The impact of elevated lithium concentration 3.5 ppm on the corrosion rate of zirconium

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ABSTRACT

Corrosion of zirconium in presence of LiOH was studied by cyclic potentiodynamic polarization technique. SEM was used to observe the visual appearance of oxide film after the procedure. The measurements were carried out at room temperature and open to air. Our investigations show the accelerated electrochemical corrosion is caused by 3.5 ppm rather than 2.2 ppm. The important observation is the steep decrease in corrosion rate at 2.2 ppm Li ion.

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1. Short communication

In light water-cooled and –moderated reactors boric acid H_3BO_3, is added as chemical shim and the alkali, Lithium hydroxide (LiOH), is also added to the primary coolant for pH control. A number of utilities are adopting even higher pH levels, 3.5 ppm Li. That resulted in an accelerated corrosion rates of cladding material so many hypotheses were proposed to interpret the phenomenon.

The equipment consisted of a potentiostat (EG&G Princeton Applied Research, Model 352/252 Corrosion Analysis Software, version 2.23), computer, and an electrolytic cell (Fig. 1). A two graphite electrodes and saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. Cyclic potentiodynamic polarization (CCP) scan was employed for these tests. Zirconium sheet was supplied by Nuclear Manufacture and Materials division, EAEA, Egypt. The experimental technique applied in this work and sample preparation have been described in detail in previous publication [1]. The visual appearance of the oxide was evaluated using SEM model Using SEM Model Quanta 250 FEG (Field Emission Gun).

Using Faraday's Law, we can convert the results of electrochemical measurements (I_{corr}, $\mu A/cm^2$) to rates of uniform corrosion (CR, mm/yr) [2].

Corrosion Rate (CR), mmpy
K (constant) = 3.27×10^{-3}, mm.g/(μA.cm.yr)
Corrosion Current Density (I_{corr}), $\mu A/cm^2$
Equivalent Weight (EW); EW = atomic weight of the metal/valence of the metal
Density of the metal (ρ), g/cm^3

$$\text{Corrosion Rate (CR)} = \frac{K \cdot I_{corr} \cdot EW}{\rho}$$

For pure elements, the equivalent weight is given by Ref. [2]:

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Fig. 1. Potentiostat, computer system and electrochemical cell.

$$Equivalent\ weight = \frac{Atomic\ weight\ of\ the\ element\ (W)}{the\ number\ of\ electrons\ required\ to\ oxidize\ an\ atom\ of\ the\ element\ in\ the\ corrosion\ process,\ that\ is,\ Valence\ of\ the\ element}$$

Standard atomic weight of zirconium element (Zr) = **91.224** U. Valence of zirconium = 4

$$Equivalent\ weight\ of\ zirconium = \frac{91.224}{4}$$

$$= 22.806\ gm/equivalent$$

Density of zirconium at room temperature = **6.52** gm/cm^3 [3]

$$Corrosion\ Rate\ (mmpy) = \frac{0.00327 \times 22.806 \times I_{corr}(\mu A/cm^2)}{6.52}$$

Unlike hydrogen precipitation, metallurgical variables, radiation effect and thermal feedback, the implication of lithium hydroxide in the accelerated waterside corrosion phenomenon of zirconium alloy under PWR water chemistry conditions is somewhat controversial. Many studies of the effect of lithium hydroxide on the corrosion rate have been done and were well documented. Witness from these studies led to dichotomy so there are divisions in the opinions. The argument for the possibility of an increase in rate of corrosion due to lithium in reactor divided into three opinions; a-major effect or primary role, this primary effect is supported by investigations in Ref. [4–8], b-minor effect or secondary role, this non-negligible effect is supported by investigations of [9], c-absence of effect i.e. the accelerated corrosion in PWR by high concentration, 3.5 ppm Li is unlikely by each of [10,11].

In the work presented here, we try to introduce a simple extrapolation for the results obtained under tests of simple conditions and correlate it with the previously published works at these simple conditions. Based on the data obtained, we introduce couple of terms here; ameliorating operator (2.2 ppm Li) and accelerating operator (3.5 ppm Li).

For the results from the electrochemical corrosion tests with LiOH and H$_3$BO$_3$ (Table 1) which are consistent with previous investigations [1] and [12], although the tests were conducted at a simple conditions (room temperature, open to air, and lack of radiation effect) however, we encounter two of extraordinary predicaments:-

1 **Erratic results**, this unpredictable behavior of zirconium and its alloys in lithiated water environments was also reported in our previous work [1] and [12]. Some investigators reported the same conclusion when they conducted the tests in autoclave [6] and [13–15]. The interpretation of this vagueness is unbeknownst however, it's very significant.

2 **Abrupt decrease of corrosion rate**, the sudden and steep decrease of corrosion rate at 2.2 ppm Li ion than those in deionized water, we are not able to foretell the mechanism of how this "**ameliorating operator**" leads to sharp decrease in the corrosion rate. It is not clear and difficult to understand at the present time. The relationship between the lithium hydroxide and the corrosion rate of zirconium and its alloys is probably more complex than we thought and we need deeper insight. In other words, there is no simple relationship between LiOH and corrosion.

In addition, localized corrosion at the 3.5 ppm Li "**accelerating operator**" due to the positive hysteresis loop was observed (Figs. 2–3). This localized corrosion will aggravate the failure of corrosion resistance of zirconium and its alloys. The positive hysteresis loop and the susceptibility to localized corrosion were reported at the same value, 3.5 ppm Li in the case of Zr-4 [12]. Consequently, 3.5 ppm lithium increases the corrosion rate and might lead to localized corrosion, worse type than general corrosion.

From Table 1, at moderate concentrations of lithium hydroxide, a slight increase in the corrosion rate is reported with respect to corrosion rate in water. With an increase in LiOH concentration, corresponding to 7000 ppm lithium, a high corrosion rate is seen. At this high concentration of lithium hydroxide, the entire surface is completely covered by pores (Fig. 4). This vulnerable oxide film (not impervious oxide film is ascribed to the generation of porosity) will results in perpetuation the oxygen diffusion through the oxide film and provides different and easy paths for oxygen diffusion to reach the metal oxide interface and hence, the high corrosion rate. Oxygen diffusion is a rate determining step in the corrosion process [16]. For accelerated uniform corrosion, the porosity generation