

## 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 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.

**Keywords:** Coolant, pH, Light water

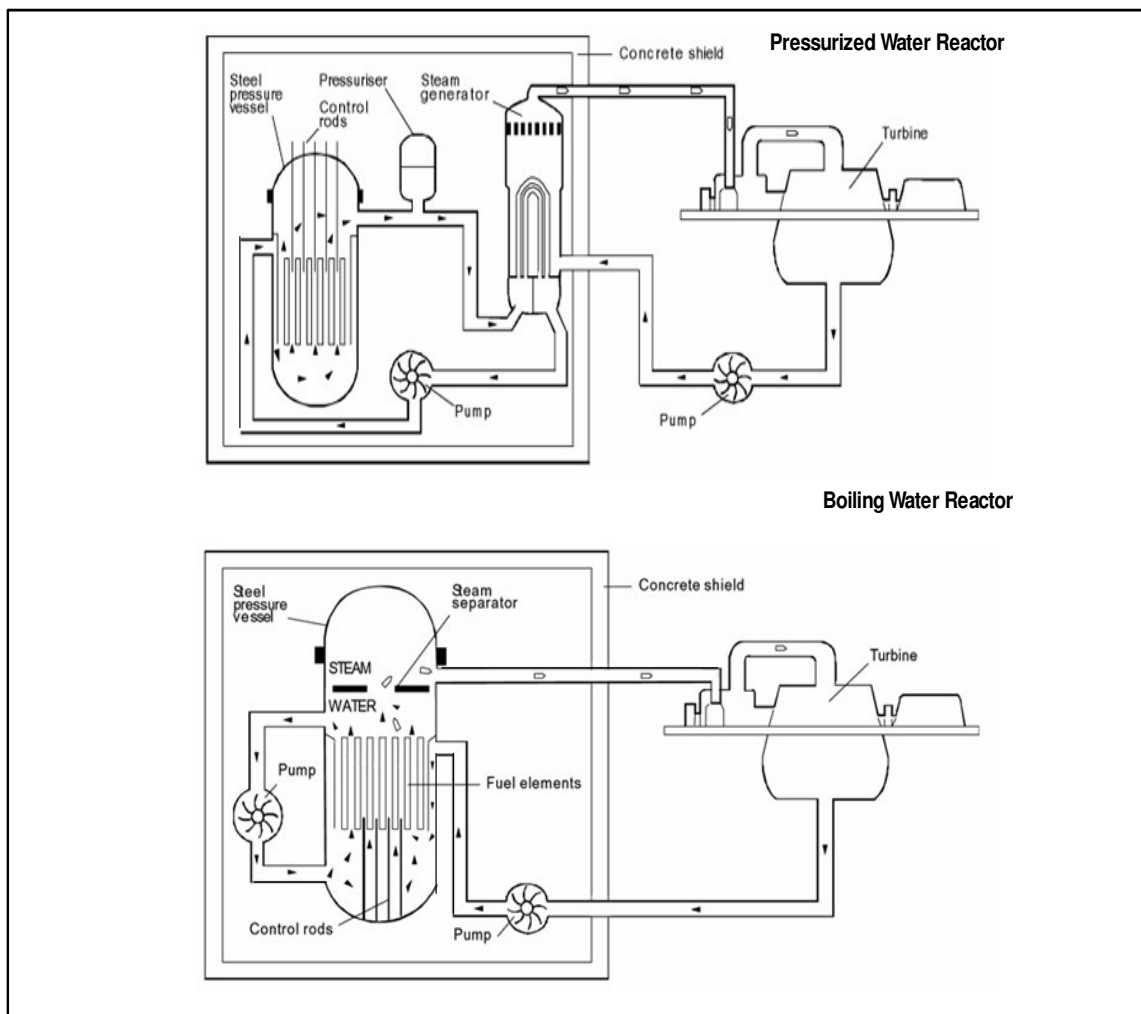
## 1. INTRODUCTION

### 1.1. General

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. Nearly half of forced or unplanned power plant shutdowns today can be attributed to impurities and other cycle chemistry problems. Hereupon, water coolant chemistry and corrosion problems are issues of special importance for the safe and reliable operation of nuclear power plants. So that water regimes for commercial water cooled reactors must be developed to be

satisfactory. Studies are continued and being conducted based on operational experience for further improvement of the technology and a better understanding of the physico-chemical nature of those processes.

In pressurized water reactor (PWR) power plants, the focus is on secondary system chemistry, while in boiling water reactor (BWR) power plants, the indicators focus on reactor coolant chemistry control. 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), AREVA [1]. Figure 1 shows a simplified schematic diagram for PWR and BWR nuclear power plants (NPPs).



**Fig. 1: Simplified schematic diagram for PWR and BWR**

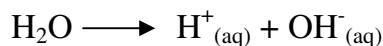
## 1.2. Objectives

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 coordination of lithium and borate concentrations in the primary circuit, which affect the pH of the water during reactor operation. 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.

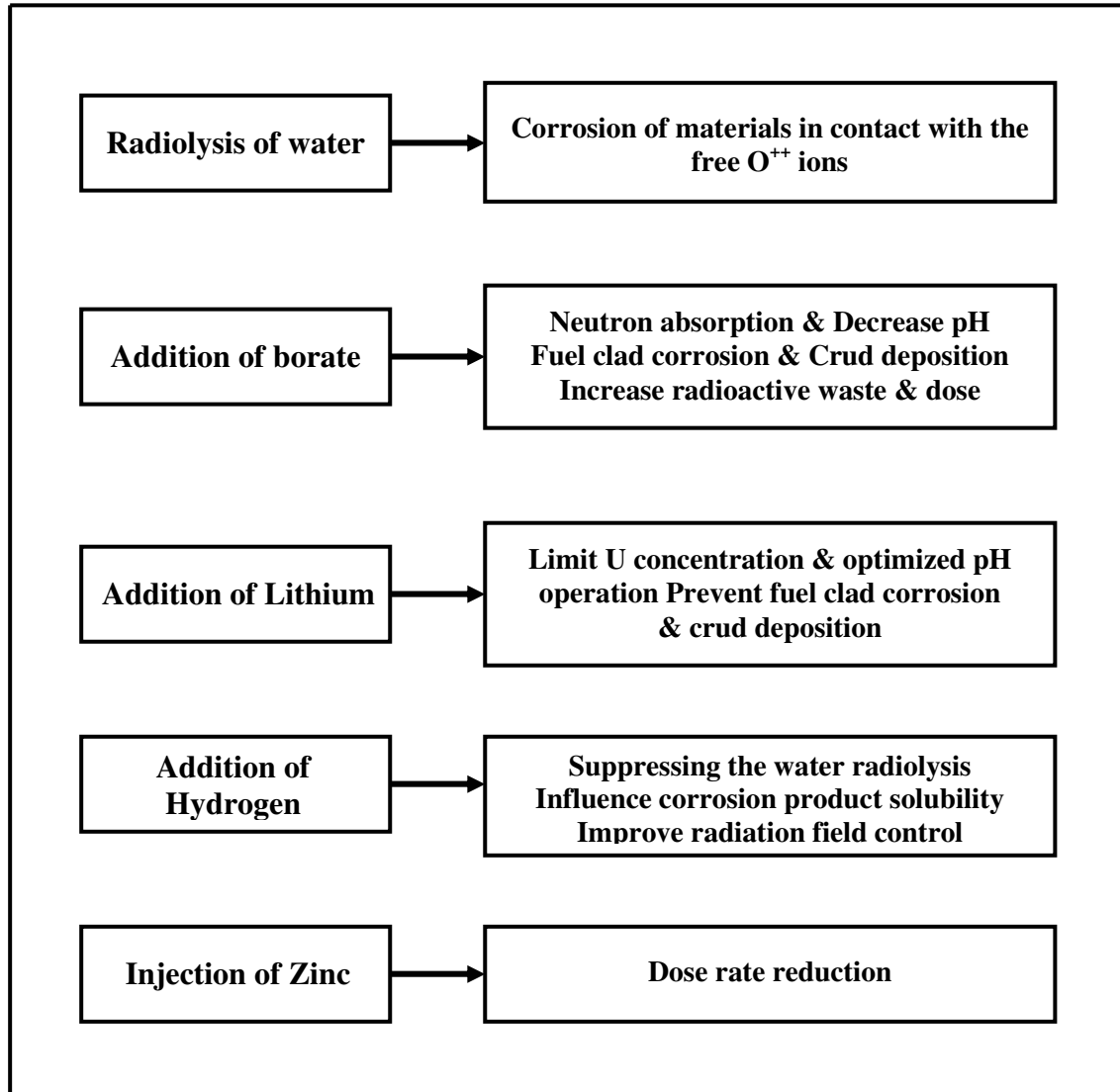
## 2. SCOPE OF THE ASSESSMENT AND INPUTS

In (PWR), the primary system within the water coolant is a closed system as shown in the below diagram. Water in the reactor core reaches about 325°C, Pastina and LaVerne [2]; hence, it must be kept under about 150 times atmospheric pressure to prevent it from boiling. Pressure is maintained by steam in a pressurizer. In the primary cooling circuit, the water is also the moderator, if any of it were converted to steam, the fission reaction would slow down. This negative feedback effect is one of the safety features of PWRs. The secondary shutdown system involves adding boron to the primary circuit. The design of boiling water reactors (BWRs) is similar to that of the PWR, except that there is only a single circuit in which the water is at lower pressure (about 75 times atmospheric pressure) so that it boils in the core at about 285°C, Pastina and LaVerne [2]. The reactor is designed to operate with 12-15% of the water in the top part of the core in steam form, equipping the reactor with less moderating effect and thus efficiency, The Encyclopedia of Earth [3]. The impact of important and common interactive parameters and additives in the cooling water chemistry in nuclear power plants (NPPs) is depicted in Fig. 2.

During high temperature operations, demineralized water in the primary circuit (the coolant) is decomposed according to the following equation:

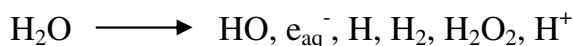


Boron is added, to the primary circuit in the form of boric acid, to the coolant to control reactivity. Natural boron contains only 20% of the B-10 isotope with the remaining 80% B-11 isotope. Accordingly, pH can not be maintained as high more than 5 to 7. On the other hand, above 300 °C of the coolant, pH is below the accepted minimum of 6.9 during a certain period of time, Venz and Weidmann [4]. 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, Frattini et al. [5]. 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, Min and Kun [6]. 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, Peter et al. [7].

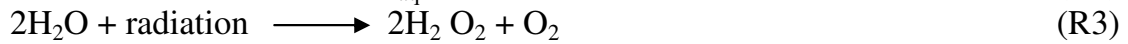


**Fig. 2: Impacts of important conditions and additives in the water coolant in NPPs**

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, Spinks and Woods [8].



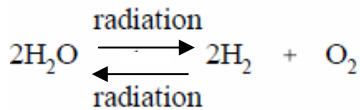
Other reactive species such as  $HO_2$ ,  $O_2$ , and  $O^-$  are also formed through reactions as secondary products are illustrated by the following reaction. In case of pure water;



The electron produced in (R2) 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 HO and 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, Spinks and Woods [8].

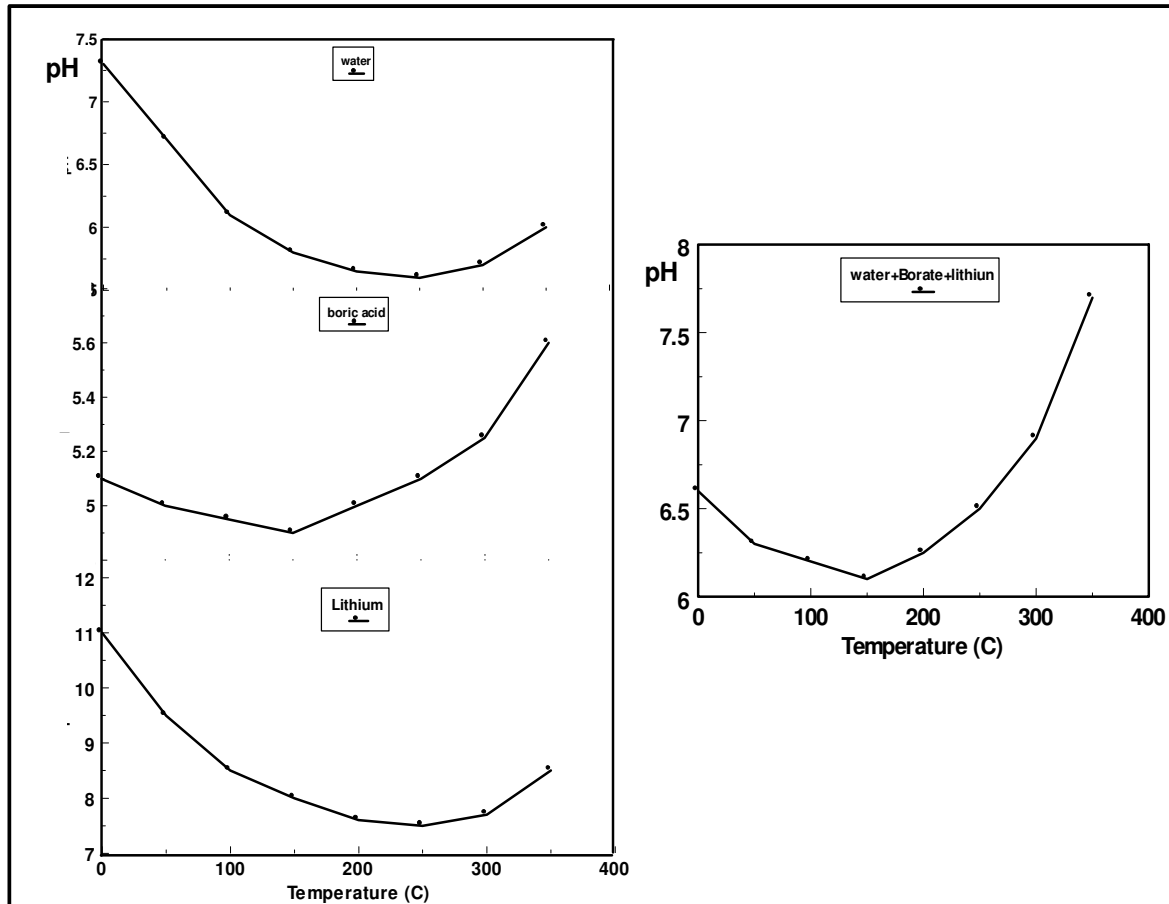


Oxidation is the loss of electrons and the electrons are transferred to the oxidizing agent, which becomes reduced (gain of oxygen or loss in hydrogen). Reduction is the addition of electrons, which may involve the addition of electron only, or the addition of hydrogen together with an electron (loss of oxygen or gain in hydrogen), Wikipedia [9]. Since the radiolysis products range from oxidizing to reducing ions, these species, even at low concentrations, strongly influence corrosion kinetics, Langelier [10].

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.

### 3. RESULTS AND DISCUSSION

In Fig. 3, 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, AREVA [1].



**Fig. 3: Effect of boric acid and lithium on the pH of coolant**

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, David and Edwar [11]. This is not true after 270 °C, which form a turn point and pH increases again as shown in Fig. 4, AREVA [1] and Pastina et al. [12]. The pH temperature dependence data from experimental investigations are distributed in several literatures, AREVA [1] and Pastina et al. [12]. Table 1 is an example of these data.

**Table 1 pH values at different temperature for pure water**

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

The curve fitting representation depends on these data are shown in Fig. 4. 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.

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, Frattini et al. [5]. The pH of borate acid continues to decrease slowly until the temperature reaches 150 °C as shown in Fig. 3. 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.

Figure 5, from data given in Joseph et al. [13], 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  $\text{H}^+$  radical over  $\text{OH}^-$  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 shows the 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 overcome the effect of high temperature.

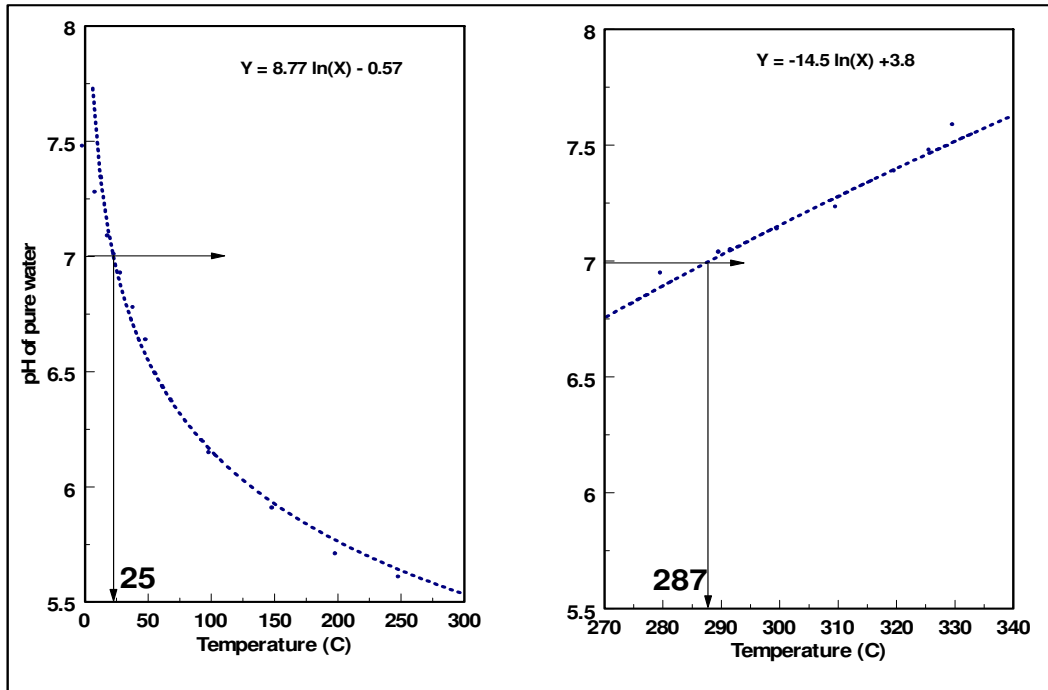


Fig. 4: Effect of temperature on pH of pure water

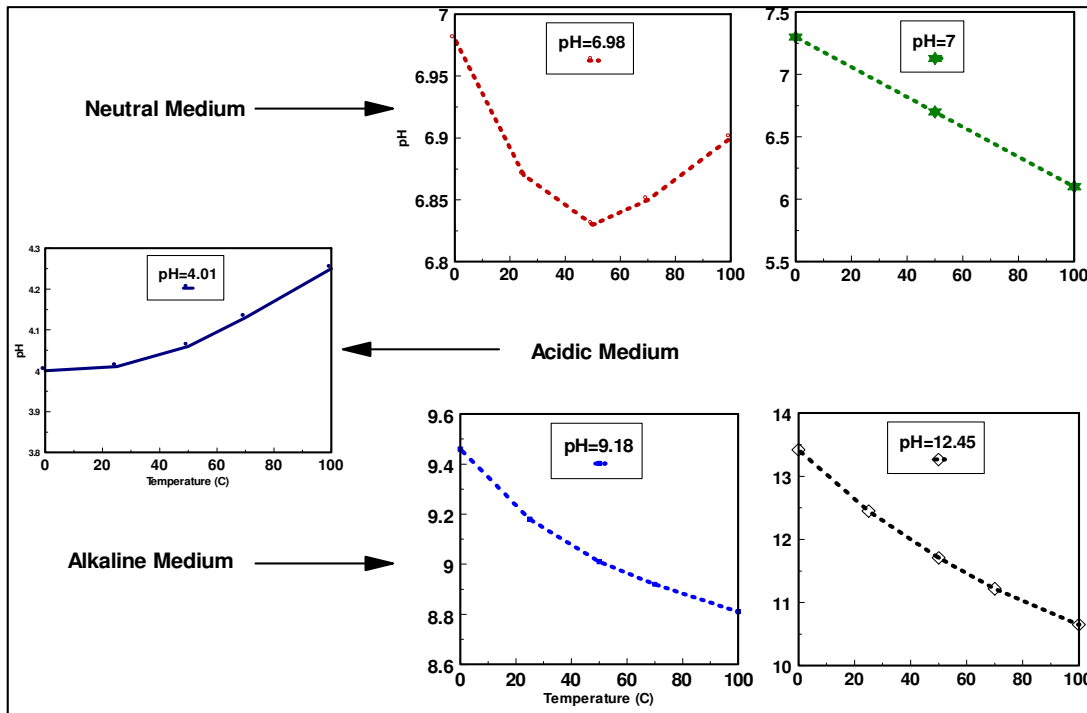
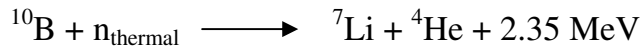


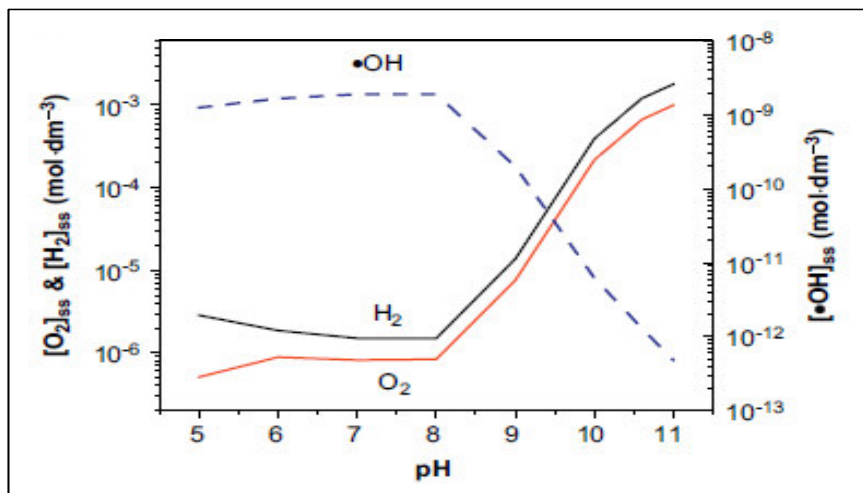
Fig. 5: Effect of temperature on different water pH



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, Nasir et al. [14].

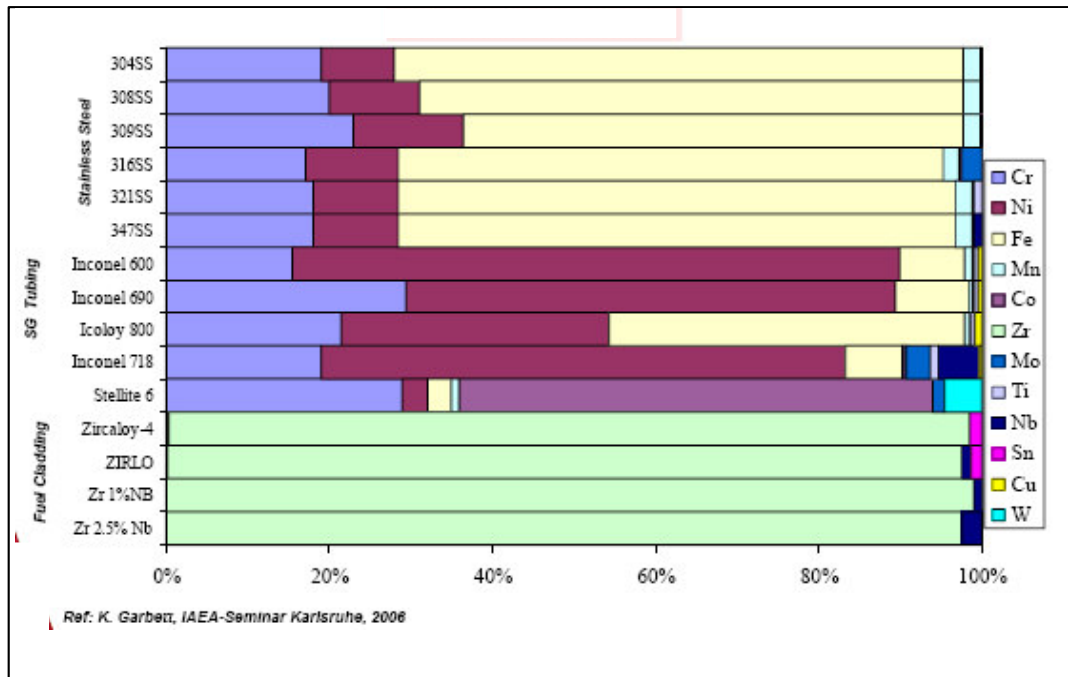


At higher pHs (pH = 10) transient species such as  $\text{O}_2^-$  and  $\text{O}_3^-$  play a major role in determining the steady-state concentration of molecular products  $\text{H}_2$  and  $\text{H}_2\text{O}_2$ . Additionally, radiolytic production of  $\text{O}_2$  and, hence,  $\text{O}_2^-$ , plays a major role in determining the radical behavior, DOE [15]. 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, Frederick [16]. 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  $\text{O}_2$ , KANUPP [17].



**Fig. 6: Predictions for the steady-state concentration of  $\text{H}_2$  along with  $\text{H}_2\text{O}_2$  along with  $\text{OH}$  as a function of pH under deaerated conditions**

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. Different materials, in use in the light water reactors, are presented in Fig. 7.



**Fig. 7: Materials used worldwide in reactor coolant system**

Since steel and inconel are common structural materials used in PWRs, 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 and Predominant corrosion product activity during operation is due to Mn-56, and cobalt isotopes dominate the activity after shutdown of reactor.

During normal operation of PWRs, 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, KANUPP [17]. Even though, the extreme small amount of released corrosion products can be deposited and activated in the core; causing an increase in radiation field and risk for fuel corrosion.

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, Venz and Weidmann [4]. 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. 8, IAEA [18].

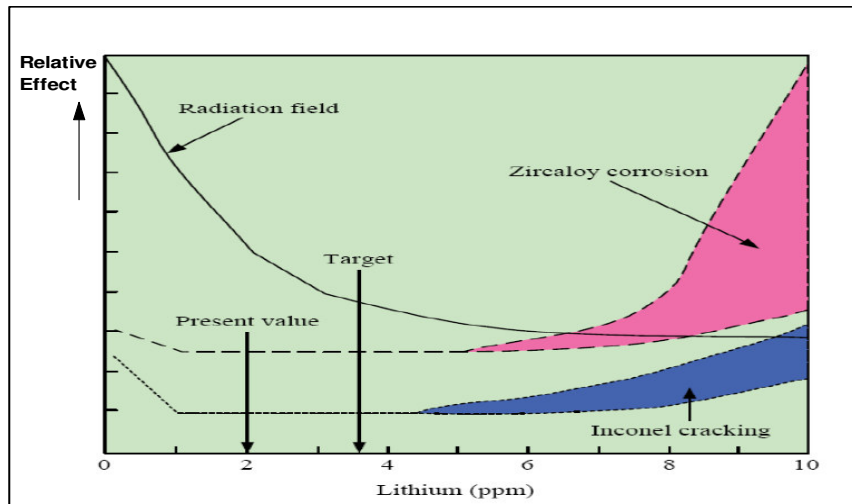


Fig. 8: PWR primary coolant chemistry effect of lithium concentration

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; alkaline and acid as shown in Fig. 9, Rolf et al. [19].

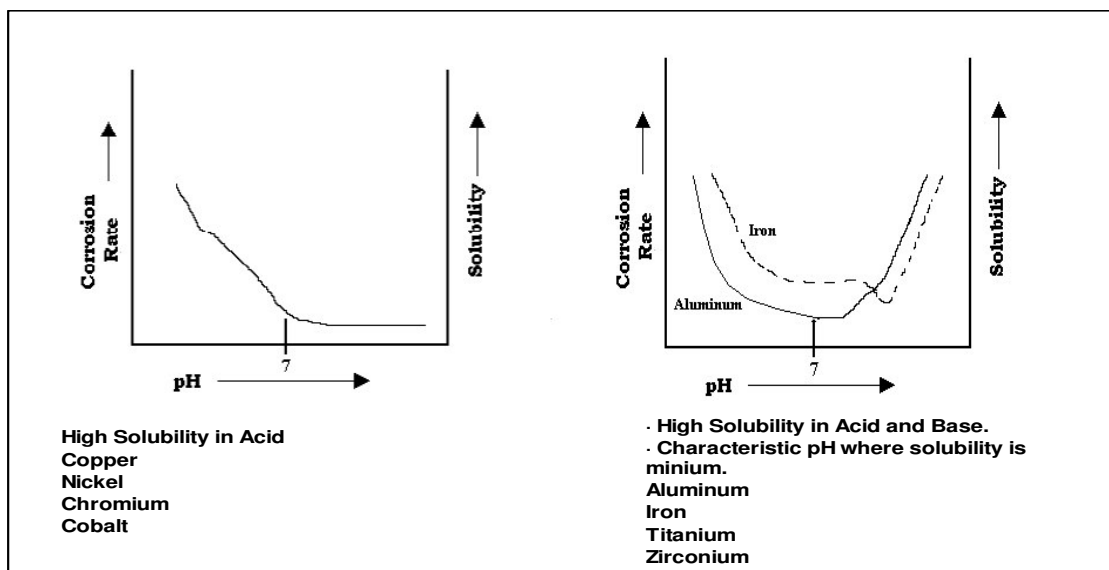
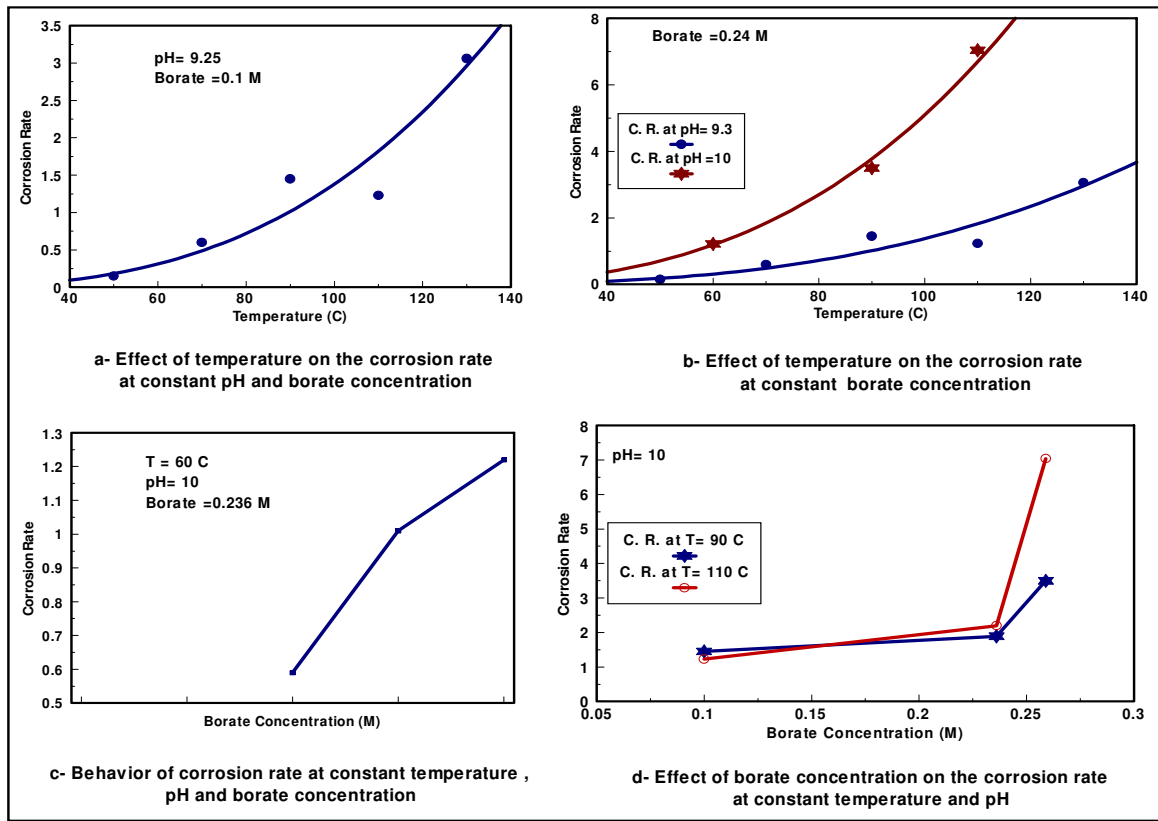


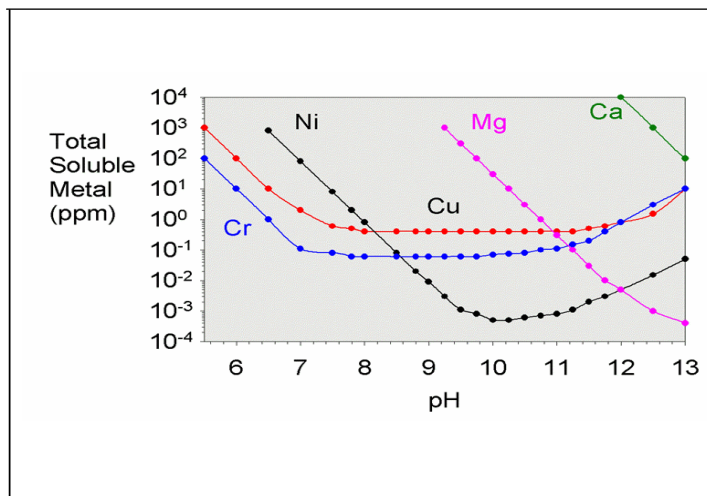
Fig. 9: Effect of pH on Metals

In some cases and for certain metal, the corrosion rate increases in the alkaline medium. Figure 10 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 g m<sup>-2</sup> h<sup>-1</sup> when the solution pH increased from 8 to 10 at 60 °C, Tabrizi et al. [20].



**Fig. 10: Effect of different concentrations of boric acid on the corrosion rate**

Figure 11 describes corrosion rate of some metal at different pH, Randy [21]. It is obvious that there no a definite pH value can be selected to prevent the corrosion of all metals involved in the reactor building.



**Fig. 11: Effect of pH on total soluble metals**

#### 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 to decrease as possible the severe effects of pH by:

- 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 – 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; on the other hand, radiolysis of water is other that impact the rate of material corrosion.

#### REFERENCES

- [1] AREVA, Primary Coolant Chemistry: Fundamental Aspects & Improvements/Optimizations, Areva, Fundamentals & Developments, Nov. 2008.
- [2] Pastina B., and LaVerne J.A., "Effect of Molecular Hydrogen on Hydrogen Peroxide in Water Radiolysis", *J. Phys. Chem. A*, 105, 9316, 2001.
- [3] The Encyclopedia of Earth, Last Updated December 11, 2009, [http://www.eoearth.org/article/Nuclear\\_power\\_reactor](http://www.eoearth.org/article/Nuclear_power_reactor).
- [4] Venz H., and Weidmann U., "Influence of Extended Cycles on Reactor Coolant Chemistry and Collective Dose at Nuclear Power Plant", *Proceedings of International Conference on Water Chemistry of Nuclear Power Systems* 7, BNES, London, pp. 16-27, 1996.
- [5] Frattini P.L., Block J., Chauffriat S., Sawicki J., and Riddle J., "Axial Offset Anomaly: Coupling PWR Primary Chemistry with Core Design", *Nuclear Energy*, 40 (2), pp. 123-135, 2001.
- [6] Min C.S., and Kun J.L., "The Evaluation of Radioactive Corrosion Product at PWR as Change of Primary Coolant Chemistry for Long-Term Fuel Cycle", *Annals of Nuclear Energy* 30, pp. 1231-1246, 2003.
- [7] Peter M., Wood C., Frattini P., Ocken H., and Gaudreau T., "Plant-Specific Optimization of LWR Water Chemistry", EPRI Nuclear Power Group, TR-

- 107329, Final Report, October, 1997.
- [8] Spinks J.W., and Woods R.J., "An Introduction to Radiation Chemistry". John Wiley, New York, 1990.
- [9] Wikipedia, the free encyclopedia, last modified on 19 January 2010. <http://en.wikipedia.org/wiki/Redox>
- [10] Langelier W.F., "Effect of Temperature on the pH of Natural Water". J. Am. Water Works Assoc., 38, pp. 179-280, 1946.
- [11] David M.G., and Edwar, P.S., "Cycle Chemistry pH Measurement, Electric Utility Chemistry", Workshop, Champaign, Illinois, May 12-14, 1998.
- [12] Pastina B., Isabey J., and Hickel B., "The Influence of Water Chemistry on the Radiolysis of the Primary Coolant Water in Pressurized Water Reactors", J. Nucl. Mater. 264, pp. 309-214, 1999.
- [13] Joseph J.M., Choi B.S., Yakabuskie P., and Wren J.C., "Combined Experimental and Model Analysis on the Effect of pH and O<sub>2</sub>(aq) on  $\gamma$ -Radiolytically Produced H<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>, Radiation", Physics and Chemistry Journal, Vol. 1, pp. 1-14, 2008.
- [14] Nasir M.M., Rafiquea M., Mirzaa S.M., and Hyder M.J., "Simulation of Corrosion Product Activity for Nonlinearly Rising Corrosion on Inner Surfaces of Primary Coolant Pipes of a Typical PWR Under Flow Rate Transients", Applied Radiation and Isotopes Journal, Vol. 6, pp. 361-372, 2004.
- [15] DOE (U.S. Department of Energy), FSC-6910, Washington, D.C. 20585 DOE-HDBK-1015/2-93, "DOE Fundamentals Handbook", Chemistry, Volume 2, pp. 101-113, January 1993.
- [16] Frederick J.K., "What is pH, and How is it Measured?", A Technical Handbook for Industry, Hach Company, 2003.
- [17] KANUPP– International Atomic Energy Authority (IAEA), Training Primary Heat Transport System Chemistry Control, IAEA web pages.
- [18] IAEA (International Atomic Energy Authority), TECDOC-1196, "Mitigation of Hydrogen Hazards in Water Cooled Power Reactors", February 2001.
- [19] Rolf R., Ford F.P., Lundgren K., and Sandklef S., "LCC-2 Annual Report, Advanced Nuclear Technology International, Sweden", December 2006.
- [20] Tabrizi M.R., Lyon S.B., Thompson G.E., and Ferguson J.M., "Corrosion of Aluminum in the Aqueous Chemical Environment of a Loss-of-Coolant Accident at a Nuclear Power Plant", Corros. Sci. 32, pp. 733-742, 1991.
- [21] Randy H.F. "Advanced Aquarist's", online magazine, Chemistry and the Aquarium, copyright, 2003. <http://www.advanceaquarist.com>