



Impact of iron (Fe) phases on the reactivity of calcined clays under reductive conditions

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Abstract Most kaolinitic clays have accompanying minerals such as iron (Fe) phases that impact the color of the material before and after calcination. The pinkish color in the calcined product, resulting after the formation of the phase Hematite, changes the color of the resulting cement. The industry is reluctant to produce a cement with a color other than gray, thus color control techniques need to be implemented. The most common approach to control color is to carry out cooling under reductive conditions to favor the formation of the dark color Fe phase magnetite. This paper evaluates the properties of three different clays with varying Fe_2O_3 content, which have been cooled under reductive conditions. Results prove that for Fe_2O_3 content around 20% (sample C2), there

is a significant drop in specific surface that leads to a poorer reactivity of the calcined product. Mineralogical studies confirm the formation of a new spinel phase, hercynite, which is dark in color. This phase apparently immobilizes part of the alumina of the system and thus cripples the amount of reactive alumina in cement. Mössbauer tests were done to study both valence and the coordination of iron on the product under different cooling regimes. The cooling process under neutral/reducing conditions induces iron reduction from Fe^{3+} to Fe^{2+} state, which impact material coloration. The contribution of hematite is considerably reduced, and ferrous oxide (Fe^{2+}) contributions clearly appear under 3 distinct crystallographic

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environments. Strength results of cement pastes confirm the loss of reactivity of the calcined material.

Keywords Kaolinitic clays · Reactivity · Reductive cooling · Iron phases · Calcination

1 Introduction

The cement industry is facing unprecedented challenges related to its environmental footprint and, despite the efforts in recent years, is still responsible for around 6% of all man-made global carbon emissions [1, 2]. If present development trends continue uninterrupted, it may be responsible for generating 24% of the total world CO₂ emissions by 2050 [3, 4]. The substitution of conventional Portland cement with alternative materials is one of the most promising options to lower the environmental impact and costs of cement manufacturing [5, 6].

Clays, especially from the kaolinite group, appear as a solution to this problem as they are unique among the supplementary cementitious materials [7, 8] because of their wide abundance and the excellent pozzolanic properties shown when calcined under specific conditions [9]. They are mainly composed by aluminosilicates, and they exploit both the filler effect and the pozzolanic reaction to replace Portland cement clinker, enhancing the mechanical and durability properties of concrete [6]. In their natural state, kaolinitic clays have a stable crystal structure that inhibits the release of reactive components [10]. However, during the calcination process, a series of structural and morphological changes occur due to the loss of structural hydroxides, which causes the destabilization of the crystalline structure, the liberation of Al and Si reactive phases and changes in the specific surface. This usually happens at calcination temperatures around 700–800 °C [11].

Due to their complex formation mechanisms, clay deposits are generally composed of a combination of clay types, clay purities and companion minerals, with a great variety of crystallographic structures and chemical compositions [9]. The presence of accompanying phases may cause modifications in the temperature range where dehydroxylation occurs and on the characteristics and properties of the final product [11]. The presence of calcite can reduce the specific surface area and reactivity of calcined clay,

due to the formation of a new phase during reaction between the free lime and metakaolinite, when the decomposition of calcite and kaolinite overlap during the calcination process [12]. Muscovite and feldspar impurities provoke additional sintering of the sample during the calcination process as a result of respectively partial dehydroxylation and pre-fluxing properties [13]. When iron sulfides are present, they transform into other mineral phases through a complex process which involves several simultaneous transformations, that can lead to the formation of hematite and the release of SO₂, toxic gas [14].

It is also common for clays to contain iron mineral phases such as hematite, magnetite, maghemite, goethite, lepidocrocite and ferrihydrite, in addition to structural iron in clay minerals [15]. Recent studies reveal that amorphous iron phases can have a beneficial effect in the pozzolanic reactivity [16]. On the other hand, the presence of these minerals, especially hematite (Fe₂O₃), can impart a pinkish coloration to the calcined clay and, consequently, to the “blended cement” [10]. The oxidation state and percentage of the iron present in the raw clay, the susceptibility of iron phases to oxidation–reduction reactions and the availability of oxygen throughout the calcination process can influence in the color development of calcined clays [17, 18] varying from pinkish to shining red.

In the cement industry, color is treated as a quality parameter that responds to technical, regulatory, and market factors, historically showing a preference for gray tones in its products. Gray cement is traditionally associated with quality and consistency, while colors in different shades of red are perceived as contaminated or lower-quality products, which generates rejection in consumers [19]. This perception is reflected in international standards, which do not explicitly prohibit the color red; but establish chemical parameters that indirectly limit its appearance [20]. Furthermore, the variability in the geological origins of clay minerals generates differences in the contents of iron phases that may be present, which results in a spectrum of red tones that prevents the manufacture of a consistent colored cement [21] and limits its applicability in design projects, where aesthetics are a key factor [22]. A group of scientists proposed a way to obtain a dark color calcined clay by regulating the atmosphere during the calcination, especially during the cooling process [17]. When



temperatures rise above 650 °C, magnetite is the main iron phase formed, regardless of the presence of oxygen [23–26]. However, if the material reaches temperatures below 600 °C while cooling in a reducing atmosphere, magnetite will prevail, providing a black color to the final product [17, 25, 26].

The strategy for color control treatments focusses on promoting a reducing atmosphere during cooling to favor the formation of magnetite rather than hematite [17]. Patented systems, that allow a homogeneous grayish color, have been developed based on exhaustive studies in pilot plants, where the performance of different clays is evaluated under various conditions [27]. Another innovative method that has been implemented is injection of vaporized fuel into the kiln discharge area, where the residual temperature causes auto-combustion, consuming the available oxygen and generating an atmosphere rich in CO and CO₂, which results in a dark colored clay [17].

The present investigation aims to evaluate the influence of color control treatments on the mineralogical and morphological properties and pozzolanic reactivity of calcined clay.

Table 1 Chemical composition using X-ray fluorescence (XRF)

Oxides (wt%)	A1-R	C2-R	C3-R
LOI	16.30	13.20	7.34
SiO ₂	45.31	36.38	69.13
Al ₂ O ₃	18.24	22.99	19.01
Fe ₂ O ₃	6.22	20.52	1.42
CaO	6.62	0.24	0.37
MgO	1.27	0.01	0.09
MnO	0.03	4.80	0.01
SO ₃	2.40	0.06	0.12
K ₂ O	1.81	0.26	1.41
Na ₂ O	0.77	0.10	0.07
TiO ₂	0.76	0.94	0.90
P ₂ O ₅	0.19	0.25	0.07
V ₂ O ₅	0.06	0.13	0.04
Cr ₂ O ₃	0.03	0.12	0.01

2 Materials and methods

2.1 Materials

Three distinct clay samples, designated A1, C2, and C3, were sourced from different geological deposits, each one exhibiting unique chemical profile shown in Table 1. Sample C2 exhibits the highest kaolinite content (45.7%) as well as iron oxide content (20.52%). Sample A1 is characterized by a kaolinite content of 37.0%, a medium to low iron oxide (Fe₂O₃) concentration (6.22%), and presents calcium oxide (6.62%). Sample C3 is the one with the simplest mineralogical

Table 2 Chemical composition and physical properties of LC3 system components

Components	OPC	Gypsum	Limestone
<i>Oxides (wt%)</i>			
LOI	1.43	21.70	41.40
SiO ₂	21.00	0.69	1.16
Al ₂ O ₃	5.50	0.15	0.22
Fe ₂ O ₃	2.63	0.09	0.18
CaO	63.70	35.00	55.30
MgO	1.51	0.57	0.98
MnO	0.06	0.01	0.01
SO ₃	2.91	41.7	0.01
K ₂ O	0.80	0.10	0.17
Na ₂ O	0.04	0.01	0.01
TiO ₂	0.28	0.01	0.01
P ₂ O ₅	0.17	0.01	0.54
V ₂ O ₅	0.01	0.01	0.01
Cr ₂ O ₃	0.01	0.01	0.01
<i>Phases (wt%)</i>			
C ₃ S M ₃	67.50	–	–
C ₂ S beta	14.80	–	–
C ₃ A cubic	2.50	–	–
C ₃ A orthorhombic	2.00	–	–
C ₄ AF	11.60	–	–
Calcite	1.60	0.60	99.40
Gypsum	–	95.30	–
Dolomite	–	2.70	–
Quartz	–	1.50	0.60
<i>Physical properties</i>			
BET SSA (m ² /g)	1.31	3.18	3.64
D10 (μm)	1.10	1.10	0.50
D50 (μm)	10.3	5.90	5.70
D90 (μm)	40.1	48.0	36.1

composition and has 37.5% of kaolinite. The characterization of the components used for the preparation of LC3 systems is shown in Table 2.

2.2 Experimental methods

2.2.1 Characterization of raw and calcined clays

Rietveld analysis was used to determine crystalline phases of materials from X-ray diffraction (XRD) diffractograms. A rutile external standard method was applied in order to obtain the absolute mass fractions of the crystalline phases according to [28]. A Bragg–Brentano configuration in a Panalytical X'pert pro diffractometer working at 40 kV and 40 mA with a CuK α X-ray tube and an X'celerator detector for recording the diffracted X-ray intensity signal was used. The measurements for clay samples were carried out at an angular range of 4–60° 2 θ with a step size of 0.0167° and an equivalent scan speed of 0.0356°/s, corresponding to a total measurement time of about 28 min. A similar step size and scan speed were used between 5 and 70° 2 θ and the total measurement time was 31 min for cement, limestone and gypsum. In both cases an incidence slit of 1/4°, a divergence slit of 1/8° slit and a beam knife were used. Rietveld refinement was conducted using the HighScore Plus v4.8 software. Chemical composition (XRF, Table 1) was used to calculate the X-ray mass absorption coefficient (MAC) used in the external standard method.

Thermogravimetric analysis (TGA) was carried out for all calcined clays. Equipment from NETZSCH (STA 449F5) was used. About 50 mg of sample was placed in open alumina crucibles and then heated at a rate of 10 °C/min from 30 to 1000 °C. The step-wise method was used to determine the mass loss during kaolinite dehydroxylation with the first derivative of the mass loss curve (DTG) being used to precisely determine the temperature range (usually between 350 to 600 °C). The measurement cell was flushed with 50 mL/min nitrogen gas. A similar protocol was used for all TGA measurements.

The particle size distribution (PSD) of all calcined clay samples was assessed by laser diffraction using Betsizer S3 from 3P instruments. A dispersion time of 3 min in isopropanol at a speed of 2000 rpm was used. Specific surface area (SSA) was measured by the BET method using equipment from 3P

instruments. Approximately 5 g of sample was first degassed for 16h at 40 °C under a N₂ flux and afterwards an average of three BET measurements was taken.

The qualitative and quantitative studies of both the valence and the coordination of iron were performed using ⁵⁷Fe Mössbauer spectroscopy [29]. Measurements were done at room temperature in a transmission geometry and constant acceleration mode in the range of $\pm 125 \text{ mm s}^{-1}$. The velocity scale was calibrated with a ⁵⁷Co Rh matrix source and a metallic iron foil. The evaluation of the Mössbauer spectra was performed by the least-square fitting of lines using the WinNormos-for-Igor (version 7, Wissel) program. The experimental error on ⁵⁷Fe Mössbauer spectra was $\pm 0.1 \text{ mm s}^{-1}$.

Optical absorption spectra were recorded with a spectrometer Lambda 1050 from Perkin-Elmer using two light sources: a deuterium lamp for the range 200–320 nm and a W-halogen lamp for the range 320–3300 nm and three detectors: a photomultiplier from 200 to 860 nm; a photodiode InGaAs from 860 to 2500 nm and a photoconductor from 2500 to 3300 nm. Spectra were recorded on the range 200–2500 nm; which is adequate for identifying Fe³⁺ transition (UV domain) and Fe²⁺ transition NIR domain. In the spectrophotometric analysis, the colorimetric CIE L*a*b* parameters were calculated from the optical absorption spectra registered on powder with a C-based code using D65 illuminant and CIE 1931 2° observer provided by the CIE recommendations. *L** describes the brightness of the color (*L**=0 for black; *L**=100 for white), *a** describes the red (*a**=120) green (*a**=−120) component and *b** describes the yellow (*b**=120)-blue (*b**=−120) component of the color.

The morphology of the clay specimens calcined with and without color control was analyzed using SEM. The analysis was carried out on a Zeiss Supra 55 equipped with a Schottky-emitter electron gun operating at an acceleration voltage of 5 kV. A 5 nm tungsten coating was used due to the availability of the equipment. Morphology is reported at a magnification of 20,000.



2.2.2 Preparation and characterization of cement pastes

The LC3 binders were prepared using a 50 wt% OPC, 30 wt% calcined clay, 15 wt% limestone and 5 wt% gypsum. The powders were dry-mixed for about 1 min before the addition of water at a water to binder ratio of 0.5, after which paste mixing was done using a TURBULA mixer (IKA MINISTAR) for 2 min at 1600 rpm. This mixing condition was applied to ensure homogeneous dispersion of particles and reproducible consistency.

For the preparation of OPC reference pastes, 100% OPC was used with a water to binder ratio of 0.5. The same mixing protocol was followed.

Specimens for XRD and TGA were cast in rubber molds with a height of about 90 mm, and a diameter of 30 mm to match the diameter of the XRD samples holder. The samples were demolded after 1 day and the first measurements were carried out immediately (as described below). Samples for later ages were cured in 40 ml HDPE bottles. A small piece of the specimens was cut, crushed and placed at the bottom of the curing bottles to act as a sacrificial sample to avoid leaching from the actual specimen. At the designated ages (1, 3, 7 and 28 days) 3 mm discs were cut for XRD and TGA measurements. The top and bottom samples were discarded.

For TGA of cement paste, hydration was stopped using solvent exchange with isopropanol as recommended in [30]. A disc of about 3 mm (cut at the required age) was immersed in 30 ml of isopropanol for a total of 7 days. The isopropanol was replaced after 1 day and 3 days. The discs were then stored in a desiccator with silica gel beads and under vacuum for 7 days to evaporate the isopropanol while minimizing the potential of carbonation. At the time of measurement, the slices were gently crushed and ground to fine powder. A similar protocol to the one used for powder clay samples was used (a heating rate of 10 °C/min from 30 to 1000 °C).

Qualitative and quantitative studies of hydrated paste samples were performed by XRD following the same measurement parameters described above section for clay samples. Diffractograms were recorded on stopped hydration samples at 1, 3, 7, and 28 days.

TGA–DSC measurements of hydrated pastes were performed following the same protocol described in above section for clay samples, using a heating rate

of 10 °C/min from 30 to 1000 °C. The mass losses associated with different hydrate phases (ettringite, C–S–H, AFm, portlandite) were identified from the DTG curves.

For the determination of the pozzolanic reactivity of the calcined clays by isothermal calorimetry, the specifications followed are established in the ASTM C1897-20 standard “Standard Test Methods for Measuring the Reactivity of Supplementary Cementitious Materials by Isothermal Calorimetry and Bound Water Measurements” [31], using the isothermal calorimetry protocol, also known as R3 protocol. Once the components were weighed in the proportions specified in the standard, the pastes were mixed using a high-speed mixer at 1600 rpm for 2 min. For the test according to the isothermal calorimetry protocol, TAM Air 3238 and Calmetrix I-Cal 8000 isothermal calorimeters were used indistinctively. The pastes were introduced in the calorimeter, where they remained for a period of 7 days (168h) at 40 °C.

To evaluate the influence of calcined clays in the hydration kinetics of a mixed system, isothermal calorimetry tests were carried out, for which 50 wt% OPC, 30 wt% calcined clay, 15 wt% limestone and 5 wt% gypsum with a water / solid ratio = 0.5 pastes were made, and 100% OPC pastes were prepared as a reference. The pastes were mixed at 1600 rpm for 2 min. A TAM AIR 3238 calorimeter was used and the readings were performed for 120h at 20 °C.

Compressive strength tests were performed on standard mortars. Specimens were demolded after 24h and cured in water at 20 ± 2 °C until testing at 28 days. Results are reported as the average of three specimens.

2.3 Experimental design

The raw clays were dried at 200 °C and were reduced to particle size smaller than 236 μ m. The calcination was carried out in a Tryte Technologies TR-MFL7301 programmable laboratory furnace heating the sample from ambient temperature up to 800 °C. The heating rate was set at 10 °C per minute and the time of residence at high temperature was 60 min. When the calcined clay was cooled down in air atmosphere, a normal calcined clay was obtained (NC). However, when it was cooled down in a reducing atmosphere, the final product was a color controlled clay (CC).



The reductive conditions were achieved by placing charcoal inside the furnace chamber to exhaust the oxygen in the interior. After calcination, the samples were ground to a sieve residue $R_{45\mu m}$ of $\sim 20\%$. A total of 6 series were obtained.

In order to assess if there was an influence on the calcination conditions, sample C2 with the highest iron content, was submitted to different calcination regimens, varying the calcination temperature (700 °C, 800 °C) and residence time (20 min, 60 min). The reductive cooling conditions were also applied. A total of 8 series were obtained.

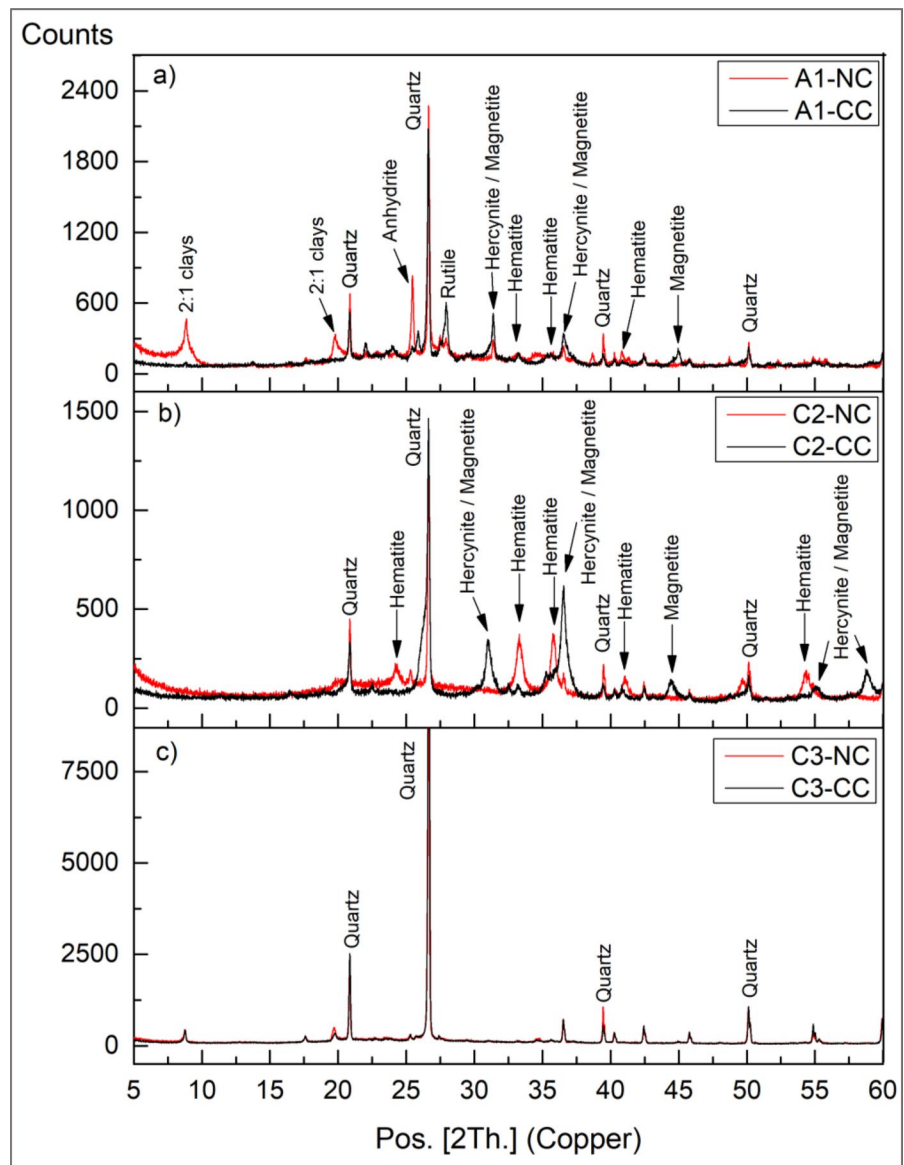
3 Results

3.1 Changes in physico-chemical properties due to color control

3.1.1 Phase assemblage changes

Figure 1 shows the diffractograms of the normally calcined clay (NC) and the color control clay (CC) for the three samples. Independently of the calcination protocol followed, the kaolinite peak is absent in all diffractograms, which indicates that the temperature

Fig. 1 X-ray diffractograms of clay samples under study, comparing normal calcination (NC) and color control (CC). The '2:1 clays' label indicates muscovite/illite peaks, which overlap due to structural similarity. **a** Sample A1; **b** Sample C2; **c** Sample C3



used was sufficient to cause the dehydroxilation of the clays. Also, the graphite phase was not identified in the diffractograms of any of the samples (A1, C2, C3) subjected to color control; indicating that the disproportion of $CO_{(g)}/CO_{2(g)}$, gases generated in the furnace's atmosphere due to the calcination protocol followed, was not significant enough to promote carbon deposition on the calcined clay [32]. Consequently, the dark coloration observed in these samples cannot be attributed to the presence of carbon, but rather to other phase transformation occurring during calcination.

Sample C3 exhibits narrow peaks with high intensity, proof of its simpler mineralogical composition, and there is no significant variation in the results when comparing between NC and CC series.

Samples A1 and C2 exhibit wider peaks with lower intensities in the diffractograms, indication of a more disordered crystalline structure and a more complex mineralogical composition. There are evident differences between NC and CC series in both cases. The formation of spinel iron phases (magnetite/hercynite) instead of hematite when color control treatments are applied is evident for both clays, more noticeable for C2 due to the higher amount of iron oxide in the raw sample. This transformation occurs because under oxygen-deficient conditions, the reaction pathway diverges, leading to the preferential formation of ferrous iron-containing spinels [33, 34]. The ferrous oxide (FeO) resulting from the reduction of ferric oxide (Fe_2O_3) reacts preferentially with alumina (Al_2O_3) from metakaolin to form hercynite ($FeAl_2O_4$) [35]. Also note the disappearance of the 2:1 clay peak in A1-CC sample could be related to the presence of Fe^{3+} substitutions in the structure of muscovite and illite, as both are present in the raw clay. It is well documented that structural iron in clay minerals such as illite and muscovite can be reduced under reducing conditions, destabilizing the crystalline lattice [36, 37]. The Fe^{2+} released from this reduction, along with that from hematite reduction, may react with alumina from metakaolin to form hercynite, while the collapsed 2:1 clay structure may transform into a vitreous phase.

Another structural change, unrelated to the Fe phases, occurs in sample A1-CC and it consists in the decrease of the intensity of the anhydrite peak in A1-CC. This could be a consequence of the reducing atmosphere, which may induce the carbothermic

reduction of anhydrite ($CaSO_4$) to form calcium sulfide (CaS) [38, 39]. However, the presence of CaS was not confirmed by XRD, suggesting it may be present in low quantities, be poorly crystalline, or that the anhydrite partially decomposed under the thermal treatment.

It is also worth noting a slight increase in the intensity of the rutile (TiO_2) peaks in the A1-CC sample compared to A1-NC. This increment could be attributed to the catalytic effect of ferric oxide (Fe_2O_3) on the transformation of anatase to rutile, which is promoted under reducing conditions [40]. The presence of iron, even in trace amounts, has been reported to significantly lower the activation energy for the anatase-to-rutile phase transition, facilitating this transformation at temperatures around 700–800 °C. Additionally, the reducing atmosphere may favor the formation of rutile over other titanium oxide phases, as rutile is the thermodynamically stable polymorph of TiO_2 at high temperatures [41]. This is consistent with the observation that the A1 sample, which contains a moderate amount of iron oxide (6.22% Fe_2O_3 , Table 1), exhibits this effect more clearly than C2, where the high iron content may lead to the formation of other Ti-bearing phases such as iron titanates (e.g., $FeTiO_3$) [42].

Table 3 illustrates the mineralogical composition of sample C2 after a quantitative analysis of the XRD results. In the color control series, the presence of both spinel phases, magnetite and hercynite, is confirmed however the highest percentage corresponds to hercynite. Results of A1 with and without color control (Table 3) show lower amounts of hercynite and magnetite. This is due to the lower iron oxide content of A1 compared to C2 (Table 1). The difference in observed hercynite quantities between A1 and C2 makes it clear that the amount iron oxide in each raw clay had a direct bearing on the formation of hercynite. This observation is consistent with previous studies on iron-rich kaolinitic systems, where higher Fe_2O_3 content promotes spinel phase formation under reducing conditions [34, 43, 44].

Sample C2 was further analyzed due to its high Fe_2O_3 content which facilitated the observation of the transformation of hematite into hercynite at different calcination conditions. In Fig. 2 the diffractograms for this clay, calcined varying temperatures and residence time, are shown. The disappearance

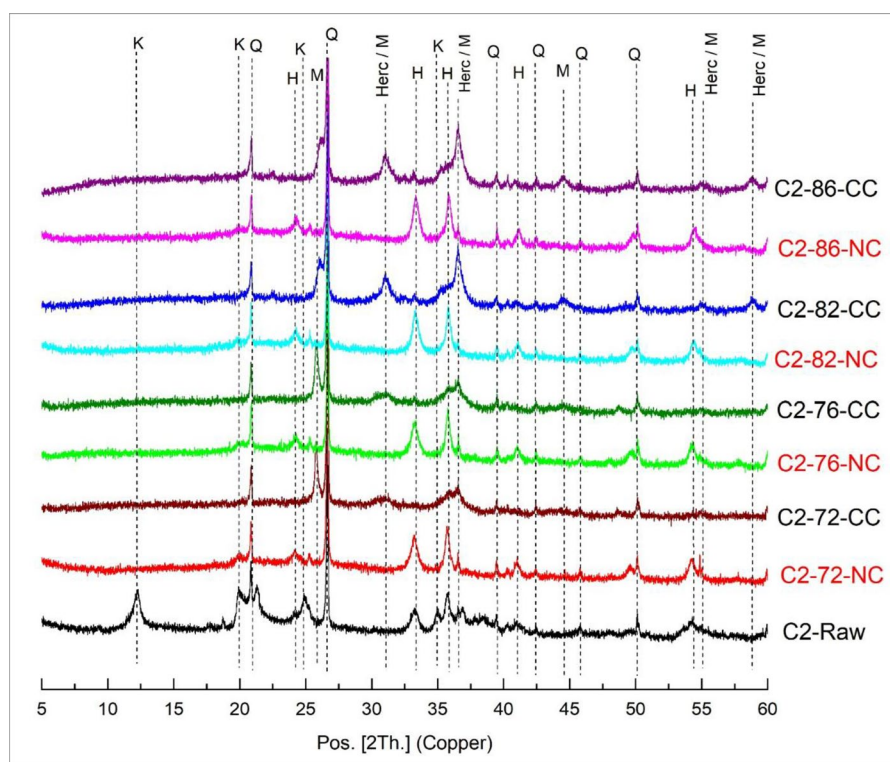


Table 3 Mineralogical composition of A1 and C2 samples

Phases (wt%)	A1-Raw	A1-NC	A1-CC	C2-Raw	C2-NC	C2-CC
Quartz	20.6	19.2	20.1	21.0	22.8	17.2
Kaolinite	24.1	—	—	56.6	—	—
Illite	13.3	7.2	2.6	3.80	—	—
Muscovite	15.4	6.2	—	—	—	—
Hematite	3.1	4.4	1.1	8.90	22.1	2.70
Goethite	—	—	—	9.70	—	—
Hercynite	—	—	3.4	—	—	20.5
Magnetite	—	—	0.2	—	—	1.50
Calcite	11.7	—	—	—	—	—
Gypsum	6.1	—	—	—	—	—
Anhydrite	—	4.4	3.2	—	—	—
Rutile	1.9	1.5	2.3	—	—	—
Amorphous	3.8	57.2	67.0	— ^(*)	55.2	58.1

^(*)Not quantifiable due to mineralogical complexity or below detection limit

Fig. 2 Diffractograms of sample C2 calcined varying temperature and residence time. (7:700 °C; 8: 800 °C; 2: 20 min; 6: 60 min; NC: Normal Calcination; CC: color control). (K: kaolinite, Q: quartz, H: hematite, M: magnetite, Herc: hercynite)

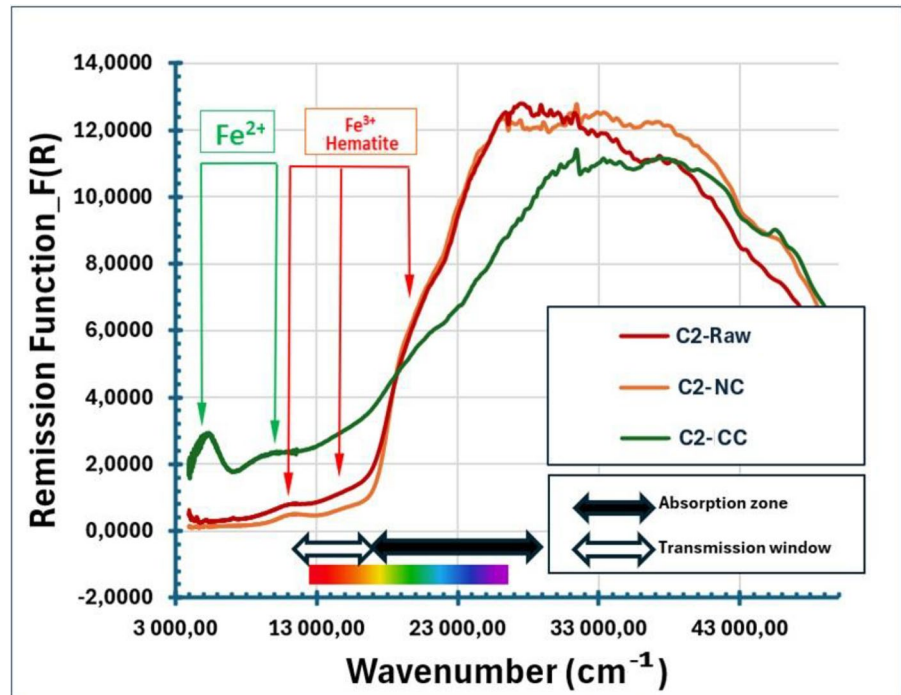


of the kaolinite peak is evident in all calcined samples, regardless of the calcination protocol followed. There is clear evidence of disappearance of hematite peak and formation of magnetite and hercynite in CC samples. The residence time has no apparent effect on the transformation, but calcination temperature does favor the occurrence of hercynite/magnetite, which

increases with the raise of the temperature. This temperature-dependent behavior is consistent with the thermodynamic stability of hercynite, which is favored at higher temperatures under reducing conditions [43, 45].

Figure 3 gives the remission function $F(R)$ versus the wavenumber (cm^{-1}) and shows a remarkable

Fig. 3 Optical absorption spectra of raw clay (C2-Raw), normally calcined clay (C2-NC) and color control clay (C2-CC)



contrast in optical characteristics of the sample C2. The natural clay (C2-Raw) and the normally calcined (C2-NC) show similarly two relatively weak absorption bands in the near IR and Red-VIS at 11,000 and 15,000 cm^{-1} , followed by a huge absorption band in the UV region, centered on 20,000 cm^{-1} . The absorption bands correspond to transition $E_g \rightarrow T_{2g}$ of Fe^{3+}

in octahedral site, coherent with hematite, and the intense one is corresponding to a charge – transfer $\text{Fe}^{3+}-\text{O}$. In other words, the huge absorption in the UV-mid VIS region means violet, blue and green radiations are absorbed, leaving a transmission window for orange-red radiations. This explains the red

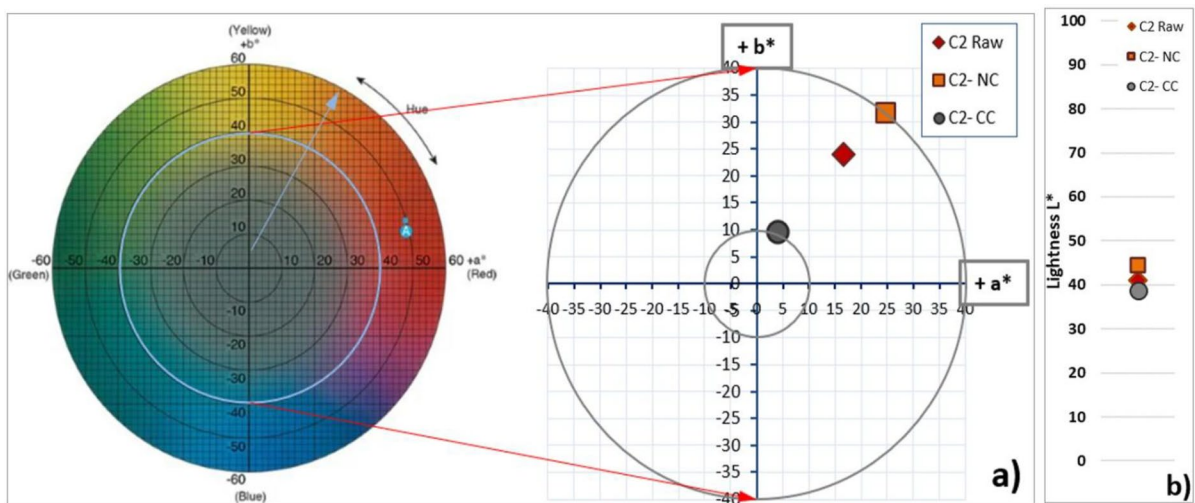
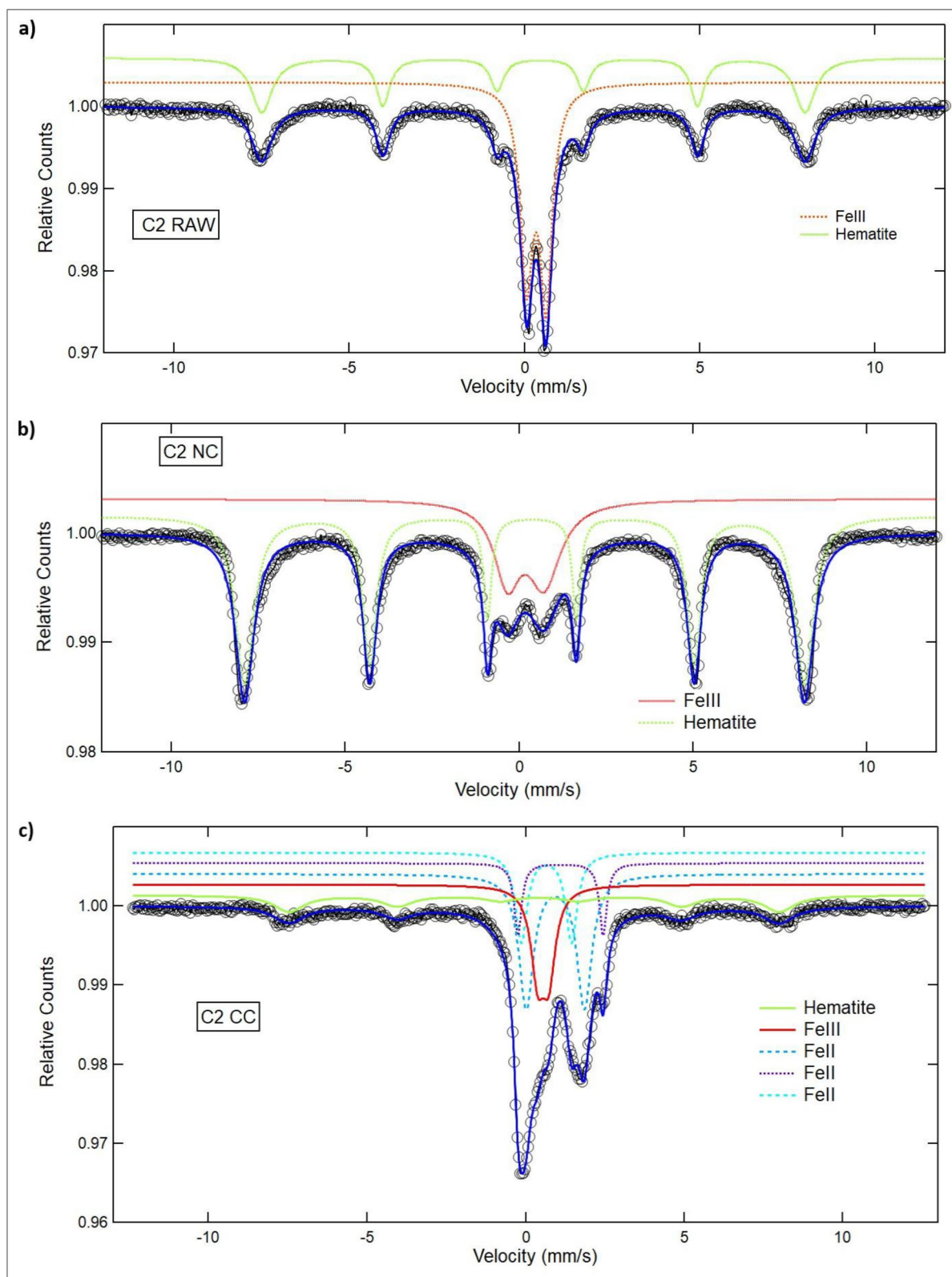


Fig. 4 Spectrocolorimetric characteristics of the sample C2: **a** colored plan (a^* , b^*); **b** Lightness scale



◀**Fig. 5** ^{57}Fe Mössbauer spectra, recorded at room temperature (293 K) of: **a** raw clay (C2-Raw), **b** normally calcined clay (C2-NC), **c** color control clay (C2-CC)

color of these two samples which are driven by ferrous oxide present as hematite.

The sample C2-CC exhibits a notably weaker overall slope compared to the previous samples, suggesting partial light absorption across the entire wavelength range, which explains the grey color of this sample. This change in the slope is due to the vanishing absorption bands linked to Fe^{3+} with a correlative appearance of Fe^{2+} (ferrous iron) absorption bands at 5000 and 10,000 cm^{-1} . This spectral signature is very coherent with Fe^{2+} in hercynite [46].

The calculated values from DRS data are plotted in the 1939 CIE $L^* a^* b^*$ color space. Figure 4 is giving the positions of the samples in the colored plan (a^*-b^*). The evolution of the colorimetric characteristics of the representative points clearly shows the trend from relatively saturated colors (C2-Raw and C2-NC) toward undersaturated color (C2-CC), hence expressing the grey color (Fig. 3a). Correlatively, the lightness factor (L^*) is decreasing from more than 44 to 39%, indicating a dominant grey color (Fig. 4b).

Mössbauer spectra of all samples are shown in Fig. 5a, b and c. All samples exhibit sextuplets and doublets with varying intensities. The spectrum of C2-Raw is dominated by a doublet whose parameters ($\text{IS}=0.33$; $\text{EQ}=0.55$) are coherent with isolated Fe^{3+} ions in a tetrahedral coordination site. The remaining spectrum exhibits a sextuplet whose parameters ($\text{IS}=0.35$; $\text{EQ}=0.19$) correspond to ferric iron engaged in hematite structure. The relative proportions of these species are 54 and 46% respectively.

In the calcined clay without color control C2-NC, the proportion of hematite increases with a correlative decrease of isolated ferric iron. Its corresponding parameters ($\text{IS}=0.20$; $\text{EQ}=0.99$) and the band width at half height (FWHM) are coherent with isolated ferric iron in an octahedral coordination site. In the calcined clay with color control C2-CC, the contribution of hematite is considerably reduced with a relative area passing from 72% in C2-NC to 18% in C2-CC. Correlatively, ferrous oxide (Fe^{2+}) contributions clearly appear under three distinct crystallographic environments according to the Mössbauer parameters, shown in Table 4.

The three Fe^{2+} environments identified in the C2-CC sample (Table 4) are assigned as follows, based on parameters from the literature [43, 46]:

1. Environment 1 ($\text{IS}=0.93$ mm/s, $\text{EQ}=1.82$ mm/s, 35%): Fe^{2+} in tetrahedral site in the hercynite structure.
2. Environment 2 ($\text{IS}=1.09$ mm/s, $\text{EQ}=2.69$ mm/s, 9%): Fe^{2+} in distorted octahedral site, possibly in magnetite or in an iron-rich spinel phase.
3. Environment 3 ($\text{IS}=0.65$ mm/s, $\text{EQ}=1.58$ mm/s, 18%): Fe^{2+} in an amorphous or vitreous phase, suggesting incorporation of reduced iron into the silicate network, consistent with XRD results showing high amorphous content (58.1%) in C2-CC.

The coexistence of these three environments indicates that the reduction of Fe^{3+} to Fe^{2+} during cooling under reducing conditions is not limited to the formation of crystalline spinel phases, but also involves the incorporation of Fe^{2+} into the amorphous phase, which could additionally affect the material's reactivity.

3.1.2 Physical changes

Figure 6 presents a relation between the specific surface area (SSA) and particle size distribution (PSD). Sample C3 shows a slight increase of around 11% in D_{90} , and a decrease of approximately 22% in SSA when color control techniques are applied. However, these changes are notably more for samples C2 and A1, with a complex mineralogical composition. They exhibit a significant drop in the specific surface of 94.57 and 96.12% in their respective color control series, due to the presence of magnetite and hercynite that have smaller SSA than hematite [47, 48]. In addition, there is also an increase in particle size of 49.65 and 132.89% respectively, that could be related to the presence of spinel phases and the fluxing effect of iron phases [49]. This phenomenon is more intense for sample A1, because of the dehydroxylation of the 2:1 clays during color control treatments causing more agglomeration in the calcined clay [50].

Table 4 Mössbauer parameters (IS: Isomer Shift, EQ: Quadrupole Splitting, FWHM: Full Width at Half Maximum, B(T): Magnetic Hyperfine Field, A%: Abundance)

Parameters	IS (mm.s ⁻¹)	EQ (mm.s ⁻¹)	FWHM	B (T)	A%	Interpretation
C2-Raw	0.33	0.55	0.43	48.1	54	Fe ³⁺ Tetrahedral
	0.35	0.19	0.45		46	Hematite
C2-NC	0.20	0.99	0.83	50.25	28	Fe ³⁺ Octahedral
	0.26	-0.21	0.35		72	Hematite
C2-CC	0.36	-0.15	1.15	48	18	Fe ³⁺
	0.55	0.35	0.51		20	Fe ³⁺
	0.93	1.82	0.56		35	Fe ²⁺
	1.09	2.69	0.30		9	Fe ²⁺
	0.65	1.58	0.44		18	Fe ²⁺

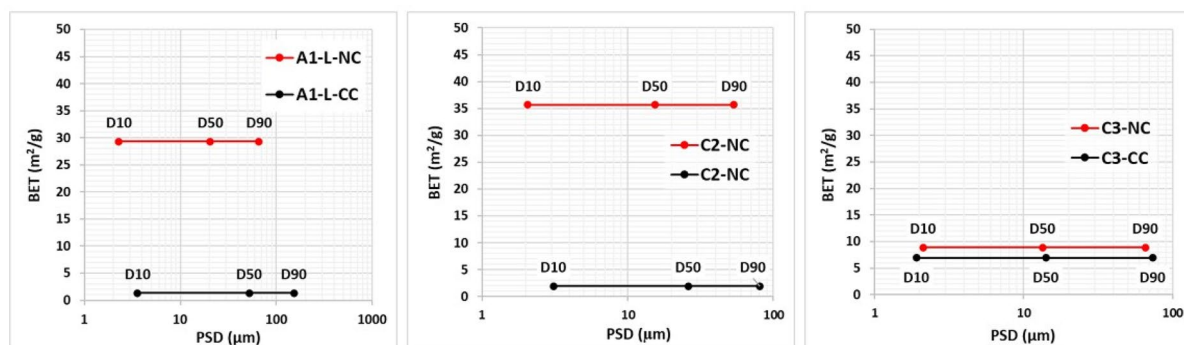


Fig. 6 Change of specific surface area (BET) and PSD (d10, d50 and d90) for the different samples as function of the calcination conditions

3.1.3 Morphology changes SEM

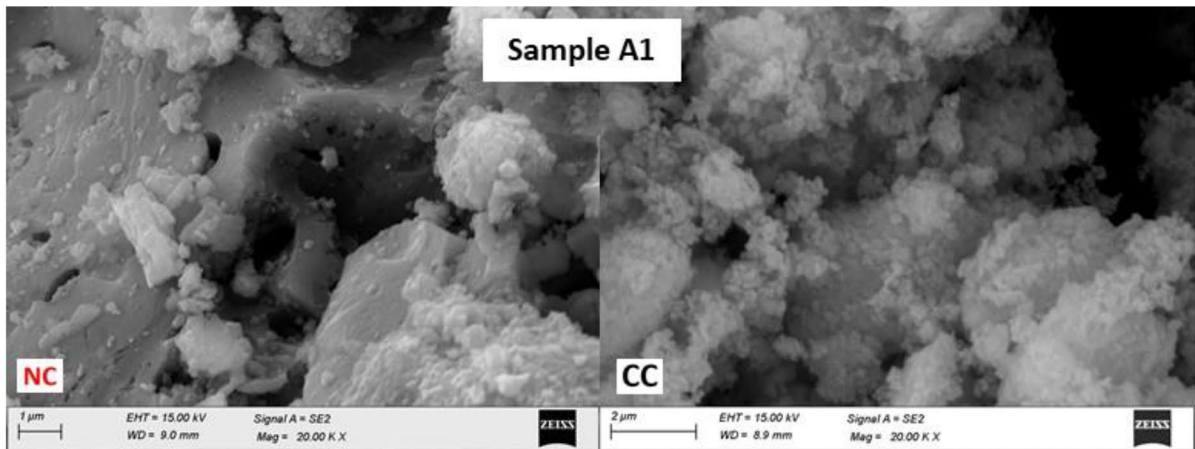
The results of the SEM analysis are shown in Fig. 7 a, b and c for samples A1, C2 and C3, respectively. No signs of agglomeration can be observed in the series sample C3, calcined with and without color control. But there are clear signs of this behavior in color control samples of clays with complex mineralogical composition (A1-CC, C2-CC), especially for sample A1, which can be related to the phase arrangement in the material. The fluxing effect of Fe rich phases and the formation of new mineralogical phases, magnetite/hercynite, could be the cause of the agglomeration in C2-CC, because it can be happening at lower temperatures than usual, which is a consequence of the procedure followed in the color control treatments. However, it is difficult to assess the structural differences between the NC and CC series of C2 due to the high iron content of this sample [51].

The agglomeration phenomena is more noticeable in samples A1-CC when compared to A1-NC, because of the combination of the disappearance of the 2:1 clay phases and the fluxing effect caused by the presence of Ca bearing phases [52] together with the Fe rich phases.

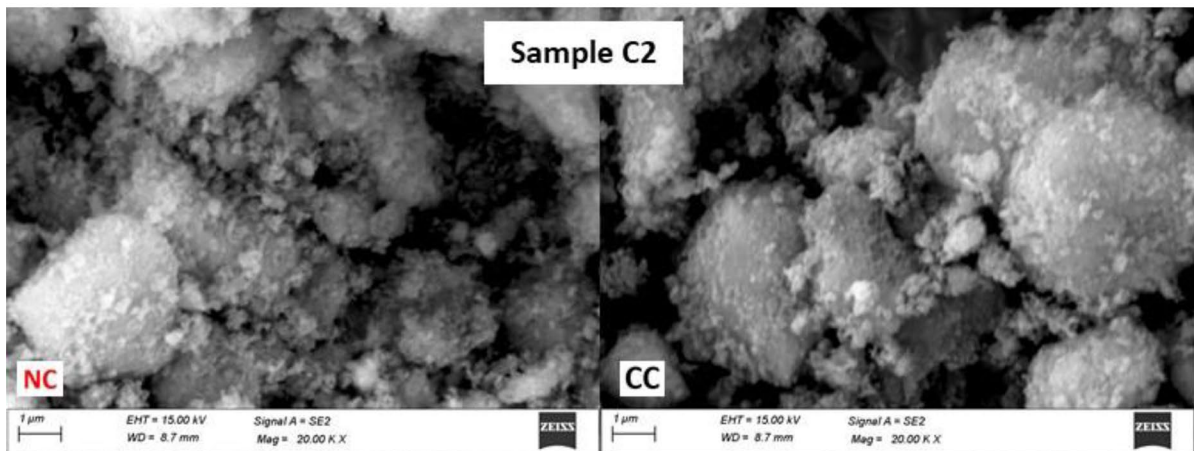
3.2 Impact on the reactivity of calcined clays

3.2.1 Reactivity (R3 protocol)

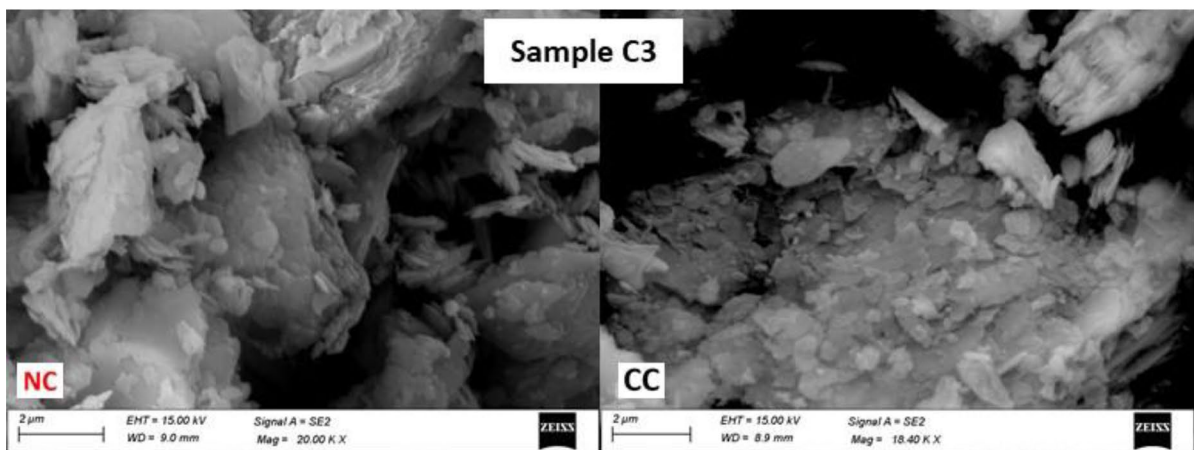
Figure 8 shows the values of cumulative heat at 7 days measured using R3 protocol. Sample C2-NC exhibited the highest cumulative heat release over seven days, reflecting superior pozzolanic reactivity associated with the higher content of kaolinite (45.7%) in this clay compared to the others. The heat of hydration has a significant drop for color control clays when compared with normally calcined clays, which increases with increment of iron oxide



a). SEM images for samples A1, calcined without (NC) and with (CC) color control.



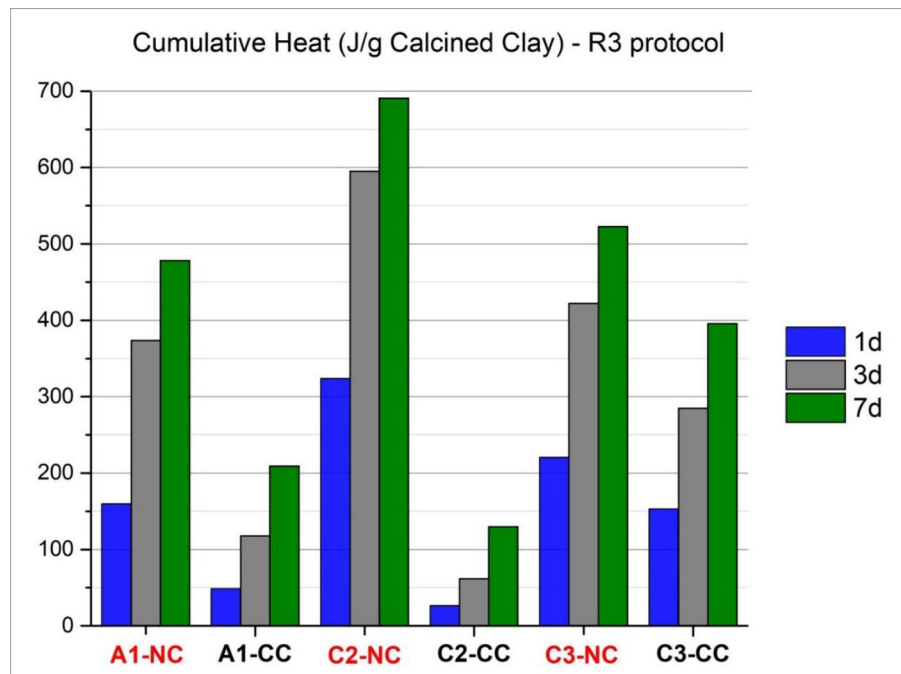
b). SEM images for sample C2, calcined without (NC) and with (CC) color control.



c). SEM images for sample C3, calcined without (NC) and with (CC) color control.

Fig. 7 a SEM images for samples A1, calcined without (NC) and with (CC) color control. b SEM images for sample C2, calcined without (NC) and with (CC) color control. c SEM images for sample C3, calcined without (NC) and with (CC) color control

Fig. 8 R3 reactivity of samples A1, C2 and C3, calcined with (CC) and without (NC) color control. Measured in TAM Air 3238 isothermal calorimeter



content in natural clay ($C3 < A1 < C2$). The percentage of reduction of pozzolanic reactivity is 24.24, 56.29 and 81.23% respectively. The loss in specific surface and the formation of the hercynite phase that captures reactive alumina in its spinel structure during the color control treatments are the main factors affecting the reactivity of the calcined clays in reductive conditions.

3.2.2 Cement hydration

In Fig. 9, the results of reactivity studies for the LC3 systems using isothermal calorimetry are shown. The sulfation of the pastes was kept constant at 5% of gypsum to avoid adding a new variable to the study, which caused undersulfation on some of the systems. The differences between the cumulative heat of hydration (20 °C) of clays calcined with and without color control at 1 day are close or less than 5%. At 3 days this percentage increases up to 7.75% for C2 series. However, these differences are more noticeable at the 5 days mark, when the reactivity of CC samples is lower than NC for all clay samples and behave like $C3 \approx A1 < C2$. The percentage of reduction of pozzolanic reactivity is 5.7%, 5.4% and 15.34% respectively. This effect is enhanced in sample C2-CC due to the greater loss

of reactive alumina associated with the presence of hercynite. Nonetheless, the reactivity values are still higher than the OPC reference system at every age.

The comparative analysis of LC3 hydration profiles, shown in Fig. 10 a, b and c for samples A1, C2 and C3 respectively, reveals a consistent impact of calcination with color control strategy on the development of hydrated phases. Clays subjected to standard calcination (NC) demonstrate rapid ettringite formation within the first few hours as proof of aluminate reactivity. The portlandite peaks remain relatively small in the first 24h, signaling that is being consumed in the second ettringite formation.

In contrast, clays processed under color control calcination protocols (CC) behave differently, especially the series A1-CC and C2-CC. Gypsum tends to be consumed between 6 and 8h later than in the corresponding normally calcined samples and the ettringite formation is slower, with broader and less intense peaks, indicating reduced early reactivity. This is mainly caused by a decreased in intrinsic clay reactivity, potentially due to a decrease in specific reactive surface effect [53]. Portlandite peaks appear early and intensifies swiftly until 24h, suggesting a prevalence of the reactions of the clinker phases.



Fig. 9 Reactivity of LC3 systems of samples A1, C2 and C3, calcined with (CC) and without (NC) color control. Measured in Calmetrix I-Cal 8000

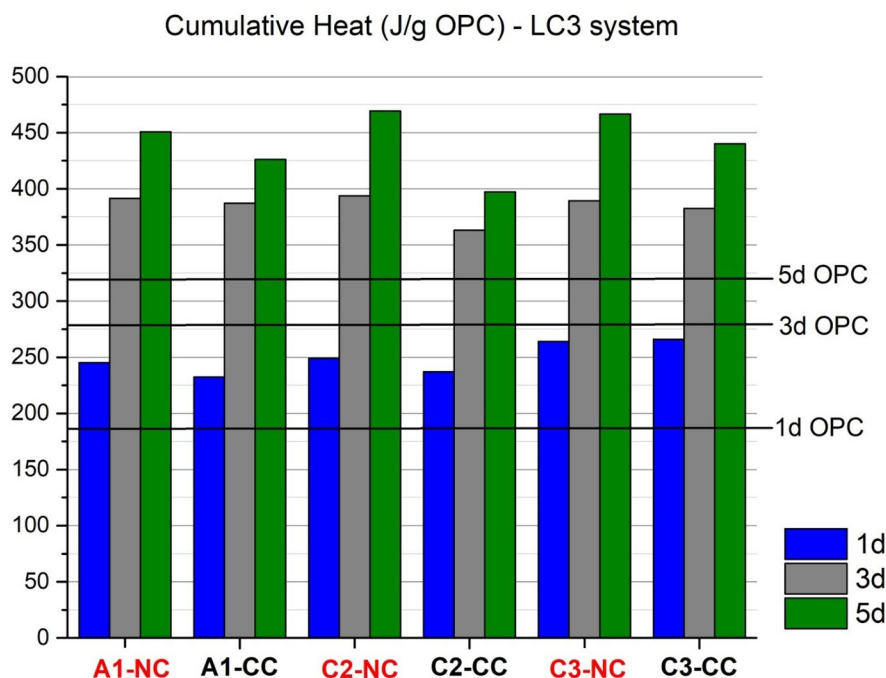


Figure 11 shows the thermal analysis of LC3 pastes elaborated with samples C2 following the two calcination protocols containing (C2-NC and C2-CC). At 3 days, both samples exhibit typical endothermic signals associated with early hydration products (ettringite, C-S-H) and emerging AFm phases. C2-NC shows sharper and more defined events, indicative of rapid hydration kinetics, in contrast with C2-CC. At 28 days, sample C2-NC shows an almost complete disappearance of the portlandite to form Ettringite, AFm and carboaluminates phases. But C2-CC maintains a strong, nearly unchanged portlandite signal, suggesting much slower pozzolanic reaction.

The diffractograms of LC3 pastes elaborated with samples C2 following the two calcination protocols containing (C2-NC and C2-CC) are shown in Fig. 12. In C2-NC, ettringite forms rapidly but begins to slowly decline by 28 days, while portlandite is scarcely detected at this moment, which indicates the transformation into hemicarboaluminate and monocarboaluminate phases, presents since day 3 and with an enhanced content at 28d. This suggests a typical LC3 system early-stage reactivity. In contrast, the color-controlled calcined clay (C2-CC) displays broader, more persistent ettringite peaks at 28 days, indicative of a slower hydration

process. Portlandite is clearly present and intensifies over time, while the hemicarboaluminate and monocarboaluminate peaks remain quite small. This indicates a possible change in the hydration mechanism when color control techniques are applied due to the reduced presence of reactive alumina and the changes in the morphology of the calcined clays.

3.3 Strength of cement pastes

The trend observed in the results from isothermal calorimetry (Fig. 9) is mirrored in the compressive strength results of LC3 pastes at 28 days (Fig. 13). A1 and C2 pastes exhibit significant strength reductions of 33.5 and 47.9% respectively when color control is applied during calcination. These losses align with the reduced reactivity observed in calorimetry, confirming that the diminished pozzolanic reactivity directly affects mechanical performance. So, while color control may offer aesthetic benefits, it can compromise reactivity and strength development, particularly in clays with high Fe_2O_3 content in their composition.

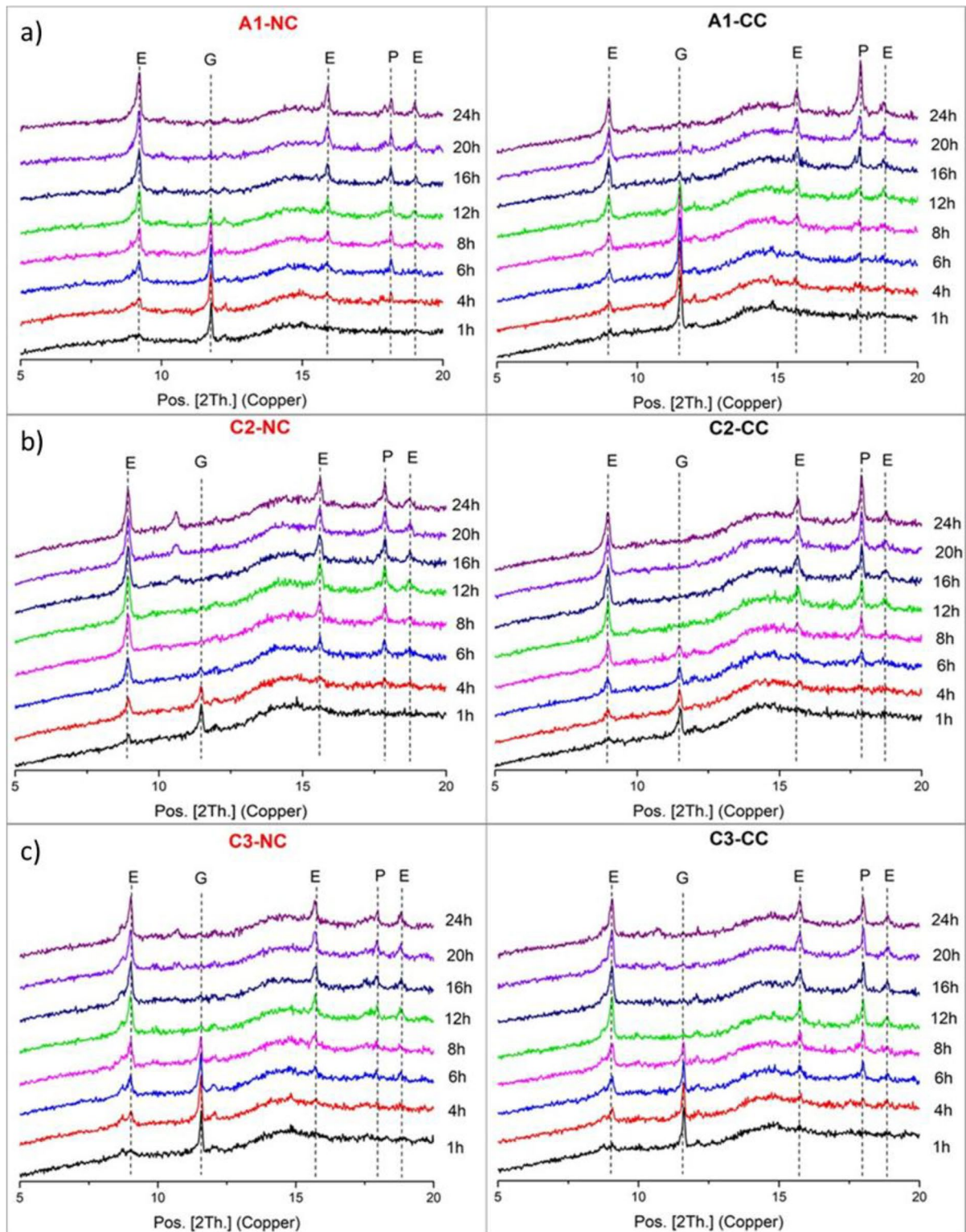


Fig. 10 In-situ XRD of stopped hydration samples of LC3 systems prepared with clays, calcined with (CC) and without (NC) color control. (E: ettringite, G: gypsum, P: portlandite). **a** Sample A1; **b** Sample C2; **c** Sample C3

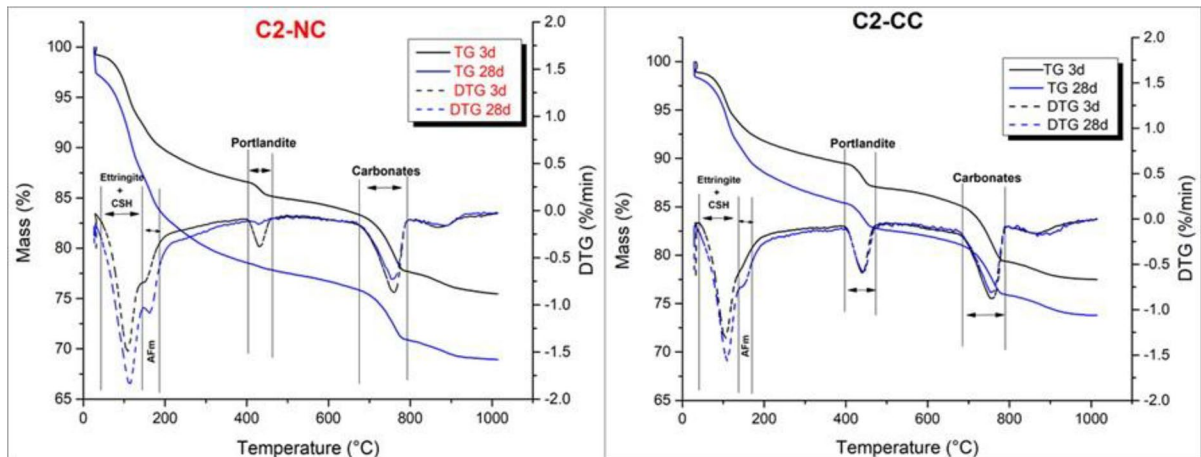


Fig. 11 TGA–DSC of LC3 pastes of sample C2, calcined with (CC) and without (NC) color control, with hydration stopped at 3–28 days

4 Discussion

4.1 Impact of reducing conditions on phase assemblage

The presented results evidence that the mineralogical composition and the calcination conditions, especially during the cooling process, have an influence in the characteristics of the final reaction products after calcination. The first effect is the grayish–black color of calcined clays. This originates from the conversion from hematite to magnetite/hercynite, characterized

by their black color, and it is especially noticeable in clays with significant amount of Fe_2O_3 in their composition (A1, C2) and it becomes more evident with the increase of Fe_2O_3 content. Temperature showed to be an aspect to take into account in the calcination protocol with color control treatments, as higher values stimulate the formation of hercynite/magnetite, but residence time doesn't have a noteworthy effect.

In one hand, magnetite structure consists of an inverse spinel, of a closed packed oxygen arrangement where Fe^{2+} ions are in tetrahedral coordination with oxygen and Fe^{3+} ions are in an octahedral coordination [54]. While hercynite presents an Al–Fe spinel structure where the Fe^{2+} ions occupy tetrahedral

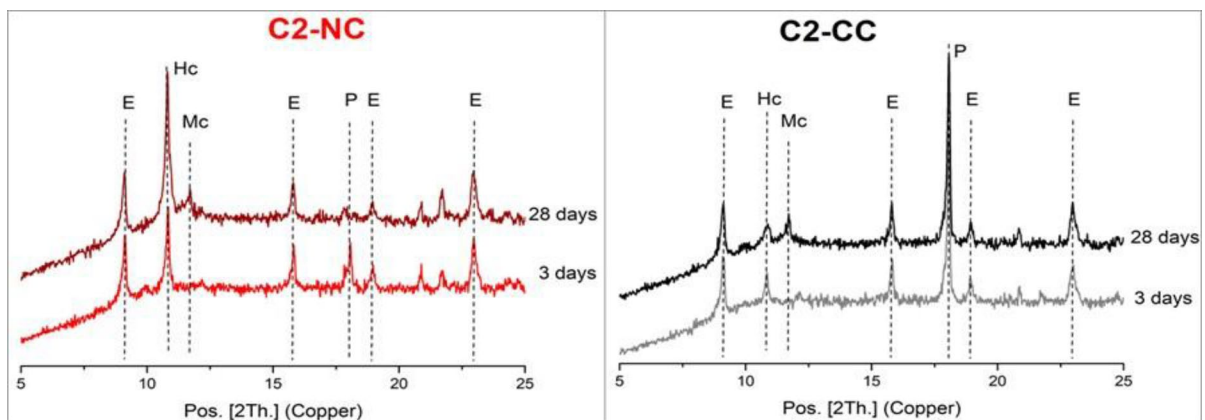


Fig. 12 Diffractograms of LC3 pastes of sample C2, calcined with (CC) and without (NC) color control, with hydration stopped at 3 and 28 days (E: ettringite, G: gypsum, P: portlandite, Hc: hemicarboaluminates, Mc: monocarboaluminates)

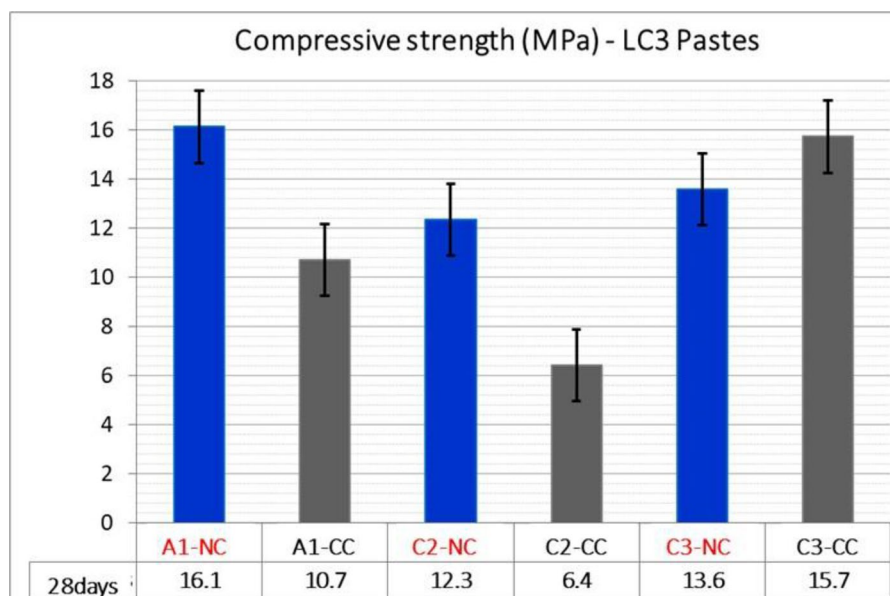
sites and Al^{3+} fills up the octahedral sites [43, 45]. Both of them have reported less specific surface area than hematite [47, 48], which consists in a dense arrangement of Fe^{3+} ions in an octahedral coordination with oxygen atoms in and hexagonal closed packing [54]. This contributes to the greater decrease in the specific surface of iron rich clays. Also, during the formation of hercynite, very stable crystalline phase, occurs a partial subtraction of Al^{3+} from the kaolinitic phases and, as a consequence, the availability of reactive alumina phases is reduced. Hercynite (FeAl_2O_4) formation during cooling under reducing conditions has direct implications for the availability of reactive alumina. Considering the stoichiometry of hercynite (FeAl_2O_4 , molar mass ≈ 173.8 g/mol), the Al_2O_3 content in this phase is approximately $54/173.8 \approx 31.1\%$. For the C2-CC sample, which presents 20.5% hercynite according to XRD quantification, this implies that approximately 6.4% of the total material corresponds to Al_2O_3 immobilized in the hercynite structure. Given that the total Al_2O_3 content in C2-Raw is 22.99% (Table 1), this represents approximately 28% of the total Al_2O_3 present in the clay that has been sequestered in the spinel structure. This alumina sequestration, combined with the reduction in specific surface area (Fig. 6), explains the decrease in pozzolanic reactivity observed for the C2-CC sample. For the A1-CC sample, with 3.4% hercynite and 18.24% Al_2O_3 , the immobilized alumina represents

approximately 1.1% of the total (6% of available Al_2O_3), resulting in a less pronounced reactivity reduction, although still significant due to the combined effects with specific surface area reduction.

The agglomeration observed in the samples with moderate – high content of Fe_2O_3 in the composition of the raw clays could be related to the fluxing effect of Fe rich phases that can be happening at lower temperatures as a consequence of the applications of the color control techniques. In the specific case of sample A1-CC, there are factors contributing to the significant higher agglomeration observed that are not related to the iron phases and is an indication that mineralogical composition has an impact on the properties of calcined clays.

In addition to alumina immobilization in hercynite, the reduction in specific surface area observed in color-controlled samples (Fig. 6) contributes to lower pozzolanic reactivity. The decreased specific surface area limits the area available for dissolution of reactive phases. Furthermore, the presence of reducing conditions during cooling could induce changes in the glass/metakaolin structure, incorporating Fe^{2+} into the amorphous network and modifying its reactivity. The Mössbauer spectra of the C2-CC sample (Fig. 5c, Table 4) show Fe^{2+} in three distinct crystallographic environments, suggesting that part of the Fe^{2+} could be incorporated into the amorphous phase, modifying its structure and reducing its reactivity. Additionally,

Fig. 13 Compressive strength at 28 days of LC3 pastes of samples A1, C2 and C3, calcined with (CC) and without (NC) color control



the absence of significant morphological changes in the C3-CC sample (Fig. 7c), which has low iron content, suggests that sintering induced by reduction is mediated by the presence of iron-rich phases and is not a generalized phenomenon. These hypothesis deserves investigation in future studies.

Analysis between reactivity loss (measured by R3) and mineralogical and physical parameters shows that reactivity reduction is determined by both hercynite formation and specific surface area reduction. The combination of both factors suggests that alumina immobilization in hercynite and specific surface area reduction act synergistically to decrease the pozzolanic reactivity of clays subjected to color control treatments.

An important finding, with significant practical implications, is that despite the reactivity reduction induced by color control treatment, all LC3 systems prepared with calcined clays (both NC and CC) outperform the Portland cement reference in terms of cumulative heat at all ages (Fig. 9). This suggests that although color control may compromise the pozzolanic reactivity of the clay, LC3 systems still maintain superior performance to conventional cement, supporting the feasibility of using color control treatments in applications where the color is a relevant factor.

4.2 Recommendations to mitigate the impact of high Fe_2O_3 clays under color control

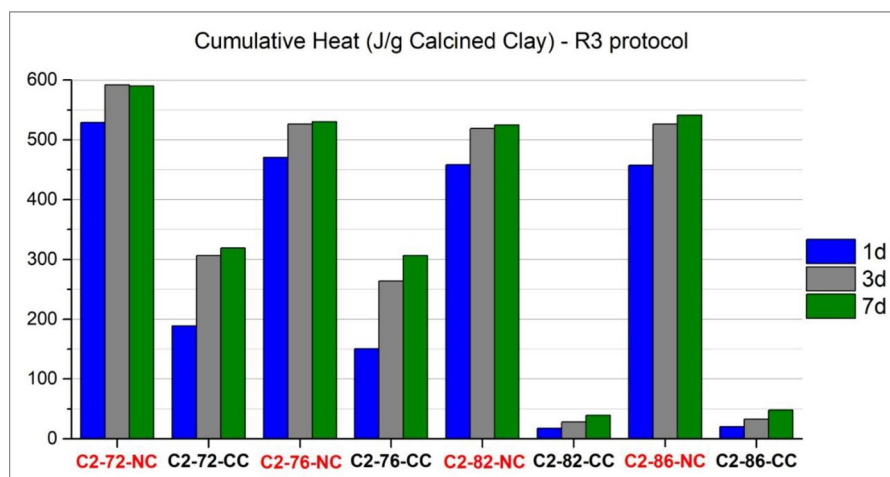
The R3 protocol was employed to evaluate the pozzolanic reactivity of sample C2, calcined under varying temperatures and residence times. As discussed before, all calcined samples undergo dehydroxylation, confirming effective thermal activation. However, residence time has no apparent effect on the transformation mechanisms. In contrast, the rise in calcination temperature favors the formation of hercynite/magnetite, causing agglomeration and reducing specific surface area in the color control samples. These temperature-driven effects are reflected in the reactivity results shown in Fig. 14. When comparing CC and NC series calcined at 700 °C, a decrease in the reactivity around 45% is observable; but at 800 °C this increases to 90% loss of reactivity.

So, in order to mitigate the adverse effects of high Fe_2O_3 content in clays subjected to color control treatments, the main recommendation is to reduce the peak calcination temperature establishing a compromise with the values required for an effective dehydroxylation while avoiding the formation of spinel phases and reducing the fluxing of iron.

5 Conclusions

The findings presented highlight the critical role that mineralogical composition, particularly Fe_2O_3 content,

Fig. 14 Reactivity of LC3 systems of sample C2 calcined varying temperature and residence time. (7: 700 °C; 8: 800 °C; 2: 20 min; 6: 60 min; NC: Normal Calcination; CC: color control). Measured in Calmetrix I-Cal 8000



and calcination parameters play in the properties of calcined clays, especially those subjected to color control treatments. The transformation of hematite to darker spinel phases (magnetite and hercynite), especially pronounced in iron-rich clays, contributes to the desirable aesthetic of the material but it is accompanied by a marked decrease in specific surface area and reactive alumina availability. These transformations negatively impact the pozzolanic reactivity and hydration dynamics of LC3, and even though, these systems surpass the results of the OPC reference, there might be other unfavorable consequences depending on the use of the blended cement elaborated with color control clays.

Further studies are required to quantify the clay compositions that are susceptible to this effect, in particular the maximum iron content that should be used with color control. In addition, other analytical techniques that can show the consumption of alumina from metakaolin will be considered for future work.

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