

Environmentally benign and novel management route for radioactive corrosion products by hydroxyapatite

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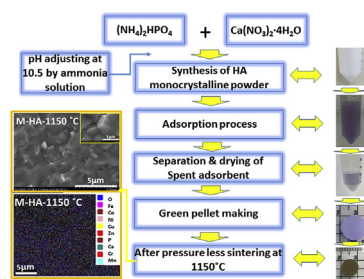
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HIGHLIGHTS

- The direct solidification of the captured corrosion products by HA has been investigated.
- No organic binders were used for solidification of M-HA matrix.
- The sintered matrix showed good densification and mechanical properties.
- ASTM PCT test approved the chemical durability of sintered matrix.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 19 January 2018

Received in revised form

4 May 2018

Accepted 6 May 2018

Available online 7 May 2018

Keywords:

Waste immobilization

Nano-ceramic

Hydroxyapatite

Radioactive corrosion products

ABSTRACT

A novel and environmentally benign route for the direct solidification of captured corrosion products (Co, Cr, Fe, Ni, Cu, Zn, and Mn) generated from the primary coolant system of nuclear power plants is introduced in this study. Synthesized calcium hydroxyapatite was used to remove individual and mixtures of corrosion products from aqueous solutions. The results show more than a 95% removal of these corrosion products for both cases. The direct solidification of adsorbed corrosion products was done by pressure-less conventional sintering. The sintered matrix revealed a good hardness (3.70 ± 0.60 GPa) and a relative sintered density $> 98\%$ after heat treatment at 1150°C . The measured compressive strength (207.3 ± 9.5 MPa) was significantly higher than the established waste immobilization criteria of the US (3.5 MPa) and Russia (4.9 MPa). The corrosion products consolidated matrix had a normalized leaching rate ranging from 3.4×10^{-2} to 3.1×10^{-6} g/m²/day. Moreover, no additional chemical treatments, additives (gypsum, slaked lime, sodium silicate, etc.), and sophisticated equipment were needed for the adsorption and solidification process. Therefore, the proposed waste management route has no adverse effects on the ecosystem and can be highly efficient to immobilize adsorbed waste and to reduce the secondary waste volume.

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1. Introduction

Corrosion products, known by Chalk River Unidentified Deposits (CRUD), such as ^{58}Co , ^{60}Co , ^{51}Cr , ^{64}Cu , ^{54}Mn , and ^{59}Fe are the main

sources of radiation build-up inside nuclear reactor vessel and pose serious problems in routine overhaul maintenance work. CRUD are released into the primary coolant due to the degradation of mechanical parts of the primary coolant system in nuclear power plants. The CRUD are transported to the reactor core and get activated under the high neutron flux. These are called radioactive CRUD which consequently increase the radiation level. CRUD can

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deposit on the surface of fuel rods and cause a reduction in the thermal conductivity. In certain cases, they may also damage the fuel rods due to stress corrosion cracking phenomena [1–3]. Therefore, it is necessary to use efficient adsorbents to maintain the coolant chemistry and to remove any metal ions that form due to the corrosion of structural materials of the nuclear power plant.

Many natural wastes, organic matter, and synthesized adsorbents have been successfully used to capture cobalt/CRUD from contaminated water [4–8]. For example, Granados et al. reported on the adsorption behavior of cobalt as a function of pH, contact time and initial metal ion concentrations for Fe–Mn oxide synthetic material [9]. Oliva et al. used commercial apatite to remove trace levels of Cd, Cu, Ni, Co and Hg, which are hard to remove by calcite or other organic adsorbents [8]. Yoonjin et al. used ammonium molybdophosphate–polyacrylonitrile to remove Co, Sr and Cs which come from radioactive laundry waste water [10]. However, the solidification of Co/CRUD captured adsorbents (secondary waste produced) was not addressed in the aforementioned studies.

Radioactive waste management procedures can be simplified and more cost-effective if the material being used as an adsorbent also acts as a matrix for the consolidation of captured nuclear waste. In addition, a significant reduction of secondary waste could be achieved with an adsorbent that can capture metal ions from waste and simultaneously solidify them thus eliminating the need for additional chemical treatments (addition of binders, excessive acid/base treatments or conditioning), loading to other matrices like Portland cement, glass or unsaturated polyesters.

Calcium hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) is a phosphate-based hard ceramic belonging to the apatite family and has the general chemical formula $\text{A}_5(\text{XO}_4)_3\text{Z}$. The apatite structure has two cationic positions (A and X) and one anionic position (Z) [11–14]. On ionic sites, different ions can be accommodated without affecting the apatite structure due to its ion exchange properties [11]. Calcium hydroxyapatite (HA) has excellent biocompatibility and is being widely used as a bio ceramic material for making artificial dental roots, teeth implants and artificial bones similar to those living bodies [15–17]. The HA is also abundantly present in nature in the form of waste bones and phosphate-based minerals. Both natural and synthetic HA have been extensively investigated for their adsorption and substitutional properties to remove pollutants and toxic heavy metals [8,18,19].

In terms of environmental pollution, it is always desirable to use waste management methods that are the least harmful to the environment and nature. The use of organics, lime and cementitious binders for the stabilization and solidification of contaminants has been considered the best available technology [20]. The additional binders such as biochar, starch and carbodiimide have been used during green shaping of ceramic body to make it easier to obtain a desired density with less defects while pressing. During sintering at higher temperatures, the pyrolysis of these binders results in the emission of carbon dioxide or other hydrocarbon gases [21,22]. Nowadays, geo-polymers, slag, cement kiln and hydroxyapatite have also been tested for the consolidation process [23].

In this study, we applied the synthesized HA to remove single metal ions and a mixture of CRUD metals from an aqueous system. This study further investigated the possibility of binder-free immobilization of a CRUD captured adsorbent in a form of the highly dense and durable sintered matrix. This technique involves the adsorption of CRUD onto the surface of ceramic (calcium hydroxyapatite) nanoparticles. The adsorbent was separated from liquid by centrifugation and ultrafiltration. Then the compaction and consolidation of separated CRUD captured adsorbent was achieved by using conventional pressure-less sintering method.

2. Experimental procedures

2.1. Synthesis of the adsorbent

The wet precipitation method has been used to synthesize crystalline apatite as described elsewhere [13]. Anionic and cationic solutions were prepared by dissolving each of the di-ammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ and calcium nitrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 200 ml of ultrapure deionized water, respectively. The Ca/P molar ratio of both the reactants was theoretical set as 1.67. The anionic solution was dropwise mixed with the cationic solution at a speed of 0.06 ml/s under continuous stirring at 200 rpm. During mixing, the temperature and the pH of the solution were continuously monitored and maintained at 30 °C and 10.5, respectively. To maintain the pH of the solution, a concentrated ammonia solution was used. The aging of white gel type precipitates that formed during the synthesis was done inside the parent solution for 3 h. During the first hour, the stirring continued at 100 rpm and the temperature was maintained at 30 °C, whereas at the end of the first hour, the reaction vessel was removed from the hot plate and kept without stirring at room temperature for 2 h. After that the suspension was filtered, thoroughly washed and dried overnight at a temperature of 100 °C in a vacuum oven. The dried precipitates were ground to fine powder with a mortar and pestle.

2.2. Adsorption procedures

A detailed adsorption study of HA can be found elsewhere [24]. First, the maximum removal of Co(II) was optimized by varying the solid to liquid ratio (S: L ratio) from 2 to 5 g/L with 1 mM of Co(II) at pH 6. The adsorbent-liquid contact time was set as 24 h with constant stirring at 150 rpm at 25 °C. More than 90% removal of the Co(II) was observed for S:L ratio of 4 g/L. By using the optimized S:L ratio, a single element Co(II) solution and a series of corrosion products (Co(II), Cr(III), Cu(II), Ni(II), Mn(II), Fe(II) and Zn(II)) were removed from the contaminated aqueous solution. In the mixture of corrosion products, the concentration of each metal ion was kept constant at 1 mM in 100 ml of deionized water. After 24 h, the solid and liquid phases were separated with a 0.45 μm syringe filter followed by a 5 min centrifugation at 3200 rpm. The concentration of the metal ions in the separated dried adsorbent and the supernatant were measured by ICP-OES. The percentage removal (% R) of the metal ions was calculated by equation (1),

$$\%R = (C_o - C_e)/C_o \times 100 \quad (1)$$

where C_o and C_e are the initial and final metal ion concentrations (mM), respectively.

2.3. Sintering of pure HA and corrosion product adsorbed HA

After the separation and drying of the adsorbent in a vacuum oven at 100 °C overnight, the powder was shaped into cylindrical pellets with a stainless steel mold 13 mm in diameter. The pressing at room temperature was conducted under 100 MPa for 30 s by a Carver(R) uniaxial press. For each pellet, 1.20 g of pure HA and the metal adsorbed HA (Co-HA and M-HA) powder was used. The pressure-less conventional sintering of the as-pressed pellets of pure HA Co-HA and M-HA was carried out in the box furnace (Model: S-1700, HANTECH) under an air environment. In the first step, the pure HA was studied for a range of temperatures (500 °C, 800 °C, 900 °C, 1000 °C, 1150 °C and 1300 °C) for 120 min at a heating ramp of 4 °C/min to optimize the sintering temperature. After the sintering, the samples were left inside the furnace to cool

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