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Potential–temperature (*E*–*T*) diagrams for iron, nickel, and chromium in sulfate solutions up to 473 K

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ABSTRACT

The electrochemical corrosion behavior of high purity iron, nickel, and chromium is evaluated in sodium sulfate solutions at temperatures up to 473 K. The thermodynamic stability regions of the species involved in the X—H_2O system (X = Fe, Ni, Cr) were evaluated. The stability regions were presented in a new form of potential vs. temperature diagrams in specific solutions rather than conventional *E*–pH diagrams. The open circuit potential and polarization resistance experiment data were used to demonstrate the viability and usefulness of the newly developed diagrams.

1. Introduction

The potential–pH diagrams known as Pourbaix diagrams are widely used to predict the thermodynamic stability of a metal—H_2O system in various conditions of solution oxidizing power and proton concentration. They were originally developed at room temperature where the most available and reliable thermodynamic measurements are available. The diagrams present a concise presentation of the stability regions of metal at a wide range of pH and potential. They are also constructed in various environments relevant to for example LiBr absorption refrigerators [1,2], leaching solutions [3], Sulfite reducing agent [4] and iron phenanthroline complexes [5]. The other field of expansion is the consideration of adsorbed species and developing the Pourbaix diagrams for the adsorbed species [6–10]. These diagrams have become so popular that some studies were focused on development of computerized methods for construction of diagrams [11,12].

As more aqueous processes were developed at higher temperatures, the diagrams were generated at higher temperature and pressures [13,14]. These diagrams were utilized to predict the corrosion in high temperature high pressure systems like geothermal brines [15]. These high temperature *E*–pH diagrams are particularly developed up to 573 K for Fe [16,17], Cr [18,19], Ni [20–22], S [23,24], Pt [19], Ti [19], Mo [19], Co [25] and Zn [26]. There are also attempts to develop the diagrams at supercritical conditions [27–29]. Furthermore, there have been attempts to develop multi component Pourbaix diagrams [30–37]. The methods of development of such diagrams are similar to room temperature with the exception of the calculation of the thermodynamic data at higher temperatures and the assessment of stability of new phases as temperature increases. The thermodynamic data were historically extrapolated using the Criss–Cobble model [38,39], applicable typically up to 473 K, and more recently using the HKF model with a significantly higher range of applicability [40]. New phases become more stable at higher temperatures. For example, oxides are generally more stable than hydroxides at high temperatures and they are usually considered at high temperatures [41]. The measurement of potential and pH at high temperatures is more challenging. The dissociation constant of water, in particular, is highly temperature dependant so the neutral pH position is conventionally marked on high temperature diagrams to address the significance of the pH at a given temperature.

There have been some attempts to modify the E–pH diagrams to better demonstrate the relationship between process parameters. For example, Subrata Roy et al. [42] developed a thermo-kinetic *E*–pH diagram. Nila and Gonzalez developed the "Pourbaix-type" E-pCl diagrams for the copper leaching system [3] Jung incorporated the effects of microstructure on the stability lines [43] and Mohr and McNeil developed modified log-activity diagrams which could be incorporated with Pourbaix diagrams [44].

The high temperature, high pressure aqueous systems are a closed loop in a number of processes, such as the cooling system of the supercritical water reactor. Therefore, the solution has a fixed analytical composition and is subjected to temperature variation during the process. In the particular case of the supercritical water reactor coolant, it consists of pure water and could

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have varying electrochemical potential due to water radiolysis [45]. Since the pH of closed loop processes can be readily calculated, development of the potential–temperature diagrams instead of potential–pH diagrams at given analytical composition is possible. It may more conveniently present the effect of temperature on metal–water equilibria. It should be noted that such diagrams are not simply the projection of E–pH–T diagrams on the E–T plane, as the pH is not an independent variable and is itself a function of temperature.

The aim of this paper is to develop such diagrams for iron, nickel, and chromium, as the most involved elements in material selection for the cooling system of supercritical water reactor. Experimental measurements of potential and corrosion rate up to 473 K were performed to compare with the E–T diagrams.

2. Experimental

A 1.8 L autoclave with titanium alloy internal lining was used for the electrochemical tests. A glass liner contained the solution. The autoclave is controlled with a PARR 4843 controller system. The accuracy of the temperature and pressure reading is ±2 K and 42 psi, respectively. The solution was purged with argon for 0.5 h in the glass liner before starting the test while the oxygen content of the solution was being checked with a dissolved oxygen sensor (Omega DOB21 accuracy 12 ppb) to confirm the oxygen-free solution. Afterwards, the autoclave was sealed and heated to the set temperature.

The working and counter electrodes were connected to copper wires with a high temperature silver paste. Then the wires were passed through alumina tubing. The whole assembly was then mounted using a high temperature epoxy (MG Chemical 832HT, maximum operating temperature 523 K) along with an appropriate fitting (Swagelok). The fitting was used to assemble the electrodes on a titanium shaft passing through the lid of the autoclave.

An external pressure balanced Ag/AgCl ($[Cl^-] = 1$ M) electrode was used as the reference electrode. The details of construction of the reference electrode and the characterization of the measured potential are published in Ref. [45]. The reference electrode bridge, subjected to a temperature gradient, is designed to be filled with the test solution. Therefore, the thermal junction and liquid junction potential calculations were performed, relevant to the solutions used in this work. All the potentials reported in the following are versus the standard hydrogen electrode at the operating temperature (vs. SHE_T).

The working electrodes were wires of iron (Alfa Aesar, 99.995%, $D = 1$ mm), nickel (Alfa Aesar, 99.995%, $D = 1$ mm), and chromium (American Elements, 99.9%, $D = 2$ mm). The counter electrode was platinum foil with an area of 12 cm^2. The platinum surface was prepared by degreasing in ethyl alcohol + acetone for 5 min, cleaning in an HNO_3 + HCl mixture (ratio 3:1), and rinsing with deionized water. Surface preparation of wires consisted of grinding up to 600 SiC emery paper, degreasing with ethyl alcohol + acetone, pickling in 10% sulfuric acid, and rinsing with deionized water. The test solutions consisted of 0.25 M sodium sulfate solution as the background electrolyte, and 10^{-4} M hydrogen peroxide which was added to the solution after argon purging. Hydrogen peroxide was added to the solution to simulate the water radiolysis. Sodium hydroxide or sulfuric acid was added to the solution to change the pH. The electrolyte compositions are presented in Table 1.

A Princeton Applied Research (PAR) Versastat 4 potentiostat/galvanostat was used for all the electrochemical measurements. The electrochemical behavior of the elements was evaluated by the OCP and linear polarization resistance (LPR) method. The OCP was measured for 0.5 h before the LPR test. The LPR was measured at OCP ±20 mV with a scan rate of 0.167 mV/s.

Table 1
The composition of the solutions.

Name	$[Na_2SO_4]$ (M)	$[H_2O_2]$ (M)	$[H_2SO_4]$ (M)	[NaOH] (M)
Solution I	0.25	1e−4	5e−3	0
Solution II	0.25	1e−4	5e−5	0
Solution III	0.25	1e−4	5e−7	0
Solution IV	0.25	1e−4	0	1e−6
Solution V	0.25	1e−4	0	1e−4
Solution VI	0.25	1e−4	0	1e−2

3. Results and discussion

3.1. The pH–temperature relation

The diagrams are developed for sodium sulfate solutions for experimental validation and for pure water relevant to the cooling system of the supercritical water reactor. The sodium sulfate solutions contain varying amount of sulfuric acid or sodium hydroxide to cover a wide range of proton concentration. The first step is to calculate the dependency of pH on temperature. Reactions (1)–(4) were considered in acidic and alkaline solutions. The concentration of hydrogen peroxide is low compared to the other species, it does not affect the pH to a large extent and therefore was not taken into account [52].

$$H_2SO_4 = HSO_4{}^- + H^+ \tag{1}$$

$$HSO_4{}^- = SO_4{}^{2-} + H^+ \tag{2}$$

$$H_2O = H^+ + OH^- \tag{3}$$

$$NaOH = Na^+ + OH^- \tag{4}$$

The equilibrium point in acidic solutions (solutions I, II, and III in Table 1) is calculated based on the following:

$$\frac{[H^+][HSO_4{}^-]}{[H_2SO_4]} = K_1 = \infty \tag{5}$$

$$\frac{[H^+][SO_4{}^{2-}]}{[HSO_4{}^-]} = K_2 \tag{6}$$

$$[H^+][OH^-] = K_w \tag{7}$$

Given the analytical composition of the solution as:

$$C_{Na_2SO_4} = a, \quad C_{H_2SO_4} = b$$

The mass balance for sulfur and electron balance are:

$$a + b = [SO_4{}^{2-}] + [HSO_4{}^-] \tag{8}$$

$$2a + [H^+] = [OH^-] + [HSO_4{}^-] + 2[SO_4{}^{2-}] \tag{9}$$

The concentration of the proton is finally calculated as:

$$[H^+]^3 + (a - b + K_2)[H^+]^2 - (K_w + 2K_2 b)[H^+] - K_w K_2 = 0 \tag{10}$$

The equilibrium point in the alkaline solutions (solutions IV, V, and VI in Table 1) is calculated based on the following:

$$\frac{[Na^+][OH^-]}{[NaOH]} = K_3 \tag{11}$$

Given the analytical composition of the solution as:

$$C_{Na_2SO_4} = a, \quad C_{NaOH} = c$$

The mass balance for sodium and electron balance are:

$$2a + c = [Na^+] + [NaOH] \tag{12}$$