CaO Absorbent Development for ¹⁴C Immobilization Generated From Waste Resin of Heavy-Water Reactor and Mechanism Study

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1. Introduction

Domestic Heavy-Water Reactor Nuclear Power Plants (NPPs) produce a lot of spent resin in the process of operation. Nuclides are captured in a spent resin by ion exchange. It is treated using a unique method different from a method to treat general radioactive waste. Conventional methods of treating the spent resin include activity stripping, the PLO process, acid stripping and thermal stripping, and all of them aim to selectively separate ¹⁴C, a long halflife nuclide, and reduce the volume of spent resin. Currently in Korea the method of treating the spent resin is not determined, and it is stored in storage tanks inside the NPPs. Looking at the spent resin treatment process under investigation, gaseous ¹⁴C, generated from the spent resin, is immobilized again, and disposed of as a solid. The existing CO₂ removal technique has an advantage in terms of volume reduction, but it is not enough to stabilize the radionuclide.

CaO has been considered as a good absorption material for CO_2 capturing process due to high efficiency of CO_2 capturing and high stability of CaCO₃, final product. However, there is a disadvantage to handle a CaO as absorbent because it exists as powder form without support material.

In this study, CaO was synthesized as cylindrical form without support. Porosity of CaO structure was controlled using organic solvent. FT-IR analysis was conducted for mechanism study of CaO structure formation.

2. Experimental

To make the absorbent for removing gaseous ¹⁴C, desorbed from the spent resin, calcium acetate was dissolved in the DI water, and ethylene glycol was added to it. Calcium hydroxide was added to the

resulting mixture, and the mixture was mixed, and aged for 24 hours at room temperature. An organic solvent was added to the aged mixture, and a paste was made. It was treated with heat, i.e. 90°C, 300°C and 900°C, and the absorbent was made. Ethanol and isopropyl alcohol (IPA) were used as organic solvents, and a paste without the organic solvents was also assessed to compare properties. The physical properties of the absorbent were analyzed through the XRD and SEM analysis, and the FT-IR analysis was conducted to analyze the changes in the absorbent formation mechanism.

3. Result and discussion

3.1 Comparison of properties by absorbent manufacturing method

To analyze properties depending on the heat treatment temperature of the absorbent, samples, plasticized at 300°C and 900°C, were used to conduct the XRD analysis. Fig. 1 illustrates the result of the XRD analysis of properties depending on the temperature of the absorbent. When the absorbent was treated at 300°C, it existed in the form of Ca(OH)₂, and there was a small quantity of CaCO₃. CaCO₃ is thought to have been formed by CO₂ or Calcium acetate in the air. When the absorbent was treated at 900°C, Ca(OH)₂ and CaCO₃, which existed at 300°C, were turned into CaO through dehydration and decarbonation. What follows are the reaction formulas.

$$Ca(OH)_2 \rightarrow CaO + H_2O$$
 (1)

$$CaCO_3 \rightarrow CaO + CO_2 \tag{2}$$

The SEM analysis was conducted with regard to the differences in the porosity of absorbents depending on the organic solvent added when absorbents are manufactured, e.g. alcohol-free, ethanol and IPA. Fig. 2 illustrates the result of the SEM analysis by organic solvents. It was confirmed that when alcohol-free was added, no porosity was formed, and when ethanol was added, porosity was formed, but it was less than the porosity resulting when IPA was used.

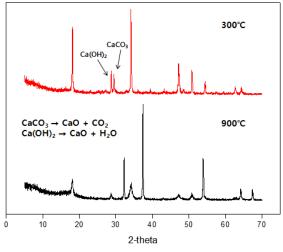


Fig. 1. XRD patterns of Calcium absorbent.

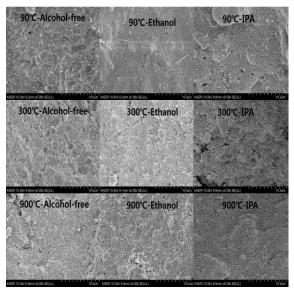


Fig. 2. SEM images by organic solvent and temperature.

3.2 Changes in the absorbent formation mechanism

The esterification between ethylene glycol and calcium acetate was used to manufacture an absorbent with free porosity without using any inorganic support or polymer. The FT-IR analysis was conducted to see if this esterification affected the absorbent formation mechanism. Fig. 3 shows the result of FT-IT by aging time. It was similar to the result of FT-IT analysis of calcium acetate. The peak

appearing at 3630 cm⁻¹ was reduced, indicating that $Ca(OH)_2$ reacts and decreases with time. As FT-IR alone did not show much difference, however, it was difficult to analyze the mechanism. Accordingly, the mechanism will be analyzed using additional methods like NMR.

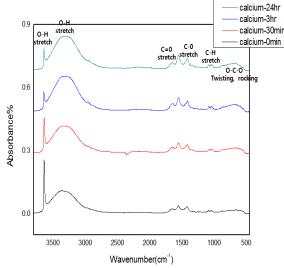


Fig. 3. FT-IR analysis of calcium absorbent by aging time.

4. Conclusion

In this study, CaO structures for CO₂ capturing were successfully synthesized. Porosity of CaO structure was controlled by organic solvent. IPA shows the high and uniform porosity. Form XRD results, it was confirmed that calcium hydroxide still exist after heat-treatment at 300°C and calcium oxide was formed after heat-treatment at 900°C. Uniform and porous surfaces of absorbent were indicated from SEM images. The FT-IR analysis was not enough to analyze changes in the absorbent formation mechanism. Accordingly, the mechanism will be analyzed using additional methods like NMR.

REFERENCES

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