Performance test of 3D printed ceramic filters for capturing of radioisotopes from a nuclear reactor coolant

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1. Introduction

The purpose of Chemical and Volume Control System (CVCS) is for controlling water chemistry in the reactor coolant system (RCS) of nuclear power plants[1]. Some functions of CVCS are controlling boron concentration, maintaining the level of pressurizer, and using filters and demineralizers for purifying the reactor coolant system[2].

Filters and demineralizers are used for capturing the activated corrosion products in reactor coolants. Specifically, iron was the dominant corrosion product, nickel is the second long-lived radionuclide, and cobalt could be activated by neutron at reactor core and thus it affects workers negatively with radiation dose[3,4]. Moreover, it is necessary to remove the main elements of Chalk River Unidentified Deposit (CRUD). According to the EPRI guideline, they recommended removing Fe, Ni, and Co for CRUD-induced fuel failures[5].

Ion exchangers were used for adsorption heavy metal ions in primary coolant but the operation temperature of them is 120 °F for keeping capability of ion exchangers[6].

For overcoming the limitation of ion exchangers, this study investigated the feasibility of the fabrication of cost-effective zeolite filters which are stable at high temperatures and have high adsorption capacity for the constituent elements of CRUD.

2. Methods/Experimental

2.1 Materials

The condition of inks used for 3D printing was obtained from Nishant's work. A mixture of bentonite, methyl cellulose, poly vinyl alcohol were added as binders and viscosity controlling agent[7]. The inks were homogenously mixed by a ThinkyMixer ARE-310 centrifugal mixer.

Table 1: The mixing ratio of a slurry for 3D printing

	Zeolite 4Å Zeolite 13X	Bentonite	Methyl Cellulose	Poly Vinyl Alcohol
Wt.%	85	10	3.5	1.5

2.2 Modelling and Printing

The design of a filter was made by 3D modeling software. There were two designs for printing, one was a simple hollow wall shape and the other was twisted honeycomb shape.
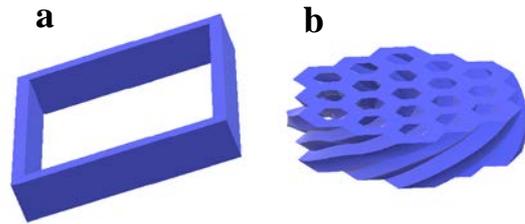
Fig. 1. Modeled structures a) a simple wall shape, b) a twisted honeycomb structure.

2.3 Mechanical properties of printed filters

The compressive strength of printed zeolite 4Å filters sintered at 700, 800, 900, 1200 °C were measured by the Universal Testing Machine at a cross-head speed of 0.2 mm/min with a 10 kgf load cell.

The hardness of 3D printed filters with zeolite 13X which were sintered at 700, 750 °C were measured using the micro-Vickers hardness method at a 25 gf loading.

2.4 X-ray Diffraction(XRD) and Differential Scanning Calorimetry(DSC) characterization

XRD and DSC were analyzed to characterize the zeolite structure at high temperatures. XRD data were collected using a SmartLab (RIGAKU, Cu Kα-radiation, room temperature). Samples were ground to fine powders and investigated for angle 2θ in the range from 3° to 65° with 0.02°/step at room temperature.

DSC measurements were conducted by using DSC404 F1 (NETZSCH). The samples with masses in the range of 8.4-11.4 mg were sealed in a crucible. Scans were performed from 30 to 1400 °C at 10 °C min^{-1}.

2.5 Adsorption test with Fe and Ni

Adsorption behavior of Fe and Ni ions onto 3D printed zeolite filter were performed using a batch-adsorption test with a shaker at 140 rpm. Initial concentrations were respectively 10 ppm of Fe, 10 ppm of Ni and 300 ppm of Co. The solid to liquid ratio was

1:50 for all cases. Contact time was 24 hours which showed enough time for reaching an equilbrium[8]. The pH level of solutions was measured with a Thermoscientific pH meter before and after the adsorption test. The concentration of ions was measured by using ICP-MS.

3. Results and Discussion

3.1. Printed samples

The printing conditions were optimized based on the rheology of the inks by considering shear-thinning and cross points in the modulus and storage curves. Fig. 2 shows the zeolite filter products printed as the model structures.
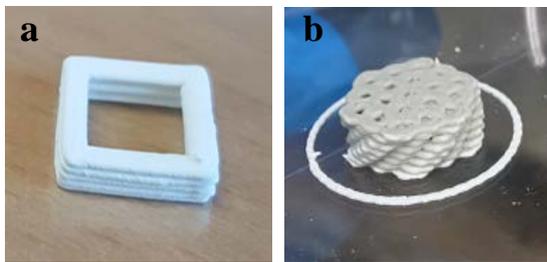
Fig. 2. Fabricated ceramic filters by a 3D printer a) a simple wall shape, b) a twisted honeycomb structure

3.2. Compressive strength and Hardness

The results of the compressive strength of printed zeolite 4Å showed that the strength was increased with the increasing sintering temperature, but it was still quite low value less than 10 MPa. In the case of printed zeolite 13X samples which sintered at 700 and 750 ℃, hardness values ($HV_{0.025}$) were around 13-14. The larger error bar of 900 ℃ in Fig. 3 was obtained because of one abnormal measurement.
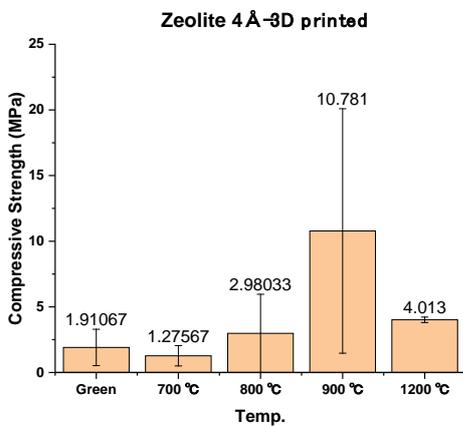
Fig. 3. Compressive strength of printed zeolite 4Å
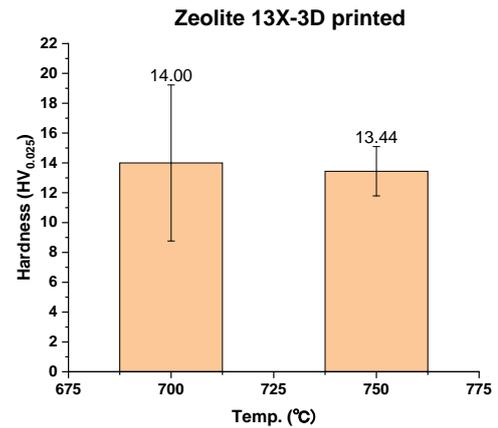
Fig. 4. Micro-Vickers Hardness value of printed zeolite 13X

3.3. XRD

The results of XRD showed that the original structure of zeolite4Å was changed from sodium aluminum silicate (according to the X-ray Powder Diffraction File, PDF Card No.: 01-086-6671 of the ICDD) to nepheline (PDF Card No.: 01-075-2935). In the case of zeolite 13X, the sodium tecto–aluminosilicate (PDF Card No.: 01-074-2512) to a mostly amorphous phase. It means that if we sintered our samples over 800 ℃, the adsorption capability of zeolite could be changed.
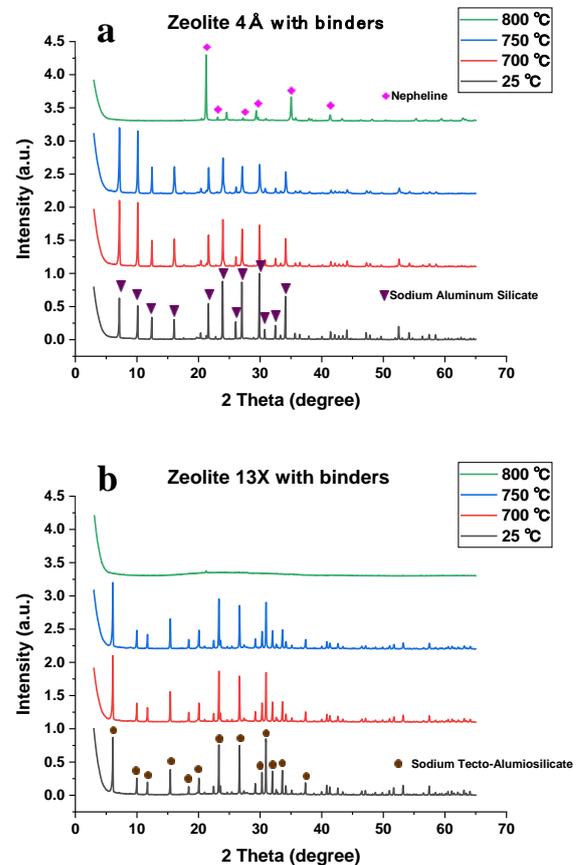
Fig. 5. XRD results a) zeolite 4Å, b) zeolite 13X

3.4. DSC

The results of DSC data for zeolite 4Å and zeolite 13X showed two exothermic peaks over 800 °C. After these reactions, original structures of zeolite were collapsed, then the properties of samples could be changed.
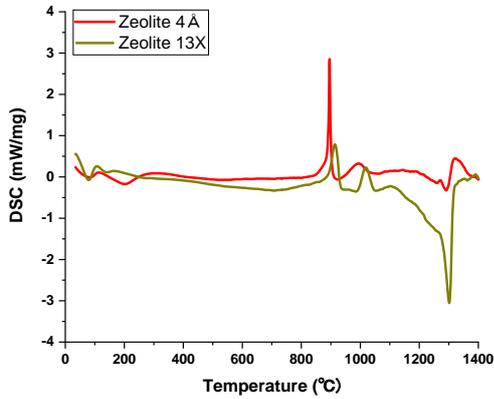
Fig. 6. Graph of DSC results

Table 2: Reaction temperature of DSC

	1st (Exothermic)	2nd (Exothermic)	3rd (Endothermic)
Zeolite4Å	895.6 °C	992.1 °C	1291.1 °C
Zeolite13X	913.8 °C	1017.5 °C	1301.5 °C

3.5. Adsorption test

The removal percent of ions was calculated using equation (1) and the decontamination factor was calculated by equation (2). C_i is the initial concentration of ions and C_e is the equilibrium concentration of ions after adsorption[9].

$$Removal \ \% = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

$$Decontamination \ Factor = \frac{C_e}{C_i} \quad (2)$$

Printed filters showed a higher removal efficiency compared to zeolite powder. Zeolite 4Å filter had over 99.9 percent of removal performance of Ni and Fe ions in solutions.

Measured pH level indicated that the higher value of pH brought less adsorption for targeting ions in powder samples because hydrogen ions which were dissolved could make competitive adsorption. Otherwise, in the case of the filter formed, lower pH levels were measured with higher adsorption capacity. It meant that the filter formed had a strong affinity to captured ions compared to powder formed. In this regard, the effects of binders should be investigated further.
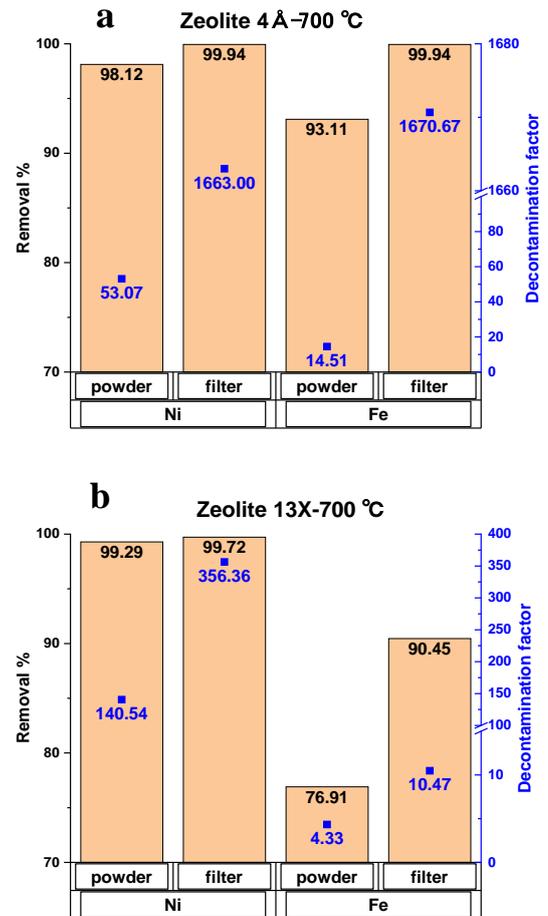
Fig. 7. Removal % and DF a) zeolite 4Å, b) zeolite 13X

4. Conclusions

The study demonstrated that zeolite-based ceramic filters could be printed into a complex 3D model, such as a twisted honeycomb structure. Moreover, with an additional heat treatment, the filters were partially sintered for using in an aqueous environment with excellent adsorption capacity. However, a higher temperature higher than 800 °C could disintegrate the porous structure of ceramic powders. For the enhanced mechanical strength of the printed filters, the control of additives is necessary.

a **Zeolite 4Å–700 ℃**

b **Zeolite 13X-700 ℃**

Fig. 8. pH level after adsorption a) zeolite 4Å, b) zeolite 13X

Acknowledgments

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