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Elevated-Constant pH Control Assessment at TXU's Comanche Peak Steam Electric Station

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Abstract

Industry experience with axial offset anomaly (AOA) has raised the importance of crud management strategies. Elevated-constant pH control is recognized as one potential solution. Additionally, minimizing radiation fields remains a high industry goal which is supported by this strategy. An investigation of industry experience and experimental data has supported a strategy of constant at-temperature pH of 7.4, requiring as much as 6-ppm lithium at the beginning-of-cycle (BOC). This approach, in a modern high temperature plant with high boron requirements, necessitated a careful assessment of potential risk for increased susceptibility to corrosion for both fuel cladding and RCS structural materials. This paper presents results of the assessment [1] for Comanche Peak Steam Electric Station (CPSES) and plans for a demonstration of this practice. Both activities are co-sponsored by EPRI and TXU Electric.

The principle of constant-elevated pH has already proven successful for radiation field control for plants with shorter operating cycle's [2], which require less lithium to achieve desired conditions. Recently, several plants with longer operating cycles have raised lithium to the current EPRI maximum recommended concentration of ~3.5 ppm, to achieve an at-temperature BOC pH in the range of 7.1 to 7.2. The preliminary results encouraged the current investigation, which seeks to qualify operation at lithium concentrations up to 6 ppm to provide a constant at-temperature pH of 7.4 for modern PWR core designs. Operation at this pH is thought to be the optimum chemistry regime for crud management.

The recently experienced AOA phenomenon is considered to be a barrier to designing reactor cores for optimal economic performance. AOA is the result of a combination of factors including fuel rod sub-cooled boiling, crud deposition, and boron hideout inside the crud deposits. The charter of the EPRI Robust Fuel Program includes developing mitigative solutions for AOA. Reactor coolant chemistry controls have been identified as one potential means of reducing AOA susceptibility. This issue is illustrated in Figure 1.

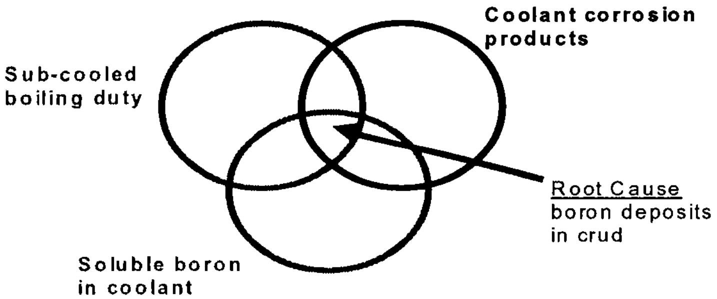

Figure 1
Root Cause of AOA

Elevated pH, held constant throughout the fuel cycle, is a possible path for such a solution. For example, elevated pH is known to reduce ex-core corrosion release, transport, and deposition of corrosion products on nuclear fuel. However, the increased boron requirements for modern core designs require significant increases in lithium concentration to attain desired constant-elevated pH conditions. Therefore, a careful engineering evaluation of the possible impact of these lithium increases on corrosion susceptibility of both fuel and structural components is necessary.

Introduction

The assessment of risk for lithium enhanced corrosion of nuclear fuel clad was performed independently by Westinghouse and Framatome-ANP for their respective fuels. The assessments included the expected power histories, to be employed in a possible demonstration at TXU's CPSES. The key results and conclusions of these assessments are as follows:

1) Zircaloy-4 clad fuel, supplied by Westinghouse, was predicted to have an increase in oxide thickness up to ~40%, when lithium was raised to 6 ppm, but remain within the design corrosion allowance. This analysis was specific to the planned assembly power history at CPSES.

2) ZIRLO^{TM} clad fuel, a low tin alloy clad material supplied by Westinghouse, was predicted to experience a very small (~5%) increase in oxide thickness when lithium was raised to 6 ppm.

3) Optimized Zircaloy-4, a low tin alloy clad material supplied by Framatome-ANP, was evaluated for constant pHs of 7.2, 7.3 and 7.4. The predicted increase in corrosion was small and did not exceed the design corrosion allowance for the power histories specific to the proposed demonstration. However, power histories having higher duties were excluded by the fact that the corrosion model predicted lithium enhanced corrosion, and the current model was not benchmarked for these conditions.

Both the Westinghouse and Framatome-ANP assessments caution that the results of their evaluation are specific to the proposed core designs for the demonstration and that the potential for lithium enhanced corrosion should be evaluated on a plant and cycle specific basis, prior to instituting an elevated lithium program.

Westinghouse performed an evaluation of the potential impact for the proposed chemistry changes on stress corrosion cracking (SCC) of the primary system materials. The key results and conclusions of this assessment include the following:

1) There is no basis to judge that IASCC of austenitic stainless steel will occur in either of the Comanche Peak units and no technical basis to suggest an effect due to higher-than-previous concentrations of lithium.

2) The precise role of primary chemistry on PWSCC is not well established. It is known and generally accepted, however, that the effects of reasonable variations in water chemistry are modest compared to those associated with temperature and stress factors.

3) The proposed change in primary water chemistry is not anticipated to have a discernible effect on the corrosion resistance of the following components at either unit:
   - Alloy 690 SG tubing mechanical plugs
   - Alloy 600 CRDM penetration adaptors or bottom-mounted instrumentation penetrations
   - Cold-worked type 316 stainless steel core baffle former bolts
   - Alloy X-750 (Rev. B) guide tube support pins.

For the Unit 1 steam generators, with mechanically-expanded Alloy 600 MA tubing, the change in water chemistry was estimated to increase the tubing susceptibility to PWSCC by about 9% relative to the current practice of coordinated pH 7.1-7.2. This component was judged to be the most susceptible material evaluated. For the Unit 2 steam generators, with hydraulically expanded Alloy 600 TT tubing, the corrosion resistance is expected to be much greater

Background

The nuclear industry has sponsored numerous experiments and investigations to better understand the role of elevated pH to limit crud deposits and the residence time of deposits on nuclear fuel, as a mitigative strategy for radiation field growth at ex-core surfaces. The demonstration of this principle has been quite successful at one nuclear station in Sweden [2, 3, 8] with operation up to an at-temperature pH of 7.4 held constant for a twelve month fuel cycle. However, most U.S. PWRs typically operate with eighteen-month fuel cycles and have much higher BOC boron requirements. These PWRs have been unable to achieve a constant pH_t 7.4 due to existing limitations on lithium concentration.

The industry trend toward lower leakage core designs and higher sub-cooled nucleate boiling (SNB) in peak channels is recognized to increase susceptibility to AOA. In an attempt to avoid AOA, several modern plants, operating longer fuel cycles have increased BOC pH in recent cycles by raising lithium to the full extent of current limits and have implemented constant pH to replace the conventional modified pH regime. These plants, including TXUs CPSES, have shown some benefit through this chemistry control principle and their progress is being followed and reported by EPRI [4]. Internal studies by TXU suggested that raising the BOC pH further to constant 7.4 provided added benefit while maintaining acceptable risk. This led to the proposal of a co-sponsored initiative with the EPRI Robust Fuel Program and the present assessment project [1].

This project was initiated with the objective of demonstrating a solution for (AOA). Corrosion product deposits at the fuel clad surface have been identified as a key contributor to the onset of AOA as depicted by Figure 1. These deposits tend to accumulate to the greatest extent in the higher SNB regions of the core [5]. Therefore consideration of methods to minimize crud formation offer a preventive strategy, as depicted in Figure 2, for AOA and possible relaxation of core design constraints for AOA. Based on plant specific evaluations, current AOA prevention strategies cost utilities between $500K to $2M per operating cycle.

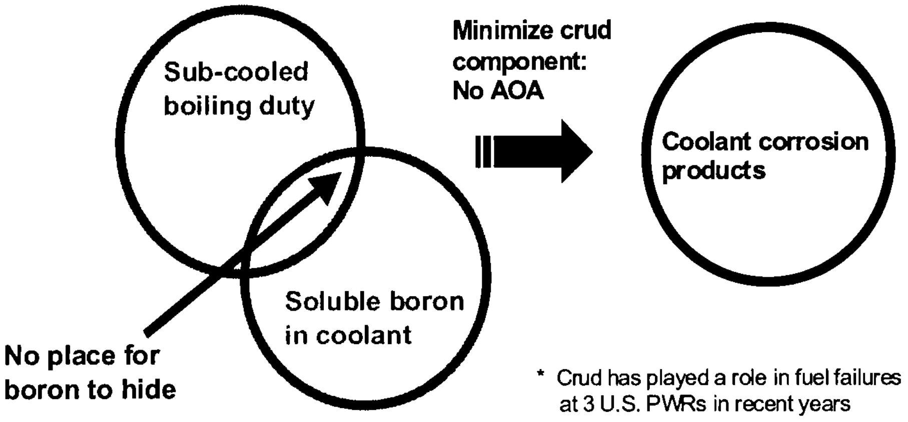

Figure 2: Mitigation Strategy

The BOC lithium requirements for at-temperature pH 7.4 at CPSES was determined to be ~6 ppm. The current industry experience base is ~3.5 ppm lithium. Therefore, the primary objective of the assessment phase of the project was to evaluate the influence of this higher lithium concentration on the corrosion performance of both the nuclear fuel and structural components of the reactor coolant system (RCS). The approach investigated existing laboratory and operating experience and predicted the impact of elevated lithium through current modeling capabilities. The second phase, assuming a favorable assessment and TXU internal approval, is to include a demonstration with appropriate fuel surveillance's, as recommended by the EPRI PWR Primary Water Chemistry Control Guidelines [6], to confirm the results.

The assessment report [1] combines independent evaluations by Westinghouse and Framatome-ANP. Westinghouse performed an evaluation for the effect of elevated lithium on Westinghouse supplied nuclear fuel and RCS structural components, while Framatome-ANP performed an evaluation for Framatome ANP supplied nuclear fuel. Both fuel vendors participated in the assessment because both suppliers' fuel will be present in the upcoming core cycles under consideration at CPSES. Although performed independently using proprietary methods, both vendors' conclusions for risk to their respective fuels were similar. Both contractor evaluations conclude that the risk of lithium enhanced corrosion is relatively small for the plant specific power histories expected in the demonstration cycles for the respective fuel designs. However, greater risk of enhanced corrosion is identified for fuel duties that exceed the planned power histories for CPSES. This reflects the critical importance of plant specific assessments.

Westinghouse performed the RCS structural component assessment for both units at CPSES. The findings of these evaluations included a small enhancement of PWSCC susceptibility for the Unit 1, Alloy 600 MA, steam generator tubes material. This was the most susceptible component evaluated. The steam generator tubes for Unit 2 are manufactured of Alloy 600 TT material and were judged to have much lower susceptibility, consistent with the excellent long term performance of this material.

TXUs role included providing the bases for constant-elevated pH 7.4 operation and evaluating the approach and conservatism in the respective contractor assessments. This was done through review and evaluation of numerous references, particularly published EPRI Reports [5-12, 14]. A recent paper by Billot, et al. [14], was very timely for this assessment and offered a thorough and independent evaluation of operation at elevated lithium concentrations. The numerous references used in the evaluation provide substantive data and conclusions useful for evaluating the risk associated with the proposed elevated-constant pH program and supported the approach and conclusions of the present assessment. TXU Electric has considered the contractor findings to be conservative but will be implementing a two step approach for transitioning to the proposed optimum constant pH. This approach will begin with the next full cycle at Unit 2, operating at constant pH 7.3. Once this cycle is concluded, TXU will evaluate operating the next cycle at constant pH 7.4. This position does not challenge the contractor assessments and only reflects the conservative philosophy of the utility.

Discussion

The following discussions are based on TXUs internal evaluations on strategies for RCS chemistry control and provided the starting points for the contractor assessments. Additionally, TXU considered the independent approaches and results of the respective contractor evaluations in view of the many related published references. TXU arranged peer reviews, and carefully weighed the data and conclusions they individually provided. It was found that the present assessment was consistent with widely accepted principles, while the approach may have been slightly different between the contractors and within the industry. Therefore, this discussion integrates the theories and mechanistic aspects, instead of offering a comparison of the methodologies and theories.

It should be considered that the present assessment did not include a penalty or benefit from the presence or absence of crud deposits, although one main purpose of the elevated constant pH proposal is to minimize in-core deposits. It should be noted that the relatively low levels of crud deposits historically observed on Comanche Peak fuel was taken into consideration. Hopefully, the planned demonstration will provide results to support inclusion of a specific crud term in future corrosion models.

Crud Deposition: The literature includes extensive information on the role of pH control regimes to influence corrosion release rates by ex-core materials, to affect residence time of crud on nuclear fuel, and to influence crud stability during operation. There is substantial evidence, from operating experience, of the benefit from increasing pH and maintaining it constant during the operating cycle. Results have included reduction in specific activity of in-core and ex-core deposits resulting in lower radiation fields. The amount of crud observed during shutdown inspection and scraping is also lowest for plants using this chemistry regime. Also, shutdown chemistry results indicate lower amounts of nickel removal through controlled crud decomposition as well as its lower specific activity.

The accepted theories of elevated pH influence on crud behavior include maintaining a positive temperature coefficient of solubility for iron compounds in the core, as temperature rises with axial height. This is illustrated in Figure 3, which supports the conclusion that the at-temperature pH of 7.4 is near the optimum point to limit deposition by precipitation [14]. This conclusion was developed after review of operating experience [2-4], consideration of the industry guideline position [6] and exhaustive review of numerous reports detailing experimental research results. Perhaps the most important of the latter category included review of nearly two decades of experimental research by AECL, all directed at crud management strategies. A summary report [15] provided the essence of the program results as given in the exceptional pH correlation with core crud mass, shown in Figure 4. The fact that boric acid is not used in CANDU plants enabled higher pH's with low lithium requirements.

The contrast in lithium requirements is large for a modern PWR core design having extended cycle length versus plants operating 12-month cycles. For example, the lithium requirements to achieve a given pH at typical BOC boron conditions for Comanche Peak operating with a T_{avg} of 309 °C is given in Figure 5. The estimated cycle lithium exposure, in ppm-days, is given in Figure 6 for each case. This provides the background for performing evaluations of potential risk for enhanced corrosion of fuel cladding and RCS materials and components.

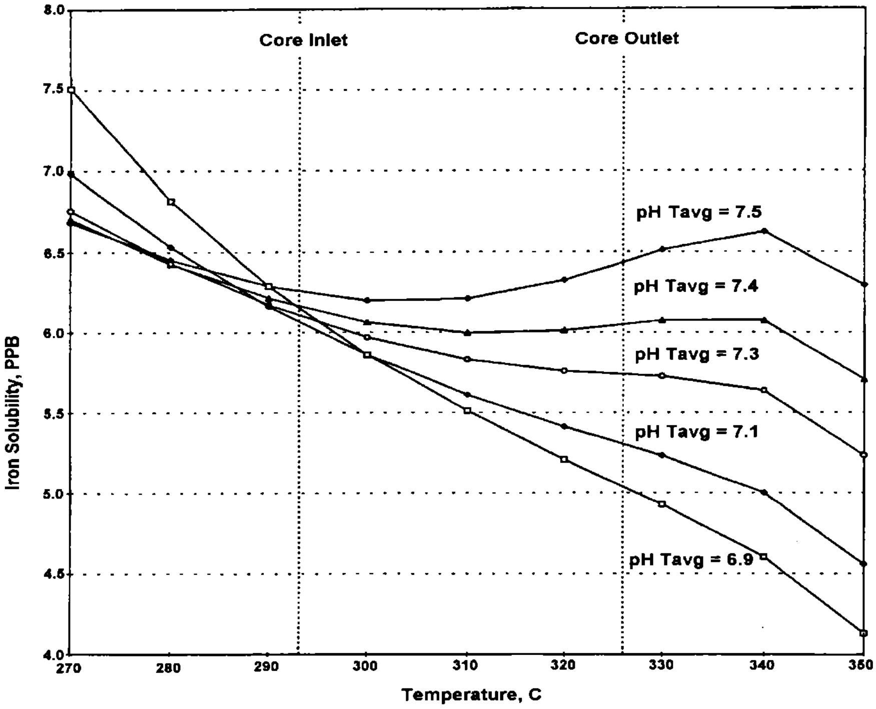

Figure 3
Iron Solubility from Core Inlet to Outlet as a Function of PH_t at the Coolant T_{avg} (Ref. 14)

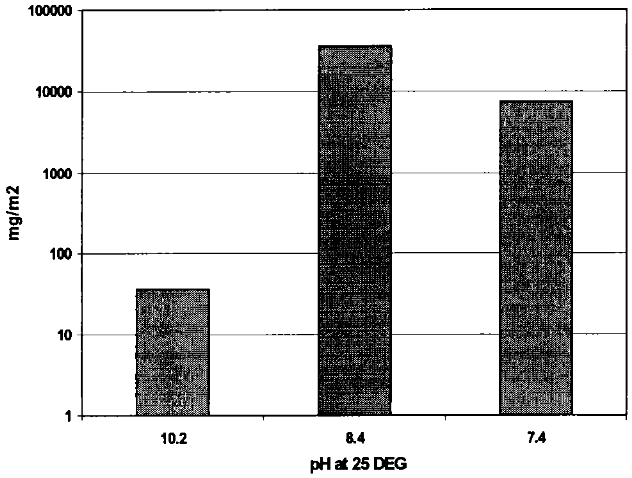

Fig. 4.a - Effect of pH on Deposit Wt.
BWR Tests

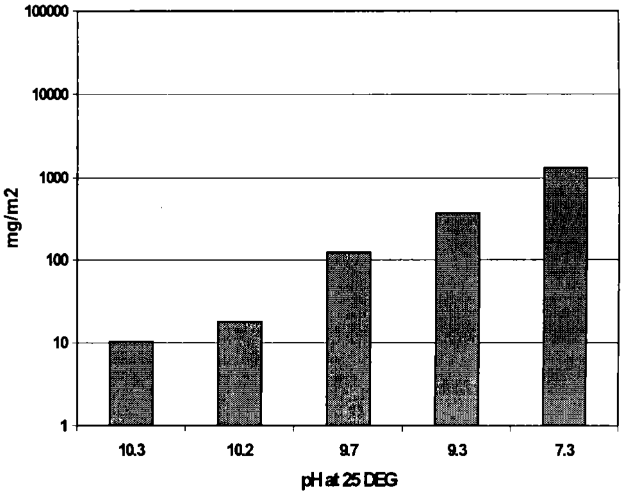

Fig. 4.b - Effect of pH on Deposit Wt.
PWR Tests

Figure 4
AECL 6952, May 1980

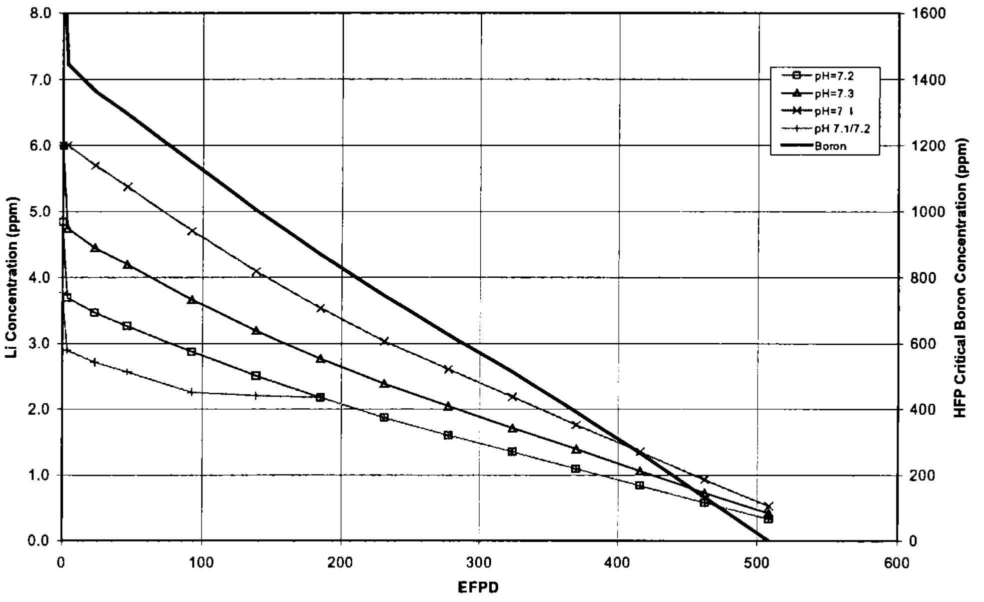

Figure 5: Alternate pH Control Program (U2C5)

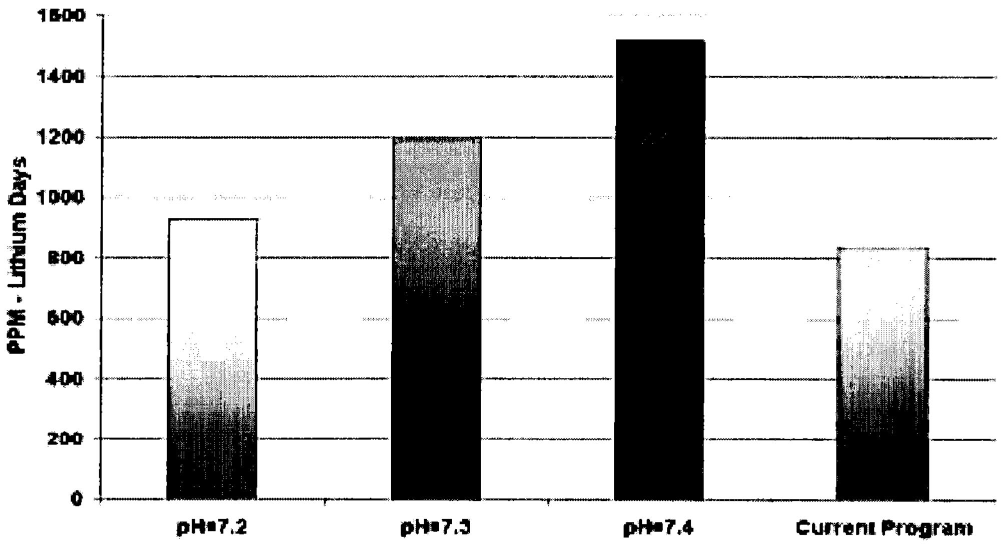

Figure 6
Cumulative Lithium Vs pH Regime

Crud Effect on Fuel Clad Corrosion: The principal factors in nuclear fuel corrosion include temperature, irradiation, and the chemistry environment. The formation of crud deposits on nuclear fuel is known to contribute to enhanced oxidation of the cladding through both temperature and chemistry environment effects. One aspect of this process is the concentrating mechanism for solute chemistry, primarily lithium and boron, which increases locally in proportion to SNB rates and crud deposits. The characteristic of crud may change, particularly thickness and near-surface porosity, to further enhance SNB rates and produce higher solute concentrations at the clad surface. Both boron and lithium deposit or "hide-out" within the crud layer resulting in local depression of the power or onset of AOA.

The presence of thick and/or low porosity crud can interfere with effective heat transfer and present high local lithium concentrations at the clad surface, both having the potential to increase corrosion rates. Therefore, strategies that limit crud deposition or loss of porosity are beneficial to reducing the probability of unacceptable corrosion of the cladding.

Lithium Effect: There has been extensive corrosion testing of zirconium alloys in autoclave environments and in experimental reactors with elevated levels of lithium as discussed in the 1998 IAEA review [16], which included 118 references. The general interpretations of the many reported results suggest that lithium concentrates in the oxide and reaches some critical level. The lithium buildup is affected by the initial concentration of lithium in the water. It has been found that corrosion accelerates as the oxide thickness increases. Relatively high concentrations of lithium in the oxide layers impacts the corrosion rate by dissolving some local areas of the oxide, forming pores and effectively allowing more oxygen to penetrate the film. High levels of lithium in the oxide layer near the metal interface also cause grain morphology changes that result in an increased corrosion rate and may also influence the diffusion of the elements through the oxide.

The sensitivity to the lithium effect is known to increase with temperature, heat flux, local quality and to decrease with additions of boron [1,16]. When boron is present, the boron or boric acid tends to lower the pH and neutralize the effects of lithium. This effect is quite large and supporting information on the beneficial effects of boron additions is found in the literature [10, 13, 16]. Thus, even if there is a potential for a slight corrosion rate enhancement due to a change in lithium from 3.5 to 6 ppm, the boron effect helps offset that impact

Most of the lithium-related corrosion data has been generated for Zircaloy-4 or tertiary type materials. However, the current industry trend to select alternate alloys, including quaternary type zirconium alloys such as ZIRLO^{TM} cladding, is addressed in the current assessment. Further, it is planned to include lead assemblies with this cladding in the planned demonstration.

Based on the published data and the current evaluation, a change in reactor coolant lithium level from 3.5 to 6 ppm will not have a significant effect on the corrosion rates of the Zircaloy-4, Optimized Zircaloy-4, or ZIRLO^{TM} materials for the proposed power histories. The amount of predicted corrosion increases with fuel duty and SNB. Therefore, the potential for increased corrosion in plants with high boiling duties should be evaluated before instituting an elevated lithium program. The present evaluation applies only to the TXU units, and caution should be used in applying these evaluations to plants with higher core mass evaporation rates.

Corrosion Effects on RCS Materials and Components: The influence of elevated pH and lithium concentrations on primary system materials and components has been pursued rather vigorously in prior research programs. Some of the impetus for this interest was due to the impact of PWSCC on Alloy 600 MA steam generator tubing. This subject is thoroughly addressed with each revision of industry guidelines for chemistry control of primary systems [6]. Due to the higher order effects of other parameters, including temperature, stress, and microstructure, it is difficult to assign a pH or lithium term to SCC predictions. It appears that the larger variation in the dominant factors mask any discernible effect of most chemistry parameters studied and has made data interpretation ion for pH and lithium effects quite difficult. In response to this circumstance, EPRI sponsored a project to investigate a multivariable analysis of chemistry parameters on PWSCC initiation [17]. This database analysis concluded that material susceptibility to PWSCC, in a pH 7.4 and 3.5 ppm lithium environment, does not increase with higher values of either lithium or pH.

Westinghouse performed a thorough and complete evaluation of the potential impact of the proposed chemistry changes on stress corrosion cracking of primary system materials. The key results and conclusions of the assessment include the following:

> **IASCC:** There is no basis to judge that an enhancement of IASCC of austenitic stainless steel will occur in either of the Comanche Peak units and no technical basis to suggest an effect due to higher-than-previous concentrations of lithium.
>
> **PWSCC:** The precise role of primary chemistry on PWSCC is not well established. It is known and generally accepted, however, that the effects of reasonable variations in water chemistry are modest compared to those associated with temperature and stress factors.
>
> **RCS Components:** The proposed change in primary water chemistry is not anticipated to have a discernible effect on the corrosion resistance of the following components at either unit:
>
> - Alloy 690 SG tubing mechanical plugs
> - Alloy 600 CRDM penetration adaptors or bottom-mounted instrumentation penetrations
> - Cold-worked type 316 stainless steel core baffle former bolts
> - Alloy X-750 (Rev. B) guide tube support pins
>
> **Unit 1-SG:** For the Unit 1 steam generators, with mechanically-expanded Alloy 600 MA tubing, the change in water chemistry is estimated to increase the susceptibility to PWSCC by about 9% relative to

the current practice of coordinated pH 7.1-7.2. This component was judged to be the most susceptible material evaluated.

Unit 2-SG: For the Unit 2 steam generators, with hydraulically expanded Alloy 600 TT tubing, the corrosion resistance is expected to be much greater. An analysis similar to that for Unit 1, within the limited framework of the analytical approach and the available data, would yield the same estimates. However, the superior resistance to PWSCC of the Model D5 SGs and Alloy 600 TT tubing demonstrated to date, suggest that the increased risk is small.

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References

1. Assessment of Elevated pH Program for Comanche Peak Steam Electric Station, EPRI, Palo Alto, CA, and TXU Electric, Glen Rose, Tx: 2001. 1006282.
2. P-O Anderson and JG Svenson, The Ringhals PWRs Demonstrate the Benefits of High Constant pH, Nuclear Engineering International, p 22-24, October 1987.
3. AOA Chemistry Diagnostics: Fuel Deposit Source Term Reduction by Elevated pH, EPRI, Palo Alto, CA: Interim Report December 1999. TR-110073
4. Evaluation of Dose Rate and Chemistry Data from Plants Operating with Increased BOL pH Chemistry Control, EPRI, Palo Alto, CA: Interim Report July 2000
5. Rootcause Investigation of Axial Power Offset Anomaly, EPRI, Palo Alto, CA: June 1997. TR-108320.
6. PWR Primary Water Chemistry Guidelines, EPRI, Palo Alto, CA: Final Report March 1999. TR-105714-V1R4
7. Zircaloy Corrosion Properties Under LWR Coolant Conditions, EPRI, Palo Alto, CA: March 1992. NP 7562-D
8. Effect of Lithium Hydroxide on Zircaloy Corrosion in the Ringhals-3 PWR Plant, EPRI, Palo Alto, CA: March 1992. TR-100389
9. In-Pile Zircaloy Corrosion Tests with High Coolant Lithium Content, EPRI, Palo Alto, CA: Final Report May 1995. TR-104516
10. Zircaloy Corrosion on PWRs: Effect of Additives, EPRI, Palo Alto, CA: Final Report July 1996. TR-104517
11. Primary Water Chemistry, Fuel Rod Corrosion, and Crud Deposition in PWRs: A Comparison of European and U.S. Plant Performance, EPRI, Palo Alto, CA: Final Report December 1999. TR-107255
12. Assessment of PWR Fuel Cladding Corrosion for Extended Cycle Operation, EPRI, Palo Alto, CA: Final Report November 1997. TR-109047
13. P. Billot, et al., Corrosion of Zircaloy-4 Under Demanding PWR–type Conditions, 13th International Symposium on Zirconium in Nuclear Industry, June 11-14, 2001, Annecy, France.
14. Impact of PWR Primary Chemistry on Corrosion Product Deposition on Fuel Cladding Surfaces, EPRI. Palo Alto, CA: Final Report November 1997. TR-108783
15. AECL Experimental Database, AECL-6952, May 1980
16. Waterside Corrosion of Zirconium Alloys in Nuclear Power Plants, IAEA-TECDOC-996, January 1998, Vienna, Austria,
17. Multivariable Analysis of the Effects of Lithium, Hydrogen, and pH on PWR Primary Water Stress Corrosion Crack Initiation, EPRI, Palo Alto, CA: 1996. TR-105656