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Color control in industrial clay calcination

Fernando Martirena[1]*, Roger Almenares[2], Franco Zunino[3], Adrian Alujas[1], Karen Scrivener[3]

[1] Universidad Central "Marta Abreu" de las Villas, Cuba
[2] Universidad de Moa, Cuba
[3] Ecole Polytechnique Federal de Lausanne, EPFL, Switzerland

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Abstract

Low grade clays often have iron in their composition. The iron hydroxides in original clay decompose at 300°C and, depending on the availability of oxygen, the iron oxides occur in different phases. For an oxygen rich environment, hematite formation prevails, but at around 650°C it converts to magnetite. In an oxygen free environment hematite does not form during calcination at any range of temperature. During cooling, the presence of oxygen can revert the formation of magnetite back to hematite at temperatures in the range 650-300°C, thus the resulting material can have a reddish color. Color is a quality parameter and it is a matter of concern for the cement producers. If hematite is the main iron phase, calcined clay has a reddish color, which could modify cement's final color. This paper proposes a method to modify color during calcination by controlling the atmosphere during the cooling. The focus is the cooling phase, where the presence of oxygen is avoided, in order to keep magnetite as the main iron phase in the calcined product. The procedure to control color consists of injecting liquid fuel at the carcass of the kiln while the calcined material exits, so that it combusts and exhausts the oxygen available during the cooling process. The procedure was successfully implemented at a pilot kiln in India. Controlling the calcination atmosphere enabled the production of a black calcined clay, instead of a red material. The reactivity and properties of both red and black clay are very similar, and no side effects have impacted properties of LC3 cements produced with the treated clay. The reactivity and properties of both red and black clay are very similar; compressive tests testes were carried out with both clays and show that differences in strength of LC3 cement produced with the grey clay when compared with the red clay are not significant.

Keywords: Cement; Calcined clays; Color; Calcination; Performance

1 Introduction

Portland cement is one of the most frequently used materials in modern life and is today associated with the level of development of a country. Cement production exceeds 4 billion tonnes per year [1,2]. Because of the huge production of cement, its emissions represent approximately 6-8% of the world's CO_2 emissions. A path to improving sustainability is the use of Supplementary Cementitious Materials, SCM as partial replacement for clinker [3,4].

The trend for clinker substitution, however, has reached a plateau during the last decade (in the range of 25-35%), mainly due to the poor availability of some of the SCM, especially Granulated Blast Furnace Slag, GBFS and Pulverized Fly Ash, PFA [5]. Environmental demands are urging coal power plants to be phased out, thus there is less PFA available. The increase in recycling metals has significantly reduced the availability of GBFS [5].

Due to the availability and low CO2 emission, calcined clays become a sustainable solution to substitute Ordinary Portland Cement (OPC). Clay deposits, though non-renewable, can be exploited within certain limits without inflicting a severe damage to the environment, and their availability exceeds that of any of the other SCMs known by far [6].

A clay thermal treatment is necessary to obtain a calcined material for the cement industry. The reactivity of the clay depends mostly on kaolinite content and the firing temperature [7–9]. The limitations of the system are the reactivity of the calcined clays, and the availability of portlandite for the pozzolanic reaction. This limits the clinker substitution rate to around 35% according to EN 197.

Recent developments have proven that low grade kaolinitic clays can be successfully used to produce reactive pozzolans when thermally activated [7,8]. Moreover, studies have proven the synergy between calcined clays and limestone to produce AFm phases, basically hemi or mono carboaluminate [10–12]. This enables higher clinker substitution, up to 50% by the blend of calcined clay and limestone, a system commonly known as Limestone-Calcined Clay-Portland Cement "LC3" [11,12].

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* Corresponding author: Fernando Martirena, Email: martirena@uclv.edu.cu

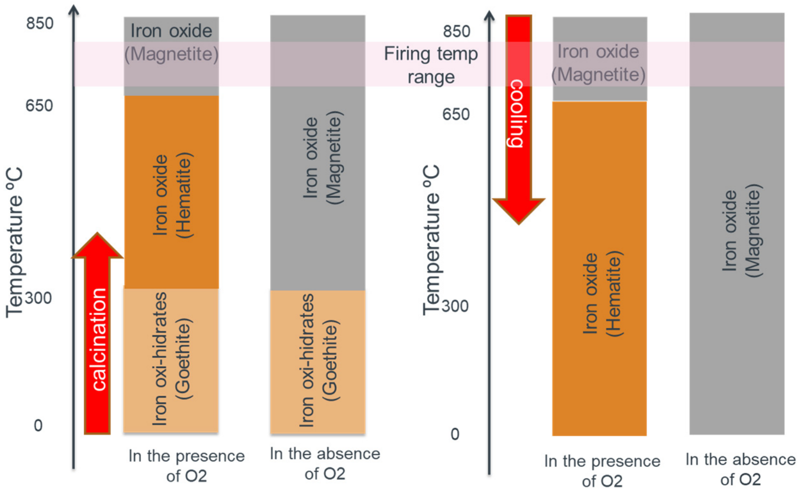

Figure 1. Transformation of Iron bearing phases during calcination.

One of the limiting factors for the use of clay is the fact that most low grade kaolinitic clays have Fe_2O_3 content around 2-9%, or even higher, and this has an impact on color of the material when calcined, which turns to a shining red depending on iron content and the availability of oxygen during calcination.

This paper presents an approach to control the conditions during calcination of kaolinitic clays to avoid the formation of a reddish calcined clay. The idea is to control the atmosphere in which calcination takes place. The theory behind this is discussed and practical experiences are presented.

2 The role of Iron in clays

Iron (Fe) is the fourth most abundant element on Earth's crust (6% mass). It is therefore very common to find it in the chemical composition of clay minerals. Clay often contains iron (hydr)oxides as associated minerals [13]. The most common phases are hematite, magnetite, maghemite, goethite, lepidocrocite and ferrihydrite. Iron is present also as structural form on clay mineral and may occur in both the octahedral and tetrahedral sheets of 1:1 and 2:1 clay minerals, and, in the gibbsite/brucite sheet of 2:1 chlorites [14].

Iron oxide is the primary colorant in the clay materials. Most clay materials contain more than 5% Fe_2O_3, mainly as impurities which strongly influence the reddish color of clays [15,16]. This can affect their industrial application, in fine ceramic, paper, pigment industries, and civil construction [18]. In many cases it is necessary to perform a treatment to make these materials suitable for application in various industries [18]. Although the beneficiation process gives a significant added value to the clay, the high cost of production and the complexity of the processes can affect its viability.

Clay materials containing iron oxide turn a predominantly red color after heated. In the cement industry, the reddish color of the calcined clay may discourage commercial use as SCMs [19,20]. Color development in calcined clays is mostly depending on: (a) oxidation state of the iron oxide present in the original clay, and (b) the phases in which iron occurs in clay its susceptibility to oxidation and reduction reactions. [21].

3 Color control during clay calcination

The dehydroxylation of the clay (removal of the OH-) takes place at temperatures between 350-650°C, thus leading to disorder in the structure of the clay and activation of the clay. In most industrial applications the calcination temperature ranges from 750-800 °C [7,8]. Transformations occur not only at clay minerals but also at other accompanying phases, such as the iron bearing phases, while quartz remains unchanged [22].

The transformation of iron oxides in reducing atmospheres is very complex and there are possibilities of several reactions, which usually take place simultaneously, i.e. hematite (Fe_2O_3) to magnetite (Fe_3O_4) to wüstite (FeO) to iron (Fe). This sequence takes place at temperatures between 550°C and 1000°C [23–26], where Fe_2O_3 to FeO proceeds by a fast reaction forming intermediate oxide (Fe_3O_4) and reduction of Fe_3O_4 to FeO is slower. In clay materials heated at the temperatures range 550–850°C hematite forms in the presence of oxygen in the temperature range 300-650°C. In a low oxygen environment, hematite is reduced to form magnetite, which can be stable even at temperatures close to 300 °C [27–29] (see Fig. 1) For temperatures above 650°C, regardless the presence of oxygen, the main iron phase formed is magnetite [16,22,28,30].

During cooling, magnetite can convert back to hematite if oxygen is available, see Fig. 2, and the calcined material will have a reddish color. If oxygen is not available, magnetite will remain as the main stable phase [31,32].

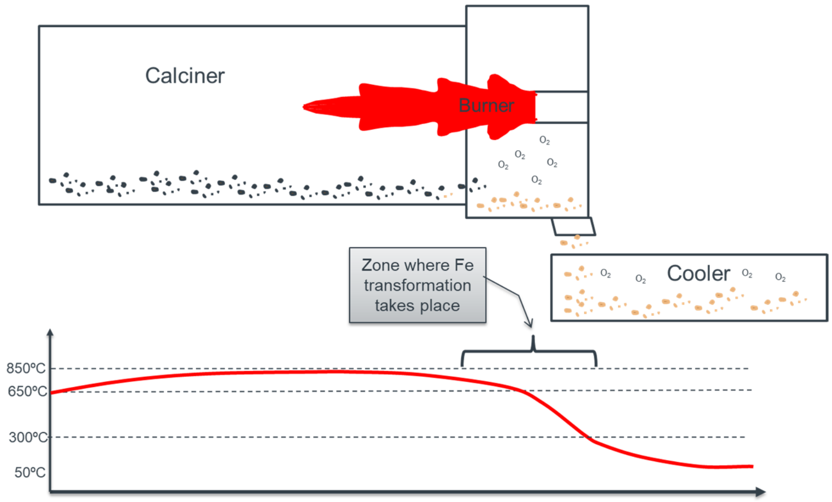

Figure 2. Changes in the iron phases during calcination at oxidizing atmosphere.

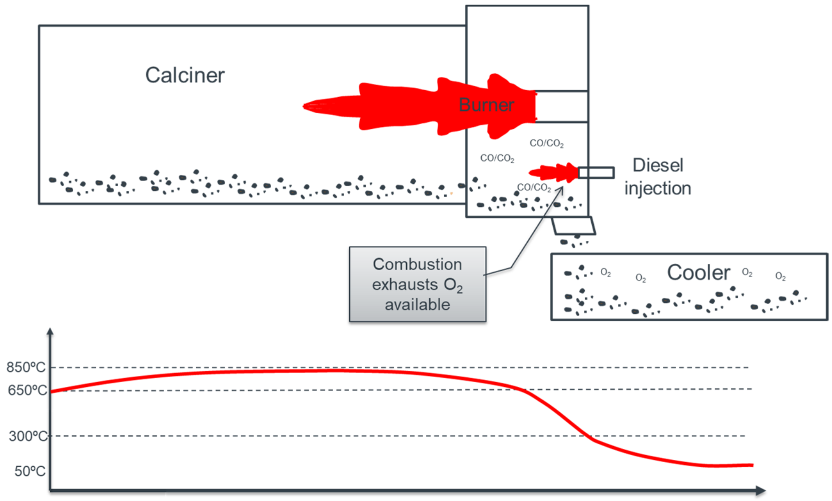

Figure 3. Favoring a reducing atmosphere during cooling.

The strategy for color control during calcination must focus on favoring a reducing atmosphere during cooling to avoid the conversion of magnetite to hematite. Temperatures at cooling chamber in industrial kilns are in the range of 650-300°C, and below 300°C no further transformation takes place [16].

The company IPIAC (www.ipiac.com) has developed a very interesting procedure to guarantee a reducing atmosphere during cooling of the calcined material. See details in Figure 3. An inlet is created at the carcass of the kiln, where the calcined material exits for cooling. Liquid fuel is injected through this inlet, and the high temperature in this region enables self-combustion of the fuel which exhausts all oxygen available and imposes reducing conditions during cooling. The system is very robust, and the extra fuel consumption is under 1% compared to the fuel used for calcination. If temperature drop is not enough, an extra inlet can be built in for a water spraying to cool the system further.

A trial to test the system was done at the workshop of the NGO "TARA" in India, where the color control system described above has been implemented. This paper will present the results of the trials, as well as the assessment of the properties of the color-controlled calcined material.

4 Materials & methods

4.1 Characterization of materials

A kaolinitic clay from an African country was chosen for the tests. This clay was formed through a weathering process. The chemical composition was determined by using X-Ray Fluorescence (XRF) technique as shown in Table 1. Kaolinite content was determined by Thermogravimetric analysis TGA-DTA by measuring the weight losses that occur in the temperature range of 350°C-650°C, normalized by dry weight (see Fig. 4). Methods of calculation based on TGA curves are always subjected to minor interferences by partial overlapping with the dehydroxylation of 2:1 clay minerals. Kaolinite content was calculated in 49.3±3 % [7,8] (see Table 2). The mineralogical phases of raw clay samples were identified by X-Ray Diffraction (XRD). Quartz and kaolinite were identified as major phases while iron-bearing phases and clay minerals from the mica group were identified as minor phases. Based on similar structural models, a semi quantitative analysis of major phases was done by the Rietveld method (Good ness of Fit = 3.5), showing a clear predominance of kaolinite and quartz over the rest of the mineral phases in the sample. All results are presented in Table 3.

Table 1. XRF composition of raw clay sample.

SiO_2	54.52
Al_2O_3	28.88
Fe_2O_3	3.76
SO_3	0.17
K_2O	0.95
CaO	0.05
MgO	1.22
TiO_2	0.42
MnO	0.42
LOI	9.84

Kaolinite content in the clay falls within the recommended range (40-60%) for cement applications [33]. Further, MgO and Fe_2O_3 are present only in small amounts. In the raw clay sample the $Al_2O_3/SiO_2 = 0.53$ and the LOI ≥ 7%. For samples with kaolinite contents higher than 40%, the lower limit values for those ratios are 0.3 and 0.1 respectively [34]. Therefore, kaolinite content values as determined by TGA are in good agreement with chemical composition.

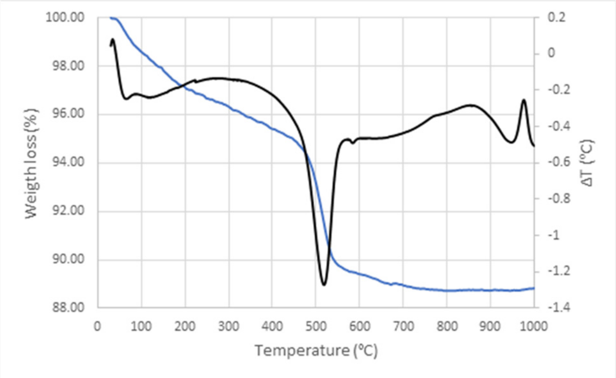

Figure 4. TGA-DTG curves for raw clay composite sample.

Table 2. Weight loss and kaolinite content of clay sample by TGA.

	Weight loss (%)	Kaolinite content (%)
Raw clay	6.9	49.3 ± 3%

Table 3. Mineralogical composition by XRD of the raw clay subject of this study.

Mineral phases	Content (%)
Quartz	31.6
Kaolinite	42.8
Muscovite	23.9
(Hematite + Goethite)	1.7

4.2 Implementation of color control process

The original kiln operation and process were modified to implement the color control. Fuel rate was increased in around 2-5% with the purpose of having an excess fuel which would induce an incomplete combustion in a CO/CO_2 rich atmosphere, and thus avoid oxidation of the iron phases. Calcination temperature was not affected since the air flow was kept constant, see Fig. 5.

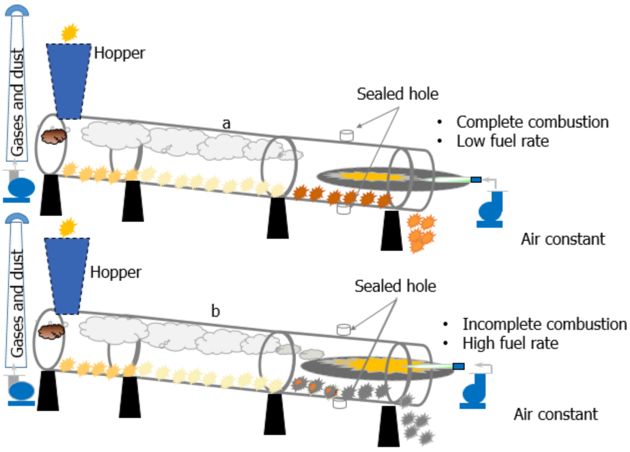

Figure 5. Modification of kiln operation to implement color control.

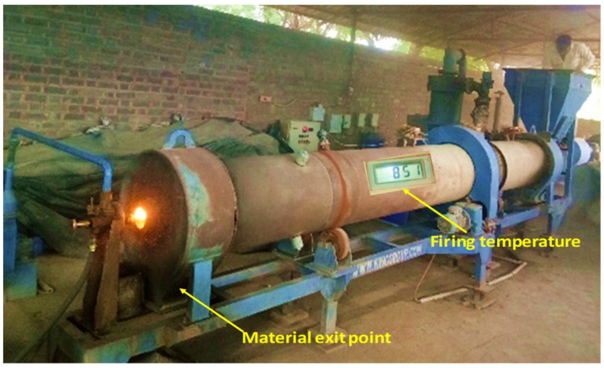

Figure 6. Kiln used during the trials presented in this paper.

The feed particle size of raw clay was in a range of 0-5 mm. The feed rate was fixed at 30 kg/h. The temperature at the firing zone was maintained at 850°C ± 20°C after kiln stabilization. Diesel was used as fuel. Calcination was conducted at normal kiln-atmosphere as well as at controlled conditions. In order to control color, the reducing atmosphere in the cooling zone was established. The atmosphere was maintained by a controlled flow of fuel, thus avoiding the formation of a stable hematite phase, and consequently making the color grey/ blackish. Total residence time for the clay inside the kiln was 18-20 minutes (see Fig. 6).

5 Results & discussion

5.1 Clay Calcination

The assessment of the calcination degree in both batches was performed aided by the measurement of the loss on ignition (900 °C), combined with TGA-DTA and XRD analysis. Finally, standard mortars were prepared as a means of confirming the reactivity of the material.

TGA-DTA tests carried out in the temperature range diagram of 30°C-1000°C for both clays (with and without color control) do not show any Loss on Ignition (LOI), thus the dehydroxylation of kaolinitic phases was complete in both cases [35].

XRD analysis of red and black calcined clay samples confirm the presence of traces of the iron phase hematite in the reddish clay (calcined without color control) and the black clay (with color control) showed traces of magnetite. Fig. 7 presents the XRD diagrams for both clays, and for reference the raw clay. Major mineral phases identified were quartz (low) and 2:1 clay mineral from the mica group (muscovite, phengite). The kaolinite peak appears to have disappeared, meaning that a high degree of structural disorder was achieved. Fig. 8 presents the color of the raw clay and the calcined clay without color control (red) and with color control (dark grey).

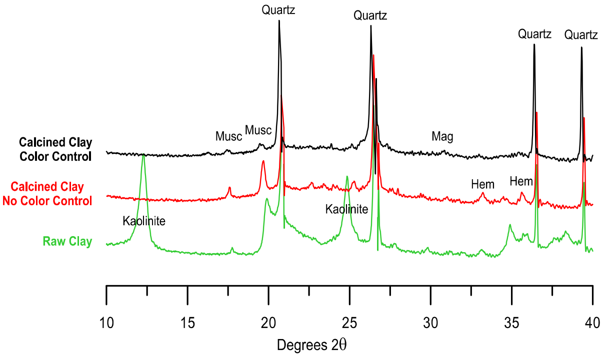

Figure 7. Comparison of XRD diffractogram of raw and calcined clays.

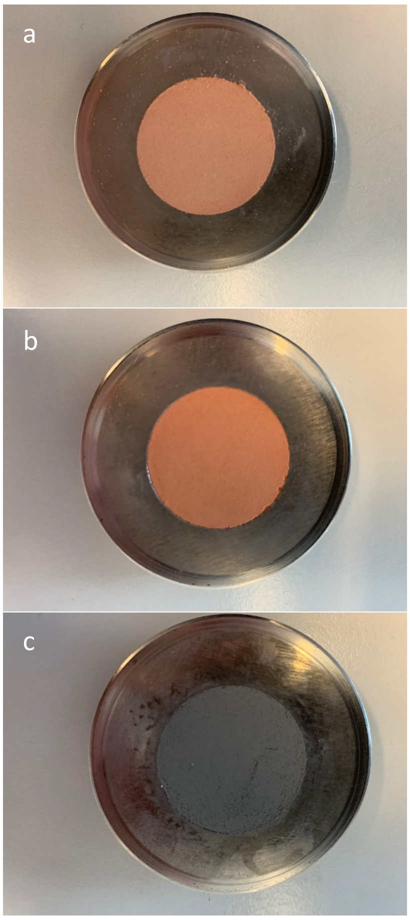

Figure 8. Picture of the materials: (a) original raw clay, (b) clay calcined without color control, (c) clay calcined with color control.

5.2 Reactivity of the calcined clay

Both red and black calcined clays were ground to powder in a ball mill and Laser granulometry and Sieve residue at 90 micros were carried out to characterize physical aspects of the clays: PSD (particle size distribution) curves and particle size. The criteria for fineness was to have material passed under 90 µm sieve around 98 %. The particle size distribution of each material was evaluated, see PSD curves in Fig. 9. The red calcined clay had maximum particles distributed within a range of 5-60 µm whereas maximum particles for black calcined clays were lying in the range of 5-50 µm. However, distribution patterns in both cases are almost similar which largely exist within a narrow range of 5-60 µm. Minor differences in PSD could also be due to the different refractive index of both red and black clay.

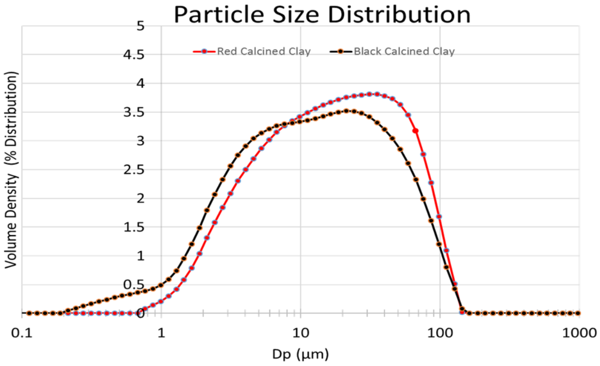

Figure 9. Particle size distribution of red and black calcined clays.

Pozzolanic reactivity of calcined clay samples was assessed using the protocol for the lime reactivity established at Indian standard IS 1727 [36]. This method of test covers the procedure for determining the reactivity of the pozzolanic material with hydrated lime, as represented by compressive strength of standard mortar test cubes prepared and tested under specific conditions. In this case it was used to compare reactivity of the red and black calcined clay and assess whether there are differences induced by the color control process.

For the tests, mortars made with lime: pozzolana: standard sand in proportion 1: 2M: 9 by weight blended intimately. The water to binder ratio is dictated by the flow, determined after 10 drops in 6 seconds at the flow table, and should give a flow of 70 ± 5 percent. The temperature of the water and that of the test room at the time when the mixing operation is being performed shall be from 27 ± 2°C [36].

Mortar cubes were cast in 50×50×50 mm^3 cubes and the surface of the specimen in the mold was covered with a smooth and greased glass plate. The specimens were kept with the molds along with the cover plates under wet gunny bags for 48 hours. Then they were removed from the molds and cured at 90 to 100 percent relative humidity at 50 ± 2°C for a period of eight days. The reactivity of each pozzolan is associated with the 8 days compressive strength of the mortars described above [36].

Table 4 presents the lime reactivity of calcined red and black clay samples. The black clay has a slightly lower reactivity compared to the red calcined clay, but this difference falls within the range of the experiment error. Therefore, it is fair to say that the color control process does not have a major influence on reactivity of the calcined clay.

Table 4. Lime reactivity of red and black calcined clays.

Sample	Lime reactivity (MPa)	
	Individual	Average
Calcined red clay	7.6	7.7
	7.5	
	7.9	
Calcined black clay	6.9	6.8
	7.3	
	6.3	

5.3 Assessment of properties of standard mortars made with calcined clay and limestone

For the preparation of the ternary binder LC3, it was decided to make a separate grinding of each component. A mineral addition made by a combination of calcined clay, limestone[a] and gypsum[b], named after "LC2" was prepared. Table 5 presents the proportions between the components of LC2.

Table 5. Proportions for LC2 2:1 (% mass).

	Proportions					SO_3 min
	Clinker	Calcined clay	Limestone	Gypsum	Total	
LC2 2:1	0%	63%	30%	7%	100%	2.80%

The ternary cement LC3 was produced through blending 50% of LC2 (mass) with 50% of a reference ordinary Portland cement (OPC 43 Grade). For each clay LC3 was produced and standard mortars were cast following the procedure described in EN 196-1 [37] to assess compressive strength. Other properties, such as Blaine's specific surface, density and water demand for LC3 were also tested. All results of the tests are presented in Table 6.

Table 6. Physical properties of LC2 blends.

Sl.	LC3 ID Code	SR 45 µ (%)	SR + 90 µ (%)	density (g/cc)	Blaine Value (m2/kg)	Normal Consistency (%)
1	Red	12.1	2.0	2.85	511	33.5
2	Black	12.0	2.0	2.88	505	35.5

Fig. 10 presents the strength results for standard mortars made with LC3 using the red and black calcined clay. Slight differences in compressive strength are observed at all ages 3, 7 and 28 days. This could imply that the color treatment did not influence the reactivity of the resulting calcined clay. Compressive strength values remain in the zone of high strength cements, even at the earliest ages.

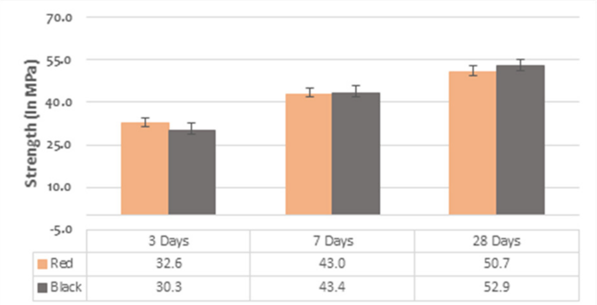

Figure 11. Compressive strength of standard mortars made with LC3.

6 Conclusions

The investigation report presented in this paper can confirm that it is possible to modify color of calcined clay by controlling the atmosphere during calcination and cooling.

The high calcination temperature (750-850°C) favors the formation of dark color magnetite in the calcination phase, regardless the availability of oxygen. However, during cooling, as the material temperature drops below 650°C, red color hematite can be formed if oxygen is available. A reducing atmosphere during cooling would keep the dark color magnetite as the main stable phase.

Therefore, controlling the cooling process is crucial in terms of modifying the color of the calcined clay. A simple and cost-effective procedure of igniting the oxygen available at the cooling chamber favors a reducing atmosphere, where dark color magnetite would remain stable.

The new process was implemented at a pilot plant, semi-industrial kiln in India, and it proved to be very effective. Controlling the calcination atmosphere enables the production of a black calcined clay, whereas when the control does not take place, a red product is produced. The reactivity and properties in general of both red and black clay are very similar, and no side effects can impact properties of LC3 cements produced with the treated clay.

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[a] CaO minimum content 40%; the material was ground separately using the same fineness criteria as calcined clay.

[b] SO_3 minimum content 38%; the material was ground separately using the same fineness criteria as calcined clay.

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