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Cumulative pore volume, Pore size distribution and Phases percolationin porous inorganic polymer composites: relation microstructure and effective thermal conductivity.

Abstract: Two different sources of amorphous silica (volcanic ash and rice ash) were exploit to improve the homogeneity of inorganic polymer pastes before the expansion with aluminum powder. The fine powder were found to be appropriate in enhancing the expansion and the lightweight structure with pore size and pore distribution easily correlated to the viscosity, the concentration of porogent agent, and the nature of the amorphous. From the Stereo optical microscope, Environmental Scanning Microscope and the mercury intrusion porosimeter used for the characterization, it appeared that for a well considered interval of concentration of porogent agent and viscosity, optimum expansion is obtained together with the closed round pores resulting in a microstructure that the effective thermal conductivity is described with the Maxwell-Eucken model. The detailed analysis of the microstructure also correlated with the novel effective medium theory proposed recently.

Keywords: geopolymer, viscosity, pore size, pore shape, microstructure, effective thermal conductivity.

1. Introduction

Amorphous to semi-crystalline alumino-silicates will dissolve into the high alkaline solution forming high colloidal pastes with viscosity linked to the liquid/solid ratio, the Si/Al ratio and the degree of dissolution which can be correlated itself to the amorphous content[1-3]. The intrinsic properties of these inorganic polymer cement pastes allow extensive modification of the microstructure of the ended consolidated products. Many researchers have used these recent time this advantage to design new class of porous matrices[4-8]. The global mechanism of the consolidation is resumed to the conversion of the high viscous suspension into a rigid and porous solid. The addition of porogent agents changes the porosity from nanometric and meso to nanometric, meso and ultra-macro sizes. Hydrogen peroxide as blowing agent[5], redox reaction of aluminum powder in alkaline solution[4, 9] or that of metallic Si[5-8] have been used as low temperature, low-energy , environmentally-friendly and sustainable processes for the production of ultra porous inorganic matrices in comparison to the high temperature treatment for burnout of fugitive additives and sintering with the aim to achieve porous ceramics[10-12]. Although the effective possibility of the

above techniques to be used for the production of porous inorganic polymer without thermal treatment, the final products still suffer homogeneity and the difficulty for the control of the pore shape, pore size and correlation of the properties of the fresh paste to the to the final microstructure in relation with the bulk chemical composition of the initial formulation. Moreover, the description of the microstructure in most cases suffer lack of details and some key informations that can allow the reader to understand and correlate the microstructure to thermal properties via analytical models. Medri et al.[5], Bourret et al.[6] and Kamseu et al.[4] used the mathematic equation (1) to calculate the total porosity of the obtained foams.

$$Vp = 1 - \frac{\rho_{bulk}}{\rho_{true}} \qquad (1)$$

With Vp the total volume of pore, ρ_{bulk} the bulk density and ρ_{true} the true density evaluated with helium picnometer.

The first two authors did not present any detailed informations concerning the macropores albeit they are the main part of the porosity of the foams. Bourret et al.[6] affirmed that the pores of the foams produced were having size > 5 µm and that they Knudsen diffusion should not be consider. However, a better consideration of the microstructure of porous geopolymers demonstrated that the materials even with the ultra macroporosity maintain the nanometric pores in their structure specially into the interpore partitions where the solid skeleton still have the initial microstructure or not significant modification. Medri et al.[5] present the total porosity of the foams measured by Mercury intrusion porosimetry (MIP) with values from 29 to 56%. Evidently these constitute a partial total porosity since the MIP used by the authors do not consider pores above 100 µm. Kamseu et al.[4] used MIP, microtomography and SEM micrographs to analyse the pore size distribution of the IPC foams and give some informations about the descriptive structure of porous matrices. However it remained difficult to use the method for the quantitative evaluation of the total porosity and particularly to estimate the volume of fine and larger pores. In the microstructural point of view, SEM is not appropriate to analyze the ultra porous materials since it does not allow the collection of a representative area suitable for the description of the structure. Intensive pores percolation, the dispersion into the pores shape and the some high particles agglomeration hinder the efforts to use analytical models to describe the porous materials.

The activity of the porogent agent into the fresh paste is sensible to the gradient of concentration, the degree of reactivity (connectivity) of the geopolymer system, the viscosity, the chemical equilibrium and the homogeneity. Soluble silica is appropriate to balance the Si/Al ratio and produce high colloidal paste capable to favor the formation of rounded pores. In the presence of

well balanced matrix with appropriate Si/Al, Na/Al and good viscosity, the densification without porogent agent conduces to a highly percolated matrix where nanoporisty is homogeneously dispersed where a small fraction of capillary pores acts as impurities. The high connectivity remains even with the introduction of the a certain concentration (C_1-□) of porogent agent. In the case of Co (1- □ = 0), the capillary pores remain isolated in a high percolated H-M-A-S (with M = Na or K). The increase of the concentration of the porogent agent, the compactness of the H-M-A.S decreases and the increase of size and number of the larger capillary pores, the interpore partitions appear with very high thickness. The thickness of the interpore decreases progressively up to a limit at which there is larger capillary pore coalescence, we are at concentration C_{1-n}□ ($n \geq 0$). The values of C_{1-}□ and C_{1-n}□ are determined in relation with the rheology properties of the pastes as well as the concentration of the residues of alkalis into the pore solution. The value of the concentrations describe in the interval C_{1-}□ and C_{1-n}□ are an arithmetic suite with r = □.

Particularly the rheology parameters are assessed with the amount of water which prepare the medium for the dissolution and polycondensation aids with various ions transfer. After the geopolymerization, water remains entrapped into the pores or bonded to the developed 3D geopolymer network and possibly silanol and aluminol within the structure[1]. For these reasons, the liquid/solid ratio in the initial paste might have stronger effect on the course of consolidation affecting the volume expansion, the pores shape and size, the stability of the foam after the formation and eventual deformation of pores already formed under the pression of the expansion or the mass of the part already expanded.

The particle of metakaolin takes a dinner-plate like shape, with a very high surface area per unit volume and reactive sites on the particles surfaces. This results on a high reactivity which is desirable in geopolymer formation, but also leads to an extremely high water demand, high probability of particles agglomeration and gradient of concentration. In this work we use rice and volcanic ashes for partial replacement to metakaolin firstly to reduce the impact of the environment on the IPC formulations, producing more sustainable porous matrices. Moreover, both amorphous sources of silica are used as flow-enhancing additives. Their particles shape, allow them to reduce both the yield stress and viscosity in presence of water. Elements important for the development of pores by porogent agent. Combing these addition with the Water/metakaolin ratio, our objectives were to present optimum parameters for the development of better expanded structures with pore shape and pore size distribution achieved for a better description of the porous structure by existing analytical models available in the literature.

2. Materials and Methods

2.1 Materials and Preparation of porous IPC

A standard kaolin form Mayouom[13,] Cameroon was calcined at 4h at 700°C and ground to fine powder under 80 µm. The Si/Al molar ratio of the standard metakaolin is 1.14 far from the ideal Si/Al ratio for solid geopolymer precursors which is described to be between 2 and 3. To fulfill the gap, amorphous rice ash was added corresponding to a Metakaolin:rice ash volume ratio of 2.5:1 and a Metakaolin:rice ash wt. ratio of 1:1. For comparison volcanic ash was added with the same volume ratio of 2.5:1. Eventhough the volume of volcanic ash added correspond to a metakaolin wt.% ratio of 7:1, theorically there was not hypothetical silica residue to remain since volcanic ash contains an amount of Alumina and has been described as potential 100% raw materials for geopolymer matrices.

Sodium hydroxide solution, 8M, was prepared by dissolving NaOH pellets, Sigma Aldrich, 96 wt% into the appropriate amount of water. A 1:1 volume mixture of sodium hydroxide solution and sodium silicate (SiO_2/Na_2O = 3; L.O.I = 60 wt%) was used at 40 ml for 100g of solid precursor. In the first part of this work, we identified the concentration of alumina powder at which the geopolymer matrix remains with thick interpore partitions ($C_{1-□}$, …$C_{1-n□}$) and the concentration at which the capillary pores percolation deform the matrix and does not allow their proper description. C1 and C2 form an interval within which the porous structure present a well ordered structure with round larger capillary pores and low percolation. Deux concentrations were considered in this interval for the preparation of MKPC1 for the lower concentration and MKPC2 for the upper concentration when the amorphous silica was volcanic ash. Similarly MKRC1 was prepared for the lower concentration and MKRC2 for the upper concentration for rice ash as amorphous addition. The effects of viscosity of the pastes was asses using the variation of the Water/Metakaolin ratio for all the four formulations.

2.2 Microstructure, qualitative and quantitative analysis of porosity

The Environmental Scaning Electron Microscope (ESEM) technique was used to determine the 2D morphological features of the fresh fractured pieces of porous IPC. However this technique was limited since it was not possible to analyze larger surface simultaneously. The detailed features of the porous structure was appreciated using the stereo optical microscope: the SZX10 type. An Autopore IV 9500, 33000 psi (228 MPa) Mecury Intrusion Porosimeter (MIP) covering the pore diameter range from approximately 360 to 0.005 µm having two low-pressure ports and one high-

pressure chamber was used for the pores analysis. Pieces were prepared from the bulk of each sample with specimens of ~ 2 cm^3 of volume for the MIP.

The investigations on the larger capillary pores distribution and their size done using stereo optical microscope permitted to evaluate the concentration (in term of number) of the larger capillary pores and their mean size. Additionally, considering that with MIP we could analyzed just pores under 360 µm in size, we combined both technique to determine: the total pore volume that we compare with results from the difference of bulk and true density. This permit to express the total pore volume of the porous IPC as follow (2):

$$Vp = V_{MIP} + V_{LP} \qquad (2)$$

With $V_{MIP}$the volume of the pores measured by the MIP and $V_{LP}$the volume of larger capillary pores evaluated by the stereo microscope considering that they are those with diameter > 360 µm. We considered prism of porous IPC of 3 cm of side. The number n of larger in each size is determined alone with the mean pore size d_{LP} =2r_{LP}. The V_{LP} is written considering the mean pore size as (3):

$$V_{LP} = \boldsymbol{n^3 \frac{4\pi}{3} r_{LP}^3} \qquad \textbf{(3)}$$

For each formulation, 20 specimens of prism were considered to insure the validity and reproductvity of the results. The coefficient K was also determined for each specimens as the fraction (in volume percent) of the volume of pores evaluable into the prism using MIP. The total porosity can then be written as follow (4):

$$Vp = \boldsymbol{n^3 \frac{4\pi}{3} r_{LP}^3 + K V_{MIP}} \qquad (4)$$

2.3 The thermal conductivity

2.3.1 TPS theory and specimens preparation

The thermal conductivity of the specimens investigated through the transient plane source (TPS), method is determined from the time dependent temperature increase. The basic principle of this method relies on a plane element (an electrically conducting pattern of thin nickel foil of 10µm, spiral shaped, embedded in an insulating layer usually made of kapton sensor and heat source. The TPS is located between two specimens with similar intrinsic (bulk composition and microstructure) and extrinsic (geometry) characteristics: 8 cm of diameter and 2-3 cm thickness. The use of sensor diameter of 3, 6 and 9 mm allow to consider the sample to behave as an infinite medium, samples were polished in order to reduce the thermal contact resistance.

- **The TPS theory**

A constant electric power supplied to the sensor results in an increase in temperature ΔT(t)which is directly related to the variation in the sensor resistance R(t) by the equation(5):

$$R = R_0[1 + \alpha\Delta T(t)] \quad (5)$$

Where$R_0$is the nickel electrical resistance in the beginning of the recording (initial resistance), α is the temperature coefficient of resistance of the nickel foil, and $\Delta T(t)$ is the temperature increase of the sensor with time.

Assuming an infinitesample and the conductive pattern being in the XY plane of a coordinate system, the temperature rise at a point (XY) at time t is obtained by solving the equation for the heat conduction, which relates change in temperature with time[14]. In the particular case of our sensor geometry, n concentric ring sources, the spatial average $\Delta T(\tau)$can be obtained through the equation (6)[18,19].

$$\overline{\Delta T(\tau)} = P_0(\pi^{3/2}a\lambda)^{-1}D(\tau) \quad (6)$$

Where P_0 is a Bessel function, $D(\tau)$ is a geometric function characteristic of the number "n" of concentric rings,and$\overline{\Delta T(\tau)}$is the temperature increase of the sensor expressed in terms of only one variable τ, defined as (8):

$$\tau = (\frac{t}{\theta})^{1/2};\ \theta = \frac{a^2}{k} \quad (7)$$

Where t(s) is the measurement time from the start of the transient heating, θ is the characteristic time, which depends both on parameters of the sensor and the sample, a(mm)is the sensor radius and k(mm^2/s) is the thermal diffusivity of the sample. The characteristic time needs to be in the range 0.5-1.5 to guarantee that the theoretical assumptions are kept, thus the heat flow is an ellipsoid of neither too high nor too low sphericity.

- **TPS procedure**

To minimize the thermal contact resistance, a special care was taken for the samples preparation, the good transition trough two different materials in mainly associated to contact pressure and surface roughness[14-16]. The above parameters were kept constant during the measurements. Three different sensors with 3, 6 and 9mm of diameter were used to investigate on the homogeneity of the microstructure of IPC porous composites. Two different humidity contexts were also used to assess the impact of the environmental fluctuation on the thermal behavior of IPC porous composites.

The TPS equipment is able to compensate the heat capacity of the sensor and other thermal delays of the heat flow by introducing a time correction. Nevertheless, it is necessary to suppress the first 10-20 point of each measurements (of a total 300 points of the tea curve) to eliminate the heat capacity of the sensor that cannot be fully compensated by the time correction[14,16].TPS method offers some advantages as fast and easy measurements, a control of accuracy of the results, a wide range of thermal conductivities accessible, flexibility in sample size and a porosity to perform local or bulk measurement with only changing the sensor diameter. These advantages present the TPS methods more promising comparing to the conventional methods.

3. Results

3.1 Cummulative pore volume: variation of the fine and capillary pores with water/metakaolin ration and porogent agent content.

In the first part of this work, we demonstrated that it is possible to determine two thresholds of percolation in a system of H-M-A-S in which progressive amount of porogent agent is added modifying the volume expansion, the pore size distribution and the cumulative pore volume: (i) the lower amount of porogent agent that does not alter the percolation of solid matrix and (ii) the limit at which initiate the depercolation of the solid phase. The first threshold correspond to a relative expansion with fine pore size still small enough to insure their total isolation and depercolation while the second is at the limit of the structural description of the matrix in term of pore organization and connectivity between them.

The results present in the Figure 1a are data of investigations in the interval where we consider C1 and C2 situated at the extremity of the slope of the expansion curve with C2 > C1. The concentrations C1 and C2 correspond to ~ 2 and ~ 2.5 volume expansion with volcanic ash based pastes being slightly more expansive with regard to rice ash. Globally as observed in the Figure 1a, the pore volume is important for MKP series compared to MKR series. The difference was explained by the semi-crystalline behavior of the volcanic ash that do not allow complete dissolution of the silica available maintaining a certain rigidity when considering similar viscosity of the pastes. The colloidal phase more important in rice ash based pastes act on the total porosity by closing some pores or compacting the matrix. Moreover the rice present a very low density compared to volcanic ash, which favors the formation of more larger pores but also more pores coalescence and deformation of the expanded matrix under its proper weight. The results presented in the Figure 1a were focused on the final volume obtained with each specimen and could be

diversely interpreted if we want to consider the expanded phase without the volume contraction presented by almost all rice ash based specimens after expansion; volume contraction linked to the low density of the paste, pore coalescence and consequent deformability of the expanded matrix under its proper weight. The cumulative pore volume of MKPC1 increases from 76.9 vol.% to 80.32 vol.% with the increases of the water/metakaolin ratio from 0.100 to 1.33. Futher increases of the water/metakaolin to 0.66 does not change significantly the cumulative pore volume which value became 81.88 vol.%. By increasing the concentration to C2, the cumulative volume was 84.29 and 83.75 vol vol.% respectively for 0.100 and 0.133 water/metakaolin ratio and reach 86.78 vol.% with the water/metakaolin molar ratio of 0.166. The cumulative pore volume was 64.19 vol.% for MKRC1 with water/metakaolin ratio 0.100. This value increases to 74.37 vol.% for MKRC1y and MKRC1z with 0.133 and 0.166 water/metakaolin ratio respectively. With the increase of the concentration of the porogent agent to C2, the cumulative pore volume changed as from 75.45 vol.% for MKRC2x to 77.45 vol.% for MKRC2y. No specimen of the MKR series reach 80 vol.%. Moreover the increase of the water/metakaolin molar ratio from 0.133 to 0.166 conducted to the a reduction of the cumulative pore volume due to the volume contraction that becomes important after volume expansion. The high concentration of porogent contribute for the production of high volume of gas which reduce significantly the interpore partitions while the size of larger capillary pores becomes more and more important with an significant increases of the probability of pores coalescence.

Figure 1b and 1c illustrates the variation of the volume of solid matrix with the increase of the volume of the larger capillary pores; the volume of solid matrix which contains essentially the pores that can be evaluated using the MIP. A global look into the Figure 1b and 1c let observed that an increase of the porogent agent conduct to the increase of the volume of larger capillary pores with the reduction of the volume of the MIP pores per unit. The increase of the volume and size of larger capillary pores is correlated with the reduction of the thickness of the interpore partitions. The global trend is the significant increase of the volume of the larger capillary pores when the value of the water/metakaolin ratio changes from 0.100 to 0.133 for MKPC1 and MKRC1. The volume of the larger pores changed from 10.14 vol.% to 23.43 vol.% for MKPC1x and MKPC1y respectively and remained almost unchanged with further increase of the water/metakaolin to 0.166 (from 23.43 to 25.90 vol.vol.%). Similar trend is observed with MKR6: the volume of larger which is 27.31 vol.% for MKRC1x (water/metakaolin = 0.100) and increases to 41.51 vol.% with water/metakaolin of 0.133 before remains almost unchanged with further increase of the water/metakaolin to 0.166 (from 41.51 vol.% to 45.68 vol.%).

The increase in concentration of the porogent agent from C1 to C2 increases the volume of larger pores for MKP at water/metakaolin of 0.100 to 33.96 vol.% but with no further increase with the increase of the water/metakaolin ratio to 0.133 (the volume of larger pores remained at 30.57 vol.%). Further increase in the volume of larger capillary pores was however observed with the increase of the water/metakaolin from 0.133 to 0.166; the value of the larger capillary pores passed from 30.57 to 57.73 vol.% (Figure 1b). For MKRC2 series, the volume of the larger pores were 45.68, 49.19 and 48.35 vol.% respectively for 0.100 (MKRC2x), 0.133 (MKRC2y) and 0.166 (MKRC2z) as it can be observed in the Figure 2c. These values do not correlate with the trend presented by MKPC2 series. Due to the important volume contraction observed with the specimens MKRC2z, it was difficult to compare the behavior of the two formulations with high concentration of porogent agent. From the above mentioned, one can evaluate the parameters to consider during the design of the porous inorganic polymer composites taking into account the alkalinity of the medium which is significative as governing the dissolution of the solid precursors. It is from this dissolution that will depend the global chemical equilibrium important for the stability and durability of the matrices. The Si/Al of the effective dissolved species will affect the viscosity of the pastes, the pore size distribution and pore volume, the strength of the final product, etc… It is with these elements that we can interpret the difference of behavior between the volcanic ash and the rice ash based porous inorganic polymer composites.

The results describe here permit to understand the interpretation of the cumulative pore curves of MIP analysis. In general the increase of the pore size increase the difficult of the corresponding matrix to have it porosity study by the mercury intrusion porosimeter (MIP). The evaluation of the cumulative pore volume by the difference of densities as did by many authors (references) studying the porosity of the porous geopolymers seem to be inappropriate since more detailed qualitative and quantitative description of the different classes of pores present in the porous matrix are determinant in evaluate the relation between the porosity of a matrix and its thermal behavior. Particularly, the complete description of the porosity is helpful in understanding the appropriate analytical model for the evaluation of the effective thermal conductivity.

3.2 Description of the different classes of pores in the porous inorganic polymer composites

We classed the pores from the porous inorganic polymer composites into two groups: (i) Fines (nano and meso) pores and capillary pores with size from 0.005 to 360 µm which we could able to

describe using the MIP; (ii) the larger capillary pores that we assessed using a stereo optical microscope with size from 0.361 to 4-5 mm.

3.2.1 Pores between 0.006 and 360 µm

Regarding the pores ranging from 0.006 to 360 µm, Figures 2 and 3 show the spectrums of their spatial distribution for the MKP and MKR series as function of the water/metakaolin molar ratio and the concentration of the porogent agent. Figures 2a and 3a describes the pores between 0.006 and 0.68 µm, pores between 0.68 and 10 µm are described in the Figures 2b and 3b while those between 10 and 360 µm are describe in the Figures 2c and 3c respectively for MKP and MKR series. It is observed that the band of the pores present at 0.01 µm as the principal and almost unique pore band (reference) disappeared and a new band is formed with the principal peak around 0.1 µm for MKPC1 with water/metakaolin of 0.100. The band increase in proportion and width with the increase of the water/metakaolin with a slight shift of to low values of pores at water/metakaolin molar ratio of 0.166. Increasing the concentration of MKP from C1 to C2, more larger band is observed with peak at 0.13 µm. The band increase in intensity with the increase of the water/metakaolin molar ratio with progressive shift to lower values of pores size: peaks at 0.13 µm for MKPC2x, 0.10 µm for MKPC2y and 0.88 µm for MKPC2z. The smaller bands that appeared respectively at 0.43 µm and 0.56 µm in the MKPC1 series increased the intensity with the concentration C2. In the MKRC1 and MKRC2 series, the principal peak is observed at 0.05 µm with water/metakaolin ratio of 0.100, the intensity being more important in the MKRC2 specimens (Figure 2). Increasing the water/metakaolin molar ratio, the intensity of the peak increase for both MKRC1 and MKRC2 with the shift of to higher values of pores size: 0.07 µm for MKRC1y and 0.07 and 0.089 µm respectively for MKRC2y and MKRC2z. The peaks observed at 0.43 and 0.56 µm in MKP series were absent in the MKR series.

Between 0.68 and 10 µm, series of bands with peaks at 0.83, 1.05, 1.32, 2.29, 2.57, 7.41 µm are observed for MKPC1 and MKRC1. The variation of the water/metakaolin ratio is at the origin of the shift of the peaks in MKPC1 firstly to high values of pores size (MKPC1y) and to low values (MKPC1z). as it can be observed in the Figure 3. For MKRC1, the principal peak is observed at 7.32 µm with water/metakaolin molar ratio of 0.100 but important bands are observed at 2.6, 3.26, and 4.1 µm. At water/metakaolin molar ratio of 0.133, the bands with significant intensity are at 2.6 and 9.09 µm. The increase of the concentration of porogent agent from C1 to C2 resulted in a sharp decrease of the intensity of many small bands apart from that at 3.6 µm and the formation of the band centered at 9.15 µm with the intensity 5 times that of those with concentration C1. This for the series MKPC2 (Figure 3). The higher proportion of pores being possible with the water/metakaolin

molar ratio of 1.66. In the series MKRC2, few peaks are observed at 1.63 µm and 4.19 µm for MKRC2x, 4.19 µm and 4.7 µm for MKRC2y and no peak is observed for MKRC2z (Figure 3). Although significant similitude was identified in both MKP and MKR series regarding the position of bands and sometime their intensity, the part of difference in the behavior of both pastes should be linked to the degree of dissolution of the silica added: higher the degree of amorphization of the silica of rice ash conducted to high degree of dissolution in alkaline medium with consequent impact on the water demand, the plasticity and deformability compare to that of semi-crystalline phases of volcanic ash. The above details can explain the appearance of the important bands at 9.15 µm for MKP with the corresponding in term of volume at 33.10 µm for MKR series (Figure 3). This contrast with MKRC1 where the concentration of pores between 10 and 360 µm was very low (Figure 2)

Pores with size between 10 and 360 µm were those with lower concentration in MKPC1 and MKPC2 (Figure 3). They were 6 times lower with respect to those between 0.006 and 0.68 µm and more than 20 times lower compared to those between 10-17 µm and 95 µm for MKPC1 and between 10-17 µm, 62 µm and 154 µm for MKPC2.

3.2.2 Pores between > 360 µm

The pores with size > 360 µm were for the quasi totality voids formed during the action of the aluminum powder. Hence their volume and size were for the specimens under study linked to the viscosity of the paste, the concentration of the aluminum powder and the nature of the amorphous silica added as reinforcement of the matrix. For the MKP series, the use concentration C1 conducted to 10.14, 23.43 and 25.90 vol.% of larger pores respectively for the water/metakaolin ratio of 0.100, 0.133 and 0.166. The mean size for these larger pores were in the same order: 0.513, 0.640 and 0.770 mm. The roundness coefficient was 0.76 for the three serie of sample. Value evidently linked to the fact that up to the water/metakaolin ratio of 0.166, the paste maintain it structure after expansion due to the aluminum powder. Figure 3221 show the distribution of the pores as observed with the stereo microscope (Figure 4a) and the ESEM (Figure 4b). In this serie, the probability of the pores coalescence was very low. As observed in the micrographs of the Figure 4, the geometrical isolation of the single pore was effective. The larger size of pore collected was 2.44 mm for MKPC1x, 2.57 mm for the MKPC1y and 2.69 for MKPC1z. However these size of pores were very rare in the MKPC1 series. Increasing the concentration of the aluminum powder (MKPC2), the volume expansion increased as the result of the increase of size and volume of capillary pores: 33.96 vol.% of larger pores characterized the matrix with water/metakaolin ratio of 0.100. The change in the water/metakaolin ratio to 0.133 did not change significantly the volume of

larger pores. Figure 5 shows the micrographs of the MKPC2 where it can be evidenced the increase of the size of pores. Geometrical isolation of pores are still ensured even though it can be noticed an increase of the probability of pores coalescence. The average pore size increased to 0.91 mm for MKPC2x and 0.93 for MKPC2y. The change in water/metakaolin ratio from 0.133 to 0.166 increased the average pore size to 1.1 mm (MKPC2z). The volume expansion was very high for MKPC2z as the result of the increase of almost 50% of the volume from 31 vol.% to 57 vol.%. The roundness of the pores increase to 0.84 and the series could be describe as a real sponge-like structure with a significant decrease of the concentration of the fine pores as the volume the part of the skeleton containing the fine pores. Larger size of pores as 2.86 mm for MKPC2x, 3.40 mm for MKPC2y and 3.89 mm MKPCz were observed as maximum from the series of matrices of MKPC2.

For the series of porous geopolymer with rice ash (MKR), the expression of the expansion as from the reaction of aluminum powder with geopolymer paste was different from that of the MKP series. The volume of larger pores was 27 vol.% for MKRC1 with water/metakaolin ratio of 0.100. Almost three time the volume of the larger pore in the similar composition with volcanic ash as source of amorphous silica. This value increased to 41.51 vol.% with the increase of the water/metakaolin ratio to 0.133. Further increase of this ratio to 0.166 made the volume of large pores passed to 45.68 vol.%. The average pore size was found to be 0.79 mm for MKRC1x, 0.98 mm for MKRC1y and 1.15 mm for MKRC1z largely above the 0.513, 0.64 and 0.77 mm observed with MKPC1 series. Figure 6 shows the micrographs of a typical specimen of the series MKRC1. The complete amorphous form of the silica in rice ash reduced the exigency of the final matrix in water. Consequently the MKRC1 series develop extensive expansion with very larger size of pores compared to MKPC1. The increase in the concentration of the aluminum powder from C1 to C2 conducted to an increase in the pore size but with high probability of the pores coalescence and important deformation of pores shape. The volume contraction was very important in this series. In general the sample of porous geopolymer containing the amorphous silica presented volume contraction as from MKRC1z. With the increase of the expansion the low density of the paste result to the deformation of pores due to the compression by their proper weight. The volume of larger pores was > 45 vol.% in the MKRC2x, MKRCy and MKRz but it was really difficult to determine the real volume expansion of this serie because of the extensive pore coalescence and volume contraction together with the deformation of the structure and pore shape (Figure 7). Figure 7 shows the variation in size and concentration of the larger pores with the variation of the water/metakaolin.

4. Description of the porous inorganic polymer composites using analytical models

The first basic consideration for the definition of the thermal conductivity of porous geopolymer have been the description of the matrix as two-phase system: a skeleton and air[17-19]. For this, the introduction of the appropriate amount of the amorphous silica to ensure optimum chemico-physical equilibrium contribute to the homogeneity of the skeleton and avoid residue of alkalis, phase agglomeration or segregation. In the previous work[4,6], Maxwell-Eucken model was found to be one of the model more suitable for the description of the thermal conductivity of porous geopolymers. The thermal conductivity of porous inorganic polymer materials can be written as follow (8):

$$k_e = k_1 \frac{2k_1 + k_2 - 2(k_1 - k_2)v_2}{2k_1 + k_2 + (k_1 - k_2)v_2} \qquad (8)$$

Where k_e is the effective thermal conductivity, k_1 and k_2 the thermal conductivity of the skeleton and the air respectively; v_2 the volume of pores. K_e, k_1, k_2, v_2 here described is valid also for the equations (9), (10) and (11).

Here we are in the situation where there is a percolation of the inorganic polymer matrix and pores, geometrically isolated as describe above, are homogeneously dispersed. For the porous geopolymers under study, this equation (9) should be valid up to the limit of the percolation of the skeleton: where the pore coalescence becomes important creating a situation of the percolation of pores and highly depercolation of the skeleton. The introduction of the amorphous silica from rice ash and volcanic ash can conduct to the presence of some residual grains into the matrix and some consideration of grain boundaries is needed. When the amorphous silica is from the rice ash, grain boundaries should act as scattering sites and decrease the thermal conductivity. Smith et al[20], explain this situation with the change of the crystallite orientation across the boundary which leads to the change in the velocity of vibrational propagation in the direction of the heat flow. Since the grain boundary constitutes a disordered region, local change in phonon velocity is expected[20].

When the pores coalescence become important, the microstructure becomes inhomogeneous and pores percolation can results continuous at the level to give possibility to heat flux to follow a free path without any obstacle from the matrix (skeleton). This situation reflect the specimens with high water/metakaolin ratio together with higher concentration of porogent agent. So the microstructure is that of skeleton with higher concentration of open porosity, with interpartion pores completely porous. The effective thermal conductivity is written as the equation (9):

$$k_e = k_2 \frac{2k_2 + k_1 - 2(k_2 - k_1)(1 - v_2)}{2k_2 + k_1 + (k_2 - k_1)(1 - v_2)} \qquad (9)$$

This model will be valid for any situation of the concentration of aluminum powder above C2 (C >>> C2). As it can be observed in the Figure 8a, our results were more centered around Maxwell-Eucken 1 and the equation 10 can be assimilated only to the case of MKRC2 where extensive pore coalescence were identified. When the pores coalescence is at the level, the roundness of pores are not more ensured. Another suitable model in this situation is the effective medium percolation theory (EMPT), which predicts the equivalent conductivity of a random mixture of particles with two different conductivities. There is applied the percolation of the skeleton at the limit of the situation of depercolation while the percolation of larger pores is established. The effective thermal conductivity is written with the equation (11):

$$k_e = \frac{1}{4}(k_2(3k_2 - 1) + k_1(2 - 3v_2) + [(k_2(3k_2 - 1) + k_1(2 - 3v_2)^2 + 8k_1k_2]^{\frac{1}{2}}) \quad (10)$$

Referring to the Figure 8a, it is observed that at the level of the volume of porosity > 80 vol.%, the equation 10 and 11 presented almost the same values.

A novel effective medium theory for modeling the thermal conductivity of porous materials proposed by Gong and al[18,19] consider the basic structural models including the series, parallel, Maxwell-Eucken in the situations describe above and EMPT. They consider that phases in porous materials are small spheres dispersing into an assumed uniform (two-phase) with thermal conductivity K_m[18-19]. For porous geopolymers under study, their model can be written as (11):

$$(1 - v_2)\frac{k_1 - k_e}{k_1 - 2k_m} + v_2\frac{k_2 - k_e}{k_2 - 2k_m} = 0 \qquad (11)$$

The rounded pores describe for the porous structures allow to consider $K_m = K_1$ in the first time when the continue phase is the solid and $K_m = K_2$ when the continue phase is the porosity. In these option, the novel effective medium theory correspond with Maxwell-Eucken (1) and (2) respectively. Situations of $K_m = 0$ or $K_m = \infty$ that will correspond to the series and parallel models respectively are not realistic for the porous composites under study. According to the microstructure , the porosity and pore size distribution, evidenced in this study, when the pores are geometrically isolated in a continue skeleton as we observed with MKPC1, MKPC2 and MKRC (Figures 4-9) the porosity is described with intraparticles pores, interparticles pores, intraggregation pores, intracluster pores all of them without any communication with the external surface (closed pores). The uniformity of the medium is ensured by the chemico-physical equilibrium of the geopolymer matrices reinforced with appropriate amount of amorphous silica to control the Si/Al and Na/Al ratios significant in determining the effective thermal conductivity of geopolymer materials[22]. It can be noted that noted that when the pores coalescence remains under control, there is a direct relation

between the pore-size and the cumulative pore volume and the discussion about the pore size is inclusive when consider the above models.

Conclusion

This work propose an microstructural approach to define the suitable model for the description of the effective thermal conductivity of porous geopolymer composites. The approach is based on the detailed description of the microstructure, the pore volume and pore size distribution including pore shape. Description that allows to correlate the appropriate model to the indicated microstructure obtained with the design of porous geopolymer composites through the use of porogent agent. We focused on the influence of the phases percolation on microstructure and their influence on the effective thermal conductivity. Designed homogeneous porous structure of gopolymer was found possible applying a control of the viscosity (water/metakaolin), the expansion behavior, and the pore size to project the microstructure easily descriptible with analytical model. Closed porosity also called in this case latent pores are not associated with the permeability or absorption of molecules so will help to obtrude the thermal flow and will help improving the thermal insulation of the porous composites.

References

1. Davidovits J., Geopolymers chemistry and applications. In Davidivits J. (Eds), institut of Geopolymer, Saint-Quentin, France.
2. **Duxson P., Provis J.L., Lukey G.C., Malicoat S.W., Kriven W.M., Van Deventer J.S.J., Understanding the relationship between geopolymer composition, microstructure and mechanical properties, Colloids Surf. A: Physicochem. Eng. Aspects 269(2005)47-58.**
3. ElieKamseu, Maria Chiara Bignozzi, U C Melo, Cristina Leonelli, Vincenzo M Sglavo, Design of inorganic polymer cements: Effects of matrix strengthening on microstructure Construction and Building Materials 38(2013):1135–1145.
4. **E. Kamseu, B. Nait-Ali, M.C. Bignozzi, C. Leonelli, S. Rossignol, D.S. Smith, Bulk composition and microstructure dependence of effective thermal conductivity of porous inorganic polymer cements, Journal of the European Ceramic Society 32(2012)1593-1603.**

5. **Medri V., Ruffini A., The influence of the process parameters on the in situ inorganic foaming of alkali-bonded SiC based foams, Journal of the European Ceramic Society 32(2011)538-545.**
6. **J. Bourret, N. Tessier-Doyen, B. Nait-Ali, F. Pennec, A. Alzina, C.S. Peyratout, D.S. Smith, Effect of the pore volume fraction on the thermal conductivity and mechanical properties of kaolin-based foams, Journal of the European Ceramic Society 33(2013)1487-1495.**Prud'homme
7. **Prud'Homme E., Michaud P., Joussein E., Peyratout C., Smith A., Arrii-Clacens S., Clacens J.M., Rossignol S., Silica fume as porogent agent in geomaterials at low temperature, Journal of the European Ceramic Society 30 (2010)1641-1648.**
8. **Prud'Homme E., Michaud P., Joussein E., Peyratout C., Smith A., Rossignol S., In situ inorganic foams prepared from various clays at low temperature, Applied Clay Science 51(2011)15-22.**
9. Bell J.L., Kriven W.M., Preparation of ceramic foams from metakaolin-based geopolymer gels. In: Lin H.T., Koumoto K., Kriven W.M., Garcia E., Reimanis I.E., Norton D.P., (Eds), developments in strategic materials: ceramic engineering and science proceedings, vol. 29(10), pp.97-111.
10. Studart A.R., Gonzenbach U.T., Tervoort E., Gauckler L.J., Processing routes to microporous ceramics: a review, Journal of the American Ceramic Society 89(2006)1771-1789.
11. Van Bonin W., Nehen U., Von Gizycki U., Hydrogen peroxides blowing agent for silicate foams, US patent 3,(1975), 864, 137.
12. Woyansky J.S., Scott C.E., Minneay W.P., Processing of porous ceramics, American Ceramic Society bulletin 71(1992), 1674-1682.
13. A. Njoya, C. Nkoumbou, C. Grosbois, D. Njopwouo, D. Njoya, A. Courtin-Nomade, J. Yvon, F. Martin, Genesis of Mayouom kaolin deposit (western Cameroon), Applied Clay Science 32 (2006) 125–140
14. S.E. Gustafsson, Transient plane source (TPS) technique for the thermal conductivity and thermal diffusivity measurements of solid materials, Rev. Sci. Instrum 62(1991)797-804.
15. T.Log, S.E. Gustafsson, Transient Plane Source (TPS) technique for measuring thermal transport properties of building materials, Fire Mater. 19(1995)39-43.
16. M. Gustavsson, E. Karawacki, S.E. Gustafsson, thermal conductivity, thermal diffusivity and specific heat of thin samples from transient measurements with hot-disk sensors, Rev. Sci. Instrum. 65(1994)3856-3859.

17. B. Nait-Ali, K. Haberko, H. Vesterghen, J. Absi, D. Smith, Thermal conductivity of highly porous zirconia, J. Eur. Ceram. Soc. 26(16)3567-3574.
18. L. Gong, Y. Wang, X. Cheng, R. Zhang, H. Zhang, Thermal conductivity of highly porous mullite materials, International Journal of Heat and Mass Transfer 67 (2013)253-259.
19. L. Gong, Y. Wang, X. Cheng, R. Zhang, H. Zhang,A novel effective medium theory for modelling the thermal conductivity of porous materials, International Journal of Heat and Mass Transfer 68 (2014)295-298.
20. D. S. Smith, S. Fayette, S. Grandjean, C. Martin, R. Telle and T. Tonnessen, Thermal resistance of grain boundaries in alumina ceramics and refractories, J.Am. ceram. Soc., 86(1)(2003)105-11.
21. R. Landauer, The electrical resistance of binary metallic mixtures, J. Appl. Phys., 23, (1952)779-84.
22. Kamseu JTAC

Figures and Tables Captions

Figure 1a: Variation of the cumulative pore volume in MKP and MKR with the water/metakaolin ratio.

Figure 1b: Variation of the V_{MIP} and V_{LP} in MKP series with the water/metakaolin ratio.

Figure 1c: Variation of the V_{MIP} and V_{LP} in MKR series with the water/metakaolin ratio.

Figure 2: Pore-size distribution (ϕ < 360 µm) in MKP series

Figure 3: Pore-size distribution (ϕ < 360 µm) in MKR series

Figure 4: Micrographs showing larger pores shape and distribution in MKPC1

Figure 5: Micrographs showing larger pores shape and distribution in MKPC2

Figure 6: Micrographs showing larger pores shape and distribution in MKRC1

Figure 7: Micrographs showing larger pores shape and distribution in MKRC2

Figure 8: Typical distribution of larger pores showing the maximum size of pores of 3 mm in series with aluminum content of C1 and appearance of larger pores with 4 and 5 mm of diameter for C2 series.

Figure 9a: Variation of the effective thermal conductivity (k_e) with the volume of porosity (v) according to the basic models of the literature.

Figure 9b: Proposed microstructure model corresponding to the specimens under study.

Figure 10: Variation of the effective thermal conductivity of the specimens under study with the cumulative pore volume.

Table 1: Formulations of the different specimens under study.