

Recent Advances in Water Chemistry Control at US PWRs

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INTRODUCTION

Corrosion problems historically have caused substantial losses of power generation, resulted in large repair and maintenance costs, and contributed to significant personnel radiation exposures in Pressurized Water Reactors (PWRs) operating throughout the world. Water chemistry control plays an important role in the degradation of materials, including; steam generators, reactor components, fuel cladding and balance of plant piping. Water chemistry is one of the few methods available to plant operators to control the degradation. This paper reviews the major developments in water chemistry control which have been developed and implemented to minimize corrosion and radiation exposure in US PWRs.

EPRI publishes Water Chemistry Guidelines for the primary and secondary systems of PWRs. All US PWR utilities and many other utilities worldwide implement these guidelines. The Water Chemistry Guidelines were designed to be living documents, which are revised at two to three year intervals as new technology is developed and implemented in the field. The focus of these documents has shifted from a prescriptive set of specifications to a toolkit for developing a site-specific optimized water chemistry program. In late 1997, the US PWR industry under the leadership of NEI issued the SG Initiative (NEI 97-06). The objective of this initiative is to standardize SG operation, inspection and repair efforts. The initiative has major implications for water chemistry control in the US, as EPRI's PWR Primary and Secondary Water Chemistry Guidelines are defined as "directive guidelines" by the initiative. The initiative prescribes that all US PWRs will meet the intent of the EPRI Guidelines.

The tremendous change in the US utility industry is a result of deregulation of the electricity marketplace.

Competitive pressures are causing utilities to strive to reduce O&M and capital costs. Since corrosion is a major contributor to the O&M costs, utilities must pursue the most cost-effective solutions to their corrosion problems. Mitigation strategies developed over the past few years reflect a trend towards plant specific solutions to corrosion problems. As many corrosion problems are economic issues and are not safety concerns, utilities can focus their strategies on their unique financial situation. The focus on R&D has shifted from the development of more expensive, prescriptive solutions to corrosion problems to the development of cost-effective mitigation options.

In developing new water chemistries, a systems engineering approach is preferred. In the past, a water chemistry strategy would be designed around a single component. Today, it is recognized that the chemistry needs to be optimized for the entire power plant. Since each of the major systems in PWRs contain a number of different materials of construction and are exposed to varied environmental conditions, no one chemistry can be best for the entire system. The concept of optimization applied to mitigation strategies means that the overall economic impact on the entire plant is considered when pursuing a given strategy. Much emphasis is being focused on developing tools, which the LWR operators can use to perform these evaluations.

HISTORICAL PERFORMANCE

Overall, the US utility industry has been quite successful in reducing the impact of corrosion in nuclear power plants in recent years. Figure 1 shows the loss of output due to corrosion in PWRs.

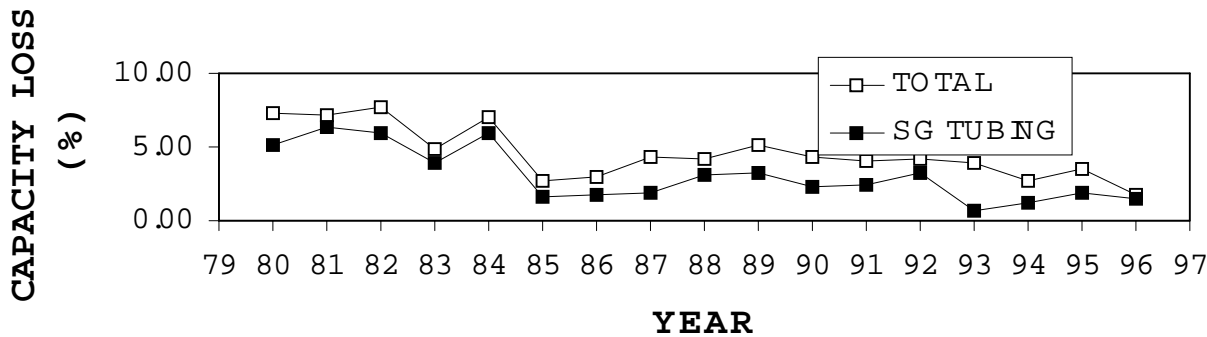


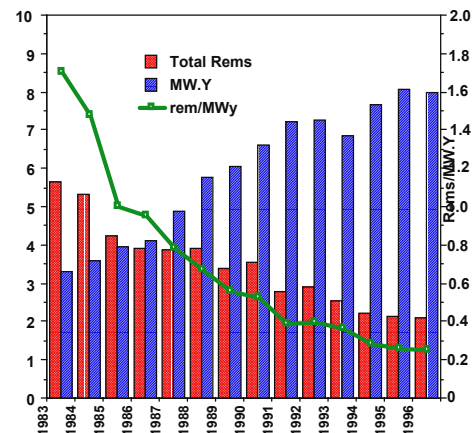
Figure 1 Capacity Loss in US PWRs

As shown in Figure 1, Steam generators (SG) have been the largest single source of output loss in PWRs. The overall trend over the past 10 years has been downward, however, specific damage processes, such as intergranular attack/ stress corrosion cracking (IGA/IGSCC) of SG tubing at tube support crevices and at the top of tubesheets, are becoming increasingly prevalent as the PWR fleet ages. Many of the original SGs which use “mill annealed” Alloy 600 for the tubing material have been or will be replaced much earlier than their original 40 year design life. However, the lifetime of these earlier SG designs has increased from nominally 10 to 20+ years, partially as a result of improvements in water chemistry. In addition to SG corrosion, the other major corrosion concerns in PWRs include; fuel cladding corrosion, flow accelerated corrosion of carbon steel components in the balance of plant and reactor vessel penetration cracking.

Water chemistry also has a significant influence on out-of-core radiation fields, which are the main cause of occupational radiation exposures of nuclear power plant workers. Radiation exposures of nuclear plant workers are determined by the radiation dose rate and by the amount of maintenance and repair work required in radiation areas. Both factors have declined over the past 10 years, with the result that exposures are only about 25% of the peak PWR values experienced in the early 1980’s, as shown in Figure 2. Water chemistry control improvements have focused on minimizing activity generation and transport and at the same time reducing corrosion damage thereby reducing the need for maintenance work and the radiation exposure incurred by personnel performing the work.

The remainder of this paper will focus on specific issues associated with secondary and primary chemistry control. The discussion will center on those initiatives that are either in wide use throughout the US industry or are under development and will be tested in US PWRs in the near future.

**Figure 2
U.S. Nuclear Power Plants
Radiation Exposures and Electric Generation**



ADVANCES IN SECONDARY WATER CHEMISTRY

In recent years, the focus of Secondary Water Chemistry has been on the development and implementation of water chemistry options and tools for PWRs to eliminate or reduce SG damage, in particular IGSCC and to minimize corrosion and O&M costs in the remainder of the secondary system. A number of cost effective mitigation options (e.g. molar ratio control, alternate amines, boric acid treatment, etc.) have been developed and implemented in US PWRs. Tools have been developed to help utilities select and implement the most appropriate water chemistry program for their plant. These tools take the form of water chemistry application guidelines and computer programs such as EPRI chemWORKS™(1).

Several initiatives to control IGA/IGSCC in US PWRs were developed and widely implemented in the early nineties as shown in Figure 3. These initiatives are discussed in detail in the latest revision of EPRI’s Secondary

Water Chemistry Guidelines (2). Table 1 taken from Revision 4 to the EPRI Secondary Water Chemistry Guidelines shows current SG blowdown water chemistry specifications to control IGA/IGSCC and other localized

forms of corrosion. It should be noted, that these guideline limits do not reflect typical plant impurity levels. The average levels of sodium, chloride and sulfate reported are much lower and are on the order of 1-2 ppb.

Figure 3
Implementation of Advanced Water Chemistry Programs in US PWRs

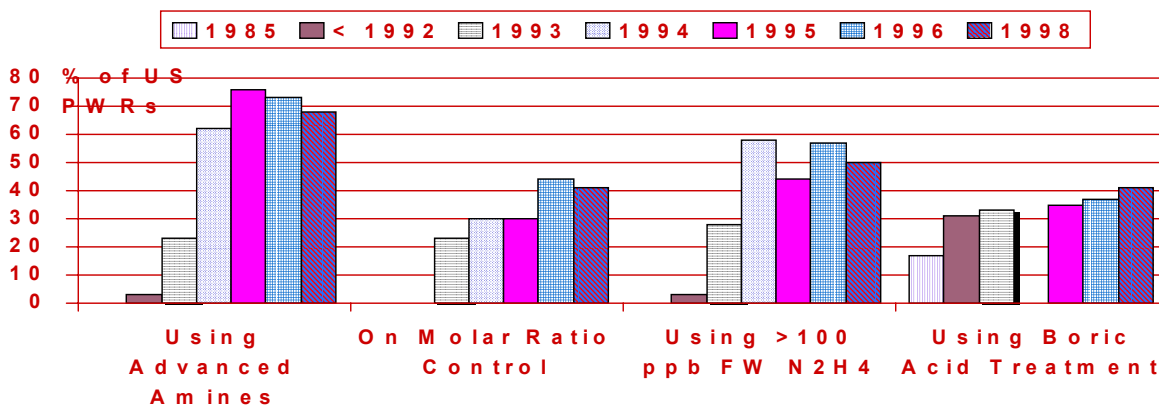


Table 1
Recirc. Steam Generator Power Operation (> 5% Reactor Power) Blowdown Sample CONTROL PARAMETERS

Parameter	Action Levels (d)		
	1	2	3
pH @ 25C	(c)		
Cation Conductivity (μS/cm)	>0.8	>2	>7
Sodium, ppb	>5	>50	>200
Chloride, ppb	>10	>50	>200
Sulfate, ppb	>10	>50	>200
Boron, ppm ^a	(b)		
Phosphate ^a	(b)		

Footnotes: (a) If used. (b) As specified in site-specific chemistry program. (c) Per station pH program. (d) action levels correspond to specific plant actions including power reduction for Action Level 2 and plant shutdown for Action Level 3.

All of the initiatives are directly or indirectly designed to influence crevice chemistry. Molar ratio control (MRC) is designed to control the local pH in PWR crevices by controlling the ratio of anions to cations in the bulk water. Since local crevice chemistry cannot be measured directly, operators depend on hideout return chemistry to optimize the molar ratio during operation. Molar Ratio Control Guidelines (3) describe the design and implementation of MRC programs throughout US PWRs.

Elevated hydrazine defined as >100 ppb in the final feedwater is designed to maintain reducing conditions in the final feedwater. Most forms of SG corrosion are accelerated under oxidizing conditions. To insure elevated hydrazine is working properly, utilities are monitoring the relative fractions of reducible iron (e.g. hematite) to reduced iron (e.g. magnetite) in the feedwater and blowdown. A high fraction of hematite and other reducible metal oxides is indication of oxidizing conditions. Although reducing conditions can be maintained by using elevated hydrazine during operation, a new EPRI research program is looking at oxidizing conditions during shutdown and startup. Some empirical data suggests that much of the IGSCC growth may be occurring during startup when oxidizing conditions are present in the SG. Further evaluation will be performed and it is expected that this work will lead to more stringent

startup and shutdown chemistry requirements. This topic will be addressed in the next revision of EPRI's Secondary Water Chemistry Guidelines planned for 1999-2000.

A new test program in 1998-1999 is focused on evaluating the benefit of injecting hydrazine closer to the SG's. PWRs generally inject hydrazine just downstream of the condensate polishers (or after the condensate pumps in plants without polishers). It is believed that flow accelerated corrosion of carbon steel components can be reduced in the condensate and somewhat in the feedwater system by injecting hydrazine just prior to the SG's. This would create stronger oxidizing conditions in the condensate and feedwater system. Unlike Alloy 600 where oxidizing conditions are deleterious, carbon steel FAC rates are reduced under oxidizing conditions. Tests will be performed at several US PWRs to see how much FAC rates and corrosion product transport rates can be reduced when hydrazine is injected further upstream. To insure the SG's are not adversely impacted, electrochemical potential (ECP) and iron redox measurements will be made during the test program.

Corrosion products, which deposit in the crevices and on tube support and tube sheet surfaces aggravate corrosion by promoting the concentration of impurities. Organic amines are being used in the secondary water to reduce the transport of iron, which contributes to sludge buildup. Amines such as, ethanolamine provide better pH control and thereby reduce carbon steel corrosion in the balance of plant. In recent years, US utilities have adopted a wide variety of amines. Today over 80% of US plants are using one or more of the following amines for pH control; ammonia, dimethylamine, ethanolamine, methoxypropylamine, and morpholine. Another amine, pyrrolidine is under test at a US PWR. Plant specific designs and constraints result in a variety of approaches to pH control. The only specific guidance provided to US PWRs in EPRI's guidelines is that plants optimize their pH control program based on minimizing corrosion product transport. pH control using advanced amines is a good example of how a systems approach to chemistry control is being pursued to address SG corrosion control issues. EPRI's Advanced Amine Guidelines (4) provide qualification data for amines and describe how to optimize a site specific pH control program. A new initiative for corrosion product control involves the use of organic dispersants to increase blowdown removal efficiency and to reduce deposition on SG surfaces. A specific dispersant has been qualified for a short term test in a US PWR planned for 1999.

Boric Acid Treatment (BAT) has been used since the late 80's for both denting control and IGSCC inhibition. More recently, it has been shown that the use of titanium oxides strongly inhibit caustic IGSCC in static autoclave testing. Since, titanium compounds have extremely low solubilities, it is difficult for them to penetrate fouled crevices. In fact, the titanium additives were found to be less effective in the model boiler testing when the crevices

were prepacked to simulate fouling. The titanium additives were more effective at inhibiting cracking in initially open crevices. These results suggest that implementation of a titanium based inhibitor may be more effective immediately following a chemical cleaning or before the crevices are significantly fouled. Several US plants have gone forward with full scale additions of titanium oxides. As with BAT, the potential benefits of adding the inhibitor may greatly outweigh the small risk of deleterious side effects.

ADVANCES IN PRIMARY WATER CHEMISTRY

PWR primary chemistry control aims to maintain primary system pressure boundary and fuel-cladding integrity, to provide for reactivity control, and to minimize ex-core radiation fields. Primary chemistry control is optimized to insure that the fuel and pressure boundary integrity objectives are achieved and radiation fields are manageable. This optimization concept guides the PWR primary coolant chemistry program. Specifically, operation at elevated pH can reduce ex-core radiation fields but the accompanying elevated lithium concentrations can lead to an increased likelihood of Alloy 600 cracking, although the effect of lithium on Alloy 600 is now believed to be smaller than originally thought. In contrast, at a lower operating lithium concentration, the likelihood of Alloy 600 integrity problems will be minimized but an increased buildup rate of radiation fields may result. The fuel cladding situation is even more complicated. Specifically, heavier crud deposits are expected on the cladding at low pH, possibly leading to increased cladding failure rates. Higher pH operation minimizes the rate of crud deposition, while the possibility of accelerated cladding corrosion in regions of the core where subcooled boiling occurs may increase as the local lithium concentrations increases. As a result of considerations such as the above, the pH control program as specified in EPRI's PWR Primary Chemistry Guidelines (5) must achieve a balance among the three goals.

The major consideration for material integrity in the primary system is the Steam Generators. Alloy 600 tubed SG's have experienced considerable IGSCC, which has led to replacement of many units. More recently, Alloy 600 penetrations in PWR pressurizers and reactor vessel heads have experienced cracks. Such cracking has occurred at both US and foreign plants. A recent EPRI study evaluated the literature data on the effects of dissolved hydrogen, pH and lithium on PWSCC of Alloy 600 (6). As indicated previously, lithium and pH levels are controlled per the optimization principles set in the pH control program.

Tables 2 shows the current Reactor Coolant Control Parameters for operating conditions.

Table 2
Power Operation (Reactor Critical)
CONTROL PARAMETERS

Action Levels (c)

Parameter	1	2	3
Chloride, ppb	>50	>150	>1500
Sulfate, ppb	>50	>150	>1500
Fluoride, ppb	>50	>150	>1500
Lithium, ppm	(a)		
Hydrogen, cc(STP)/kg H ₂ O	<25	<15(b)	<5
	>50		
Dissolved Oxygen, ppb	>5	>100	>1000

Footnotes: (a) Limits are based on plant specific pH control program. (b) Corrective action is recommended if this value is exceeded but no plant shutdown is suggested (c) see Table 1 footnote for action level definition.

Primary Chemistry Initiatives

EPRI is currently revising the PWR Primary Chemistry Guidelines. Several of the initiatives discussed below will be incorporated into the revised guidelines. The major focus of primary chemistry programs today is pH control. As previously discussed operation at low lithium (and pH) produces crud deposits. Specifically, operation below $pH_{(Tave)} = 6.9$ is not desirable because of the expected decrease in corrosion product solubilities in the core, which may lead to heavier core crud deposits. At the present time, almost all plants operate at $pH_{(Tave)} = 6.9$ or above.

With the advent of higher power fuel with subcooled boiling, the potential for additional crud to be deposited on the core has increased. Recently, several plants operating with localized boiling in some parts of the core have experienced an axial offset anomaly (AOA), which has been attributed to concentration of lithium boron compounds in crud deposits. The current guidelines recommend operation above a $pH_{(Tave)}$ of 6.9 to a maximum of 7.4 with the requirement that lithium not exceed 2.2 ppm for long periods to achieve $pH > 6.9$ due to fuel corrosion concerns. These principles are based on corrosion product solubility considerations and ex-core radiation fields. Beyond this basic operating principle, reducing the source term for crud (e.g. minimizing corrosion rates of system materials) is considered especially important for plants susceptible to AOA. Corrosion product release rates are reduced as the $pH_{(at\ temperature)}$ is increased from 6.9 to 7.4. The change in release rate becomes less dependent on $pH_{(at\ temperature)}$, as the $pH_{(at\ temperature)}$ approaches 7.4. This dependence is observed for both stainless steel and Alloy 600. This effect is more pronounced for Alloy 600, which is important because of the large surface area of SG tubing. Additionally, the release rates are expected to be highest at the beginning of the cycle and decrease as protective oxides on system materials stabilize. These two findings indicate that corrosion product generation and transport will be greatest during the earliest parts of the fuel cycle when the $pH_{(at\ temperature)}$ is lowest under current practices.

The current guidelines recommend a fuel and materials review for extended operation above 2.2 ppm

lithium, although operation up to 3.5 ppm will likely be considered acceptable in the next revision of EPRI's guidelines. Current fuel corrosion models suggest that the fuel cladding corrosion rate is proportional to the integrated lithium exposure (e.g. ppm x days) during a fuel cycle. As such, many US PWR operators have shifted to a constant pH throughout the fuel cycle. Concurrence from the fuel vendor for an increase in the cycle lithium ppm x days, has been obtained by some plants. Several US utilities have already moved to a constant $pH_{(Tave)}$ of 7.1-7.2.

EPRI is evaluating the costs and benefits of boric acid enriched in B-10. This will allow higher $pH_{(Tave)}$'s to be maintained without increasing the lithium concentration. Already in use for nucleonic control at some German and Swiss PWR's the main impediment is the cost of enriched boric acid.

Another major concern in the primary system is silica, due to deposition on the fuel as a zeolite compound with magnesium, calcium and or aluminum. Silica may be found in high concentrations in the spent fuel and refueling pool waters due to decomposition of Boraflex. During refueling operations, silica contaminates the refueling water via fuel movement through the transfer canal. Removal of silica can be expensive and appropriate limits, giving consideration to balancing the risks and the economics have been established. Existing chemistry guidelines limit the silica to 1 ppm in the reactor, but a couple of US utilities are allowing the silica limit to increase to 3 ppm and monitoring for adverse effects. The silica limit will likely be changed to 3 ppm in the Primary Chemistry Guidelines.

The first field test of zinc in a PWR was conducted at Farley 2 during the last nine months of fuel cycle 10 (1996). Initial examination of the fuel after the trial suggested that the fuel cladding oxide thickness was greater than anticipated. However, additional analyses led to the conclusion that the higher than expected corrosion values were caused principally by the fuel duty and the inherent variability in Zircaloy cladding corrosion. The presence of zinc had little effect on Zircaloy cladding corrosion. With regards to PWSCC inhibition, the available data (eddy current test results) suggests that improvements were observed after nine months of zinc addition. Channel head dose rates were also 15-20% lower than would have been anticipated without zinc addition. As with BWRs, the use of natural zinc does not provide the maximum benefit due to the activation of Zn-64. Farley has initiated the addition of depleted zinc in Unit 2 during Cycle 12. One other US PWR, Diablo Canyon began adding zinc in late 1998. Other US PWRs will begin adding zinc in 1999.

Shutdown and startup chemistry has become another major issue for the primary system. The main objective of shutdown chemistry is to control the release of radioactive species during the shutdown evolution so that they can be removed via cleanup systems and not create dose problems during the refueling outage. US PWRs follow a procedure of maintaining acid reducing conditions during the cooldown followed by forced oxidation with

hydrogen peroxide. This procedure first removes metal oxides from fuel and ex-core surfaces then dissolves the reduced metals (particularly nickel) so that they may be removed via the cleanup system. This approach is followed by most US PWRs with slight variations relative to the timing and specifics of each phase (e.g. lithium removal, hydrogen levels, etc.). In the past year, some US PWRs operating with sub-cooled boiling have experienced large crud burst during shutdown despite following these procedures. This may be related to a more nickel rich fuel crud in these plants (and AOA plants in general) compared to non-boiling plants.

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