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Removal of Chalk River unidentified deposit (CRUD) radioactive waste by enhanced electrokinetic process

Won-Seok Kim[a], Seongsik Nam[a], Seeun Chang[a], HyunJu Kim[a], Wooyong Um[a,b,*]

[a] Division of Advanced Nuclear Engineering, Pohang University of Science and Technology (POSTECH), 77 Cheongam-ro, Pohang, South Korea
[b] Pacific Northwest National Laboratory, Richland, WA 99354, USA

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ABSTRACT

Decontamination techniques proposed and used to remove Chalk River unidentified deposit (CRUD) in radioactive waste management. In cases of huge volumes of metal or radionuclides contaminated by CRUD, removal of CRUD by mechanical or chemical decontamination is difficult. An advanced electrokinetic process combined with chemical decontamination was applied to remove CRUD and experimentally evaluated. Oxalic acid was used for CRUD removal, and cobalt (Co) released from the CRUD was transferred to the cathode in an electrokinetic reactor. Results indicate that the combined system is efficient for CRUD removal with enhanced, efficiency by use of the cation exchange membrane and zeolite.

Introduction

Decommissioning and decontamination of nuclear power plants (NPPs) release intermediate and low-level radioactive wastes. Because radionuclides are hazardous to human health and the environment, and the costs of decommissioning an NPP and any related nuclear materials are enormous [1], an effective and economical remediation method is needed for radioactive waste decontamination. During NPP operation, a corrosion product called Chalk River unidentified deposit (CRUD) accumulates on the Inconel and stainless steel surfaces. CRUD is an accumulation of materials and corrosion products that is composed of either dissolved ions or solid particles such as Ni, Fe, and Co on fuel rod cladding surfaces in NPPs [2]. CRUD degrades heat production by nuclear fuel because it is slowly eroded by the circulation of the hot (~300 °C) pressurized water and later deposited on the cladding or outer housing of fuel rods [3]. Generally, the chemical composition of CRUD varies depending on the types of refueling cycles and the constituents of the basic metal material. Irradiation can produce radionuclides in the CRUD, such as ^{60}Co and ^{63}Ni [4]. Ni, Cr, and Fe are the major elements of the outer layer of CRUD, and Zn is a major element of its inner layer [5]. Ni may be released from the cladding surfaces into the coolant system due to constant interaction between the CRUD and cooling water [6]. The most representative compound in CRUD is nickel ferrite ($NiFe_2O_4$); under irradiation, Ni can be transmuted to ^{60}Co so the nickel ferrite changes to $^{60}CoFe_2O_4$ [4]. When an NPP is decommissioned, decontamination of radiologically contaminated metals should be conducted prior to disposal. Because $^{60}CoFe_2O_4$ exists on metal surfaces, several methods to decontaminate CRUD are being studied in many countries [3,7,8].

CRUD decontamination can be performed using mechanical or chemical methods. Mechanical decontamination includes scraping, washing, and swabbing, and foaming agents used in wet or dry abrasive blasting and grinding of surfaces [9]. These techniques are most adaptable to the decontamination of structural surfaces, but produces a mixture of dust and liquid droplets that might be difficult to treat. Chemical reagents are used to remove the contamination from metal surfaces [9]. Chemical decontamination has proved to be effective for removing radionuclides from large metal surface areas. Oxidizers and detergents can be used to remove CRUD from the metal surfaces to reduce the amount of solid radioactive waste and the radiation dose rate. They also can be used on complex geometries to provide a uniform process for inner and outer pipe surfaces. However, these techniques can also produce a large amount of secondary solution waste [9]. When large contaminated metal components are decommissioned and cut into reasonably-sized pieces, an electrokinetic (EK) process can be used to decontaminate them for waste volume reduction before their disposal.

* Corresponding author at: 790-784, 77 Cheongam-ro, Nam-gu, Pohang, Gyungbuk, South Korea. Fax: +82 54 279 9559.
E-mail address: wooyongum@postech.ac.kr (W. Um).

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The EK technology has been successfully applied to remove heavy metals and radionuclides from contaminated soils [10–13]. When direct current (DC) electric fields are applied to the EK reactor, ions of heavy metals and radionuclides migrate to the electrodes respectively [10–13]. A combination of EK with chemical decontamination methods can increase the amount of contaminant removed from CRUD. In the combined system, Co ions released from CRUD by chemical reagents migrate to their respective electrode in the EK reactor for Co extraction from CRUD. Application of DC through electrodes immersed in solution results in oxidation at the anode, generating an acid front (H^+), and reduction at the cathode, producing a base front (OH^-) [14]. Radionuclide release rate from CRUD is limited because the OH^- generated at the cathode disrupts maintenance of low pH in the EK cell. However, if a cation exchange membrane (CEM) is installed between the EK cell and the cathode electrolyte, the OH^- cannot pass through to the EK cell, so the pH remains low [12] and the rateof radionuclide removal from CRUD increases. Although EK process is effective to decontaminate CRUD, the process generates secondary waste solution, which can contain radionuclides such as ^{60}Co. Secondary waste solution contaminated by radionuclides must be reduced in volume, and stored sustainably. There are several conventional methods for the removal of radionuclides from waste solution, including adsorption, precipitation, electrochemical methods, and membrane treatment [15–18]. Although those methods have some benefits, most of them have limits, including high cost and poor removal efficiency [19–21]. Including adsorption method by zeolite to the combined chemical and EK process was proposed to increase the removal efficiency of radionuclides.

The objective of this study is to combine EK and chemical decontamination processes to increase the efficiency of CRUD decontamination for decommissioning of large contaminated metal components from NPPs; the combination system was evaluated with and without enhanced scheme including zeolite and CEM.

Experimental

Synthesis of cobalt ferrite powder

CRUD is a common byproduct of reactor operation, yet its decontamination has not yet been carefully elucidated. It is important to have information about the chemical composition and crystalline structure of CRUD to decontaminate it properly. Simulated CRUD ($CoFe_2O_4$) was synthesized in powder form. Nonradioactive cobalt (^{59}Co) was used. $FeCl_3$ (97% reagent grade, Sigma–Aldrich) solution (0.4 M in 50 mL) and $CoCl_2$ (98%, purum p. a., Sigma–Aldrich) solution (0.2 M in 50 mL) were mixed in deionized water (DIW). NaOH (98%, Samchun) solution (3 M in 50 mL) was slowly added to the solution and constantly stirred by a magnetic stirrer until the pH reached 11. Oleic acid ($CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$, extra pure, Junsei; weight fraction of aqueous phase to surfactant = 0.34:0.12) was added to the solution as a surfactant and coating material to prevent change in the oxidation state of cobalt. The mixture was reacted at 80 °C for 1 h using a heating plate, then cooled to room temperature. After reaction, the mixture was rinsed twice with DIW and then centrifuged for15 min at 3000 rpm (Centrifuge 5702, Eppendorf). The supernatant was decanted and the remaining solid material was rinsed with ethanol to remove excess surfactant. The mixture was centrifuged again for 15 min at 3000 rpm and the supernatant was decanted. The resulting black precipitate was dried at 105 °C for 12 h, then ground to fine CRUD powder with size fractions of 0.0–0.5 mm (11.90%), 0.5–2.8 mm (56.46%), and 2.8–5.0 mm (31.63%). Before use, the CRUD powder was heated at 600 °C for 10 h to remove moisture [22].

Synthesized CRUD on metal specimen

The simulated CRUD was coated on a specimen of metal [SUS304 stainless steel that includes Ni (8–11%), Cr (18–20%), and lesser quantities of C, Si, Mn, P, and S] that is a component material of NPPs [23]. The surfaces of the metal specimen were abraded with SiC paper (1200 grit), then washed with acetone (99.5%, Kanto) in an ultrasonic cleaner (Branson 1510) for 5 min. Then 0.25 mL of cobalt nitrate solution (150 mg/mL, Sigma–Aldrich) was spread on the metal specimen and dried at 105 °C for 24 h. This procedure was repeated three more times (total of four coatings), to leave 1 mL of cobalt nitrate solution doped on the metal specimen. Then the specimen was heated at 700 °C for 24 h inside a furnace to create an oxide layer.

Chemical decontamination method

Chemical decontamination was applied to synthesized $CoFe_2O_4$ powder. Oxalic acid was used because it is better chemical reagent for $CoFe_2O_4$ powder than are malonic acid, citric acid, and nitric acid [24]. Synthesized $CoFe_2O_4$ powder (2 g) was placed in a 4 L beaker, then a peristaltic pump (Masterflex, Cole Parmer Instrument Company) was used to circulate oxalic acid solution (2.5 L, pH = 3.5) in the beaker. The amount of oxalic acid solution used during chemical decontamination was the same as used in the EK process. The test was run for 10 h. Decontamination results were checked by calculating mass balance. The mass of Co in solution was obtained as the product of Co concentration and solution volume. The mass of Co in the CRUD powder was determined from the Co concentration after acid digestion of CRUD powder in 0.1 N HNO_3 and 0.1 N HCl (1:3 in volume basis).

Enhanced CRUD decontamination method

To compare the chemical decontamination method using oxalic acid with the decontamination method with EK process, the same amount of oxalic acid solution was used in both methods as well as, the same reaction time (24 h) was applied. The experimental apparatus (Fig. 1) consists of four principal parts: the cell, electrode compartments, electrolyte solution reservoirs, and the power supply. Each electrode compartment contained 2.5 L of oxalic acid, which was sufficient to dissolve the Co from CRUD that was put in the cell of the EK reactor, and to avoid sudden variations of pH in the electrolyte solution. At the end of each side of the cell (anode and cathode compartments), a glass microfiber filter (grade GF/C, Whatman® International Ltd.) was installed to prevent scattering of the CRUD powder. A glass microfiber and a CEM (CMX, Neosepta®, Tokuyama Corp.) was set on the frame in the cell and fixed by a glue; no leaking between the cell and the electrode compartment was found before use. Peristaltic pumps were used to recirculate the oxalic acid solution in both electrode compartments, and a DC power supply (BioRad PowerPac™ 200) was used to create an electric field. When the chemical reagent (oxalic acid) is circulated in the EK system, Co ions dissolve from the CRUD; they are driven to the cathode by the electric field. The combined system with the chemical reagent and EK process was tested.

Three EK tests for powder and three EK tests for metal specimen (Table 2) were conducted respectively, and the results were compared. A set of control (conventional) and enhanced (using zeolite and CEM) EK tests were undertaken for powder and metal specimen. In the EK tests for powder, 2 g of synthesized $CoFe_2O_4$ powder was used, while the metal specimen coated with CRUD was placed at the center of the cell in the EK tests for metal specimen. The CRUD coated on surface of metal specimen was treated by oxalic acid in the cell and Co ion from CRUD was transferred by EK process to cathode compartment. 2.5 L of oxalic

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