new fuel options
	Limited Li (K) concentration	Nickel base alloys (600, etc.) sensitive to SCC	Not concerned	Longer fuel cycles, High enrichments with less refueling, MOX in some cases.
		304 SS corrosion	Unclear interest	
	Fuel corrosion meaning limited Li or K	If advanced fuel options with high B-10	Likely advanced fuel options with high B-10	
	AOA mitigation	Unclear benefit due to concentration and deposition process for B/Li(K)		Likely beneficial
	Tank volume or concentration	May avoid expensive or difficult replacement	Saves design and manufacturing costs	May be a solution for Regulatory requirements
	Lower Li-7	Decreases expensive Li-7 needs		Some cost savings
	Lower wastes, mainly B and Tritium but in general	Mainly B and Tritium from Li-7 due to lower B and Li concentrations. Wastes in general :due to higher recycling		B and T but wastes in general
	B-10 recovery	Whatever the plant, either with natural boron or EBA		Use of higher B-10 enrichment
	Recycling	High recycling mandatory, may create some difficulties for some impurities		
Inconve- niences	Cost of EBA	Initial load + annual costs		The main concern
	Switching to EBA	Needs a good preparation and accurate process	Not concerned, thus better with initial design	A burden but existing feedback

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1.4 The behaviour of Co-58 and nickel in a high duty core

Some units in the U.S. have experienced high concentrations of Co-58 and nickel in the reactor coolant during the cycle. The increase in concentrations has occurred at approximately one hundred effective full power days (EFPD) into the cycle. Nickel is of concern in the coolant because it can increase the probability of Axial Off-set Anomaly (AOA). Furthermore it can lead to an increase in the production of Co-58 which is a radiation dose concern through the $^{58}Ni(n,p)^{58}Co$ reaction.

The sampling lines characteristics may have an impact on the measured values and should be appropriately designed and the results considered carefully when interpreting the results.

Measurements that have been performed at McGuire Unit One (PWR) where zinc has been added resulted in the following conclusions [Sawochka, 2008]:

- The increase in the Co-58/60 ratio at the beginning of the cycle and the high ratio during power operation clearly indicate the source of the Co-58 and Co-60 is release of deposits from the fuel surfaces.

- The high values of Co-58 specific activity indicate the nickel is also coming primarily from the fuel surfaces. The specific activity of Co-58 at saturation is 1 to 1.4 at the McGuire core flux conditions after ~150 days of operation.

- Variations in the Mn-54 to Fe-59 ratio confirm that the source of the particulates is release from the core of deposits formed during prior cycles.

- The nickel in the primary coolant is undoubtedly insoluble/particulate notwithstanding sample temperature, pH and precipitation effects. The soluble nickel concentration in the coolant is limited to <0.1 ppb by thermodynamic considerations.

- The nature of the released material, primarily insoluble/particulate, indicates the release mechanism from the core fuel surfaces is primarily driven by physical forces associated with particle deposition and erosion.

- **Local variations in boiling duty and fluid shear appear the most likely cause of the release from the reload fuel.**

- Zinc incorporation into out-of-core and fuel surface deposits has decreased the tendency for deposition of particulates, but is not considered the likely cause of the McGuire Cycle 19 chemistry variations.

- It is not possible to quantify particulate and soluble concentrations in a primary coolant sample by taking a grab sample, exposing it to air, filtering it for particulate analysis and analysing the filtrate for soluble species or analysing the raw sample for total concentration and subtracting the filterable fraction to obtain a value for solubles. Effects of co-precipitation of radionuclides can be very significant.

- The correlation of shutdown releases to tubing manufacturer has recently been reconsidered, and the reviewers concluded that the initially observed relation could also be explained by core boiling duty variations. The French have also indicated that although it is clear that the tubing manufacturing process has an effect on shutdown releases and particularly their variation with EFPY, exceptions to the expected patterns have recently been reported.

In conclusion, the behaviour of Co-58 and nickel in a high duty core is largely governed by core physics rather than reactor coolant chemistry. The migration of fuel crud is a function of boiling rates of the feed, once burned and twice burned fuel during the cycle. Correlation is shown and the technical basis for this is provided.

1.5   Degradation of concrete structures in NPPs

Among the concrete structures used in nuclear power plants (NPPs), concrete containment buildings (CCBs) play a critical role performing multiple functions including, maintaining load carrying capacity, radiation shielding and leak tightness.

1.5.1   Aging of CCBs

The constituents used in CCB construction include concrete mix, steel reinforcements, pre-stressed steel and steel or non-metallic liner materials. Concrete is a durable material and its performance in containment function in NPPs has been quite good. However, aging degradation of CCBs can occur due to factors such as poor design, use of poor quality materials, poor construction, exposure to aggressive and weathering environments (thermal and freeze/thaw cycles), use of excessive structural loads. The use of non destructive evaluation (NDE) methods will be of high value to a successful aging management program (AMP).

1.5.2   Chemistry related concrete degradation mechanisms

Degradation of concrete can occur in the aggregate material/cement matrix as well as in the embedded steel rebar reinforcements. Chemical degradation may occur as a result of chemical interactions between aggregate/cement paste and/or embedded steel rebar reinforcements.

The chemical degradation may be due to acid or base attack, to carbonation, to chloride and finally to alkali-silica reaction (ASR).

Acids present in ground water such as sulphuric and carbonic can react with calcium compounds in the hydrated cement paste to form soluble compounds that are readily leached from the concrete to increase its porosity and permeability.

In general, concrete is resistant to base attack, however, in the presence of high levels of sodium and potassium hydroxides (> 20%) cement paste can undergo degradation.

Chloride attack can cause excessive oxidation of the rebar material leading to cracking of the concrete matrix and gradual debonding of the reinforcement lowering the load bearing capacity of the structure. This type of attack is easily detectable visually from rust stains on the exterior surfaces of the concrete. Typically, corrosion of rebars in concrete is not significant for pH > 11.5 in the concrete matrix and for Cl < 500 ppm. Chlorides may come from concrete additives such as calcium chloride added to accelerate the concrete setting time, sea water exposure, salt spray or from de-icing salts.

A schematic of corrosion of a steel rebar embedded in concrete is shown in Figure 1-2 with associated electrochemical reactions. Localized pitting corrosion initiated by the presence of chloride ions releases Fe^{2+} ions and electrons, and the driving force for corrosion is the reduction of oxygen that consumes the released electrons. Thus, as long as oxygen is available, corrosion of the steel rebar will continue to occur.
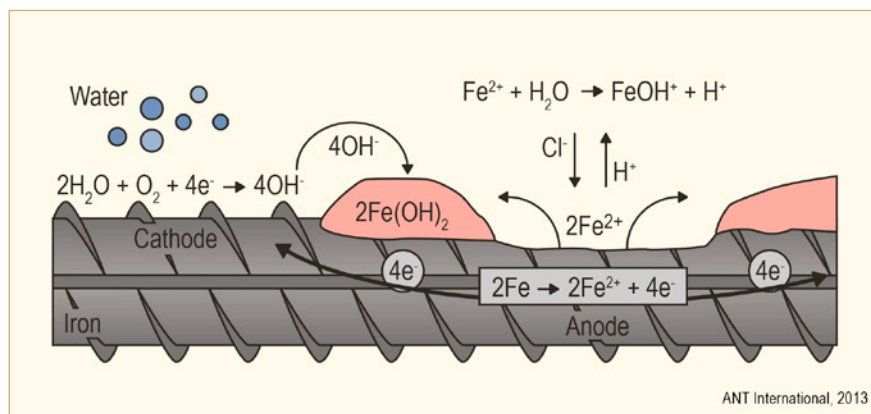
Figure 1-2:   A schematic of steel rebar corrosion in an embedded concrete matrix in the presence of chloride ions, adapted from [Concrete Technology, 2013].

Carbonation attack occurs when carbon dioxide present in the atmosphere reacts with $Ca(OH)_2$ and other calcium bearing compounds forming calcium carbonate leading to densification (shrinkage) of the matrix.

Reaction of alkali ions in cement with some silica mineral aggregates can lead to degradation of concrete by a process called alkali-silica reaction (ASR) which has been known since 1930's. The reaction forms an alkali-silica gel that expands or swells when it comes into contact with water generating excessive pressure on the concrete matrix [ASTM, 1986]. ASR requires the simultaneous presence of sufficient moisture, sufficient alkali and reactive silica. ASR can be detected visually by expansion of the concrete structure and surfaces, cracking, surface discoloration, ASR-gel exudations, occasional pop-outs. ASR is more precisely detected by petrographic examination of concrete core samples that includes scanning electron microscopy (SEM). Typically, ASR may initiate within 10 years of construction, but advanced deterioration may not occur until 15 to 25 years after construction. At the construction stage, ASR can be mitigated by restricting the cement alkali content to less than 0.6% by weight of Na_2O equivalent, and application of barriers to minimize moisture ingress.

Among the chemistry related concrete degradation mechanisms, the most common issue in the recent times has been degradation due to ASR.

There are many mechanical factors that can affect the structural integrity and life of concrete structures used in NPPs. These could potentially include fatigue due to cyclic loading, creep due to sustained loading, abrasion, cavitation and surface erosion.

1.5.3 Concrete inspection, aging detection and monitoring [IAEA- TECDOC 1025, 1998]

Concrete cooling towers exposed to chlorides and sulphates have experienced degradation of the steel rebar material leading to cracking and spalling of concrete. Some cooling tower operators use corrosion inhibitors and biocides to control corrosion and bacterial growth.

Despite the variability of the concrete matrix, some of the NDE methods can be used to evaluate the strength, density and quality of concrete. They can also locate and characterize voids or cracks in concrete, locate steel reinforcement, and indicate depth of the concrete cover. Typically used NDE methods include, 1) visual inspection, 2) Integrated leakage rate measurement, 3) audio responses, 4) rebound hammer, 5) infrared thermography, 6) acoustic methods, 7) radiation and nuclear techniques, 8) tomography, 9) short pulse radar and 10) other instrumentation methods [IAEA, 1998].

The commonly used instrumentation methods used in NPPs include vibrating-wire strain gauges, thermocouples, pendulums, extensometers, load cells, liquid level gauges, and humidity gauges. These instruments are useful in detecting and monitoring overall local stress, strain, deformation and temperature changes in CCBs.

Destructive testing can be used to determine concrete strength, density and quality: locate voids or cracks; locate steel reinforcement; detect corrosion of steel reinforcement, and determine depth of concrete cover. Destructive techniques include, 1) air permeability, 2) core testing, 3) probe penetration, 4) chloride ion content, 5) carbonation depth, and 6) petrography.

Besides above methods, electrochemical methods available for corrosion monitoring and inspection of steel reinforcements include the four electrode method, half cell potential measurement and the galvanostatic pulse technique.

1.5.4 Concrete mitigation technologies

The two major areas of concrete degradation are corrosion of the reinforcing steel and degradation of concrete by the alkali-silica reaction (ASR).

For newly built concrete structures [Liu & Shi, 2009] numerous proactive methods are available for protecting steel reinforcements from corrosion. These include, low permeable concrete to impede the ingress of aggressive species such as chloride ions, application of polymer overlays and sealers (paints and coatings), increased concrete cover depth, use of epoxy coated rebars, and addition of corrosion inhibitors to the fresh concrete. However, for already existing concrete structures that have undergone chloride induced corrosion but retains sufficient strength, the traditional repair method involves the replacement of chloride containing concrete with fresh chloride free concrete, which is quite expensive. This is not a durable solution since it is impossible to remove all of the chloride containing concrete.

There are three electrochemical based methods available for mitigation of reinforcing steel from corrosion. They are cathodic protection (CP), electrochemical chloride extraction (ECE), and electrochemical injection of corrosion inhibitors (EICI).

2 Mitigation of various types of corrosion encountered in the second containment barrier of PWRs (François Cattant)

2.1 Forewords

The second containment barrier of Pressurized Water Reactors (PWRs) is the interface between the contaminated primary water and all the other environments (secondary steam/water, cooling water, air...). The second containment barrier is composed of various components such as vessels, capacities, pipes, elbows, fittings, tubes, valves, and pumps. Most of these components are able to withstand the Reactor Cooling System (RCS) high pressure (typically: 155 bars in operation). Although this study will mainly focus on the RCS (including some RCS internals), we will cover some corrosion failures of other systems such as Reactor Heat Removal system (RHR), High Pressure Safety Injection System(HPSIS) or Chemical and Volume Control System(CVCS). Note that the secondary face of the Steam Generator (SG) tubes, in contact with the secondary water, is out of scope.

2.2 Various types of corrosion encountered in the second containment barrier of PWRs.

2.2.1 Stress Corrosion Cracking

2.2.1.1 Overview

Stress Corrosion Cracking (SCC) initiates at the material surface. This cracking occurs when specific material, environment and stresses conditions are met as shown on Figure 2-1. SSC is much more significant than the cracking that would have been obtained under separate actions of the same aggressive environment and the same applied stresses.
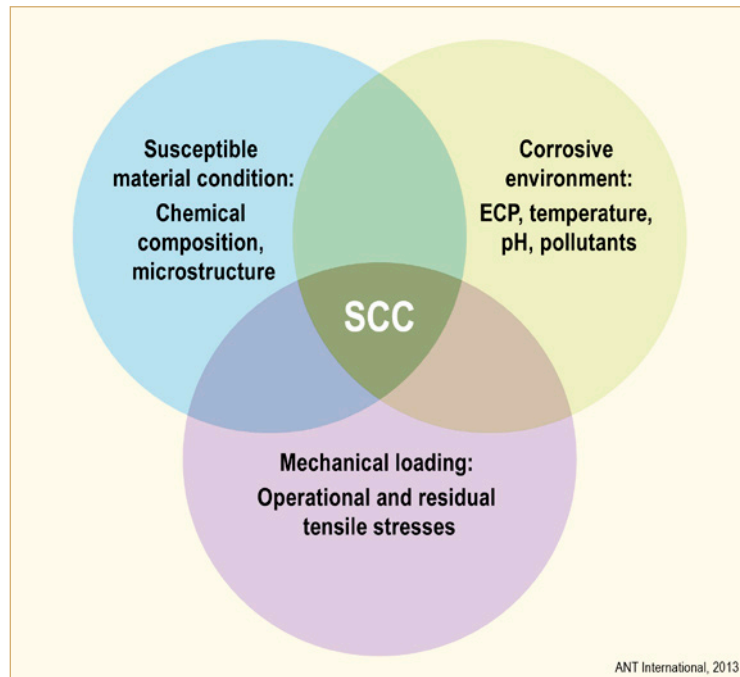
Figure 2-1:   Material, environment and stresses conditions to initiate SCC, drawn by [Cattant F., 2013].

SCC is a 3-step process. The first one is initiation; it can last from one hundred to several thousand hours, depending on the material susceptibility. The second one is slow propagation until the crack reaches a size large enough to be detected by Non Destructive Examination (NDE) (typically: 100 µm); it can last from several hundred to several thousand hours, depending on the load. The third one is the rapid propagation phase.

SCC cracks present fragile features (Figure 2-2), although the material mechanical behaviour remains ductile.
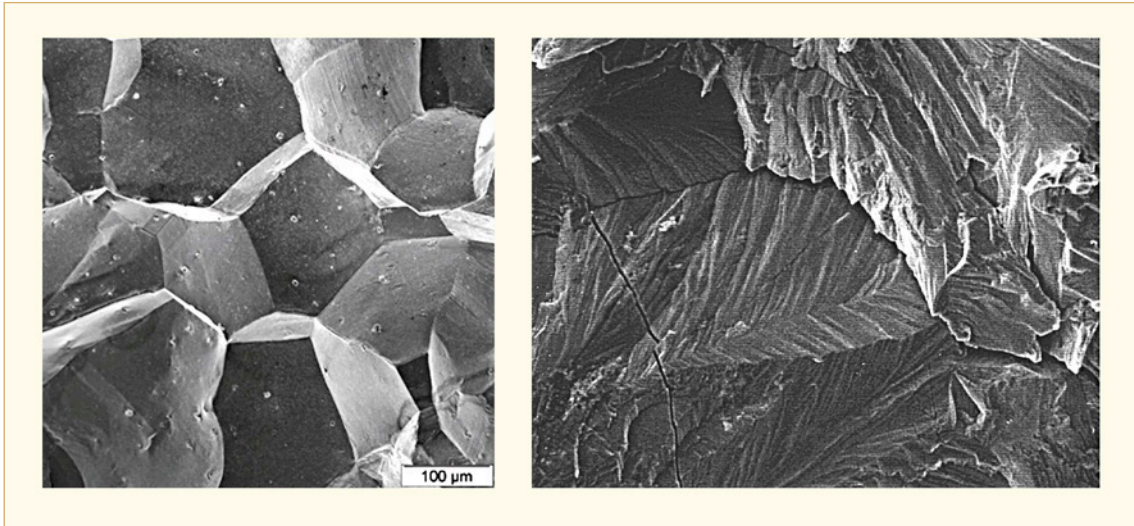
Figure **2-2:**   Scanning Electron Microscope (SEM) views of typical SCC cracks faces. Left: intergranular, MA600, [Dove et al, 2007]. Right: transgranular, Stainless Steel (SS), x715, [Boursier et al, 2002].

Depending on the material/environment association, cracks can be intergranular (Ni alloys in primary water, (Figure 2-3)), transgranular (stainless steels quite often (Figure 2-4)) or both (MA600 in polluted environment (Figure 2-5)).
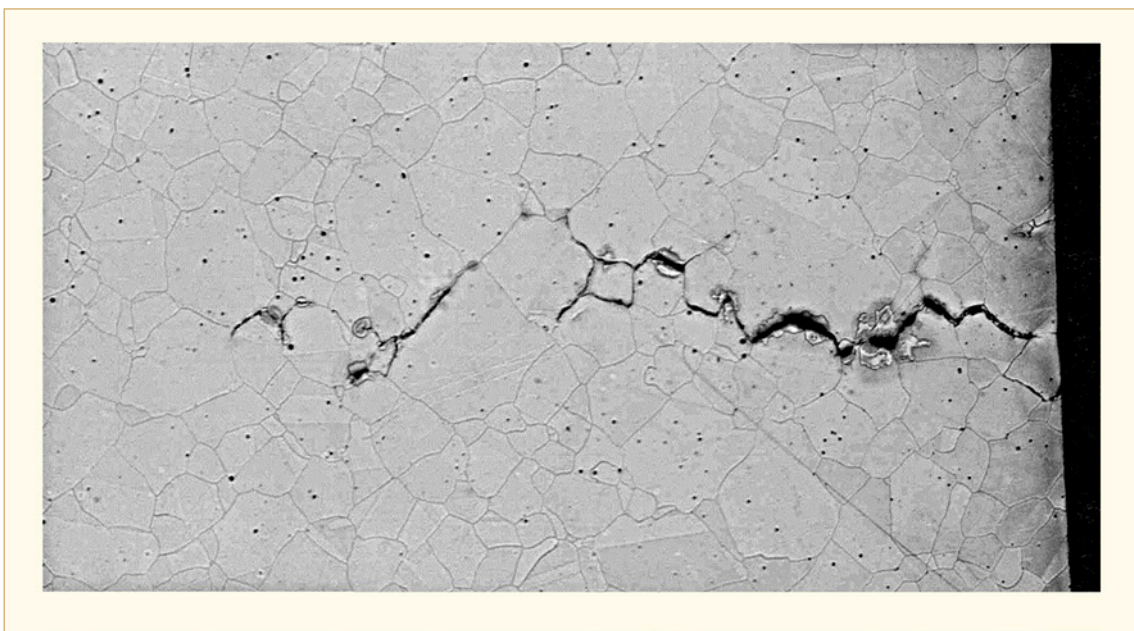
Figure **2-3:**   Cross section of a typical intergranular SCC crack, head penetration, MA600, x40, [Xu et al, 2005a].

Figure **2-4:** Cross section of a typical TransGranular Stress Corrosion Cracking (TGSCC) crack, SS, x48, [Boursier et al, 2002].
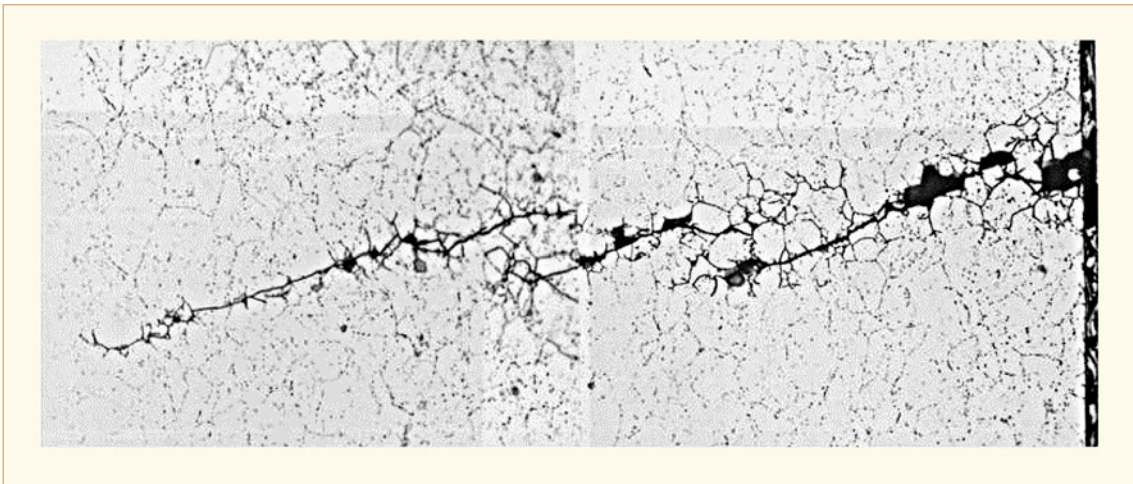
Figure **2-5:** Mix of InterGranular Stress Corrosion Cracking (IGSCC) and TGSCC cracks, MA600, x370 [Nordmann et al, 1990].

2.2.1.2   Primary Water Stress Corrosion Cracking

Primary Water Stress Corrosion Cracking (PWSCC) is SCC occurring in primary water. PWSCC has been the prevalent form of corrosion over the past 30 years on PWRs.

Regarding the material, the major influent parameters are: carbon and chromium contents, carbides precipitation, grain size, thermal treatments, mechanical properties and Cold Work (CW). For example, regarding MA600, small grains, high carbon content and heavy intergranular carbides precipitation are detrimental. Nickel alloys with a chromium content exceeding 25 Wt% are very PWSCC resistant.

3 Enriched Boric Acid (EBA) (Francis Nordmann)

Fuel of higher enrichment, longer fuel cycles or use of mixed oxide fuel (MOX), requires increased amounts of neutron poison to maintain reactivity control. This can be achieved either by control rods, consumable poison or higher content of boron-10 at the beginning of fuel cycles and in some safety injection tanks. The inconveniency of a higher concentration of natural boric acid, with only ~19.6% to 20 % of B-10, may be counteracted by using Enriched Boric Acid, with typically ~40% B-10, which means a twice lower total boric acid concentration.

The chapter is covering the fuel issues, including use of MOX, the various advantages of using EBA, particularly associated with the possibility of achieving the optimum pH_T (close to 7.4 at 300°C) with an acceptable lithium concentration, i.e. (i) lower dose rates, (ii) lower risk of corrosion of Alloy 600 and other nickel base alloys, (iii) lower risk of corrosion of 304 stainless steel. The key issue of impact of EBA on Axial Off-set Anomaly (AOA) and on waste amounts will be discussed. The benefit of using tanks with lower boric acid content will be explained, both for new PWR/VVER units and for avoiding heavy modification in tanks of already operating units. The process for switching from natural boric acid to EBA will be also described.

Finally, the interesting use of high enrichment of EBA (>90%) to recover the B-10 depletion from neutron reaction in operating units will be explained, with very low primary water coolant renewal, thus generating much lower liquid wastes.

3.1 EBA principle and objective

The economics of operating pressurized water reactors (PWRs) demand increased fuel economy which in turn places increasing demands on the primary coolant chemistry. Higher energy production can be achieved by using increased enrichment of the nuclear fuel, higher fuel burn up and longer fuel cycles, which in turn requires increased amounts of neutron poison to maintain reactivity control. In addition, greater amounts of chemical shim are required when utilizing alternative, high-reactivity fuels such as mixed uranium/plutonium oxide (MOX) fuels.

Boron is used as a chemical shim in the primary coolant of Pressurized Water Reactors (PWR) to control nuclear reaction according to the very high neutronic capture section of the B-10 isotope.

$$^{10}_5 B + {}^1_0 n \rightarrow {}^7_3 Li + {}^4_2 He$$
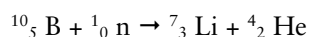
which may also be written as ^{10}B (n, α) ^7Li

Natural boron only contains ~20% of B-10 isotope. On the opposite of most isotope ratios in ore, B-10 proportion is slightly different from one to another. This must be taken into account when natural boron is used to ensure that the same origin is used for make up or to modify the total boron content in the considered system. In other words, whatever it is, the B-10 percentage of the natural boric acid that is provided, must be accurately known.

The B-10 isotope of boron has a high cross section for the absorption of thermal neutrons. However, this isotope comprises only ~19.6% to 20 % of natural boron while the ~ 80 % of B-11 isotope is of no use and even potentially undesirable since it is increasing the total boron concentration that is required to get the target B-10 isotope content.

The cross section of neutron capture through the reaction below on B-11 is almost 1000 lower than on B-10 above:

$$^{11}_5 B + {}^1_0 n \rightarrow {}^{12}_5 B \rightarrow \beta^- \rightarrow {}^{12}_6 C$$
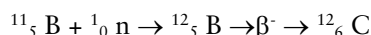
It is a curiosity and something very specific to Boron to note that the isotopic composition B-10 and B-11 is slightly different in the 2 main ores on earth; with a slightly higher B-10 proportion in the one from Turkey as compared to the one from California. Besides this curiosity, this may be taken into account when adjusting the total boron concentration.

If the boric acid is enriched in the B-10 isotope, then the maximum amount of chemical shim can be increased without exceeding the chemistry limits set by the acidity of boric acid or the concentration limit of lithium (PWR) or potassium (VVER). With sufficient isotopic enrichment, it therefore becomes possible to operate the entire PWR fuel cycle with the constant $pH_{300°C}$ at the favoured value of ~ 7.2-7.4, depending on the materials in presence, as highlighted on Figure 3-1 [Riess & Odar, 2012].
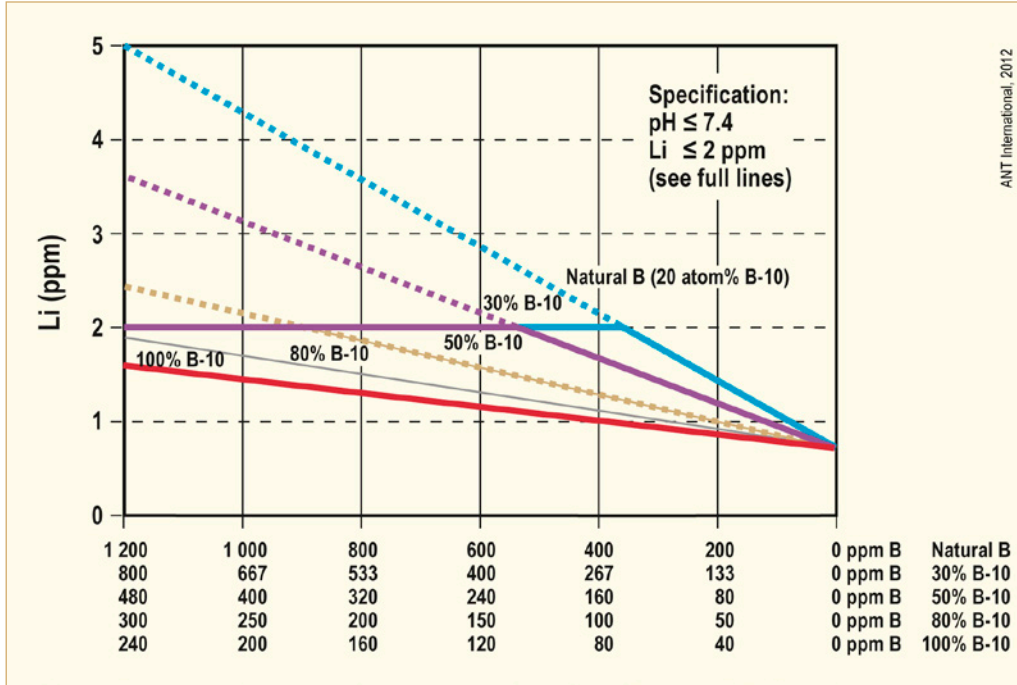
Figure 3-1:   PWR primary system chemistry with B-10 enriched boric acid, after [Riess & Odar, 2012].

The use of Enriched Boric Acid (with ~40% B-10 instead of ~ 20% in natural boron) consequently provides many advantages in enhancing operational safety and life time of several components, as well as facilitating dose rate reduction programs in PWRs and VVER Nuclear Power Plants. When lowering the total boron concentration in the primary coolant, it is possible to minimize:

- The dose rates during maintenance activities - optimal pH_T from the beginning of the fuel cycle (BOC) can mitigate corrosion products that become activated;

- The risk of corrosion of various materials of the Reactor Coolant System - allowing a lower lithium (or potassium) concentration mainly at BOC;

- The sensitive materials are fuel cladding (zirconium alloy), stainless steels (AISI 304 type), nickel-based Alloy 600;

- The risk of Axial Offset Anomalies - resulting from precipitation of boron compounds on the fuel cladding;

- The need for design modification to support either larger volume or higher boric acid concentration of safety tanks;

- The concentration or volume of safety and other tanks containing boric acid; if the concentration is decreased, this may potentially decrease the need to heat some tanks;

- The concentration or volume of sodium hydroxide in spray tank for neutralization of boric acid in the containment;

- The amount of solid wastes and liquid effluents released into the environment, mainly boron wastes due to the lower concentration and the improved recycling associated with the use of EBA.

Finally, EBA may also be added in units operated under natural boron, when B-10 becomes depleted, to more easily adjust the B-10 proportion within the specified value by only adding a small quantity of EBA with in this case a much higher enrichment ($\sim$ 96%) instead of replacing a large quantity of natural boron.

The major constraints of EBA in operating units are the cost and modification requirements. If the benefits of EBA deserve economic and technical evaluation in operating plants (which are more difficult and costly to transition), then it seems clear that any new plant should consider a design with the EBA option.

This chapter provides an overview of the benefits of Enriched Boric Acid (EBA) on PWR radiation field development, increased safety margins and structural component corrosion as well of other potential advantages, such as volume or concentration of tanks or wastes reduction in support of advanced fuel management trends.

3.2 Boron 10 content versus Fuel and fuel cycle options -MOX

For economical reasons, several plants are applying longer fuel cycles with higher fuel burn up, or less renewed fuel element during refueling and thus shorter refueling, or higher plant power and performance.

This is why EBA may be considered either when the plant is operated with fuel of higher enrichments, associated or not with MOX, with longer fuel cycles, lower proportion of replaced fuel during shutdown (e.g. 1/4 instead of 1/3 of the core replaced, allowing shorter shutdown duration) or with higher power.

A higher fuel burn up or fuel cycle length may induce a higher core reactivity at BOC by increasing the concentration of fissile material which requires a higher B-10 concentration at the Beginning of Fuel Cycle (BOC). Such an increase may be of a few hundreds of ppm total boron with natural boric acid at BOC which is the cycle part where the boron and lithium (or potassium) are the highest with potential difficulty to get the desired pH_T as shown on Figure 3-2 [Riess & Odar, 2012]. With for example the historical value of 2ppm Li, the $pH_{300°C}$ is only of 6.8, which is very insufficient, for 1600 ppm B. On the contrary, with EBA and a twice higher B-10 enrichment (40 %), the required boron concentration will be twice lower, i.e. 800 ppm and the $pH_{300°C}$ will be of 7.0, hardly acceptable. With 3.5 ppm Li, the use of EBA will raise the $pH_{300°C}$ to 7.2 instead of ~7.0 with natural boron. Consequently, the EBA enrichment may be defined depending on the desired pH and fuel characteristics that are defining the B-10 required concentration. Then, during the fuel cycle, when the fuel becomes partially burnt, B-10 content is progressively decreasing.

MOX is a fuel containing from 3 to 12 % of Plutonium (Pu) obtained from the 1 % of Pu generated in standard fuel and is particularly of interest in countries which are reprocessing their fuel. Indeed, Pu produced during the fuel cycle is used as a new part of the fuel where it is mixed with U of lower enrichment (lower proportion of the fissile U-235 isotope). France and other European countries are reprocessing their fuel while US PWR units do not. Consequently, if MOX means the questionable reprocessing of the used fuel, it has the main advantage of much better using the resources of natural uranium which is containing mainly non fissile U-238 (99.28%) and much less fissile U-235 (0.71 %) which needs to be enriched or mixed with Pu to get the fuel to be used in PWR units. The remaining 0.01 % is U-234.

4 The behaviour of Co-58 and nickel in a high duty core (Dewey Rochester)

At McGuire Unit One during Cycle 19 Chemistry personnel observed the concentrations of both cobalt -58 (Co-58) and nickel (Ni) increasing. These observations set off an investigation over several years that involved both Duke Energy and industry personnel in an attempt to understand this phenomenon.

McGuire Units 1 and 2 are four loop Westinghouse designed pressurized water reactors (PWR) with replacement steam generators (SG) manufactured by Babcock & Wilcox Canada. The replacement SG have approximately 30% more surface area than the original SGs and are made of Alloy 690 tubing.

Nickel and cobalt have very similar chemical properties (Group VIIIB). Furthermore, nickel is the "parent" of the radioactive Co-58. This occurs according to:

$$\text{Ni-58}(n,p)\text{Co-58}$$
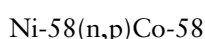
The nonradioactive Ni-58 picks up a neutron in the reactor core and decays by releasing a proton to become radioactive Co-58. Co-58 then decays by releasing a 0.811 MeV gamma ray and is therefore a significant source of radiation dose rates and radiation exposure to plant personnel. The source of the nickel is the Inconel steam generator tubing.

Nickel can form compounds that can be deposited on the fuel rod surfaces. If these compounds contain boron (specifically B-10, a neutron moderator) such as bonaccordite (Ni_2FeBO_5), Axial Offset Anomaly (AOA) or Crud Induced Power Shift (CIPS) can occur. This phenomenon can lead to power reductions or in severe cases to an early shutdown. Any increase in RCS nickel concentrations, which is an indication of crud movement, are of concern. The addition of zinc presents a special situation. There is no evidence that zinc by itself, which can also form mineral compounds in concert with other species and boron, increases the risk of AOA/CIPS. However, due to the lack of a zinc innocuousness demonstration, as a precaution, it is recommended to add zinc cautiously in PWR units that AOA/CIPS may be of risk.

At both McGuire units Chemistry personnel usually take reactor coolant samples from the hot leg. Normally, this is not a preferred sample point unless it is continuously flowing such that equilibrium between the coolant and the piping wall is established. In the case of McGuire, the sample point is located off of a line from the hot leg that feeds a radiation monitor that is always in service. This ensures that the samples taken from this line are representative (or as much as can be) of the RCS. See [Riess et al, 2008] for more information on sampling issues. McGuire routinely uses this hot leg sample point for chemical and radiochemical analyses. Experience has shown that this sample point is superior for many analyses, but especially radioactive crud samples.

A review of McGuire sampling issues to understand crud behaviour at McGuire better was performed [Riddle et al, 2008]. No U.S. PWRs have been designed to deliver representative reactor coolant samples for characterizing corrosion products because of transformations during sample delivery and interactions with the corrosion products and the sample line. Long reactor loop sample lines with isolation valves, temperature gradients during sample delivery in a boric acid matrix, and intermittent use limit representative loop samples in most PWRS.

The hot leg sample at McGuire initiates as a 0.75 inch tap with a 0.234-inch flow restrictor on the RCS Loop l. The location of the tap is at 90 degrees on the pipe and ~9 feet from the hot leg nozzle. It is located ~1.4 feet before the three hot leg thermocouples. The sample line travels ~120 feet before exiting the reactor building, reducing to ½ inch at a valve and is field routed to the sample sink. This is in contrast to other PWRs which may have as much as 600 feet or longer of 3/8 inch tubing, which is routed through containment to a sample cooler in a central sample station. Double isolation valves must be opened to initiate sample flow. The hot leg sample usually (but not always) has a delay coil to provide a 60-second or longer decay of N-16 (7.13 second half-life). However, this feature was not incorporated in the McGuire hot leg sampling line. At 1 gallon per minute sample line flow, the velocity in the 0.75 inch hot leg sample line is only ~0.25 feet/second (f/s). ASTM D3370-07, Standard Practices for Sampling Water from Closed Conduits, recommends sample line stability in addition to linear flow rate considerations, although an optimum of 6 feet/second is recommended. Even with continuous sample flow, the sampling conditions are not optimum.

Letdown is taken from RCS Loop 3. Fluid in the 3-inch letdown line is cooled by a three-pass regenerative heat exchanger followed by the letdown heat exchanger. Flow velocity in the 3-inch letdown line is ~1 f/s or less. Letdown flow is on the shell side and charging flow on the tube side of the regenerative heat exchanger. The letdown sample line initiates as a 0.75 inch tap >84 feet after the letdown heat exchanger. This line is field routed to the sample sink. This arrangement provides for opportunities for settling and/or plate out of particulate material prior to sampling. Letdown heat exchanger local dose rates are consistent with such a mechanism. At McGuire, although certainly not perfect for particulate sampling, the hot leg sample is considered a better sample location than the letdown sample.

McGuire-1 has significant hot leg streaming, which refers to non-uniformity in the hot leg temperature profile. The non-uniform temperature is a result of non-uniformity in the coolant flow distribution, neutron flux distribution, reactor head bypass flows, and core internals leakage flows. In general, the streams exiting the fuel channels on the perimeter of the core are cooler than those closer to the centre of the core. Three temperature detectors are installed at 120-degree intervals around each hot leg. Assuming that the particles are being generated in the core from only a small number of assemblies and then plate out relatively rapidly, hot leg streaming could result in the hot leg sample not being representative of the actual average core particulate concentration. Plant data indicates that significant mixing should have occurred prior to the sample tap. It was concluded that the oscillating character of the coldest streams would suggest that the average fluid being sampled is representative of more than just a narrow static stream. Therefore, the hot leg sample is considered to be a better sample location for particulates than the letdown sample, which has passed through four heat exchangers prior to the sample cooler in the sample room. Figure 4-1 compares the hot leg and letdown line (BIX) Co-58 concentrations.
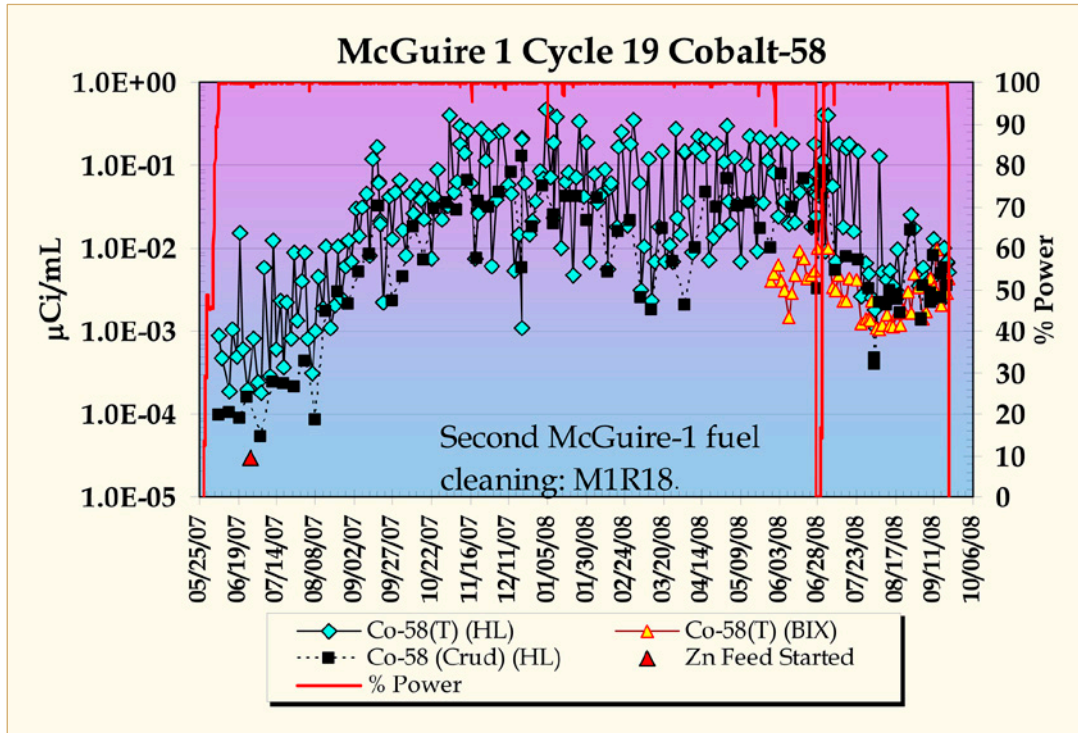
Figure 4-1:   Comparison of McGuire Unit One Hot Leg vs. Letdown Line (BIX) Co-58 [Riddle et al, 2008].

A note about the McGuire sampling terminology is found in Table 4-1 below:

Table 4-1:   McGuire Sampling Terminology.

Sample Point Name	Description
Grab sample	Liquid sample taken directly from RCS hot leg sample point and analyzed
Crud sample	Liquid sample taken from the hot leg sample point, filtered through a 0.45µ filter and the filter analyzed for radioactivity
BIX	Sample taken upstream or Before the letdown (Ion EXchange) demineraliser and analyzed
	ANT International, 2013

Table 4-2 contains the conversion factors that are used in the U.S. and Europe and will be useful in this section. While the units in the graphs are generally in English units, it is the trends that are important and not the absolute values.

5 Degradation of concrete structures in NPPs (Samson Hettiarachchi)

Among the concrete structures used in nuclear power plants (NPPs), concrete containment buildings (CCBs) play a critical role performing multiple functions including, maintaining load carrying capacity, radiation shielding and leak tightness. They are designed to separate the reactor and other systems and equipment important to safety from the outside environment. External events could include earthquakes and weather related conditions such as floods, tornadoes, tsunamis, as well as aircraft impact. Internal events include loss-of-coolant accidents (LOCAs), high energy line breaks and unexpected radiation releases. Therefore, potential age-related degradation of CCBs needs to be periodically assessed to ensure their leak tightness and structural integrity.

5.1 Aging of CCBs

The optimum design life of current NPPs was chosen to be about 40 years. However, there have been and there are moves to extend the life of operating NPPs up to 60 and even up to 80 years. Besides, during the decommissioning stage of NPPs it is expected that the CCBs will perform the safety functions for up to 100 years, i.e. a significantly longer period of time than the originally planned 40 year design life.

The constituents used in CCB construction include concrete mix, steel reinforcements, pre-stressed steel and steel or non-metallic liner materials. Typically, concrete used in these applications consists of a moderate heat of hydration cement, fine aggregates/sand, water, and various chemical and mineral additives for improving properties of the concrete. Mild steel reinforcements are used primarily to provide tensile and shear load resistance. The pre-stressed systems consist of tendons that are tensioned and then anchored to the hardened concrete. The pre-stressed tendons counteract tensile loadings to minimize or prevent concrete cracking. They also improve the resistance to shear forces such as those that could develop due to loadings during an earthquake. The pre-stressed tendons can be post-tensioned, once they are installed in the containment structure, as needed after the concrete has achieved sufficient strength. Corrosion protection is provided by corrosion inhibiting agents or bonding with Portland cement grout. Metallic or non-metallic liners are installed on the inside surface of many single-wall containments to provide a barrier against the leakage of gas. Metallic liners are typically carbon steel sheets welded and anchored to the concrete by steel studs. Typical non-metallic liners consist of epoxy or polyurethane paints applied to a thickness up to one millimetre. The drywell liners are typically carbon steel, while wet well liners consist of stainless steel plates. Some facilities have used carbon steel plates with stainless steel clad material for the liner. The primary function of the liner is to provide a leak tight barrier.

Concrete is a durable material and its performance in containment function in NPPs has been quite good. However, aging degradation of CCBs can occur due to factors such as poor design, use of poor quality materials, poor construction, exposure to aggressive and weathering environments (thermal and freeze/thaw cycles), use of excessive structural loads that could impair the expected public health and safety functions. Therefore, an adequate aging management program (AMP) for CCBs is critically important to assure their expected performance throughout the service life of the plant. The use of non-destructive evaluation (NDE) methods will be of high value to a successful AMP.

The International Atomic Energy Agency (IAEA) initiated an activity in 1989 and issued a report in 1998 [IAEA,1998], to address issues associated with the aging management of CCBs. The IAEA conducted a study in the form of a Coordinated Research Program (CRP) with the following objectives.

- Produce a summary of current aging management practices and experiences of CCBs

- Compile a report on concrete repair techniques specifically applicable to NPPs

- Develop a crack mapping/repair guidelines applicable to NPPs

- Develop practical indicators for monitoring aging of CCBs

The study included over 150 NPPs and the results are summarized in the IAEA report [IAEA, 1998]. The report addressed the first three bulleted items, however, information available on the 4th bulleted item is limited since results on monitoring and interpretation were not adequately provided. The report basically summarized aging mechanisms, age related degradation, aging management (including inspection, monitoring, assessment and remedial action) for materials and components used in CCBs.

5.2 Chemistry Related Concrete Degradation Mechanisms

Degradation of concrete can occur in the aggregate material/cement matrix as well as in the embedded steel rebar reinforcements. Such degradation can occur as a result of prolonged exposure to environmental factors such as freeze-thaw cycles, radiation, chemical exposure and static or dynamic loading. In many instances one or more of these factors may be operative causing gradual degradation of concrete. This report limits its focus only to chemistry related degradation mechanisms.

5.2.1 Freeze-Thaw Cycles

Freeze-thaw cycles may cause thermal fatigue associated with changes in states of water entrained in the concrete matrix. Freezing of water causes the matrix to expand due to the hydrostatic pressure generated while thawing causes the matrix to contract. This type of damage is more common with concrete in contact with water, particularly on horizontal surfaces, causing internal cracking [Jacobsen et al, 1995], that may lead to reduced load-bearing capacity and loss of tensile strength [Marzouk & Jiang, 1994].

Freeze-thaw damage of concrete NPP structures is not significant if the weathering conditions are minimal, i.e. < 100 day-inch/year, where "day-inch" is the number of rainfall days multiplied by the depth of rainfall in inches [NUREG, 1996b]. Furthermore, freeze-thaw damage is minimal if the concrete mix meets ACI-318 [ACI, 2008] or ACI-349 [ACI, 2006] specified by the American Concrete Institute. Plants that satisfy these two criteria do not currently require an aging management program related to freeze-thaw damage. However, for plant license renewals beyond 60 years, further review may be necessary.

5.2.2 Radiation Damage

Concrete structures around NPPs provide shielding against radiation that can appear as fast or thermal neutrons as well as gamma radiation that can affect the properties of concrete. Radiation can cause heating of concrete due to energy transfer as atoms in the concrete that moderate the incident radiation via atomic collisions. The extent of heat generated is a function of the energy of the incident radiation, and heating beyond 100°C over long periods of time can cause dehydration of the concrete. A significant loss of water and hence loss of hydrogen will reduce the neutron moderating capacity and hence diminishes the radiation shielding effectiveness. In addition, prolonged heating may affect the mechanical properties of the concrete as well. Minimal nuclear heating is expected at an energy threshold of $< 10^{10}$ MeV/cm^2-s [ANSI/ANS-64, 2006]. In addition, high levels of gamma radiation can also cause radiolysis of water [Naus, 1986] that can affect the cement paste in concrete leading to its degradation. High levels of neutron exposure can cause swelling of aggregates due to atomic displacement leading to change in mechanical properties of concrete.

Neutron irradiation can also change the mechanical properties of rebar steel embedded in the concrete increasing its yield strength and reducing the fracture toughness. The threshold neutron fluence that can affect mechanical properties of rebar steel is 10^{18} n/cm^2. Under normal operating conditions, this level of neutron fluence is unlikely to be experienced by most concrete structures in NPPs. However, rebars in the concrete biological shielding outside the reactor pressure vessel could experience high neutron fluences [IAEA, 1998]. There are no regulatory requirements for US NPP operators to characterize radiation damage to rebars embedded in concrete.

5.2.3 Chemical Degradation

Chemical degradation may occur as a result of chemical interactions between aggregate/cement paste and/or embedded steel rebar reinforcements. Chemical attack may occur from exposed surfaces including surface cracks that can lead to internal degradation of the concrete.

5.2.3.1 Degradation by Acid and Base Attack

Acid and base attack on concrete can lead to increased porosity and subsequent degradation. It is mostly the below ground structures such as foundations and intake structures that are susceptible to this kind of attack, depending on the ground water chemistry.

Acids present in ground water such as sulphuric and carbonic can react with calcium compounds in the hydrated cement paste to form soluble compounds that are readily leached from the concrete to increase its porosity and permeability. The key factor here is not the acid, but the solubility of the resulting calcium salt.

In general, concrete is resistant to base attack, however, in the presence of high levels of sodium and potassium hydroxides (> 20%) cement paste can undergo degradation. Embedded rebar steel is susceptible to attack by high levels of chlorides which can lead to cracking and spalling of the concrete matrix. Typical chemical environments that can affect concrete degradation are [EPRI, 1994c], [EPRI, 2010] and [ACI, 1990]:

- Acidic environments with pH < 5.5

- Chloride concentrations > 500 ppm

- Sulphate concentrations > 1500 ppm

Chloride attack can cause excessive oxidation of the rebar material leading to cracking of the concrete matrix and gradual debonding of the reinforcement lowering the load bearing capacity of the structure. This type of attack, in an advanced state, is easily detectable visually from rust stains on the exterior surfaces of the concrete. Typically, corrosion of rebars in concrete is not significant if the concrete matrix has a pH > 11.5 and the chloride concentration is < 500 ppm.

5.2.3.2 Degradation by Sulphate Ion Ingress

Sulphates of sodium, potassium and magnesium present in soil, groundwater, and sulphur containing acid rain can react with the cement paste in concrete. Excessive reaction can cause swelling and irregular cracking leading to reduced structural integrity. Susceptible structures for this type of attack in NPPs are intake structures, the foundation slabs and below grade exterior concrete.

6 Colloids, Zeta potential and activity transport in PWRs and BWRs (Samson Hettiarachchi)

6.1 Colloids and Their Characteristics

The origin of colloid science may be dated back to Michael Faraday's time when he made colloidal gold back in 1845 [Faraday, 1845]. However, the term "colloid" was coined much later by Graham in 1861 [Graham, 1861]. Colloids are present as dispersed systems, characterized by a dispersed phase and a dispersion medium. The dispersed phase could be solid, liquid or gas, and the dispersion medium could also be solid, liquid or gas. An example of a liquid dispersed phase and a gas dispersion medium is mist, where the liquid phase is water droplets and the gas phase is air. An example of a solid phase suspended in a gaseous phase is smoke or dust. An example of a solid phase suspended in liquid medium is what is often encountered in nuclear power plants (NPPs) as colloidal suspensions. There are many other combinations of dispersed phases and dispersion media that result in emulsions (liquid/liquid), foams (gas/liquid), gels (liquid/solid) etc. However, because of the broadness of this topic, the focus in this section will be confined only to solid/liquid combination that is common in nuclear heat transport systems. The solids (colloids) could be oxides, oxyhydroxides, mixed oxides, hydroxides, carbonates etc., that act as the dispersed phase suspended in flowing water which acts as the dispersed medium.

In nuclear reactor heat transport circuits where water acts as the coolant, colloids arise as a result of the slow, but gradual corrosion of metals in contact with the high temperature water. The first step in this process is the release of metal ions into the aqueous medium followed by cation hydrolysis forming various charged species such as sub-hydroxides or stable hydroxides. These species may undergo further oxidation to oxides or mixed oxides. Thus, at any given instance the reactor water may have a multitude of charged species consisting of colloids and aggregates of colloids. Colloids are particles of molecular dimension whose size varies from 1 to 1000 nm [Degueldre et al, 1996], species less than 1 nm in size are considered soluble while those that are greater than 1000 nm are called suspended particles.

Due to the interaction of metal components with reactor water, colloidal species are being continuously generated in various forms and sizes. The form depends on the stability of different oxides, hydroxides, mixed oxides and oxyhydroxides in the aqueous environment while the size depends on many factors such as the age of the particles and their tendency to aggregate depending on the acid/base properties (pH) of the water. The size distribution can be evaluated by sampling water through different filter sizes using a normal sampling point. Plots can be made between the number distribution and the size distribution to understand the cumulative particle distribution. Such a plot provides valuable information on the most prominent particle distribution in a given population of colloids that can influence activity transport.

Colloids are species that have unique optical properties. They exhibit the Tyndall light scattering [Overbeek, 1981], thus a normal beam of light does not pass through a colloidal solution, but is reflected back due to light scattering. This is different from a true solution (species with ionic dimensions) and a suspension (with particle sizes greater than 1000 nm), both systems allowing the passage of light. Colloids also have very large surface area to mass ratio and hence do not settle out easily on standing, thus exhibiting the stability of colloidal systems within their stability pH range. The large surface area of colloids is partly responsible for their strong interaction with radionuclides in nuclear heat transport systems that act as a carrier in activity transport, which will be described in a later section.

Colloids can be broadly separated into two categories, those that interact with the solvent strongly (lyophilic), and those that do not have a tendency to interact with the solvent (lyophobic). If the solvent is water, the corresponding terms used are hydrophilic and hydrophobic respectively. However, it must be noted that in some cases there are colloids where one part is hydrophilic and the other part is hydrophobic. Therefore, one must be careful in categorizing colloids distinctly as hydrophilic or hydrophobic.

Regardless of the type of colloid, and more particularly hydrophobic colloids can typically be subjected to two main types of forces, van der Waals attraction and electrostatic repulsion owing to the presence of surface charge according to the DLVO theory [Deryaguin & Landau, 1941] and [Verwey & Overbeek, 1948]. The surface charge generation may be due to surface dissociation of the solvent during its interaction with the colloid, or due to preferential adsorption of ions by the colloid. The balance between these two forces keeps the colloidal system in a stable condition depending on the pH of the solution. The presence of Brownian motion (kT) or thermal energy also helps to maintain colloidal stability where k is Boltzmann constant and T is absolute temperature. The system can be destabilized by changing the pH of the medium that may result in flocculation of the colloidal particles. Thus, pH of the medium plays a major role in maintaining colloidal stability. The influence of pH on colloidal stability is described in the next section.

Unlike the case of ionic species that are single valent or multi-valent, exhibiting a charge of up to about six, colloidal surfaces can sustain much higher surface charges all around its surface. These surface charges impart unique electrochemical properties on to colloidal systems resulting in a variety of electrokinetic phenomena because of the presence of electrical double layers around the colloidal particles. The presence of electrical double layers on colloidal surfaces (Figure 6-1) is manifested by the electrokinetic phenomena exhibited by colloidal systems that include, electrophoresis, electro-osmosis, streaming potential, zeta potential and sedimentation potential [Hunter, 1988].

In reactor water, colloids can be measured or monitored by particle counting as has been done at the Philippsburg BWR (KKP-1) [Degueldre et al, 1994]. The normal approach is to combine filtration with scanning electron microscopy (SEM) [Degueldre et al, 1996]. Typical filter sizes used are 0.2 or 0.45 micron filters, and a typical reactor water volume could be about 2 litres for BWRs, and much larger volumes may be needed for PWRs. The filter sample is dried and covered with a film before SEM investigation at various magnifications. The dried samples could also be counted to determine which particle size retains most radionuclides. For KKP-1 reactor water colloids, a mass concentration of 4 ml/ng was evaluated for the colloidal size distribution from 100 to 1000 nm, and for a colloid density of 5 g/cm³. Figure 6-2 [Degueldre et al, 1996] shows the specific activity size distribution of the colloids from KKP-1 BWR. The study also showed that under steady state conditions, the colloid concentration was not affected by the flow rate at the sampling point. This observation led to the conclusion that the aggregation of colloids is much less likely compared to deposition on to stainless steel oxide surfaces and zircaloy surfaces.
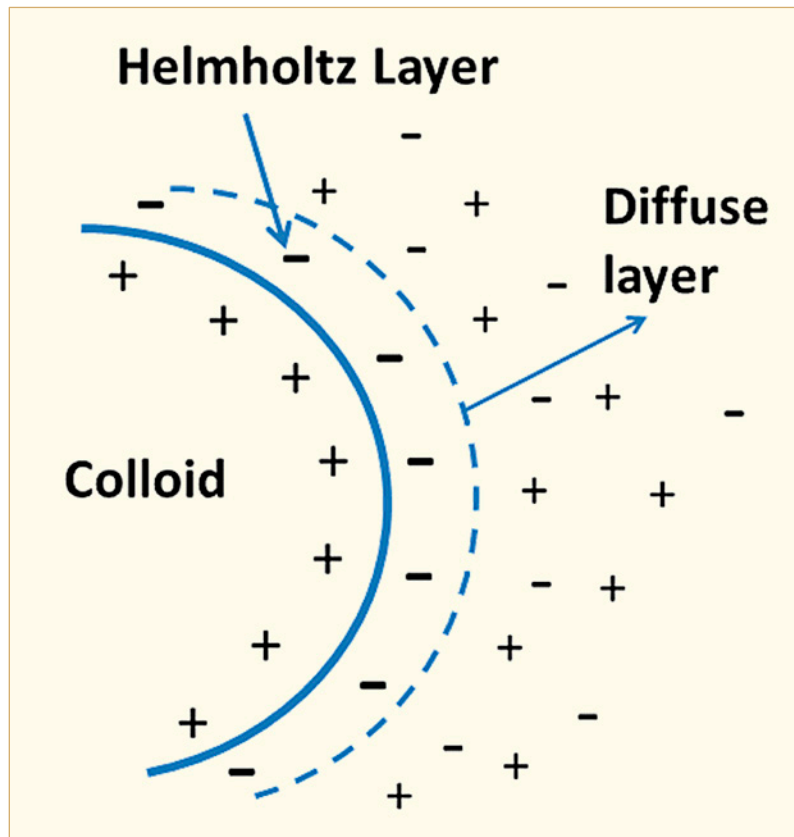
Figure 6-1:   A schematic of electrical double layer generation around a colloidal particle [Hettiarachchi, 2013].
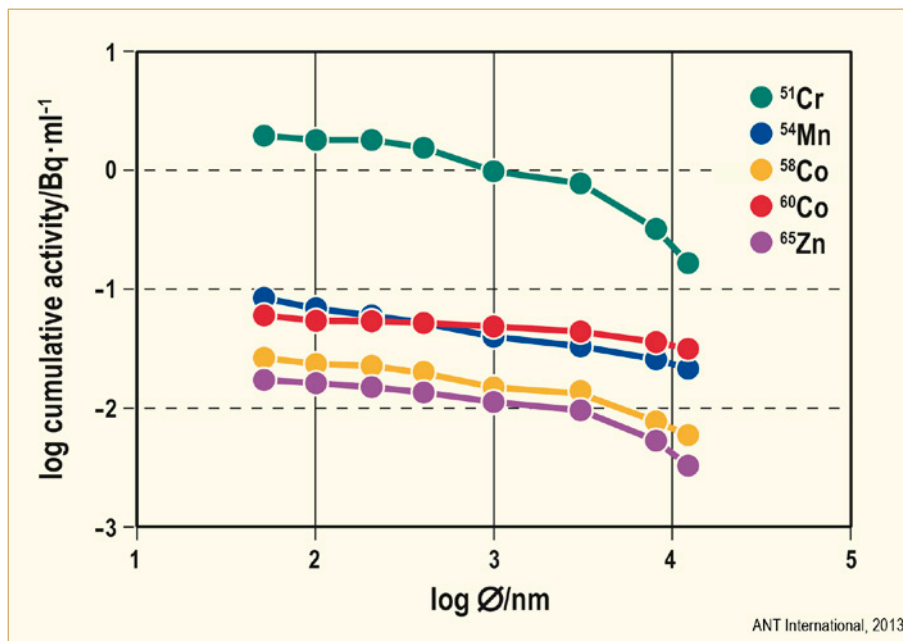

Figure 6-2:   Specific activity and size distribution of the colloids from KKP-1 NPP, after [Degueldre et al, 1996].

7 Electrochemical Corrosion Potential (ECP) measurements in PWR and BWR (Samson Hettiarachchi)

7.1 Introduction and Background

Electrochemical corrosion potential (ECP) monitoring has gained increasing acceptance in many nuclear power plants (NPPs) because it is the single most important quantitative parameter that can be used to understand whether wetted internal metal components of the reactor have achieved the conditions necessary for mitigation against corrosion or stress corrosion cracking, particularly in the case of BWRs. Current day ECP sensors are able to accurately monitor the oxidizing and reducing nature of the reactor coolant environment that enables plant operators to take adequate measures quickly, and sometimes in real time. The measurement is made by having the active end of the ECP sensor close to the desired component location and measuring the potential difference between the ECP sensor and the metal component using a high impedance electrometer and then converting the measured potential difference to the standard hydrogen electrode (SHE) scale for ease of comparison with other data.

ECP monitoring has been widely used in BWRs since the early 80's to optimize hydrogen addition, which is one of the early methods used to mitigate intergranular stress corrosion cracking (IGSCC) of internal components used in BWRs. More than 40 BWRs worldwide have monitored ECPs and have taken appropriate measures to achieve the desired ECP goal of < -230 mV(SHE) in order to mitigate reactor internal components from intergranular stress corrosion cracking (IGSCC). In BWRs, ECPs have been measured at numerous locations since different locations are subjected to different oxidizing conditions.

PWR ECP monitoring has not been very extensive, with only a few plants having monitored or continuing to monitor ECP of primarily two locations in the Secondary Side of the plant, feed water piping and the steam generator tubing either internally, or externally by drawing water to the measurement location using long sample lines. The latter approach can lead to errors due to decomposition and consumption of oxidants in the sample line, although in some cases representative samples have been drawn using short sample lines or by increasing the flow velocity to reduce the transit time to the measurement location. In addition to these ECP measurements in the Secondary Side, primary side ECP measurements have also been made in a few PWR plants. For example, ECP monitoring in the Reactor Pressure Vessel (RPV) of one Japanese PWR has been performed in order to understand the effect of decreasing the coolant Dissolved Hydrogen (DH) concentration on the reducing conditions in the reactor core.

7.2 ECP Monitoring Objectives

The ECP monitoring objectives are different for BWRs and PWRs because the needs are different.

In BWRs, ECP monitoring is performed to achieve industry established IGSCC mitigation criteria of < -230 mV(SHE) on BWR structural materials using a variety of SCC mitigation technologies. In general, BWRs use continuous ECP monitoring of the selected location, through the fuel cycle, in order to obtain inspection relief from the regulators.

On the other hand, in the case of PWRs, a very limited number of ECP monitoring studies have been performed in the primary side to define the required dissolved hydrogen (DH) concentration to suppress radiolysis of water in order to minimize the oxidizing conditions in the reactor coolant system (RCS). Yet another objective has been to determine the corrosion potentials of different materials in PWR primary water to study their corrosion potential behaviour during plant start-up, steady state operation and shut down [Molander et al, 1986].

In the secondary side of PWRs (feed water and the steam generator), in the early days, ECP monitoring studies have been performed to ascertain the presence of sufficient hydrazine concentration to minimize IGA/SCC, and also to check the efficiency of different reducing agents as alternatives to hydrazine addition. More recently, ECPs have also been monitored to define the amount of oxygen addition required to raise the carbon steel potential and also minimize FAC while maintaining a sufficiently reducing condition in the final feed water and in the SG (secondary side).

Thus, once the reducing conditions are identified, continuous ECP monitoring in PWRs has not been considered a necessary requirement.

7.3 PWR ECP Monitoring

7.3.1 Background

PWR ECP monitoring has not been extensive, with only a few plants having monitored or continuing to monitor ECP in the secondary side, and in the reactor coolant system (RCS or the primary side). In the secondary side, the ECP monitoring have been performed primarily at two locations, feed water system and the secondary side of the steam generator tubing either internally, or externally by drawing water to the measurement location using long sample lines [Beyer et al, 1988], [Molander et al, 1992] and [Kassen, 1995]. The latter approach can lead to errors due to the decomposition and consumption of oxidants in the sample line, although in some cases representative samples have been drawn using short sample lines or by increasing the flow velocity to reduce the transit time of the coolant to the measurement location.

Feed water chemistry control in PWRs is important for mitigating corrosion and corrosion product transport. Many PWRs have experienced water chemistry related corrosion issues such as flow accelerated corrosion (FAC) of carbon steel and ingress of oxidants in the feed water system. Oxygenated water chemistry (OWC) is used as an effective means to reduce FAC issues in the feed water systems of PWRs [Takiguchi et al, 2004] and [Takiguchi, 2008]. The oxygen addition amount is too small to be monitored by oxygen analysis, and therefore, electrochemical methods such as redox potential monitoring are required to detect the presence of sufficient oxygen in the feed water system and simultaneous presence of reducing conditions in the steam generators.

Figure 7-1 illustrates the response of FAC to oxygen addition [Ullberg et al, 2009]. The main goal of adding oxygen is to reduce FAC of carbon steel components by raising the corrosion potential. In PWR feed water environment, only a very small addition of oxygen in the sub ppb range is required to raise the corrosion potential and decrease FAC as illustrated in Figure 7-1
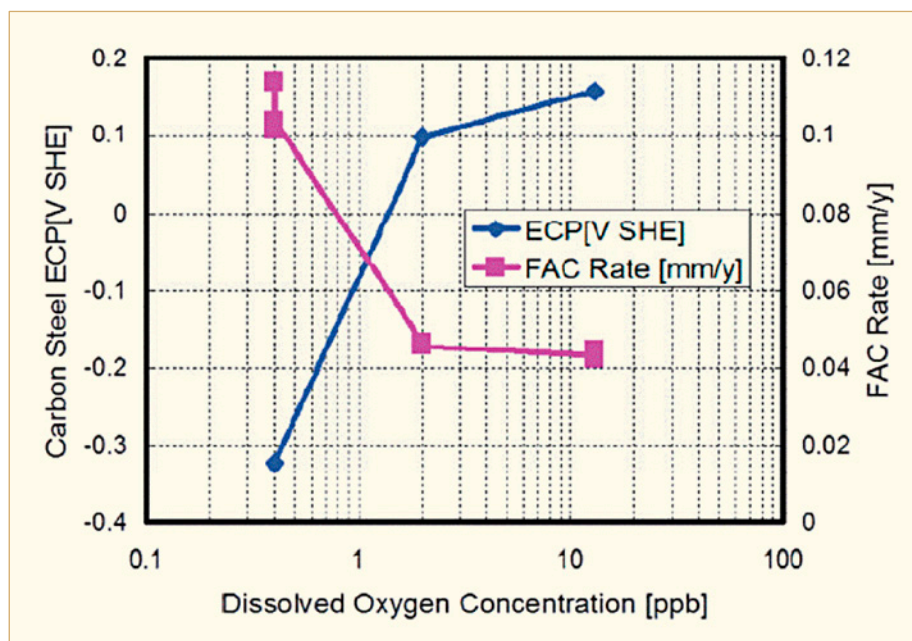
Figure 7-1:   ECP of carbon steel and FAC rates as a function of the dissolved oxygen content in simulated secondary feed water [Ullberg et al, 2009].

ECPs in PWRs have also been measured in the steam generator (SG) tube bundle area and also at the periphery in the down comer region in one case [Beyer et al, 1988]. But, in most cases, ECPs have been measured in external side-stream autoclaves or in-pipe systems where in-pipe monitoring is more sensitive than autoclave monitoring to water chemistry changes as expected [Molander et al, 1986], [Molander et al, 1990] and [Ullberg et al, 2009]. However, in-pipe monitoring requires penetration of the pressure boundary of the system for ECP sensor installation, which is rather costly. The redox conditions of the secondary system in a PWR is largely determined by the balance between hydrazine addition and the residual oxygen concentration. ECP monitoring has been able to better characterize the prevailing redox conditions in the secondary system, and helped to ensure minimizing of corrosion of the secondary side components.

Only a limited amount of PWR ECP data is available in the public domain, and they are presented chronologically in this report, to the extent practical.

The following Table 7-1 provides a list of PWRs and VVERs that have performed ECP monitoring in some parts of the feed water system, in the steam generator of the secondary system or in the reactor coolant system (primary side) with the ECP monitoring year and ECP monitoring location indicated.

8 Review of 2013 Radiation Reduction and Source Term Conferences (Robert Cowan and Dewey Rochester)

8.1 BWR (Robert Cowan)

8.1.1 US Industry Collective Radiation Exposure (CRE) Status through 1st Quarter 2013 by Jeff Foster, INPO Senior Radiation Protection Evaluator

The collective radiation exposure (CRE) statistics for the period beginning in the year 2000 were reviewed for both BWR and PWR units. On a per unit basis, the BWR collective exposure is currently more than double that for PWR units, with median values currently at 114 and 45 person-rem respectively. The U.S. fleet CRE performance is shown in Figure 8-1. The trend shows a steadily decreasing CRE for both BWR and PWR units with a reduction of about 32% and 45% respectively. There is quite a spread in person-rem values for both the US BWR and PWR fleets as shown in Figure 8-2. Note that even the current best BWR unit value would not meet the 2015 goal of 55 person-rem for PWRs, while more than half of the PWR fleet already meets that goal! Hopefully, the 2015 BWR goal of 110 person-rem will be met by the median BWR.
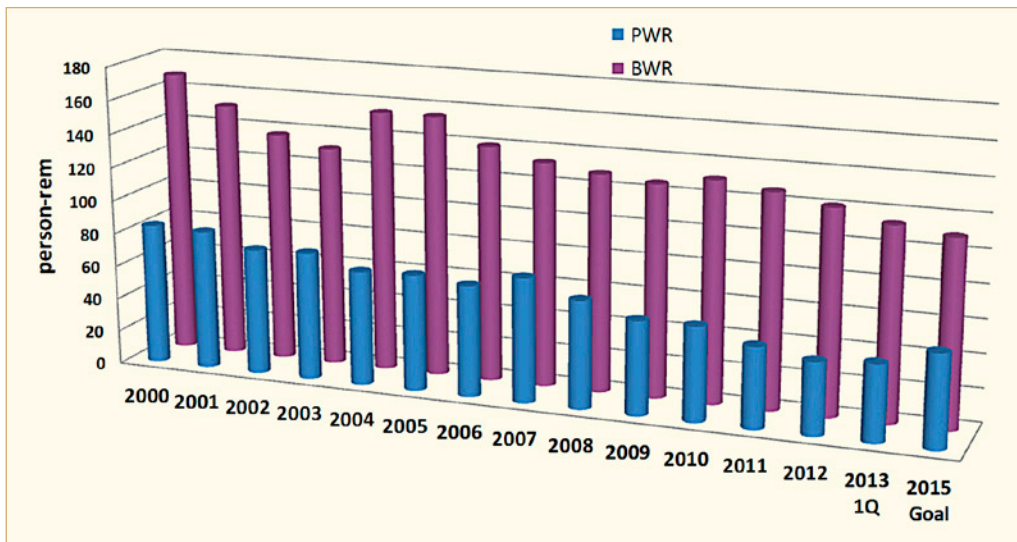
Figure 8-1:   U.S. collective radiation exposure for BWRs and PWRs as adapted from Foster's presentation [Foster, 2013].
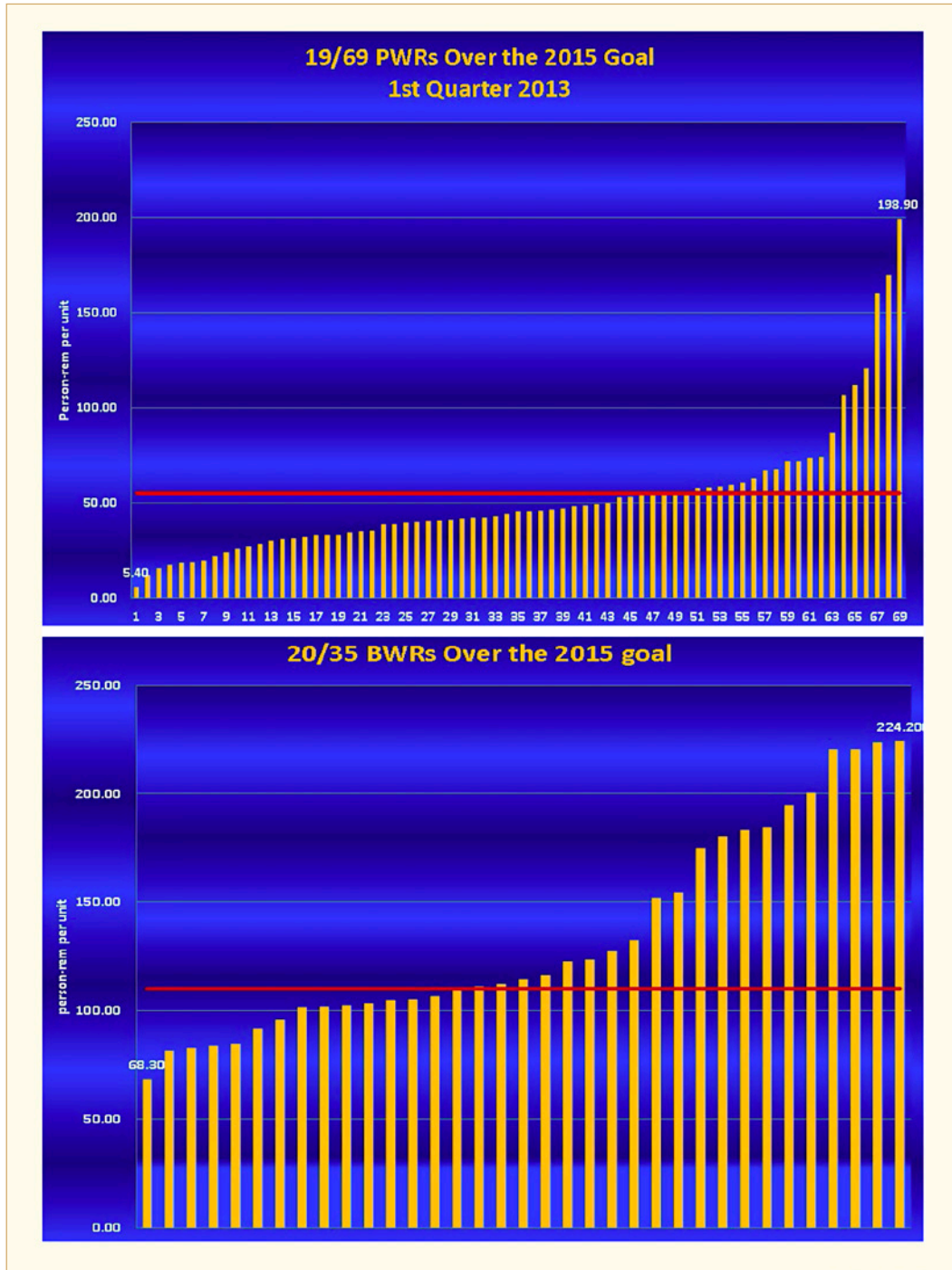
Figure 8-2 :   Distribution of CRE among U.S. BWR and PWR units as presented by Foster [Foster, 2013].

A list of new practices that have helped the downward trend in CRE are shown below.

1)   A unique method to eliminate steam generator entries for nozzled dam installation associated with extended drain down activities...saving approximately 1 person-rem.

2)   Cross functional teamwork and collaboration among multiple departments at one station reduced the cycle average dose for both units more than 10 person-rem below the 2015 industry goal. Effective benchmarking resulted in improved shutdown crud burst management, system flushing and permanent shielding.

3) An ALARA group, working with a medical group, was able to obtain injection-molded, flexible shielding containing tungsten or iron powder mixed with a silica polymer. This flexible shielding was used extensively on two recent jobs and saved a total of 61 person-rems of exposure.

4) Using an engaged ALARA subcommittee and the use of ALARA planning at the task level, in-progress reviews using real-time dose rate tracking and detailed analysis of dosimeter dose and dose rate data improved dose performance was achieved for several high-exposure on-line equipment repairs.

8.1.2　　EPRI BWR Water Chemistry Guidelines Revision Status By Susan Garcia, EPRI

The EPRI BWR Water Chemistry Guidelines are under review with an expected publication date of early 2014. The progress report presented by Garcia listed the key technical changes that are to be made to the current version, EPRI publication BWRVIP-190, issued in 2008. The new version will be published as BWRVIP-190, Rev. 1. Since most EPRI BWR members are or will be utilizing On-Line Noble metal Chemistry (OLNC), many of the changes address operation with this technology. Key revision items follow.

Sulphate and Chloride: Recent investigations have reported that low levels of both chloride and sulphate (<5ppb) may accelerate the IGSCC crack propagation of low alloy steel. Since some parts of the vessel are not under reducing conditions even when HWC or NMCA/OLNC is employed, the chloride and sulphate levels previously used for NWC are now applied for all modes. A summary of the new values is shown in Figure 8-3.

9 Summary of the important BWR items from the 16th International Conference on Environmental Degradation of Materials in Nuclear Power Systems (Robert Cowan)

The *16th International Conference on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors* was held in Asheville, North Carolina (USA) from August 11-15, 2013. The conference operated with three simultaneous sessions covering many topics. Only those topics either directly or indirectly involving BWR related issues are summarized in this review. For example, there were 7 sessions addressing PWR primary SCC and one that addressed PWR secondary side issues that are not reviewed. These sessions represented 1/3 of the conference agenda. All of the other topics of the conference were reviewed, although only the papers with significant new findings or interesting approaches were included.

9.1 Noble Metal Technology

d) Effect Of Flow and Surface Structure on the Pt Deposition on Stainless Steel During Simulated Noble Metal Applications by P.V. Grundler, A. Ramar, L. Veleva, I. Günther-Leopold, S. Ritter, Paul Scherrer Institut(PSI), Switzerland

This paper presents the latest results from a Swiss program entitled NORA, which is studying noble metal deposition behaviour in boiling water reactors. In the present work, a simulation of on-line NobleChem™ (OLNC) was conducted by injecting $Na_2Pt(OH)_6$ into a loop under simulated BWR conditions (288 °C, $H_2/O_2 > 2$). Deposition specimens were coupons of Type 316L stainless steel that had been pre-filmed in either the as received (AR) condition (with a ≈ 0.4 μm surface finish) or a pre-oxidized (PO), which was the same as the as-received plus 2 weeks exposure to simulated BWR/HWC conditions. In the test loop the specimens were exposed in a "low flow autoclave" and in two special "flow test" specimen holder capsules (SH1 and SH2) which were in series after the autoclave. Pt chemical solution was added to the system at a concentration of 2-10 μgm/hr into the main flow of 10 kg/h. The post exposure Pt loadings were determined by Lasar Ablation A-ICP-MS. The results of the testing are summarized in Figure 9-1.
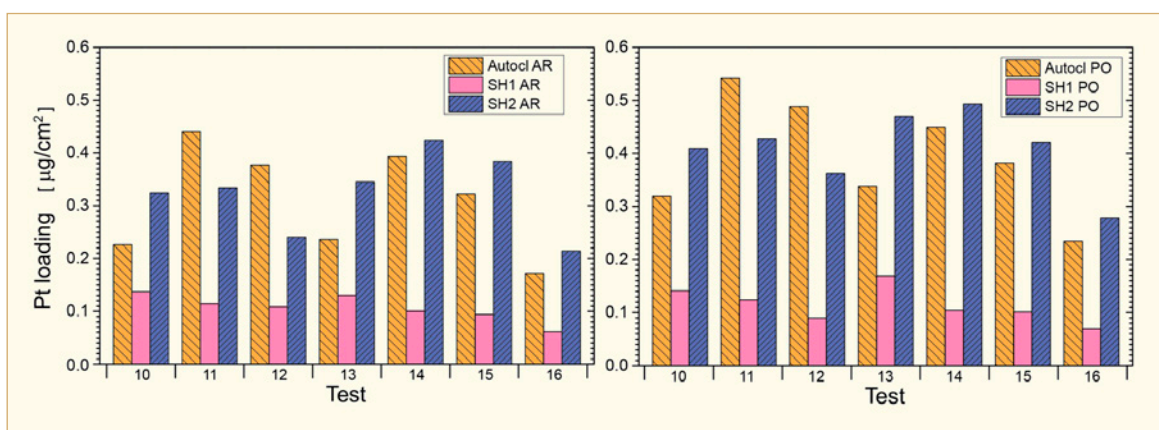
Figure 9-1: Typical test run results of Pt loading for the three locations and two sample surface finishes [Grundler et al, 2013].

The results show that the pre-oxidized samples consistently have higher loading than the as-received samples and this was attributed to the morphology of the PO samples, which had a higher concentration of oxide crystals on the surfaces. A well-developed oxide layer accumulates more Pt nanoparticles due to its larger specific area.

In *all* the tests, the lowest Pt loading was found in SH1, independent of injection rates, water chemistry or surface condition. The critical factor distinguishing the three locations is the bulk flow velocity whish was as follows: Autoclave = a few mm/s, to quasi-stagnant conditions, SH1 = an intermediate velocity of 0.1 m/s, and SH2 = high velocity of 0.52 m/s. A Reynolds Number analysis showed that the SH1 samples saw mostly transitional flow while the SH2 samples saw turbulent flow. These results imply that Pt particles would behave as shown in Figure 9-2, in which particles in the core of the laminar flow have a long way to diffuse to the duct wall and most will leave the duct before reaching the wall and depositing. For the case of turbulent flow, eddies carry particles quickly in all direction, including very close to the duct wall, and these particles only have only a minimal distance to cover by diffusion before depositing.
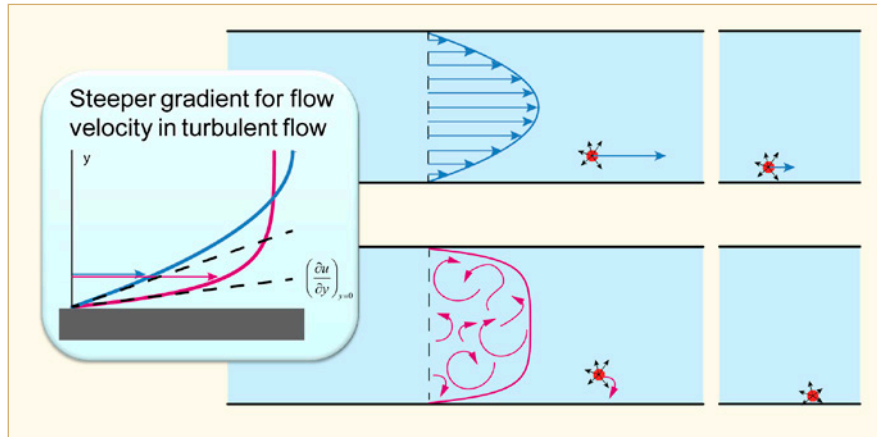
Figure 9-2:   Particle deposition: laminar vs. turbulent [Grundler et al, 2013].

Assuming that the injected $Na_2Pt(OH)_6$ decomposed into Pt particles, the authors suggest that the particle relaxation time τ_p quantifies the inertia of the particles with respect to the fluid by the following:

$$\tau_p = \frac{\tau_p d_p^2}{18 \cdot \eta}$$

Where:

ρ_p = density of particle material (Pt21090 kg/m³)
d_p = diameter of particle
$\eta\eta$ = dynamic viscosity of fluid (94.360 µPa s @ 270°C, 90 bar)

$$\tau^+ = \frac{\tau_p (u^*)^2}{v}$$

Where:

τ^+ = adimensional relaxation time
v = kinematic viscosity (η/ρ) (1.2761 x 10⁻⁷ m²/s @ 270°C, 90 bar)
u^* = friction velocity (for SH2 ~0.025 m/s)

τ can be used to estimate the deposition velocity using the model proposed by [Fan & Ahmadi, 1992]

$$u_d^+ = \frac{1}{2} \frac{D_H}{l} \frac{U_B}{u^*} \ln\left(\frac{C_{in}}{C_{out}}\right)$$

Where:

Estimation of the ratio of particles entering and leaving a section of duct of length/and hydraulic diameter D_H.

When applied to Pt particles in their experimental setup, the authors calculated the result shown in the following Table 9-1. The smaller the particle the higher its probability of being deposited on the surface.

Table 9-1:   Calculated deposition in turbulent flow for Pt particles of different diameters, after [Grundler et al, 2013].

Pt particle size	5 nm	20 nm	50 nm	200 nm
$\tau+$	1.510^{-6}	2.510^{-5}	1.510^{-4}	2.510^{-3}
u_d^+	$>10^{-2}$	1.710^{-3}	2.510^{-4}	$\sim 310^{-5}$
C_{in}/C_{out}	>1.14	1.023	1.003	1.0003
% deposited	~60	2	0.3	0.03
				ANT International, 2013

Experimental results and computations show that a turbulent flow regime provides better conditions for deposition of Pt nano particles. In the absence of strong turbulences, deposition will take place essentially by the slower diffusion transport. Smaller particles diffuse faster than larger ones under the same conditions. Since turbulence does not enter very far into narrow cracks, it is important to produce the smallest possible particles, because they diffuse into a crack is faster.

9.1.1 Effects of DO Depletion in External ECP Measurements by J. A. Varela, H. H. Huie, R. A. Seeman, and T. A. Caine, GE Hitachi Nuclear Energy

The primary "measure of efficacy" used by most BWRs employing OLNC for IGSCC mitigation is the Mitigation Monitoring Systems (MMS) supplied by GE-Hitachi. A schematic diagram of the placement of this device is shown in Figure 9-1. It consists of a method to measure ECP on either coupons or the stainless steel surface of the monitoring unit itself. The coupons can be easily removed and replaced. The coupons are used to monitor the amount of Pt deposited during an NMCA or OLNC application, the latter currently being the preferred method for noble metal application. The ECP measurement tells the "quality of the deposit" and can indicate when early re-application is warranted.

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