Fabrication of FeOOH nanoparticle via anodization as an adsorbent material for nuclear reactor coolant decontamination system

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1. Introduction

Flow in Primary system of nuclear power plant contains various waste and radioactive contaminant including fission products (e.g., ^{137}Cs and ^{90}Sr) and activation products (e.g., ^{60}Co, ^{63}Ni, or ^{55}Fe) [1]. Fission products are produced during chain reaction and diffuse out of fuel cladding and dissolved into the coolant flow [2]. Acidic and high-temperature coolant environment induces fuel cladding and structure materials to be corroded and popped out of the structure surface [3]. These corrosion products are activated by neutron to be activation products with radioactivity [4]. One of the major activation product is ^{60}Co, which forms cobalt (II) in reactor coolant, which have long half-life (5.27 years) and high energy (2.5 MeV) gamma emission [1,5]. Those contaminants are deposited on the surface of the structure materials to make the system radioactive, which can trigger irradiation issue of nuclear workers [1].

To prevent this problem, the coolant should be continuously decontaminated [6]. Through the coolant decontamination process, coolant in the primary system is collected in chemical and volume control system (CVCS), and the undesirable materials, for example, radioactive products and waste, are removed with suitable treatment [2]. Typical cleanup techniques of this treatment are filtration, ion exchange and adsorption [6]. Filtration is for particulate material and undissolved solid removal, while ion exchange is suitable for dissolved radioactive and chemical contaminants. Adsorption is usually utilized in combination with ion exchange in coolant waste treatment. Adsorption can be divided into physical and chemical adsorption, where physical adsorbent uses Van der Waals force while chemical adsorbent involves chemical attraction [7]. In typical waste removal system, filter material and ion exchange resin is utilized together [6].

Even though ion exchange resin have taken roles of radioactive ion remover in coolant system, poor resistance and selectivity of ion exchange resin were problematic [8]. Despite existing ion exchange resin have good ion exchange capacity, its poor selectivity let this exchanger to remove any ionic material regardless of radioactivity, such as non-radioactive ferrous ions, while actual amount of radioactive material is relatively small [1]. At the end of the treatment, spent resin become radioactive waste, which is actually the main source of low-intermediate level waste (LILW) of nuclear power plant system [9]. Thus, removal of radioactive material involving fission product and activation product requires suggestion of new material with high selectivity and stability.

FeOOH nanoparticle is a promising adsorbent for metal cations with some noble properties such as interlayered structure and ferromagnetism [10,11]. Interlayered structure of FeOOH nanoparticle allows it to have high specific surface area, which results in high adsorption capacity. Presence of hydroxyl group at the surface of FeOOH gives high chemical affinity. Moreover, adsorption sites at the surfaces can be easily functionalized with the presence of functional group, which gives selectivity for a certain target material. Ferromagnetic nature is also a fancy property that helps easy recovery in coolant system [10,11].

In this study, FeOOH nanoparticle was selected as adsorbent of cobalt (II), which was aforementioned as a major activation product. As a nanoparticle fabrication method, anodization process was adopted. It had been already studied that anodization provides economic, safe, and efficient procedure to fabricate nanoparticle, within short time and relatively large amount of result [12,13]. Some evaluation plan of adsorption performance and selectivity will be provided in the latter section. The specialties of FeOOH nanoparticle based adsorbent that existing ion exchangers do not have make it as a very promising agent for nuclear coolant decontamination project, which provides safer and more effective nuclear working environment.

2. Method

2.1 Equipment and Materials

1.0 mm diameter iron wire was purchased from Sigma-Aldrich. Potassium Chloride (KCl) powder of purity higher than 99% was supplied by Sigma-Aldrich. Distilled Water was purchased from Daejung, Korea. 45 mm neck size *Steritop* of pore size 0.22 μm was used as vacuum filtration equipment. This is obtained from Sigma-Aldrich. Stainless steel Cathode frame as a counter electrode and anodization stand to hold the frame and adjust the level of iron wire was custom-made from Gumto Engineering, Korea.

2.2 FeOOH nanoparticle Fabrication

0.1 M KCl was dissolved in 300 mL distilled water as an electrolyte material. This solution was sonicated for few minutes and stirred in 100 rpm. Iron wires and stainless steel frame were placed into electrolyte as a working electrode and counter electrode, respectively, with surface level of the electrolyte and each electrodes are adjusted. Iron wires were prepared with length of 3 cm. System power was set to have fixed potential of 15 V DC and initial electric current of 4 A. During anodization process, effective surface of working electrode and electrolyte was adjusted with anodization stand lever to maintain 4 A of current [14].

After the anodization process ended, electrolyte with FeOOH nanoparticle was filtered with *Steritop*. During the filtration, deionized water is continuously supplied to filter out KCl component. This filtered FeOOH was wrapped with experimental wiper and dried in an oven at 50 °C for 24 hours. Dried sample was grinded with 45 µm sieve.

2.3 Characterization and Evaluation Plan

Size of nanoparticle and aggregation was obtained by Field Emission Scanning Electron Microscope (FE-SEM) (Magellan400, FEI company, US). Diffraction patterns of the prepared nanoparticle will be obtained by X-ray diffractometer (SmartLab, RIGAKU, Japan) to observe the crystallization structure of prepared FeOOH nanoparticle. The absorption and transmission spectra will be obtained by Fourier transform infrared (FTIR) spectrometer (Nicolet iS50, Thermo Fisher Scientific Instrument, US) to observe the formation of FeOOH [12].

Adsorption capacity of FeOOH to cobalt (II) is known to be differed by acidity of the environment. The adsorption evaluation method will follow the method of SCHENCK et al. (1983). Prepared FeOOH will be equilibrated with different concentration of $Co(NO_3)_2 \cdot H_2O$ and acidity will be controlled by addition of 0.1 M NaOH or 0.1 M HNO_3 [15]. Selectivity test will be also conducted with different concentration of cobalt (II) and iron (II) content.

3. Results

As-prepared FeOOH nanoparticle after sieving was black, fine powder with agglomerating property. For characterization of base particle, Fe-SEM imaging was prepared. 0.003g of sample was diluted in 3 mL of chloroform, and the diluted sample was prepared on Al plate and fixed by copper tape.
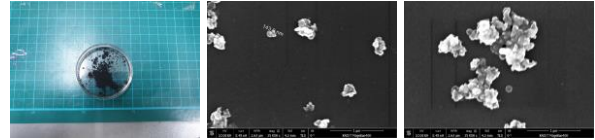

Fig. 1. Prepared FeOOH nanoparticle powder (a) and FE-SEM image of the powder (b, c). Large agglomeration is observable in (c).

In the result FE-SEM image, base particles of size around 150 nm were observed. Large agglomeration was also observed which is not desirable for adsorption. Suppression of this agglomerating property also need to be provided in the later study.

4. Conclusions

In this study, FeOOH nanoparticle adsorbent was suggested as an alternative of existing ion exchange resin. Some properties of FeOOH nanoparticle such as interlayer structure, selectivity due to functional group, and ferromagnetic nature was provided as a clue for replacement. Fabrication of FeOOH nanoparticle was proceeded by anodization, and black fine powder was obtained as result. FE-SEM image of the powder showed that base particle of size 150 nm was obtained, but large number of agglomeration was observed which is not desirable. In the following study, adsorption test for cobalt (II) according to pH change and selectivity test against the presence of iron (II) will be conducted, with decoration of additional functional group for enhancing selectivity and preventing agglomeration. This newly invented adsorbent can provide much safer working environment and much effective coolant purification system in nuclear reactor system operation.

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