

Primary Coolant pH Control for Soluble Boron-Free PWRs

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1. Introduction

Water chemistry control for nuclear power plants plays an important role in the degradation of materials, fuels integrity, and radiation control. The plant designs should consider implementation of state-of-the-art, industry-developed water chemistry controls. pH is one of the important parameters that should be considered in water chemistry control. There is a dilemma in controlling an optimum pH to meet the conflicting requirements of material integrity, fuels integrity and radiation control [1]. These should be considered when evaluating and designing the operating pH program for nuclear power plants.

This paper discusses the advanced water chemistry strategies to keep pace with the recent global trends related to pH control in the primary water system for soluble boron pressurized water reactor (PWR) plants. Finally, the objective of this work is to study primary coolant pH control for soluble boron-free PWR plants.

2. Review of pH Control Strategy for Soluble Boron PWR Plants

Nuclear power plants control pH in the primary coolant as part of a balancing act between mitigating material degradation and controlling radiation fields. Boric acid is added to the primary coolant to control core reactivity, but the resulting acidic (low pH) environment can increase the formation and transport of corrosion products that deposit on fuel rod surface, especially in high-duty PWR. PWRs use lithium hydroxide to raise the pH to a target value as a mitigation of this process. Operation at higher pH levels reduces the risk of crud deposition associated with fuel reliability issues. However, higher lithium concentration is known to accelerate the corrosion of zirconium alloy fuel cladding.

Fig. 1 shows the schematic representation of (a) solubility of magnetite and Ni-ferrite and (b) relationship between lithium concentration and chemistry optimization problem. This schematic shows that proper range of pH should be between 6.9 and 7.4 to reduce the solubility for magnetite and Ni-ferrite. The target pH has to place the dissolution regime where it is increasing with temperature. This pH must maintain the solubility as low as possible. This leads to limit the life duration under flux of the corrosion products and the activation. Also, susceptibility of Zircaloy to accelerated

corrosion in concentrated solutions of LiOH in the absence of boric acid is well known. According to Reference 2, the lithium concentration should not exceed 4.5 ppm due to initiation of Inconel cracking and Zircaloy corrosion. Recently, however, a corrosion effect was measured at concentrations as low as 7 ppm in out-of-pile tests per EPRI Guidelines [1]. Improvements in fuel economy, longer cycle lengths and dose reduction initiatives have led to the use of higher lithium concentrations. Therefore, there have been substantial efforts by the industry to quantify the effects of increasing lithium and pH_T in the RCS on fuel cladding corrosion [1].

Fig. 2 shows the U.S. PWR trend to raise beginning-of-cycle (BOC) lithium in order to maintain pH levels that minimize out-of-core material corrosion, corrosion product transport and deposition in-core.

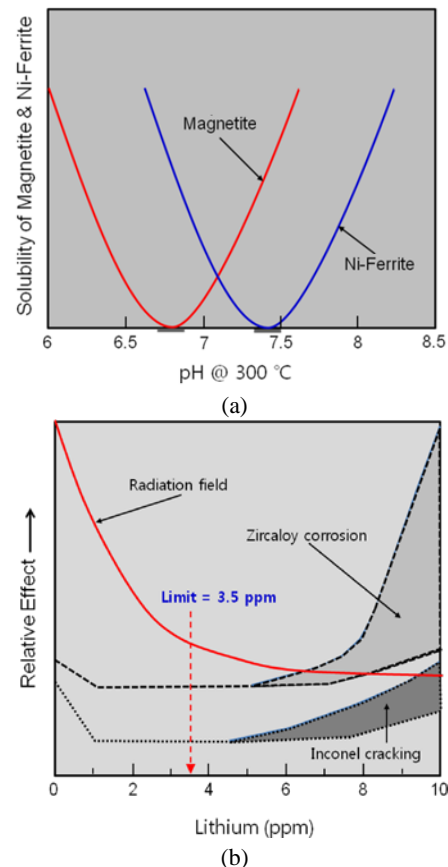


Fig. 1. Schematic representation of (a) solubility of magnetite and Ni-ferrite and (b) relationship between lithium concentration and chemistry optimization problem [2]

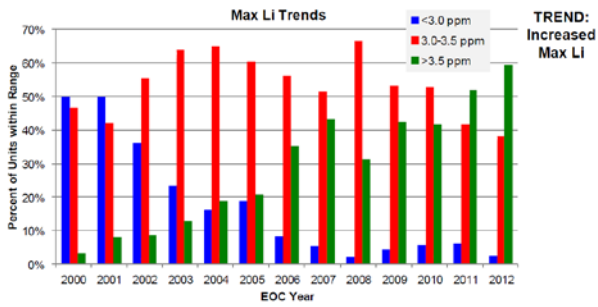


Fig. 2. Lithium trend for U.S. PWRs [1, 3]

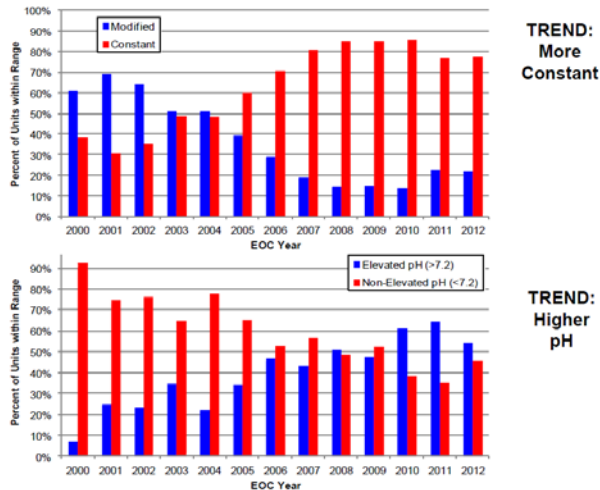


Fig. 3. U.S. PWRs trend for primary coolant pH program [3]

One major strategy of the primary chemistry program is to select an appropriate operating pH_T regime in order to minimize negative impacts of chemistry on material integrity, fuel reliability and radiation fields. Minimizing crud deposition onto the core is the key to achieve fuel reliability and radiation field goals. This is also very important for plants with a history of crud induced power shift (CIPS) phenomenon or potential susceptibility to CIPS.

U.S. PWRs trend for primary coolant pH program is shown in Fig. 3. The new pH chemistry trend for the primary coolant is towards the constant and elevated pH chemistry to decrease dose rate. It is bound a large portion of PWRs wishing to raise pH so utilities do not have to pay for costly fuel surveillances.

The primary water pH control program (Li/B control program) for APR1400 has been managed and designed according to industry approved pH control schemes depicted in Fig. 4. Fig. 4 (a) shows the modified chemistry regime, in which lithium concentration is maintained at a constant value of 2.2 ppm in the range of pH_T 6.9 to 7.4 and thereafter coordinated with boron to maintain a target pH_T value for the remainder of the cycle. Fig. 4 (b) shows the elevated pH_T regime. The pH_T is maintained as close to constant and as high as practical within fuel vendor constraints (no greater than 3.5 ppm lithium) throughout the full cycle. These approaches are to mitigate the process of corrosion product deposition onto the core in plant experiencing

CIPS. Recently, APR1400 plants have adopted the latter to keep pace with the recent global trends related to pH control in the primary water chemistry system for soluble boron PWR plants.

3. pH Control for Soluble Boron-Free Plants

A soluble boron-free PWR which does not use soluble boron for reactivity control is being studied because it offers a number of potentially significant improvements, e.g. to eliminate boric acid induced corrosion, and system and components related to boron control [4]. Another benefits of boron-free primary water chemistry is to avoid CIPS which is a flux depression caused by boron accumulation in fuel clad. In particular, soluble boron-free operation has been widely applied for small-sized reactors which system simplification is essential as well as economics.

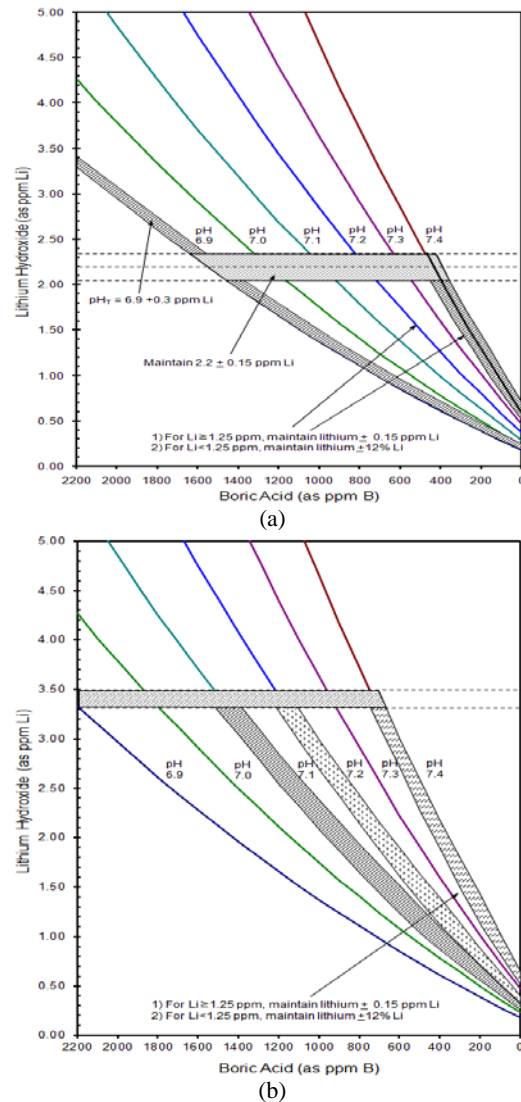


Fig. 4. pH control curves: (a) modified chemistry regime and (b) elevated pH_T regime at 307 °C

Table I: Comparison of the Primary Coolant Chemistries Related to pH Control

Units	Chemistry parameter	Normal Range	Remarks
APR1400	pH at 307 °C	6.9 - 7.4	
	Lithium, ppm	0.2 - 3.5	
	Boron, ppm	<2,500	
	Ammonia, ppm	≤2.0	
	Hydrogen, cc/kg H ₂ O	25 - 50	
	Dissolved Oxygen, ppm	≤0.005	
VVER	pH at 300 °C	7.1 - 7.3 * 7.0 - 7.2 **	* for VVER-440 ** for VVER-1000 *** related to pH ₃₀₀
	Potassium***, ppm	0.8-20	
	Boron, ppm	As required for reactivity control	
	Ammonia, ppm	>5 (normally 10~15)	
	Hydrogen, cc/kg H ₂ O	30 - 60	
	Dissolved Oxygen, ppm	<0.005	
SMART-P	pH at 25 °C	9.5 - 10.6	
	Ammonia, ppm	10 -100	
	Hydrogen, cc/kg H ₂ O	20 - 60	
	Nitrogen, cc/kg H ₂ O	<2000	
	Dissolved Oxygen, ppm	<0.1	

The specifications of comparison of the primary coolant chemistries related to pH control are shown in Table I. It has been reviewed to use ammonia and potassium, which are used in VVER [5,6] and SMART [7~14] for pH control for new soluble boron-free power plants.

3.1 Ammonia-Based Water Chemistry

One strategy of the pH control for boron-free operation is to use the ammonia. Some of ammonia is decomposed to hydrogen and nitrogen by radiation in the reactor core. The produced hydrogen gas is used for the removal of dissolved oxygen in the coolant. Some of nitrogen gas for N₂ blanket of tank and pressurizers is dissolved into the primary water. Because ammonia, hydrogen and nitrogen which are produced by ammonia radiolysis exist in the coolant, ammonia chemistry is different from lithium-boron chemistry at commercial PWR. In this strategy, the pH characteristics of ammonia and the solubility characteristics of hydrogen and nitrogen has been analyzed for the management of primary water chemistry [7,8]. The basic study about gas solubility, pH and radiolysis of ammonia in water should be considered in the chemistry design and chemistry management for the primary water for soluble boron-free nuclear power plants.

Fig. 5 shows the pH changes with ammonia concentration and temperature. This is useful as operating and design data for pH control by ammonia based water chemistry. Also, this strategy is particularly useful in new power plants such as SMART-P to control the pressurizer with nitrogen.

Also, the corrosion characteristics and kinetics of ammonia in the primary water have been studied for soluble boron-free operation [9~14]. However, ammonia-based water chemistry is not recommended for the following reasons;

- To avoid fluctuation of the pH value by ammonia radiolysis.
- To reduce C-14 production in reactor coolant from reaction with dissolved nitrogen.

3.2 Potassium-Based Water Chemistry

Another strategy of the primary water pH program for boron-free operation is to use the potassium which is different from existing commercial PWR using lithium. According to Reference 15, an evaluation of the use of KOH as a replacement for LiOH as the pH control agent in PWRs has been performed based on information in the literature and VVER experience. Sufficient data exists to indicate good compatibility with Zr-based alloy fuel cladding. Use of KOH for pH control in PWRs appears very promising, and its use offers the potential for mitigation of CIPS in high boiling duty plants. Specially, some reactor types, notably the Russian-designed VVER reactors, use potassium hydroxide, KOH, instead of LiOH to adjust the primary coolant pH. These plants have not experienced CIPS [5,6,15]. VVER experience also indicates good compatibility with the KOH coolant and stainless steel components. However, Ni-based alloys used in steam generators have not been tested in KOH solutions and evaluation of SCC concerns with these materials may be necessary prior to full plant implementation. Also, Wally H Huijbregts has reported that the corrosion of carbon steel in KOH is certainly lower than in the NaOH and LiOH [16]. In terms of radiation control, there is absolutely no problem, nor concern, with ⁴⁰K causing high activities [15].

Fig. 6 shows the calculated pH changes with potassium concentration and temperature. This is useful as an operating and design data for pH control by potassium based water chemistry.

Coolant pH as shown in Fig. 7 is adjusted by KOH addition so that pH value at 286.5 °C lies in range of 6.9-7.4, i.e. potassium concentration should be in range of 1.7-5.0 ppm. Also, pH at 25 °C in this conditions is 9.6-10.1.

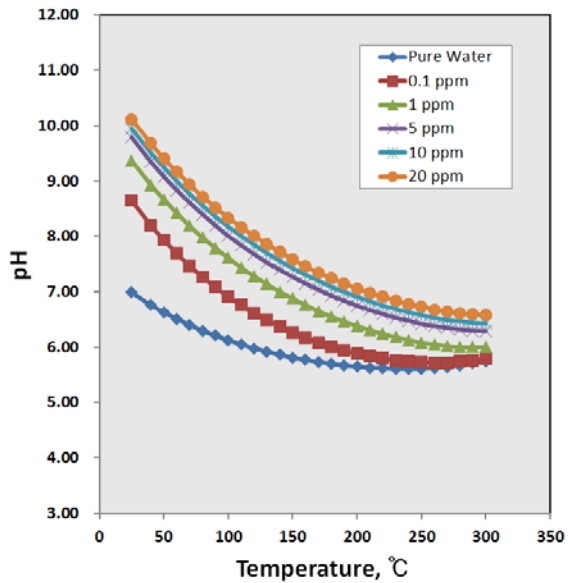


Fig. 5. pH changes with ammonia concentration and temperature.

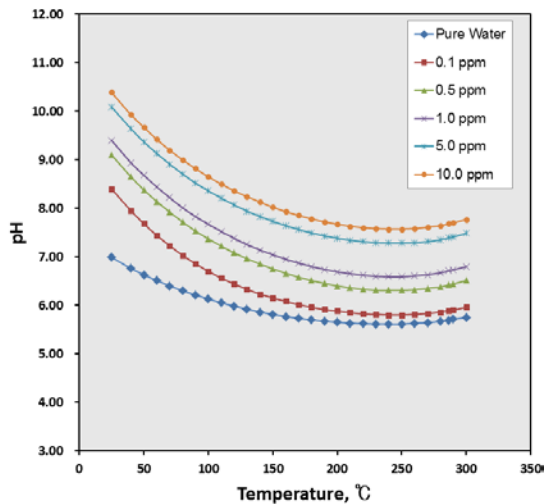


Fig. 6. Calculated pH changes with potassium concentration and temperature.

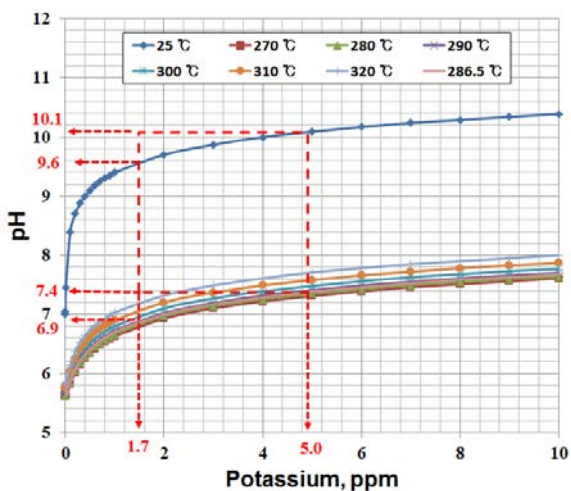


Fig. 7. pH control strategy at primary coolant temperature 286.5 °C.

4. Conclusions

This paper reviewed the advanced water chemistry strategies to keep pace with the recent global trends related to pH control in the primary water chemistry system for soluble boron PWR plants. The new chemistry trend for the primary coolant is towards adaptation of the constant and elevated chemistry.

Finally, this work studied primary coolant pH control for soluble boron-free PWR plants. The ammonia-based water chemistry related to pH control for boron-free PWR plants was discussed. The ammonia-based water chemistry is not recommended to avoid fluctuation of the pH value by ammonia radiolysis and to reduce C-14 production in reactor coolant from reaction with dissolved nitrogen. Also, the potassium-based water chemistry related to pH control for boron-free PWR plants was discussed. KOH has a potential as an alternative pH control agent for soluble boron-free PWR plants. The potassium-based water chemistry related to pH control is recommended for boron-free operation as follows.

Chemistry parameter	Normal Range	Remarks
pH at 286.5 °C	6.9 - 7.4	
pH at 25 °C	9.6 - 10.1	
Potassium, ppm	1.7 - 5.0	
Ammonia, ppm	≤2.0	
Dissolved Hydrogen, cc/kg H ₂ O	25 - 50	
Dissolved Oxygen, ppm	≤0.005	

However, the systematic study to use KOH for PWR is necessary because, according to References 15, 17, and 18, KOH may induce the stress corrosion cracking in the steam generator and other primary components.

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