Performance of Cold Sintered Zeolite 13X for Removing Cs^+

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1. Introduction

Zeolites are widely used in the fields of adsorption and ion exchange due to their larger specific surface area and low cost [1]. Specifically, the structure of zeolite is negatively charged, which attracts cations such as Cs^+ in radioactive liquid waste. Commercial ion-exchanger with zeolites was fabricated on a styrene-DVB matrix and zeolite powders mixed with an amount of binder into a specific shape [2]. Furthermore, it should be fired at a high temperature (700-800℃) for sustaining the structure.

Cold sintering is recently suggested by Randall et al. and this new concept is economical and safer rather than other conventional sintering techniques because of using low temperature (<300℃). Recently, cold sintering has been suggested to apply to the decontamination of radionuclides by the Ryu group [3][4][5]. However, there is no study for applying cold sintering to zeolite till now.

From this study, we tested the performance of cold sintered zeolite 13X (faujasite structure) as an adsorbent to understand how to apply cold sintering to nano porous-crystalline materials. Furthermore, fabricating zeolite pellet through cold sintering is possible without any inorganic binder powders, meaning no need for additional calcination at high temperatures.

2. Methods and Experiment

2.1 Materials

Zeolite 13X powder ($Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]\cdot xH2O$, 283592), cesium chloride (CsCl, 289329), sodium hydroxide (NaOH, solution, 415413) were supplied by Sigma Aldrich. 0.01 M of NaOH solution was used for the titration test. 125 ml of polypropylene (PP) wide neck bottles (WH.209667) was from the Wheaton, 0.45 ㎛ of PTFE filter was used.

2.2 Cold Sintering

The cold sintering process was divided into dry and wet conditions. For setting the wet condition, 17 wt.% of liquid agents (deionized water or 5M of NaOH solution) were added into dry powder and then homogeneously mixed through a mortar and pestle [6].

The powder was poured into the steel mold and loaded the pressure, 500MPa for 10 min at 200 ℃ under the hydraulic pressing as shown in Fig. 1.

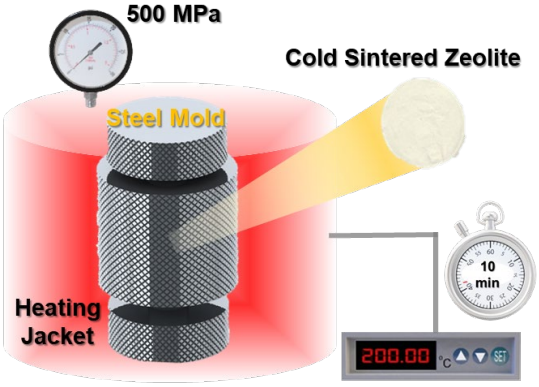

Fig. 1. Schematic of cold sintering.

2.2 Batch Adsorption Test

Measuring the adsorption capacity of cold sintered zeolite pellets was done by the batch adsorption test following the OECD guideline[7]. For comparing the conventional zeolite 13X pellet, the conditions of adsorption test were set (S/L = 5 g/L, 100 ppm of CsCl, pH 7, 24 hr) [2]. After 24 hr, used cold sintered zeolite pellets were separated from the liquid and treated water was filtered by 0.45 ㎛ of PTFE. The final concentration of Cs was measured by ICP-MS.

2.3 Characterization

The crystal structure of zeolite before and after cold sintering was investigated by X-ray diffractometry (XRD) (SmartLab, RIGAKU) with CuKα radiation at 45 kV and 200 mA. Data were collected in the range of 2Θ 3-60° with a 0.01°/step and a scanning time of 5 s/step.

The microstructure of fractural surface of sintered zeolite was characterized by a Scanning Electron Microscopy (SEM) using a SU8230 (Hitachi) with 3 kV electron beam. The measured data were binarized by the Otsu model.

3. Results and Discussion

3.1. Cold sintered zeolite pellets

The relative density of cold sintered zeolite pellets were 56.9±1.56, 65.0±1.34, 72.7±1.62, 77.15±3.50, and 82.5±1.40 for compressed, 700℃, dry cold sintering, cold sintering with H_2O and cold sintering with NaOH.

The transparency of pellets showed in Fig. 2. and the most transparent one was with NaOH. Transparency is one indexing for the degree of sintering because the light scattering comes from the discontinuity of the body[8]. Thus, the relative density and transparency indicated the most densified matrix was cold sintered with NaOH.The crystal structure of treated samples was analyzed by comparing with the PDF card # 01-083-7118. Both 700℃ heat treatment and cold sintering maintained the zeolite's structure as shown in Fig. 3.

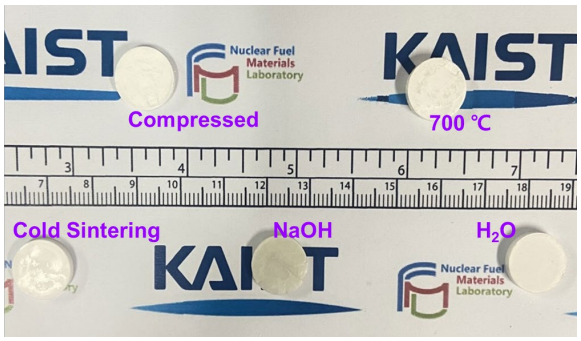

Fig. 2. Cold sintered zeolite pellets.

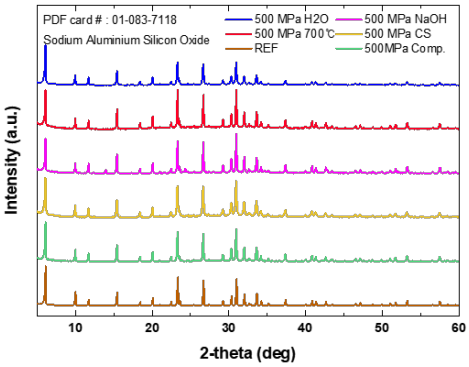

Fig. 3. XRD results of all samples.

However, the microstructure of each sample was quite different stemming from the difference of densification as shown in Fig. 4. For more insightful rather than original SEM images, binarization images on Fig. 4. represented the fewer boundaries (black line) on the densified matrix.

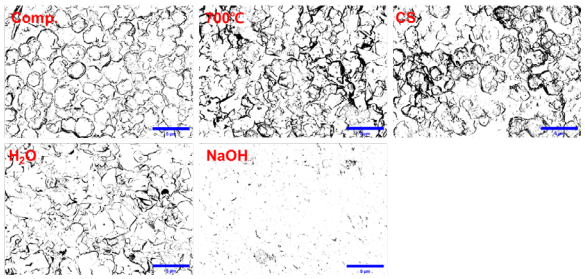

Fig. 4. Binarization SEM images of all samples.

3.2. Adsorption performance of cold sintered zeolite pellets

Even if the same crystal structure, processing might affect the original porous structure of the zeolite, which participates in the adsorption mechanism. The result showed that the highest adsorption capacity was with the cold sintered sample with H_2O and the lowest adsorption capacity was with the cold sintered sample with NaOH as shown in Fig. 5.

With the NaOH, the route of cesium ions might be blocked by the densified matrix matching with Fig. 4, but with H_2O, it was an astonishing result because it was still densified but provided the most adsorption sites compared with other matrixes.

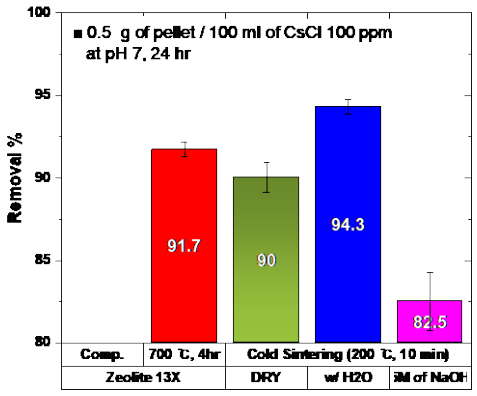

Fig. 5. The adsorption capacity of cold sintered zeolite pellets

4. Conclusions

This study provided that cold sintering did not affect the crystal structure but it affected the densification and adsorption capacity of the zeolite 13X matrix depending on the presence of liquid agents. However, for deciding the cold-immobilized matrix, further research about measuring the leaching resistance of Cs^+ is required.

Acknowledgments

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