The effect of zinc injection on the increasing of Inconel 600 TT corrosion resistances

Febrianto, Sriyono, Surip Widodo, Geni Rina Sunaryo
Puspiptek Area Building 80, Serpong, South Tangerang City, 15310, INDONESIA
febri@batan.go.id

Abstract. Many failures were found in reactor pressure vessel head penetration (RPV) head material. Those failures caused by boric acid corrosion, and from visual examination were found a big hole and white deposit crystal of boric acid during shutdown maintenance at David Besse reactor. Zinc Oxide addition in BWR reactor known as Zinc Injection that has purposed to reduce radiation exposure cause of Hydrogen addition. Beside reducing the radiation exposure, Zinc injection also has an effect in reducing material corrosion. The purpose of study is to determine the effect of zinc addition, boric acid, temperature also the effects of Cobalt Nitrate and Zinc Oxide addition to Inconel 600 TT as RPV head penetration material. The result in the BWR reactor experience will be implemented at PWR reactor, whether zinc oxide addition also has an effect in reducing the corrosion of Inconel 600. The method that used in this research is to observe the corrosion rates for Inconel 600 material using Potentiostat. Examination were conducted in 30, 40, 60, 70, 80 and 90 °C using 1000, 1500, 2000, 2500 and 3000 ppm boric acid concentration. The results showed that the corrosion rate for the material were very small, but the highest corrosion rate occurred in 3000 ppm boric acid concentration at 90 °C with Cobalt Nitrate addition, around 5.210 x 10^{-1} mpy. In the same condition at 3000 ppm boric acid concentration for temperature at 90 °C, Inconel 600 TT corrosion rate is smaller with Zinc oxide addition, around 4.631 x 10^{-1} mpy.

Keywords : corrosion, zinc injection, radiation, Inconel 600, resistance

1. Introduction
Since the beginning of operational the PWR (Pressurized Water Reactors) reactor, corrosion problems have caused substantial losses of power generation, resulted in large repair and maintenance costs throughout the world. Water chemistry is one of the few methods available to plant operators to control the materials degradation after the reactor being operated, including; steam generators, reactor components, and balance of plant piping. Since corrosion is a major contributor to the O&M costs, utilities must pursue the most cost-effective solutions to their corrosion problems [1,2].

Boric acid could be caused in the degradation of carbon steel and low alloy. Currently, many research programs conduct a study concerning corrosion effect of boric acid to reactor components. Many material failures causing on boric acid corrosion, one of famous failure caused by boric acid corrosion is reactor pressure vessel head leak at David Besse reactor in US. Material degradation that occurs at Davis Besse reactor RPV head is an example of consequence boric acid corrosion [3]. Reactor Beznau unit 1 in Swiss also has an experience of boric acid corrosion at RPV head. It was
found boric acid crystal deposit at above part of RPV head. After cleaning of boric acid crystal it was seen hole with 50 mm width and 40 mm depth at Control Rod Drive Mechanism (CRDM) nozzle penetration part [4]. Currently, PWR reactor operates with higher burn up, lithium concentration addition, high coolant temperature to reduce fuel cladding corrosion risk. Many PWR reactors operated at pH between pH 6.9 and 7.4 during fuel cycle. Reactor coolant pH value is controlled by boric acid (H$_3$BO$_3$) and lithium hydroxide (LiOH) combination [5].

Lithium maximum concentration at beginning fuel cycle is 2.2 ppm. Higher lithium concentration will initiate fuel cladding corrosion and nickel alloy primary water stress corrosion cracking (PWSCC). Fuel cladding controll is more complicated, at low pH many corrosion products will deposit at fuel surface and increase of cladding failure risk [6]. At higher pH, corrosion product deposit rate at fuel surface will decrease but rate of corrosion fuel will increase by increasing lithium hydroxide concentration [7,8].

Boric acid is added into reactor coolant to control reactor reactivity and reactor coolant pH. During reactor operation, material and component will be degraded and corroded. From the reactor operation experiences, degradation and corrosion can cause coolant leakage in several degree. One of material degradation example can be initiated by boric acid [1, 3, 5]. This degradation has a potential to reduce system integrity and can initiate loss-of-coolant accident. Material degradation also occurs at Bugey reactor 3 and 4 Reactor Pressure Vessel Head Penetration Material which made of Inconel 600.

The purpose of this study is to determine the effect of boric acid, temperature and Cobalt Nitrate and Zinc Oxide addition to alloy 600 TT corrosion as RPV head penetration material. The method that used in this research to observe the corrosion is Potentiostate technique. Various researches report that the beneficial effects of Zn on the radiation reduction can be attained in PWR also [4]. In this study will be determine the effect of zinc addition and temperature increasing to Inconel 600 corrosion rate. The purpose of this study is to determine the effect of boric acid, cobalt nitrate, zinc oxide addition and temperature to alloy 600 corrosion resistance.

2. Theory
In BWR reactor zinc addition is known as Zinc Injection that has purposed to reduce radiation exposure cause of hydrogen addition. Hydrogen addition is well known as HWC (Hydrogen Water Chemistry). HWC is effective in reducing the corrosion of material, component and reactor structure. Because the hydrogen addition can reduce the coolant oxidizing power. Even if Hydrogen addition can cause of reactor coolant became more reductive but it has an negative impacts such as [5];

1). Increasing the radiation doses at main steam way cause of N-16 change from stabile form (NO$_3^-$ and NO$_2^-$) to volatile form (NH$_3$) and goes to turbine area.

2). Radiation dose increase until 3 – 4 times during shutdown and increase radiation exposure risk will be accepted by worker especially during yearly inspection and maintenance activity. This condition occurs cause of change of oxide form Fe$_2$O$_3$ (hematite) in oxidation environment to Fe$_3$O$_4$ (magnetite) in reduction environment. Change of this oxide form can cause activated corrosion product such as Co-60.

Zinc addition can reduce radiation exposure through [5, 9]

1. Inhibit the corrosion at surface material and resulting the thinner film layer
2. Zinc will compete with cobalt at the same place and reducing cobalt concentration in oxide structure film
3. Repress cobalt release from deposition place into primary coolant.

Boric acid can cause low alloy and carbon steel degradation. Currently, many research programs conduct study concerning boric acid corrosion effect to reactor components. Boric acid is weak acid
but boric acid leak to hot surface material and water will disappear and leave concentric boric acid. Boric acid saturated solution will occur at temperature above 95°C with solution pH around 3 and this solution is very corrosive and causes the local corrosion. RPVHP reactor structure can be seen at figure 1 and boric acid crystals deposit at figure 2 [10].

![Figure 1. Reactor PWR RPVHP Structure [11]](image)

![Figure 2. Deposits of boric acid crystals on reactor pressure vessel head from leaking CRDM nozzles [10, 12]](image)

### 3. Methodology
The experiment was conducted in several steps:
- Specimen preparation
- Inconel 600 TT material corrosion test using Potentiostat.
- Data analysis and report.

Inconel 600 TT was used as specimen in this experiment (produced by Inco Alloys Services PTE LTD). The specimen dimension is 19.05 mm in diameter, 1.09 mm in thickness and 10 mm in
length. The specimen dimension is the same as steam generator tube dimension. The specimen surface was polished with polished paper from grade 400, 600, 800 and 1000 and then polished with diamond paste Metadi II. Specimen was conditioned in Autoclave in 100 ppb cobalt nitrate at temperature 250 °C for 250 hours and to this solution was added 25 ppb zinc oxide at the same temperature for 250 hours.

Specimens that have been conditioned in cobalt nitrate, with zinc oxide and without zinc oxide will be measured its corrosion rate in various boric acid concentrations (1500, 2000, 2500 and 3000 ppm) at various temperatures (30, 40, 60, 70, 80 and 90 °C). The potential was automatically varied at a constant rate between two preset levels. Data that found by Potentiostat will be analysed to get corrosion rate.

4. Results and Discussion

4.1 Temperature Effect on Inconel 600 Corrosion Rate

Change of temperature can modify the interaction between the metal and the electrolyte. Increasing temperature will increase corrosion rate by increasing the diffusion of soluble oxygen from solution to the metal surface.

From Figure 3, it is shown that temperature increasing tend to increase corrosion rate of Inconel 600 material. Inconel 600 corrosion rate at 30 °C in 1500 ppm containing boric acid solution is 4.02 x 10^{-6} mpy and corrosion rate at 40 °C in the same boric acid solution concentration is 3.11 x 10^{-5} mpy. At the same boric acid concentration, at 60 °C corrosion rate is 2.69 x 10^{-5} mpy an increase become 4.43 x 10^{-12} mpy at 70 °C. Inconel 600 corrosion rate continue to increase with temperature increasing, is 4.57 x 10^{-1} at 80 °C and 4.74 x 10^{-1} mpy at 90 °C. In the other boric acid concentration also has the same tendency where temperature increasing also increase the corrosion rate of Inconel 600 TT.

From the experiment results can be seen that temperature increasing and corrosion rate has linear relation. Increasing temperature tend to increase the corrosion rate. Change of temperature can modify the interaction between the metal and the electrolyte. Increasing temperature will increase corrosion rate by increasing the diffusion of soluble oxygen from solution to the metal surface.

From the experiment results can be seen that the corrosion rate of Inconel 600 TT is small. Inconel 600 TT has a good resistance to corrosion at high temperature and for this reason this material can be used and operated as component and structure at high temperature and pressure. Inconel 600 TT has nickel composition around 58 % so this material can be operated at high temperature and pressure.

Table 1. Inconel 600 corrosion rate in conditioned Cobalt Nitrate at temperature 250 °C for 250 hours at several concentrations of Boric acid and temperature

| Material  | Temperature (°C) | Boric Acid Concentration (ppm)/Corrosion Rate (mpy) |
|-----------|-----------------|--------------------------------------------------|
| Inconel 600 |                 | 1500        2000        2500        3000        |
|           |                 |    30        | 4.02 x 10^{-6}       | 5.12 x 10^{-6}       | 2.16 x 10^{-3}       | 2.6820 x 10^{-3}       |
|           |                 |    40        | 3.11 x10^{-5}        | 3.53 x 10^{-5}        | 5.55 x 10^{-5}        | 1.1961 x 10^{-4}        |
|           |                 |    60        | 2.69 x 10^{-4}       | 3.48 x 10^{-4}        | 2.18 x 10^{-4}        | 4.19 x 10^{-2}         |
|           |                 |    70        | 4.43 x 10^{-1}       | 4.47 x 10^{-1}        | 4.53 x 10^{-1}        | 4.56 x 10^{-1}         |
|           |                 |    80        | 4.57 x 10^{-1}       | 4.60 x 10^{-1}        | 4.61 x 10^{-1}        | 4.63 x 10^{-1}         |
|           |                 |    90        | 4.74 x 10^{-1}       | 4.91 x 10^{-1}        | 5.12 x 10^{-1}        | 5.21 x 10^{-1}         |
Table 2. Inconel 600 corrosion rate in Cobalt Nitrate and Zinc oxide conditioned at temperature 250°C for 250 hours at several concentration of Boric acid and temperature

| Material  | Temperature (°C) | Boric Acid Concentration (ppm)/Corrosion rate (mpy) |
|-----------|------------------|------------------------------------------------------|
|           |                  | 1500   | 2000   | 2500   | 3000   |
| Inconnel 600 | 30                | 3.81 x 10⁻⁷ | 7.21 x 10⁻⁷ | 7.46 x 10⁻⁷ | 1.412 x 10⁻³ |
|           | 40                | 2.69 x 10⁻⁴ | 3.11 x 10⁻⁴ | 3.34 x 10⁻⁴ | 3.34 x 10⁻⁵ |
|           | 60                | 2.12 x 10⁻⁴ | 3.48 x 10⁻⁴ | 4.17 x 10⁻⁴ | 4.19 x 10⁻² |
|           | 70                | 3.91 x 10⁻¹ | 4.19 x 10⁻¹ | 4.42 x 10⁻¹ | 4.47 x 10⁻¹ |
|           | 80                | 4.53 x 10⁻¹ | 4.54 x 10⁻¹ | 4.54 x 10⁻¹ | 4.56 x 10⁻¹ |
|           | 90                | 4.59 x 10⁻¹ | 4.61 x 10⁻¹ | 4.63 x 10⁻¹ | 4.63 x 10⁻¹ |

4.2 Effect of Boric Acid Addition to Inconel 600 TT Corrosion Rate

From the experiment results can be seen that the Inconel 600 TT corrosion rate increases with increasing boric acid concentration. Inconel 600 corrosion rate at 30°C in 1500 ppm containing boric acid solution is 4.02 x 10⁻⁶ mpy, in the 2000 ppm boric acid solution concentration at the same temperature is 5.12 x 10⁻⁶ mpy, in 2500 ppm boric acid concentration, corrosion rate is 2.16 x 10⁻⁵ mpy and increase become 2.6820 x 10⁻⁵ mpy in 3000 ppm boric acid at 30°C. Increasing the boric acid concentration also increases the Inconel 600 TT corrosion rate. Increasing the corrosion rate of Inconel 600 with boric acid addition can be explained that increasing the boric acid in will make the solution more acidic. Increasing the solution acidic will make the more aggresive its solution toward corrosion. This would explain the temperature dependence of the corrosion rate shown in Figure 3 as well as its dependence on boric acid concentration. For a thermally activated process, corrosion rates are expected to increase with increasing temperature.

4.3 Cobalt Nitrate and Zinc oxide Addition Effect on Inconel 600 Corrosion rate

Figure 3 and Figure 4 show the measured corrosion rates for Inconel 600 TT in several boric acid solutions after conditioned in Cobalt Nitrate and Zinc oxide.

In this step can be compared the Inconel 600 corrosion rate in two conditions:
1. In several boric acid concentrations after the specimen was conditioned in Autoclave in cobalt nitrate10 ppb at temperatur 250 °C for 250 hours (A condition).
2. In various boric acid concentration after the specimen was conditioned in Autoclave in cobalt nitrate 10 ppb at temperatur 250 °C for 250 hours and addition of 25 ppb zinc oxide at the same temperature for 250 hours (B condition).
Figure 3. Inconel 600 corrosion rate in conditioned Cobalt Nitrate at temperature 250 °C for 250 hours at various concentrations of Boric acid

Figure 4. Inconel 600 corrosion rate in Cobalt Nitrate and Zinc oxide conditioned at temperature 250 °C for 250 hours at various boric acid concentrations

4.4 Zinc oxide Addition Effect on Inconel 600 material Corrosion rate
At temperature 30 °C, Inconel corrosion rate after conditioned with cobalt nitrate 10 ppb addition at temperature 250 °C for 250 hours in 1500 ppm boric acid is 4.02 x 10^{-6} mpy. The Inconel corrosion rate after addition 25 ppb zinc oxide at the same temperature for 250 hours to the above solution is 3.81 x 10^{-7} mpy. Also at temperature 30 °C in 2000, 2500 and 3000 ppm boric acid, the Inconel corrosion rate which conditioned with cobalt nitrate 10 ppb addition (A condition) are bigger comparing with the Inconel corrosion rate with zinc oxide addition (B condition).

At temperature 40, 60, 70, 80 and 90 °C in the same boric acid concentrations, the Inconel corrosion rate which conditioned with cobalt nitrate 10 ppb addition (A condition) are bigger comparing with the Inconel 600 corrosion rate with zinc oxide addition (B condition).
A smaller of Inconel 600 TT corrosion rate with zinc oxide addition comparing cobalt nitrate addition can be explained by D. Lister using Site Preference Energy view. Ion Zinc (Zn$^{2+}$) has an ability to fill the same place in oxide layer faster than other oxide, such as Co$^{2+}$. This behaviour can reduce the other oxide metal with two valence concentration in corrosion layer. Zinc oxide layer is more protective that has tend to to form passive layer and can reduce the next corrosion process [13].

From the view of site preference energy concept be explained that zinc has high bond energy at tetrahedral interstitial position in crystal lattice comparing with Co$^{2+}$ and other two valence metal ions. Cause of high the value of site preference energy (Table 1), Zin ion can substitute for other two valence metal ions positions in corrosion film [13]. From the result of experiment found that Inconel 600 TT corrosion rate is smaller with zinc oxide addition comparing with cobalt nitrate addition in the same boric concentration. It can be explained by using site preference energy. Zinc has an ability to fill the same place in oxide layer faster than other oxide because zinc has high bond energy at tetrahedral interstitial position in lattice oxide.

| Ion  | Site Preference Energy (kJ/mol) |
|------|---------------------------------|
| Fe$^{2+}$ | - 3.35                        |
| Ni$^{2+}$ | - 51.04                       |
| Co$^{2+}$ | 14.64                          |
| Zn$^{2+}$ | 33.89                          |
| Fe$^{3+}$ | 20.51                          |

5. Conclusion
From the result of experiment can be seen that Inconel 600 TT corrosion rate is a relative small. Increasing the temperature and boric acid concentration also increase the Inconel 600 TT corrosion rate. From the experiment data found that Inconel 600 TT corrosion rate is smaller with zinc oxide addition comparing with cobalt nitrate addition in the same boric concentration. It can be explained by using site preference energy. Zinc has an ability to fill the same place in oxide layer faster than other oxide because zinc has high bond energy at tetrahedral interstitial position in oxide lattices. The alloy 600 TT corrosion rate decreases with the addition of zinc oxide in high temperature water. There are some suggested explanations for the improvement of SCC resistance by several researchers. Most arguments are based on the modifications of oxide structure with the impregnation of Zn in the oxide.

The results from the present study, the highest corrosion rate occur in boric acid 3000 ppm solution at temperature 90 °C, around 6.31 x 10$^{-1}$ mpy with cobalt nitrate addition.

It can be explained that the decrease of Inconel 600 corrosion rate with the addition of Zn is related to the change of properties of the oxide structure in passive film. By using the Site Preference Energy view, it is possible explanation that the improvement of Inconel 600 corrosion properties with the addition of Zn is due to the substitute the other two valence ion positions in passive film. Kawamura indicates that Zn addition stabilizes the ZnCr2O4 oxide spinel and increases the corrosion resistance of Alloy 600.
Acknowledgment
This work has been carried out under Center for Nuclear Reactor Technology and Safety program, National Nuclear Energy Agency of Indonesia (BATAN).

References
[1] Millett, P.J. and C.J. Wood 1998 Recent advances in water chemistry control at US PWRs in 1998 JAIF international conference on water chemistry in nuclear power plants, proceedings.
[2] Ford, F. 2006 Environmentally-Assisted Degradation of Structural Materials in Water Cooled Nuclear Reactors, vol 11, pp 213-218
[3] Fruzetti, K. and C. Wood 2007 Developments in nuclear power plant water chemistry Power Plant Chemistry, vol 9(4): p. 209-215.
[4] Wilson, P.L.A. 2006 Use of primary Water Chemistry in PWRsTo Mitigate PWSCC of Ni-Base Alloys. in International Conference on water Chemistry of Nuclear Reactor system. Jeju, Korea, pp 134-140.
[5] Riess, R., et al., 2006 LCC-2 annual report. Advanced Nuclear Technology International, pp 25-29
[6] J.-H. Park, O.K.C., K. Natesan, and W. J. Shack 2006. Boric Acid Corrosion of Light Water Reactor Pressure Vessel Materials. in International Conference on Water Chemistry of Nuclear Reactor system. Jeju, Korea.
[7] Grimmel, B. and W. Cullen 2005 US Plant Experience with Alloy 600 Cracking and Boric Acid Corrosion of Light Water Reactor Pressure Vessel Materials, US Nuclear Regulatory Commission, Office of Nuclear Regulatory Research, Division of Engineering Technology.
[8] Bennetch, J., et al. 2002 Root Cause Evaluation and Repair of Alloy 82/182 J-Groove Weld Cracking of Reactor Vessel Head Penetrations at North Anna Unit 2. in ASME 2002 Pressure Vessels and Piping Conference American Society of Mechanical Engineers.
[9] Wolter, D. 2006 Ten Years Zinc Injection for Radiation reduction at The Biblis Power station in International Conference On Water chemistry of Nuclear Reactor system. Jeju, Korea.
[10] Series, I.N.E., 2011 Stress Corrosion Cracking in Light Water Reactors: Good Practices and Lessons Learned. No. NPT-3.13, IAEA, Vienna, Austria
[11] Park, J.-H., et al. 2005 Boric acid corrosion of light water reactor pressure vessel head materials, Argonne National Laboratory (ANL), USA.
[12] Commission, N.R. 2004 Final Safety Evaluation Report Related to Certification of the AP1000 Standard Design, NUREG-1793, Initial Report, USA
[13] Lister, D. 1992 Activity transport and corrosion processes in PWRs, Water chemistry of nuclear reactor systems., Vol 2: p. 49-49.
[14] Navrotsky, A. and O. Kleppa 1967 The thermodynamics of cation distributions in simple spinels, Journal of Inorganic and Nuclear Chemistry., Vol 29(11): p. 2701-2714.