The copper-assisted dissolution of magnetite in hydrazine-based inorganic solution

[†]Ayantika Banerjee [1,2], [†]Wangkyu Choi[1*], [†]Byung-Seon Choi[1], Seon-Byeong Kim[1]

[1]*Decontamination and Decommissioning Division, KAERI, Daejeon, 34057, Korea*
[2]*Quantum Energy Chemical Engineering, University of Science and Technology (UST), Daejeon, 34113, Korea*
[*]*Corresponding author:* nwkchoi@kaeri.re.kr

[†]Authors have the same contribution to this paper

Abstract

A protective oxide layer forms on the material surfaces of a Nuclear Power Plant during operation due to high temperature. These deposited oxides are iron oxides such as Fe_3O_4, Fe_2O_3, 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. To improvise this chemical decontamination technology for the Pressurized Heavy Water Reactor (PHWR) system, we investigated the role of Cu in magnetite dissolution. The redox cycle of copper in the presence of hydrazine and magnetite in the solution does provide a good dissolution behavior of magnetite.

Keywords: Redox cycle, magnetite dissolution, PHWR, reaction mechanism, hydrazine

1. Introduction

Copper is the noblest of the 3rd transition metals. It can form two stable passivating oxides at neutral pHs, depending on the potential (Parsons, 1967). The fabrication of copper oxides and copper ions in different morphologies has attracted increasing attention in recent years due to their potential application in so many fields such as energy conversion, electrode materials, catalysis, etc (Gawande et al., 2016; Zhang et al., 2014). The main feature of the copper-enhanced mechanism for the dissolution of synthetic magnetite is the electron transfer between Cu^+/Cu^{2+} and a surface Fe^{3+} species (Zeng et al., 2012).

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 (Lee et al., 2020). Of the various metal oxides formed in NPPs, magnetite is one of the major corrosion products. Magnetite is formed under high temperatures (>270[O]C) and pressure (around 16 MPa) on the surfaces of the reactor coolant system. Magnetite dissolution and

deposition are significant problems in NPPs. In the case of the Pressurized Heavy Water Reactor (PHWR), as this reactor is made up of mainly carbon steel, the oxide layer deposition consists of magnetite. The circulating CRUD in CANDU-PHWR is Fe_3O_4 and the thickness of the oxide layer film on the carbon steel surfaces is about 75µm. Korea Atomic Energy Research Institute (KAERI) has developed a chemical decontamination process called <u>Hy</u>drazine <u>B</u>ased <u>R</u>eductive metal <u>I</u>on <u>D</u>econtamination (HyBRID) process to decontaminate the PWR system. In this process, the oxide layers containing metal ions Fe, Ni, etc. are dissolved in the reductive step using hydrazine, H^+, and Cu^+ as functional chemicals. In the HyBRID process chemistry hydrazine breaks as hydrazinium ion, $N_2H_5^+$ in the acidic solution (Jung et al., 2015). Typical HyBRID solution can be able to dissolve 0.624g/l of magnetite (~400ppm of Fe ion) after 9 hours of dissolution time. Later, this HyBRID process is optimized to dissolve much amount of magnetite by enhancing the dissolution rate to make this process applicable for PHWR system decontamination. To optimize the typical HyBRID system for developing this process applicable to PHWR decontamination, various experimental tests were performed to screen the most efficient conditions on the magnetite dissolution. Those studies explained and concluded that, by increasing the addition of Cu ion concentration (0.5mM to 10mM), it is possible to get a high dissolution of magnetite (~1350ppm of Fe) within 4 hours of dissolution time.

In this dissolution study, an interesting trend of Cu was observed. In the case of high Cu^{2+} concentration in the presence of hydrazine, Cu^{2+} is reduced to Cu^+ by generating CuO and Cu_2O. Later, when the concentration of hydrazine is low, and the full dissolution of magnetite of the initial amount is completed, Cu_2O/CuO breaks to Cu^+ and Cu^{2+} ions in the solution. A reasonable assumption is that the first step of the overall reduction process involves the one-electron reduction of Cu^{2+} to Cu^+ by hydrazine. This study proposed that the presence of cupric ions enhances the abstraction of a proton from the hydrogen with concomitant reduction of the cupric ion to the cuprous ion. Several studies also reported the synthesizing of Cu_2O in hydrazine reduction conditions. As hydrazine is a strong reducing agent, some experiments showed that, in the excess of hydrazine, it can not only reduce the metal ions but also integrate within the lattice of nanoparticles, which may form some copper coordination compound-oxide composite nanostructures.

In this study, the behavior of Cu ions in the presence of hydrazine and magnetite is studied. The interaction of copper oxide in a hydrazine-based solution is studied well. With the addition of high Cu concentration, the changes in the oxidation state of Cu or Fe are observed. Due to the redox cycle of Cu ion in the solution, the reaction mechanism of Fe dissolution under high Cu and hydrazine conditions is derived and shown in this study. The reason for pH changes in the solution according to the dissolution time is also discussed.

2. Experimental

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 the magnetite dissolution were performed in a stirred batch glass reactor using the solution. Since hydrazine is basic, H_2SO_4 was used to reach a pH of 2.6 (±0.05), to prepare an acidic HyBRID solution.

The typical HyBRID solution usually contains 0.5 mM of Cu ions. At first, to understand the copper effect in magnetite dissolution, the experiment of magnetite dissolution according to initial Cu ion concentration was conducted. In this series of experiments, Cu ions were added to the solution at concentrations from 0.5 to 10 mM and the dissolution behavior of magnetite was tested.

To understand the behavior of copper in a hydrazine-based solution, the changes in copper concentration with reaction time have been analyzed, when the initial concentration of copper was different in the solution. In all experiments, the amount of magnetite was fixed to 1.87g/l (1350ppm, as Fe ions). Hydrazine monohydrate was used as the main dissolution agent. The copper concentration changes are also monitored when the initial hydrazine concentration was varied (1mM~50mM). Both these conditions have been checked in the absence and presence of magnetite in the solution. Magnetite powder was added to 250ml 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 the prepared solutions were tightly closed. Periodic samples were taken with a syringe and then filtered through a 0.2μm pore filter during the entire experimental period, and the dissolved concentration of Cu ion in the solution was analyzed by atomic absorption spectrophotometer (AAnalyst 400, Perkin Elmer). The changes in pH and hydrazine concentration with time were checked for the reaction mechanism study. To analyze XRD or XPS for understanding the composition of the oxidation state of ions, the sample was taken at a different time of dissolution test and filtered and dried in the air atmosphere at 60°C.

Several thermodynamical calculations have been done by using the HSC Chemistry program (HSC Chemistry is a product of Outokumpu Research (ORC)).

3. Results and Discussions

3.1 Dissolution of magnetite according to the changes in copper concentration

Copper helps to accelerate the dissolution rate of magnetite. It was stated from previous studies that, of the metal ions, Cu^{2+} was the most effective in catalyzing the oxidation of hydrazine. The Cu^+ ion and hydrazine bond can facilitate an electron transfer from the Cu^+ ion to the Fe^{3+} of magnetite. Previous studies on the HyBRID decontamination process stated that Cu^+/Cu^{2+} ion acts as a redox couple (Won et al., 2014). The characteristics of Cu^+/Cu^{2+} ion pairs as redox media and the deposition by reducing Cu^{2+} ions were also investigated (Choi et al., 2015). The reduction of Cu^{2+} ions oxidized by reacting with Fe^{2+} to Cu^+ is effective for the further oxidation of hydrazine. Fig. 1 shows that the higher the concentration of Cu^{2+} ions in the solution, the faster the dissolution

rate of magnetite. Evolution tests were performed in two different pH of the solutions (Fig 1). In both solutions, around 63% of magnetite was dissolved in 9 hours when the concentration of Cu ion was 0.5mM in the solution. Compared with typical HyBRID conditions it was evaluated to dissolve 800~1,000ppm of Fe after 9 hours when Cu ion concentration was increased from 1.0mM to 5.0mM in two pH conditions. In the case of 10mM Cu ion, 1200~1300ppm of Fe was able to dissolve within 3~4hours of dissolution test in two pH conditions. Fig 1 (a) and (b) show that a 10mM concentration of Cu ion in the solution consisting of 50mM of N_2H_4 could dissolve up to 89% and 75% of magnetite dissolution within 30min, in two different pH conditions. Compared to the dissolution result without Cu ions, it can be stated that the increasing amount of Cu^{2+} ions in the solution increased the magnetite dissolution rate accordingly. Besides, the possible explanation of the Cu effect in dissolution is that Cu^+ ions are reduced from Cu^{2+} ions by the oxidation process of hydrazine as hydrazine plays a vital role in reducing Fe^{3+} ions into soluble Fe^{2+} ions, as well. The oxidation process of hydrazine also produces hydrogen ions and electrons, which affects the acceleration of the Fe dissolution rate. The concentration of Fe reduced in the solution after the full dissolution of Fe to the initial concentration (Fig 1 (a), (b)) after 4~6hours of dissolution test due to the reason of hematite formation, which is not part of this study.
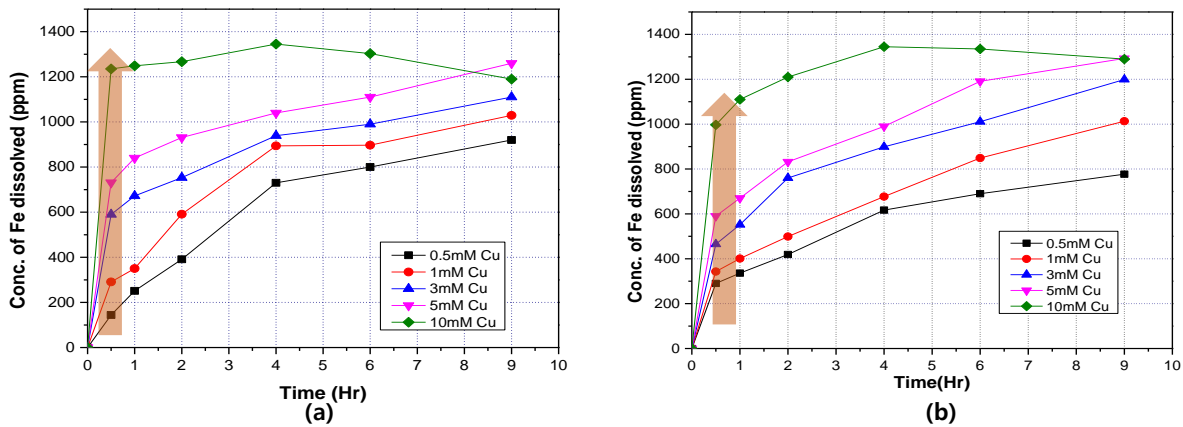

Fig. 1. Dissolution behavior of magnetite with 50 mM of hydrazine hydrate, according to the concentration of Cu ions, T= 95ºC, an initial amount of magnetite= 1.87g/l (1,350ppm) (a) when solution pH was 2.0, (b) when solution pH was 2.5

3.2 Changes of copper concentrations according to the initial concentration of Cu ion with the dissolution time

In the 9 hours of magnetite dissolution under improved HyBRID condition (50mM N_2H_4/10mM Cu^{2+}/28mM H_2SO_4), several changes in copper compositions are observed. In this study, it is observed that the initial concentration of Cu changes according to reaction time. For the detailed observation, the changes of Cu ion concentrations (0.5mM~10mM) with reaction time under two different conditions of the solution were analyzed. The changes in Cu concentration and the pH

with time are observed in two conditions: a) the absence of magnetite in the solution, and b) the presence of 1.87g/l of magnetite in the solution.

Figure 2 (a) and (c) was shown the changes of Cu ion and pH with reaction time when no Fe was initially added to the solution, respectively. Figure 2 (b) and (d) was shown the changes of Cu ion and pH with reaction time when 1.87g/L magnetite is added to the solution.

In Fig. 2 (a) it is observed that in the case of the absence of magnetite in the solution a depletion of Cu ion concentrations occurred after 30min of reaction time when the initial amount of Cu is ≥3mM.

After 9 hours of dissolution time, the hydrazine concentration is around 700ppm in the solution and the Cu ion concentration doesn't reach the initial amount. After 9 hours of dissolution test, it is observed that Cu ion's final concentration was 1mM and 3mM, whereas the initial concentration of Cu was 5mM and 10mM, respectively.
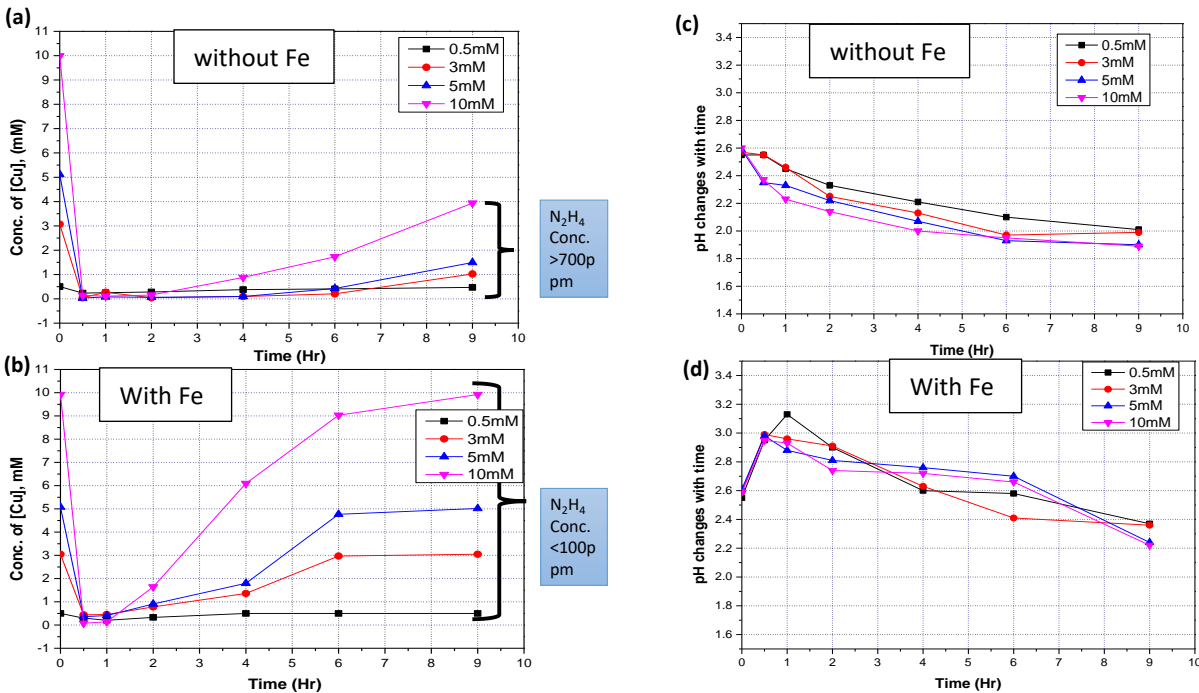

Fig 2. Changes of the concentration of Cu ion and pH with reaction time, according to different initial Cu concentration, $[N_2H_4]$ = 50mM, T = 95°C, initial amount of magnetite = 1.87g/l. (a) Changes of Cu concentration according to the dissolution time (in the absence of magnetite in the solution), (b) Changes of Cu concentration according to the dissolution time (in the absence of magnetite in the solution), (c) Changes of pH according to the dissolution time (in the absence of magnetite in the solution), (d) Changes of pH according to the dissolution time (in the presence of magnetite in the solution)

In Figure 2 (b) it is observed that in the presence of magnetite in the solution the Cu concentration was dropped to nearly zero after 30min of dissolution time regardless of initial Cu concentrations,

and then recovered to the initial concentration after 9 hours of reaction time. This hide-out return behavior of copper appears when there is magnetite in the solution. The pH trend was at first higher than the initial pH and then it went down again (Fig 2 (C) and (d)). The initial pH of the solution is 2.5, it increases to 3.0 within 1 hour of reaction time, but gradually goes down and after 9 hours of dissolution test the pH reaches 1.9 when there is the presence of magnetite. But, in the absence of magnetite in the solution, the pH doesn't increase but goes down gradually with reaction time (Fig 2 (d)). After 9 hours of reaction time, the final concentration of Cu ion was the same as the initial concentration (when Cu concentration was 3mM or more than that). The concentration of hydrazine was checked after 9 hours of dissolution time and the result showed that the concentration of hydrazine left in the solution is lower than the previous condition, less than 100ppm (shown later in Fig. 5 (b)). As, in this case, magnetite is present in the solution, so high amount of hydrazine is used to dissolve the magnetite by reducing Fe^{3+} to Fe^{2+}. It is noted that, when the Cu concentration is lower (0.5 mM or lesser than that), this hide-out return pattern cannot be observed. The concentration of Cu stays the same as the initial amount when the initial Cu concentration is low(~0.5mM) in the solution.

In Figure 3 the pourbaix diagram of copper is shown. The diagram was developed at 100°C when the concentration of copper is also high. Previous studies related to the diagram stated that in the presence of oxidizing agents the potential will increase and a solid reaction product form on the surface in the form of either Cu_2O or CuO (depending on the potential) (Beverskog, 1995).
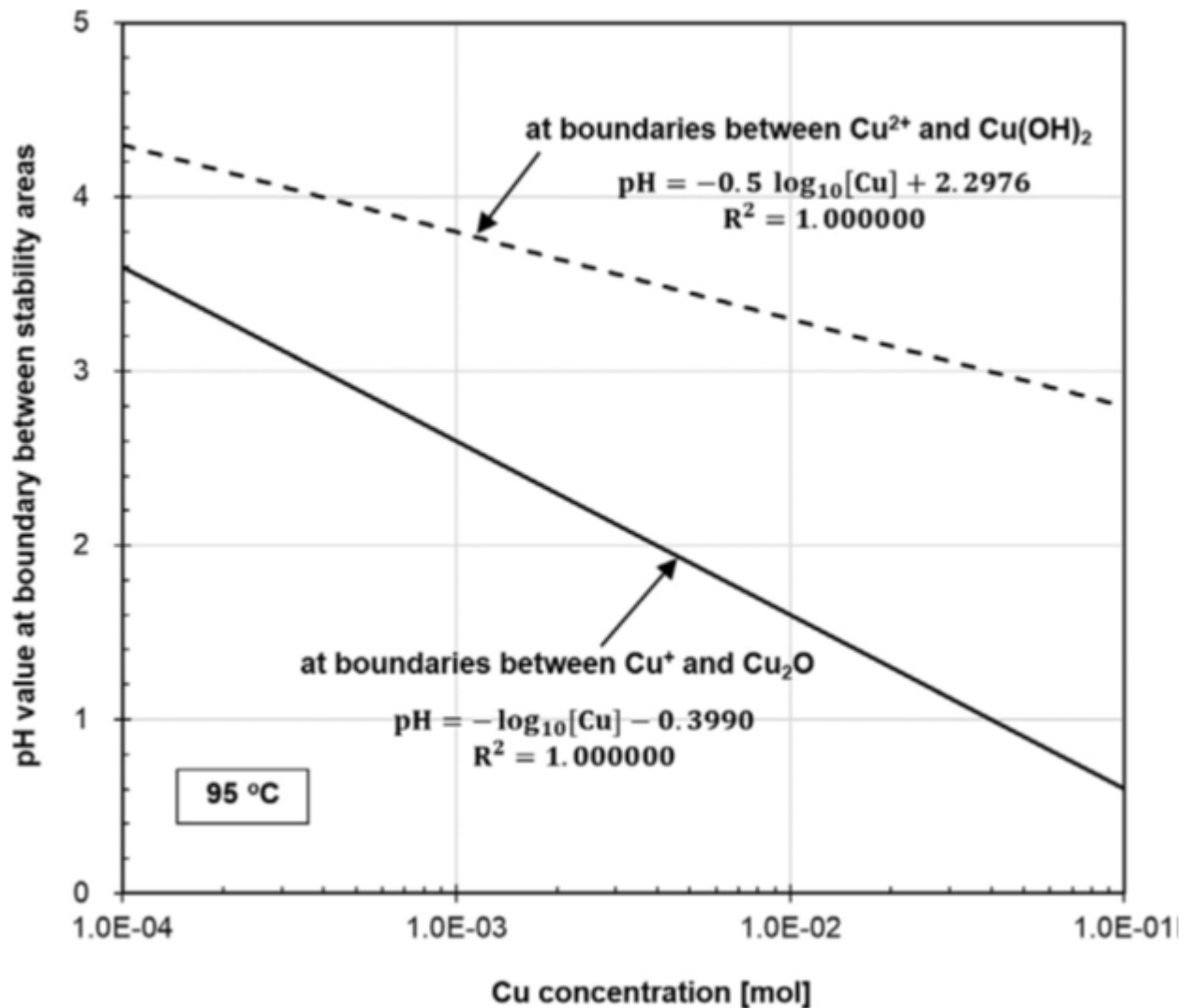
Fig 3. Pourbaix diagram for copper at 100°C (Bjorn et al., 1995)

The color changes of the solution were observed when the initial concentration of Cu was 1mM, 5mM, and 10mM. In this case, when the initial Cu concentration is low (~1mM), the color changes of the solution aren't profound at all, and the Cu concentration from the initial time to the end of the reaction remains almost the same. But, when the initial concentration of Cu was higher (≥5mM), the color changes of the solution were observed. The color of the solution appears yellow or yellowish red and becomes colorless or light blue after 9 hours of reaction time. This change of color is assumed due to the formation of copper (II) oxide/copper (I) oxide in the solution. Many studies developed the idea about the speciation of dissolved copper species at its' high concentration (Beverskog & Puigdomenech, 1997). The generation of Cu_2O or CuO is possible through reduction by hydrazine and also the generation of hematite after full magnetite dissolution was observed. The image of color changes in solution according to the initial concentration of Cu is provided in supplementary data [S1].

To be confirmed the formation of Cu oxide by analyzing the oxidation state of Cu, the sample was collected and filtered after a two-time duration (initial time and 30min of dissolution test). This dissolution test was performed in the presence of 50mM of N_2H_4, 10mM of Cu ion, and 1.87g/l of Fe_3O_4 in the solution at pH 2.5. XRD and XPS characterizations are done at the initial time and after 30 minutes of reaction time. Figure 4 (a) and (b) show the XRD spectra of a sample consisting of both Cu and Fe at the initial time and after 30min of reaction time, respectively. From these two figures, Cu_2O and CuO formations are confirmed. Cu_2O formation is higher after 30 minutes of reaction time (Fig 3 (b)), the highest XRD peak shows evidence of the presence of Cu_2O.
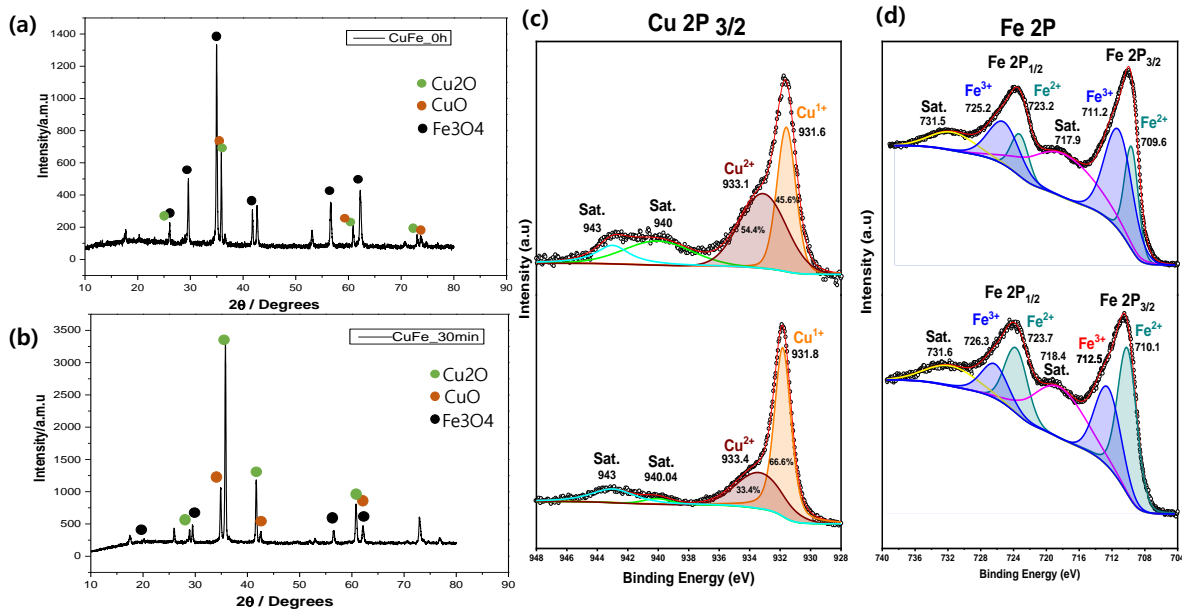

Fig 4. The XRD and XPS spectra on Cu and Fe of two times (0min, 30min)

Figures 4 (c) and (d) show the XPS peaks for the oxidation states of Cu and Fe. It is shown in Fig. 4 (c) that, at the initial time when the high concentration of copper is added, Cu presents both as +2 and +1 oxidation states (as $CuSO_4$ added in the solution where Cu presents as +2 oxidation state). After 30min of reaction time, the Cu oxidation state went down from +2 to +1, so the generation of Cu_2O became high. The percentage of the Cu^+ is 45.6% (initial time) increased to 66.6% after 30min of reaction time, whereas the percentage of Cu^{2+} ion is 54.4% (initial time) decreased to 33.4% after 30min of reaction time. Figure 4 (d) shows the oxidation state of Fe at two times of dissolution test. At the initial stage, the Fe oxidation state presents as +2 and +3 (Fe2P 1/2 and Fe2P 3/2 both have been shown). After 30min of reaction time, the +3-oxidation state of Fe is lower than the +2-oxidation state of Fe, in the solution. From this XPS spectra of two elements, it can be concluded that hydrazine reduces both Cu and Fe strongly. The fast reduction of Fe^{3+} to Fe^{2+} confirms the dissolution of magnetite at a high dissolution rate, in the presence of a high concentration of Cu ion within 30min of the dissolution test.

3.3 Changes in copper concentrations according to the initial hydrazine concentration through dissolution time

The changes in Cu concentration depending on the Fe ions and initial hydrazine concentration in the solution are shown with the reaction time in Fig. 5. The Cu concentration in the solution was kept the nearly same as the initial concentration during all the reaction time when hydrazine concentration was in low ranges (1.0 ~10mM).

In the case without magnetite, the Cu concentration in the solution did not change at all with the reaction time when there is less concentration of hydrazine (≤10mM). As the hydrazine concentration are increased to 50mM, the concentration of Cu dropped but it didn't reach the initial concentration of Cu after 9 hours of dissolution test shown in Fig. 5 (a). However, this phenomenon of hide-out return of Cu in the solution appeared to show the same patterns shown in Fig. 5 (b). The Cu concentration is dropped within 30 minutes of dissolution time due to the reductive dissolution of Fe_3O_4 with hydrazine and returns to the initial concentration after the full dissolution of magnetite. The time and magnitude for the hide-out return phenomenon of Cu were different depending on the hydrazine concentration in the solution.
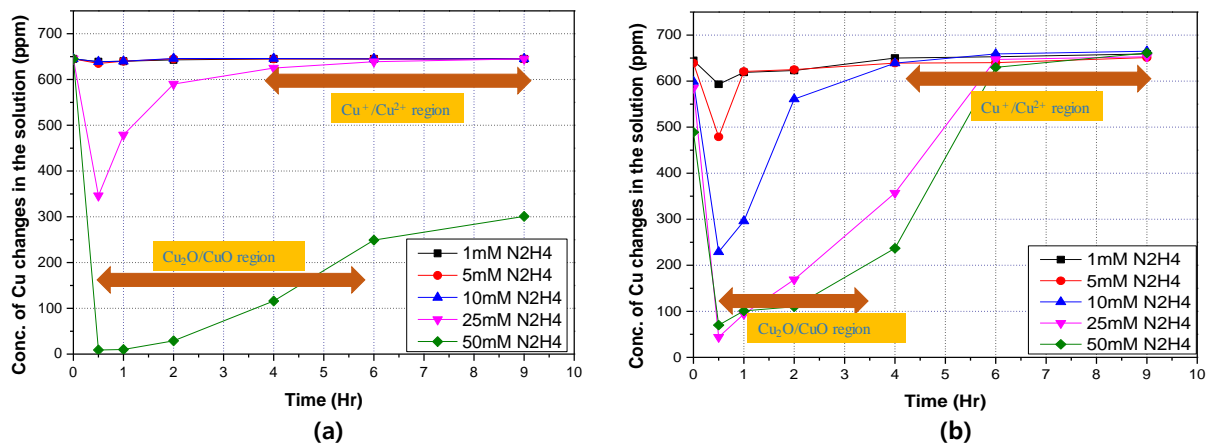

Fig 5. The changes of Cu ion concentration (10mM) according to the concentration of hydrazine in the solution according to the dissolution time. (a) No presence of magnetite in the solution, (b) presence of magnetite is the solution (initial amount = 1.87g/l)

Figure 6 shows how the concentration of hydrazine changes with dissolution time, in the presence and absence of magnetite in the solution. The initial concentration of Cu was high (~10mM) in the solution. These results state that, as there is no presence of magnetite in the solution, the hydrazine concentration didn't decrease much after 9 hours of dissolution test, when the initial concentration of hydrazine is 50mM (Fig. 6 (a)). So, Cu concentration didn't reach to initial concentration, after 9 hours of dissolution test, as the presence of hydrazine is still high in the solution. But, when there is the presence of magnetite in the solution, after 9 hours of dissolution test, the presence of hydrazine concentration in the solution is lesser than 100ppm (the initial concentration of hydrazine is 50mM) shown in Fig 6 (b) and the hide-out return pattern for Cu appeared profoundly,

in this case. In the case of less hydrazine concentration initially (1mM~10mM), the hydrazine concentration goes to almost zero within a short period, so, the Cu concentration changes were not profound. No hideout return pattern is observed, in this case. Some previous studies (Littrell et al., 1987) explained about the behavior of Cu_2O or CuO in the hydrazine-based solution. They described that CuO possesses a relatively unstable d9 configuration, while Cu_2O although having a complete 'd' shell, is uniquely unstable as assessed by the d-s promotion energy (Zeng et al., 2012).
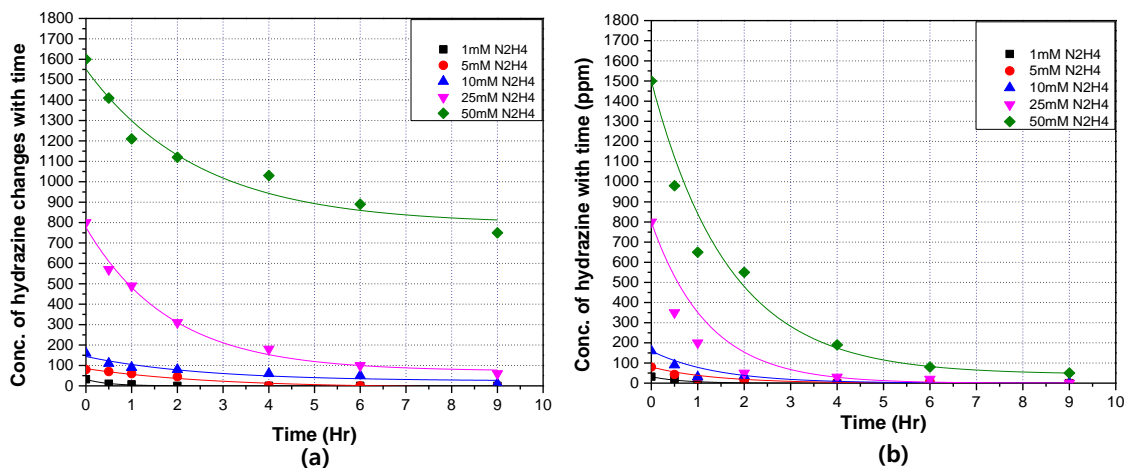

Fig 6. The changes of hydrazine concentration according to the dissolution time, when the initial hydrazine concentration is different, in the presence of 10mM Cu concentration. (a) absence of Fe_3O_4 (b) presence of $Fe_3O_4 = 1.87g/l$

Figure 7 (a) and (b) were plotted by using HSC chemistry modeling. These two graphs simulated the experimental conditions according to the absence and presence of magnetite, both in low and high hydrazine concentrations. From these two figures, the assumption of generations of different compositions of Cu can be confirmed. It can be stated from this computational simulation that, when hydrazine concentration is higher than 10mM, the concentration of Cu^+ ion goes down, but the presence of Cu_2O goes higher (both in the presence of magnetite and the absence of magnetite conditions). This simulated data does support the experimental findings related to Cu_2O formation which is described previously. Also, this simulated result provides a supportive explanation about the hide-out trend of Cu in the presence of magnetite in solution.
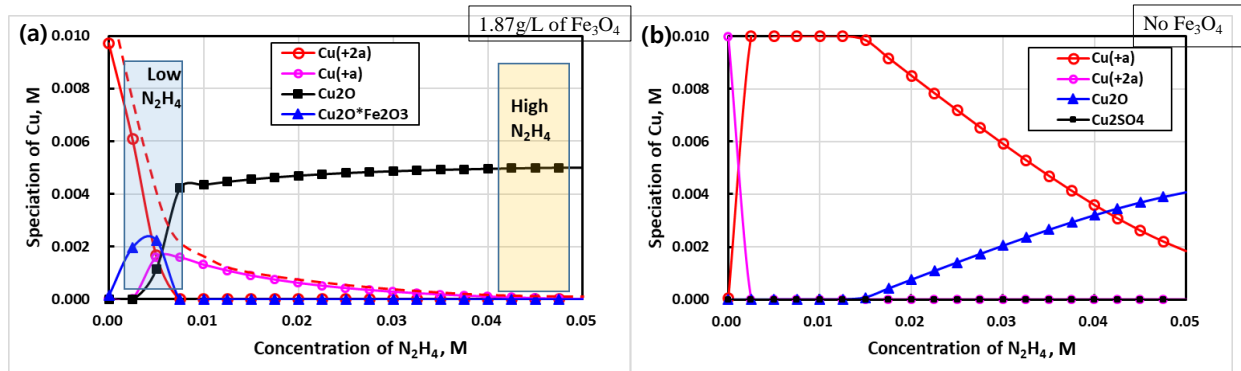
Fig 7. HSC modelling study to know the speciation of Cu according to the concentration of hydrazine (a) $[Cu^{2+}]$ = 10mM, Fe_3O_4 = 1.87g/l (b) $[Cu^{2+}]$ = 10mM, No Fe_3O_4

3.4 Reaction mechanism for copper-assisted Fe dissolution in the hydrazine-based solution

By observing the changes in copper concentrations according to the concentration of hydrazine and the presence of magnetite, a possible reaction mechanism of magnetite dissolution may be suggested through a reaction pathway shown below (reactions 1 to 6). This mechanism was observed in the presence of a high concentration of Cu in the hydrazine-based solution. The calculation of Gibb's free energy also is stated along with reactions. Fig 9 emphasizes the experimental findings regarding copper-assisted magnetite dissolution in the hydrazine-based inorganic solution.
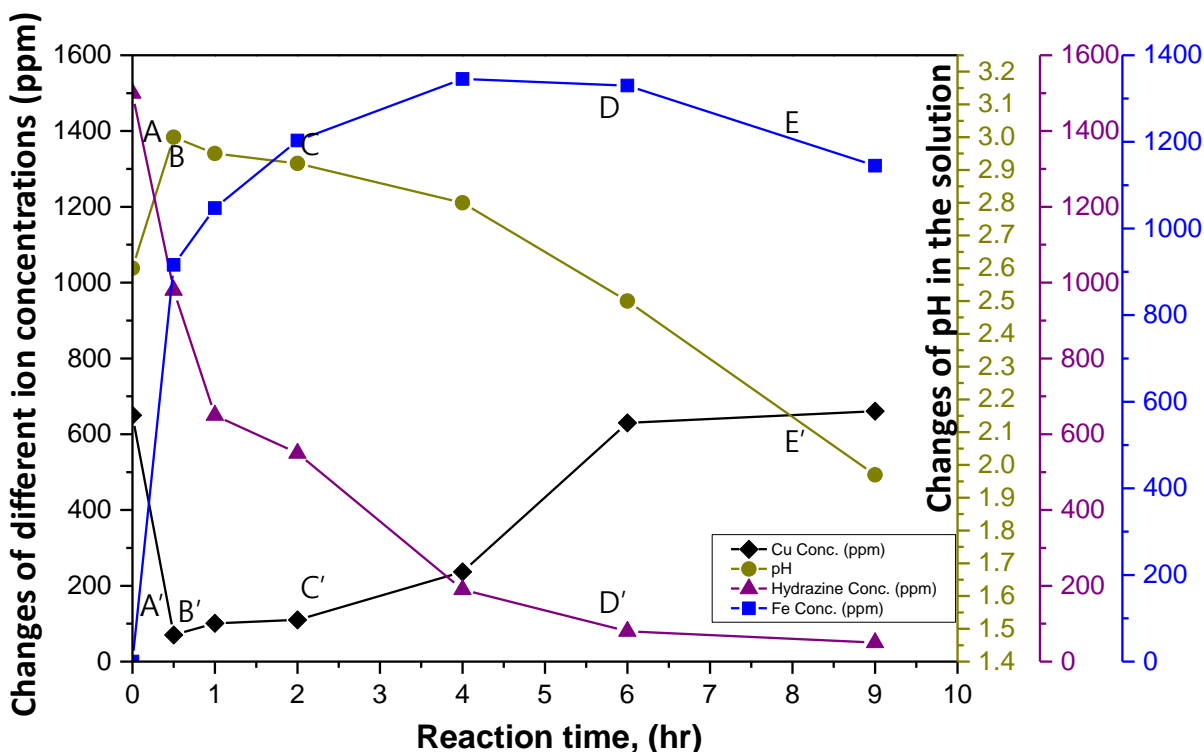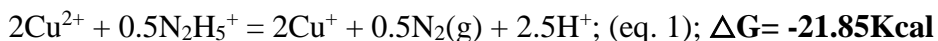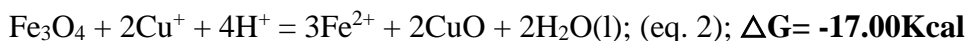
Fig 9. The changes of different ion concentrations according to the dissolution time. $[N_2H_4]$ = 50mM, $[Cu^{2+}]$ = 10mM, Fe_3O_4 = 1.87g/l (1350ppm, as Fe ion), T = 95°C, initial pH= 2.5

Figure 9 shows the dissolution of Fe, the changes in Cu concentration, and the changes in hydrazine concentration through reaction time when the initial hydrazine concentration was 50mM, the initial Cu concentration was 10mM in the solution and the initial pH was 2.5. The temperature of the solution was kept at 95°C. The pH changes of the solution are also described in this mechanism by producing H^+ ions in the solution (eq 1, 3 & 4). This figure can emphasize the reaction mechanisms described below:
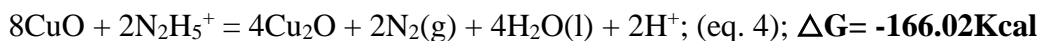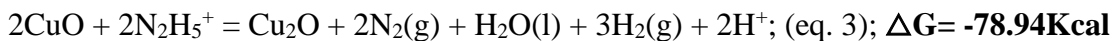
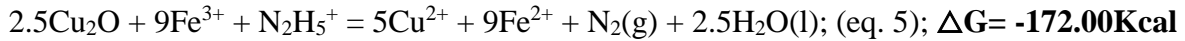**Formation of Cu^+ from Cu^{2+} ($Cu^{2+} \rightarrow Cu^+$: A~A′)**

$$2Cu^{2+} + 0.5N_2H_5^+ = 2Cu^+ + 0.5N_2(g) + 2.5H^+; \text{ (eq. 1)}; \triangle G= \textbf{-21.85Kcal}$$

Formation of CuO from Cu^+ ($Cu^+ \rightarrow CuO$: B~B′)

$$Fe_3O_4 + 2Cu^+ + 4H^+ = 3Fe^{2+} + 2CuO + 2H_2O(l); \text{ (eq. 2)}; \triangle G= \textbf{-17.00Kcal}$$

Formation of Cu_2O from CuO (CuO $\rightarrow Cu_2O$: C~C′)

$$2CuO + 2N_2H_5^+ = Cu_2O + 2N_2(g) + H_2O(l) + 3H_2(g) + 2H^+; \text{ (eq. 3)}; \triangle G= \textbf{-78.94Kcal}$$

$$8CuO + 2N_2H_5^+ = 4Cu_2O + 2N_2(g) + 4H_2O(l) + 2H^+; \text{ (eq. 4)}; \triangle G= \textbf{-166.02Kcal}$$

Formation of Cu^{2+} from Cu_2O ($Cu_2O \rightarrow Cu^{2+}$: D~D′)

$$2.5Cu_2O + 9Fe^{3+} + N_2H_5^+ = 5Cu^{2+} + 9Fe^{2+} + N_2(g) + 2.5H_2O(l); \text{ (eq. 5); } \triangle G= \text{-172.00Kcal}$$

Formation of hematite (E~E′)

$$2Fe^{3+} + 3H_2O = 3Fe_2O_3 + 6H^+; \text{ (eq. 6); } \triangle G = \text{-6.139 kcal}$$

According to this reaction mechanism it can be stated that the redox cycle of copper in the presence of hydrazine (Medvedeva et al., 2019) and magnetite in the solution does provide a good dissolution behavior of magnetite. The formation of hematite after the full dissolution of magnetite was discussed in a previous study.
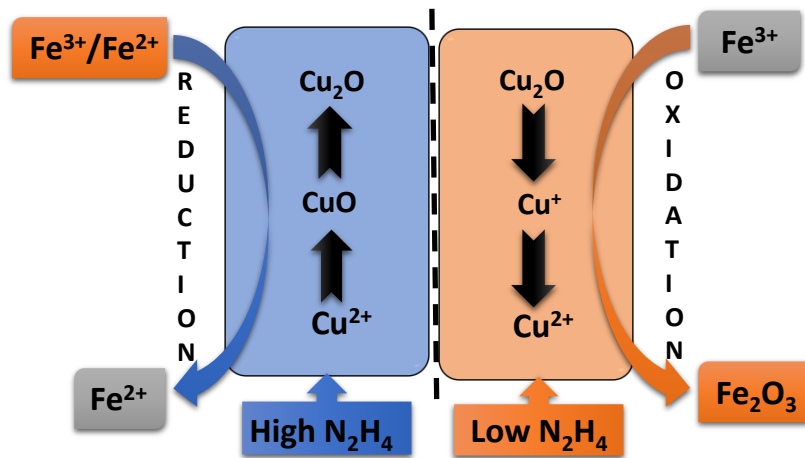

Fig 10. Schematic diagram of Cu redox reaction according to the concentration of hydrazine in the solution

Fig 10 showed a schematic diagram of copper changes behavior according to the concentration of hydrazine present in the solution. Also, the behavior of Fe ion was displayed.

4. Conclusion

This study revealed the redox reaction of Cu in the presence of hydrazine on magnetite dissolution. The results have clearly demonstrated that the presence of copper oxides does influence the dissolution of magnetite. The enhancement of the dissolution behavior of magnetite in the presence of the copper oxides indicates that the copper species either modify the kinetics of the process (possibly through a catalytic mechanism) or participate directly as a reactant. These findings imply that; the redox reaction of Cu is directly connected to the magnetite dissolution. This redox behavior of Cu depends on temperature, pH, initial concentration, etc. Further, by accounting for dissolution, the total Cu oxidation and reduction charges were balanced.

This Cu redox reaction mechanism is followed to get a high dissolution of magnetite with a high dissolution rate. These data altogether with detailed information on the capability of transition metal, copper-assisted dissolution of magnetite can be confirmed.

References

1. Ballester, A., González, F., Blázquez, M. L., & Mier, J. L. (1990). The influence of various ions in the bioleaching of metal sulphides. *Hydrometallurgy*, *23*(2–3). https://doi.org/10.1016/0304-386X(90)90006-N
2. Beverskog, B. (1995). Revised Pourbaix Diagrams for Copper at 5-150 °C. *SKI Report*, *27*.
3. Beverskog, B., & Puigdomenech, I. (1997). Revised Pourbaix Diagrams for Copper at 25 to 300°C. *Journal of The Electrochemical Society*, *144*(10). https://doi.org/10.1149/1.1838036
4. Choi, W. K., Yang, H. B., Won, W. H., Jung, C. H., Park, S. Y., Moon, J. K., Hwang, S. B., Yoon, I. H., Lee, K. W., & Maeng, W. Y. (2015). *Development of Advanced Decontamination Technology for Nuclear Facilities*. https://inis.iaea.org/search/search.aspx?orig_q=RN:49108228
5. Gawande, M. B., Goswami, A., Felpin, F. X., Asefa, T., Huang, X., Silva, R., Zou, X., Zboril, R., & Varma, R. S. (2016). Cu and Cu-Based Nanoparticles: Synthesis and Applications in Catalysis. In *Chemical Reviews* (Vol. 116, Issue 6). https://doi.org/10.1021/acs.chemrev.5b00482
6. Jung, J. Y., Park, S. Y., Won, H. J., Kim, S. B., Choi, W. K., Moon, J. K., & Park, S. J. (2015). Corrosion properties of Inconel-600 and 304 stainless steel in new oxidative and reductive decontamination reagent. *Metals and Materials International*, *21*(4). https://doi.org/10.1007/s12540-015-4572-x
7. Kim, S., Park, S., Choi, W., Won, H., Park, J., & Seo, B. (2018). Magnetite Dissolution by Copper Catalyzed Reductive Decontamination. *Journal of Nuclear Fuel Cycle and Waste Technology(JNFCWT)*, *16*(4). https://doi.org/10.7733/jnfcwt.2018.16.4.421
8. Lee, B. C., Kim, S. B., Moon, J. K., & Park, S. Y. (2020). Evaluation of reaction spontaneity for acidic and reductive dissolutions of corrosion metal oxides using HyBRID chemical decontamination. *Journal of Radioanalytical and Nuclear Chemistry*, *323*(1). https://doi.org/10.1007/s10967-019-06962-3
9. Littrell, D. M., Bowers, D. H., & Tatarchuk, B. J. (1987). Hydrazine reduction of transition-metal oxides. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, *83*(11). https://doi.org/10.1039/F19878303271
10. Medvedeva, X., Vidyakina, A., Li, F., Mereshchenko, A., & Klinkova, A. (2019). Reductive and coordinative effects of hydrazine in structural transformations of copper hydroxide nanoparticles. *Nanomaterials*, *9*(10). https://doi.org/10.3390/nano9101445
11. Parsons, R. (1967). Atlas of electrochemical equilibria in aqueous solutions. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, *13*(4). https://doi.org/10.1016/0022-0728(67)80059-7
12. Won, H. J., Lee, W. S., Jung, C. H., Park, S. Y., Choi, W. K., & Moon, J. K. (2014). A feasibility study on the decontamination of type 304 stainless steel by N2H4 base solution. *Asian Journal of Chemistry*, *26*(5). https://doi.org/10.14233/ajchem.2014.17221

13. Zeng, G., Deng, X., Luo, S., Luo, X., & Zou, J. (2012). A copper-catalyzed bioleaching process for enhancement of cobalt dissolution from spent lithium-ion batteries. *Journal of Hazardous Materials*, *199–200*. https://doi.org/10.1016/j.jhazmat.2011.10.063

14. Zhang, Q., Zhang, K., Xu, D., Yang, G., Huang, H., Nie, F., Liu, C., & Yang, S. (2014). CuO nanostructures: Synthesis, characterization, growth mechanisms, fundamental properties, and applications. In *Progress in Materials Science* (Vol. 60, Issue 1). https://doi.org/10.1016/j.pmatsci.2013.09.003