

# The effect of pH adjuster type on general corrosion characteristics of Alloy690TT in pressurized water reactors

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## 1. Introduction

Boric acid is used as a chemical shim to control excess reactivity in the fuel assemblies in pressurized water reactors (PWR) [1]. Although natural boric acid is generally used, only the <sup>10</sup>B isotope is involved in reactivity control, via <sup>10</sup>B(n,α)<sup>7</sup>Li reaction which produces the alkali <sup>7</sup>LiOH [2]. Thus, LiOH is selected as a pH adjuster to ensure the integrity of reactor coolant system materials. pH<sub>T</sub> in PWR operation environment has been recommended in the range of 6.9 - 7.4 to minimize the corrosion rate of primary coolant system materials and to avoid a heavy fuel crud buildup [3].

However, the global lithium demand is significantly being increased, leading to supply instability and rising price, due to extensive applications in ceramic, glass, steel, nuclear, chemical industries and medicine [4]. Because of that, there is a growing demand for finding alternative alkali hydroxides, which will facilitate better pH control, as opposed to LiOH in nuclear industry. Particularly, KOH is considered as a possible candidate because the K<sup>+</sup> ion has a smaller charge density compared to Li<sup>+</sup> and therefore, it exhibits a lower affinity for the negatively charged OH<sup>-</sup> ion, making water chemistry control more manageable. Furthermore, KOH is substantially cheaper than LiOH and can be sourced much more readily than nuclear grade LiOH. The use of KOH as compared to LiOH would result in substantial reduction in plant operational costs. The Water Water Energetic Reactor (WVER) in Russia has used potassium hydroxide (KOH) as a pH adjuster for H<sub>3</sub>BO<sub>3</sub> and the Electric Power Research Institute (EPRI) in US has recently been considering KOH as a potential alternative for LiOH in PWRs [4].

Alloy690TT (60Ni-30Cr-10Fe) is a strong corrosion resistant material which has not experienced a corrosion damage in steam generator tubing application for longer than 40 years. However, the results on the corrosion characteristics of Alloy690TT in a PWR K-B environment have not been reported yet.

In this work, we compare the general corrosion behavior of Alloy690TT in K-B and Li-B solutions to

obtain its integrity data for using KOH as an alternative alkali hydroxide of LiOH.

## 2. Experimental Methods

### 2.1 Preparation of specimens

Alloy690TT was thermally treated (TT) at 715 °C for 10 h after mill annealing. The chemical composition of specimens is investigated as summarized in Table 1. For the corrosion test, a specimen was machined in half tube having a dimension of 50.0 mm x 19.05 mm x 1.15 mm and an analysis specimen was prepared with a size of 13.47 mm x 10.0 mm x 1.15 mm.

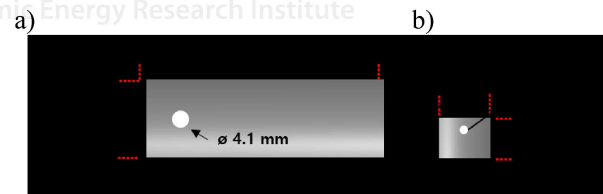


Fig. 1. Schematic of corrosion test specimens; a) corrosion test specimen and b) analysis specimen

Table.1 Chemical composition of Alloy690TT (wt.%)

Element	Cr	Ni	Fe	Mn	Si	Cu	C
	28.0	Bal.	10.2	0.3	0.1	0.01	0.02

### 2.2 Corrosion test

Corrosion tests were performed in a primary water recirculating loop system as shown in Fig. 2. Two different types of solutions were prepared by dissolving 1,000 ppm B and 2.9 ppm Li, 1,000 ppm B and 16.4 ppm K, respectively, into the deionized water, in which pH is 7.4 at 320°C. Prior to the test, the dissolved oxygen and dissolved hydrogen in test loop were controlled to less than 5 ppb and 35cc/kg-H<sub>2</sub>O, respectively. Under these conditions, corrosion tests were conducted for 300, 1,000, 1,500, and 2,000 h, respectively, at a temperature of 320°C.

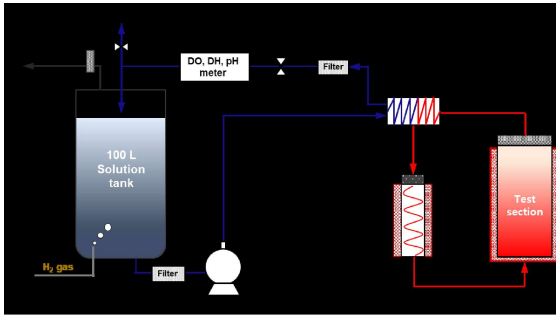


Fig. 2. Schematic of the simulated primary coolant loop for the corrosion test.

### 2.3. Specimen analysis

After corrosion tests, the corrosion and release rates were evaluated by gravimetric method through two-step descaling process. In the first step, a solution of 1% KMnO<sub>4</sub> and 5% NaOH was used for 1 minute. In the second step, a 5% ammonium citrate solution was applied for 1 minute. oxide films of the Alloy690TT corrosion specimen was examined in surface morphology and chemical composition by using scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS)

## 3. Results and Discussion

Fig. 3 shows corrosion and release rates calculated through the chemical descaling process for corrosion specimens tested in K-B and Li-B solutions, respectively, for 300, 1,000, 1,500, and 2,000h. Corrosion rate value was similar with  $1.36 \times 10^{-7}$  g/cm<sup>2</sup>h for specimens tested in both solution of K-B and Li-B for 300h. However, corrosion rate of specimens tested in Li-B shows slightly high with increasing test time after 500h, comparing that of specimens tested in K-B. In addition, the release rate also slightly higher on specimens tested in Li-B solution than on that tested in K-B solution. This means that pH adjuster can affect somewhat to corrosion and release behavior.

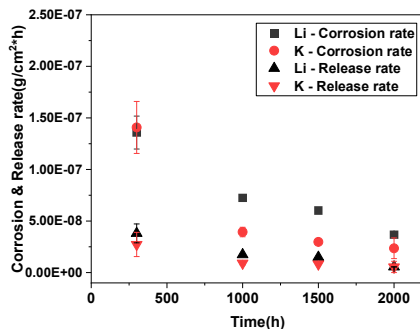


Fig. 3. Corrosion and release rate in K-B and Li-B solutions

Fig. 4 shows the SEM morphologies of the outer oxide film formed on Alloy690TT specimens in different solutions with increasing test time. The small particles covered the specimen surface after corrosion test and the density of oxide particles increased with increasing test time on specimens tested in both solutions. However, it is seen that the particle size on specimen tested in Li-B solution is larger than that in K-B solution. Furthermore, the growing rate of oxide particles in Li-B solution is faster than in K-B solution with increasing test time.

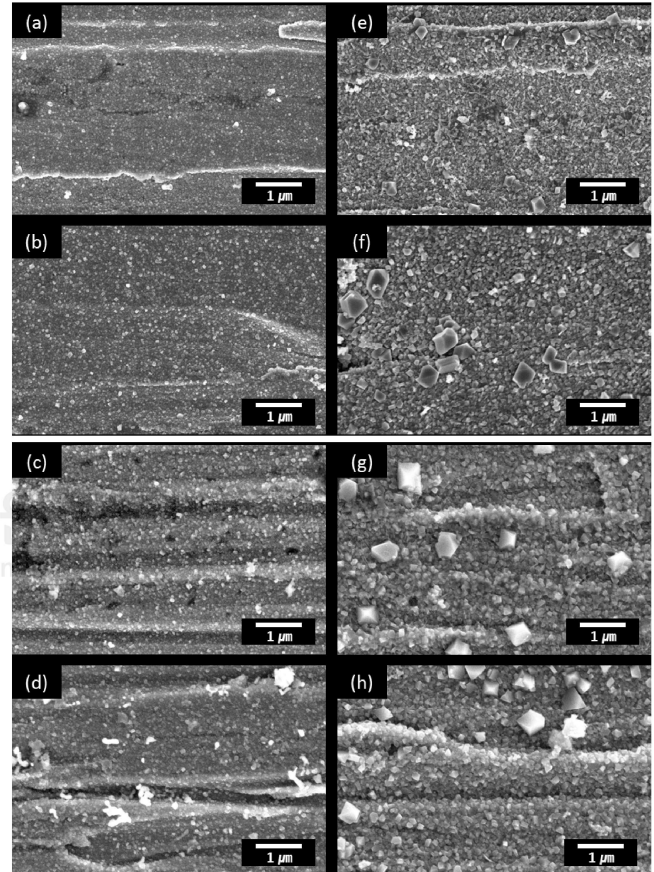


Fig. 4. SEM images of the specimens after corrosion test in K-B (a, b, c, d) and Li-B (e, f, g, h) solutions: (a, e)300h, (b, f)1000h, (c, g)1500h, (d, h)2000h.

## 4. Conclusions

We compared the corrosion behaviors of Alloy690TT in both solutions of Li-B and K-B in this work. The corrosion rate and release rate of Alloy690TT is slightly higher in Li-B solution than in K-B solution. The size and density of oxide particles are larger in Li-B than in K-B solution. These results depict that the corrosion resistance of Alloy690TT can be improved through replacing pH adjuster from LiOH to KOH.

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