

Comparative Study on Water Chemistry Properties controlled with LiOH and KOH Additions for Corrosion Behavior Evaluation

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1. Introduction

South Korea is currently developing an Innovative Small Modular Reactor (i-SMR), which employs a distinctive boron-free water chemistry environment. In conventional Pressurized Water Reactor (PWR) designs, lithium hydroxide (LiOH) is commonly used as a pH control agent. This is primarily to manage the concentration of Li-7, which is produced through the interaction between boric acid used for reactivity control and neutrons [1].

However, the use of boric acid presents several limitations, such as the inability to control reactivity in real time, the induction of axial power offset, and the generation of liquid radioactive waste. To overcome these issues, the newly developed i-SMR adopts a boron-free water chemistry approach, aiming to enhance system safety and reduce radioactive waste production. The absence of boron in the coolant chemistry also enables the consideration of alternative pH control agents in place of LiOH. Among potential alternatives, potassium hydroxide (KOH) has been suggested as a promising candidate based on previous studies [1,2].

KOH has been successfully employed as a pH control agent in Water-Water Energetic Reactor (VVER) systems [1,2]. However, while VVERs typically use stainless steel for steam generator tubes, PWRs and i-SMRs utilize Ni-based alloys. As a result, it is essential to evaluate the corrosion behavior of Ni-based alloys, particularly in KOH environments.

Several studies have investigated the corrosion characteristics of Ni-based alloys in KOH-based water chemistry. For example, the corrosion behavior of Alloy 690 in boron-free KOH environments was reported to be similar to that observed in conventional PWR chemistry where LiOH is used as the pH control agent [3]. In contrast, Alloy 600 exhibited superior corrosion resistance in KOH compared to LiOH environments [2]. Nonetheless, the overall effects of LiOH and KOH environments on the corrosion of nuclear materials have not yet been clearly established. Therefore, a more

comprehensive understanding of the corrosion behavior in LiOH and KOH aqueous solutions is needed.

The present study investigates the fundamental differences between Li⁺ and K⁺ ions and their impact on aqueous solution properties relevant to corrosion processes. The properties of alkaline aqueous solutions that influence corrosion can be broadly classified into those related to hydration phenomena and those associated with ionic transport. For some parameters, data from existing literature were used, whereas contact angle and electrical conductivity were either experimentally measured or calculated using water chemistry prediction software. Based on these results, the corrosion rate of Alloy 690 in both LiOH and KOH environments was predicted.

2. Methods

Some properties associated with hydration phenomena include the structure and stability of hydration shells, hydration energy, and the wettability of the metal surface. In addition, properties such as ionic mobility, viscosity, dielectric friction, and solution conductivity are closely related to ionic transport behavior.

In this study, various physicochemical properties of water modified with LiOH and KOH were investigated under the operating and water chemistry conditions relevant to the i-SMR system. When direct measurements under operating conditions were not feasible, alternative approaches such as literature review and experiments at ambient temperature were employed.

Table I summarizes the water chemistry conditions used in this study. All analyses were conducted at a pH of 7.4 at 303.5 °C, which falls within the expected operational range of i-SMR systems. The cation concentrations of LiOH and KOH required to achieve the target pH were calculated using the MULTEQ code, developed by the Electric Power Research Institute (EPRI). The calculated cation concentration for KOH was approximately 5.67 times higher than that of LiOH.

Table I. Concentrations of LiOH and KOH required to achieve pH 7.4 at 303.5 °C, calculated using the MULTEQ.

pH agent	pH _T (303.5 °C)	Cation concentration (ppm)	Alkali hydroxide concentration (mM)
LiOH	7.4	0.67	0.1
KOH		3.8	

To evaluate the wettability of Alloy 690 in the two alkaline solutions, static contact angle measurements were performed. The experiments were conducted at 25 °C, where a droplet of each solution was placed on the surface of Alloy 690 ten times, and the average contact angle was calculated.

The viscosities of the LiOH and KOH aqueous solutions were measured at 70 °C, following the ASTM D7042-25 standard test method. Additionally, the electrical conductivities of both solutions at 25 °C were calculated using the MULTEQ software.

3. Results

3.1. Properties associated with hydration phenomena

The ionic radius of Li⁺ is smaller than that of K⁺ [4]. A smaller ionic radius results in a higher charge density, which in turn leads to greater hydration energy. Hydration energy is defined as the amount of energy released when one mole of ions is solvated by water molecules. A higher hydration energy indicates a stronger tendency for hydration. Due to this difference, the hydration shell of Li⁺ is classified as a kosmotrope (structure maker), whereas that of K⁺ is considered a chaotrope (structure breaker). Kosmotropic ions tend to disrupt the existing hydrogen-bond (HB) network by removing surrounding oxygen atoms and forming a new, stronger, and more structured network of water molecules. In contrast, chaotropic ions are unable to form stable and well-organized hydration structures. Table II presents the ionic radii and hydration energies of the cations in the alkaline aqueous solutions

Table II. The ionic radii and hydration energies of the cations in the alkaline aqueous solutions.

pH agent	Cation radius (pm)	Hydration energy (kJ)
LiOH	76	-515
KOH	152	-312

Kosmotropic ions are typically attracted to hydrophilic surfaces and repelled from hydrophobic ones, whereas chaotropic ions are generally attracted to hydrophobic surfaces. As a result, kosmotropes exhibit strong ion-surface interactions, which can influence the stability of the electric double layer (EDL) formed on a metal surface when it is immersed in an aqueous solution. Figure 1 shows the structure of the cation hydration shells. In the diagram, yellow circles represent Li⁺ ions, purple circles represent K⁺ ions, and blue circles represent H₂O molecules.

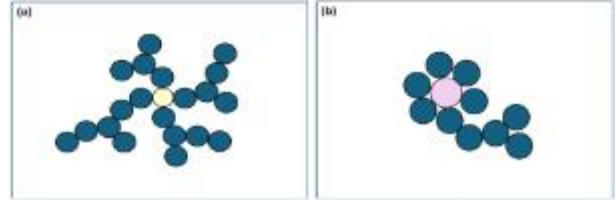


Fig. 1. Structure of cation hydration shells: (a) Li⁺ hydration shell and (b) K⁺ hydration shell [4].

The hydration shell of 10mM LiOH aqueous solution induces disruption of EDL, which was demonstrated to increase the corrosion rate as evidenced by the Tefal polarization curve [4]. To investigate whether the characteristics of the hydration shell in alkaline aqueous solutions used in this study could also affect stability of EDL on the metal surface, contact angle measurements were performed on the surface of Alloy 690. The contact angle is defined as the angle formed at the junction of liquid, vapor, and solid phases when thermodynamic equilibrium is established on a solid surface. It serves as a key indicator of wettability. A contact angle greater than 90° generally corresponds to reduced wettability of the solution on the surface, whereas a contact angle less than 90° corresponds to enhanced wettability.

Figure 2 shows the static contact angles of Alloy 690 measured in this study. The contact angle of the LiOH aqueous solution on Alloy 690 was 78.74° ± 0.24°, indicating greater affinity to hydrophilic surfaces. In contrast, that of the KOH aqueous solution was 92.69° ± 0.39°, indicating lower hydrophilicity.

As previously discussed, a stronger attraction to hydrophilic surfaces can disrupt the structure and stability of the electric double layer (EDL) formed on the metal surface, thereby promoting corrosion. Therefore, in terms of wettability, the LiOH aqueous solution is expected to accelerate the corrosion of Ni-based alloys.

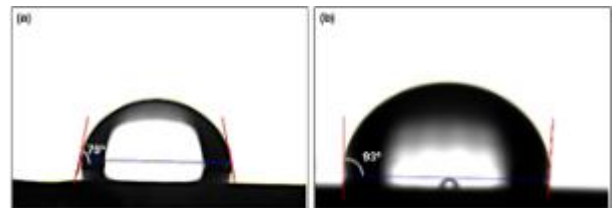


Fig. 2. Static contact angle measured on Alloy 690 substrate in two alkaline aqueous solutions: (a) the aqueous solution with LiOH addition and (b) the aqueous solution with KOH addition.

3.2. Properties associated with ionic transport

Ionic mobility, viscosity, and dielectric friction are the key parameters governing ionic transport in the aqueous solutions. Although these factors do not directly determine corrosion, they collectively determine the conductivity of the solution, which is the principal property influencing corrosion behavior [5].

First, Li⁺ has a smaller ionic radius than K⁺, resulting in higher charge density and more structured hydration

shell. The structured hydration shell limits the mobility of the ion. Consequently, in infinitely diluted LiOH and KOH aqueous solutions at 25 °C, the ionic mobility of Li^+ and K^+ are $38.7 \text{ cm}^2/\Omega$ and $73.5 \text{ cm}^2/\Omega$, respectively. As the temperature increases, the activation energy decreases, resulting in enhanced ionic mobility. Accordingly, at 303.5 °C, the ionic mobility of these cations is expected to increase.

Second, the viscosity of alkaline aqueous solution retards ionic mobility and the product of viscosity and ionic radius is proportional to the Stokes friction resulting from viscosity [6]. Stokes friction can be expressed by the following equation.

$$(1) \zeta_{\text{Stokes}} = 6\pi\eta r$$

Table III presents the viscosity and Stokes friction of the alkaline aqueous solutions at 70 °C. The measured viscosities of the solutions were found to be nearly the same, which is presumed to be due to the low concentration of the cations. When the ionic radius is considered, KOH exhibits greater Stokes friction.

Table III: Viscosity and Stokes friction of the alkaline aqueous solutions at 70 °C.

η_{LiOH} (cP)	η_{KOH} (cP)	ζ_{LiOH} (cP*pm)	ζ_{KOH} (cP*pm)
0.468	0.461	670.1011	1320.156

As temperature increases, the viscosity of the solution decreases. Consequently, the Stokes friction is expected to decrease at 303.5 °C, thereby reducing its influence on corrosion under i-SMR operating conditions.

Dielectric friction refers to the resistance encountered by a charged particle as it moves through a polar liquid, such as water. Evaluation of dielectric friction in alkaline aqueous solutions requires consideration of the ion's self-dynamic structure, the dynamic properties of the dipolar solvent, and ion-dipole interactions. In infinitely dilute solutions at 25 °C, the dielectric friction experienced by Li^+ is approximately three times greater than that of K^+ [6]. In dilute alkaline solutions, the influence of the ion itself can be neglected [7], and only the effects of the dipolar solvent and ion-dipole interactions would be considered. Moreover, as temperature increases, both contributions are known to decrease [8,9]. Therefore, under the concentration and temperature conditions considered in this study, the dielectric friction is expected to be reduced, and its impact on corrosion correspondingly diminished.

The combined effects of ionic mobility, viscosity, and dielectric friction determine the conductivity of alkaline solutions. At 25 °C, the conductivities of 0.1 mM LiOH and KOH aqueous solutions, calculated using the MULTEQ code, were $23.00 \mu\text{S}/\text{cm}$ and $26.42 \mu\text{S}/\text{cm}$, respectively. Ho et al. [10] experimentally measured the conductivities of 0.26 mM LiOH and KOH solutions at 300 °C, reporting values of $297.08 \mu\text{S}/\text{cm}$ and $337.98 \mu\text{S}/\text{cm}$, respectively. These results demonstrate that solution conductivity increases with temperature and confirm that, at equivalent

temperature and concentration, the conductivity of KOH solutions is higher than that of LiOH solutions. Accordingly, from the perspective of conductivity, Ni-based alloys are expected to exhibit a higher corrosion rate in KOH aqueous solutions under i-SMR water chemistry conditions.

4. Conclusions

The present study focused on the fundamental differences between Li^+ and K^+ ions and their influence on aqueous solution properties relevant to corrosion under i-SMR water chemistry.

(1) From the perspective of hydration, the LiOH aqueous solution may tend to promote corrosion of Ni-based alloys, as Li^+ with its stronger hydration tendency could increase the wettability of the Ni-based alloy surface and destabilize the EDL. In contrast, in terms of ionic transport and conductivity, the KOH aqueous solution may promote corrosion of Ni-based alloys. This is due to high mobility and conductivity of K^+ .

(2) It is difficult to determine which properties exert dominant influence on corrosion, and the dominant factor may vary depending on temperature and concentration of alkaline aqueous solutions. Therefore, predicting corrosion behavior and identifying the alkaline solution with higher corrosion resistance solely based on solution properties remains limited.

(3) To address these limitations, the electrochemical and immersion tests will be performed to evaluate the corrosion behavior of Alloy 690 material under water chemistry conditions of i-SMR.

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