



Bulk modulus of basic sodalite, $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, a possible zeolitic precursor in coal-fly-ash-based geopolymers

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ABSTRACT

Synthetic basic sodalite, $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, cubic, P43n, (also known as hydroxysodalite hydrate) was prepared by the alkaline activation of amorphous aluminosilicate glass, obtained from the phase separation of Class F fly ash. The sample was subjected to a process similar to geopolymerization, using high concentrations of a NaOH solution at 90 °C for 24 hours. Basic sodalite was chosen as a representative analogue of the zeolite precursor existing in Na-based Class F fly ash geopolymers. To determine its bulk modulus, high-pressure synchrotron X-ray powder diffraction was applied using a diamond anvil cell (DAC) up to a pressure of 4.5 GPa. A curve-fit with a truncated third-order Birch–Murnaghan equation of state with a fixed $K'_0 = 4$ to pressure-normalized volume data yielded the isothermal bulk modulus, $K_0 = 43 \pm 4$ GPa, indicating that basic sodalite is more compressible than sodalite, possibly due to a difference in interactions between the framework host and the guest molecules.

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1. Introduction

Engineering the recycling of coal fly ash for use in cement and concrete manufacturing has been studied extensively and continues to be an active area of research [1–3]. Although its incorporation into cementitious materials is on the rise, a large amount of fly ash is still disposed of into landfills or deposited in the ocean. In 2004 in the United States, according to the American Coal Ash Association (ACAA) [4], 70.8 million tons of coal fly ash was produced and 42.7 million tons of that coal fly ash was disposed into the ground or ocean. In 2007 in Europe (EU 15), 41 million tons of coal fly ash was generated, with a reutilization rate of only 47% [5]. As the cost of disposing of fly ash continues to rise, strategies for the recycling of fly ash is environmentally and economically critical. The geopolymer science and zeolite synthesis fields that use fly ash as source materials are two emerging areas for the recycling of coal fly ash [6,7]. Interestingly, the science of zeolite formation using fly ash has been regarded as an analogue of fly-ash-based geopolymer synthesis in terms of synthesis methodologies [8].

The reaction product of geopolymerization is, clearly, the zeolite precursor [9]. The similarities in terms of their nanostructure between zeolites and geopolymers synthesized from coal fly ash have been discussed in earlier studies [10,11]. Provis et al. [12] suggested the widespread existence of nanocrystalline-size zeolites with no more than four unit cells, which corresponded to approximately 8–10 nm as the

main phase, resulting in the broad $\sim 28^\circ$ peak of characteristic in the X-ray diffraction pattern of geopolymer. Table 1 presents the most frequently observed crystalline zeolitic phases in geopolymer studies. Zeolites belonging to the “ABC-6 family” framework were often found when Class F fly ash was activated by a high concentration of a NaOH (or a mixture with Na-silicate) solution ($>5\sim 8$ M) [6], which is a strong geopolymerization activator. These zeolites include hydroxysodalite, herschelite (= Na-chabazite), nepheline, and hydroxycancrinite. Other types of zeolites not belonging to the ABC-6 family (e.g., zeolite Na-P1, analcime) were also observed in geopolymers; however, these zeolite usually formed when a low concentration of NaOH solution ($< 2\sim 3$ M) was used [6]; this is a weak geopolymerization activator. This observation seems to indicate that the geopolymer reaction product, also called the zeolitic precursor, possess a similar structure as the ABC-6 family of zeolite minerals when a high concentration of Na-based alkali-activating solution is used [7]. This hypothesis is also supported by the observation that the ^{29}Si NMR spectrum of aged fly ash geopolymers is identical to herschelite [13].

The framework of ABC-6 family zeolites, known as a “six-membered ring”, consists of Al- and Si-tetrahedra. Only nineteen members of zeolite framework types are categorized as ABC-6 family among the known 176 zeolite framework types. The main difference between zeolites belonging to the ABC-6 family is only in the stacking sequence of the six-membered rings [14]. Of the zeolitic materials belonging to the ABC-6 family framework type, hydroxysodalite and hydroxycancrinite were suggested as the best candidates to represent the structure of a zeolitic precursor [7] and to play a similar function as the role that 14 Å tobermorite and jennite play in C–S–H in cement science.

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