

## Study of Chemical Decontamination Process for CRUD Removal

Seongsik Nam<sup>a,\*</sup>, Won-Seok Kim<sup>a</sup>, Jungjin Kim<sup>a</sup>, Wooyong Um<sup>a,b</sup>

<sup>a</sup>Division of Advanced Nuclear Engineering, POSTECH, Pohang, Korea

<sup>b</sup>Pacific Northwest National Laboratory (PNNL), Richland, WA, USA

\*Corresponding author: spoppower@postech.ac.kr

### 1. Introduction

Chalk River Unidentified Deposit (CRUD) is a technical term in nuclear engineering which is an accumulated material on external fuel rod cladding surfaces in nuclear power plants. It is a corrosion product which is composed of either dissolved ions or solid particles such as Ni, Fe and Co. It consists mainly of NiO and NiFe<sub>2</sub>O<sub>4</sub>. It can affect to reduce fuel lifetime, degrade heat transfer to the coolant, and threaten human health and environment. Therefore, decontamination process is essential for reducing occupational exposures, limiting potential releases and uptakes of radioactive materials, allowing the reuse of components, and facilitating waste management process.

In this paper, we have conducted the synthesis of Cobalt ferrite as power foam to use for decontamination process. In addition, oxide layer foam on the metallic coupon (SUS 304) was prepared and used. Dissolution test of the simulated CRUD was conducted with different chemical reagents and electro kinetic (EK) process was applied to investigate for the cobalt, nickel and iron removal from CRUD.

### 2. Materials and methods

#### 2.1 Synthesis of Cobalt ferrite powder

Iron chloride (FeCl<sub>3</sub>, 97% reagent grade, Sigma-Aldrich) solution (0.4M in 50ml) and Cobalt chloride (CoCl<sub>2</sub>, 98%, purum p.a., Sigma-Aldrich) solution (0.2M in 50ml) were mixed in tri-distilled water. Sodium hydroxide (NaOH, 98%, Samchun) solution (3M in 50ml) was prepared and slowly added to the salt solution drop-wise until pH of solution reached 11. And oleic acid was added with specified amount (weight fraction of aqueous phase : surfactant = 0.34 : 0.12). The slurry was heated up to a reaction temperature of 80°C for 1hour and then cooled to room temperature. And pour the supernatant into another beaker to get precipitate. To get free particles from solution, the precipitate was rinsed twice with distilled water before centrifugation and then washed with ethanol to remove the excess surfactant. To isolate the supernatant liquid, the beaker contents were then centrifuged for 15 minutes at 3000 rpm. After that, heating at 600°C for 10 hours to remove moistures associated with powder [1].

#### 2.2 Synthesis simulated CRUD on metallic coupon

Stainless steel SUS 304 (Ni: 8~11%, Cr: 18~20%, Fe), a component material of nuclear power plant, is used to make CRUD on the metal surface using doping process. Cobalt nitrate solution (50 mL of 0.82M concentration) was prepared for doping at surface of SUS 304 metallic coupon. And spread with 0.25 ml cobalt nitrate solution on metallic coupon and dried at 100°C. Repeat this procedure 4 times. To make oxide layer on the surface of metallic coupon, heat treatment carry out at 700°C for 24 hours [2].

#### 2.3 Solubility experiment for CoFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub>

Tri-distilled water (100mL) in glass beaker was used for dissolution experiments of synthesized CRUD ferrites. The beaker is wrapped in two sheets of aluminum foil for blocking the light. About 20mg of Ni and Co ferrite powders were poured into the beaker. The suspension was magnetically stirred and acids were added periodically using a micropipette to adjust solution pH to different pHs (1.8, 2.5, 3.5, 4.5, 5.5, and 6.5). The reactions were carried out 1 hour at different temperatures (25°C, 70°C, and 90°C) [3].

#### 2.4 Electro – Kinetic (EK) process

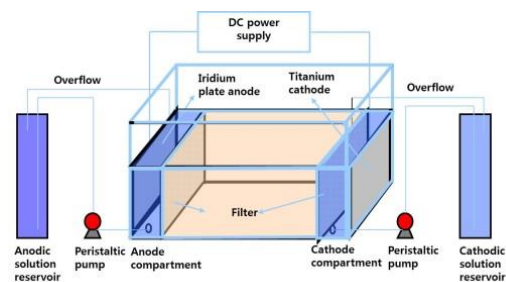


Fig. 1. Schematic diagram of Electro-Kinetic (EK) process [4].

Experimental apparatus consists of four principal parts : cell, electrode compartments, electrolyte solution reservoirs, and the power supply. Schematic diagram of EK process is presented in Fig. 1. About 2g of cobalt ferrite and nickel ferrite inside paper bag respectively which was placed at center of the cell and different solutions were circulated during 10 hours. Oxalic acid, Malonic acid, Citric acid, or Nitric acid solution with pH 1.8 or 3.5 was used at two different temperatures (25°C and 90°C).

### 3. Results and Discussion

#### 3.1 Characterization of synthesized materials

The XRD results of synthesized CRUD are shown in Fig. 2, and Co based CRUD was well synthesized in our method. It is identified as Co-ferrite,  $[\text{CoFe}_2\text{O}_4]$ . X-Ray Fluorescence (XRF) data of Co-ferrite powder is shown in Table I. XRF analyses shows normalized concentration of Fe : Co = 65.61% : 31.44% in the obtained powder, which is similar to the molar ratio of Fe : Co = 2 : 1.

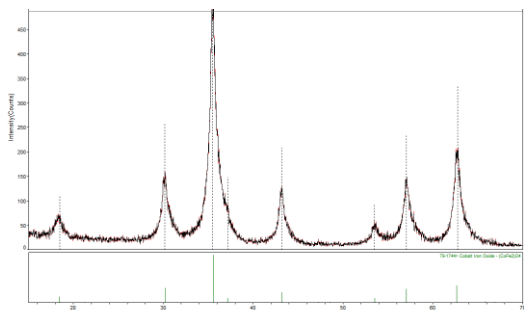


Fig. 2. XRD data of synthetic cobalt ferrite.

Table I: XRF data of synthetic cobalt ferrite

Compound Formula	Original Concentration	Normalized Concentration
$\text{Na}_2\text{O}$	0.35	0.34
$\text{Fe}_2\text{O}_3$	66.4	65.61
$\text{CoO}$	31.8	31.44

#### 3.2 Dissolution test of cobalt ferrite

Amount of dissolved cobalt in cobalt ferrite at various pHs and at  $70^\circ\text{C}$  is shown at Fig. 3. Dissolved amount of cobalt is higher in lower pH solution. The highest dissolved amount of Co was found when pH was titrated with oxalic acid. Temperature dependent dissolved amount of iron and cobalt in Cobalt ferrite is shown in Fig. 4 and the amount of dissolved cobalt and iron is increased as temperature increases.

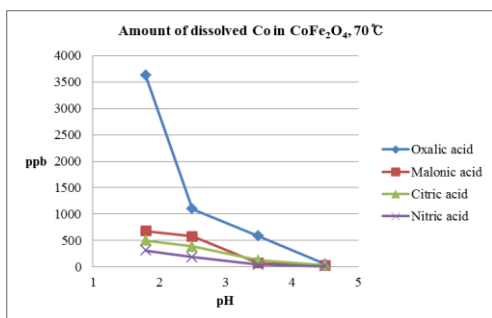


Fig. 3. Dissolved amount of cobalt from Cobalt ferrite at different pHs.

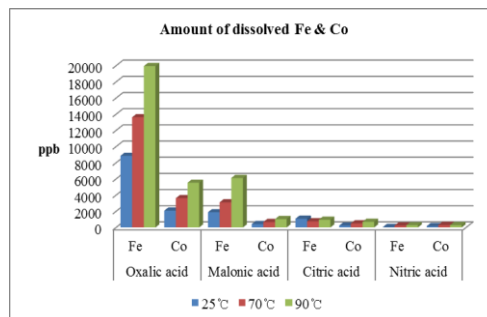


Fig. 4. Dissolved amount of iron and cobalt at different temperatures.

#### 3.3 Dissolution test of nickel ferrite

Amount of dissolved nickel in nickel ferrite at various pHs and at  $70^\circ\text{C}$  is shown at Fig. 5. At lower pH, the dissolved amount of nickel is higher. And, oxalic acid shows the highest dissolved amount of Ni compared to other acid solutions at the same pH.

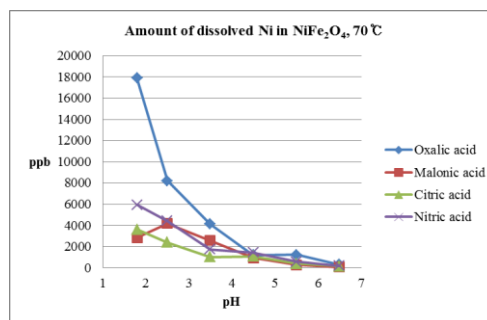
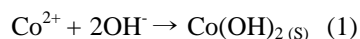


Fig. 5. Dissolved amount of nickel from nickel ferrite at different pHs and  $70^\circ\text{C}$ .

#### 3.3 Electro-Kinetic process

Amount of dissolved cobalt from cobalt ferrite using different acids at cathode of Electro-kinetic (EK) process under the pH 1.8 is shown at Fig. 6. Fig. 7 shows the amount of dissolved cobalt from cobalt ferrite using acids at cathode of Electro-kinetic (EK) process under the pH 3.5. When pH 3.5 titrated with oxalic acid, most of dissolved cobalt is precipitated. The Cobalt (II) ions which were moved to cathode reacted with hydroxide ion ( $\text{OH}^-$ ) and precipitation reaction occurred like eq. (1)



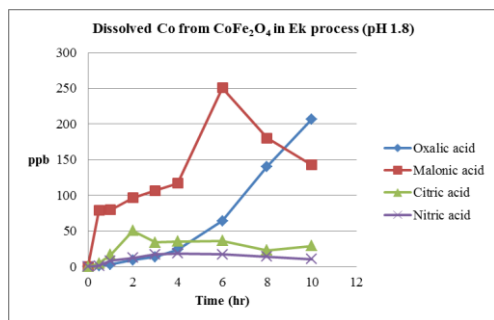


Fig. 6. Electro - kinetic process data of cobalt from cobalt Ferrite at pH 1.8

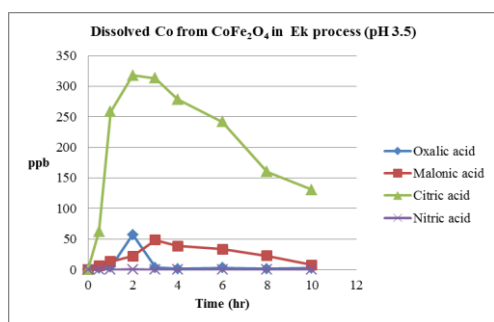


Fig. 7. Electro - kinetic process data of cobalt from cobalt Ferrite at pH 3.5

The amount of dissolved cobalt and iron from cobalt ferrite using oxalic acid at cathode of Electro-kinetic (EK) process at pH 1.8 controlled temperature (25 °C and 90 °C) by heating mantle is shown at Fig. 8. The amount of dissolved cobalt and iron increased as temperature increased.

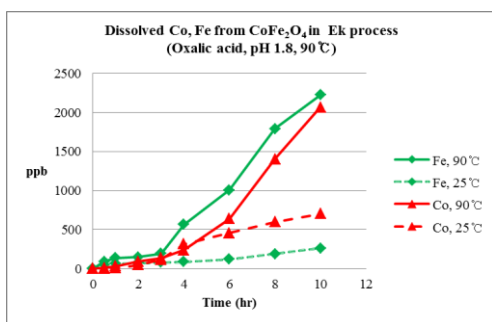


Fig. 8. Electro - kinetic process data of cobalt and iron from cobalt ferrite at pH 1.8 and different temperature (25 °C, 90 °C).

### 3. Conclusions

In dissolution test of Co ferrite and Ni ferrite, oxalic acid shows the most effective chemical decontamination reagent to remove the contaminants. Generally, the dissolved amount of cobalt and nickel increases at low pH condition and as the temperature goes higher, dissolved amount of cobalt and iron are much higher. In EK process for cobalt ferrite, under the condition of pH 1.8, there is no precipitation phenomena occurred but at

pH 3.5, when titrated with oxalic acid, precipitation phenomenon is occurred. Consequently, EK process is valid to remove Co from CRUD metal solid at pH 3.5.

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