3D printing of zeolite for adsorption of radioisotopes from a nuclear reactor coolant

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1. Introduction

In operating nuclear power plants, the radionuclides are present in the reactor coolant system. These radionuclides are generated primarily by activation of dissolved ions released from structural components into the coolant [1]. These isotopes should be removed for treating liquid wastes in aspect of safety and economically. There are many studies on the adsorption of dissolved Co (Ⅱ) and Ni (Ⅱ) ions by inorganic adsorbents (e.g. molecular sieve, kaolinite clay) [2,3]. Treatment of the liquid wastes with the inorganic adsorbent is preferred because of its high exchange capacity, possible selectivity and specificity, good resistant to radiation [4].

Manufacturing of ceramic filters is difficult because of brittleness of ceramics. Furthermore, fabrication cost for ceramics is five times higher than fabricating of polymers [5].

Thus, ceramic 3D printing based on extrusion of slurry ink has an advantage in making a filter of adsorbents, because 3D printing can reduce processing time and cost to form a complex filter structure. [6]

2. Experimental Procedure

2.1. Materials

For making a slurry ink of 3D printing, zeolite 4 Å (Sigma Aldrich) powder was mixed with bentonite clay (Sigma Aldrich) as a binder, methylcellulose (Sigma Aldrich) as a plasticizing organic binder, and poly(vinyl) alcohol (Sigma Aldrich) as a co-binder [7] with the ratio presented in Table 1. The slurry was mixed in a ThinkyMixer ARE-310 centrifugal mixer at 2000 RPM for 8 min and defoamed at 2200 RPM for 90 s. After making a slurry, for stabilizing, it was aged for 24 h at room temperature.

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

	Zeolite 4Å	DI-water	Binders
Vol.%	20~32	68~80	<1

2.2. Modelling

Using 3D modeling software, the 3D model was designed as a wall shape with two layers per each step.

2.3. Printing

After loading the ink in the barrel, the designed structure was printed by using INVIVO 3D Printer (ROKIT), which operates in a slurry extrusion mode. Printing conditions were set as follows: pressure 250~300 kPa; temperature of bed 45 ℃; diameter of nozzle 609 ㎛;

2.4. Drying and Sintering

After drying at 25 ℃, for 24 h under vacuum, printed samples were sintered in a temperature controlled furnace in an air environment at 700/800/900 ℃ for 2 h, respectively, at a heating rate of 10 ℃/min. Sintering removes the organic content [7]. Before and after sintering, the apparent density of samples was measured.

2.5. Rheology test

The rheological properties of the slurries were characterized by HAAKE RS 6000 (ThermoFisher) with a cone plate geometry with 1° Angle, a 0.106 mm gap. For gaining shear-thinning behavior, flow ramps were conducted at 25 ℃ over a strain rate from 1~100 s^{-1}. The storage modulus (G') and loss modulus (G'') were measured by dynamic mechanical analysis (DMA) with the oscillation stress from 1 to 5000 Pa at 1 Hz[8].

2.6. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) of material printed was carried out by using Hitachi SU5000. The measurement was done with 5 kV to reduce charge accumulation on the ceramic samples.

3. Results and Discussion

3.1. Slurries for printing

As a result of using a centrifugal mixer, inks were mixed homogeneously as shown in Fig.1.

Figure 1. Mixed inks with deionized water

3.2. Printed a structured sample

Using an appropriate condition of 3D printing, the sample were printed as a wall shape with 1.2 mm thickness completely.

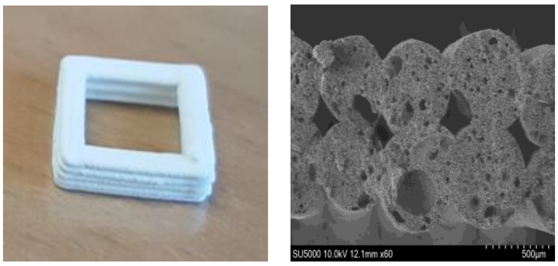

Figure 2. Printed a bulk sample and cross-section image

3.3. Drying and Sintering

With a mixing ratio of 28 vol.% of zeolite 4 Å, the mass fraction of remained samples were measured 41 wt.% of the original ink which matches a theoretical amount of zeolite powders. Thus, it means that all of water and binders were totally evaporated.

After sintering of samples, density was further increased because of densification as shown in Figure 3. It means that the volume fraction of pores (porosity) is lower in the sample with a higher sintering temperature.

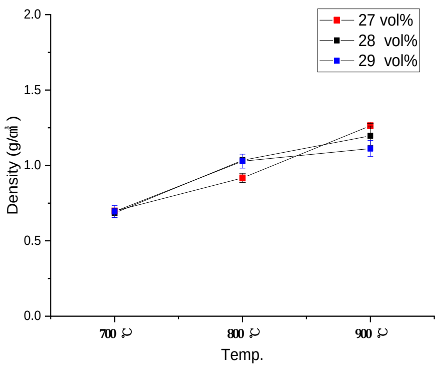

Figure 3. Different density depending on sintering temp

3.4. Rheology test

Based on Figure 4, the state of slurries can be divided into solid-like behavior and liquid-like behavior by the cross over point of G' and G''. Shear-thinning happens as shown Fig. 5, thus ink could be printable because of the low viscosity at high pressures.

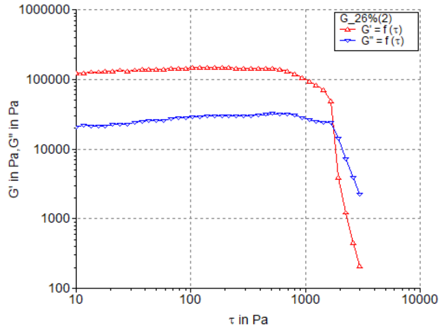

Figure 4. Storage modulus and loss modulus of inks

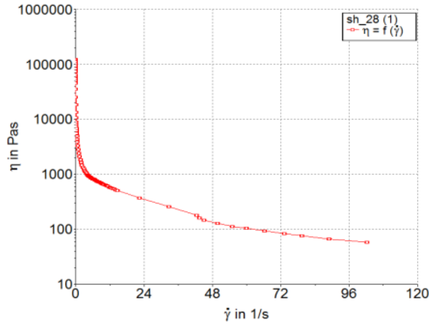

Figure 5. Shear-thinning of inks

3.5. SEM images

Based on SEM images in Fig. 6, as the sintering temperature increases, more zeolite particles are connected to each other. Sintered microstructures which are treated at over 700 ℃ have more pores than the green state because binders were evaporated. .

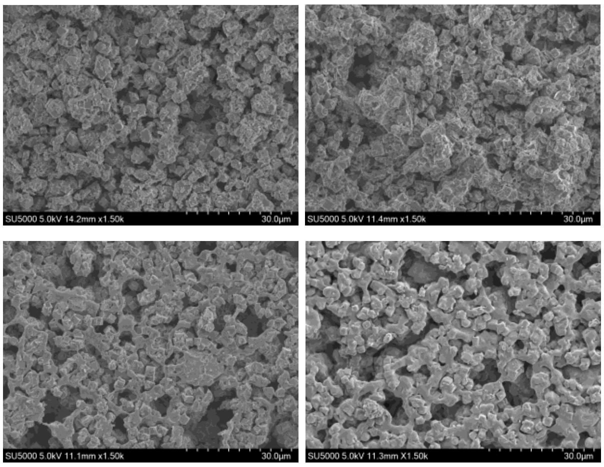

Figure 6. Green state, 700℃, 800℃, 900℃ (left to right)

4. Conclusions

3D printing behavior of zeolite was investigated to make a ceramic filter for adsorption of radionuclides. Properties of printed zeolite were evaluated in terms of microstructure, rheology, and sintering behavior.

Through analyzing the rheology properties, printable concentrations of slurries were set between 27-29 vol.% of zeolite powders. The density of printed filter increased from 0.6843 g/㎤ to 1.197 g/㎤ as sintering temperatures were increased from 700 ℃ to 900 ℃. Moreover, the porosity of printed filter could be controlled by adjusting the sintering temperature.

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