



Transformation of the geopolymer gels to crystalline bonds in cold-setting refractory concretes: Pore evolution, mechanical strength and microstructure

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ABSTRACT

Two K_2O – MgO – Al_2O_3 – SiO_2 based geopolymer gels with bulk chemical composition corresponding to cordierite (Co) and 1:1 mullite-cordierite (MuCo) were successfully transformed to crystalline bonds in high temperature service of cold-setting made refractory concretes. Kyanite aggregates changed the flexural strength of the gels from 11 to 28 MPa due to the development of good adhesive bonds. Under thermal cycles, up to 1250 °C, the cumulative pore volume remained at 0.09 mL/g, as from the absence of important densification/shrinkage. However, the behavior of the cumulative pore volume curves changed from that of a matrix with a wide range of distribution of pore sizes to that, of matrix, consisting of relatively coarse grains. The latter exhibits a rise at 10 μm as void spaces created around the contact points among the coarse kyanite grains and that at 0.054 μm as pores within the crystalline phases (cordierite, kalsilite, leucite, mullite, enstatite) formed. The microstructural observations confirmed the transformation of gel pores (size around 0.01 μm) to interparticle and intergranular pores due to the crystallization. The flexural strength of refractory concretes increased from 28 MPa to 40 MPa in agreement with the increase in the elastic modulus from 9 to 30 GPa. The crystallization was enhanced by the MgO content (being important in Co compared to MuCo) and the kyanite concentration as particles of kyanite effectively acted as phase separation and nucleation sites.

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1. Introduction

Projection of the use of K-geopolymer binder as refractory bonds essentially has objectives to propose alternatives to traditional silicate or aluminosilicate bonds, derived from the vitrification reactions, for more sustainability in the production of refractory materials [1–4]. The technology is based on the transformation of the geopolymer gels to ceramic bonds upon firing. However unlike the formation of kalsilite, mullite and leucite, formulations available into the literature have proved to develop a considerable amount of liquid phase detrimental for the thermo-mechanical stability of the final products [2]. The thermal behavior of the K_2O – MgO – Al_2O_3 – SiO_2 geopolymer gels designed recently as refractory bond [5] proved to have different sintering behavior with an improvement in thermal stability, significant reduction of the vitrification and shrinkage. While K_2O – Al_2O_3 – SiO_2 gels presented vitrification as from 1000 °C, the cordierite and mullite-cordierite shown optimum

dimensional stability up to 1250 °C [5]. The new geopolymer refractory bonds conduct to the formation of concretes with the microstructure that will alter in service: transformation of the geopolymer gel to crystalline bond ensuring to the refractory composites low cost, low energy consumption for the processing and more sustainability.

The cordierite and mullite-cordierite geopolymer based refractory concretes fall in classification within refractory castables that can be produced in situ. The microstructure that will be finalized upon firing imposed the control of the particle size distribution of the raw powders solid precursors of the geopolymer gels as well as that of the fine aggregates responsible for the skeleton of the refractory matrix. Fine particles of metakaolin and meta talc as well as metastable alumina from bauxite will control the rheology of the wet system, packing and establishing hydraulic bonds to insure the consolidation for the mechanical properties of the unfired system. In general, similar results are obtained with the K_2O – Al_2O_3 – SiO_2 system. However the originality of the new formulations of cordierite and mullite-cordierite refractory concretes is found in the difference in densification and sintering of the amorphous gel, their capacity to withstand high temperature and favor crystallization maintaining the control of their pore system up to 1250 °C. The good

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adhesion bonds established between the geopolymer gel and the aggregates, the particular sintering behavior of the composites can allow the achievement of a microstructure in which micro cracks are reduced to the minimum providing useful toughening while increasing the resistance to cracks propagation and the thermal shock resistance. Heindl and Pendergast [6] found excellent agreement between the flexural strength and the elastic modulus for fired plastic refractories. Mong and Pendergast [7] easily correlated the elastic modulus E determined in four-point flexural and resonance methods for fired plastic refractories. In the applications where strength is important, impact-erosion or crack initiation resistance need to be high. For this reason it is critical to achieve high density in the matrix phase of a refractory with bond phase having optimum adhesion with denser aggregates [1]. In cordierite and mullite-cordierite geopolymer based refractory concretes, the evolution of the flexural strength between the pastes (11 MPa) and the refractory products (21 to 28 MPa) demonstrated that good compatibility was achieved between the matrix and the kyanite aggregates [5], then the porous and coarsening microstructure of the latter were found to be contributive for the toughening and strength enhancement. According to Williams E and Robert Moore [1,8], aluminosilicate bricks formulated from coarse grains and unfired bonds are likely to survive thermal shock. The loose texture of these bricks and the presence of numerous cracks made it difficult for cracks to extend. The use of K_2O – MgO – Al_2O_3 – SiO_2 systems and not K_2O – Al_2O_3 – SiO_2 should significantly modify the leucite formation give priority to more MgO -based crystalline phases as from low temperature as 800 °C with the reduction of the thermal expansion mismatch due to the absence of extensive liquid phase. When a leucite reinforced ceramic matrix is cooled, leucite contracts along the α axis during both the phase transformation from the cubic to tetragonal form and the cooling. The evolution of the bi-axial four-point flexural strength of the cordierite and mullite-cordierite geopolymer concretes is investigated in relation with the kyanite aggregates content and the temperature development. The changes in elastic modulus are correlated to the phases transformation to understand the microstructure and the flexural strength of the composites under thermal cycles. The variation of the pore volume and pore size distribution are used to complete the mechanical, mineralogical and thermal behavior providing a comprehensive understanding of the refractoriness and behavior in service of the geopolymer refractory concretes.

2. Experimental procedures

The formulations of cordierite (Co) and mullite-cordierite (MuCo) were designed as improvement to K_2O – Al_2O_3 – SiO_2 geopolymer refractory systems described in the literature [2,3,9]. The refractoriness of kyanite aggregates [5], the sintering behavior of K_2O – MgO – Al_2O_3 – SiO_2 gels with high probability of crystallization, the polymorphous behavior of cordierite and its capacity to integrate alkaline ions like potassium and exists in a large range of temperature as from 800 °C render the formulations under study theoretically promising for the design of high temperature refractory castables through the geopolymerization route [10–14]. The phase evolution with the kyanite aggregates and temperature as well as the thermal behavior were detailed in the first article of this project [5]. The informations referring to the phase evolution and the sintering behavior will be used here just for support the physico-mechanical properties and microstructure results.

2.1. Geopolymer refractory concretes processing

Two powders with bulk chemical formulae of cordierite (Co) and 1:1 mullite-cordierite (MuCo) were prepared as solid precursors for the production of the refractory bonds. Bauxite [14], Kaolin [5] and Talc [15] from Cameroon were collected calcined, pulverized and mixed in appropriate proportions in order to develop cordierite ($Mg_2Al_4Si_5O_{18}$) and 1:1 mullite-cordierite ($3Al_2O_3 \cdot 2SiO_2$ – $Mg_2Al_4Si_5O_{18}$). The powders obtained were ball-milled under 80 μm and mixed with alkaline

solution in porcelain jar still with ball-mill to obtain an homogeneous paste. The alkaline solution was a mixture of potassium hydroxide (8 M) and potassium silicate (SiO_2/K_2O molar ratio of 3.01). The potassium hydroxide and potassium silicate were provided by Ingessil, Verona, Italy. The proportions of each constituents in both Co and MuCo formulations are presented in the Table 1. Kyanite aggregates were crushed and granulated at 2 mm > ϕ > 100 μm . The solid/liquid ratio of 1.7 was considered [5]. 20, 25 and 30 wt.% of each geopolymer bond obtained (Co and MuCo) were combined to 80, 75 and 70 wt.% of kyanite aggregates to have Co20, Co25 and Co30 for the cordierite series, MuCo20, MuCo25 and MuCo30 for the mullite-cordierite series. Highly viscous slurries were obtained and pressed using uni-axial hydraulic press at 5 MPa to form disks of 4.2×0.7 cm. For each formulation and temperature, a series of 5 specimens was considered to ascertain the reproducibility of mechanical testing. The pressed specimens were sealed immediately in plastic films for 72 h at ambient temperature (21 ± 2 °C; 54% humidity). The curing continue up to a stable weight. The refractory concretes were fired to different temperature: 800 °C, and from 1050 °C to 1350 °C with an interval of 100 °C, in an electric furnace at 5 °C/min with 1 h soaking time at maximum temperature. This thermal treatment has the objective to simulate the thermal behavior of the refractoriness. See Table 2

2.2. Bi-axial four-point flexural strength and elastic modulus

The mechanical properties of the cylindrical specimens were determined according to ASTM F-373 [16], the piston-on-three balls, using a testing machine (MTS 810, USA) with maximum loading of 10,000 kN for all the experiment. For the execution of the test a load is applied to the specimen centered by a right circular cylinder of hardened steel. The test specimen was supported on three ball bearings with a diameter of 2.67 mm and positioned at 120° to each other on a circle of 9.5 mm diameter. The specimens were loaded centrally at a rate of 3 mm/min, using a spherical indenter with a diameter of 1.66 mm. The result presented for each formulations and temperature is the average for 5 specimens considered.

The Young modulus was measured using the ultrasonic method described by Tessier-Doyen et al. [18]. The ultrasonic waves propagation in the “infinite medium” with contact transducers is used. Low frequency (1 MHz) was applied in order to limit the attenuation effects. The time delay τ between the two echoes was determined by intercorrelation [19]. T is the travel time of the wave in the sample. Young's modulus is calculated using both the transit duration of ultrasonic waves (τ_L for longitudinal waves, τ_T for the transversal waves) and the apparent density of the material:

$$V_T = \frac{e}{\tau_T} \quad (1)$$

$$V_T = \frac{e}{\tau_T} \quad (2)$$

$$E_{exp} = \rho \cdot \frac{3 \cdot V_L^2 - 4 \cdot V_T^2}{\left(\frac{V_L}{V_T}\right)^2 - 1} \quad (3)$$

Table 1

Formulation of mixture before the calcination at 700 °C (Note: The fractions of raw materials are on the basis of raw oxides including the water that would not appear in the calcined products. It is why the apparent total is above 100 wt.%).

Proportion (wt%)	Cordierite mixture (Co) ($Mg_2Al_4Si_5O_{18}$)	Mullite-cordierite (MuCo) $Al_{4.5}Si_{1.5}O_{9.75}$
Kaolin	53.36	77.51
Talc	42.21	21.61
Bauxite	21.07	34.73

Table 2

Phases, Cumulative pore volume, principal pore bands and pores description in MuCo and Co refractory concretes.

	Cumulative pore volume/mL·g ⁻¹		Peaks of principal pore bands/μm		Pores description	
	25 °C	1250 °C	25 °C	1250 °C	25 °C	1250 °C
Co20	0.093	0.098	0.01	0.054	Predominance of gel pores with small amount of larger capillary pores	Interparticle pores
Co25	0.086	0.094		and		
Co30	0.074	0.088		7		
MuCo20	0.087	0.100			Interparticles pores + closed pores	
MuCo25	0.085	0.099				
MuCo30	0.081	0.084				

In order to obtain significant values over the whole sample, several measurements are carried out on various zones. The scattering of the experimental values was 3.5% and the measured Young's modulus increases with the inclusion content.

2.3. Pore volume, pore size distribution and microstructure

One important aspect of the microstructure of ceramics and refractories is the porosity. The interconnected, open pore size distribution in a porous material is most easily assessed using the technique of Mercury Intrusion Porosimetry (MIP) in which a holder is partially filled with weighed, dried sample, evacuated and filled with Hg [17]. Optical microscopy remains not only the easiest but also the most important method for refractories characterization. The resolution allows an overall impression of the microstructure [8]. However, to fully characterize a complex microstructure as that of geopolymer refractory concretes, scanning electron microscope (SEM) is necessary to determine the grains morphology, crystals structure, the relation of kyanite aggregates with the geopolymer bonds (interfaces), porosity and morphology. The environmental SEM is particularly useful, in conjunction with a heating stage. The microstructure of the as prepared and fired specimens of cordierite and mullite-cordierite based geopolymer composites was studied by SEM (mod. XL40, Philips, The Netherlands). Freshly fractured surfaces and polished specimens were used for each sample. The polished specimens were etched in 5% HF-HNO₃ solution for 30 s for crystalline phases identification. All the specimens for SEM analysis were mounted on aluminum stubs and sputter-coated with 10 nm of Au/Pd to facilitate imaging. The microanalysis was performed using EDS (X_EDS INCA, Oxford Inst.).

The stereo optical microscope type SZX10 was used for the collection of the global impression of the MuCo and Co refractory concretes. SZX10 motorized focus drive makes the digital documentation with extended focal imaging (EFI) efficient. 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. In addition the SZX10 allows 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 Mercury Intrusion Porosimeter (MIP) used was an Autopore IV 9500, 33,000 psia (228 MPa) MIP covering the pore diameter range from approximately 360 to 0.005 μ m having two low-pressure ports and one high-pressure chamber [17]. Pieces collected from the mechanical test were used to prepare specimens of ~1 cm³ of volume for the MIP.

3. Results

3.1. Correlation of the sintering behavior and phases evolution with physico-mechanical properties

Figs. 1 and 2 show the variation of the bi-axial flexural strength of cordierite and mullite-cordierite based geopolymer refractory concretes

as function of the kyanite content and temperature. It is observed that the refractory binders used for the design of the concretes have bending strength value of ~11 MPa which is the value generally observed for the metakaolin based inorganic polymer cement [2,5,16]. The effective development of 3D network of geopolymer gels were verified using NMR investigations. The introduction of the Kyanite aggregates resulted for MuCo series in an important increase in bending strength from 11 to 20 MPa with 75 and 80 wt.% of aggregates. The bending strength even reached 23 MPa for 70 wt.% of kyanite aggregates. For the similar content of aggregates, Co series showed up to 28 MPa of bending strength [5]. This improvement of the mechanical properties of the refractory concretes correspond to a variation of the bulk density of the pastes from 1.5 g/cm³ to 2.7 g/cm³. Both increase in densification and mechanical properties were ascribed to an important reduction of the open porosity from 33 to 14 vol.% for Co series and 35 to 13 vol.% for MuCo series. The good interfacial bonds established between the geopolymer pastes and coarse kyanite explains the increase in mechanical strength. The interfacial bonds benefit from the porous structure of kyanite aggregates and contribute to improve the adhesion behavior between the components [5].

Under thermal treatment, MuCo paste shown a relative high rate of the increase of the bending strength that moved from 10 to 40 MPa between the room temperature and 1250 °C. Further increase in temperature above 1250 °C reduced the mechanical strength and promoted micro cracks: enhancement of the porosity (due to the expansion of the volume as characteristics of the K₂O–MgO–Al₂O₃–SiO₂ systems [20,21]), with appearance of liquid films. Differently, the increase of the flexural strength of Co paste with the temperature was continue up to 1350 °C. It was observed a decrease in strength between 1150 °C and 1250 °C with another scale of improvement between 1250 °C and 1350 °C that contrast with the MuCo series. The difference in mechanical behavior of Co and MuCo series between 1250 °C and 1350 °C was

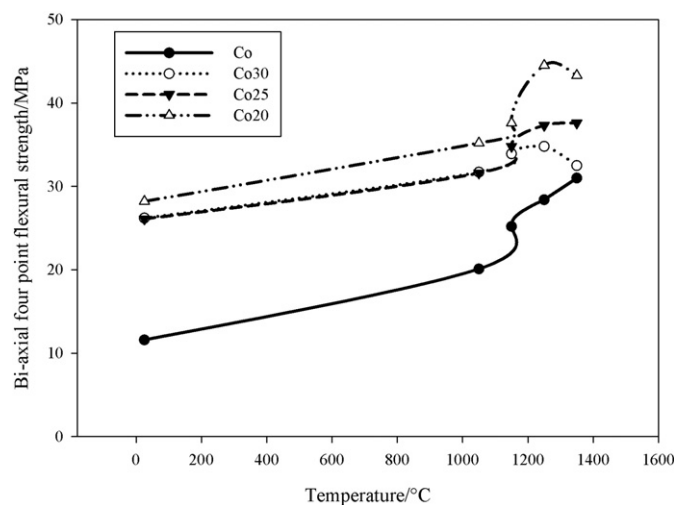


Fig. 1. Variation of the bi-axial four point flexural strength of geopolymer concretes MuCo as function of the kyanite content and the temperature.

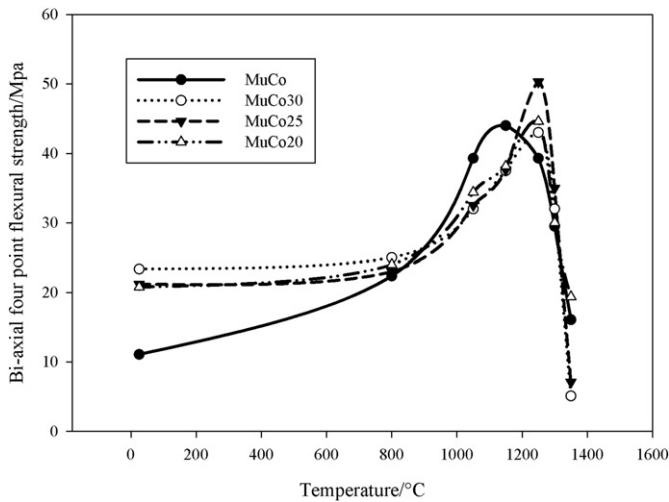


Fig. 2. Variation of the bi-axial four point flexural strength of geopolymer concretes Co as function of the kyanite content and the temperature.

ascribed to the relative amorphous phase (liquid) slightly important in MuCo compared to Co and sufficient to decrease the mechanical strength. The Co series resulted with very low expansion with respect to MuCo. In the MuCo series there was not a real difference in mechanical behavior at high temperatures linked to the variation of the kyanite aggregates content between 70 and 80 wt.% (MuCo20, MuCo25 and MuCo30). As it can be observed into the Fig. 2, all the three formulations showed ~30 MPa at 1150 °C, ~40 MPa at 1250 °C and ~20 MPa at 1350 °C. In Co series, similar values of 30 MPa is observed at 1150 °C. The increase of the flexural strength between 1150 °C and 1250 °C was not as important as in the MuCo series: Co20 with 80 wt.% of kyanite aggregates showed value of flexural strength above 40 MPa; the sample Co25 presented a value slightly above 30 MPa and Co30 with value under 30 MPa. At 1350 °C, Co20 and Co25 still have their flexural strength above 30 MPa while that of Co30 is relative down to 30 MPa. This difference in mechanical behavior between MuCo and Co series follows that of physical properties as shrinkage of MuCo and Co pastes: 7.0% for Co and 8.0% for MuCo [5]. The change in dimensions is one of the most important parameters that is used to evaluate the sintering behavior of the refractory castables. This change in dimensions was not visible in MuCo and Co refractory concretes up to ~500 °C, temperature at which all the samples showed expansion (<0.5%). At temperature above 1000 °C samples return to develop shrinkage and evidently the value of expansion decrease near to 0 as described into the previous work [5].

The value of the elastic modulus (E) of MuCo series increased from 9.9 to 13.13.7 GPa between 20 and 25 wt.% of geopolymer cement and decreased to 11 GPa when the content of geopolymer cement reached 30 wt.%. The value of the elastic modulus of Co series increased from 14.9 to 17.1 GPa when the geopolymer cement increased from 20 and 25 wt.% of geopolymer cement (Co20 and Co25) before decrease to 13.7 with 30 wt.% of geopolymer cement Co (Figs. 3 and 4). For the samples treated thermally, the increase in the geopolymer cement continuously increase the elastic modulus (Fig. 3). The variation of the value of E for the as prepared geopolymer concretes seem to be comparable for Co and MuCo series (Figs. 3 and 4). Conversely, the thermal treatment at 1250 °C evidenced a net difference in mechanical behavior between the two series (Figs. 1 to 4). The values of E are 30.3, 34.7 and 29.8 GPa for MuCo (20, 25 and 30 wt.% of geopolymer cement respectively) treated at 1250 °C; values two times higher with respect to Co series (13.3, 14.2 and 16.4 GPa respectively) as it can be observed in the Figs. 3 and 4.

The variations bi-axial flexural strength values with the geopolymer cement and temperature as that of the elastic modulus can be interpreted considering the intrinsic structure of each formulations.

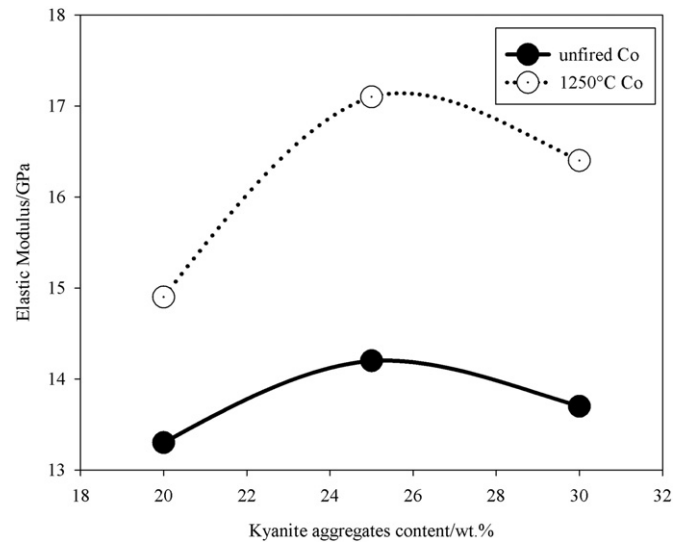


Fig. 3. Variation of the elastic Modulus (E) of geopolymer concretes Co with kyanite content and temperature.

These, in relation with the phases development and the adhesion contact between the geopolymer cement and kyanite aggregates. The correlation between the four-point flexural strength and the elastic modulus was already established by Mong and Pendergast [7] for the refractory castables. The structure and phase evolution into the two refractory systems can be described as follow: (i) transformation of amorphous gels to crystalline phases at the range of the temperature between 1000 and 1250 °C preceded by a continuous dehydration and densification; (ii) brittle-to-ductile transition as from 1150 °C from the formation of liquid films. This softening is accompanied by a significant volume expansion in the case of K_2O – MgO – Al_2O_3 – SiO_2 under study [18–21]. Above 1250 °C the liquid content became detrimental for the mechanical strength for MuCo series while it relative low amount in Co explains the low expansion and the continue increase of the mechanical strength.

As detailed into the first part of this study, the geopolymer cement Co developed cordierite as principal crystalline phase together with kalsilite, enstatite, leucite and mullite. Residual quartz and talc were still present. All enveloped in a high fraction of amorphous phase. Upon thermal treatment, the same crystalline phases remained but with important increase of the peaks cordierite, kalsilite and mullite.

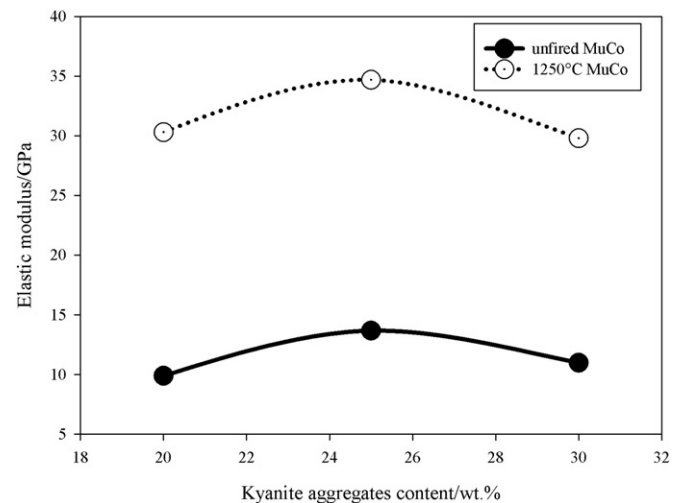


Fig. 4. Variation of the elastic Modulus (E) of geopolymer concretes Co with kyanite content and temperature.

MuCo shown similar crystalline phases of cordierite, kalsilite, mullite and enstatite with quartz and talc as residual unreacted minerals that remained after geopolymerization. The principal difference between the MuCo and Co geopolymer cement treated between 1050 °C and 1250 °C is the amorphous content more important in MuCo [5]. Both formulations belong to the quaternary system $K_2O-MgO-Al_2O_3-SiO_2$. System that can be identified as modified $K_2O-Al_2O_3-SiO_2$ with kalsilite, leucite and amorphous mullite in the process as geopolymer refractory materials [2,9]. The high rate of densification/shrinkage of the latter system enhances the formation of liquid phase and reduced the crystallization activities yet at low temperature. The presence of the MgO (for the newly system under study) reduced the shrinkage, densification and by the way the liquid phase formation. The reduction of the liquid and amorphous phase was important as the content of MgO was high considering the MuCo and Co formulations. In fact the introduction of MgO changed the sintering behavior of both formulations. In the absence of liquid phase or their significant reduction, the pore evolution is favorable to the crystallization. Numerous techniques have been described into the literature for the synthesis of porous cordierite [23]. Most of the techniques are based on the gel casting that can be compared to the geopolymerization. The phase separation that accompanied the process allows the reduction of the densification rate and improve the crystallization phenomenon [23]. The polymorphous forms of cordierite is favorable for the objectives of this work as cordierite exist in a large interval of temperature. In fact peaks ascribed to saphirine ($Mg_8Al_9Si_6O_{20}$) is described in the cordieritic gels as from 800 °C [23]. Sapphirine will transformed to β -cordierite ($Mg_2Al_4Si_5O_{18}$) at 1250 °C. At low temperature metastable μ -cordierite is possible to be formed as well as β -cordierite. At high temperature, hexagonal form is developed [23,24]. The kyanite aggregates act to improve the phase separation playing the role of nucleation sites and enhance crystallization.

3.2. Porosity and pore size distribution and microstructure

The cumulative pore volume, the pore size distribution and detailed informations relative to the pores present in the geopolymer refractory concretes are summarized into the Table 1, Figs. 5, 6, 7 and 8. The Co series showed values of 0.093, 0.086 and 0.074 mL/g for the cumulative pore volume respectively for 70, 75 and 80 wt.% (30, 25 and 20 wt.% of geopolymer cement) as it can be observed in the Fig. 5a. For the similar geopolymer content, MuCo showed values of 0.087, 0.085 and 0.081 mL/g for the cumulative pore volume (Fig. 6a). The decrease of the cumulative pore volume with the increase of the amount of the kyanite aggregates is linked to the difference of porosity between the geopolymer gels (with higher volume of pores) and the kyanite aggregates more dense and less porous. So for the range of formulations under study, the higher the aggregates content, lower is the cumulative pore volume. The curves of the cumulative pore volumes of Co (Fig. 5a) and MuCo (Fig. 6a) vs the pore diameters are characteristics of a single piece of material in which there is a wide range of pore sizes. The good adhesion developed between kyanite aggregates and the geopolymer cement conducted to a relative homogenous matrix considered by the MIP as a single piece of material. The thermal treatment of the geopolymer concretes up to 1250 °C did not affect in significant manner the cumulative volumes: the cumulative pore volume for Co series remained at 0.098, 0.094 and 0.088 mL/g respectively for 70, 75 and 80 wt.% kyanite content (Fig. 5b); that of MuCo presented 0.100, 0.099 and 0.084 mL/g respectively (Fig. 6b). However, the curves of the cumulative pore volumes of Co and MuCo series treated at 1250 °C shown a change in their structure. Actually, curves are characteristics of samples with relatively coarse grains. They exhibited two distinct parts with a first rise at high diameter of pores (10 μ m) due to the void spaces created around the contact points among the coarse grains of kyanite aggregates and the second rise (0.1 μ m) due to pores within the crystalline phases formed at the interfaces of aggregates during the sintering of the refractory concretes.

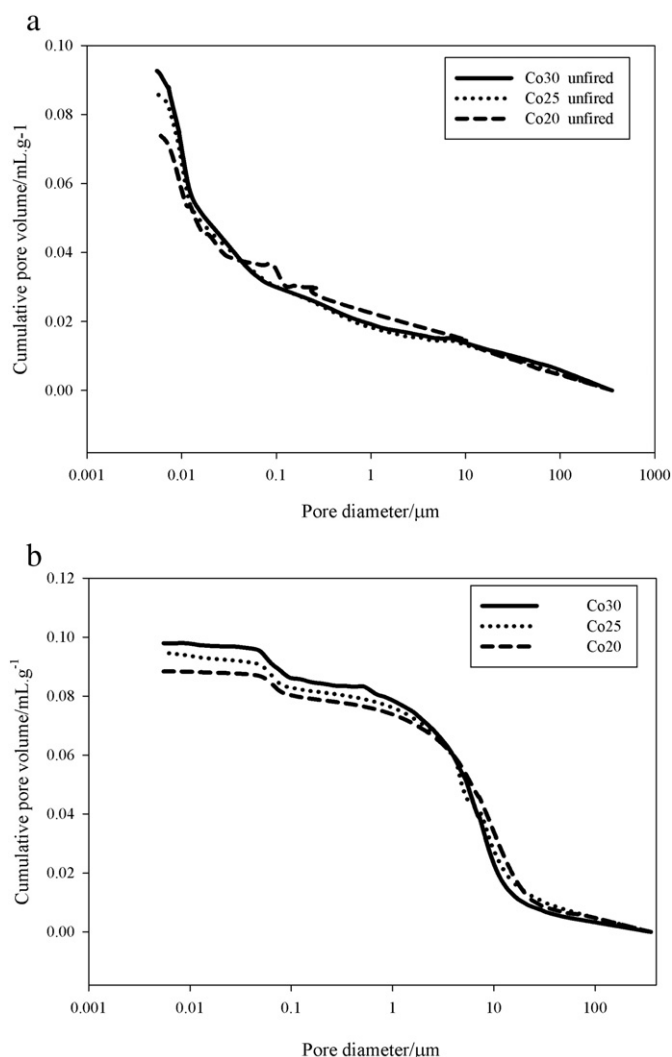


Fig. 5. Variation of the cumulative pore volume of the geopolymer refractory concretes with the kyanite aggregates content: (a) as prepared Co series; (b) Co series treated at 1250 °C.

Figs. 7a (Co series) and 8a (MuCo series) confirm the characteristics of the curve of the cumulative pore volumes of as prepared geopolymer concretes. It is observed peaks of pores at 0.01, 0.013, 0.02, 0.036, 0.052, 0.36, 9.76 and 84.13 μ m confirming the wide distribution of pore sizes for Co and MuCo series. The intensity of peaks at 0.036, 0.052, 0.36, 9.76 and 84.13 μ m are not as important in MuCo as in Co. This can be ascribed to the relative difference in the viscosity of the two gels linked to their bulk chemical compositions: particularly the action of MgO. When the specimens of geopolymer concretes are treated thermally to 1250 °C, the changes in pore structure are illustrated with the Figs. 7b and 8b. For both Co and MuCo composites, two pore bands are observed: one with peak at \sim 0.054 μ m and the second more larger with high intensity centered at \sim 10 μ m. The pores around 10 μ m characterize porosity between coarse kyanites aggregates that dominate the matrix (70 to 80 wt.%) and the band at 0.054 μ m describe the interparticle pores from the crystalline structure existing in the interparticle regions of matrices as already evidenced above. The concentration of the pores in both bands justify the behavior of the cumulative pore volume organized in two rises (Figs. 5–8). The results discussed here have been verified for 10 firing cycles. Cycles during which the mechanical properties remained constant as illustrated into Figs. 1 to 4. This can be described as a significant improvement for the thermal behavior of $K_2O-Al_2O_3-SiO_2$ geopolymer systems described in the literature [2,9]. The improvement includes the stability of the pore volume upon firing, significant

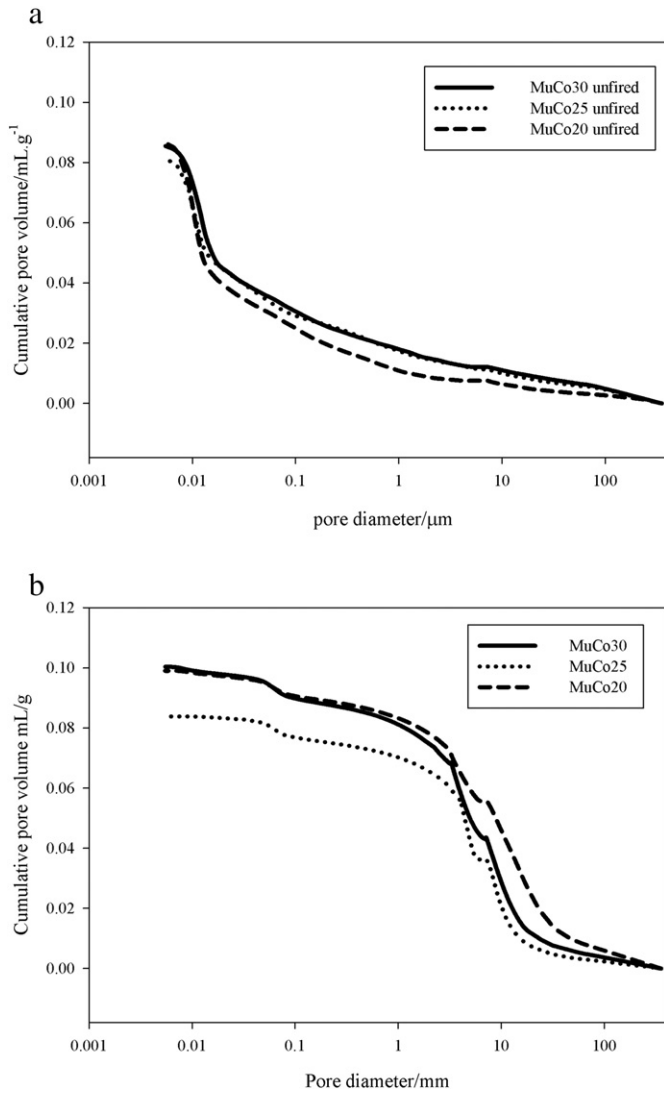


Fig. 6. Variation of the cumulative pore volume of the geopolymer refractory concretes with the kyanite aggregates content: (a) as prepared MuCo series; (b) MuCo series treated at 1250°C.

reduction of the fraction of liquid phase and disappearance of micro cracks and deformation. Apart from the MgO that acts to favor the crystallization and delay densification, Kyanite aggregates play in the system the role of phase separation and nucleation sites. The kyanite aggregates are closely bounded to the paste providing a pathway for more rapid and complete dehydration without damage (shrinkage, micro cracks, creeps, ...) of the microstructure (Fig. 9). This resulted in a particular network of pores that can withstand thermal transformation at high temperature. The pore network as described in the Figs. 5 to 8 are contributive for the thermal shock resistance and thermal stability of the geopolymer refractory concretes. The changes of the position of the pores bands from 0.01 to 0.054 and 10 μm are correlated to the transformation, during sintering, of the geopolymer gels that are generally characterized by an important band of pores with peak centered at 0.01 μm [25–28]. As already indicated above, before sintering, the geopolymer refractory concretes present homogeneous macrostructure with kyanite aggregates bound together through the good contact adhesion with the geopolymer cement (Fig. 9). During the thermal treatment, the amorphous geopolymer gel is transformed to crystalline grains and the band of pores at 0.01 μm disappeared with the formation of new classes of pores with band centered at 0.054 μm characterizing the pores between the crystalline phases and that centered at

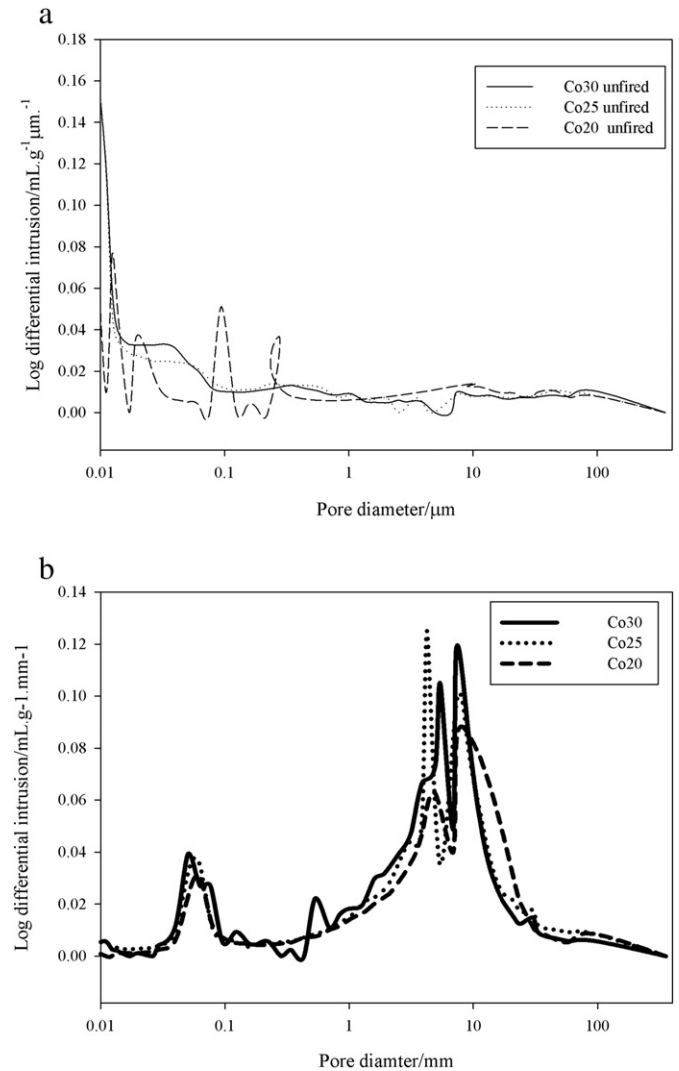


Fig. 7. Pore-size distribution in the matrices of geopolymer refractory concretes as function of the kyanite aggregates content: (a) as prepared Co series; (b) Co series treated at 1250°C.

10 μm characterizing the porosity around the coarse aggregates of kyanite which are not covered by the gel but by crystalline phases.

The geopolymer refractory concretes can be described as refractories designed with properties to alter in service through sintering reactions that enable complete transformation of the amorphous geopolymer gel to well crystallized phases capable to withstand further thermal cycles. Thermal reactions improving the properties and refractoriness of the castables (geopolymer refractory concretes) are the targeted evolution of those matrices through thermal cycles in service. For these reasons the microstructure detailed here is that of the heat treated specimens where the mechanical properties and the pore structure were verified up to 10 cycles of the firing-cooling at 1250 °C. For these, the typical microstructure of the cordierite and mullite-cordierite geopolymer refractory concretes consists of grain and bond phases [1,8]. The bond phases are made from the transformation of amorphous gel to crystalline aggregations with binding properties and the grains are kyanite aggregates. In the Fig. 10, bond phases and kyanite grains are not altered during the firing process up to 1250 °C. Impurities such as TiO₂ and Fe₂O₃ are visible and present an even contrast in micrographs (Fig. 10). These impurities together with local inhomogeneity (local concentration of K⁺) can facilitate the liquid sintering and enhance bonds between kyanite grains and crystalline phases formed. The transformation of the amorphous gel to crystalline phases and the

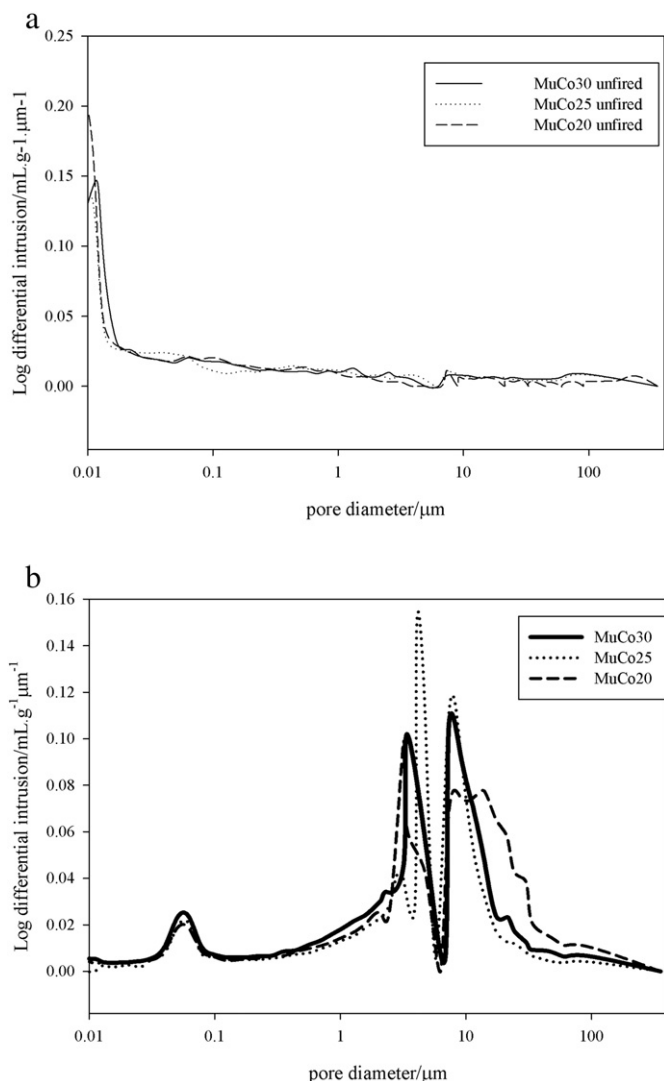


Fig. 8. Pore-size distribution in the matrices of geopolymer refractory concretes as function of the kyanite aggregates content: (a) as prepared MuCo series; (b) MuCo series treated at 1250°C.

possible development of liquid film act together to make the adhesion bond in the matrix more important and resistant after firing. For Co series, crystallization predominated with relatively low probability of

liquid phase formation. Consequently the flexural strength and elastic modulus remained with lower values with respect to MuCo series (Figs. 1–4). Co series remained with more coarsening microstructure that justify a relative grow in porosity with respect to MuCo (Figs. 5–8).

The binding properties of the as-prepared gels and their successful transformation upon thermal cycles to crystalline (refractory) bonds permit to evaluate as promising the cold-setting process that provide useful refractory phases at high temperature improving strength to the final products. Fig. 11 shows the crystallization feature in the Co20 and MuCo20. The interparticle spaces between kyanite grains are completely filled with crystalline phases: complex aggregations of cordierite, kalsilite, enstatite, mullite and leucite. The level of crystallization in MuCo is affected by the predisposition of the matrix bonds to develop liquid phase. Cordierite one of the principal crystalline phases exists with various morphologies in relation with the temperature [1,8,23]. Establishing that refractory processing from large particle size distribution leads to a complicated microstructure, we can understand the large, discrete aggregates (fillers) refractory grains held together by a continuous bonding matrix with extensive porosity, so-called grain and bond microstructure. The common features of such microstructure are micro cracks from the thermal expansion mismatch of different phases, and from sintering of the fine particles fraction causing shrinkage and opening up cracks between the larger particles which do not sinter as rapidly [1,8]. One of the advantage of the cordierite and mullite-cordierite geopolymer refractory concretes is the sintering behavior which does not favor the shrinkage and the highly limitation of liquid phase which maintains the matrix with a relative porosity, contributive for the resistance of the materials for thermal shock, micro cracks and deformations. The compatibility between the kyanite aggregates and the matrix bond was effective [5]. The difference between the two matrices is the ability more pronounced for Co series to develop crystalline phases, with consequent grow of porosity. As it can be observed in the Fig. 12. The significance of the liquid film in the MuCo reduced the probability of crystallization. The increase in strength and elastic modulus seem to be linked to the growth of tabular grains with liquid film that results in an increase in the fraction of closed porosity. Fraction important for the improvement of the toughness and strength.

4. Discussion and conclusion

The need to protect the environment and, therefore people, from unhealthy waste and emissions has motivated the orientation to technologies, raw materials for ceramics and processes of ceramics and refractories more sustainable. The production of the refractory castables through geopolymerization of cordierite and mullite-cordierite systems can be classified as in situ refractories [1]. In fact the achievement of

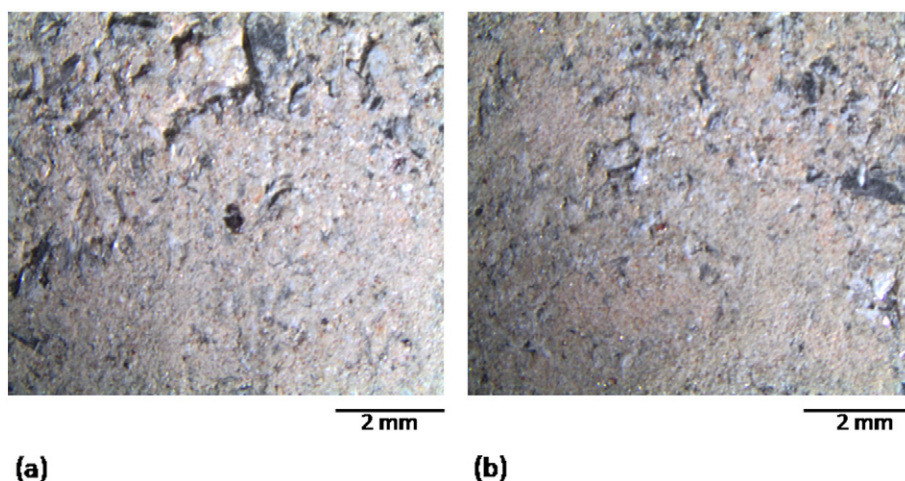


Fig. 9. Optical micrographs of the geopolymer concretes: (a) Co20; (b) MuCo20.

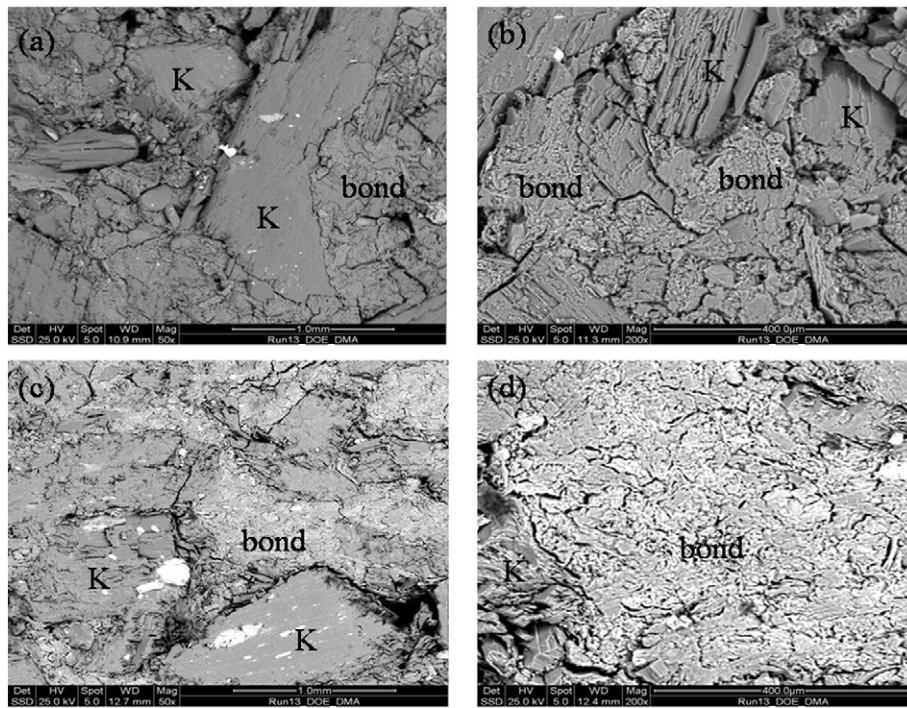


Fig. 10. Low magnification micrographs showing the constitution of the geopolymer based refractory concretes after 10 cycles of firing at 1250°C: (a) and (b) Co20 and (c) and (d) MuCo20: K = kyanite aggregates, bond = cordierite and mullite-cordierite crystalline matrices.

final properties of refractories including porosity, microstructure and mechanical strength is performed during the first firing cycle although the shrinkage, the initial strength and the stability of the system throughout thermal cycle allow the consideration of the non-fired geopolymer refractory concretes as a proper and effective refractory [5]. The grains and bond microstructure of the cordierite and mullite-cordierite geopolymer refractory concretes included kyanite aggregates which are natural and low cost grains that do not require any pre-

treatment, so sustainable and environmentally-friendly compared to grogs (from clays and Magnesia), chamotte, calcined bauxite, fused alumina, etc. The MuCo and Co bonds are designed using cold-setting process. The setting established a good adhesion between aggregates with geopolymer gels that is transformed at high temperature to high strength bond due to the crystallization of the amorphous geopolymer gel to complex, crystalline structure including cordierite, kalsilite, mullite, enstatite and residual quartz.

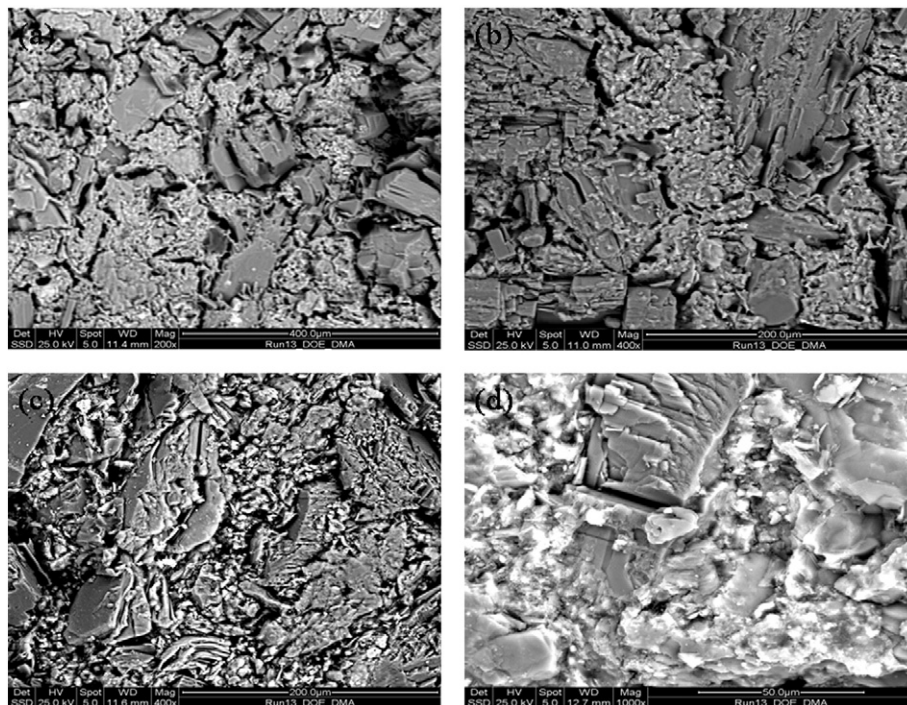


Fig. 11. Micrographs of Cordierite and Mullite-cordierite based geopolymer concretes evidencing the difference in crystallization behavior between Co series, (a) and (b); and MuCo series, (c) and (d).

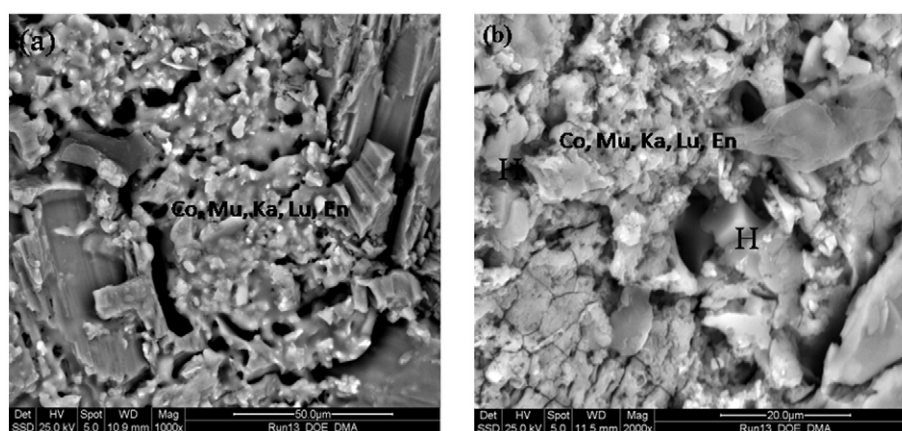


Fig. 12. Effects of the liquid films on the ceramic bonds and formation of closed porosity at $T > 1250^{\circ}\text{C}$: (a) Co_2O and (b) MuCo_2O ; Co = cordierite, Mu = mullite, Ka = Kalsilite, Enstatite, Lu = Leucite, H = hexagonal cordierite.

In the MuCo series, crystallization is accompanied or is in competition with the formation of liquid film that promoted closed porosity and additional bonds at the origin of the improvement of the elastic modulus and the flexural strength. A good correlation was established between the variation of the elastic modulus E and the four-point flexural strength. Changes in the E modulus of Co and MuCo could be explained by the constitutional transformation such as dehydration, conversion of the amorphous geopolymer gel to crystalline phases, important in MuCo with respect to Co. Results in agreement with those obtained by Mong and Pendergast [7] and Heindl and Pendergast [6]. Both Co and MuCo were then successfully identified as significant basic formulations for the design of refractory bricks and in situ monolithic castables applicable in various field where refractoriness and thermal shock resistance are critical.

Kyanite resists relatively more than quartz and others feldspar aggregates at high temperature. Their good adhesion contact with the MuCo and Co geopolymer bonds let them play the role of phase separation conducting to an improvement of the resistance to densification and vitrification. Moreover the kyanite particles act as nucleation sites for the cordierite, kalsilite, mullite, leucite, enstatite. The MuCo and Co geopolymer binders with the K_2O – MgO – Al_2O_3 – SiO_2 quaternary system can be described as the improvement of K_2O – Al_2O_3 – SiO_2 with an enhancement of the crystallization behavior, the reduction of densification/shrinkage, a particular sintering behavior with a hierarchical porosity compatible with the thermal behavior refractory materials.

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References

- [1] W.E. Lee, R.E. Moore, Evolution of in situ refractories in the 20th century, *J. Am. Ceram. Soc.* 81 (6) (1998) 1385–1410.
- [2] E. Kamseu, A. Rizzuti, C. Leonelli, D. Perera, Enhanced thermal stability in K_2O –metakaolin-based geopolymer concretes by Al_2O_3 and SiO_2 fillers addition, *J. Mater. Sci.* 45 (2010) 1715–1724.
- [3] J.L. Bell, P.E. Driemeyer, W.M. Kriven, Formation of ceramics from metakaolin-based geopolymers part 2: K-based geopolymer, *J. Am. Ceram. Soc.* 92 (3) (2009) 607–615.
- [4] V.F.F. Barbosa, K.J.D. Mackenzie, Synthesis and thermal behavior of potassium sialate geopolymers, *Mater. Lett.* 57 (9–10) (2003) 1477–1482.
- [5] C.N. Djangang, C. Tealdi, A.S. Cattaneo, P. Mustarelli, E. Kamseu, C. Leonelli, Geopolymer paste as binder for the design of cold-setting cordierite and mullite-cordierite refractory composites, *J. Chem. Phys. Mater.* 154 (2015) 66–77 (accepted for publication in).
- [6] R.A. Heindl, W.L. Pendergast, Results of laboratory tests of high-duty and super-duty fire-clay plastic refractories, *Am. Ceram. Soc. Bull.* 36 (1) (1957) 6–13.
- [7] L.E. Mong, W.L. Pendergast, Dynamic and static tests for mechanical properties of fired plastic refractories and other more-resilient materials, *J. Am. Ceram. Soc.* 39 (9) (1956) 301–308.
- [8] W.E. Lee, S. Zang, Refractories: controlled microstructure composites for extreme environments, *J. Mater. Sci.* 39 (2004) 6675–6685.
- [9] P. Duxson, G.C. Lukey, V.D. SJJ, J. Non-Cryst. Solids 353 (22–23) (2007) 2186.
- [10] M. Fukushima, M. Nakata, Y. Yoshizawa, Fabrication and properties of ultra highly porous cordierite with oriented micrometer-sized cylindrical pores by gelation and freezing method, *J. Ceram. Soc. Jpn.* 116 (12) (2008) 1322–1331.
- [11] H.M. Alves, G. Tari, A.T. Fonseca, J.M.F. Ferreira, Processing of porous cordierite bodies by starch consolidation, *Mater. Res. Bull.* 33 (10) (1998) 1439–1448.
- [12] J.K. Park, J.S. Lee, S.I. Lee, Preparation of porous cordierite using gel casting method and its feasibility as a filter, *J. Porous. Mater.* 9 (2002) 203–210.
- [13] S. Izuhaara, K. Kawasumi, M. Yasuda, H. Suzuki, Highly porous cordierite ceramics fabricated by in situ solidification, *Ceram. Trans.* 112 (2000) 553–558.
- [14] C. Nkombou, F. Villieras, D. Njopwouo, C. Yonta Ngoune, O. Barres, M. Pelletier, A. Razafitianamaharavo, J. Yvon, Physicochemical properties of talc ore from three deposits of Lamal Pougue area (Yaounde Pan-African Belt, Cameroon), in relation to industrial uses, *Appl. Clay Sci.* 41 (2008) 113–132.
- [15] A.B. Tchamba, U.C. Melo, E. Kamseu, R. Yongue, D. Njopwouo, Thermal and sintering behavior of bauxite from Haleo-Danielle Mimim-Matap (Cameroon), *Ind. Ceram.* 3 (2010) 1–9.
- [16] C. Leonelli, E. Kamseu, V.M. Sglavo, Waltraud M. Kriven, Bi-axial four points flexural and compressive strength of geopolymer materials based Na_2O – K_2O – Al_2O_3 – SiO_2 systems In: Developments in Strategic Materials Edited by, in: Hua-Tay Lin, Kunihito Koumoto, Edwin Garcia, Ivar E. Reimanis, David P. Norton (Eds.), Ceramic Engineering and Science Proceedings, Journal of the American Ceramic Society Wiley InterScience, The American Ceramic Society, 2009.
- [17] P. Webb, C. Orr, Analytical Methods in Fine Particle Technology, Micrometrics Instrument, Norcross, GA USA, 2011 (301 pp.).
- [18] N. Tessier-Doyen, J.C. Glandou, M. Huger, Untypical Young's modulus evolution of model refractories at high temperature, *J. Eur. Ceram. Soc.* 26 (2006) 289–295.
- [19] I.D. Kashcheev, S.N. Sychev, A.Y. Elizarov, Effect of oxides RO , R_2O_3 , RO_2 and impurity materials on decomposition during heating of kyanite in oxidizing and reducing atmospheres, *Refract. Ind. Ceram.* 52 (1) (2011) 44–47.
- [20] S. Izuhaara, K. Kawasumi, M. Yasuda, H. Suzuki, Highly porous cordieriteceramics fabricated by in situ solidification, *Ceram. Trans.* 112 (2000) 553–814.
- [21] M. Valášková, J. Zdrávková, G. Simha Martynková, B. Smetana, J. Vlček, S. Študentová, Structural variability of high purity cordierite/steatite ceramics sintered from mixtures with various vermiculites, *Ceram. Int.* 40 (6) (2014) 8489–8498.
- [22] X. Guo, K. Nakanishi, K. Kanamori, Z. Yang, H. Yang, Preparation of macroporous cordierite monoliths via the sol–gel process accompanied by phase separation, *J. Eur. Ceram. Soc.* 34 (2014) 817–823.
- [23] S.J. Schneider, L.E. Mong, Elasticity, strength, and other related properties of some refractory castables, *J. Am. Ceram. Soc.* 41 (1) (1958) 27–32.
- [24] F.G.M. Aredes, T.M.B. Campos, J.P.B. Machado, K.K. Sakane, G.P. Thim, D.D. Brunelli, Effect of cure temperature on the formation of metakaolinite-based geopolymer, *Ceram. Int.* 41 (2015) 7302–7311.
- [25] P. Duan, C. Yan, W. Zhou, W. Luo, C. Shen, An investigation of the microstructure and durability of a fluidized bed fly ash–metakaolin geopolymer after heat and acid exposure, *Mater. Des.* 74 (2015) 125–137.
- [26] P. Posi, C. Teerachanwit, C. Tanutong, S. Limkamoltip, S. Lertnimoolchai, V. Sata, P. Chindaprasit, Lightweight geopolymer concrete containing aggregate from recycle lightweight block, *Mater. Des.* 52 (2013) 580–586.
- [27] P.K. Sarker, S. Kelly, Z. Yao, Effect of fire exposure on cracking, spalling and residual strength of fly ash geopolymer concrete, *Mater. Des.* 63 (2014) 584–592.