

Physical Assessment of Pozzolanic Activity of Saudi Kaolinitic Clays for Use in Sustainable Cement-based Materials

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Abstract— presently, there is a growing concern in calcined clays as supplementary cementitious materials SCM, because of their relatively great geographic distribution and their demonstrated pozzolanic properties once calcined under specific conditions. In this study, two different Saudi kaolinitic clays (from KHUSHAYM RADI DEPOSIT) were calcined at three different temperatures 650, 700 and 750 °C, the influence of calcination temperature on the mineralogical compositions and micro-morphologies were investigated by X-ray diffraction spectrometer XRD and the scanning electron microscope SEM respectively. The pozzolanic activities were studied using hydrated lime as an activator. 80% clay – 20% hydrated lime pastes were prepared using water/solid ratio = 1 (on basis of mass) and hydrated for 3 and 7 days. The phase composition/decomposition of the hydrated pastes was identified by using differential scanning calorimetry (DSC) and XRD. The microstructure characteristics and x-ray microanalysis were examined by SEM equipped with energy dispersive analytical x-ray unit (EDAX). Significant modifications in the micro-morphologies have been observed due to calcination. The investigated clay samples showed different pozzolanic activities.

Index Terms— kaolinite, calcination, Pozzolanic Activity, DSC, XRD, SEM, EDAX

1 INTRODUCTION

Nowadays, due to economical and environmental goals, concrete industry is looking after an optimization to replace clinker cement by other supplementary cementitious materials. Such is the case for pozzolans, which constitute a possibility of attaining a reduction in cement consumption either as the addition in the cement production process or as its replacement in the concrete. In both cases, it's well known that pozzolans modify concrete physical and mechanical properties, which supply several benefits to the use engineers, civil constructors and researchers design for it [1,2]. Presently, one of the most used and studied supplementary cementitious materials are calcined clays in the form of metakaolin. Such materials are obtained from thermal-treated natural kaolin mineral deposits, which have excellent pozzolanic properties mainly because of their chemical composition, amorphous structure, and high specific surface. During this thermal treatment, factors such as temperature, calcination time, shape and size of particles influence metakaolin reactivity (MK) [3-7]. The mineralogical composition, particle size distribution, and degree of amorphousness are the main factors affecting the pozzolanic activity of clays [8]. Natural materials like volcanic ash where artificial pozzolans such as clay, shales, bauxite waste have to undergo heat treatment before they become pozzolanic. Metakaolin is obtained from thermal-treated natural kaolin mineral deposits, which have excellent pozzolanic properties mainly because of their chemical composition, amorphous structure, and high specific surface [9]. Portland cement (PC) if adequately hydrated produces CH of about 28% of its own weight. The CH (portlandite) liberated by the hydration of PC does not make a significant contribution to the strength and can be dangerous to concrete durability. Its

elimination or conversion by reaction with the pozzolana can result in greatly enhanced durability and strength [2]. Different methods have been carried out for improving the cement paste properties in the past such as the addition of supplementary materials into cement and concrete which has been considered by many researchers all over the world for improving the strength of cement paste and concrete, these supplementary materials including natural pozzolans as well as artificial ones such as fly ash and silica fumes. The aim of this study is to assess the pozzolanic activity of two different Saudi kaolinitic clays in order to produce highly active and amorphous pozzolana by means of thermal activation to be used as unique SCMs. the influence of thermal treatment on mineralogical composition and micro-morphologies is investigated.

2 EXPERIMENTAL

2.1 Materials (Clays Location and geological setting)

The geological setting of the outcropping Middle Cretaceous Wasia Formation with the adjacent formations is shown in Figure 1. The Wasia Formation is exposed in a discontinuous arc from latitude 20°54'N to 30°00'N, for a distance of about 1500 km and a width of about 50 km [10]. The thickness of the Wasia at outcrops increases irregularly but persistently from south (25 to 30 m) to north (about 90 m). Lithologically, the Wasia formation (Middle-Upper Cretaceous) is composed of quartzitic sandstones of thickness varying from 40 to 500 m. The upper part of this formation is composed of impermeable clays or silty clays and kaolinitic deposits, the white Kaolinitic clay in the lower member and at the top of the upper member of the Wasia Formation.

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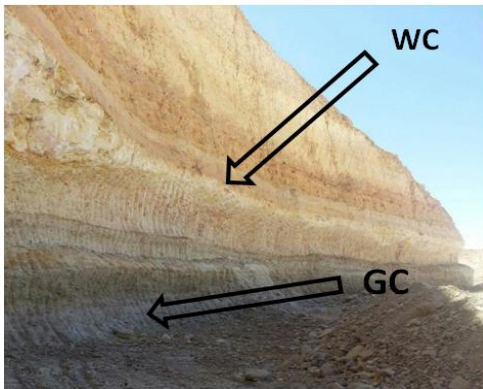


Fig.1. Clays Location

2.2 Methodology

The two clay samples (white, WC & grey, GC) were fired at different temperatures 650,700 and 750°C for 2 h. the mineralogical phase composition/decomposition of the fired clays was performed in order to determine the optimum calcination temperature. Pozzolanic activity the calcined samples were studied on 80% NMK - 20% hydrated lime pastes, mixed using absolute ethanol for 1 h in order to attain complete homogeneity of the mix, (water/solid ratio =1 by mass) at different ages of hydration 7 and 28 days. The phase composition of the hydrated NMK (80%)–CH (20%) pastes was identified using differential scanning calorimetry (DSC). The microstructure of the hardened pastes was studied by means of scanning electron microscopy (SEM), Also, the phase composition/decomposition was studied by means of X-ray diffraction (XRD).

3. Results and discussion

3.1. Mineralogical phase analysis of clays

Fig.2a,b. shows the XRD patterns after calcination at different temperatures as compared to the as received raw clays. The patterns interpretation of the as received raw clays led to identification of the kaolinite phase; furthermore, quartz has been identified in the grey clay. The sharp intense peaks indicate their crystalline nature. After calcination, significant peak broadening ($2\theta=15^\circ-35^\circ$) was occurred which points to the formation of non-crystalline (amorphous) material (i.e. the conversion of kaolinite, $2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$, into metakaolin. In addition, kaolinite peak at ($2\theta=12.41^\circ$) almost disappeared, that suggests a breaking of the bonds between kaolinite layers (001) [2] while quartz is preserved. As it can be seen, the peak broadening increases with increasing the calcination temperature which could be considered as an indication for the increased reactivity [1]. Also it could be noted that, the degree of amorphousness (the degree of disorder in the amorphous phase) of the WC sample seems to be higher than that of the GC. The pozzolanic activity depended on many factors, the most significant of which is the chemical and mineralogical composition of the metakaolin, amorphous phase content, the degree of amorphousness, average particle size (d_{50}) and specific surface area [2].

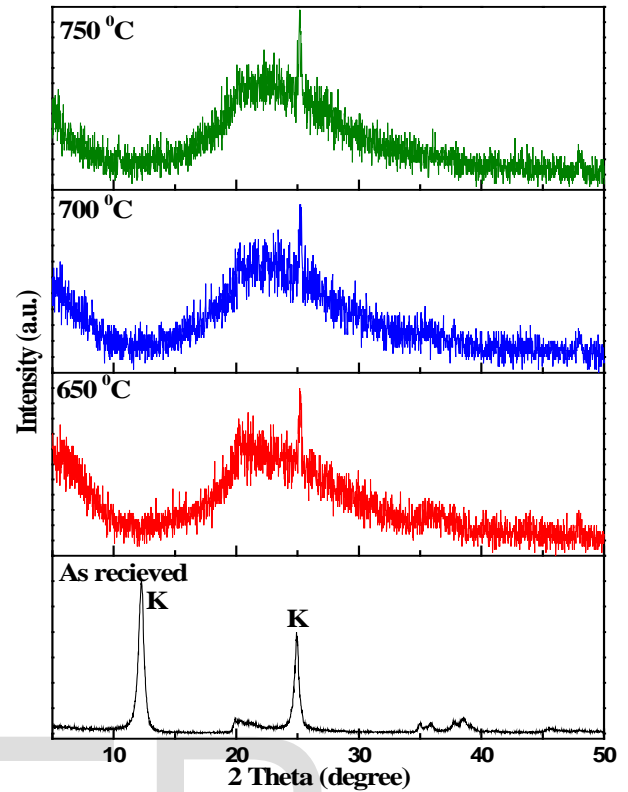


Fig.2.a. XRD patterns of WC sample calcined at different temperatures

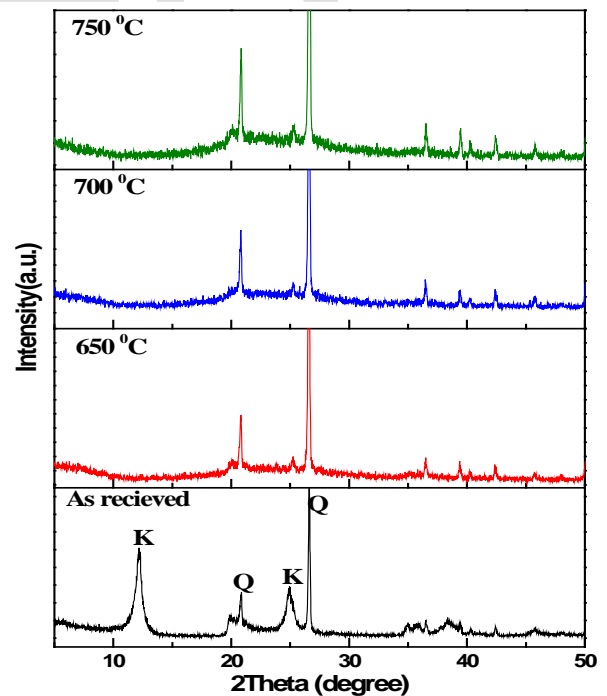


Fig.2.b. XRD patterns of GC sample calcined at different temperatures.

3.2. Micro-morphology characterization

Fig.2. shows the particles micro-morphologies of the as received raw clays and the influence of calcination on their morphologies. The structure of WC sample consisting of thin well crystallized hexagonal layers/plates stacked in parallel fashion.

The plates are characterized by large length to thickness aspect ratio; it is especially favourable in matrix reinforcement. The particle size is variable; although its dimensions in length and width can be measured in hundreds of nanometers, the platelet thickness ranges from 1-100 nm.

The GC sample showed also platy structure however stacked in completely random fashion; furthermore, the individual plates relatively showed less degree of crystallinity. The thermal treatment of the two examined clay samples showed a great modification in particles micro-morphologies. Considerable complete distortion in the platy structure of individual particles of the WC sample was seen, the GC showed less distortion as compared with the WC. This modification of surface micro-morphologies satisfies the transformation into the non crystalline/amorphous state.

3.3. Assessment of pozzolanic reactivity

3.3.1. XRD

The x-ray technique can allow monitoring in time the pozzolanic reaction process of the studied clay samples, XRD patterns of the thermally activated WC and GC blended pastes hydrated up to 7 and 28 days are introduced in fig.3a,b respectively.

The patterns demonstrating intense portlandite (CH) peaks (18° and 34°) for each paste; in Addition, a peak characterizing calcium silicate hydrate (CSH) was identified after 7 days of curing, also it could be noted that unhydrated kaolinite still detected. The XRD patterns are given for comparison of pozzolanic reactivity. As it is clear, the peaks characterizing CH in the GC blended paste is less than that of the WC paste. On the contrary, the intensity of CSH peak for the GC blended paste is higher than that of the WC paste, and this is attributed to the characteristic portlandite consumption of pozzolanic reaction. Furthermore, the amount of unhydrated kaolinite in the GC blended paste is less than that of the WC paste all these phenomena indicate that the GC is more reactive than WC after 7 days of curing.

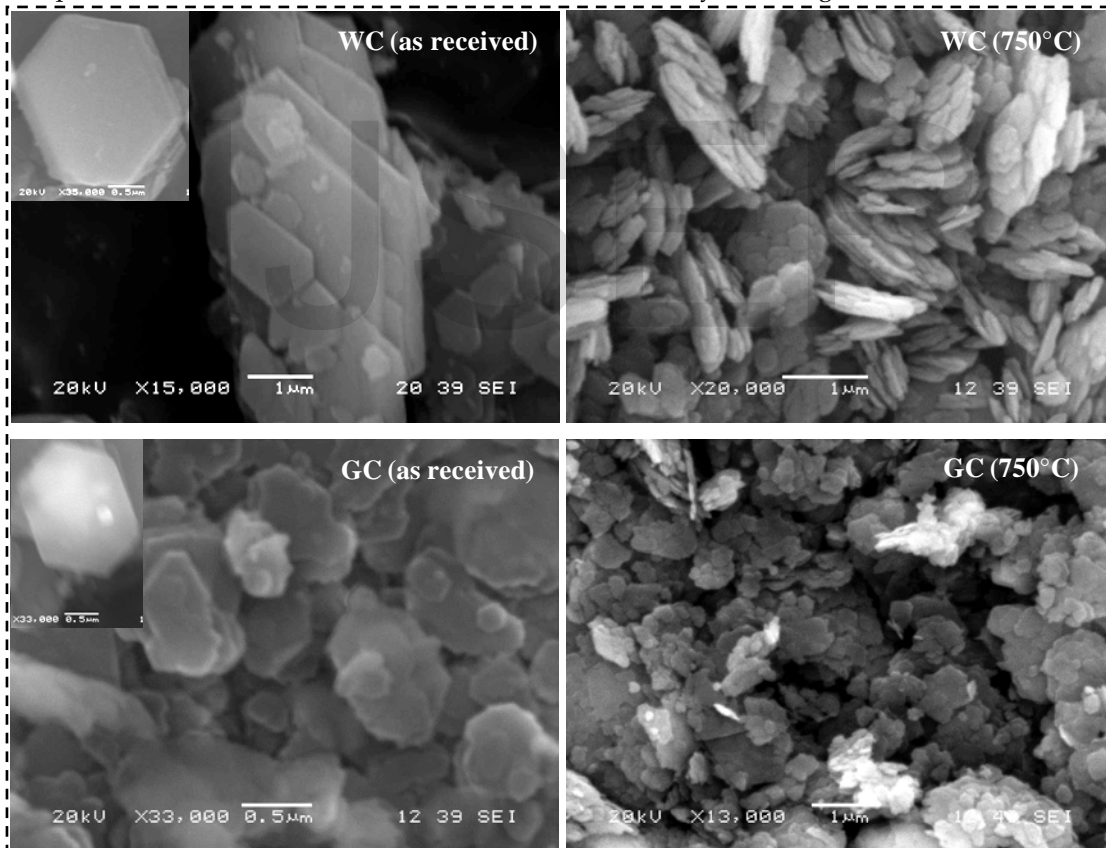


Fig.2. SEM micrographs of the as received raw (WC & GC) samples and the samples calcined at 750°C.

Since, the degree of amorphousness of the WC sample is higher than that of the GC It was thought that it will show higher reactivity than GC. The higher reactivity of the GC may be attributed to the higher content of quartz crystallites which act as nucleation centers for the hydration products and then accelerating the hydration reaction rate in the GC blended paste [3]. At 28 days of hydration more quantity of CH was consumed by the pozzolanic reaction; therefore, the peaks characterizing the CH phase are of very low intensity. Also the XRD patterns at 28days of hydration demonstrate that the GC is of higher reactivity than the WC.

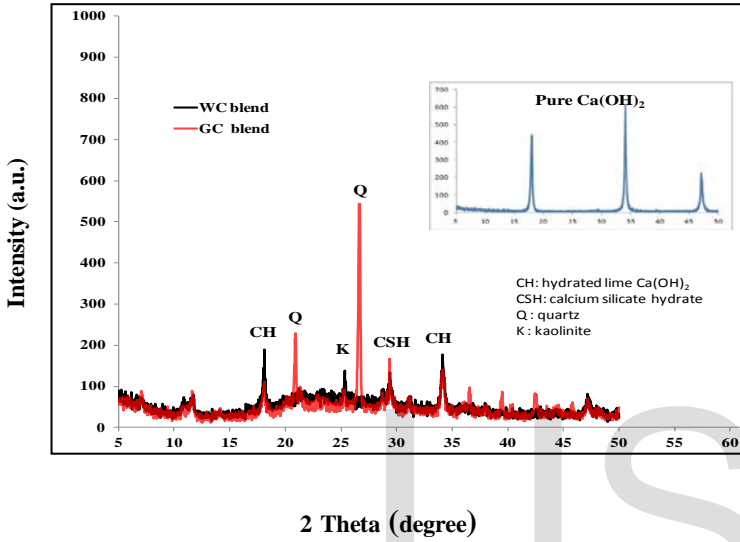


Fig.3a. XRD patterns for the blended clay pastes at 7days of curing.

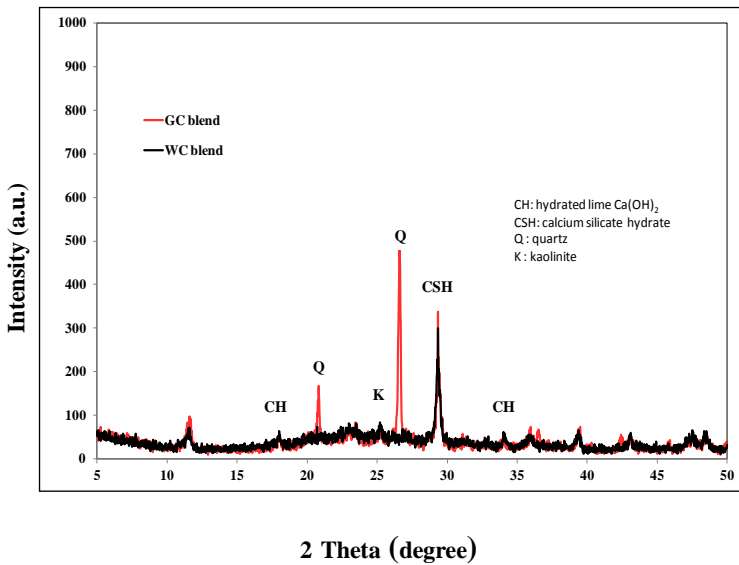


Fig.3b. XRD patterns for the blended clay pastes at 28days of curing.

3.3.2. Differential scanning calaorimetry (DSC)

The results of DSC studies of the two hydrated clay pastes at 7 and 28 days of curing are shown in Figs. 4a,b respectively. Figs. 4a,b indicate two main endothermic peaks characteristic for calcium silicate hydrates (C-S-H) and calcium hydroxide (CH). These DSC thermograms indicated that the reactivity of GC is higher than that of WC. This is clearly understood from the amount of heat required for the decomposition of the C-S-H and CH phases as shown in Table 1. So the DSC results are in good agreement with the XRD study. Evidently, the intensity of the endothermic peak characterizing the free CH phase decreases with age of hydration while the intensity of the endothermic peak characterizing the C-S-H phases increases with age of hydration as shown from the DSC Thermograms at 28days of curing (fig.4b). In addition, the amounts of heat required for the decomposition of CH decreases with the time of hydration as a result of its consumption by the pozzolanic hydration.

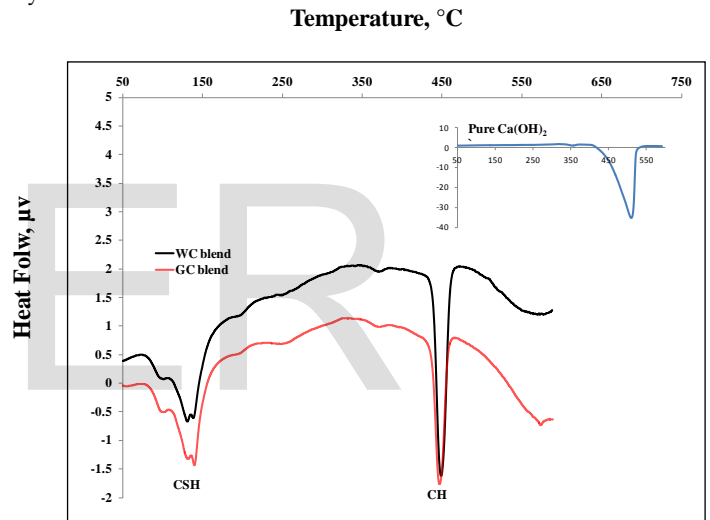


Fig.4a. DSC Thermograms for the blended clay pastes at 7days of curing.

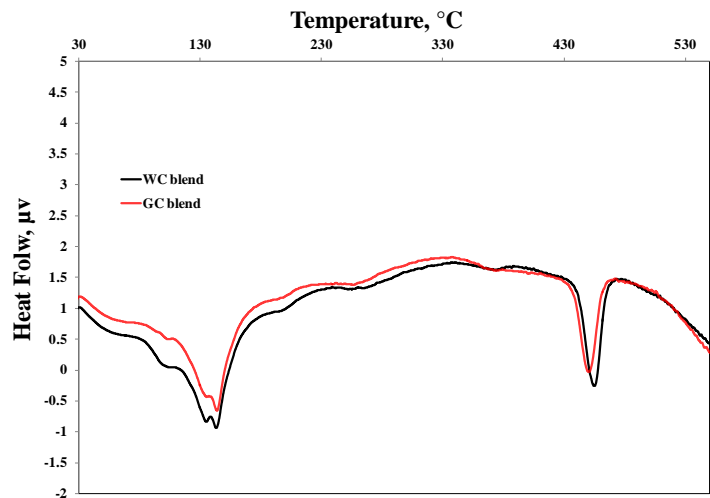


Fig.4b. DSC Thermograms for the blended clay pastes at 7days of curing

Table1. characteristics of the DSC thermograms of WC and GC blended pastes

blends		C-S-H phase		CH phase	
		Decomposition temperature (°C)	Heat (J/g)	Decomposition temperature (°C)	Heat (J/g)
GC blend	7d	105-183	17.32	423-466	11.09
	28d	105 - 179	23.17	425-465	23.13
WC blend	7d	104-184	12.95	422-467	19.19
	28d	108-177	18.74	435-470	28.27

3.3.3. Microstructure characteristics

The microstructure characteristics of both the GC and WC blends at 7days of curing in addition to the pure lime (act as an activator) are introduced in fig.5. As it is clear, CSH phase is identified in the two blends as a result of the pozzolanic reaction; however, its quantity in the GC is relatively higher than that in the WC which confirm that GC is of higher activity than the WC, this is in good agree with the DSC and XRD data. Many unreacted clay grains are present which means that the pozzolanic reaction is in progress and more curing time is needed for complete hydration. After 28 days of curing compact structures of the blends have been observed i.e. approximately all the clay particles are transformed by pozzolanic reaction into CSH with very small quantities of hydrated lime crystals

4 CONCLUSION

Based on the experimental results of this study, the following conclusions can be drawn:

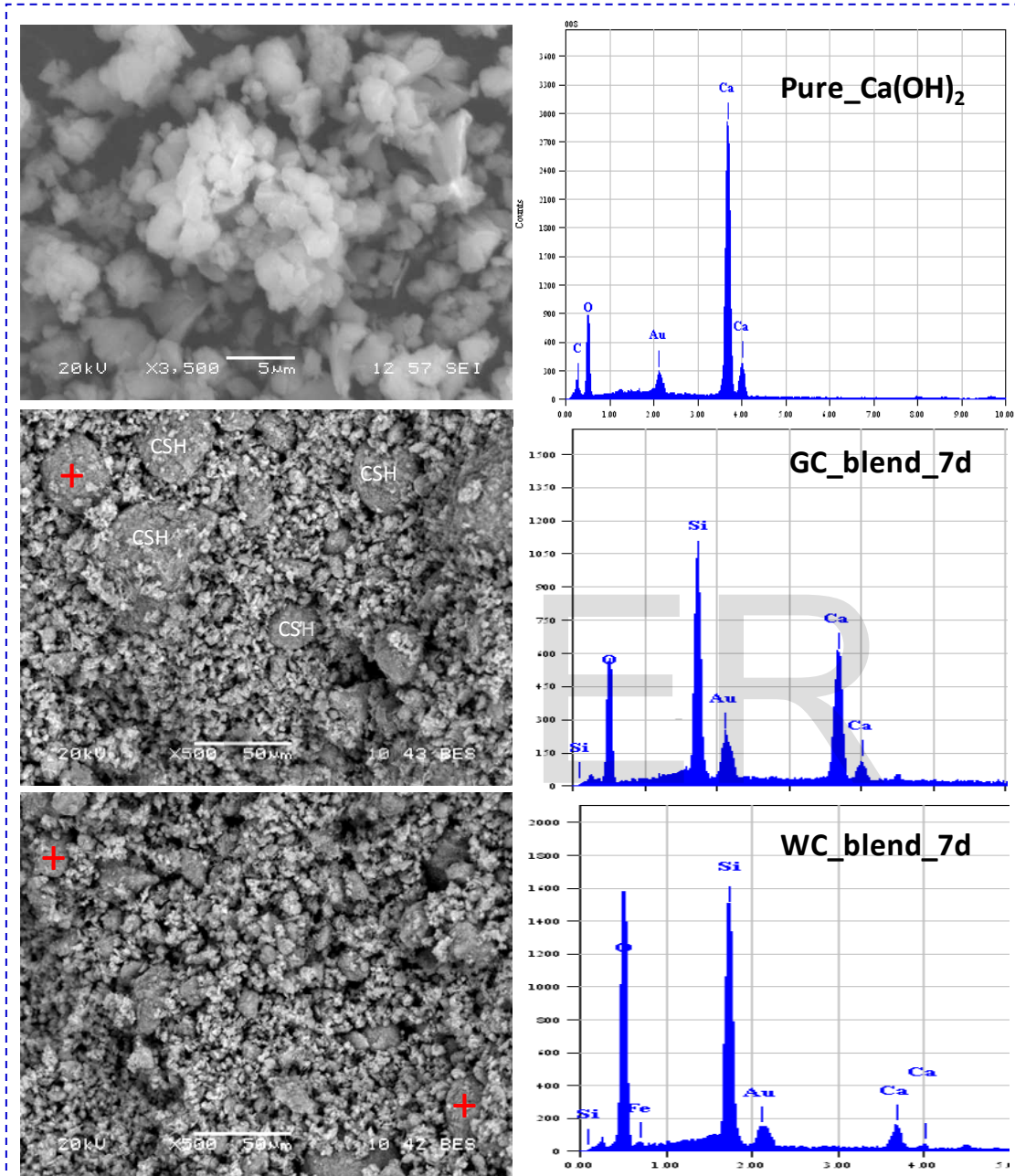
- Thermal activation of clay results in significant modifications in the micro-morphologies.
- The degree of amorphousness (the degree of disorder in the amorphous phase) is increased with increasing the calcination temperature.
- The investigated clays although they are in the same site, they possessed different pozzolanic activities.
- The assessment of pozzolanic activity of clay minerals is of great importance to determining their specific applications in the development of sustainable cementitious materials.

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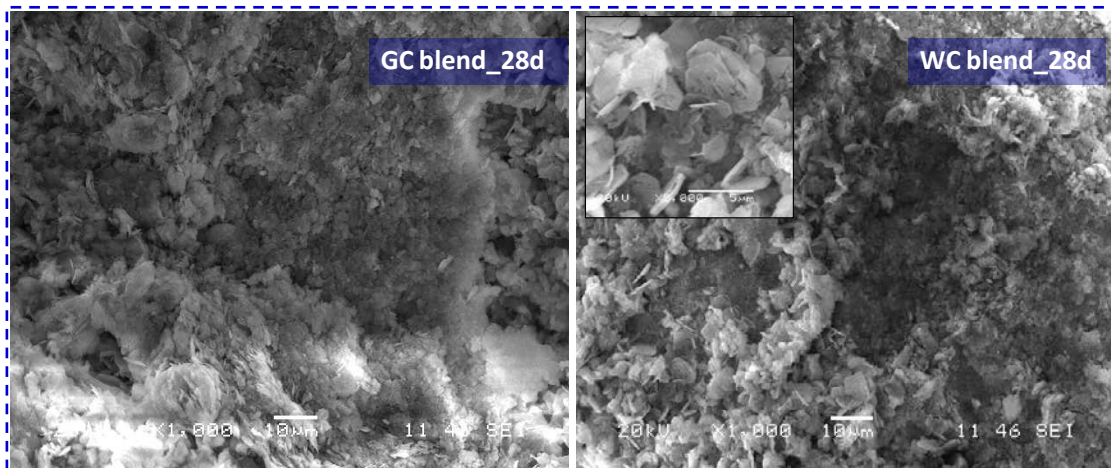


Fig.6. SEM micrographs of GC and WC blends at 28 days of curing

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