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Bulk composition and microstructure dependence of effective thermal conductivity of porous inorganic polymer cements

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Abstract

Experimental results and theoretical models are used to assess the effective thermal conductivity of porous inorganic polymer cements, often indicated as geopolymers, with porosity between 30 and 70 vol.%. It is shown that the bulk chemical composition affects the microstructure (grains size, pores size, spatial arrangement of pores, homogeneity, micro cracks, bleeding channels) with consequently the heat flow behaviour through the porous matrix. In particular, introduction of controlled fine pores in a homogeneous matrix of inorganic polymer cements results in an increase of pore volume and improvement of the thermal insulation. The variation of the effective thermal conductivity with the total porosity was found to be consistent with analytical models described by Maxwell–Eucken and Landauer.

Keywords: Thermal conductivity; Porosity; Inorganic polymer cements; Microstructure-final; Composites

1. Introduction

The porous and amorphous structure of inorganic polymer cements (IPC), often indicated as geopolymers, implies that flow in a thermal gradient will take a very tortuous route consisting of a multiple of neighboring interconnected polysialate particles.[1] The effective thermal conductivity of such a material is strongly affected by its chemical composition as well as the presence of voids in the microstructure which are pockets or cells more or less spherical in shape.[2] The microstructure of IPC is known to vary considerably with chemical composition and processing conditions. For example, related to the preparation, a controlled fine porosity can be incorporated into the skeletal framework, which also reduces the effective density of gel. In particular for geopolymers, it has been demonstrated that the pore size varies with Si/Al ratio. The porosity includes interconnected pores ranging from nano to micrometric scale (10–50 nm for Si/Al molar ratio ~1, <10 nm for Si/Al molar ratio ~1.65 and very fine pores (~5 nm) for Si/Al molar ratio ~2.5.[3,4] Apart from these fine pores, some dispersed larger-diameter pores are generally observed which can be controlled during processing. The pore structure is determined by the nature and size of polysialates formed as well as by the interactions between various phases present in the material.[4–6] The distribution and interconnectivity of pores, the short-range ordering of the gel phase, and the nominal composition are all likely to play roles in determining the heat transport properties of geopolymeric gels.[1,7] In particular the effective thermal conductivity of IPC will be controlled by the pore size distribution and pore volume.

In this work, we exploit the corrosion of aluminum powder in a highly concentrated alkali solution to form porous IPC. Normal processing of geopolymer material leads to a pore fraction of 25–30% of total porosity.[1,8] Upon introduction of a foaming agent into the geopolymer paste, the resultant steam forms bubbles within the softened matrix to produce a frothy-like structure which transforms into a cellular material. The additional pores increase the pore volume fraction up to 70%.

Previous investigations on compositions of geopolymer materials already were devoted to their suitability as structural materials.[8] In the case of the more porous materials which were obtained, first measurements indicated their potential for thermal insulation.[1] Here we investigate the relations between the bulk composition, the pore size-distribution, pore volume fraction and the effective thermal conductivity of the porous geopolymer.

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Nomenclature

λ_{eff}	effective thermal conductivity
λ_s	thermal conductivity of solid continuous phase
λ_g	thermal conductivity of dispersed phase (air)
v_s	volume of solid fraction
v_g	volume of dispersed phase
F	form factor regarding the pores
v_p	volume of pores
$\cos^2 \alpha$	orientation parameter
HB	high bound or upper bound of Hashin–Shtrikman
LB	lower bound of Hashin–Shtrikman
a and b	calibration curve constants
ΔT	difference of temperature
R	thermal resistance
ϕ	heat flux density
U	thermo electric power
r	pore radius
γ	surface tension of mercury
θ	contact angle

2. Analytical models for the effective thermal conductivity of porous geopolymers

A significant number of analytical models have been developed to predict the effective thermal conductivity of porous solid as function of pore volume fraction. They differ in the manner by which the morphology of the pore system has been taken into account. In this respect Collishaw and Evans have written a useful review.[9]

As reported in our previous work[8] and by many other authors,[3–6] the metakaolin based geopolymer is typically made of nanometric scale particles of polysialates joined to one another to form a matrix containing nanosized pores. Furthermore, a small fraction of porosity is micrometric, and micro cracks are also visible. Therefore, an analytical model yielding on equation that can be used to describe satisfactorily the effective thermal conductivity of a porous geopolymer material is difficult to identify. However in the respect we consider a matrix of porous geopolymer to be constituted of particles, cement (binding the particles of polysialates and other residues together), air inside pores and finally micro cracks. The material can be classified as bound/cemented matrix.[9] In addition, secondary effects influencing the effective thermal conductivity may include contact resistance between grains, radiation through grains or pores, convection and in the case of small pores, the Knudsen effect which can reduce the gas thermal conductivity.[9]

Studies of the effect of structure on the heat flow and effective thermal conductivity (λ_{eff}) have shown that λ_{eff} is generally higher in cemented materials.[10–12] Thus the increase in porosity for geopolymer matrices is a potential solution to maintain the strength while improving the insulating behaviour of the materials. A porous geopolymer is then considered as a continuous solid phase in which uniformly dispersed cavities are filled with fluid (air, or another gas). An approach describing this type of solid phase has been proposed by Hashin–Shtrikman.[2] The approach is based on calculating the most restrictive bounds for the value of the effective thermal conductivity. The primary parameters influencing the effective thermal conductivity are the conductivity ratio and concentration of voids. The upper bound (HB) refers to a continuous solid phase including uniformly dispersed fluid filled cavities (Eq. (1)).

$$\lambda_{eff} = \lambda_s + \frac{3p\lambda_s(\lambda_g - \lambda_s)}{3\lambda_s + (1-p)(\lambda_g - \lambda_s)} \quad (1)$$

And the lower bound (LB) refers to a continuous fluid phase including uniformly dispersed solid spheres (Eq. (2)).

$$\lambda_{eff} = \lambda_g + \frac{3\lambda_g(1-p)(\lambda_s - \lambda_g)}{3\lambda_g + p(\lambda_s - \lambda_g)} \quad (2)$$

Maxwell–Eucken[13] model can also be used as λ_s is the thermal conductivity of the continuous phase and λ_g that of the dispersed phase (air or hair saturated humidity in IPC voids). The Maxwell–Eucken model considers a random distribution of pores with different diameters (Eq. (3)).

$$\lambda_{eff} = \frac{\lambda_s v_s + \lambda_g v_g((3\lambda_s)/(2\lambda_s + \lambda_g))}{v_s + v_g((3\lambda_s)/(2\lambda_s + \lambda_g))} \quad (3)$$

In fact the Maxwell–Eucken equation (3) leads to an expression arithmetically equivalent to Eq (1).

Broadbent and Hammersley[14] studied situations of fluid flow through a porous medium where percolation becomes important. The hypothetical passage of a fluid through an uncertain porous environment. For a metallic phase randomly introduced in an insulator to form a composite, the composite behaves like an insulator in the case of a weak concentration of the metallic phase. If the volume fraction of metal increases, the current can circulate between two opposite faces of the material via the metallic phase and the composite behaves like a conductor. The volume fraction at which this change of behaviour is observed is called the percolation threshold. This can be illustrated by Landauer's expression for the effective thermal conductivity of a mixture of two phases with each phase constituted of particle sizes of roughly equivalent size[15] (Eq. (4)):

$$\lambda_{eff} = \frac{1}{4}[\lambda_g(3v_g - 1) + \lambda_s(3v_s - 1) + ([\lambda_g(3v_g - 1) + \lambda_s(3v_s - 1)]^2 + 8\lambda_s\lambda_g)^{1/2}] \quad (4)$$

The percolation model[15] assumes a completely random distribution of these components, and is equivalent to an Effective Medium Theory (EMT)[16,17] (Eq. (5)).

$$v_s\frac{\lambda_s - \lambda_{eff}}{\lambda_s + 2\lambda_{eff}} + v_g\frac{\lambda_g - \lambda_{eff}}{\lambda_g + 2\lambda_{eff}} = 0 \quad (5)$$

Nait-Ali et al.[18] have demonstrated the close agreement between predicted values of the effective thermal conductivity using Eq. (4) and experimental values for zirconia with pore volume fraction up to 70%.