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(Article begins on next page)

Recycled Natural Wastes in porous geopolymer composites: Effects on the pore size distribution and effective thermal conductivity.

Abstract: The effectiveness of two amorphous silica based wastes, rice husk ash and volcanic ash powders, to act as structural reinforcement and partial replacement of metakaolin in porous matrices for thermal isolation was assessed. Both wastes produce colloidal phases that contributed to improve the reactivity and homogeneity of the matrices enhancing the mechanical strength: rounded pores were obtained in relation with significant reduction of the interpore partitions under controlled addition of porogent agent. The bulk thermal conductivity decreased from 0.6 to < 0.15 $W.m^{-1}K^{-1}$ with the increase of porogent concentration. The final porous structure was compared to cellular materials with pore size distribution and pore connectivity that allow analytical description and prediction of their effective thermal conductivity as the modification of the Si/Al ratio with the introduction of the wastes improve the formation of highly consolidated matrices with regular and reproducible texture.

Results demonstrated that clear correlation can be established among the viscosity of the pastes, their bulk chemical composition, the concentration of the porogent agent (6-12/10000) and the volume expansion/pore size distribution

Keywords: porous inorganic polymer composites, rounded pores, pore size distribution, thermal insulation

Introduction

In the context of global warming for environment, the role played by the insulating materials for the achievement of the reduction of energy is significant and explains the continuous increase of interest of researchers and governments for this class of materials especially the low cost ones. More specifically those insulating materials that are produced with less energy consumption and that may contribute to the management of some natural or/and industrial wastes are under

investigation by many researchers [1,2]. Recent studies have proposed in this direction porous inorganic polymer matrices as from clays [3,4] or wastes [5] The motivation comes from the low values of the thermal conductivity of these materials ($<1 Wm^{-1} k^{-1}$) and their fire resistance if compared to organic polymer foams. Their room temperature manufacturing cycle is based on the ability of the raw materials, mainly in amorphous form, to be dissolved in high alkaline solution and to develop gel whose intrinsic good mechanical properties allow the introduction of a large quantity of pores while maintaining the global continuity of the skeletal body [3]. It was observed that with the low thermal conductivity of clays, and even reduced in presence of metaclay, the introduction of controlled pores volume and pore size distribution, important lowering in effective thermal conductivity of the system matrix-pores are achieved: the reduction of the resistance due to the interfaces combined with the increase in tortuosity of the route of thermal gradient.

The management of the Si/Al molar ratio is accepted as main parameter controlling the mechanical properties of inorganic polymer cements, IPC [6-8]. In the first work addressed to this subject [3], we tried to solve the problem of Si/Al by using a natural sand-rich kaolinitic clay as aluminosilicate source for the preparation of IPC. The results showed that via alkali activation of the metakaolin derived from the clay it was possible to achieve good mechanical properties with a specific pore size distribution, final pore shape, and pore volume affected by the presence of the dense quartz grains which remained unreacted or were partly embedded into the matrix affecting the movement of the gas developed with the introduction of the aluminum powder.

Being interested in the preparation of geopolymeric porous and self-supporting insulating materials, in the present work our objective is to use a standard kaolin, despite its relative low Si/Al, and to introduce amorphous silica powder to achieve the chimico-physical equilibrium for an homogeneous and resistant porous system avoiding the presence of rigid quartz grains. Volcanic ash

and rice husk ash were chosen for their contain in amorphous silica and in particular for their ability to develop frothy-like structures. By introduction these two additional raw materials, improvement in the final IPC of mechanical properties are target together with the pore size distribution, expansion behavior and a final matrix capable to resist to environmental stresses as from the stability in water and to cycles of temperature variation [3]. The processing route here appears more sustainable as the two wastes with their important fraction of amorphous silicate are usefully recycled without additional treatment. Their presence reduced the amount of clayey materials to be calcined, hence the energy consumed and CO_2 released.

The introduction of volcanic ash or rice husk ash in the system of porous IPC would allow the reduction of the amount of sodium silicate necessary to achieve good porous structure and even give possibility to use only sodium hydroxide since in the presence of amorphous silica the system NaOH-rice husk ash or NaOH-volcanic ash will develop viscous paste with binding properties capable to act as binder giving high resistance to the material. It is recognized that the presence of sodium silicate in the bulk composition of inorganic polymer cements is one of the preoccupation for this new class of materials to be defined as “green” [9]. Successful formulations in which the sodium silicate is absent or reduced sound promising for the sustainability of the final porous matrices [9]. The processing route appeared to be less exigent in term of energy (room temperature) and materials added for pore formation do not need any energy to effectively act. Usually the introduction of porosity through the use of organic matter required important quantity of energy to escape the organic matter at high temperature [4] and is detrimental for the environment due to the energy cost and CO_2 emitted [10-12].

The addition of amorphous silica to inorganic polymer paste reduces to minimum the residual alkali which has as effect the reduction of free alumina oligomers in the matrix and consequent reduction of the air bubbles since the presence of amorphous silica contributes to create more homogeneity and continuity in the matrix [3, 6-8]. When the matrix is homogeneous with limited constraints linked to the unreacted particles, like quartz grains, and residual alkalis, the movement of gas

produced from the corrosive reaction of metallic powder (here specifically: Al) is as uniform as possible contributing to more homogeneous size of pores and optimum expansion for a highly expanded structure.

Homogeneity, that helps in controlling the pore seize distribution, allows to design with more accuracy a potential model suitable for the description and prediction of the effective thermal properties of porous inorganic polymer materials. Alvarez et al. [13] showed that pores with nanometric size greatly enhance phonon scattering, introduce larger strain fields in materials and effectively obstruct the cross-sectional area for heat transfer. The homogeneity developed with the addition of amorphous silica is here expected to promote more controlled small size of pores and cellular structure with good insulating properties [3,4,14,15].

In this paper, fine powders of volcanic ash and rice husk ash have been added to metakaolin-based geopolymer paste, taking in consideration appropriate amount for the hypothetic total reduction of Al oligomers during geopolymerization. Pore volume's change has been investigated according to the water/MK ratio, the amount of aluminum powder and the amorphous silica source. The influence of these parameters on the pore evolution has been assessed using the Mercury Intrusion Porosimeter and the stereomicroscope. Finally correlation between the pore evolution and the thermal behavior was established. In this context the alkalis present in the IPC matrices act to enhance this conduction. The higher the amount of ions required for the complete balance of the geopolymerization of the solid precursors, the higher the probability of ions accumulation. The bulk thermal conductivity is discussed taking in account the reduction alkalis ions accumulation with the effectiveness of the amorphous silica to balance the chemical equilibrium and decrease the ionic thermal diffusion.

2. Materials and Experimental methods

2.1 Materials

A standard kaolin from the Mayouom deposit in Cameroon [16] was used for the preparation of the metakaolin. We selected the white variety as described by A. Njoya [16]. It is a sand-poor kaolin,

76–85% kaolinite and 2–9% quartz with illite, muscovite, anatase and hematite as secondary minerals. The kaolin was sieved to eliminate the residual quartz sand, dried and calcined at 700°C for 4 hours. The volcanic ash was from the Mungo deposit [17] in the Littoral region of Cameroon. The material presents essentially amorphous matrix in which fine grains of anorthite, quartz, entastite-augite, diopside are embedded [17,18]. Many authors consider volcanic ash as a waste since they required to be disposed of in most of the naturally occuring volcanic eruptions.Rrice husk was collected in a rice mill at Ntarikon-Bamenda in the North-West Region of Cameroon. It was considered as a valueless by-product of rice milling and thus burnt in heaps near the mill. The husks collected were burned at 700 °C for one hour in an electric furnace at a temperature rise of 3 °C/min for comparison. The kaolin from Mayouom was calcined at 700°C for 4h in electric Furnace while the volcanic ash was used as collected. The bulk chemical composition and the minerals content of the above described materials are presented in Table 1. The_aluminum powder and sodium hydroxide were laboratory grade from Sigma Aldrich, Italy. The sodium silicate solution ($SiO_2/Na_2O = 3.0$) was provided by Ingessil, Verona, Italy.

2.2 Preparation of the porous inorganic polymer composites

Preliminaries investigations (results not show here) permitted to adopt 2.5 volume of metakaolin for 1 volume of volcanic ash or rice husk ash. This ratio valid for both wastes was also adopted for necessity of comparison and interpretation of the result in term of implementation considering the potential applications of the results of this study. The above described volume ratio correspond in mass to 1:1 for the metakaolin and volcanic ash while it is 7:1 (in mass) for the couple metakaolin and rice husk ash. The relative high amount of volcanic ash by the IPC matrix compared to rice husk ash is due to the fact that the volcanic ash is an aluminosilicate source with relative high amount of alumina (15 mass% of Al_2O_3) compared to the rice husk ash (2 mass% of Al_2O_3). Moreover, volcanic ash as other the pozzolanic materials are suitable as 100% solid precursor for the production of inorganic polymer composites [18,19]. Its relative high density is responsible of the value of its mass 7 times that of rice husk ash for a determined volume. However, our

investigation presented both materials promising for porous IPC with high potential on developing frost-like structure in geopolymerization context.

Metakaolin powder was weighted and introduced in an alkaline solution (sodium hydroxide 8 M and sodium silicate -Na_2O:SiO_2 = 1:3- in 1:1 volume ratio) for a liquid/solid ratio 0.35**.** Five formulations of geopolmers, indicated as MK4, MK6, MK8, MK10 and MK12, were prepared by introducing respectively 4, 6, 8, 10 and 12 g of aluminum powder (Reagent grade, Aldrich) over 10000 g of the paste. Similarly, MKP4, MKP6, MKP8, MKP10 and MKP12 were obtained for volcanic ash added metakaolin while MKR4, MKR6, MKR8, MKR10 and MKR12 were obtained for rice husk ash.

The effect of viscosity of the final porosity of the geopolymeric paste was tested using the series MKP6, MKP8, MKR6 and MKR8. The variation of the viscosity was based on the modification of water content: water/metakaolin ratios of 0.100, 0.133 and 0.166 were considered and indicated with a,b, and c respectively. Finally MKP6a, MKP6b, MKP6c, MKP8a, MKP8b and MKP8c for volcanic ash based porous inorganic polymer composites; MKR6a, MKR6b, MKR6c, MKR8a, MKR8b and MKR8c for the rice husk ash were obtained. The pastes of the above described formulations were poured into hard plastic molds having 8 cm of diameter and 3 cm thickness. These dimensions were adopted to have specimens suitable to be considered as infinite element with regard to the sensors (with 3, 6 and 9 mm of diameter) of TPS used for this study. In prevision of the increase in volume of the paste due to the action of the aluminum powder, the initial thickness for all the formulations was 1cm. The products were keep from the contact of air during the first 24 h then curing continued at room temperature (21 ± 2°C, 55% humidity) up to 28 days before starting the characterization.

2.3 **Characterization of the porous inorganic polymer composites**

2.3.1 MIP and Volume changes

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 ~ 1 cm^3 of volume for the MIP.

The preparation of the IPC adding fine powder of volcanic ash or rice husk conducted to an homogeneous paste which was subjected to considerable increase in volume when metallic aluminum powder was added. The increase in volume is the results of the increase in the volume of gas that occupies the voids. The dimensional changes during the development of frost-like structure was measured using tubes of 2 cm of diameter for the samples preparation. Each specimen's formulation with added aluminum powder was compared to the standard ICP formulation without Al addition. The expanded fraction was then used to calculate the coefficient of expansion.

2.3.2 Stereomicroscope and Scanning Electronic Microscope Analysis

Fractured pieces from the mechanical test were collected and polished (diamond pastes after grinding with silicon carbide powders and water) to have 3 x 3 x 1 cm for the surfaces observations. The DFPlan objective series showed the shape of the specimen as it is, without any distortion. Furthermore the careful selection of lens surface coating and glass materials in the entire optical system made it possible to observe and document specimens in their original, authentic colors. The SZX10 motorized focus drive (optional) made the digital documentation with extended focal imaging (EFI) efficiently. This even allows creation of pseudo 3D images, closing the gap between documentation and what the eyes have seen before through the stereoscopic light path.

Many imaging or measuring tasks required the use of the same zoom magnification setting to ensure consistent and comparable results. In addition the SZX10 allowed the quick change between stereoscopic view and axial light path for the camera. The advantage of the axial light path setting is that measurements taken with the camera are reliable and precise in all directions making results independent from the orientation of the sample under the microscope.

The polished surfaces were gold coated after washing with acetone and dried for image analysis using scanning electron microscope, SEM (ESEM Quanta-200, Fei Company - Oxford Instruments). The scanning electron microscope equipped with EDS detector (X-EDS Oxford

INCA-350) (operating at 20 kV) was used for microstructural examination of the specimens with secondary electron images (SEI) and back scattering images (BSI). Microanalysis for phase's identification and distribution was performed using the embedded EDS digital controller and control software.

2.3.3 Thermal conductivity

The thermal conductivity of the specimens investigated through the transient plane source (TPS) method is determined from the time dependent temperature variation. 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 allows to consider the sample to behave as an infinite medium. Samples were polished in order to reduce the thermal contact resistance.

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 [20-22]. Measurement time and sensors geometry and positioning were kept constant during the measurements. 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 [21,22].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 Changes in the fresh pastes, expansion and mechanical properties of the final products

The choice of partial replacement of the MK with amorphous silica is significant with regard to the first solution [3] on the use of the sand-rich metakaolin to improve homogeneity, pore size distribution and chemico-physical equilibrium of the matrix of porous inorganic polymer composites. Apart from the pore size distribution and the bulk thermal conductivity that we are going to discuss in the next paragraphs, important improvement in the reactivity, processing of the pastes, the expansion behavior, the properties of the fresh state and the flow behavior are the first advantages describe here. Particularly, we noted significant improvement of the workability of the pastes with rice husk and volcanic ashes. The apparent density of the amorphous silica is low and can be incorporated in the cluster structure of metakaolin reducing the possibility of segregation or particles agglomeration with improvement of homogeneity and densification. The introduction of the amorphous silica from rice husk and volcanic ash resulted primarily with the dissolution of an important fraction with consequent presence of colloidal phase that is formed. This phase, prompts to contribute on the reactivity and formation of sodium aluminosilicate hydrate gels (H-N-A-S gels), modifies the silica to alumina ratio and enhances the polycondensation. The amorphous silica from rice husk and volcanic ashes transformed to reactive species, reduced the alkalis residues and reinforced the chemico-physical equilibrium of the matrix of porous IPC.

Figure 1 describes the variation of the coefficient of expansion of the pastes with the fraction of the aluminum powder for the metakaolin (MK), metakaolin- rice husk ash (MKR) and metakaolin-volcanic ash (MKP) based porous IPC matrices. The coefficient of expansion was 1.44 for the standard metakaolin based porous inorganic polymer, 1.55 for MKR and MKP when 4/10000 of Aluminum powder was added. With the increase of the aluminum at 6/10000 the coefficient of expansion increased to 1.79 for MK, 1.95 for MKR and 2.02 for MKP. These values were 2.26, 2.40 and 2.56 respectively for the value of aluminum powder of 8/10000. Further addition of

aluminum powder did not correspond to extra expansion: the results in term of expansion coefficient did not change at 10 and 12/10000. This latter value of aluminum powder seems as threshold since the extensive pores coalescence conducted to the development of some larger pores that obliged film of pastes to be handed incapable to resist to their proper weight: redensification and closure of some pores with consequent decrease in the coefficient of expansion occurred in some cases.

The addition of the amorphous silica (from rice husk ash and volcanic ashs) improved the mechanical properties as the Si/Al changed with complete reduction of the alumina oligomers and enhancement of the densification. The flexural strength of 10 MPa for the metakaolin based-geopolymer moved to 12 MPa with the addition of amorphous silica (Figure 2). Adding 4/10000 of Aluminum powder, the mechanical strength decreases to 6 MPa for MK and 7 MPa for MKR and MKP. Further increase in aluminum powder decrease linearly the flexural strength: 4, 5 and 6 MPa respectively for MK, MKR and MKP at 8/10000 and 2.5, 3.8 and 5.2 MPa in the same order at 10/10000 (Figure 2). The samples with 12/10000 Al addition showed very poor mechanical strength due to the larger pores present in the structure resulting from the extensive pores coalescence. The difference in flexural strength between the MKR and MKP was due to the important increase in pores size in the MKR compare to MKP.

By varying the water/metakaolin ratio in the systems under study, it was observed some modifications of the density, pore size, volume expansion, etc… of the frost-like structure. Figure 3 presents the variation of the apparent density of the frost-like structure obtained with the formulations MKP6, MKP8, MKR6 and MKR8 of the a,b,c serires where the water/metakaolin ratio is progressively modified from 0.100,0.133, and finally to 0.166. This modification directly affected the viscosity parameters of the fresh pastes as already demonstrated [23]. It was of our objectives to assess how this addition can affect the final structure of the porous matrix. For MKP6 and MKR6, the apparent density decreases linearly form 0.668 and 0.7886 for water/metakaolin ratio of 0.100; to 0.633 and 0.749 for 0.133; and to 0.558 and 0.724 g/cm^3 respectively for 0.166.

For both MKP6 and MKR6, the decrease in density was correlated to an increase in volume expansion. For MKP8 and MKR8, the apparent density decreases from 0.597 and 0.727 for water/metakaolin ratio of 0.100, to 0.564 and 0.666 g/cm^3; and 0.562 and 0.630 g/cm^3 respectively. There was no significant difference between the MKR8 with water/metakaolin ratio of 0.133 and 0.166 due to the pores coalescence which was at the origin of the volume contraction as described earlier. The global variation of the density and the expansion behavior can be interpreted taking in consideration the chemico-physical equilibrium between the formation of the gel, the action of the aluminum powder and the pore coalescence that affect the densification/expansion behavior.

3.2 Pore size distribution and microstructure

The introduction of up to 4 /10000 of aluminum powder was found to not be enough to reduce considerably the thickness of walls between pores while that of 10 or 12/10000 produced porous matrices with high level of percolation of capillary pores formed. At this stage (12/10000 Al added) the volume expansion was not more effective since the major part of pores formed disappeared under the effects of coalescences and volume contraction. The volume contraction was due to the difficulty of some films of pastes from the expansion to resist under their proper weight. Moreover, the bi-axial bending strength of the sample with 10 or 12/10000 was low as result of the extensive pore coalescence and depercolation of the skeleton. As observed in the Figure 1, the addition of aluminum of 6 and 8/10000 corresponded to the interval of optimum reduction of the thickness of the walls between pores and volume expansion while maintaining their roundness and low level of percolation.

Figures 4, 5 and 6 show the pore size distribution as analyzed by the Mercury Intrusion Porosimeter for the dense IPC, volcanic ash based and rice ash based expanded IPC respectively. The achievement of the expanded cellular matrices with the above described formulations depends on the realization of a homogeneous mix between the MK and rice ash or between MK and volcanic ash. The fineness of the particles and the alkaline solution was found to be significative as having great impact on the viscosity of the pastes and the expression of the frost-like structure. It is observed in Figure 3 that the porosity of the volcanic ash or rice husk ash based IPC is reduced to the important fraction of nanometric pores (5-50 nm) together with small fraction of micrometric pores as already describe with metakaolin based IPC[3]. The

microstructural investigations confirmed that some few dispersed larger capillary pores can be observed and their presence in metakaolin based geopolymer can be inhibited using appropriate amount of amorphous silica. With the introduction of 6/1000 of aluminum, the pore size was extended from 0.001 to 360 micrometer as revealed by MIP with additional larger pores (> 360 µm) but generally smaller than 2 mm for volcanic ash based IPC and 3.5 mm for rice husk ash based IPC. The detailed analysis of the pores from MIP let observed bands concentrated at 100 nm and between 0.6 and 20 µm for the expanded volcanic ash based IPC (Figure 5a); 10-100 nm and between 0.6 and 50 µm for the expanded rice husk ash based IPC (Figure 6a).

The cumulative pore volume of MKP6 is 0.36, 0.48 and 0.29 mL/g respectively for 0.100, 0.133 and 0.166 water/MK ratios (Figure 7a). These values are 0.47, 0.53 and 0.48 mL/g for MKR6 (Figure 7b). It seems that the limited volume of water necessary to achieve good expansion in correlation with the amount of aluminum powder corresponds to the water/MK of 0.133. Even with MKP8 and MKR8 series, the cumulative pore volume (Figure 7c and 7d) increases between water/MK ratio of 0.100 and 0.133 from 0.41 to 0.46 mL/g (MKP8) and 0.46 to 0.47 mL/g (MKR8), but when the water/MK ratio moves from 0.133 to 0.166, the cumulative pore volume slightly decreases. The dissolution of an important amount of amorphous silica increased the colloidal phase which affected significantly the viscosity of the final pastes. The modification of the viscosity gave a peculiarity to the matrix improving the depercolation of capillary pores up to 8/10000 of aluminum powder and the formation of more rounded shape pores as it can be observed in Figure 8 and 9. The thickness of the walls between pores decreases with the aluminum concentration as the viscosity of the paste. In fact the action of the aluminum was found to be relatively limited by the structure of the matrices. The semi-crystalline structure of the volcanic ash improved the resistance of the paste under the action of the propagation of the gases formed from the reaction of aluminum powder in alkaline solution. In Figure 8 the larger pores have an average size of 0.8 mm and 1 mm respectively for 0.100 and 0.133 water/MK ratios. The larger pore size in MKP6b was 2 mm while it was 3 mm in the MKP6a. Increasing the Al content the average pore size increase to 2 mm with water/MK of 0.100 and 2.5 mm for water/MK of 0.133: the pores remained rounded, the number of pore sites increased with the reduction of the walls between pores (Figure 9). The distribution of the larger pores and the structure of the rest of smaller pores in the walls between pores allowed us to compare the pore structure with the model of Hashin-Shrinkmann [3]. This is true even for MKR6 and MKR8 although the amorphous structure of the rice husk ash affects

relatively the size and deformation of the pores under the action of the aluminum powder. The average size of pores was 2.5 mm for MKR6b and even 3 mm MKR6a. Presence of larger pores with size up to 5 mm was also evidenced (Figure 10). The low density of the pastes that was at the origin of the extension of the pore size conducts, with high concentration of Al powder (MKR8), to larger pores with average size of 4 mm with additional intensive pore coalescence and redensification of the pastes that affected significantly the pore size distribution with deformation of some part of the matrix (Figure 11-13).

3.3 Effective thermal conductivity of porous IPC: effects of pore size distribution

The thermal conductivity of silica (SiO_2) and alumina (Al_2O_3) decrease from ~1.5 and ~30 $W.m^{-1}K^{-1}$ to 0.2 and 0.5 $W.M^{-1}K^{-1}$ following the transformation from crystalline to amorphous state respectively. This observation is particularly precious for the motivation of the design of insulating inorganic polymer matrices. The amorphous structure of metakaolin and associated additives induced to the final product a tortuous structure that oblige thermal gradient to flow through a very twisting way consisting of a complex interconnected system of H-N-A-S gel. The additives (amorphous silica) acted to balance the chemical equilibrium and as resistant bridge modifying the final structure: density and porosity (Figures 2 to 6) and the expansion behavior when considering the addition of porogent agent. As showing in the Figures 11 and 12, the phenomenon of expansion increases the pore size and the final interpore partitions are significantly reduced. Even though they are reduced, the walls of these interpore remained compact particulary for the rice husk ash based formulations.

However, the compactness of the structure of IPC, even with additions, still maintains the bulk thermal conductivity at 0.5-0.6 $W.m^{-1}K^{-1}$ as it can be observed in the Figure 14. The pores in these compact part are essentially fines pores ranging from 5 to 50 nm (Figure 3 and 7).

In the Figure 14, the error bars have to be interpreted as the variation of the thermal conductivity during the course of the investigations including the variation of the total humidity of the specimens that fluctuated around 3-4 wt%. The error bars also integrate the slight variation of the thermal conductivity linked to the diameter of the probe: we worked with three probes having respectively 3, 6 and 9 mm. These three probes induce three different probing depths and the results could be used to assess the local homogeneity of the matrices.

4. Discussion

An important change in the metakaolin-amorphous silica geopolymer systems is the significant modification of the properties of the fresh pastes with influence on the viscosity, shear behavior and yield stress. Colloidal particles formed appear to considerably impact the process of gelation and formation of porosity with reduction of setting time. The added particles of rice and volcanic powders let observed an enhancement of the agglomerates when the mix of solid precursors came in contact with the alkaline solution. The demand in water increase but the porosity (particularly the capillary pores) of the matrices is reduced with colloid of silica and alumino-silicates that fill the remaining voids inducing the increase in densification process and homogeneity that allow to reduce the porosity to interstitial fine pores (nano sizes) and controlled capillary pores from porogenic agents which in this case is aluminum powder. Moreover preparation of porous inorganic polymers indicates that we are discussing materials that can be spreading, molding or poured according to the desired application. These processes recall the rheological properties of the system. The effects of solid to liquid ratio have consequences up to the effective thermal conductivity since this affect the local concentration of alkalis, volume expansion and the pore size distribution. When only metakaolin was used for the preparation of the referent paste, changes in yield stress and shear behavior were clearly observed after 90 min of ageing at room temperature [23] The addition of amorphous silica from rice and volcanic ashes reduced the changes to 45-50 min improving the cohesiveness of the particles in fresh state.

The interpretation of the pores evolution concluded on the reduction of the volume of the nanometric pores evidently due the fact that the introduction of capillary pores with aluminum powder contribute to reduce the density of the matrix (Figure 1) means the real volume of the IPC which presents the nanometric pores. Focusing to the proportion of the two principal bands of pores, the volume of the band with pores between 5-100 nm was important for the MKR6 while that between 0.6 and 50 µm was important for the MKP6. Another observation was the shift to lower values of the band of nanomtric pores in the case of MKR6. For both MKR6 and MKP6, the high volume of pores seem to be obtained with the water/MK ratio of 1.33 (MKP6b and MKR6b). In fact the principals bands of MKP6 and MKR6 shifted to relatively high values of

pores fraction (Figure5a and 6a) with the water/MK ratio varying from 0.100 to 0.133. Further increase of water/MK ratio from 0.133 to 0.166 inhibited the increase in pore volume fraction with the reduction of the single band. The situation is similar for MKR6 series.

Focusing on the pores size distribution of the MKP8 and MKR8 series, the increases in aluminum powder content from 6 to 8/10000 did not modify the nanometric pores band between 5 and 100 nm for both series but the fraction of this type of pore decreases again while pores band at 0.6-50 µm increased in volume. The pores band with diameter centered at 7-9 µm appeared with high volume in MKP8 while in MKR8 high volume fraction was observed with pores of diameter around 20-25 µm (Figure 5b and 6b). The principal band for MKP8 was accompanied with important series of small bands with diameter from 0.6 to 50 µm. The diversification of the bands in this interval was not as important in MKR8 (Figure 6b). The overall behavior of the two series can be correlated to the viscosity behavior which is significantly affected by the addition of water independently on the amount of aluminum powder. Moreover the dissolution of amorphous silica (rice ash) in alkaline solution is different from that of semi-crystalline silica (volcanic ash) while the degree of dissolution should be affected by the water content. The extend of dissolution has affected the polycondensation and the pore size distribution. The decrease of the viscosity of the metakaolin based geopolymer with the increase in water content was extensively discussed in our previous work [3].

The distance between the pore walls is reduced and the thickness of the interpore partitions is important favoring the heat transfer by conduction [24]. The aluminum powder decreases the thickness of the interpore partitions as blowing agent reduces the bulk density with consequent reduction of the thermal conductivity through the reduction of ions accumulation and reduction and the heat capacity of the matrices (Figure 12). As demonstrated with the metakaolin based porous IPC, the decreases is correlated to the mathematical function $y = bx^{-a}$ with squared correlation > 0.95[1]. The increase in aluminum powder contributes to the reduction of the effective volume containing the nanometric pores and the formation of new pore with larger size allowing to consider multiforms of heat flow transport. Our formulations design focused the objectives of: (i) enhancement of the strength, chemical stability and reduction of the alkalis ions residues maintaining the lightweight structure of the matrix; (ii) introduction of rounded pores with the reduction of interpore partitions and the capillary pores percolation.

Figures 4 to 10 indicate that promising results have been achieved. The rounded isolated pores was effective in specimens with both rice and volcanic ashes at 4/10000 of aluminum powder. However with this concentration we were far from the maximum expansion and the thickness of the interpore partitions remained higher. The bulk thermal conductivity is reduced under 0.3 $W.m^{-1}K^{-1}$ and under 0.3 and 0.2 $W.m^{-1}K^{-1}$ when the aluminum powder increases to 6/10 000 and 8/10000 respectively. It was observed the variation of the density as that of the bulk thermal conductivity with the variation of the viscosity (Water/MK ratio) which was found to be significant parameter for the optimization of the design of porous IPC structures. The pore size under 4 mm of diameter, their roundness and the maximum reduction of the thickness of the interpore partitions allow to have matrix with bulk conductivity < 0.15 $W.m^{-1}.K^{-1}$. With aluminum powder > 10/10000, the intensive pore coalescence favored the redensification which limits the extension of the expansion specially for rice ash based specimens.

5. Conclusions

The partial replacement of the metakaolin in the formulations of the porous inorganic polymer materials by rice and volcanic ashes allowed the integration of around 30 vol.% of natural wastes. While this sound as significant contribution for the reduction of the energy and use of kaolin, which means gain in environmental impact and sustainability, the prompt dissolution of the wastes into the matrices and formation of soluble and colloidal silica induce important modification on the microstructure, improvement of the strength together with enhancement of the expansion ability. In this regard, the action of the porogent agent was influenced by the nature of the fresh paste: rounded pores were effectively probable when the appropriate viscosity and concentration of aluminum powder is controlled. The expansion was limited with the elasticity of the pastes and allows us to identify the lower concentration of aluminum powder necessary to have major expansion with limited pores coalescences and the limit at which the percolation of the pastes is no longer ensured.

The products developed bring some contributions to solve the problems of the sustainability of forming process of the foams, strength, control of the pores size, extension of capillary pores as

well as the homogeneity of the microstructure [3,4,25-27]. The rounded pores obtained and the significant reduction of the interpore partitions with the increase of the aluminum content while maintaining control on the capillary pores percolation appeared fundamentals for the analytical description of the final microstructure in relation with the effective thermal conductivity. Our results demonstrated that clear correlation can be established between the viscosity of the pastes, in relation to their bulk chemical composition, the concentration of the porogent agent, the volume expansion/pore shape and pore size distribution. These informations are contributive for the understanding and design of these promising class of materials since most of the interpretations concerning the porous geopolymers with applications as insulating materials[4, 25-30] up to date focus to the total volume of pores without details concerning the influence of the detailed microstructure: formation of the total volume of pores, control of the pores size and the interpore partitions. The models identified by Kamseu et al. [3] and Bourret et al. [4] for the description of the porous IPC are analytical models which can be accurately interpreted if the elements as pore shape, pore size and homogeneity of microstructure discussed in this work are clearly mastered and well defined. The porosity and the pore size distribution of the interpore partitions are another parameters to be considered as indicated by Russel [30] in his work on the principles of heat flow in porous insulators. The use of amorphous silica from rice and volcanic ashes significantly improved the flow behavior during processing and reduce the probability of particle packing with the enhancement of the homogeneity of the microstructure. The dissolution of the amorphous silica into the pore solution conduct to the colloidal phases that modify the viscosity while improving the roundness of the pore formed from porogent agent. We noted the ability of volcanic ash to effectively tailor the pore size and the volume expansion at high concentration of aluminum powder (> 6/10000) compared to rice ash. This is due to the semi-crystalline structure of volcanic ash and their contain of some long chains of molecules which contribute to modify the viscosity and the behavior of the fresh paste under the effects of aluminum powder. Moreover, volcanic ashes are porous materials which is contributive for the design of the structures under study.

Such matrices appeared promising as sustainable and environmentally-friendly composites capable to act with efficiency in various applications where thermal isolation, filtration, dust collection and lightweight behavior is needed [28-29]. The nanometric size of the pores into the interpore partitions greatly enhances the phonon scattering and introduces larger strain fields in materials, effectively obstruct the cross-sectional area of the heat transfer.

Appendix-TPS Theory

A constant electric power supplied to the sensor results in an increase in temperature T(t) which is directly related to the variation in the sensor resistance R(t) by the equation (1):

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

where R_o is the nickel electrical resistance at the beginning of the recording (initial resistance), α is the temperature coefficient of resistance of the nickel foil, and ΔT(t) the temperature increase of the sensor with time.

Assuming an infinite sample 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 [20]. In the particular case of our sensor geometry, n concentric ring sources, the spatial average can be obtained through the equation (2) [21,22].

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Figures Captions

Figure 1: Variation of the expansion coefficient of the porous inorganic polymer as function of the aluminum powder concentration.

Figure 2: Variation of the Bi-axial flexural strength (MPa) of the porous inorganic polymer as function of the aluminum powder concentration.

Figure 3: Variation of the apparent density (g/cm^3) of the MKP6, MKP8, MKR6 and MKR8 specimens as function of the water/metakaolin ratio.

Figure 4: MIP Pore size distribution of dense volcanic ash and rice ash based inorganic polymer composites

Figure 5: MIP Pore size distribution of the volcanic ash based porous IPC with a): 6 and b): 8/10000 of aluminum powder.

Figure 6: MIP Pore size distribution of the rice ash based porous IPC with a): 6 and b): 8/10000 of aluminum powder.

Figure 7: MIP cumulative pore volume as function of water/metakaolin ratios: a) volcanic ash with 6/10000 of aluminum powder ; b) volcanic ash with 8/10000 of aluminum powder; c) rice ash with 6/10000 of aluminum powder and d) rice ash with 8/10000 of aluminum powder.

Figure 8: Stereo microscope images of porous volcanic ash based IPC with 6/10000 of aluminum powder showing the effects of the water content on the pore size.

Figure 9: Stereo microscope images of porous volcanic ash based IPC with 8/10000 aluminum powder showing the effects of the water content on the pore size.

Figure 10: Stereo microscope images of porous rice ash based IPC with 6/10000 aluminum powder showing the effects of the water content on the pore size.

Figure 11: Stereo microscope images of porous rice ash based IPC with 8/10000 of aluminum powder showing the effects of the water content on the pore size.

Figure 12: Micrographs of volcanic ash based IPC with 8/10000 of aluminum showing the structure of the interpore partitions: a) MKP8a; b) MKP8c.

Figure 13: Micrographs of rice ash based IPC with 8/10000 of aluminum showing the structure of the interpore partitions: a) MKR8a; b) MKR8c.

Figure 14: Bulk thermal conductivity of the porous IPC as function of the formulation and the concentration of the aluminum powder.