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Effect of Dissolved Zinc in a Primary Coolant on Demineralizer Performance and Usage

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Abstract

Ionic zinc has been used to reduce reactor radiation buildup and to mitigate primary water stress corrosion cracking (PWSCC) in reactor components at several nuclear plants. An evaluation was done on the thermodynamic analysis of the aqueous zinc system. The speciation equilibrium shows that the stability of the hydrolyzed zinc species increases with pH and temperature. Adsorption kinetics and isotherm studies were carried out to investigate the mixed resin performance of the zinc adsorption. The equilibrium isotherms of the zinc adsorption onto nuclear grade resin indicate that the data correlate well with the Langmuir model and that the adsorption is physical in nature. The maximum capacity according to the Langmuir model is about 0.6meq/g for an initial zinc concentration of 100ppm at 50°C. Based on the acceptable breakthrough points observed in the kinetic tests, the operating capacity is rated at about 0.5mEq/mL.

1. Introduction

Recently, the addition of zinc to the primary coolant of a nuclear reactor has gained a great deal of attention and been seen as an attractive option because of its effective reduction of the radiation dose rates in piping systems and the prevention of cracking in certain metallic components [1-3]. Long-live isotope Zn-65 (forming from the Zn-64) provides an additional increase in the γ -radiation dose rate. Thus, Zn-64 needs to be decreased to 1-5% in the injecting Zn isotopes and results in a cost increase for the depleted zinc compounds (depleted of ^{64}Zn) [1].

Zinc depleted in Zn-64 is usually added as an aqueous solution of zinc acetate to the primary coolant system of pressurized water nuclear reactors. The zinc concentration of coolant is controlled to about 40ppb by adjusting the zinc addition rate at a zinc feed concentration of about several hundred ppm. It has been estimated that about 70% of zinc is inevitably removed by the coolant purification system from the operational experience with a

zinc addition. Accordingly, the injection rate of the costly zinc should be higher than the removal rate on the purification mixed bed.

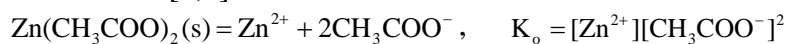
The zinc cation is readily removed from the solution by strong acid ion exchange resins such as those used in the purification demineralizers. In common with the ions of such corrosion products as cobalt, nickel and iron, zinc will be exchanged for hydrogen ions from the nuclear grade strong acid resin in the cation bed and the mixed bed. Thus, an evaluation is required for the potential effects of the zinc addition on the performance of the purification demineralizers. This evaluation is important to estimate the resin performance associated with the overall efficiency and expiration of the demineralizer resin with a zinc addition. This information is useful for use by the utilities in quantifying the potential costs and benefits of this alternative operating chemistry regime.

It is expected that aqueous zinc could form various ionic species for the range of pH and temperature when dissolved in the primary coolant. An aqueous equilibrium analysis of the dissolved zinc species is essential for this understanding.

In this work, a simple thermodynamic calculation was performed to estimate the possible reaction of the ion exchange for aqueous zinc species. The zinc adsorption on the typical mixed resin of a nuclear grade was evaluated to determine how the presence of zinc could have an adverse effect on the resin performance and expiration. Equilibrium adsorption isotherms are analyzed to obtain the Langmuir constants and the kinetic investigation at various temperature ranges is also undertaken. In addition, the generation of the ^{65}Zn activity on the demineralizer was estimated on the basis of the CVCS operating condition of the PWR.

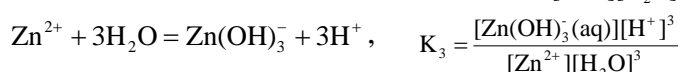
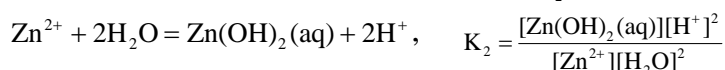
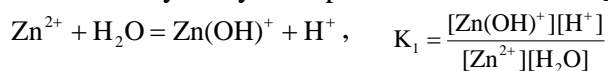
2. Dissolved Zinc Equilibrium in an Aqueous Solution

Dissolved zinc mostly forms the divalent cation Zn^{2+} when dissolved in a neutral aqueous solution and does not form complex ions except in acidic or alkaline solutions at room temperature. The basic dissolution reaction of zinc acetate in an aqueous solution can be written as follows [4,5]:



This is the solubility reaction of $\text{Zn}(\text{CH}_3\text{COO})_2(\text{s})$ to give the uncomplexed zinc ion in an aqueous solution.

Hydrolysis of the dissolved zinc ion could form zinc-hydroxyl complexes at an elevated temperature ($T > 25^\circ\text{C}$) or in an alkaline solution. The basic hydrolysis reactions of the zinc ion to form zinc-hydroxyl complexes are as follows [6]:



K_o , K_1 , K_2 , and K_3 are the equilibrium constants of the corresponding reactions. The molality of each species is assumed to be defined by the equilibrium of the relevant reactions. The existence of higher valence anions and polymer ions with other anions was also neglected.

Total charge concentration of the positive ions should be equal to that of the negative ions in the solution for the charge neutrality of the system. Total dissolved zinc concentration ($\sum[\text{Zinc}]$) is defined as the sum of the following species in an aqueous zinc acetate solution:

$$\sum[\text{Zinc}] = [\text{Zn}^{2+}] + [\text{Zn}(\text{OH})^+] + [\text{Zn}(\text{OH})_2(\text{aq})] + [\text{Zn}(\text{OH})_3^-] + [\text{Zn}(\text{CH}_3\text{COOH})_2(\text{aq})] .$$

Equilibrium constants for the hydrolysis of the zinc ion to form the zinc-hydroxyl complexes, and for the solubility reaction of $\text{Zn}(\text{CH}_3\text{COO})_2(\text{s})$ to give the uncomplexed zinc ion in a solution, were derived by Apelblat [4] and Giordano [5] in a MULTEQ-based analysis[7].

3. Experimental

The nuclear grade mixed resin of Amberlite[®] IRN150 (Rohm and Haas Co., USA) was used in this study. This mixed ion-exchange resin is generally used for the removal of radio nuclides from coolant and waste water. The physical properties and specifications of the resin as reported by the suppliers are shown in Table 1. A stock solution of 1000ppm zinc was prepared by dissolving $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (Junsei Chemical Co. Japan) in deionized water from a Barnstead triple-stage system. Adsorption isotherm and kinetic studies were carried out at elevated temperatures with different initial concentrations of zinc in an isothermal glass flask of a 2L capacity (jacketed pressure reactor of Ace Glass Inc., USA). The operation temperature range of the reactor in this work was 20-60°C. The solution of the resin dispersed was monitored by a conductivity meter (Model: PHOR-90-10V-I, Omega[®] Eng. Inc., USA) for the zinc content.

4. Results and Discussion

A calculation of the published thermodynamic data has been performed for the aqueous species described in the previous section. The speciation equilibrium for an aqueous dissolved zinc at two temperatures (20 and 60°C) with the total zinc concentration of 100ppm is shown in Fig.1. The hydrolysis of Zn^{2+} results in the form of ZnOH^+ , $\text{Zn}(\text{OH})_2(\text{aq})$ and $\text{Zn}(\text{OH})_3^-$. The zinc species related to the higher hydrolyzed zinc complexes could not be considered for the range of pH in this calculation. The trends of zinc speciation as a function of pH show that the stability of the hydrolytic zinc complexes such as ZnOH^+ and $\text{Zn}(\text{OH})_2(\text{aq})$ increase with pH and temperature even at a low total zinc concentration.

The adsorption isotherms are of fundamental importance in determining the adsorption capacity of Zn(II) onto the ion exchange resin. Results of the adsorption of zinc onto Amberlite[®] IRN150, by applying the model of Langmuir are discussed below. According to the basic assumption of the Langmuir model, the amount of zinc adsorbed can be expressed by:

$$q_e = \frac{X}{m} = \frac{Q_0 b C_e}{1 + b C_e}$$

Fig. 2 illustrates the Langmuir analysis of the experimental isotherm data at 30~60°C. The values of Q_0 and b can be calculated either by the least squares method or graphically. The maximum monomolecular capacity was found to be about 0.6meq/g for an initial zinc

concentration of 100ppm at 50°C. The adsorption is favored by a decrease in temperature, a phenomenon which is characteristic of a physical adsorption.

The selectivity of a typical mixed bed resin for the zinc cation vis-à-vis the hydrogen cation was evaluated to determine whether or not the presence of zinc would have an adverse effect on the resin performance. Fig.3 shows the effect of adsorption rate on the removal of Co(II) and Zn(II) by IRN150 mixed resins. The results of this evaluation indicated that the adsorption capacity of the mixed bed resins is essentially the same for all of the divalent transition metal cations of interest. Hence, the zinc cations will be strongly adsorbed in the same exchange zone in the demineralizer bed as the alkali earth cations such as Ca^{2+} and Mg^{2+} , and the divalent transition metal cations of the radioisotopes, such as ^{58}Co , ^{60}Co , ^{54}Mn and ^{51}Cr .

One parameter that describes the operational characteristics of an ion exchanger is the operating capacity, resulting from the effective number of the functional active groups per unit mass of the mixed resin. The theoretical value depends upon the nature of the material and the form of the resin. When the column operation mode is employed, operating capacity is usually lower than the available capacity, and depends on several operational factors such as flow rate, temperature, particle size and concentration of the feeding solution. Fig.4 graphically depicts the shapes of the dynamic capacity curves observed in the case of the same Zn concentration in the influent at different temperatures (20~60°C). An acceptable breakthrough point is observed and the operating capacity is about 0.5mEq/mL at a flow rate of 10.6mL/min.

An estimate was made of the potential effect of zinc on the resin bed usage rate of CVCS as given in Fig.5. For the demineralizer performance during the zinc addition operation, it was estimated that a mixed ion exchange bed would last for a period of time that exceeded the length of the cycle and served for the entire fuel cycle of 12 months of operation.

In addition to the effect of zinc on the demineralizer resin performance, the use of zinc results in the generation of the ^{65}Zn activity, which must be considered in waste disposal activities. The projected ^{65}Zn coolant concentration at the end of the 12 month cycle with a natural zinc addition was about 0.004 $\mu\text{Ci/mL}$. The generation of the ^{65}Zn activity on the demineralizer was estimated on the basis of the CVCS operating condition. The estimated activity of the ^{65}Zn on the mixed bed demineralizer resin was about 500 $\mu\text{Ci/mL}$ of resin after 12 months of operation with a natural zinc addition.

5. Conclusions

Thermodynamic analysis of the aqueous zinc system using reliable data shows that the stability of the hydrolyzed zinc species increases with pH and temperature. The equilibrium isotherms of zinc adsorption onto nuclear grade resin indicate that the data correlate well with the Langmuir model and that the adsorption is physical in nature. The adsorption temperature influenced the rate of adsorption. The maximum capacity according to the Langmuir model is about 0.6meq/g for an initial zinc concentration of 100ppm at 50°C. The operating capacity is about 0.5mEq/mL at a flow rate of 10.6mL/min. The use of natural zinc could result in the generation of the ^{65}Zn activity with about 500 $\mu\text{Ci/mL}$ of resin after 12 months of operation.

Acknowledgement

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Table 1 Characteristics of Amberlite® IRN150 mixed resin *

	IRN77 cation-exchange resin	IRN78 anion-exchange resin
Physical form	Uniform particle size spherical beads	
Shipping weight	800 g/L	689 g/L
Harmonic mean size	650±50 µm	630±50 µm
Matrix	Polystyrene DVB gel	
Functional groups	Sulphonic acid	Trimethylammonium
Ionic form as shipped	H ⁺	OH ⁻
Total exchange capacity	≥1.9 equiv./L (H ⁺ form)	≥1.2 equiv./L (OH ⁻ form)
Moisture holding capacity	49-55% (H ⁺ form)	54-60% (OH ⁻ form)

* Information provided by the manufacturer.

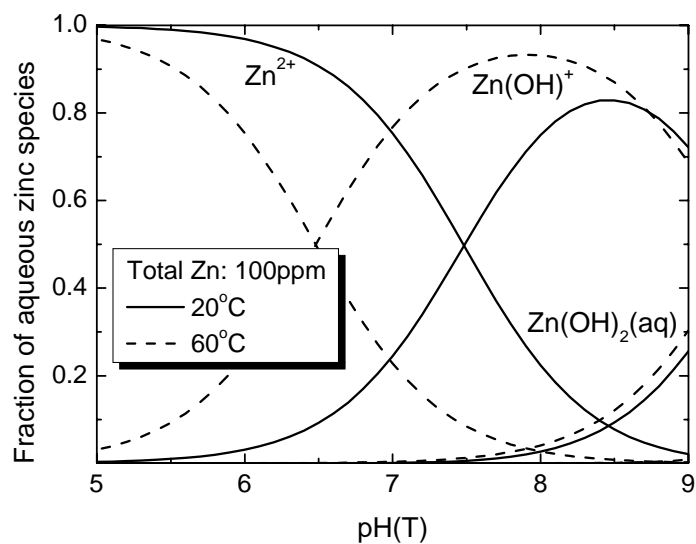


Fig.1 Aqueous equilibrium distribution of dissolved zinc species at different pH (20°C and 60°C).

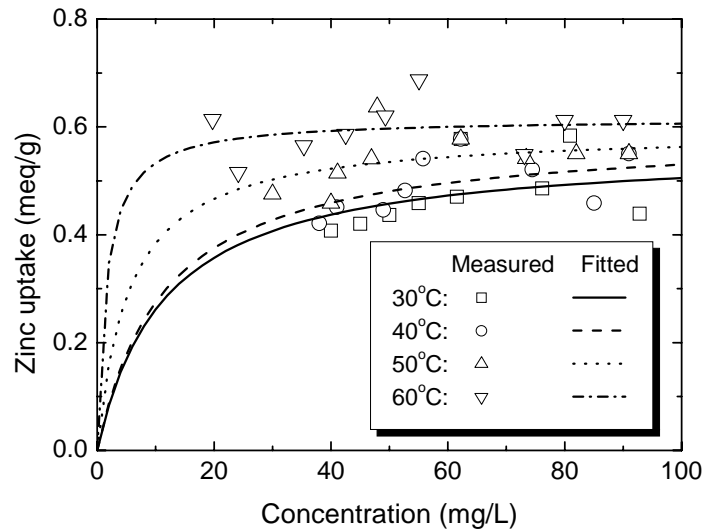


Fig.2 Langmuir equilibrium isotherm of Zn(II) onto mixed resin of IRN150 at various temperature.

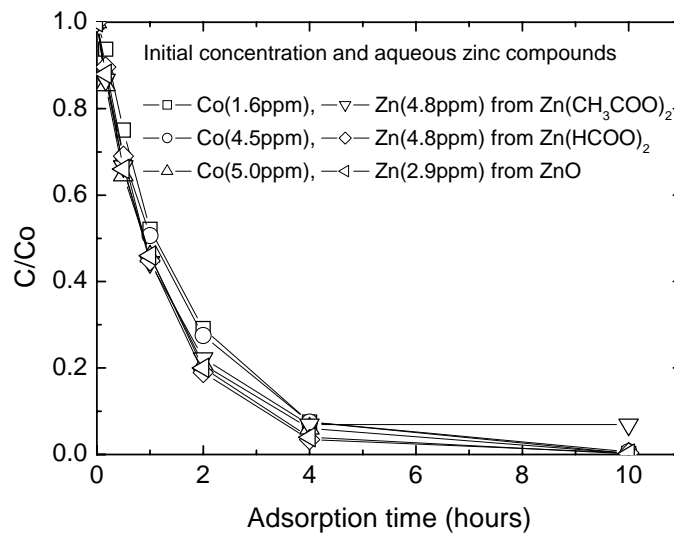


Fig.3 Adsorption rate of cobalt onto IRN 150 from aqueous zinc solution (initial concentration: 1000ppm B, 2.2ppm Li; solution volume:1.5L; adsorbent amount: 1.5g, solution temp.:25°C).

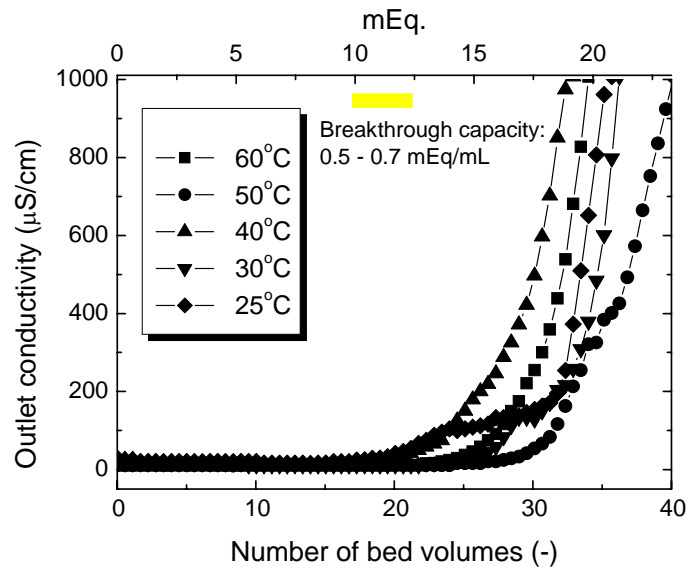


Fig.4 Dynamic capacity measurements for Zn(II) adsorption onto mixed resin of IRN150 at various temperature.

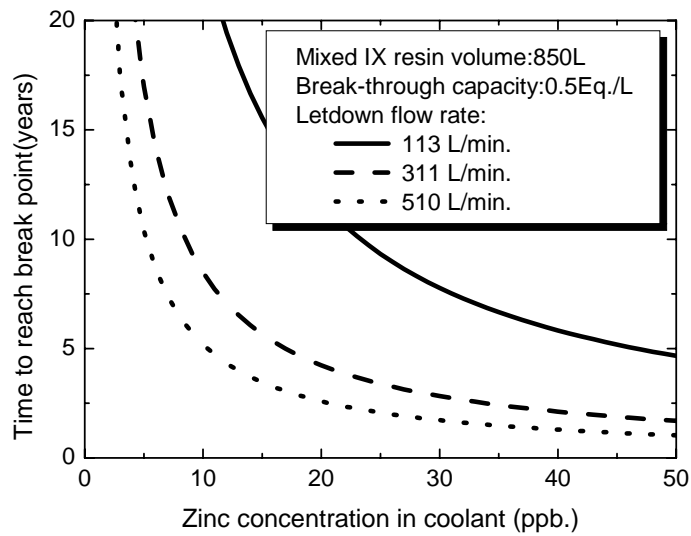


Fig.5 Time to reach break-point vs. coolant zinc concentration.