The Study on the Solidification of Radioactive Zeolite Waste Using Alkaline Active Agents for Final Disposal

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ABSTRACT

This study analyzed the compressive strength characteristics of alkaline activator–based mock solidified waste forms of radioactive zeolite and evaluated their potential suitability for final disposal. In heavy-water nuclear power plants, steam recovery systems are employed to capture heavy-water vapor released from reactor systems and to limit tritium emissions to the atmosphere, with zeolite commonly used as the desiccant. Without proper solidification and disposal, contaminated zeolite may pose a risk of secondary contamination through airborne dispersion or radionuclide leaching. Although a portion of the adsorbed tritium (^{3}H) and carbon-14 (^{14}C) can be removed by pressurization and thermal treatment, other radionuclide species may remain associated with the spent zeolite, indicating the need for stabilization in a monolithic waste form. In this study, zeolite was combined with alkaline activators to form an aluminosilicate-based geopolymer matrix. Based on a comparative analysis of compressive strength under different curing conditions and alkaline activator compositions, the geopolymer waste form prepared using a 10 M NaOH solution with a sodium silicate–to–sodium hydroxide mass ratio of 1.5 exhibited the highest compressive strength under both curing regimes. The maximum compressive strength obtained under initial thermal curing at 60 °C was 14.88 MPa, which was 12.64 % higher than that measured for specimens of the same composition cured at room temperature (RT). The proposed solidification approach exceeded the compressive strength requirements specified in the waste acceptance criteria (WAC) and achieved a waste loading of 76 wt%, which is expected to significantly reduce the number of waste drums required for disposal. Overall, these results indicate that the proposed method provides a viable option for the treatment of spent zeolite waste while satisfying the mechanical strength requirements for disposal.

Keywords: *Solidification, Radioactive waste, Waste form, Zeolite waste*

1 INTRODUCTION

Pressurized heavy water reactors (PHWRs) are operated in several countries, with a total of 47 commercial units worldwide. In the Republic of Korea, PHWRs are limited to CANDU-type reactors at the Wolsong Nuclear Power Plant, where four units were constructed, although Wolsong Unit 1 has been permanently shut down [1]. Heavy-water reactor systems often include molecular sieves for the removal of water vapor, followed by zeolite-based adsorbents to further dehydrate heavy water [2].

During operation, these zeolite desiccants accumulate radioactive contaminants, primarily tritium (^{3}H) and carbon-14 (^{14}C), which are pure beta emitters characterized by high volatility and leachability even under mild condition. As a result, spent zeolite materials become contaminated with both beta- and gamma-emitting radionuclides, necessitating effective stabilization prior to disposal. Ensuring disposal safety therefore requires solidification technologies capable of immobilizing these radionuclides under low-temperature conditions where volatilization is suppressed.

For long-term disposal, solid radioactive wastes such as spent zeolite must be immobilized in mechanically stable waste forms. According to the U.S. Nuclear Regulatory Commission's Technical Position on Waste Form, Revision 1, cementitious and polymer-based waste forms are required to satisfy waste acceptance criteria (WAC), including adequate compressive strength and structural stability [3].

In this study, a geopolymer-based solidification strategy is investigated as a potential alternative for the immobilization of spent zeolite waste. The feasibility of geopolymer solidification is evaluated with emphasis on key parameters relevant to practical waste-form development, particularly waste-loading capacity and compressive strength. The remainder of this paper describes the fabrication procedures for geopolymer waste forms and presents an assessment of their compressive strength with respect to the mechanical stability requirements specified in the WAC.

2 MATERIALS AND METHODS

2.1 Raw Materials and Fabrication of Geopolymer Waste Forms

To synthesize the geopolymer matrix, a spent inorganic ion-exchange medium based on molecular sieve 4A was employed as the aluminosilicate precursor. An alkaline activating solution was formulated using sodium hydroxide pellets in combination with a commercial sodium silicate solution. The sodium silicate solution used in this study contained 9.0–10.0 wt% Na_2O and 28.0–30.0 wt% SiO_2.

Before geopolymer paste preparation, the zeolite material was physically processed to enhance homogeneity and promote consistent reactivity during alkali activation. The molecular sieve 4A rods were subjected to ball milling to produce a fine powder with improved uniformity and reactivity. The resulting milled zeolite powder was then mixed with the prepared alkaline activator at a mass ratio of 76 wt% zeolite to 24 wt% alkaline activators to form a homogeneous geopolymer paste.

The alkaline activating solution was prepared by blending sodium silicate and sodium hydroxide solutions at sodium silicate–to–sodium hydroxide mass ratios (SS/SH) of 1.5, 2.5 [4]. A series of sodium hydroxide solutions with molar concentrations of 2, 4, 6, 8, 10, 12, and 14 M were prepared by stirring for 30 min prior to use. By combining the seven NaOH molarities with the three SS/SH ratios, a total of 14 distinct alkaline activator compositions were evaluated in this study.

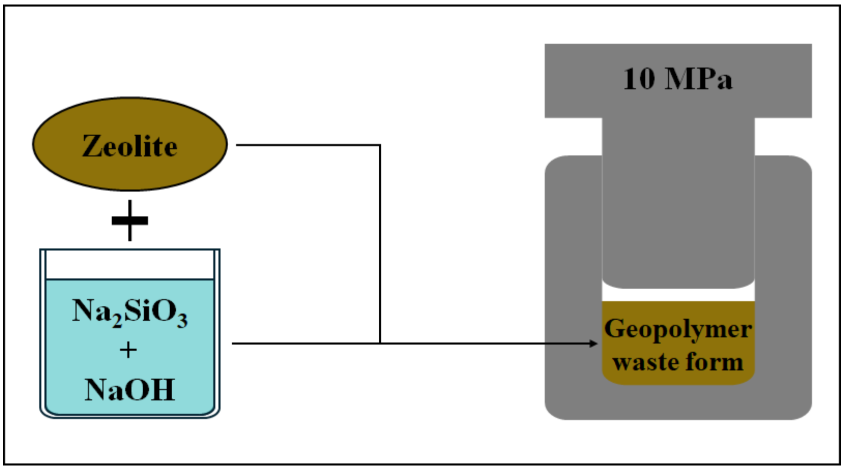

Figure 1. Schematic illustration of the geopolymer waste-form fabrication process using spent zeolite adsorbents.

The resulting geopolymer paste was placed into a steel mold and subjected to uniaxial compaction at a pressure of 5 MPa using a hydraulic press, as schematically shown in Figure 1, to fabricate cylindrical specimens. The specimens were prepared with a diameter of 14 mm and a height of 28 mm, corresponding to an aspect ratio (H/D) of 2.0 [3]. After removal from the mold, the specimens were cured under two different humidity–temperature conditions to assess the influence of externally applied thermal energy: (i) curing at room temperature (RT, 25 ± 2 °C) without any artificial heat input for 28 days; and (ii) curing with intentional thermal treatment at 60 °C for the first day, followed by storage at RT for an additional 27 days [5].

2.2 Compressive Strength Evaluation of Geopolymer Waste Forms in Relation to Waste Acceptance Criteria

The mechanical performance of the geopolymer waste-form specimens was assessed exclusively through compressive strength testing.

Compressive strength was measured in accordance with ASTM C39/C39M–21, which defines standardized procedures for testing cylindrical specimens with respect to specimen geometry, loading conditions, and failure criteria [6]. This standard was adopted because the geopolymer specimens prepared in this study had a diameter of 14 mm and a height of 28 mm (H/D = 2.0), consistent with the geometry specified in ASTM C39, and because it provides reproducible loading conditions suitable for comparison with previously reported data on cementitious and geopolymer-based waste forms.

After curing under the conditions described in Section 2.1, the specimens were tested using a universal testing machine equipped with steel bearing blocks meeting the loading uniformity requirements of ASTM C39. Axial compressive load was applied continuously without shock at a controlled stress rate of 0.25 ± 0.05 MPa s^{-1}, as specified in ASTM C39/C39M–21. Compressive strength was calculated by dividing the maximum load by the cross-sectional area based on the average measured specimen diameter. For each condition, more than three specimens were tested, and the reported values represent the average of at least two specimens that satisfied the geometric, alignment, and failure-mode criteria of the standard.

3 RESULTS AND DISCUSSION

3.1 Comparison of Compressive Strength Results for Waste Forms

Figure 2 shows the variation in compressive strength as a function of NaOH molarity for geopolymer waste-form specimens prepared with different SS/SH ratios under RT curing and under an initial 1-day thermal curing at 60 °C.

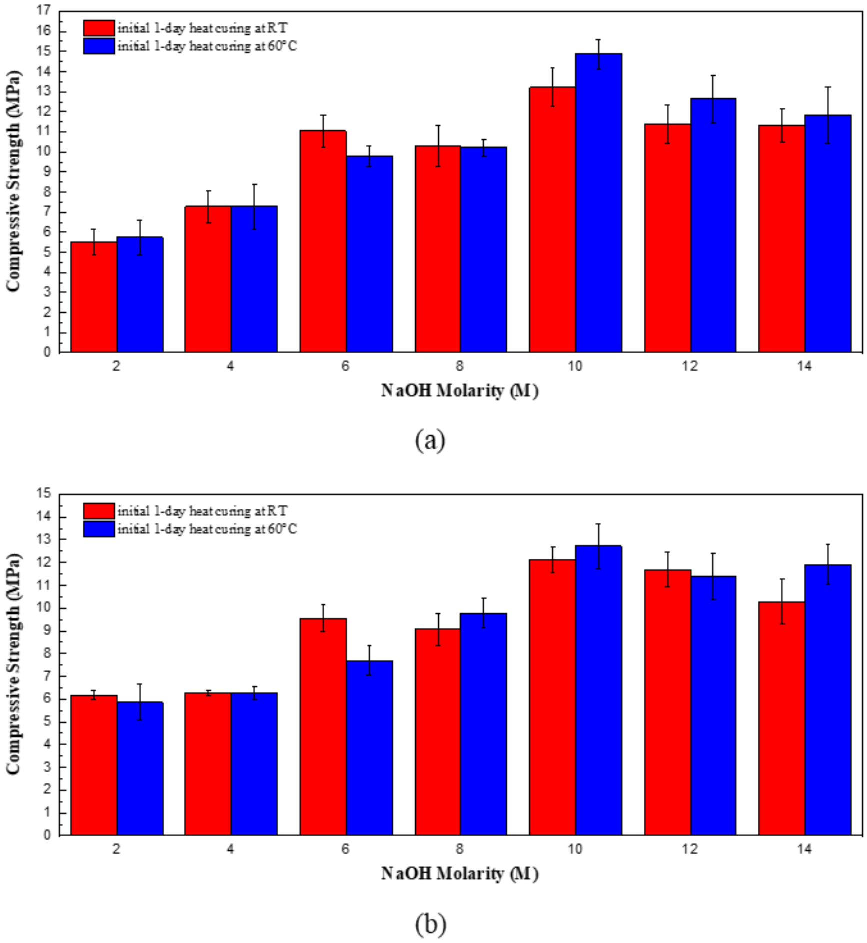

Figure 2. Variation in compressive strength of geopolymer waste-form specimens with NaOH molarity. Subfigures (a), (b) present results for SS/SH ratios of 1.5, 2.5, respectively, under initial 1-day curing at RT and 60 °C.

Overall, specimens with higher SS/SH ratios exhibited a more consistent dependence of compressive strength on NaOH molarity. For most compositions, the compressive strength increased in a non-monotonic manner up to an NaOH molarity of 10 M, followed by a gradual decrease at higher molarities. Although broadly similar trends were observed across different compositions, a certain degree of data scatter was present, and in several cases the mean compressive strength values overlapped within their respective standard deviation ranges. Accordingly, the analysis focuses on the overall compressive-strength response to changes in NaOH molarity and SS/SH ratio across the investigated range, particularly the general pattern of strength increase up to an optimum composition followed by a decline at higher NaOH molarities, rather than on isolated local fluctuations in individual data points.

The decrease in compressive strength at NaOH molarities exceeding 10 M can be interpreted as being related to the presence of excessive unreacted alkaline and silicate species within the geopolymer matrix, which may partially hinder effective geopolymer gel formation and disrupt the continuity of the reaction network.

Based on these observations, specimens prepared with an SS/SH ratio of 1.5 and an NaOH molarity of 10 M consistently exhibited the highest compressive strength under both curing conditions. Under RT curing, the compressive strength reached 13.21 MPa, whereas initial thermal curing at 60 °C for 1 day increased the compressive strength to 14.88 MPa, corresponding to an enhancement of approximately 12.64 %. Although both curing conditions satisfy the mechanical stability requirements, this difference is considered meaningful, as it may influence subsequent durability evaluations such as thermal cycling and immersion tests.

Considering both mechanical performance and curing effects, the combination of an SS/SH ratio of 1.5 and an NaOH molarity of 10 M under an initial thermal curing condition of 60 °C appears to be a favorable formulation for subsequent waste-form performance evaluations. The observed strength enhancement under thermal curing is attributed to thermally activated geopolymerization, which promotes denser gel formation through accelerated dissolution and polycondensation reactions.

4 CONCLUSION

A geopolymer-based solidification process was developed for zeolite-derived radioactive waste generated in heavy-water reactor systems, including moisture-removal desiccants used in steam recovery units. The proposed process successfully produced monolithic waste forms with stable surface integrity and geometric consistency, demonstrating the suitability of the geopolymer matrix as a durable immobilization medium. The mechanical performance of the fabricated waste forms was evaluated with respect to the mechanical stability requirements specified by the WAC.

The study indicated that the initial thermal curing could significantly enhance mechanical performance under the identified formulation, particularly achieving increase of a double-digit percentage in maximum compressive strength at an initial curing temperature of 60 °C compared to no initial thermal curing.

In addition, compared to conventional cement solidification, the proposed high-waste-loading approach (76 wt% zeolite to 24 wt% alkaline activators) was confirmed to reduce the number of waste drums generated during disposal significantly. Consistent compressive strength property across different activator compositions was thought to further support the reliability and reproducibility of the process. Overall, the developed zeolite–geopolymer solidification method provides a technically robust and scalable route for producing high-strength monolithic waste forms applicable to radioactive waste treatment and disposal.

5 ACKNOWLEDGEMENT

This work was supported by the National Research Foundation of Korea (NRF), funded by the Korean government (Ministry of Science and ICT), under Grant No. RS-2024-00431789, and by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Climate, Energy & Environment (MCEE) of the Republic of Korea, under Grant No. RS-2023–00239183.

6 COMPETING INTERESTS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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