

## Assessment of Cooling Water Chemistry on the Safety of Water Cooled Power Reactors

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**Abstract:** Recently, for economic reasons, nuclear light water-cooled reactors power plants (the Third Generation) operational practices are shifting towards long-term irradiation fuel cycle (extended fuel burn up). So, new and advanced operational measures to satisfy long-term operational safety conditions are required. Among these safety measures is cooling water chemistry control. In the field of nuclear power technology, the term "coolant technology" means a complex of methods and means assuring operation of nuclear plants under definite and possible abnormal conditions. An uncontrolled condition of the coolant contributes to an increase in radioactive waste quantities, higher exposure rate and finally advanced ageing of reactor component. The prevention of these effects can be achieved through essentially the control of the alkalinity (pH) and the radiolysis of the coolant. Adjustment of these conditions requires better understanding of their mechanisms and impact on different material and processes of the reactor. In this paper, a technical evaluation study among light water reactor type concerning cooling water specifications in case of operating experience conditions have been investigated and discussed. For further, cooling water quality improvements to reduce radiation dose, waste generated from primary circuits and to achieve higher burn up and better fuel performance, constitution of LWR chemistry guidelines and a new pH control method for primary coolant have been recommended.

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### 1. Introduction

#### 1.1. General

Nuclear and other facilities handling radioactive material are like any other industrial facility in that they generate radioactive waste materials in addition to their useful products. These wastes must be handled carefully in order to reduce potential harm to facility operators, the public and the environment.

Coolant chemistry performance is an effective indicator monitors the operational safety of the nuclear power plants (NPPs), to guarantee the integrity and reliability of the primary circuit and fuel element cladding, and control the radioactive wastes that generates. Accordingly, the main tasks related to coolant are maintaining the coolant reactivity control during operation and quality to keep impurity and corrosion conditions in the coolant within acceptable limits. These tasks are achieved essentially by additives in the water coolant as; 1) boric acid, lithium hydroxide, and excess hydrogen/oxygen. Boric acid is added for neutron absorption as required by core reactivity control during different operating modes. Lithium Hydroxide is used for optimum pH control, minimizing the corrosion product transport and radiation field, and minimizing fuel cladding corrosion. hydrogen/oxygen is added to reduce conditions and suppressing product resulting from

water radiolysis, and influence the corrosion product solubility to improve Radiation Field Control (RFC) [1].

Additionally, reactor coolant additives lithium and boron can produce tritium (H-3) through neutron capture following a nuclear reaction. Because of its relatively long half-life (12.3 y), H-3 can accumulate in reactor coolant systems, resulting in an increase of dose rates in the vicinity of systems containing reactor coolant. To decrease this problem, the reactor coolant is periodically diluted, which leads to an increase in the volume of waste generated at the nuclear power plant [2].

Meanwhile, reactor coolant radionuclides typically generated during activation of corrosion products are Cr-51, Mn-57, Ni-59, Ni-63, Co-58, Co-60, Zn-65 and Nb-94. The concentration of these radionuclides for any given plant depends on the construction materials used, the chemical regime of the reactor coolant, the power level and age of the reactor, and the oxygen content in the reactor coolant. Coolant impurities are naturally occurring nuclides that remain after processing/purification of coolant water for use in a reactor. The content of impurities varies from site to site and is strongly influenced by the minerals present in a given location. Because requirements for reactor coolant purity are extremely high, activation of such impurities occurs only infrequently. Radionuclide

typically generated in the process of impurity activation are Na-24, Mg-27, Ca-45, Ca-49, Si-31, S37 and Cl-38 [2].

The interactions among all these additives involving in controlling coolant chemistry, with respect to the water coolant, should not be ignored. One of which is the co-ordination of lithium and borate concentrations in the primary circuit, which affect the pH of the water during reactor operation. Hereupon, water coolant chemistry and corrosion problems are issues of special importance required continuous improvement. Herein, the objective of the present work; it concerns about the deep understanding of effect of these additives on the performance of water as a coolant.

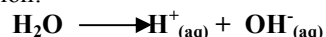
## 2. Scope of the Assessment and Inputs

In (PWR), the primary system within the water coolant is a closed system. Water in the reactor core reaches about 325°C under about 150 times atmospheric pressure [3]. The secondary shutdown system involves addition of boron to the primary circuit. In the BWR reactors, the water cycle is at lower pressure (about 75 times atmospheric pressure) so that it boils in the core at about 285°C [4]. In pressurized water reactor (PWR), the focus is on secondary system chemistry, while in boiling water reactor (BWR) power plants, the indicators focus on reactor coolant chemistry control. The impact of important and common interactive parameters and

additives in the cooling water chemistry in nuclear power plants (NPPs) is depicted in Fig. 1.

During high temperature operations, two processes are occurred; 1) water decomposition and 2) radiolysis.

In the first process of decomposition, demineralized water in the primary circuit (the coolant) is decomposed according to the following equation:



Boron is added, to the primary circuit in the form of boric acid, to the coolant to control reactivity. Natural boron contains only 20% of the B-10 isotope with the remaining 80% B-11 isotope. Accordingly, pH can not be maintained as high more than 5 to 7. On the other hand, above 300 °C of the coolant, pH is below the accepted minimum of 6.9 during a certain period of time [5]. In this period, an increased influence on the release rate of various metal ions and on the solubility of corrosion products is obvious and may be occurred [6]. Since the pH and corrosion process of the activity will buildup and the dose rate of the components could be increased, lithium is added to increase pH to 7.4 [7]. Again the addition of the lithium to the coolant can raise the pH in the coolant to more than 10. During this period, the elevated Lithium chemistry has potential effects of prolonged exposure to water stress corrosion cracking alloy 600 and zircalloy cladding [8].

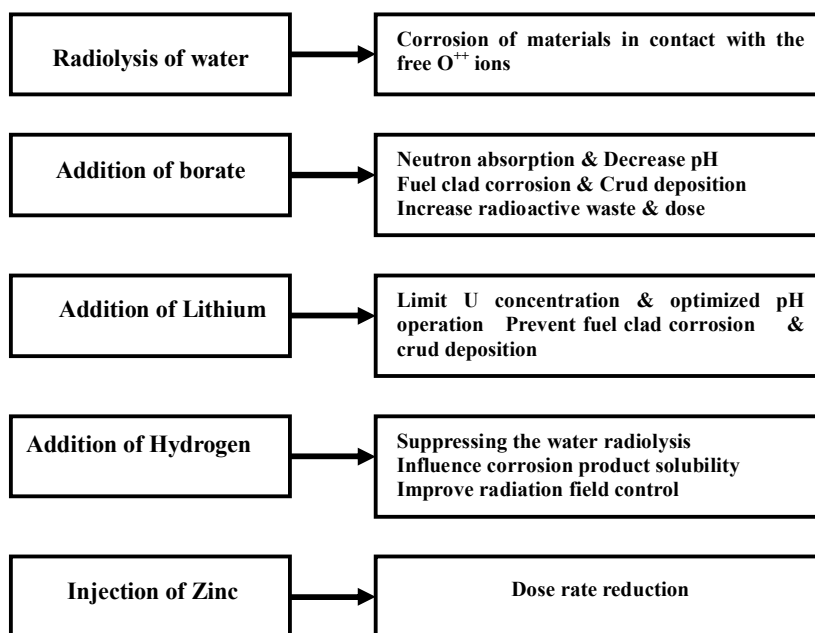
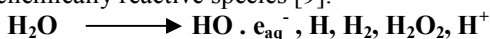
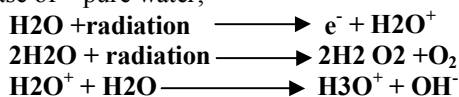


Fig. 1: Impacts of important conditions and additives in the water coolant in NPPs

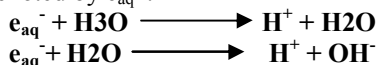
Radiolysis is the interaction of radiation with water. During operation, as reactor coolant water passes through the core region of an operating reactor, it is exposed to intense radiation. The major components of the radiation field are neutrons, protons, gamma rays, and high energy electrons (beta particles). These types of radiation interact with the coolant water primarily by an ionization process. Exposed to ionizing radiation, water decomposes to yield a range of chemically reactive species [9].



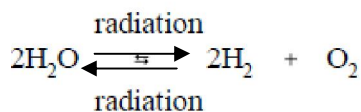
Other reactive species such as  $\text{HO}_2$ ,  $\text{O}_2$ , and  $\text{O}^-$  are also formed through reactions as secondary products are illustrated by the following reaction. In case of pure water;



The electron produced by Reaction (3-1) first forms a species called the hydrated electron, denoted by  $\text{e}_{\text{aq}}^-$ .



These reactions are followed by other reactions cited in details in Ref. 8. Water radiolysis produces highly reactive  $\text{HO}^-$  and  $\text{H}^+$  radicals. Steady-state water radiolysis provides a complex system of both reducing and oxidizing species with competing reactions occurring rapidly and the net result of these reactions is simply the decomposition of water [9].



Oxidation is the loss of electrons and the electrons are transferred to the oxidizing agent, which becomes reduced (gain of oxygen or loss in hydrogen). *Reduction* is the addition of electrons, which may involve the addition of electron only, or the addition of hydrogen together with an electron (loss of oxygen or gain in hydrogen) [10]. Since the radiolysis products range from oxidizing to reducing ions, these species, even at low concentrations, strongly influence corrosion kinetics [11]. The water radiolysis radicals react with a very large number of inorganic and organic solutes such as;  $\text{Cd}^{2+}$ ,  $\text{Cu}^+$ , and  $\text{Fe}^{2+}$ . Because of its low ionic content, pure water will quickly dissolve traces of contaminants from sample lines, flow chambers, containers and even the atmosphere. Oxygen from the air which leaks into the system can cause a perceived high dissolved oxygen reading. Also, carbon dioxide, from air leaks, ionizes in the water to form a weak solution of carbonic acid. Consequently, carbon dioxide can cause errors in both pH and conductivity readings. All carbon steel components in a system are exposed to oxygen corrosion. Also,

copper alloy corrosion in condensate and feed-water systems is a function of oxygen. Oxygen can cause corrosion fatigue of boiler tubes as well as turbine disks and blades. However, totally eliminating oxygen from the water is in fact impossible [11].

### 3. Results and Discussions

In Fig. 2, each curve represents different pH solution; pure water, natural boric acid, lithium hydroxide, and water contain natural boric acid and lithium hydroxide. For pure water, pH of coolant decreases with increase of temperature until reach a minimum value of 5.7 at 250 °C and then increase again to 6 until reach a value of 6 at 350 °C [2].

The dependency of pH of pure water with the temperature can be explained by the forward endothermic reaction of hydrogen ions and hydroxide ions to form water. According to Le Chatelier principle; increase the temperature of water, the equilibrium will move to lower the temperature again. It will do that by absorbing the extra heat. That means the forward reaction will be favored, and more hydrogen ions and hydroxide ions will be formed. Noting that, the number of hydrogen ions over hydroxide ions in the water is constant and water during this period remains neutral even with pH of 6. Solution is acidic if there is an excess of hydrogen ions over hydroxide ions; that is not the case of pure water. This ratio is always constant and no real change of pH take place.

In pure water, a constant decrease in pH of about 0.45 occurs as the temperature is raised by 25°C [12]. This is not true after 270 °C, which form a turn point and pH increases again as shown in Fig. 4 [2, and 13]. The pH temperature dependence data from experimental investigations are distributed in several literatures [2, and 13]. Table1 is an example of these data.

The curve fitting representation depends on these data are shown in Fig. 3. During temperature rising forward and backward, the two curves can follow, by best fitting logarithmic behavior:

$$y = a \ln(x) + b$$

Where :  $y = \text{pH}$ ,  $x = \text{temperature}$ , and  $a, b$  are constants

The constants  $a$  and  $b$  have the values of 8.77 and -0.57 respectively in the temperature range 0-250 °C, and -14.5 and 3.8 in the temperature range 280 – 330 °C. The different values of constants  $a$  and  $b$  are reflecting the variation in the rate of pH change with temperature. The coefficient of determination  $r^2$  for the two equations is about 0.986, which means that 98.6% of the total variation in  $y$  can be explained by the above relationship.

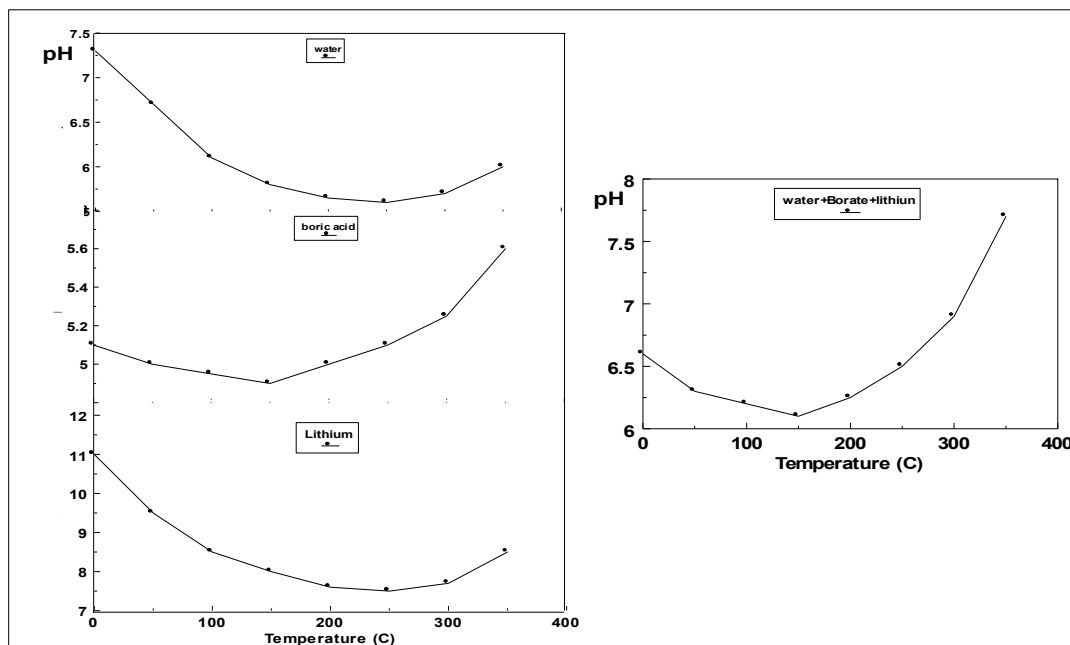


Fig. 2: Effect of Boric Acid and Lithium on the pH of Coolant

Table- 1. pH Values at Different Temperature for Pure Water

Temperature	pH	Temperature	pH
0	7.47	280	6.94
10	7.27	290	7.03
20	7.08	292	7.04
25	7	300	7.13
30	6.92	310	7.225
40	6.77	320	7.38
50	6.63	326	7.47
100	6.14	330	7.58
150	5.9		
200	5.7		
250	5.6		

Recently, for economic reasons, nuclear power plant operational practices are shifting to long-term irradiation fuel cycle. So new and advanced operational measures, which can satisfy long-term safety are required. For this purpose, increasing the borate concentration in the primary coolant is required. Typically, 12- month fuel cycles begin with no more than 1200 ppm borate at a start of a cycle [6]. The pH of borate acid continues to decrease slowly until the temperature reaches 250 °C as shown in Fig. 2. That reveals again Le Chatelier principle and the turn point is 150 °C. On the other hand, the pH of lithium tends to decrease with temperature until reach the turn point at 250 °C for water contains lithium hydroxide and pH 6.2.

Fig. 4, from data given in Ref. [14], describes the

effect of temperature range on the different water pH. At acidic medium, pH of water increases with the increasing of temperature. That reveals the decrease of  $H^+$  radical over  $OH^-$  in the solution by the effect of backward reactions. There is no appearance of turn point in this particular range of temperature. For neutral medium, the turn point of the reaction of dissolution is very obvious at 50 °C with a decrease of pH 6.83. The value of turn point temperature increases with the pH equal 7, but doesn't appear in the considered range. The alkaline medium show range same behavior as the neutral and no turn point temperature appear. Increase pH of water is increasing the value of turn point temperature, which reflects the difficulty of backward reactions to over come the effect of high temperature.

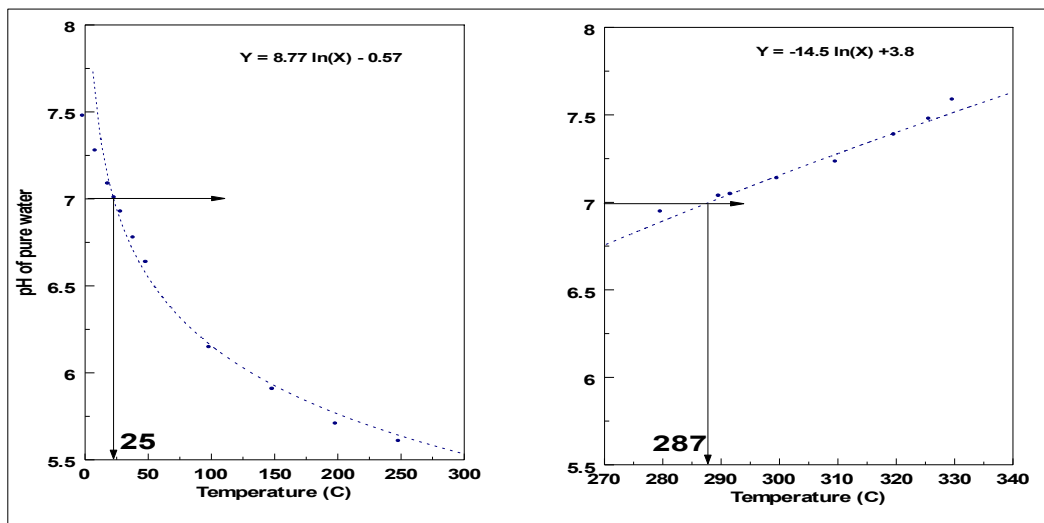
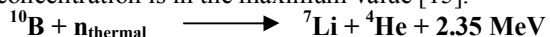


Fig. 3: Effect of Temperature on pH of Pure Water

The thermal neutrons, from water radiolysis, are captured by the isotope (B-10) of boron. An increase of the boric acid concentration leads to a higher B-10 and Li-7 dose (from borate radiolysis), which has a negative impact on the mechanism of water recombination with hydrogen. Thus water is more exposed to decomposition by radiolysis at the beginning of the fuel cycle, when the boric acid concentration is in the maximum value [15].



At higher pHs (pH=10) transient species such as  $\text{O}_2^-$  and  $\text{O}_3^-$  play a major role in determining the steady-state concentration of molecular products  $\text{H}_2$  and  $\text{H}_2\text{O}_2$ . Additionally, radiolytic production of  $\text{O}_2$  and, hence,  $\text{O}_2^-$ , plays a major role in determining the

radical behavior [16]. It also increases the time required to reach steady state, which explain the lower rate of pH increase (from 270 to 350 °C) presented in Fig. 3. As shown in Fig. 6, dissolved oxygen increases the steady-state concentrations of  $\text{H}_2\text{O}_2$  and  $\text{H}_2$  by reacting with  $\text{OH}$  and  $e_{\text{aq}}^-$ , and the impact of oxygen is more noticeable at pH below 8 [17]. The steady-state concentrations of water decomposition products are nearly independent of pH in the range 5–8. At pH equal 10, the radiolytical production of  $\text{O}_2$  becomes significant, but at a finite rate. This considerably increases the time for the irradiated system to reach a steady state, and is responsible for different impacts on  $[\text{H}_2\text{O}_2]$  and  $[\text{H}_2]$  due to radically produced  $\text{O}_2$ , compared to impacts due to initially dissolved  $\text{O}_2$  [18].

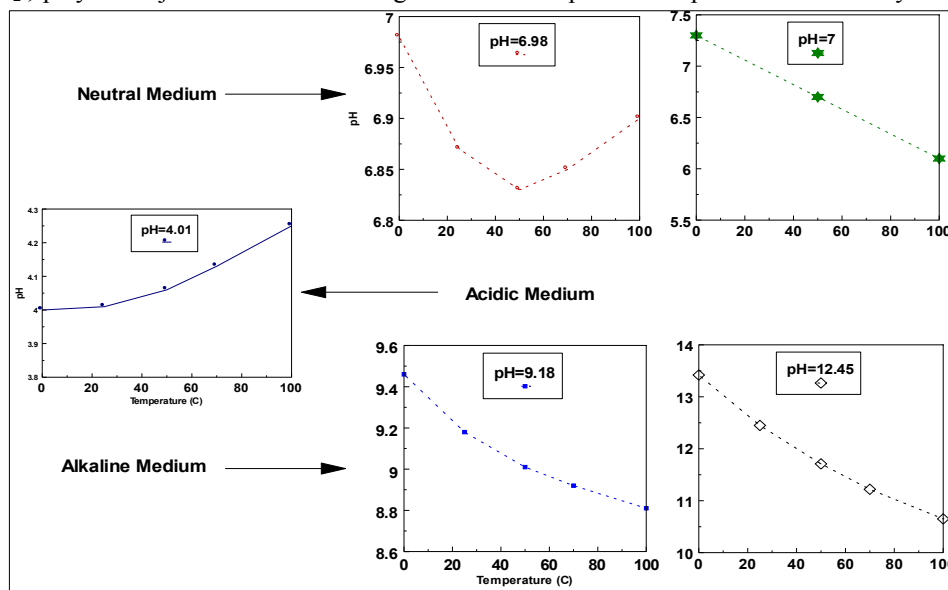


Fig. 4: Effect of Temperature on Different Water pH

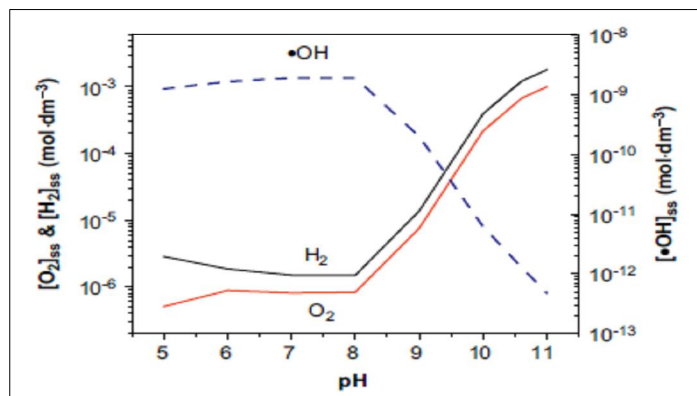


Fig. 5: Predictions for the Steady-State Concentration of  $H_2$  along with  $H_2O_2$

The corrosion in light water reactors occurs due to liquid–metal interaction and dominant constituents of the cladding and piping metals which are released into the coolant as corrosion products which may be in particulate form or in dissolved state. The corrosion products mainly contain iron, nickel, chromium and cobalt. These corrosion products become activated as they pass through the core region, and in the primary loop they may be deposited at various places. Later, these may be released again in coolant. Predominant corrosion product activity during operation is due to Mn-56, and cobalt isotopes dominate the activity after shutdown of reactor. The corrosion product activity is primarily due to short-lived Mn-56 and Na-24. Nearly, all the long-lived activity in the coolant is due to iron, molybdenum and cobalt with most significant radionuclide as Fe-95, Mo-99, Co-58 and Co-60 [18].

These radionuclides are of more concern with the problems in the radioactive waste handling and disposal. Even though, the extreme small amount of released corrosion products can be deposited and activated in the core; causing an increase in radiation field, risk for fuel corrosion, and finally waste produced.

Several PWRs implemented a 3.5 ppm Li (max.)/pH=7.4 (elevated lithium) scheme to reduce out-of-core radiation fields and corrosion materials [5]. The pH, in the coolant, is increased from 6.9 to 7.4 by the addition of lithium to minimize CRUD deposition on the core and reduce radiation fields in out-of-core regions. Solubility studies suggest that operating with pH=7.4 will minimize nickel ferrite precipitation in the core as shown in Fig. 6 [19].

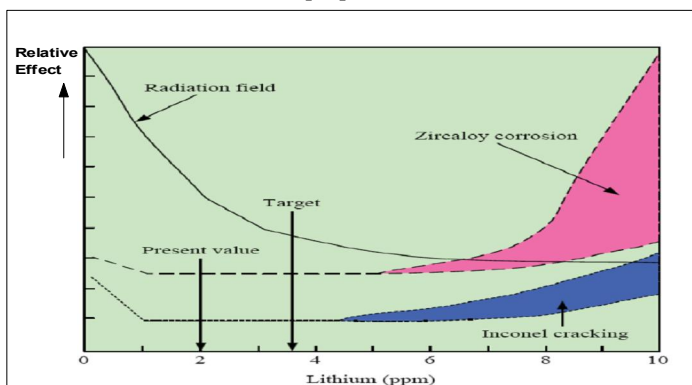


Fig. 6: PWR Primary Coolant Chemistry Effect of Lithium Concentration

The addition should be controlled, to prevent the zircalloy corrosion and inconel cracking. On the other hand, some metals can be soluble in acid media and/or both medium. In some cases and for certain metal, the corrosion rate increases in the alkaline medium alkaline and acid as shown in the Fig.7 [20]. This figure leads to one fact that at any degree of pH value, there are some metal corrosions. Fig. 9 describes the behavior of corrosion rate (C. R.) of aluminum by the

addition of boric acid in alkaline medium considering different conditions. As shown in the figure, the corrosion rate increases as temperature increases. Also, aluminum corrosion increases rapidly as pH increases above 6. It is reported that the corrosion rate increased more than five times from about  $0.009$  to  $0.048 \text{ g m}^{-2} \text{ h}^{-1}$  when the solution pH increased from 8 to 10 at  $60^\circ\text{C}$  [21].

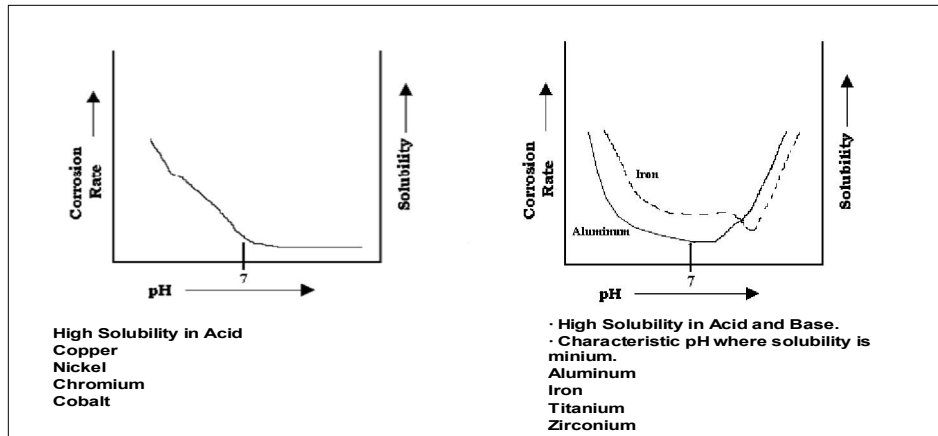


Fig. 7: Effect of pH on Metals

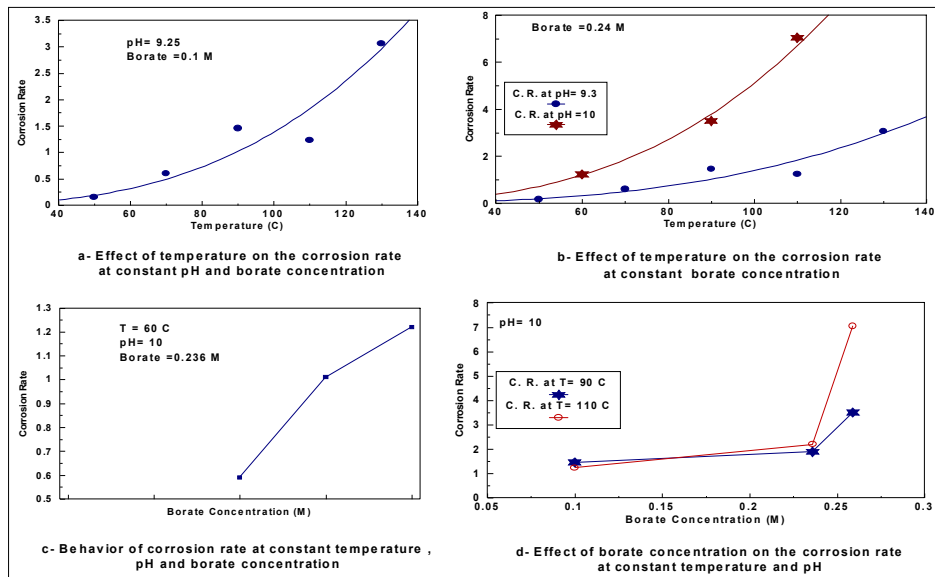


Fig. 8. Effect of Different Concentration of Boric Acid on the Corrosion Rate

#### 4. Conclusion and Recommendations

As a conclusion, it could be stated that despite the consideration of some additives such as boric acid and lithium, and some phenomena such as radiolysis effect by temperature and radiation, proper range of coolant pH is difficult to specify. Therefore, the possible recommended tools, in addition to the recommendations reported in previous study [22], to decrease as possible the severe effects of pH are:

1) Measurements; pH in high purity water can be extremely difficult. Pure water has a high resistance and a high tendency to contamination, so pH is often a very challenging measurement which can easily be measured improperly. For this reason, all pure water measurements should be

made on closed, flowing samples which are free of leaks

- 2) pH value should be selected on compromise study of metals build-in reactor and steam generator
- 3) Measurement of pH should take place continuously per day as possible.
- 4) Value of pH measured should reflect its real medium taken into consideration that the forward reaction of water will be favored, and more hydrogen ions and hydroxide ions will be formed.
- 5) Increase pH of water increases the value of turn point temperature.
- 6) Determination of pH in the temperature range 250 to 280°C needs additional experimental investigations to clarify the uncertainty in this

range.

- 7) Specify important materials in pressure vessel and steam generators to adjust pH by additives.

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