

Formation of Nanocrystalline Zeolites in Geopolymer Gels

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“Geopolymers” are aluminosilicate network structures formed when an aluminosilicate phase is added to either an alkaline silicate or alkaline based solution [1]. For example, when metakaolin is mixed with a sodium or potassium based silicate solution, a geopolymeric gel phase is formed, which hardens in less than 4h even at low temperatures ($\approx 40\text{-}50^\circ\text{C}$). Metakaolin based geopolymers generally have a Si:Al molar ratio in the range of approximately 2-4, where the lower bound is determined by metakaolin, while the upper bound is limited by the solubility of silica in the alkaline silica solution. Processing of geopolymers is analogous to that of low silica zeolite in that both require a high pH concentrated alkali solution, and can be reacted below 150°C [2]. For instance, zeolite A was synthesized by addition of metakaolin to a dilute sodium solution of sodium hydroxide [3]. In contrast, geopolymers are prepared using very concentrated alkali solutions and require much shorter processing times.

Geopolymer gels, although x-ray amorphous, may contain nanocrystalline zeolite compacted in an amorphous gel phase [4]. In order to test this hypothesis, a series of geopolymeric compositions were prepared (see Table I) and examined using high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), and synchrotron x-ray diffraction (XRD). Of the nine compositions examined, only samples with the composition $2\text{SiO}_2\text{:Al}_2\text{O}_3\text{:Na}_2\text{O}$ (sample 9 in Table 1) contained zeolite crystals. HRTEM results confirmed the presence of crystals in the size range of 6-10nm (see Fig. 1a). The high resolution structure of samples 1-8 contained nanometer sized particulate features and pores as shown in Fig. 1b, which is typical of amorphous geopolymers. Subsequent synchrotron X-ray diffraction (XRD) results confirmed that sample 9 crystallized into Zeolite A (ICDD-JCPDF # 01-073-2340). Whole pattern fitting analysis of XRD data showed that the sample was comprised of 96 wt% amorphous phase and 4 wt% crystalline Zeolite A. Therefore, the concentrated nature of geopolymer gels permitted only small amount of zeolite crystallization.

References

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TABLE 1. Geopolymer Compositions of Interest

Alkali Molar % (%Na ₂ O, %K ₂ O)	Silica to Alumina Molar Oxide Ratio (SiO ₂ :Al ₂ O ₃)		
	4	3	2
100, 0	Sample 1	Sample 4	Sample 7
50, 50	Sample 2	Sample 5	Sample 8
0, 100	Sample 3	Sample 6	Sample 9

*Water used corresponded to M₂O:H₂O=10 where M=Na+K. Curing conditions were 50°C for 48h.

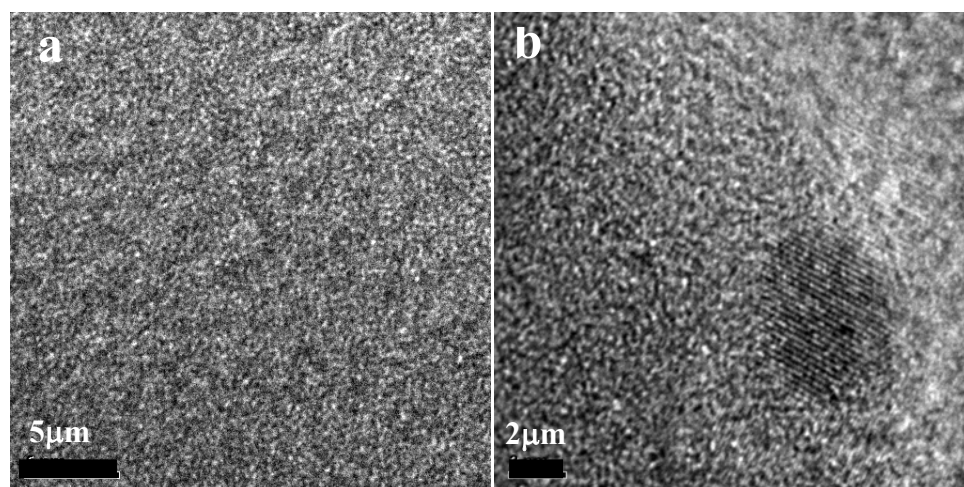


FIG. 1. HRTEM structure for (a) sample 1 and (b) sample 9. Samples 1-8 had a similar structure to that of (a). Nanocrystalline zeolite regions were found in sample 9, as shown in (b). Analysis was done using a JEOL 2010F (S)TEM. Samples were prepared by grinding with a mortar and pestle and depositing on a holey carbon grid.

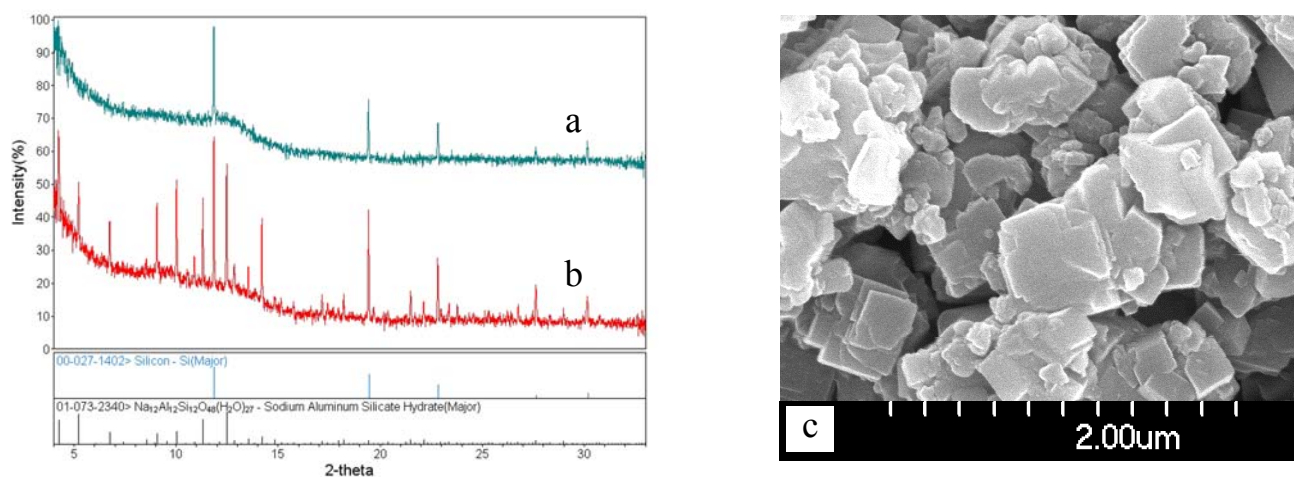


FIG. 2. Synchrotron X-ray diffraction results, using a wavelength of 0.648625 Å, for (a) sample 3, and (b) sample 9. For both samples 10 wt% silicon standard from NIST (SRM 640b) was added prior to measurements. Samples 1-8 were all amorphous with an amorphous peak at $\approx 12^\circ$ 2-theta, as shown for case (a) above. Sample 9 crystallized into Zeolite A as illustrated in (b). The SEM micrograph in (c) shows cubic zeolite crystallites in the 1-2 μm size range observed in sample 9.