Alkali- or acid-activated geopolymers and their potential application in the nuclear waste management: A review

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1. Alkali-activated geopolymer waste forms

Alkali-activated geopolymers can be fabricated by polymerization reactions between amorphous aluminosilicate materials such as fly ash or metakaolin and alkaline activators. They have good physicochemical characteristics such as mechanical strength, chemical resistance, fire resistance, and capacity to immobilize/stabilize toxic elements. The tetrahedral silicon and tetrahedral aluminum are the main building units for alkali-activated geopolymers and aluminates partially substitute silicates. The negative charge structure is compensated by alkaline cations such as sodium and potassium. The key parameters for alkali-activated geopolymers are the Si/Al ratio, M/Al ratio (M=Na or K), H_2O/Al ratio (free water content), and curing conditions. Alkali-activated geopolymer waste forms for radioactive waste disposal can be optimized and prepared considering these parameters.

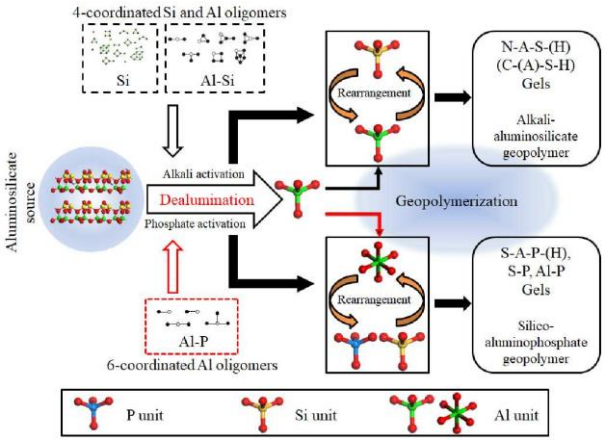

Fig. 1. Conceptual scheme for geopolymer activated by alkali or acid activators [1]

2. Acid-activated geopolymer waste forms

Recently, acid-activated geopolymers, such as phosphate-based geopolymers, fabricated through acidic activation, are now classified within the geopolymer category. While the detailed mechanism is not thoroughly investigated, it is believed that the polycondensation reaction between tetrahedral phosphorous and highly coordinated aluminum, such as six-coordinated aluminum, leads to the formation of the amorphous alumino(silico)phosphate phase.

In contrast to alkali-activated geopolymers, phosphate-based geopolymers do not require charge compensators (network modifiers) because phosphate inherently provides additional positive charge [1]. Therefore, key parameters for phosphate-based geopolymers include the P/Al ratio, free water content, and curing conditions. These geopolymers have found applications in the solidification/stabilization of toxic materials and radioactive wastes due to their excellent physicochemical characteristics, similar to alkali-activated geopolymers.

3. Case study for radioactive waste disposal using geopolymer waste forms

3.1. United Kingdom [2, 3]

In the United Kingdom, researchers at the University of Sheffield have studied the immobilization of Sr-titanate adsorbent using alkali-activated geopolymer waste form. Alkali-activated geopolymers with a low calcium content led to low Sr leaching from the encapsulated ion exchangers. The binder also occupied the voids within the ion exchangers, resulting in a compact microstructure in the waste form. The use of either potassium or sodium as alkaline activators for geopolymer waste form led to minor alterations in titanate coordination. However, the structural changes between geopolymer gel and ion exchangers did not appear to be significant.

3.2. France [2, 4]

The Callovo-Oxfordian (COx) argillite and metakaolin-blended alkali-activated geopolymer grout were developed as part of the Cigéo project in France, aimed at high-level radioactive waste disposal. In this project, 30 wt% of metakaolin was replaced by COx-argillite, and chemical additives like boric acid and

sodium tetraborate were utilized to control the pH of the paste and setting time. Additionally, the INIFUGE project was conducted with the ultimate aim of developing various forms of geopolymer materials for Cigéo packages and structures, with a specific focus on fire-resistant geopolymer binders. Furthermore, the DECIMAL project involved immobilizing Mg alloy cladding radioactive wastes generated from spent fuel in gas-cooled reactors using geopolymer.

3.3. Japan [2, 5]

The Japanese Atomic Energy Agency (JAEA) immobilized sewage sludge ash containing 10 kBg/kg of 1^{37}Cs and spent liquid scintillation cocktail using alkali-activated geopolymers. The geopolymers demonstrated low leaching of ^{137}Cs (~2%) and minimal leaching of organic compounds (~1%). Additionally, various Japanese universities developed alkali-activated geopolymers for immobilizing Cs-loaded chabazite and Sr-loaded titanate. While a previous study investigated the use of fine soils with high radioactive Cs from Fukushima as a starting material for geopolymer. The retention of radioactive anions such as iodine and selenium has been explored. However, the permanent negative charge of alkali-activated geopolymers resulted in high leaching of anions, necessitating methods to enhance immobilization efficiency.

3.4. South Korea [2, 6]

Radioactive borate waste generated from a pressurized water reactor was immobilized using alkali- or acid-activated geopolymers. Both geopolymer waste forms demonstrated high waste loading (at least 30 wt%) and good durability. Notably, they passed waste acceptance criteria tests, including gamma irradiation, thermal cycling, water immersion, and leaching tests. In alkali-activated geopolymer, boron was physically and chemically immobilized, while acid-activated geopolymer stabilized it by forming the amorphous boron phosphate phase.

Spent ion exchange resins were also encapsulated using alkali-activated geopolymer, achieving a maximum waste loading of 20 wt%. The geopolymers successfully met the waste acceptance criteria tests. Studies on the estimation of radionuclides (Co, Cs, and Sr) leaching characteristics in different sized geopolymer have been conducted, and an evaluation method for homogeneity is in progress.

4. Perspectives

Alkali- or acid-activated geopolymers with a pure aluminosilicate or aluminophosphate structure have been extensively researched worldwide for immobilizing radioactive waste and radionuclides. Particularly, challenging radioactive wastes that are difficult to stabilize using conventional cement can potentially be managed with geopolymers. However, as a relatively new material compared to cement, which has been studied for centuries, a deeper understanding of geopolymers is crucial. To apply geopolymers to the disposal of radioactive waste, thorough investigations into the chemical reactions between radioactive waste and geopolymers, as well as the long-term durability of geopolymers, are essential. For instance, the long-term leaching behavior, leaching mechanisms, and immobilization mechanisms of radionuclides or radioactive wastes must be thoroughly examined. This is because the composition of geopolymers is entirely amorphous, making it more challenging to qualitatively and quantitatively understand structural changes compared to waste forms composed of crystalline materials. Furthermore, a deep understanding of the physicochemical structural changes during long-term aging is also necessary. Geopolymers have been actively researched for less than 50 years, and their application in the disposal of radioactive waste has only recently begun. If these aspects are continuously researched and the shortcomings addressed, geopolymers could be utilized for the disposal of radioactive waste that is difficult to immobilize using cementitious materials.

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