Nano- and Microporosity in Geopolymer Gels

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Geopolymers and geopolymeric composites are a relatively new class of ceramic materials whose intrinsic properties and potential applications are still relatively under-explored.[1] Pure geopolymers are rigid, inorganic, aluminosilicate, hydrated gels, charge balanced by the presence of Group I cations such as Na^{+1}, K^{+1}, Cs^{+1}. They have a range of compositions, but a nominal composition of interest here is around $Al_2O_3 \bullet M_2O \bullet nSiO_2 \bullet 10\ H_2O$, where M = Na, K, or Cs, and n varies from 2-4.[2,3] Geopolymers are totally inorganic, and usually made by mixing a powder with a solution, forming a paste which is poured into a plastic mold or adhered on a metal, glass or ceramic surface. The mixture is allowed to set for 24h at ambient temperatures (e.g. 40 °C) and pressures. They do not adhere to polymers or graphite, so that a variety of complex shapes of near net dimensions can be fabricated. Geopolymers are acid resistant and thermal shock resistant.

The intrinsic microstructure is nanoparticulate ($\leq$ 5 nm in size) and nanoporous as seen in STEM (Fig. 1). Since the MIP technique was not responsive below 10 nm pore sizes, the nanoporosity was investigated by BET surface area analysis. The technique is able to measure surface areas and pore sizes down to below 0.2 nm. When made from natural metakaolin, geopolymers have an average pore radius of ~3.4 nm, and the porosity constitutes ~40 % by volume of the material (Fig. 2). When the geopolymer is made from a pure, synthetic alumino-silicate metakaolin in which the Al atom is in five-fold co-ordination, the average pore radius decreases to ~0.8 nm, and the pores again constitute ~40% of the volume. The porosity can be varied by selection of Na^+ or K^+ charge-balancing cation, where the latter produces a relatively homogeneous dispersion of fine, micron sized pores distributed in the nanoporous body. The porosity can be modified and enhanced by additions of Al, or by using hydrogen peroxide (H_2O_2) in the alkali metasilicate reaction solution. Fig. 3 illustrates preliminary work on producing bi-modal porosity by using hydrogen peroxide solution in a pressure vessel. The mesoporosity superimposed on the nanoporosity is of the order of 50 mm in diameter. To achieve smaller pore sizes, higher pressures are needed.

References

[1] J. Davidovits, *Journal of Thermal Analysis*, 35(2) (1989) 429.
[2] "Microstructure of Geopolymers and Geopolymer-based Materials," W. M. Kriven, J. Bell, M. Gordon and Gianguo Wen, pp 179-183 in Geopolymer, Green Chemistry and Sustainable Development Solutions, edited by Joseph Davidovits. Proc. World Congress Geopolymer,2005, St. Quentin, France.
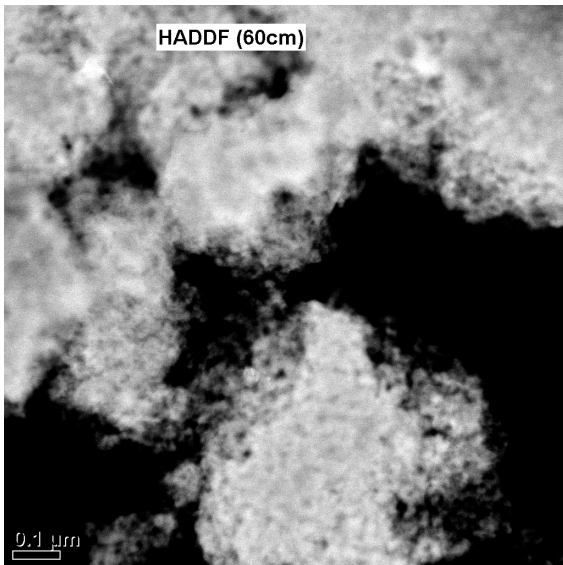
Fig. 1. STEM micrograph of crushed, Na-based geopolymer showing its nanoparticulate and nanoporous nature.
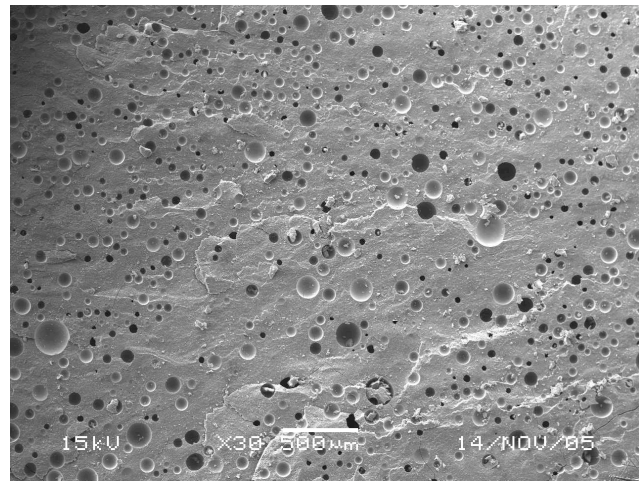
Fig. 3. SEM micrograph of fracture surface of geopolymer synthesized using hydrogen and peroxide (H_2O_2) in a sealed container at ~3.5 M Pa of pressure and 50C.

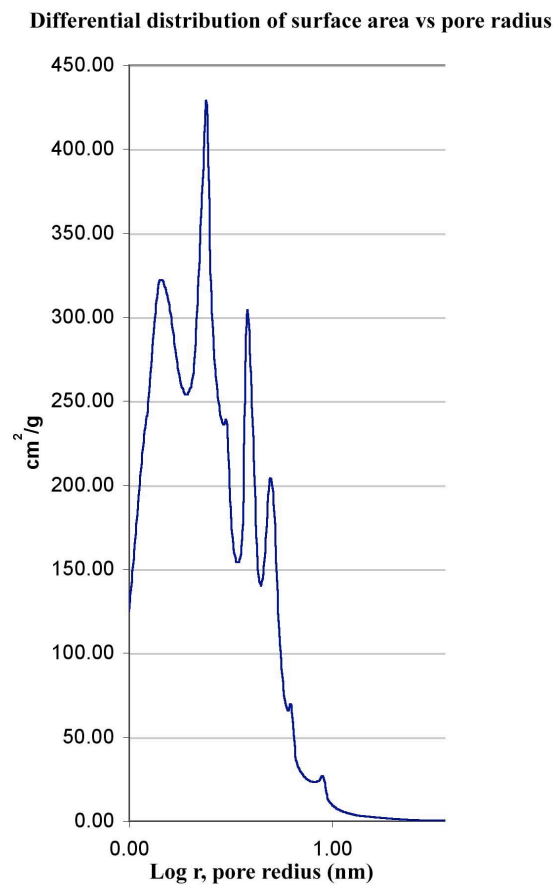**Differential distribution of surface area vs pore radius**

Fig. 2. Differential distribution of surface area versus pore radius showing a multimodal distribution