09/04/2024 23:43

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Cold-setting Refractory Composites from Cordierite and Mullite-Cordierite Design with Geopolymer Paste as Binder: Thermal Behaviour and Phase Evolution

Chantale N. Djangang[a*], Cristina Tealdi[b], Alice S. Cattaneo[b], Piercarlo Mustarelli[b], Elie Kamseu[c,d], Cristina Leonelli[c]

[a]Department of Inorganic Chemistry, University of Yaounde I, P.O. Box 812, Yaounde, Cameroon, cndjangang@uy1.uninet.cm

[b]Department of Chemistry and INSTM, University of Pavia, Via Taramelli 12, I-27100 Pavia, Italy, cristina.tealdi@unipv.it, piemus04@unipv.it, alice.cattaneo@unipv.it

[c]Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, I-41125 Modena, Italy, elie.kamseu@unimore.it, cristina.leonelli@unimore.it

[d]LAM, Local Materials Promotion Authority/MIPROMALO, P.O. Box 2396, Nkolbikok, Yaounde, Cameroon, kamseuelie2001@yahoo.fr

Abstract: Cordierite and mullite-cordierite based geopolymer binders were prepared as refractory bonds to embed coarse kyanite aggregates. Alkali activation was used to consolidate the refractory at room temperature and generate a reactive interface between the matrix and the aggregates. The flexural strength at room temperature of consolidated materials was 11 MPa without kyanite addition, whilst it reached 28 MPa when kyanite was added. The latter showed thermal expansion near to zero up to 500°C, followed by an expansion of ~0.5 % up to 1000°C, then a decrease between 1000 and 1050°C, concluding with a constant value of expansion < 0.5 % up to 1250°C. The increase in expansion was found to be linked to the transformation of the geopolymer into ceramic bond with the formation of crystalline phases, while the decrease was apparently related to the liquid phase sintering. The stability of mullite, cordierite and leucite formed up to 1250°C was responsible for the constant expansion observed up to this temperature. The mechanical properties, the phase evolution and the thermal behavior of the K_2O-MgO-Al_2O_3-SiO_2 bonds, together with the refractory behavior of kyanite aggregates, were found suitable for the design of sustainable cold-setting refractory composites.

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[*] Corresponding author: Chantale Njiomou Djangang, P.O. Box 812 Yaounde, *Tel (237) 99807896 /Fax: (237)22234496, Email: djangangc@yahoo.fr.*

1. Introduction

Cordierite, $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$, based refractory materials are extensively used as kiln furniture because of their low thermal expansion and outstanding thermal shock resistance. The low intrinsic strength of cordierite can be compensated by the presence of mullite, $3Al_2O_3 \cdot 2SiO_2$. Bodies with a high content of cordierite, accompanied in some cases with spinel and mullite, are commonly produced from mixtures of talc, plastic clay and alumina [1]. Porous cordierite represents a new class of materials for refractories, particulate filters, catalyst supports and heat insulations under severe conditions, such as high temperature and high thermal shock [2-6]. Monolithic macroporous cordierite materials were successfully prepared by combining an epoxy-mediated sol–gel reaction with an ordinary hydrolysis-polycondensation of alkoxysilanes. The presence of propylene oxide accelerates the sol–gel translation of the MgO–Al_2O_3–SiO_2 ternary system, while poly(acrylamide) mediates the phase separation of the system and improves the formation of the gel network. Heat-treatment promotes the development of crystalline phases along the path amorphous → sapphirine → β-cordierite → α-cordierite. Heat-treatments also change the macroporous morphology of cordierite monoliths, allowing production of small pores interconnected in a structure having a dense skeleton, with a shape free of cracks [7].

Geopolymer is an emerging alternative binder, an inorganic polymer which is synthesized by activating aluminosilicate materials with alkaline solutions. The polymerisation process initiates with a chemical dissolution/condensation of aluminosilicate minerals with alkaline activators and results in a three dimensional polymeric network. The chemical compositions of source materials and alkaline activators govern the chemical and microstructural properties of the final products of geopolymerisation. The thermal stability of the geopolymer has been documented [8] making the binder a promising candidate for the design of refractory aluminosilicate materials.

Geopolymer refractory concretes were prepared by reinforcing the matrix of K_2O–Al_2O_3–SiO_2 polysialate systems with quartz or alumina. During the first thermal cycle, dehydration, dehydroxylation, densification and deformation remain the principal sequence of sintering [8]. The cold-setting refractories showed, up to 900°C, shrinkage under 3% either for the paste or for the filler-reinforced pastes/composites. At 1000°C, the total shrinkage dramatically increased to 17% for the basic K-geopolymer paste, while remaining at 12 and 13% when alumina or quartz was added, respectively. The presence of fillers acted as nucleation sites for crystallization (kalsilite and leucite) and hindered the development of liquid phase. However, the presence of micro-cracks

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appearing in samples treated at 1200°C suggested the presence of sintering stresses, due to the gradient between the matrix and the newly formed liquid phase. Hence, geopolymer concretes seem to be suitable for thermal applications up to 1100°C. Even though these results represented a significant improvement with respect to the results available in the literature regarding the thermal stability of the geopolymers composites [9-14], some investigations are still needed for the optimization of the geopolymer refractory composites. The management of the interfaces between the pastes and the fillers, which totally depends on the thermo-chemical behavior of geopolymer pastes and fillers, is particularly important.

Improved geopolymer matrices suitable as refractory bonds for composites, that present excellent mechanical properties, low sintering shrinkage, and elevated temperature ranges of densification/formation of the liquid phase, together with the ability to resist to micro-cracks development and propagation, are targeted in this research. For these reasons, the cryptocrystalline aluminosilicate matrix is cordierite or mullite-cordierite based. These two crystalline compounds were chosen because of their respectively hexagonal and orthorhombic frameworks, consisting of six-member rings of tetrahedra, stacked one above the other and successively rotated of about 30° relatively to each other. These rings are laterally and vertically linked together by tetrahedra and MgO_6 octahedra, respectively. The ring stacking produces large hexagonal channels parallel to the c-axis, in which several cations or small molecules can be inserted. An insertion of alkaline cations within the large channels stabilizes the high temperature hexagonal cordierite formed [15]. The two formulation chosen, containing cordierite or mullite-cordierite, differ from the alumina content brought in the formulation by bauxite. From a physicochemical point of view, the advantage of high-alumina materials is the fact that the Al_2O_3 content is more active during heat treatment, since it is issued in the system in more active form from decomposition of bauxite and, enters in the structure of compounds (silicates, hydrates, etc.) preventing a change in the crystal lattice during heating. Geopolymer pastes are known to present high volume shrinkage above 900°C, therefore addition of a secondary phase contrasting shrinkage, and also high quality shrinkage-free fillers, are desired.

Natural kyanite, Al_2SiO_5, (theoretical weight composition 63.1% Al_2O_3 and 36.9% SiO_2) is a metastable nesosilicate, that on heating at 1100°C [16] breaks down into mullite (87.6%) and vitreous silica (12.4%) via the following reaction:

$3(Al_2SiO_5) \rightarrow Al_6Si_2O_{13} + SiO_2$.

During such a decomposition, kyanite density (3.4 − 3.6 g/cm^3) decreases to 2.9 − 3.1 g/cm^3, and correspondingly the volume increases by 17 − 23 vol%. The effects of temperature, time and kyanite grain size on its thermal decomposition parameters were studied. It was established that the

conversion proceeds from the surface toward the depth of a grain, and is limited by the relaxation of elastic stresses of the kyanite crystal lattice. After kyanite decomposition, amorphous silica crystallizes into cristobalite at low temperature [16].

From the above mentioned, we can envisage that the metastable/amorphous nature of alumina and silica of the solid precursor powders used, and the instability of kyanite at temperatures higher than 800°C (generally in equilibrium with sillimanite, $Al_2O_3 \cdot SiO_2$) do allow to predict competition between the formation of cordierite, mullite, kalsilite, leucite [17]. Sillimanite will be difficult to discriminate from mullite due to the similarity of their principal XRD patterns (3.39-3.42Å and 3.2-3.21Å, respectively). The acicular structure of both minerals can conduct to the orientations that alter the intensities of peaks, so making difficult to elucidate the exact mineralogy of the final composites [17]. However, mullite and sillimanite are two refractory systems, and cordierite will nucleate early and remains stable through the temperature development, changing only the allotropic form. Developing such refractory composites through cold-setting and sustainable processes as geopolymerization seems to be an original and innovative approach, compatible with protection of the environment in terms of reduction of the CO_2 emitted compared to the conventional high temperature process of mullite and mullite-cordierite refractory materials.

The present study aims to assess the behavior of the cordierite and mullite-cordierite based geopolymer binders in association to kyanite fillers in the preparation of refractory composites. The formation of the geopolymer was followed by means of [27]Al and ^{29}Si solid state MAS NMR spectroscopy. The expected relative stability of the cordierite based gel was evaluated in terms of thermal expansion/shrinkage at high temperature together with DTA and XRD analyses. The materials obtained are promising for the design of cold-setting sustainable refractory materials.

2. Materials and Experimental Procedure

2.1 Materials

Kaolin from Kribi, South Region of Cameroon, talc from Ngoung [18], Central Region of Cameroon and bauxite from Matap, Adamaoua Region of Cameroon [19], were used for the preparation of two amorphous geopolymer binders. Kyanite was collected from Makak in the Central Region of Cameroon and used as filler. The chemical and mineralogical composition of the different raw materials, investigated by Inductively Coupled Plasma Spectroscopy (ICP) and X-ray diffraction (XRD) respectively, are presented in Table 1. ICP accuracy is around 1-3%.

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Table 1: Chemical (ICP) and mineralogical (XRD) compostion of raw materials.

Oxides	Bauxite	Kaolin	Kyanite	Talc
Chemical composition (wt%)				
SiO_2	0.40	39.09	46.87	59.72
Al_2O_3	55.60	39.44	47.40	1.39
Fe_2O_3	1.30	0.74	0.02	5.26
MnO	0.01	0.00	0.00	0.05
MgO	<0.01	0.13	0.12	29.09
CaO	<0.01	< detection limit	0.18	0.15
Na_2O	<0.01	< detection limit	0.05	/
K_2O	0.03	0.30	1.29	/
TiO_2	0.09	1.14	3.39	/
P_2O_5	/	0.06	0.02	0.03
Loss on ignition	39.00	18.48	/	4.69
Total	96.46	99.37	99.29	100.38
Mineral composition				
	gibbsite	kaolinite	kyanite	talc
	anatase	gibbsite	anatase	chlorite
	goethite	illite	goethite	tremolite
				chromite
				magnesite

The alkaline solution used for the activation of the amorphous aluminosilicates was prepared using potassium hydroxide (KOH), 98.66 wt% from Carlo Erba, Italy and a potassium silicate solution from Ingessil, Italy having a SiO_2/K_2O molar ratio of 3.01 and a density of 1.38 g/cm^3. The solution was prepared just before the addition of the solid precursor in order to avoid any side reaction, allowing KOH acting as a dissolver and SiO_2/K_2O as a binder/cross-linker.

2.2 Preparation of the refractory composites via geopolymerization

The aluminosilicates prepared were designed following the molecular formulae of cordierite ($Mg_2Al_4Si_5O_{18}$) hereafter indicated as (Co), and mullite:cordierite ($Al_6Si_2O_{13}$: $Mg_2Al_4Si_5O_{18}$) namely (MuCo) in 1:1 weight proportion. The proportion of kaolin, bauxite and talc used for the preparation of the respective mixtures are presented in Table 2.

Table 2: Formulation of mixtures (Note: The fractions of raw materials are on the base of raw oxides including the water that would not appear in the calcined products. This is why the apparent total is above 100 wt%).

Proportion (wt%)	Cordierite Mixture (Co) (700 °C) ($Mg_2Al_4Si_5O_{18}$)	Mullite-Cordierite (MuCo) (700 °C) ($Al_{4.5}Si_{1.5}O_{9.75}$)
kaolin	53.36	77.51
talc	42.21	21.61
bauxite	21.07	34.73

Each raw material was collected directly in the deposit with the help of geologists, who performed the characterization [17]. The materials were dried, mixed and ground to fine powder having grain size below 80 μm, apart from kyanite, which was crushed and granulated at 2 mm > Φ >100 μm. The batches (Co) and (MuCo) were calcined at 700°C for 4 h, in order to remove water and have more disordered structure of the included clay minerals. The specific surface area of the batches, as determined by B.E.T. method, was 52.29 m^2/g for (Co) and 41.39 m^2/g for (MuCo). Potassium hydroxide was dissolved in distilled water to have 8M solution. An equal volume of potassium silicate was added and the final solution used to activate the solid precursors (Co) and (MuCo). The respective solid precursors were dissolved in the alkaline solution with the solid/liquid ratio of 1.7, considering that the alkaline solution was completely liquid. The resulted slurries were homogenised before adding the aggregates. Different amounts of fillers - 70, 75 and 80 wt%- were added to each (Co) and (MuCo) geopolymer pastes. The final composites were pressed using a hydraulic uniaxial press at 5 MPa to form discs of 4.2 x 0.7 cm. The pressed specimens were sealed immediately in plastic films at ambient temperature. The cordierite samples with 0, 70, 75, 80, wt% of kyanite powder were called Co100, Co30, Co25 and Co20, respectively. The mullite-cordierite samples with 0, 70, 75 and 80 wt% of kyanite were called MuCo100, MuCo30, MuCo25 and MuCo20, respectively. The choice of these amounts of aggregates was done on the following observations: 70 wt% was the minimum amount of fillers needed to tackle effectively the shrinkage; while 80 wt% was the limit after which the aggregates are no longer totally embedded in the binder. The specimens prepared were sealed in plastic bags for 72 hours, and the curing was completed at 21°C, 50% R.H. and under ambient pressure conditions until the samples weight was constant, i.e. after about 7 days.

Part of the specimens were kept as prepared for characterization, while other parts were heated at 1050°C, 1150°C, 1250°C and 1350°C in an electrical furnace at 5°C/ min, with a 1 hour isotherm at the maximum temperature. The cordierite and mullite-cordierite based geopolymer concretes were final products of the cold-setting refractory formulations. The thermal cycles applied for part of the products had the objectives to understand the behaviour of this new class of refractories at high temperatures, verifying the thermo-mechanical stability as well as the projection for the durability.

2.3 Characterization of cold-setting composites

2.3.1   Physico-mechanical and phase characterization

The mechanical properties of the specimens of cordierite and mullite-cordierite based geopolymer composites were assessed using biaxial flexural strength, obtained by the "piston-on-three ball" test.

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This test was preferred to the uni-axial bending test because thin plate structures, such as structural materials for buildings and constructions, are subjected to multi-axial stresses due to complex loading configuration and geometry structures [20]. Pieces obtained after the mechanical test were used for the determination of the bulk density and open porosity, using Archimede's method measurements.

2.3.2 Thermal behavior

Differential Thermal Analysis (DTA/TGA) was performed on the geopolymer refractory concretes using a Netzsch, STA 429 (CD) unit in air atmosphere. The operating conditions were 0–1400°C at 10°C min^{-1} for all the samples. For this analysis, samples of geopolymer concretes were ground into fine powders and a platinum-rhodium crucible was used as sample holder. Calcined alumina was used as reference.

Contactless optical dilatometry (ESS MISURA HSM ODHT model 1600/80, Expert System, Modena, Italy) measurements were performed on shaped cordierite and mullite-cordierite based geopolymer concretes (5 x 5 x 15 mm^3) up to 1250°C. The measurements were conducted under the same heating conditions (10 °C min^{-1}) for all the samples.

2.3.3 Phases evolution and microstructure

The intention of generate good bonding between matrix and kyanite aggregates using room temperature alkali activation requires to be supported by the evidence of geopolymer formation. Due to their mainly amorphous structure, geopolymers cannot be satisfactory characterized only through XRD analyses, thus an additional solid-state NMR characterization is required. The structural characterization of the geopolymers and part of the starting materials was performed using ^{29}Si and ^{27}Al solid-state NMR spectroscopy. The spectra obtained for Co and MuCo geopolymers were compared with the spectra recorded for the metakaolinite and bauxite starting materials. A Bruker Advance III 400 MHz spectrometer was used. ^{29}Si MAS NMR experiments were acquired at 79.49 MHz in a 7 mm MAS NMR probe, operating at a spinning speed of 5 kHz. A 30° pulse of 4.3 μs length and a recycle delay of 20 s were used. Chemical shifts were reported relative to TMS. ^{27}Al MAS NMR experiments were acquired at 104.26 MHz in a 4 mm MAS NMR probe, operating at a spinning speed of 10 kHz. A 30° pulse of 1 μs and a recycle delay of 2 s were used. Chemical shifts was referenced using a 1 M solution of $Al(NO_3)_3$.

Mineralogical analysis of the geopolymer cement and composites were carried out with an X-ray powder diffractometer, XRD, (PW3710, Phillips, The Netherlands) CuKα, Ni-filtered radiation (the wavelength was 1.5406 Å). The radiation was generated at 40 mA and 40 kV. The analysis was

performed on fine grains of ground samples. Specimens were step-scanned as random powder from 5° to 70° 2θ steps and integrated at the rate of 2 s per step.

The microstructure of the as-prepared specimens and those with thermal cycles were studied by SEM (mod. XL40, Philips, The Netherlands). Freshly fractured surfaces and freshly fractured polished specimens were used for each sample. The polished specimens were etched in 5% HF-HNO$_3$ solution for 30 s for crystalline phase identification. All the specimens for SEM analysis were mounted on aluminum stubs and sputter-coated with 10 nm of Au/Pd. The microanalysis was performed using EDS (X_EDS INCA, Oxford Inst.).

3. Results

3.1 Cold-set materials and geopolymerization assessment

The success of the geopolymeration process as cold binding technique was investigated using NMR characterization. The ^{27}Al NMR MAS spectra recorded for bauxite, metakaolinite and cold-set geopolymers were illustrated in Figure 1a. All the signal components are strongly affected by a quadrupolar broadening, as well as a further broadening due to the paramagnetic interactions with the iron impurities included in all starting materials. The spectrum obtained for the bauxite (Fig. 1a, spectrum 1) reveals the presence of both 4-fold and 6-fold coordinated aluminum. The peak at about 12 ppm is due to octahedral AlO$_6$ units and can be attributed to the main constituents of the bauxite: gibbsite (Al(OH)$_3$) and boehmite (γ-AlO(OH)) [21,22]. Both the shoulder at about 1.4 ppm, which can be attributed to additional Al^{VI} units, and the two signals due to different tetrahedral Al-O units in the 80-60 ppm range come from impurities. These impurities are most probably clays, having Al in tetrahedral and/or octahedral coordination, as for kaolinite or micas [23]. The metakaolinite spectrum reported in figure 1a (spectrum 2) is similar to the ^{27}Al NMR spectra already reported in the literature [23-27]. It shows an overlapping of three main signals at about 63, 30 and 20 ppm, attributable to 4-, 5- and 6-fold Al-O resonances [24-27]. The spectra recorded for the two geopolymers (Fig. 1a, spectra 3 and 4) are very similar and contain two broad peaks centered on 58 and 6 ppm. The peak at 58 ppm is typical of a geopolymer, and comes from the tetrahedral Al-O units of the sialate units [28]. The peak at 6 ppm arises from residual octahedral Al-O units, coming from an unreacted metakaolinite, as already observed for kaolinite calcined at 800°C [25]. The ^{29}Si MAS NMR spectrum of the starting metakaolinite is reported in Figure 1b. The broad and featureless signal centered at -100 ppm includes contributions of i) SiQ^4(0Al) units resonating about -105 ppm typical of calcined kaolinite [24-27]; ii) SiQ^3(0Al) units resonating in the range from -90 to -98 ppm coming from residual structured pristine kaolinite and other clays impurities [23]. However, the additional lineshape broadening due to the paramagnetic interactions with iron

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impurities included in the starting material makes practically impossible to perform any reasonable spectral decomposition. The presence of a small amount of quartz resonating at -107 ppm cannot be excluded [27]. The spectra 2 and 3 of the Figure 1b were recorded for the two geopolymers; these spectra are similar and show a single broad peak resonating at -89 ppm, which was already observed for Al rich geopolymers [28].
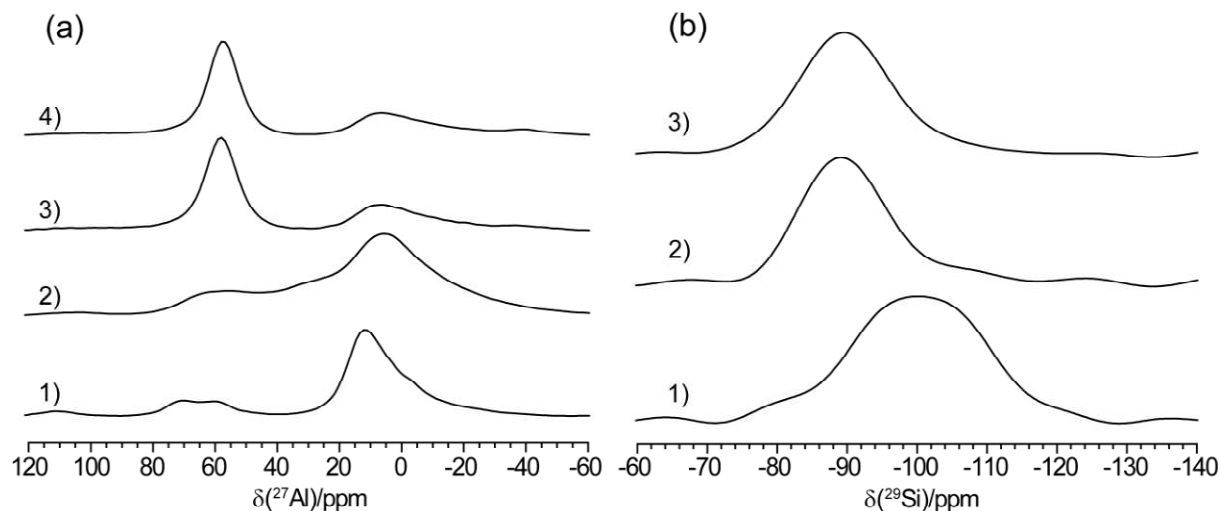

Fig. 1. (a) ^{27}Al MAS NMR spectra recorded for starting (1) bauxite, (2) metakaolinite and for the geopolymers (3) Co and (4) MuCo; (b) ^{29}Si MAS NMR spectra recorded for (1) starting metakaolinite, and for geopolymers (2) Co and (3) MuCo.

3.2 Physico-mechanical characterization of cold-set materials

The cold-set materials were tested after their weight came to a constant value and this happened after about 7 days in full agreement with what reported in literature [8-11].

Density of the refractory concretes increase with the increase in the kyanite content almost linearly from 70 to 75 wt%, then a plateau seems to be reached for Co and MuCo series (Figure 2). There were no significant differences in the bi-axial flexural strengths of the cordierite and mullite-cordierite geopolymer binders (Fig. 3). The specimens presented values around 11 MPa for MuCo and for Co; these values increase to 24 and 28 MPa, respectively, with the addition of 70wt% kyanite aggregates. At higher amount of kyanite, MuCo series shows a slight decrease in strength while Co series increases it, indicating that for MuCo series the addition of kyanite above 70wt% are deleterious for mechanical properties. The general improvement of the density and flexural strength (Figs. 2 and 3) of the refractory concretes with kyanite content, can be explained: (i) by the

difference in density between the geopolymer pastes (~1.5 g/cm^3) and the kyanite aggregates (3.65 g/cm^3); and (ii) by the good interface bonds established between the geopolymer pastes and the aggregates. Bonds enhanced with the porous structure of the kyanite. The good adhesive behavior of the MuCo and Co binders counts for the maximum load transfer to reinforcement with final improvement of the mechanical strength and density up to a certain aggregate percentage depending upon composition (Figs. 2 and 3).
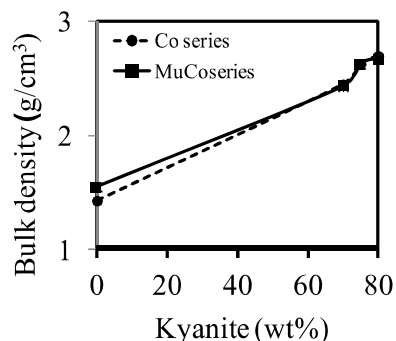
Fig. 2. Variation of the bulk density (g/cm^3) of geopolymer refractory composites as function of the kyanite aggregates content.
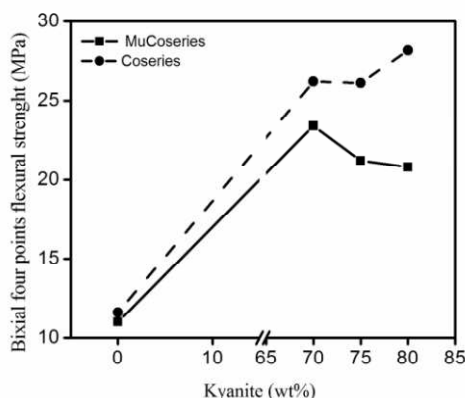
Fig. 3. Variation of the bi-axial flexural strength (MPa) of geopolymer refractory composites as a function of the kyanite aggregates content.

By adding the aggregates, the open porosity, determined after complete curing, decreased from 33 to 14 vol% for the Co series, and from 35 to 13 vol% for the MuCo series (Fig. 4).
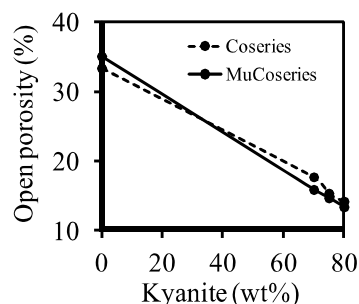
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Fig. 4. Variation of the porosity (vol%) of geopolymer refractory composites as a function of the kyanite aggregates content.

Following the variation of the flexural strength as observed in the Figure 3, the reduction of the porosity and the increase of the density contributed to improve the compactness and strength of the refractory composites. The above described bonds established between the inorganic polymer binders and the porous and coarse kyanite aggregates are essentially physico-chemical in nature. There might be formation of gels at the interface between the binders and aggregates, but not with enough crystalline structure to be interpreted through XRD.

3.3 Thermal behaviour of refractory concretes

As-prepared MuCo and Co refractory geopolymer pastes showed XRD patterns (Fig. 5) with characteristics similar to that of standard metakaolin-based geopolymer matrix: large diffuse peak centered at $2\theta=28°$, characteristic of an amorphous inorganic polymer gel from aluminosilicates [11-14]. Peaks of cordierite, kalsilite, leucite are visible above the amorphous halo indicating they are dispersed in the amorphous phases together with grains of α-quartz (see Fig. 5b). The quartz grains are residual crystalline silica not dissolved after thermal decomposition of kaolin and talc.

At 1050°C, the crystallization of kalsilite, enstatite, leucite, mullite and cordierite in MuCo, and mullite and cordierite in Co was observed (Fig. 5). The presence of a broad amorphous halo was evident at this temperature, indicating that these phases are still embedded in an amorphous matrix. The amorphous content is more important in MuCo if compared to Co matrix. For both the formulations, the increase of temperature to 1150°C and to 1250°C contributed to increase the content of newly formed crystalline phases, as revealed by the X-ray peaks intensity (Figure 5). This can be interpreted as the result of the progressive transformation of the amorphous geopolymer gel to crystalline mullite/sillimanite, kalsilite, enstatite, leucite or cordierite.

The introduction of the kyanite aggregates in the as-prepared geopolymer binders (MuCo and Co) did not result in any phase transformation, since the XRD patterns of the resulting refractory composites after complete curing at room temperature were that of kyanite and the existing peaks of

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α-quartz. These phases did not change with the variation of the kyanite aggregates content (Figures 6 and 7). The heat treatment of the different specimens of geopolymer based refractory concretes leads to an improvement of the crystallization as it can be observed in figures 6 and 7. In general, it can be concluded that the particles of kyanite act as nucleation sites for the crystallization of leucite, kalsilite, enstatite, mullite, sillimanite and cordierite and by the way reduce considerably the tendency of $K_2O-MgO-Al_2O_3-SiO_2$ system to form interfacial liquid phase. In MuCo20, MuCo25 and MuCo30, the crystallization of mullite, leucite, kalsilite, sillimanite, enstatite and cordierite was improved progressively by increasing the temperature from 1050°C to 1250°C. The observed trend was the reduction of the amorphous content and the increase of the X-ray peaks intensity of the newly formed crystalline phases.
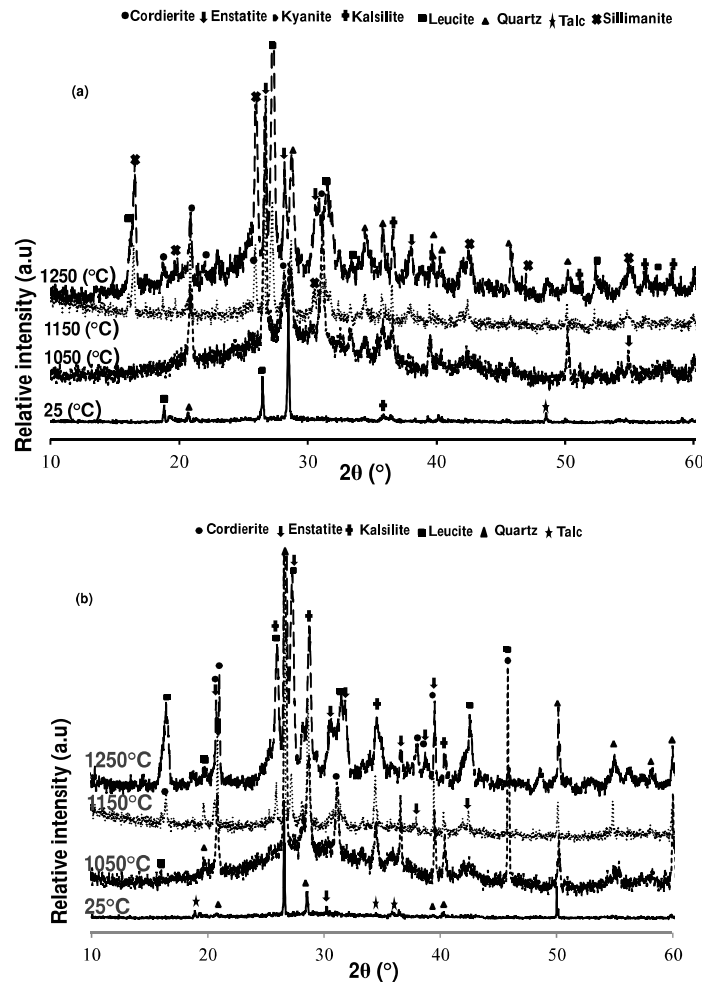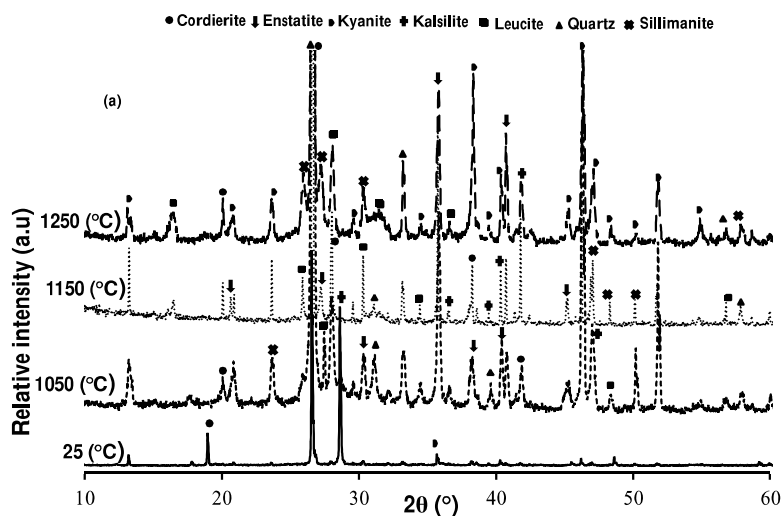

Fig. 5. XRD patterns of (a) MuCo, (b) Co as a function of temperature. (Cordierite ($MgAl_4SiO_{18}$); Enstatite ($MgSiO_8$); Kalsilique ($KAlSiO_4$); Kyanite ($Al_2O_3\cdot SiO_2$); Leucite ($KAlSiO_4$); Quartz (SiO_2); Sillimanite ($Al_2O_3\ SiO_2$); Talc ($MgSiO_{14}(OH)_2$).

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It seems that the crystalline phases occurred over a broader range of temperature, following by grain growth due to the requirement to crystallize around the kyanite particles. The choice of 1050°C for both MuCo and Co series as initial temperature for evaluating the phases evolution of the geopolymer refractory composites was in agreement with previous works [8,28,29], that did not found any significant phase transformation in the geopolymer matrices below 1000°C. Moreover, the kyanite used as aggregates would present around this temperature incongruent decomposition into mullite and amorphous silica, giving place to important modifications of the structure of the composites. Referring to the works of Bohlen et al. [17], it is expected that starting from 800°C, kyanite will establish an equilibrium with sillimanite. The existence of mullite itself takes place far above 1100°C. Changes in the intensities of diffraction peaks indicate that geopolymer composites contain kyanite, sillimanite, mullite, leucite, enstatite, kalsilite with various grains size. In the geopolymer pastes no sillimanite was found, either in as prepared or heat treated specimens. The presence of sillimanite in the specimens with kyanite confirms the finding of Bohlen et al. [17], regarding the dynamic equilibrium of kyanite-sillimanite at high temperature.
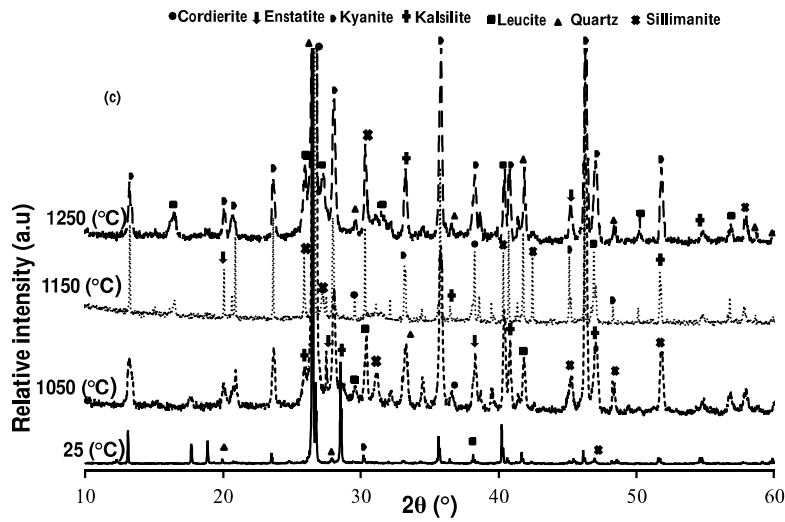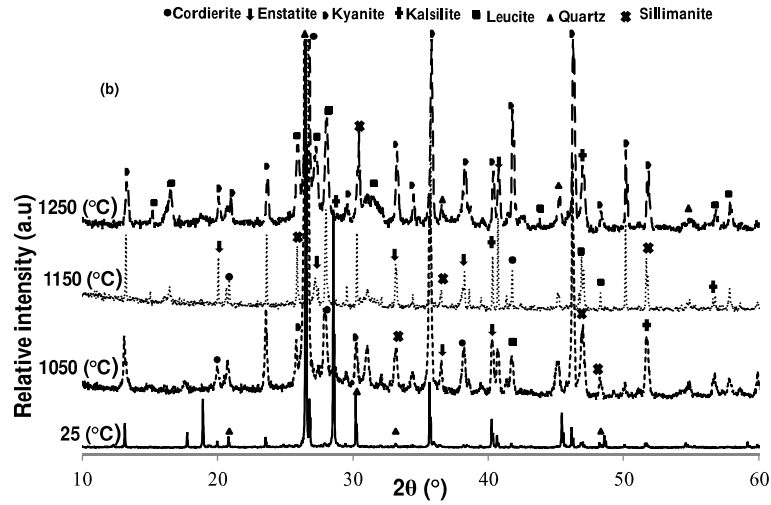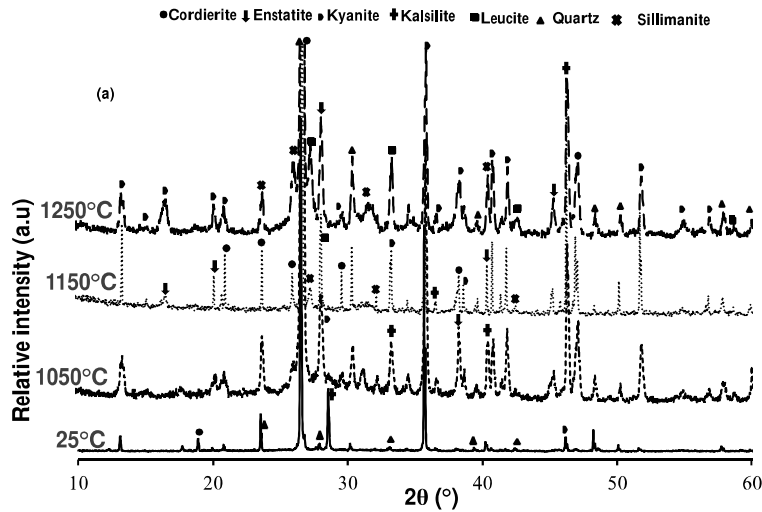
Fig. 6. XRD patterns of the (a) MuCo with 70 wt%, (b) MuCo with 75 wt%, (c) MuCo with 80 wt% of kyanite aggregates as a function of temperature. (Cordierite ($MgAl_4Si0_{18}$); Enstatite ($MgSiO_8$); Kalsilique ($KAlSiO_4$); Kyanite ($Al_2O_3 \cdot SiO_2$); Leucite ($KAlSiO_4$); Quartz (SiO_2); Sillimanite ($Al_2O_3 \cdot SiO_2$)).
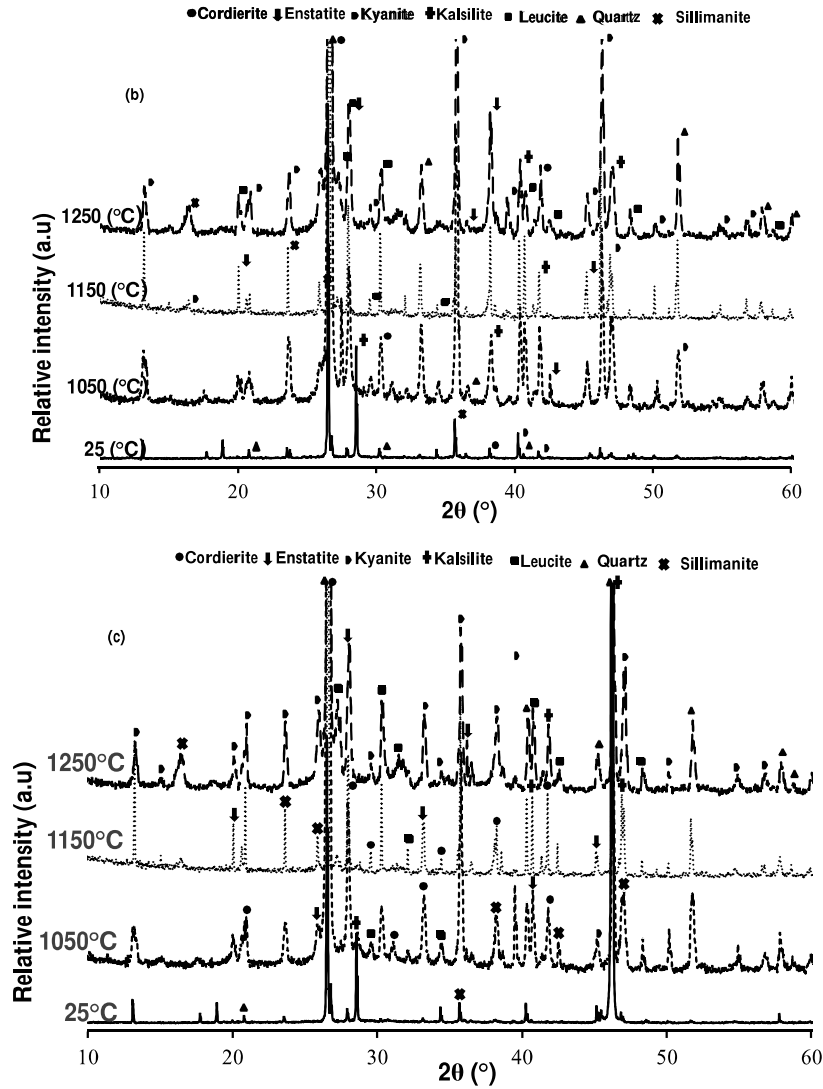
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Fig. 7. XRD patterns of the (a) Co with 70 wt%, (b) Co with 75 wt%, (c) Co with 80 wt% of kyanite aggregates as a function of the temperature. (Cordierite ($MgAl_4SiO_{18}$); Enstatite ($MgSiO_8$); Kalsilique ($KAlSiO_4$); Kyanite ($Al_2O_3 \cdot SiO_2$); Leucite ($KAlSiO_4$); Quartz (SiO_2); Sillimanite ($Al_2O_3 \cdot SiO_2$)).

For Co series (Co20, Co25 and Co30), a trend similar to that observed in MuCo series was observed. It was also seen, as already noticed with MuCo and Co binders, a sharp difference in crystalline phases content in Co series. Upon heating it was observed a progressive change of the reddish color of specimens of both refractory Co and MuCo series to grey, as the temperature increases from 1050 to 1350 °C. It is suggested that the relative iron content of the bauxite and talc is activated during the calcination. During the crystallization, this iron can insert itself into the newly formed crystalline phases as cordierite, enstatite, secondary mullite, etc.

For better understanding the transformations occurred in the samples we collected the XRD in two separate figures only (See Appendix A and Appendix B).

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In order to exploring thermal stability and refractoriness degree of the samples prepared, the thermal resistance and the occurrence of phase transformations up to 1400°C were studied using TGA-DTA analyses. Figures 8 and 9 report the DTA and TGA curves of the cordierite (Co) and cordierite-mullite (MuCo) based refractory concretes, respectively. Co and MuCo paste specimens undergo similar thermal features: endothermic peaks at about 100°C and 850°C as the only significant transformations, which can be easily identified. The first one can be correlated to the loss of the water physically absorbed on the specimens. This loss of water continues, together with dehydroxylation, up to about 700°C, for a cumulative value of 17 wt% for the MuCo and about 14 wt% for the Co based specimens (Figs. 8b and 9b). The difference between the two samples is likely related to the amount of residual hydroxyl groups associated with kaolin, talc and bauxite.
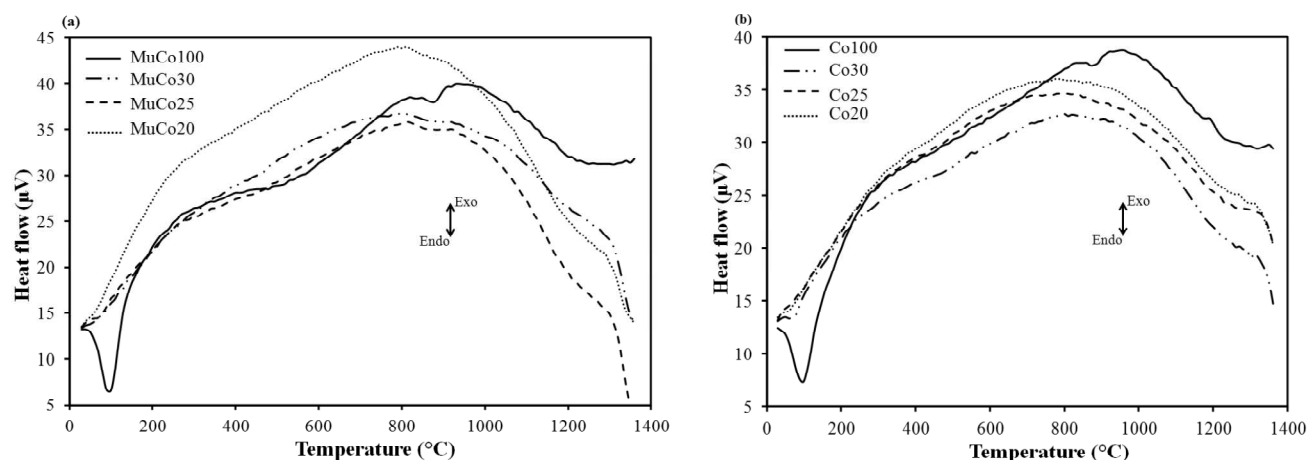

Fig. 8. DTA curves of (a) MuCo, (b) Co series of geopolymer refractory as a function of the kyanite content.

The second endothermic peak at ~ 850°C is smaller with respect to that of dehydration, and it is due to the loss of structural hydroxyl groups not totally transformed during the calcination process [8,30]. In both Co and MuCo series, the presence of kyanite aggregates considerably reduced the scale of the dehydration and dehydroxylation processes evidently resulted from dilution effects. Above 900°C no further clear thermal transformation was observed. We stress that crystallization may not be visible due to the smaller fraction of paste with respect to the kyanite aggregates. Between 1050°C and 1250°C, important degree of crystallization of kalsilite, enstatite, sillimanite, mullite, leucite and cordierite was observed in all specimens under study, even though the overall matrices remain predominant with the kyanite phases surrounded at the surface and interparticle regions with newly formed crystalline phases as we will detail below.
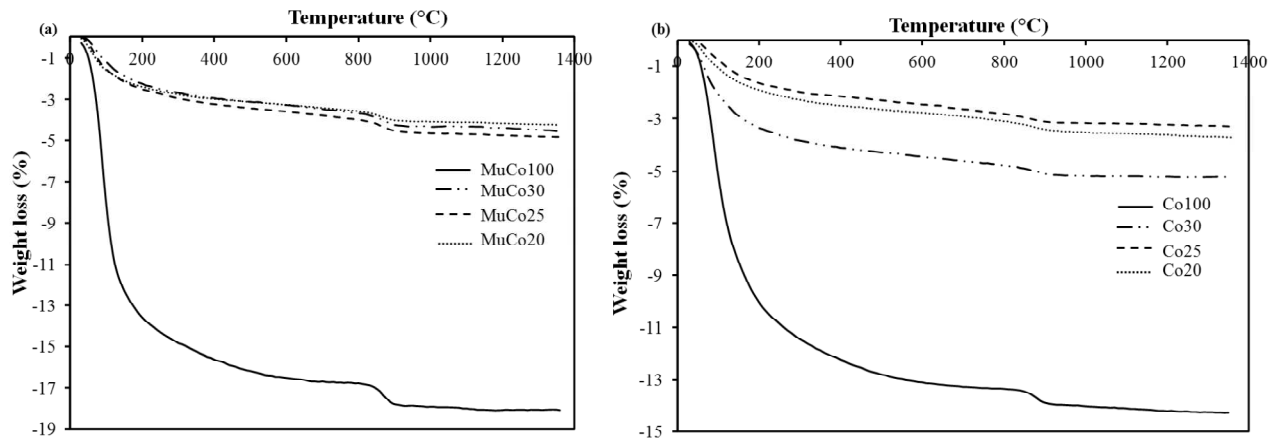
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Fig. 9. TGA curves of (a) MuCo and (b) Co series of geopolymer refractory as a function of the kyanite content.

For the Co-based series, the addition of kyanite determined a final weight loss which roughly scales with the ratio cordierite/kyanite. In the case of the MuCo-based series, the addition of kyanite determines a more complex behaviour which cannot be simply rationalized. However, in all cases the final weight loss was below 5 wt%, which confirmed the suitability of these formulations for practical uses, in particular if compared with the 8 wt% loss of the Al_2O_3-MgO-C refractory castables [31].

One of the most characteristic parameters inherent to the sintering procedure is the change of dimensions of the porous structure. This enables the analysis of the sintering procedure as a microscopic process of volume and shape deformation, caused by substance flow in the skeleton of the refractory concretes [8]. On the basis of the dilatometric curves of Figs. 10 and 11, a linear shrinkage up to 1300°C of 7.0 and 7.8% for mullite-cordierite and cordierite based geopolymer binder was estimated, with the maximum shrinkage reached after 1000°C. These values are far from the 17 to 23 % of linear shrinkage observed in the K_2O-Al_2O_3-SiO_2 based geopolymer binder [8,21].
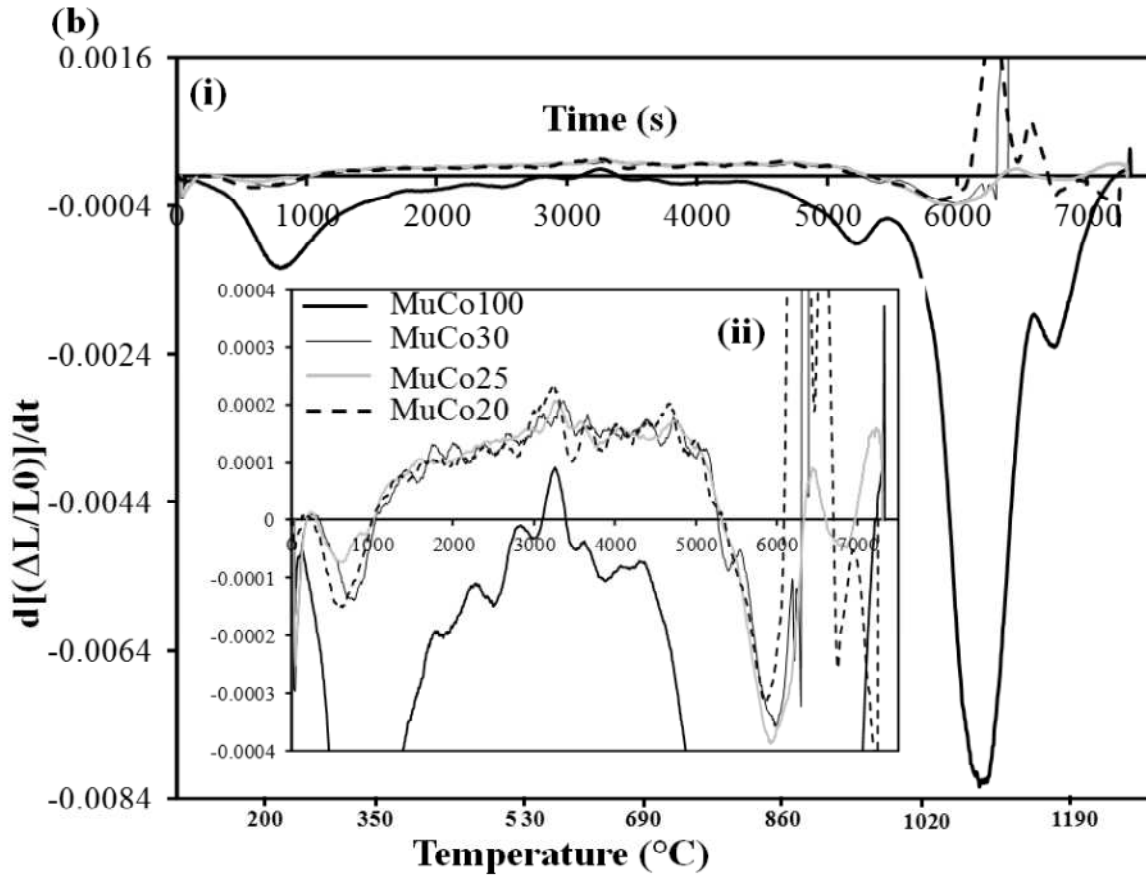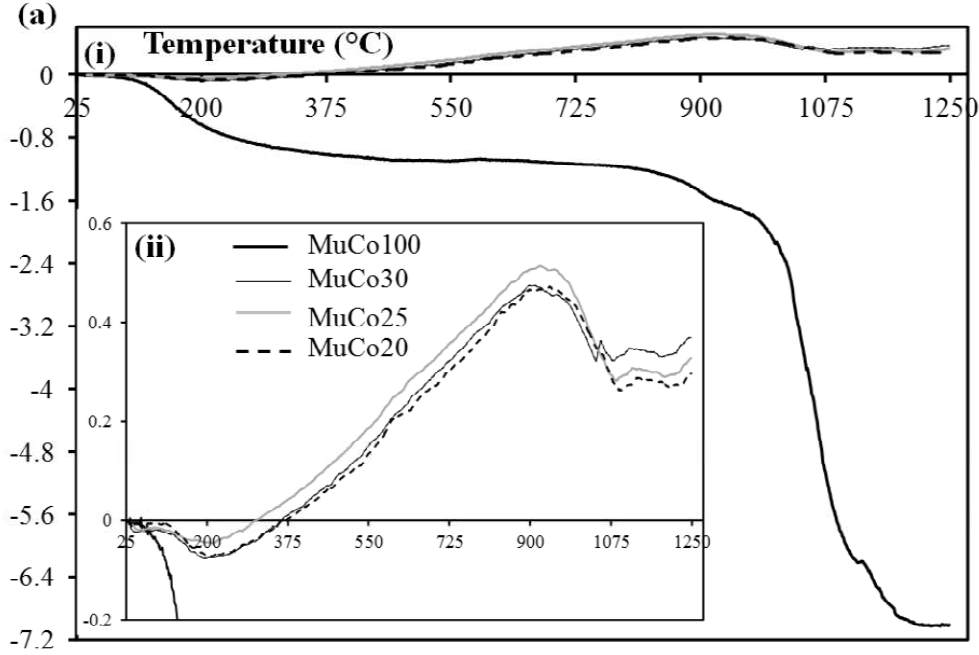
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Fig. 10. Thermal expansion curve (a) and coefficient of thermal expansion (b) curves of MuCo series of geopolymer refractory as a function of the kyanite content ((i) entire curve, (ii) zoom).

Fig. 11. Thermal expansion (a) and coefficient of thermal expansion (b) curves of Co series of geopolymer refractory as a function of the kyanite content ((i) entire curve, (ii) zoom).

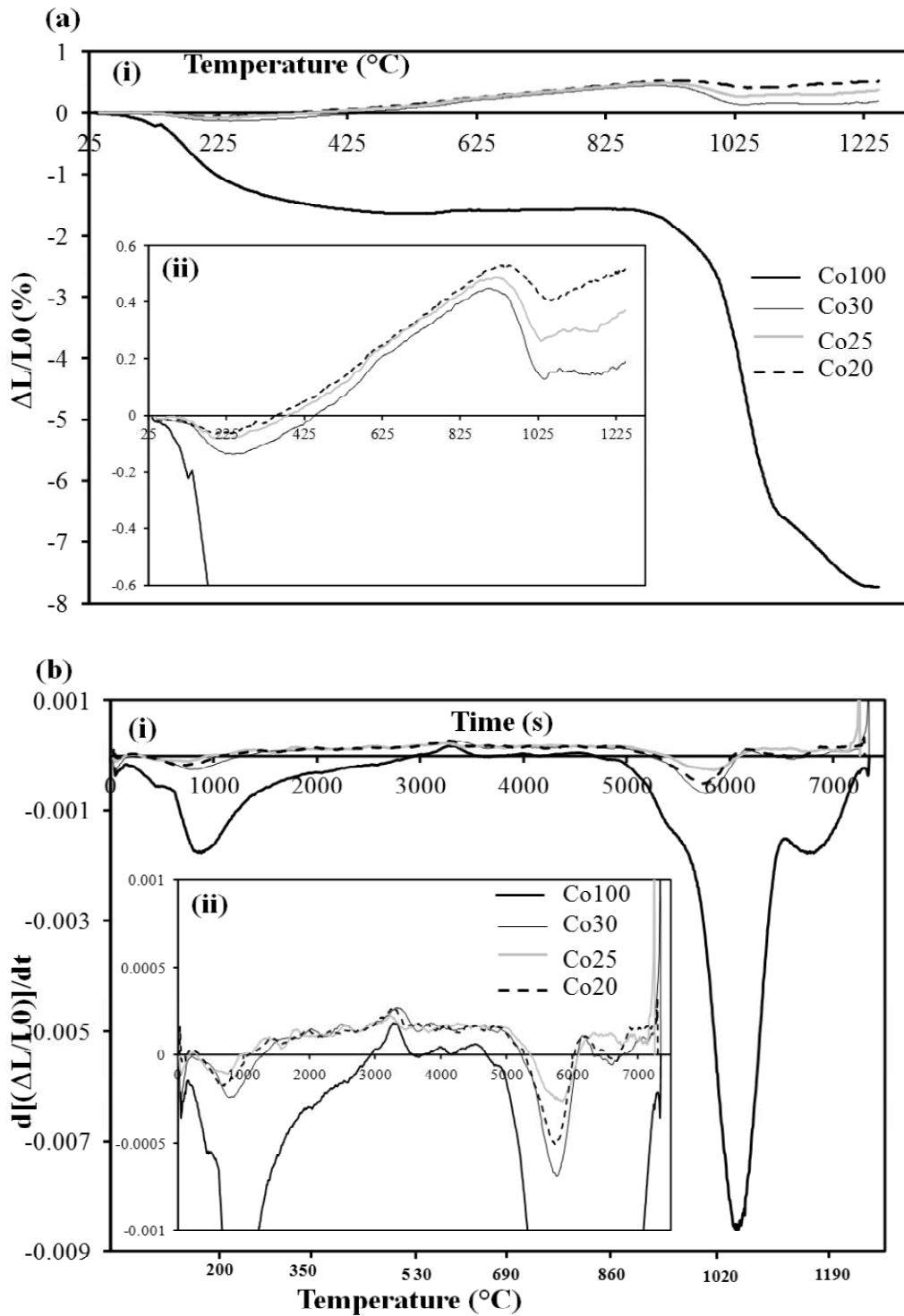In fact, although geopolymer pastes have been described to present good thermal stability [21], the detailed sintering behavior of the matrices showed that their stability is ensured only up to 800-900°C [9-13]. Above these temperatures, the formation of a liquid film in the $Na_2O-Al_2O_3-SiO_2$ and the transformation of the leucite during cooling in $K_2O-Al_2O_3-SiO_2$ systems do change the surface tension at the grains interface [8,19]. In the former case, the liquid formation induces a rapid dissolution of the grains, whereas in the latter one intensive micro cracks do appear. The densification rate increases in these formulations generally after dehydration, and the resulting shrinkage becomes more important. In this study, by changing the composition from $K_2O-Al_2O_3-SiO_2$ to $K_2O-MgO-Al_2O_3-SiO_2$, the geopolymerization processes take place successfully with a better polycondensation and good final mechanical properties (compare Figs. 3, 5 and 9). Moreover, the low linear shrinkage of the above systems is linked to the difference in their thermal behavior. Under the action of the thermal treatment, talc is transformed into a clinoenstatite-like structure and amorphous silica at T< 1000°C. The product of calcination is a lightweight powder with high reactivity and hydration behavior comparable to that of metakaolin. Hence, an optimal geopolymerization was ensured for the cordierite and mullite-cordierite based pastes. Although potassium based geopolymer pastes demonstrated a better ability to develop crystalline phases (leucite, kalsilite) with respect to the sodium based, the thermal behavior of the Co and MuCo pastes suggests an improved crystallization scenario. The presence of highly dense coarse kyanite aggregates, which are closely bound to the paste, reduces the porosity, provides a pathway for faster and complete dehydration, without damages of the structure, micro-cracks, shrinkage, creeps…, and enhances the thermal stability of kalsilite, enstatite, sillimanite, leucite, mullite and cordierite. Additionally, the ability of these matrices to crystallize is improved as far as is possible, in the case of effective formation of cordierite, to assist to the insertion of potassium ions into the structure of the cordierite at high temperature to form potassium-rich cordierite, so avoiding the formation of a liquid phase at low temperature. Moreover, the volumes of these systems show the tendency to increase under thermal treatment, so allowing us to describe the thermal behavior of the Co and MuCo geopolymer binders as a combination of shrinkage of Al-Si-rich phases and expansion of MgO-rich phases, resulting in a significant reduction of the overall linear shrinkage to 7.0% for the mullite-cordierite and 7.8% for the cordierite based materials, in comparison with the 17 to 23% of 100 wt% metakaolin based geopolymer binder [8,12]. We can note that in the Al-Si geopolymer systems, an important densification takes place after dehydration and dehydroxylation, giving place to the earlier formation of the liquid phase, while the reduction of the rate of densification observed in the cordierite and mullite-cordierite based geopolymer matrices delays the formation of the liquid phase, so favoring a better crystallization. Theoretically, the thermal conductivity of the Co and

MuCo matrices should be higher with respect to the metakaolin-based matrices. As a consequence, there would be a better homogeneity of the heat flux in the skeleton that avoids the tension stresses due to the difference in dilatation between the superficial and the internal part of the matrix. This thermal behavior was improved by the presence of the coarse kyanite aggregates, as it can be observed in the Figs. 8, 9, 10 and 11. In Fig. 11, it is observed that Co30 (70 wt.% of kyanite aggregates) displays a linear shrinkage reduced from 1.6 % (Co100) to 0.14% at 225°C. By increasing the amount of the kyanite aggregates to 75 wt% (Co25) and 80 wt% (Co20), the linear shrinkage went under 0.1% at 225°C. Between 225 and 900°C, the complex matrices exhibited a thermal expansion, which scales with the fraction of the kyanite aggregates in the composites. Higher the kyanite content in the geopolymer refractory composites is, more important is the thermal expansion: 0.42, 0.48 and 0.52% at 900°C respectively for Co30, Co25 and Co20 (70, 75 and 80 wt.% of kyanite aggregates). At 1000°C, the important rate of densification (Fig. 9b) is responsible for the decrease of the thermal expansion. The dehydration took place at relative high rate, the rate of densification appeared very important, indicating that in geopolymer these phenomena are spontaneous and typical of the nature of this material (Fig. 9b). The thermal stability should be pointed through the correct design of formulations. The reduction of the porosity in the matrices, the presence of others crystalline phases apart from leucite, as well as the coarsening of the microstructure, could be significant contributions to the improvement of the thermal behavior of the geopolymer refractory composites.

The dehydration took place at 200°C in MuCo series. The presence of kyanite aggregates reduced the linear shrinkage under 0.1% at 200°C for all the specimens. At 900°C both MuCo20 and MuCo25 presented 0.45% of thermal expansion, while it is 0.5% for MuCo30. With the densification of the matrix bonds after 900°C, all the expansion curves decrease to ~0.3% and remain constant up to 1250°C. A dispersion of the values of the thermal expansion in Co series between 1000°C and 1250°C, where the value is almost linear, can be noted. The Co30, Co20 and Co25 showed 0.1, 0.25 and 0.45% of linear shrinkage respectively. The difference in the thermal expansion, even if not so important, is linked to the higher ability of liquid film formation in the MuCo series with respect to Co one. This situation explains the delay of the expansion phenomena in Co with respect to MuCo (Figs. 10a and 11a). However, as already mentioned, the dehydration and densification were the significant characteristics of MuCo series as that of Co with a high rate of dehydration that precedes an important and significant rate of densification (Figs 10b and 11b). The shrinkage for Co and MuCo monolithic geopolymer binders and the thermal expansion of the specimens with aggregates are interpreted as the difference of the phase formation during the

crystallization and densification. Moreover, the densifications of monolithic MuCo and Co geopolymer pastes can be accompanied by the formation of liquid phase even in reduced content.

4. Discussion

The two formulations of refractory composites here presented showed a very complex microstructure evolving with the thermal cycles and the content of kyanite aggregates. On the basis of Figures 8 and 9, the expansion features of the geopolymer refractory concretes can be fractioned into three parts:

(i) from room temperature up to 500 °C. Kyanite used as aggregate was completely unaffected by the heat temperature. A slight shrinkage was observed after the dehydroxylation: the geopolymer paste was subjected to volume change and deformation, even if it was minimized due to the presence of kyanite aggregates intimately attached to the geopolymer paste, that successfully acts as a binder;

(ii) between 500 and 950 °C. A global expansion of the composites was observed. The cordierite and mullite exhibit thermal stability in this range without any transformation;

(iii) above 950 °C. At the end of the thermal stability region of the cordierite and mullite/cordierite there was an important shrinkage of the geopolymer paste, even though the values were relatively small if compared with the shrinkage of K or Na- geopolymer pastes. However, the shrinkage is counterbalanced by the significant expansion of the paste, and the expansion of kyanite resulted in a global decrease of the expansion behavior of the refractory composites. It should be noted that starting from 800°C kyanite is in equilibrium with sillimanite [17], and this equilibrium can have affected the thermal behavior of the final composites. For the Co series, Co30, which contains the highest proportion of geopolymer paste, showed an important shrinkage below 500 °C and the lowest expansion above 500 °C demonstrating, together with the behavior of pastes and those with the lower kyanite content, that the ratio geopolymer-to-aggregate is significant in determining the final thermal behavior of the cold-setting refractory composites. The phenomenon is similar for both cordierite and 1:1 mullite cordierite-based refractory composites.

The suitability of the cordierite and mullite-cordierite binders to act as refractory bonds for the cold-setting of the refractory, which can be viewed as promising matrices for kiln furniture, castable refractory, catalytic supports and heat exchanger for gas turbine engines, was confirmed by the microstructure, which remained highly crystalline at the surface of kyanite aggregates and the interparticle regions, confirming the easy transformation without damages of the geopolymer bonds to ceramic and more refractory bonds as indicated in Fig. 12.
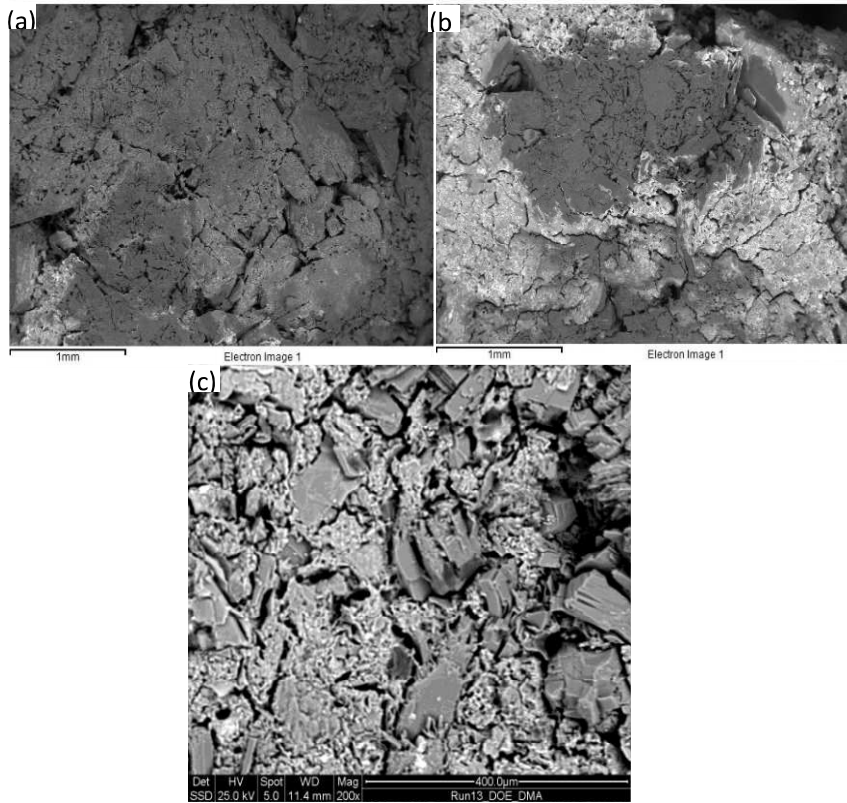
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Fig. 12. Micrographs of geopolymer refractory composites: (a) as-prepared MuCo20; (b) as prepared Co20; (c) Co20 at 1250°C showing the higher crystallization at the surface of kyanite aggregates.

5. Conclusion

Structural refractory composites can be successfully prepared using the formulations of Co or MuCo series. Since the strength and the quality of bond with aggregates depend on the degree of polymerization, the control of the rheology and the adhesive behavior of the binders are important. The porosity and the microstructure of the kyanite grains allow the development of high quality bonds with pastes. This is favored by the high reactivity of meta-kaolin and meta-talc together with their hydration behavior. The stability of the matrices through the temperature development suggests the transformation upon heating of the physic-hydraulic and/or chemical bond to ceramic bond. These transformations take place without damaging the composites, as the geopolymer pastes are known to be thermally stable upon temperature increase. The porosity of the aggregates, the difference in thermal expansion between the cordierite and the 1:1 cordierite-mullite matrices and the kyanite, as well as the packing design developed with the control of the particle size of the aggregates, likely acted synergically, giving to the final composites a good thermo-chemical and microstructural stability up to 1250°C. The thermal expansion coefficients of both the series are

very low with respect to common aluminosilicate refractory materials. These values, together with the porosity and the phase's evolution (Figs. 8, 10 and 11) are indicative of the capacity of the matrices to resist to thermal shock and spalling.

The thermal expansion, which remains less than 0.5 % for either Co or MuCo series of refractory composites, indicates the suitability of the formulations designed in this study as refractories. The variation of the thermal expansion from meta-kaolin based geopolymer refractory composites and that of cordierite-based composites demonstrate, also by including the choice of the granularity of the aggregates, the possibility to tune the final properties of refractory composites from geopolymer, having in mind the objective to reach an upgraded refractory matrix usable in the 25-1250°C range through sustainable and environmental setting processes.

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