



Original Article

Evaluation of dissolution characteristics of magnetite in an inorganic acidic solution for the PHWR system decontamination

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ABSTRACT

A protective oxide layer forms on the material surfaces of a Nuclear Power Plant during operation due to high temperature. These oxides can host radionuclides, the activated corrosion products of fission products, resulting in decommissioning workers' exposure. These deposited oxides are iron oxides such as Fe₃O₄, Fe₂O₃ and mixed ferrites such as nickel ferrites, chromium ferrites, and cobalt ferrites. Developing a new chemical decontamination technology for domestic CANDU-type reactors is challenging due to variations in oxide compositions from different structural materials in a Pressurized Water Reactor (PWR) system. The Korea Atomic Energy Research Institute (KAERI) has already developed a chemical decontamination process for PWRs called 'HyBRID' (Hydrazine-Based Reductive metal Ion Decontamination) that does not use organic acids or organic chelating agents at all. As the first step to developing a new chemical decontamination technology for the Pressurized Heavy Water Reactor (PHWR) system, we investigated magnetite dissolution behaviors in various HyBRID inorganic acidic solutions to assess their applicability to the PHWR reactor system, which forms a thicker oxide film.

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1. Introduction

The chemical decontamination of nuclear power plants (NPPs) should be performed to remove deposited oxide film from the outer core surfaces [1]. Austenitic steels are used in Pressurized Water Reactors (PWRs) because of their corrosion resistance, and stainless steel, Inconel, and carbon steels are also widely used in the construction of PWR and Pressurized Heavy Water Reactor (PHWR) systems. Zirconium-based zircaloy is also used in the coolant system of a nuclear power plant. Several metal oxides, including magnetite, nickel ferrite, and chromite, can be deposited on the surfaces of structures like pipes and other equipment, especially when they come into contact with the reactor coolant [2]. Of the various metal oxides formed in NPPs, magnetite is one of the major corrosion products. Magnetite is formed under high temperature (>270°C) and pressure (around 16 MPa) on the surfaces of the reactor coolant system. These deposited oxides are generally oxides of iron such as Fe₃O₄, Fe₂O₃ and mixed ferrites such as nickel

ferrites, chromium ferrites, and cobalt ferrites. This oxide layer also acts as a host for radioactive isotopes such as ⁶⁰Co or ⁵⁸Co [3]. Many previous studies have shown that thick magnetite layers can form during operation. In Pressurized Heavy Water Reactors (PHWRs), the typical thickness of oxide layer film on stainless steel (SS) surface is 2–3 μm, but on carbon steel surfaces, it is about 75 μm. The primary heat transport (PHT) system of a 220 MWe PHWR, such as the Douglas Point NPP, has formed very thick magnetite oxide layers of 30–35 mg/cm². Based on a report of decontamination in Maine Yankee, the concentration of Fe ions contained in 3 μm thickness of iron oxide layer in the PWR was around 50 ppm, and from this result, it can be calculated that the Fe₃O₄ concentration in a PHWR of 75 μm thickness is 1250 ppm [4].

Decontamination of NPPs should be conducted for systems that have been contaminated by activity build-up due to operating time [5]. The contamination should be removed to reduce the occupational exposure of workers and reduce waste generation and waste management costs at the time of decommissioning. Thermal and mechanical decontamination techniques have been proposed in the framework of radioactive waste management research and development programs [6]. Chemical decontamination is needed to dissolve the oxide layer. However, organic acids widely used as a

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strong decontamination reagent can achieve a faster dissolution rate [7]. Some chelating agents have also been used to improve oxide layer dissolution. To remove all the radioactive species from the target surface, dissolution of the metal oxide corrosion up to the boundary layer of the oxide and the base metal is required.

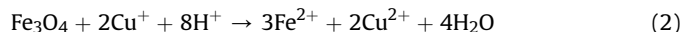
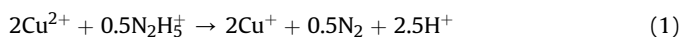
The dissolution of metal oxides in aqueous acidic solutions is mainly controlled by the protonation of the metal oxides [8]. The most critical factor determining the dissolution rates of metal oxides is the ability of the metal-oxygen bonds. The metal-oxygen bond helps to release metal ions from the oxide lattices and reduces the effects of radiation on the dissolution kinetics of magnetite and hematite in ethylenediaminetetraacetic acid (EDTA)-based and nitrilotriacetic acid (NTA)-based dilute decontamination formulations [9].

Several reductive decontamination processes, including CANDEREM, CITROX, LOMI, CORD, etc., are widely used as decontamination solutions to dissolve oxide layers from reactor coolant systems. These decontamination solutions have shown high performance in magnetite dissolution. Still, they are composed of acidic reagents such as citric acid [10], oxalic acid [11], and several chelating agents, etc. which result in vast amounts of secondary waste and affect disposal safety because they form stable complexes with radionuclides. These organic compounds also increase the probability of radioactive contamination of groundwater, and oxalic acid can cause a severe intergranular attack (IGA) of stainless steel (SUS304). Therefore, to keep the environment safe and clean, the use of organic acids for chemical decontamination must be reduced.

Korea Atomic Energy Research Institute (KAERI) has developed a chemical decontamination process called the Hydrazine Based Reductive metal Ion Decontamination (HyBRID) process, without using organic acids or chelating agents at all. In this process, the solution contains hydrazine (N_2H_4), sulfuric acid (H_2SO_4), and copper sulfate ($CuSO_4$), which helps to provide the acidic and reductive dissolution reactions needed to dissolve metal oxides like magnetite [12]. The HyBRID solution was originally developed to dissolve metal oxides formed on the surfaces of reactor coolant systems in PWR-type reactors [13]. The typical HyBRID solution can dissolve up to 1000 ppm of magnetite after 24 h (shown in the results and discussion part). As already discussed, the oxide layer deposited in PHWR is thicker than in PWR. This study aims to develop an advanced HyBRID process for the chemical decontamination of PHWRs based on the typical HyBRID process. In this study, we conducted many experimental tests to determine the most efficient and optimal conditions for magnetite dissolution by enhancing the dissolution rate. In particular, we could dissolve oxide films of 75 μm thickness from a PHWR reactor system. Also, we evaluated the dissolution capability of $N_2H_4/H^+/Cu^+$ on magnetite. Experimental approaches were based on (1) a parametric study of all concentrations of all the chemical reagents and a kinetic study of magnetite dissolution and (2) checking the experimenter's conditions, like pH.

2. Mechanism of magnetite dissolution in the HyBRID solution

Magnetite has an inverse spinel structure, and the octahedral sites are occupied by equal numbers of Fe^{3+} and Fe^{2+} atoms, while the tetrahedral sites are occupied exclusively by the smaller Fe^{3+} atoms. The oxidation of magnetite can proceed along several reaction pathways. The dissolution reactions of magnetite in an aqueous solution of hydrazine, sulfuric acid, and $CuSO_4$ (50 mM $N_2H_4/0.5$ mM $CuSO_4/28$ mM H_2SO_4) are:



From these equations, it can be easily observed that hydrazine plays an essential role in the acidic-reductive dissolution and participates in the reaction pathway of the Fe^{3+} reduction to Fe^{2+} ions. The HyBRID decontamination solution consists of hydrazine (N_2H_4) as a reducing agent, sulfuric acid (H_2SO_4) to maintain the pH of 2.6 (± 0.05), and copper sulfate ($CuSO_4$) as a catalyst. We conducted parametric studies for magnetite dissolution with the HyBRID solution in this work. These chemical agents provide acidic and reductive dissolution of metal ions of metal oxides such as magnetite [2]. In the solution, hydrazine binds with copper ions and forms a copper-hydrazine complex which transfers electrons from the cuprous ion (Cu^+) to the ferric ion (Fe^{3+}) and reduces it to a ferrous ion (Fe^{2+}) [13]. Previous studies by our research group have investigated the process of reducing Cu^{2+} ions to Cu^+ ions by hydrazine [12,14]. The Cu^+ ion is oxidized to Cu^{2+} by reducing the metal oxide, and this Cu^{2+} ion is reduced again to a Cu^+ ion, completing the redox cycle.

3. Experimental

3.1. Dissolution characteristics in relation to the initial concentration of magnetite

The chemicals used in the HyBRID solutions were hydrazine monohydrate ($N_2H_4 \cdot H_2O$, 80%, Junsei chemical, extra pure reagent), sulfuric acid (H_2SO_4 , Showa, guaranteed extra pure reagent), copper (II) sulfate ($CuSO_4$, 97.5%, Junsei chemical, extra pure), and magnetite powder (Fe_3O_4 , Junsei chemical >99%). All of the experimental solutions were made in demineralized water. Experiments on magnetite dissolution were performed using the solution in a stirred batch glass reactor. Since hydrazine is basic, H_2SO_4 was used to reach a 2.6 (± 0.05) pH to prepare an acidic HyBRID solution. The typical HyBRID solution usually contained 50 mM of hydrazine and 0.5 mM of Cu ions.

To understand the behavior of magnetite dissolution with time, the initial amount of magnetite was changed in relation to the concentration of hydrazine and Cu ions. In all experiments, magnetite was varied from 0.5–2.5 g/l (360 ppm–1800 ppm, as Fe ions). Hydrazine monohydrate was used as the primary dissolution agent and was varied from 50–100 mM. Magnetite powder was added to 250 ml of distilled water in a stirred batch glass reactor, and the solution was heated to 95°C with a rotation speed of 500 rpm. Hydrazine was then added to that solution after the temperature reached 95°C, and sulfuric acid was added to that solution to reach a pH of 2.6 (± 0.05). All of the prepared solutions were tightly closed. Periodic samples were taken with a syringe and then filtered through a 0.2 μm pore filter during the entire experimental period, and the dissolved concentration of Fe ion in the solution was analyzed by atomic absorption spectrophotometer (AAAnalyst 400, PerkinElmer). The changes in pH and hydrazine concentration with time were checked for the reaction mechanism study. Several thermodynamical calculations have been done using the HSC Chemistry program (HSC Chemistry is a product of Outokumpu Research (ORC)).

3.2. Magnetite dissolution characteristics according to the concentration of hydrazine

Hydrazine is a strong reductive reagent. In this dissolution study, we used hydrazine concentrations from 50–100 mM H_2SO_4 was added to the solution to reach a pH of 2.6 (± 0.05). The dissolution rate of magnetite in the solution with changing concentrations of hydrazine and copper was observed over time through

periodic sampling. The changes in hydrazine concentration over time were also observed and measured by UV-spectrophotometer. Table 1 lists the experimental conditions of this study. The effect of temperature on dissolution was also observed in this paper.

3.3. Magnetite dissolution characteristics according to the concentration of copper

It was determined that copper ions in the HyBRID solution act as a catalyst and play an essential role in enhancing magnetite dissolution. The typical HyBRID solution usually contains 0.5 mM of Cu ions. This study attempted to establish a more effective Cu ion concentration for magnetite dissolution. In this series of experiments, Cu ions were added to the solution at concentrations from 0 to 10 mM. The dissolution rate of magnetite in the solution was observed in relation to changes in Cu concentration in the solution. The change in Cu concentration with time were also observed using an atomic absorption spectrophotometer (AAAnalyst 400, PerkinElmer).

3.4. Magnetite dissolution characteristics according to pH

To determine the effects of pH on magnetite dissolution, different solution pH was checked to optimize the condition for good magnetite dissolution.

3.5. Magnetite dissolution characteristics according to temperature

To determine the effect of temperature on magnetite dissolution, tests were conducted at four different temperatures. This test has been conducted to calculate the activation energy using the Arrhenius equation.

4. Results and discussion

4.1. Dissolution of magnetite in the solution

The magnetite dissolution test was conducted in the HyBRID solution to evaluate the dissolution behaviors based on the initial input amount of magnetite in each stirred batch reactor. The initial amount of magnetite used for dissolutions varied from 0.5–2.5 g/l. Fig. 1 shows the dissolved concentration of magnetite with the changes in the initial amount of magnetite in the solution. Fig. 1(a) shows that the maximum amount of magnetite dissolved in the solution was about 1000 ppm in a typical HyBRID solution. Fig. 1(b) shows that the dissolved fraction of magnetite increased with the initial amount of magnetite. Fig. 1(b) shows that all magnetite was dissolved within 9 h when the initial amounts of magnetite were 0.5 g/l and 0.624 g/l in the typical HyBRID solution, which consisted of 50 mM N₂H₄ and 0.5 mM of Cu. At 1.25 g/l, 90% of the magnetite was dissolved after 24 h. However, the fraction of dissolution dropped to 65% when the initial amount of magnetite was increased to 2.5 g/l.

The results of this experimental test indicate the solution was not sufficient to meet the target capacity of dissolving a thick oxide

up to 75 μm (1250 ppm) for the decontamination of PHWRs. To improve this dissolution limit in a typical HyBRID solution, we needed a further experimental study to investigate which parameters were the most effective for magnetite dissolution.

4.2. Parametric study for improving HyBRID solution

As shown in Fig. 1 typical HyBRID solution could only dissolve 1000 ppm of magnetite in 24 h. To decontaminate a PHWR system, it would need to dissolve 1250 ppm of magnetite at least. One dissolution test cycle is 4–6 h. To dissolve 1250 ppm of magnetite using this HyBRID solution, 6–7 cycles are needed. To improve the dissolution limit of the typical HyBRID solution, we performed experimental tests to screen the most efficient parameters for magnetite dissolution.

4.2.1. Effect of hydrazine on the dissolution of magnetite

Hydrazine acts as a strong reducing agent. When liquid hydrazine is added to the solution, it is readily protonated to produce hydrazinium ions (N₂H₅⁺) that reduce Fe³⁺ ions to Fe²⁺ ions. To improve the dissolution performance of the HyBRID solution, it is necessary to understand the behavior of hydrazine in magnetite dissolution. Fig. 2 shows the concentration of the dissolved magnetite with different concentrations of hydrazine. Fig. 2(a) shows that more magnetite dissolved in the solution when the hydrazine concentration was increased from 25 mM to 50 mM. However, the dissolution was almost the same at higher concentrations of hydrazine (50 mM, 75 mM, 100 mM N₂H₄). Fig. 2(b) shows that the dissolved fractions of magnetite after 6 h were between 56% and 59%, with a higher concentration, 50 mM, of hydrazine. The results showed slight differences in magnetite dissolution when the hydrazine concentration was varied from 50 mM to 100 mM of hydrazine.

The dominant species of hydrazine in acidic solutions is the hydrazinium ion, and oxidation of the hydrazinium ion takes place in the solution. Nitrogen is also produced further [15]. The N–N bond of hydrazine breaks first, then each NH₂ fragment dehydrogenates and forms N₂ and H₂ molecules (Fig. 3).



In a hydrazine solution by itself, the dissolution of magnetite is not very significant compared to a solution with H₂SO₄. The dominant species in hydrazine is the hydrazinium ion, N₂H₅⁺. The oxidation of the hydrazinium ion and further to nitrogen in the solution takes place in the presence of half-cell reduction reaction, which has been described in equation (3) to equation (6) [15]. Reactions (3) and (4) show that the electron transfer from the

Table 1
Experimental conditions.

Fe ₃ O ₄ conc.(g/l)	Cu conc.(mM)	N ₂ H ₄ conc. (mM)	pH	Temperature
0.5–2.5	0.5	50	±2.5 (adjusted by H ₂ SO ₄)	95°C
1.87	0.5	25–100		
1.87	0–10	50		
1.87	10	50	3.0, 2.5, 2.0 (adjusted by H ₂ SO ₄)	
1.87	10	50	±2.5 (adjusted by H ₂ SO ₄)	70°C, 80°C, 90°C, 95°C

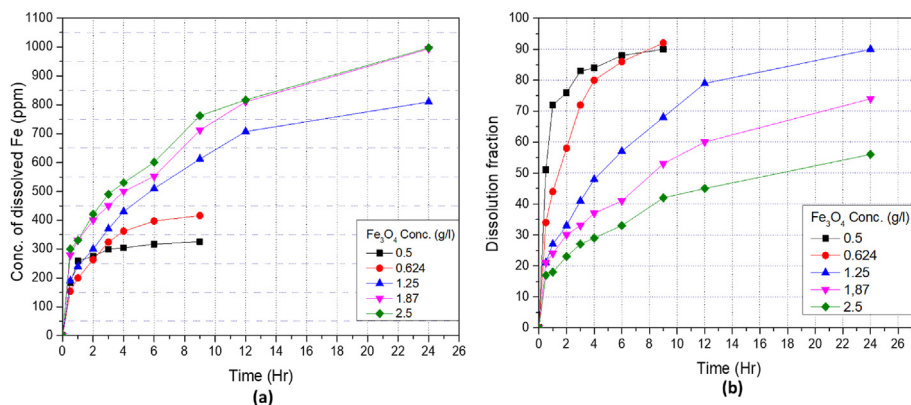


Fig. 1. Dissolution behavior of magnetite with 50 mM of hydrazine hydrate, according to the initial concentration of magnetite, when the concentration of Cu was 0.5 mM, pH = 2.5, T = 95°C (a) Concentration of dissolved magnetite in solution, (b) Dissolution fraction of magnetite.

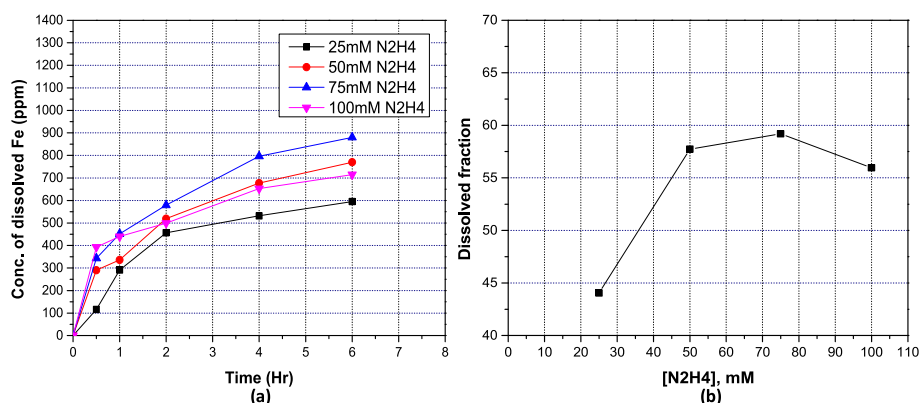


Fig. 2. Dissolution behavior of magnetite with different concentrations of hydrazine, when the concentration of Cu was 0.5 mM, the initial concentration of Fe was 1350 ppm (1.87 g/l), pH = 2.5, T = 95°C (a) Conc. of dissolved magnetite with time, (b) Dissolved fraction of magnetite with different concentrations of hydrazine after 6 h.

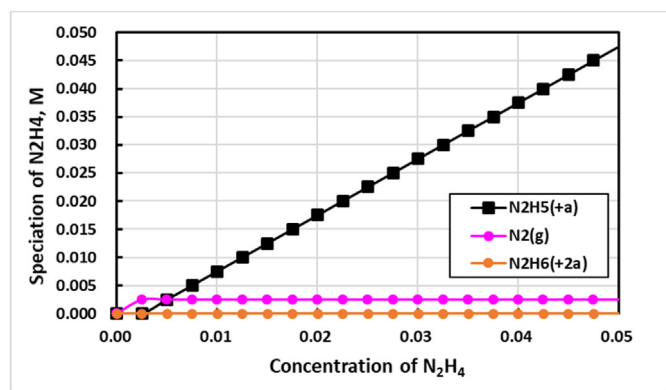
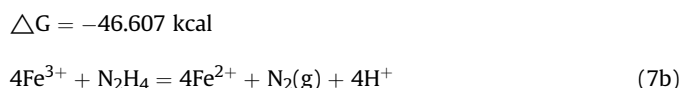
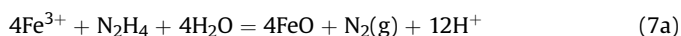


Fig. 3. Changes in hydrazine with the concentration of hydrazine produced by HSC chemical modelling.

hydrazinium ion and the overall reaction rate is a bit slow and limited, but further electron transfer process goes faster [16].

In the presence of a higher amount of hydrazine (>60 mM), there is a plausible formation of FeO in the solution, which is the reason for the lower dissolution of magnetite, as shown in Fig. 2(a) and (b).



$$\Delta G = -119.637 \text{ kcal}$$

To confirm the formation of FeO in the presence of high amounts of hydrazine, a chemical equilibrium modeling study was

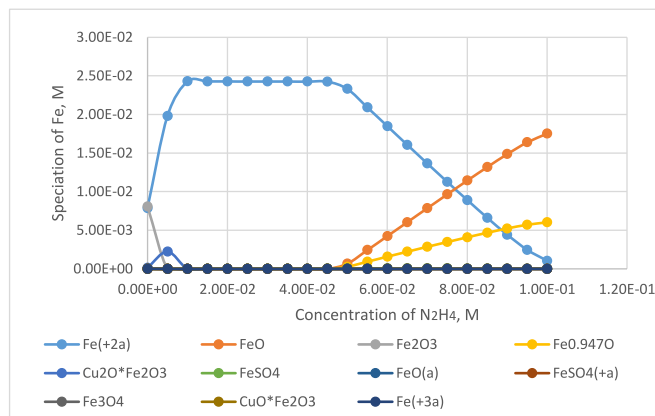


Fig. 4. Formation of Fe species with the concentration of hydrazine produced by HSC chemical modelling.

conducted using HSC chemistry, as shown in Fig. 4. Fig. 4 provides a speciation profile of ferric oxide and copper oxide in relation to changes in the hydrazine in the solution. FeO is not formed, and most of it exists as Fe²⁺ when the concentration of N₂H₄ is low (<60 mM). Because the Gibbs free energy is much lower in reaction (7b), it can occur more easily than the reaction in (7a). However, the Fe²⁺ decreased by over 50 mM N₂H₄ while the FeO gradually increased because the reductive reactions between 7a and 7b were competitive. As a result, Fe²⁺ and FeO were considered to form in a higher concentration N₂H₄ condition (>50 mM).

4.2.2. Effect of copper on the dissolution of magnetite

Copper acts as a catalyst in the solution, and it helps accelerate the dissolution rate of magnetite. The bond between the Cu⁺ ion and hydrazine can facilitate an electron transfer from the Cu⁺ ion to the Fe³⁺ of magnetite. Previous studies on the HyBRID decontamination process have reported that the Cu⁺/Cu²⁺ ion acts as a redox couple. The characteristics of Cu⁺/Cu²⁺ ion pairs as redox media and the reduction of depositions by Cu²⁺ ions have also been investigated [17,18]. The reduction of Cu²⁺ ions oxidized by reacting with Fe²⁺ to Cu⁺ is effective for the further oxidation of hydrazine.

Fig. 5(a) and (b) show that the higher the concentration of Cu²⁺ ions, the faster the rate of magnetite dissolution. Experiments were then conducted in solutions with two different pH. In both solutions, around 7% of magnetite was dissolved in 9 h when there were no Cu ions in the solution. It has been evaluated from the observation that the magnetite dissolved above 1000 ppm after 9 h when Cu ion concentration ranges from 1.0 mM to 5.0 mM. For the 10 mM Cu ion concentration, the rate of magnetite dissolution in the earlier stage was very high compared to other cases.

Fig. 5(c) and (d) show that the 10 mM concentration of Cu²⁺ ion in the solution could dissolve up to 89% and 75% of magnetite within 30 min in two different pH conditions. Compared to the dissolution result without Cu²⁺ ions, increasing the amount of Cu²⁺ in the solution increased the dissolution rate. In addition, a possible explanation for the Cu effect on dissolution is that Cu⁺ ions are reduced from Cu²⁺ ions by the hydrazine oxidation process since

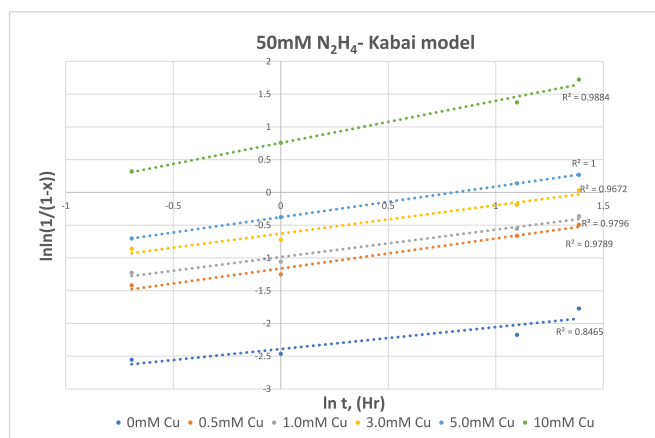


Fig. 6. Kabai fits for the dissolution of magnetite against dissolution time at different Cu ion concentrations in solution.

hydrazine plays a vital role in reducing Fe³⁺ ions into soluble Fe²⁺ ions. The hydrazine oxidation process also produces hydrogen ions and electrons, accelerating the Fe dissolution rate.

The effect of Cu ions on magnetite dissolution in Fig. 5 was investigated to build a reaction-rate model. The kinetic equations derived using the unreacted shrinking core model for magnetite dissolution were initially applied by assuming a spherical magnetite particle. However, the shrinking core model did not fit the magnetite dissolution data in Fig. 5. Thus, the Kabai model [19], which many studies have tried, was applied to explain the kinetics of magnetite dissolution [20]. The Kabai model (Eq (8)), which is either diffusion or surface controlled, was generally presented by Weibull and is derived from the Nernst equation [21].

$$\ln \ln \left(\frac{1}{1-x} \right) = a \ln k + a \ln t \tag{8}$$

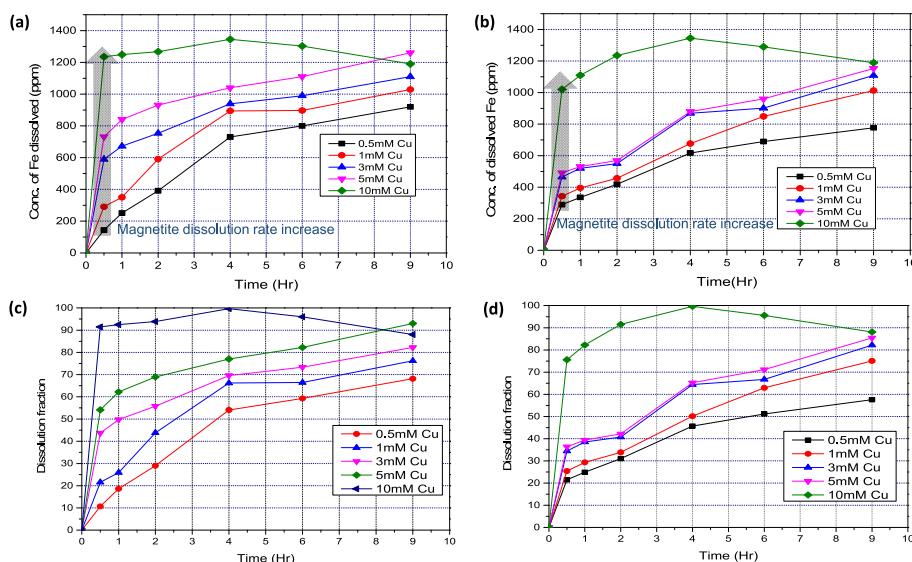


Fig. 5. Dissolution behavior of magnetite with 50 mM of hydrazine hydrate, according to the concentration of Cu ions, T = 95°C, initial amount of magnetite = 1.87 g/l (1,350 ppm) (a) Conc. of dissolved magnetite with time, when solution pH was 2.0, (b) Conc. of dissolved magnetite with time, when solution pH was 2.5, (c) Dissolved fraction of magnetite with time, when solution pH was 2.0, (d) Dissolved fraction of magnetite with time, when solution pH was 2.5.

The kinetics can be considered either diffusion or surface controlled depending on the constant a of the overall dissolution. A plot of this equation against time is presented in the following graph (Fig. 6), and in the result, a straight line with a slope of k (s^{-1}) has appeared.

The dissolution data in Fig. 5 were linearized with the Kabai model as plotted in Fig. 6, and the regression coefficient (R^2) values according to Cu ion concentrations are listed in Table 2. A plot of this equation against time was done in the following graph. As a result, a straight line with a slope k (s^{-1}) appeared. As discussed and shown previously, the high dissolution behavior of magnetite appears when the Cu concentration is high in the solution, Fig. 7 shows the reaction rate according to the concentration of Cu in the solution. The observation explained that the exponential increase of the reaction rate happened over changes of copper in the solution. The rate-determining step of the reaction can be discussed based on the solid specific constant a , as we discussed before (Eq (8)). In all of these cases, according to Cu concentration $a < 1$, that has declared that dissolution mechanism is called rounding off or spherulization. The solid is assumed to be in the lowest energy state at this point, and the background is similar to other diffusion-controlled models for spherical particles. Moreover, the table showed a good coefficient value for all conditions, which proved that the Kabai equation fit well to describe the kinetics of magnetite dissolution in the HyBRID solution.

Fig. 5(a) and (b) showed that all magnetites initially added to the solution were dissolved entirely in 4 h with 10 mM Cu ions. N_2H_4 was fully decomposed to dissolve the Fe^{3+} ion. N_2H_4 was gradually reduced depending on the reaction time, and the presence of hydrazine in the solution reached almost zero (~50 ppm), as plotted in Fig. 8(a). The remaining Fe^{3+} in the solution formed Fe_2O_3 due to the absence of hydrazine, and the solution became reddish color with hematite formation. The image of solution color changes after the complete dissolution of magnetite is shown in supplementary data [S1].

Fig. 8(b) shows changes in the solution pH with time. The pH increased from pH = 2.5 to 3.4 in 30 min at the earlier stage of the dissolution test and then slowly decreased over time. The pH increase of the solution was considered that the concentration of hydronium ion is less, so the reaction is acid-dominant, with time, H^+ ions dissociate from H_2SO_4 and form hydronium ions by forming a bond with water [H^+ (from acid) + $H_2O \rightarrow H_3O^+$ (hydronium ion)], as H^+ ions cannot exist alone. Also, with the oxidation of the hydrazinium ion (equation (2)), the concentration of H^+ increases in the solution with reaction time. A larger hydronium ion concentration simply means that the acid is more dissociated in the solution. The acidity of solution is inversely related to its pH. With the increase of hydronium ion concentrations, the solution becomes more acidic and as a result, the pH of the solution decreases simultaneously.

Magnetite sometimes produces maghematite (γFe_2O_3), a metastable spinel polymorph of hematite [22].

Table 2

Parameters for the Kabai model for different Cu ion concentrations in solution. The experiments were conducted at 95°C.

Cu concentration	k, s^{-1}	a	R^2
No Cu	6.374×10^{-4}	0.335	0.85
0.5 mM Cu	0.06521	0.458	0.98
1.0 mM Cu	0.08	0.418	0.98
3.0 mM Cu	0.2019	0.432	0.97
5.0 mM Cu	0.447	0.468	1
10 mM Cu	3.25	0.648	0.99

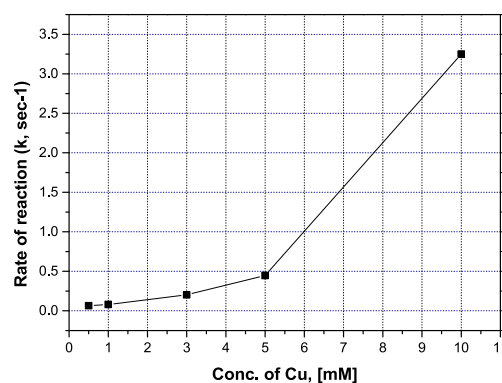
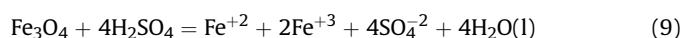


Fig. 7. Rate of reaction according to initial Cu ion concentrations in solution.



$$\Delta G = -5.47 \text{ kcal}$$



$$\Delta G = -6.139 \text{ kcal}$$

Equation (9) shows the formation of Fe^{2+} and Fe^{3+} ions with the reaction with H_2SO_4 . Equation (10) shows the involvement of the electron exchange strategy and the production of ferrous ions and water [14], when hydrazine is almost zero in the solution.

To establish the presence of hematite, a sample was taken after 9 h of the dissolution test and checked by XRD, which confirmed the presence of mag-hematite and hematite in the solution. Fig. 9 confirms the presence of mag-hematite and hematite in the solution by comparison with references.

There is another mechanism that can describe the relationship between Cu(II) ions and hydrazine. In an acidic solution, Cu(II) ions and hydrazine probably form a complex which is expected to form [$Cu^+(N_2H_5^+)$], [$Cu^+(N_2H_4)$], [$Cu^+(N_2H_5^+)(SO_4^{2-})$] [12]. The bond usually formed between Cu(I) and hydrazine helps transfer electrons from the Cu(I) ions to Fe(III). This mechanism also supports the fact that the reduction of Cu(II) ions to Cu(I), oxidized by the reaction with Fe(III), can be effective in the further oxidation of the hydrazine process.

4.2.3. Effect of pH on the dissolution of magnetite

The dissolution behavior of magnetite in different solution pHs was also checked. Fig. 10 plots the reaction rate (k) of magnetite dissolution derived from the Kabai equation (Eq (8)) for two Cu conditions. From Fig. 10, it can be concluded that 50 mM hydrazine showed the highest rate of reaction for magnetite dissolution when the copper concentration was 10 mM and the pH of the solution was 2.0, although pH 2.5 and 3.0 also showed good magnetite dissolution behavior with high copper concentration. The behavior of 5 mM Cu in the solution was checked using three different pH conditions, and the results are shown in Fig. 9. These results indicate that the reaction mechanism isn't dependent on the pH value of the solution when the pH of the solution varies between 2.0–2.5.

4.2.4. Effect of temperature on the dissolution of magnetite

The dissolution behavior of magnetite with reaction temperature was tested as plotted in Fig. 11. The reaction temperature was changed from 70 °C to 95 °C when the initial concentration of Cu and N_2H_4 concentration were 10 mM and 50 mM, respectively. The amounts of dissolved magnetite were increased as the reaction

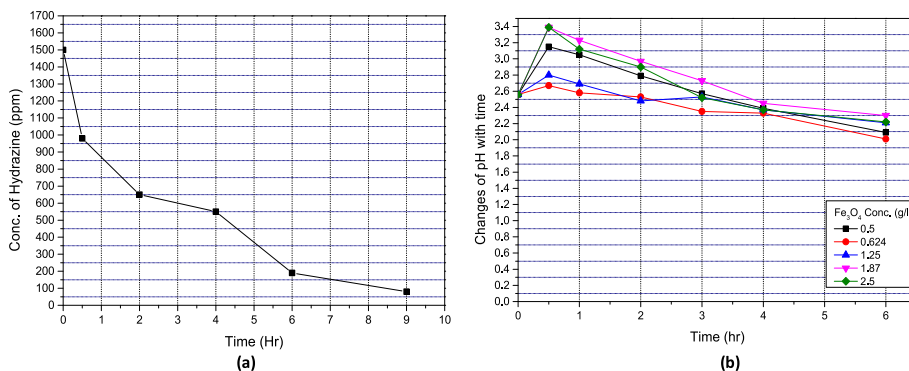


Fig. 8. (a) Changes in hydrazine concentration over time when the initial concentration of hydrazine is 50 mM, (b) Cu concentration is 0.5 mM and different initial concentration of Fe₃O₄.

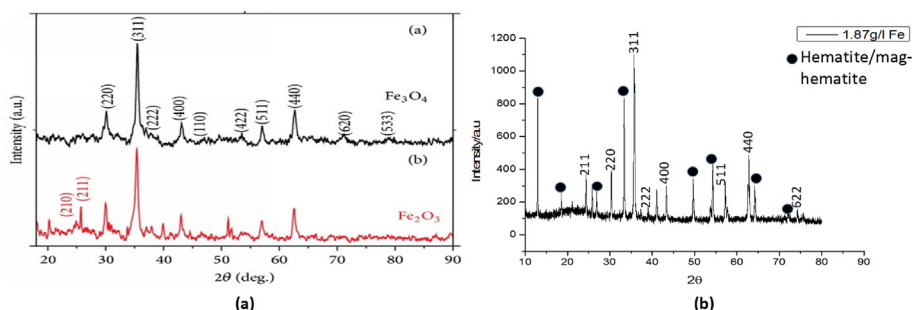


Fig. 9. (a) Reference-1 XRD of hematite and magnetite (b) XRD of sample (after 9h of reaction), 1.87 g/l magnetite.

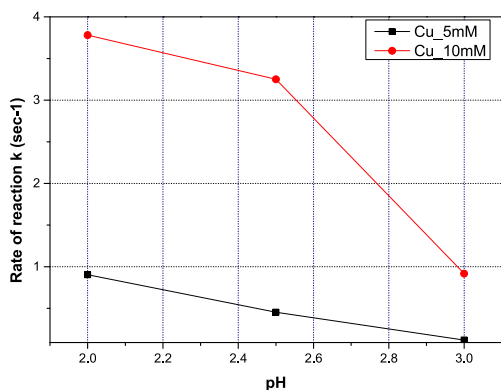


Fig. 10. Dissolution fraction of magnetite with 50 mM of hydrazine hydrate with 5 mM Cu and 10 mM Cu T = 95°C, initial amount of magnetite = 1.87 g/l, in different pH conditions (2.0, 2.5, 3.0).

temperature increased. At 90 °C and 95 °C, all of the initial amounts of magnetite were dissolved after 300 min, when there was 10 mM of Cu in the solution.

The N₂H₄/Cu/H₂SO₄ system showed good magnetite dissolution, and the high concentration of copper in the solution also increased the dissolution rate of magnetite, with a corresponding decrease in activation energy compared with the N₂H₄/H₂SO₄ system. The relationship between dissolution rate and temperature for the magnetite can be described by the Arrhenius equation (11):

$$K = Ae^{-E/RT} \tag{11}$$

whereas, K = dissolution rate, A = frequency factor, E = activation

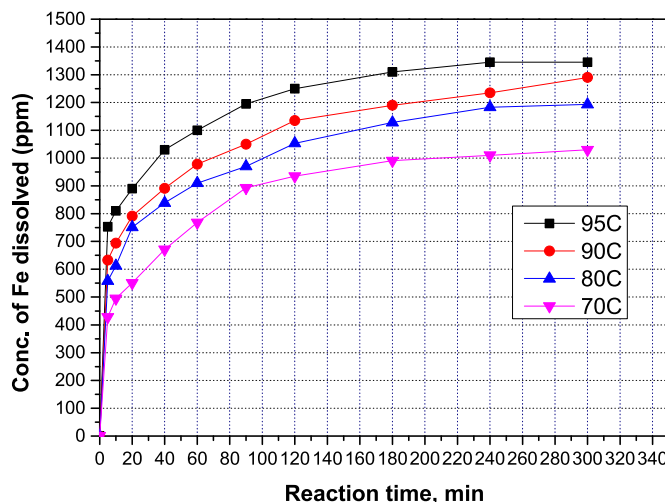


Fig. 11. Dissolution behavior of magnetite with reaction temperature (70, 80, 90, 95 °C), 50 mM of hydrazine hydrate with 10 mM Cu, initial amount of magnetite = 1.87 g/l.

energy, T = absolute temperature, R = gas constant. The value of E and A were calculated from the slope and intercept of ln(k) vs. 1/T plots for each temperature condition. The activation energy for magnetite dissolution was calculated from this equation and the following graph (Fig. 12), i.e., 122.46 kJ/mol when there is no Cu ion present in the solution and 51 kJ/mol in the presence of 10 mM of Cu. This value suggests that the reaction for magnetite dissolution is a controlled surface chemical reaction. It is reasonable that magnetite dissolution is higher at elevated temperatures.

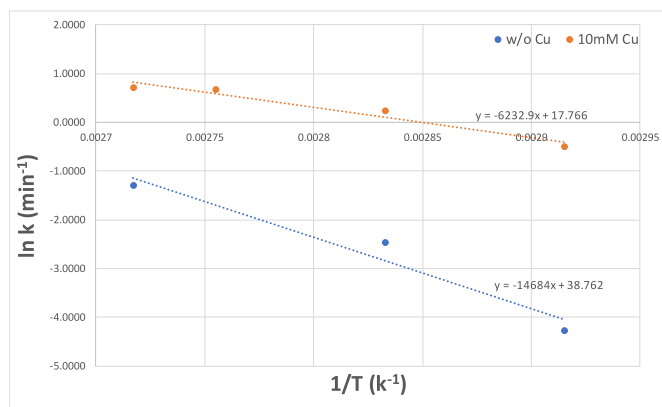


Fig. 12. $\ln k$ vs. $1/T$ plots for magnetite dissolution follow the Arrhenius equation, 50 mM of hydrazine hydrate with 10 mM Cu and without Cu, initial amount of magnetite = 1.87 g/l.

5. Conclusions

This study was originally focused on developing a decontamination technology to be applicable to decontaminate PHWR system, as a very thick oxide layer developed ($\sim 75 \mu\text{m}$) in the primary heat transport system (PHTS) of PHWR. A parametric study on magnetite dissolution was conducted based on the HyBRID process as an essential step for this. The optimization of the experimental factors for the dissolution of magnetite aimed to secure a more improved dissolution rate and dissolution capacity.

The HyBRID process for application to PWR decontamination uses a decontamination solution containing 0.5 mM copper ions and 50 mM hydrazine, and sulfuric acid is added to adjust the pH of the solution to 2.5. A new dissolution pathway appears when copper ions are added to an acidic hydrazine solution. To examine this phenomenon in detail, the effect of hydrazine and copper concentration on the magnetite dissolution behavior was investigated. The effect of pH and temperature on magnetite dissolution was also identified. The change in hydrazine concentration from 50 mM to 100 mM did not significantly affect the magnetite dissolution rate and dissolution capacity. Instead, it showed a tendency to decrease as hydrazine concentration increased. However, the magnetite dissolution rate drastically increased when the concentration of copper ions in the decontamination solution increased. The increase in copper ion concentration played an essential role in accelerating the magnetite dissolution process. The acidic solution provides protons to break the Fe–O bond, and hydrazine acts as a reducing agent for dissolving the Fe^{3+} ions into the solution. Cu^{2+} ions provide a probable bridge bond with hydrazine, which promotes dissolution by decreasing the activation energy. The equilibrium amount of Cu^{2+} was relatively small because Cu^{2+} ions were reduced to Cu^+ ions by reacting with N_2H_5^+ ions in the solution. Almost all of N_2H_4 was protonated to produce N_2H_5^+ ions. When the raw amount of added CuSO_4 in the solution containing 50 mM hydrazine was increased, the dissolution fraction changed from 22% to 75% when the dissolution test period of 30 min had elapsed.

At this time, the amount of magnetite added to the dissolution test was 1.87 g/l (about 1,350 ppm in terms of iron concentration). A dissolution model was also shown to determine the reaction rate according to the changes of hydrazine and copper concentration in the solution. The pH of the solution was changed from 2.0 to 3.0, and there was no significant difference in the magnetite dissolving capacity within this range. The low-temperature decontamination solution showed poor results in dissolving magnetite. It was found

that the temperature should be above 80°C to obtain better dissolution results of magnetite with an enhanced dissolution rate. The activation energy (E_a) decreased according to the increasing amount of Cu as a catalyst in the solution. Based on all of the above results, the dissolution of magnetite in this mixed system of $\text{N}_2\text{H}_4\text{--Cu(II)--H}_2\text{SO}_4$ is strongly dependent on the reducing effect of hydrazine and the catalytic effect of Cu^{2+} ions. The addition of copper ions to $\text{N}_2\text{H}_4\text{--H}_2\text{SO}_4$ represents a new pathway to dissolve magnetite. The improved HyBRID process, which increased the copper ion concentration to 10 mM compared to the existing HyBRID process, showed the maximum magnetite dissolution performance within the experimental range and was suggested as an optimized process.

Further study should be carried out to observe the dissolution behavior of metal oxide from different steel coupons. The improved HyBRID process needs to be applied to metal surfaces to determine its corrosion compatibility with different kinds of metals.

Credit author statement

Ayantika Banerjee: Conceptualization, Methodology, Writing, Original draft preparation. **Wangkyu Choi:** Supervision, Data interpretation, Investigation. **Byung-Seon Choi:** Writing-Reviewing and Editing, Data interpretation. **Sangyoon Park:** Software, Validation. **Seon-Byeong Kim:** Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.net.2023.01.024>.

Symbols and Abbreviations

CANDU	Canada Deuterium Uranium
CAN-DEREM	CANadian Decontamination and REMediation
CITROX	CITRic and OXalic acid
CORD	Chemical Oxidation Reduction Decontamination
E_a	Activation energy
HyBRID	the <u>H</u> ydrazine <u>B</u> ased <u>R</u> eductive metal <u>I</u> on <u>D</u> econtamination
LOMI	Low Oxidation state Metal Ion
PHWR	Pressurized Heavy Water Reactor
PWR	Pressurized Water Reactor

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