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# PETROGRAPHY AND APPLICATION OF THE RIETVELD METHOD TO THE QUANTITATIVE ANALYSIS OF PHASES OF NATURAL CLINKER GENERATED BY COAL SPONTANEOUS COMBUSTION

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## ABSTRACT

Fine-grained and mainly reddish color, compact and slightly breccious and vesicular pyrometamorphic rocks (natural clinker) are associated to the spontaneous combustion of coal seams of the Cerrejón Formation exploited by Carbones del Cerrejón Limited in La Guajira Peninsula (Caribbean Region of Colombia). These rocks constitute remaining inorganic materials derived from claystones, mudstones and sandstones originally associated with the coal and are essentially a complex mixture of various amorphous and crystalline inorganic constituents. In this paper, a petrographic characterization of natural clinker, as well as the application of the X-ray diffraction (Rietveld method) by mean of quantitative analysis of its mineral phases were carried out. The RIQAS program was used for the refinement of X ray powder diffraction profiles, analyzing the importance of using the correct isostructural models for each of the existing phases, which were obtained from the Inorganic Crystal Structure Database (ICSD). The results obtained in this investigation show that the Rietveld method can be used as a powerful tool in the quantitative analysis of phases in polycrystalline samples, which has been a traditional problem in geology.

***Key words***: Rietveld method, Cerrejón, X-ray powder diffraction, natural clinker.

## RESUMEN

Rocas pirometamórficas (clinker natural) de grano fino y coloración principalmente rojiza, compactas, y ligeramente brechadas a vesiculares están asociadas a la combustión espontánea de mantos de carbón de la Formación Cerrejón explotados por Carbones del Cerrejón Limited en la península de La Guajira (Región Caribe de Colombia). Estas rocas constituyen materiales inorgánicos remanentes derivados de arcillolitas, limolitas y areniscas originalmente asociadas con carbón y son esencialmente una mezcla compleja de diferentes constituyentes inorgánicos amorfos y cristalinos. En el presente trabajo, se llevó a cabo la caracterización petrográfica del clinker natural, así como la aplicación de la difracción de rayos-X de polvo

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(método de Rietveld) para el análisis cuantitativo de las fases minerales presentes de las rocas en estudio. El programa RIQAS fue utilizado para el refinamiento de perfiles de difracción de rayos-X de polvo, analizando la importancia de utilizar los modelos isoestructurales adecuados para cada una de las fases presentes, los cuales se obtuvieron de la base de datos Inorganic Crystal Structure Database (ICSD). Los resultados obtenidos en la presente investigación muestran que el método de Rietveld puede usarse como una poderosa herramienta en el análisis cuantitativo de fases en muestras policristalinas, lo cual ha sido un problema tradicional en el campo de las geociencias.

***Palabras clave***: método de Rietveld, Cerrejón, difracción de rayos X de polvo, clinker natural.

## Introduction

Spontaneous combustion of coal has been reported in different coalfields of the world (USA: Heffern *et al*., 1983, 1993; foit *et al.*, 1987; Cosca *et al.*, 1989; Heffern & Coates, 1997, Lyman & Volkmer, 2001; India: Prakash *et al.*, 1997; Romania: Radan & Radan, 1998; Australia: Ellyett & Fleming, 1974, New Zealand: Lindqvist *et al*., 1985, China: Zhang, 1998; de Boer *et al*., 2001). Fires associated with coal mines, which are preserved in the rock record as reduced volume burnt coal beds and pyrometamorphic rocks (natural clinker), represent global catastrophes that may be initiated for various reasons and are responsible for coronary and respiratory diseases, human death and destruction of ecosystems, contaminating air, water and soil (Stracher, 2007).

In Colombia, Candela & Quintero (2004) conducted a geological mapping of natural clinker at El Cerrejón mining operation, located in the Guajira Peninsula, northeastern Colombia. Carbones del Cerrejón Limited is dedicated to the exploration, production, transportation and shipment of high quality thermal coal), which includes monitoring and structural control at depth. According to Quintero *et al.* (2009), the “in situ” spontaneous combustion of coal, with the consequent development of natural clinker, is a phenomenon that hinders the development of coal mining, not only because it creates areas of geotechnical instability, given the characteristics acquired by the adjacent rock when subjected to high temperatures reached during combustion of coal but also because it represents a reduction in tonnage of workable coal.

The term “natural clinker” refers to a series of pyrometamorphic rocks generated as a result of thermal transformation of sedimentary protoliths from the spontaneous combustion of coal beds (Figure 1). Although many coalfields contain such rocks, there is little information regarding quantitative data about them, and almost nothing about their forming conditions. The mineralogy of natural clinker depends on physical and chemical variables, such as chemical composition of the sedimentary protolith, temperature, degree of fusion and oxidation state, among others, and how one or more of these factors affects the stability of mineral phases may vary on a microscopic scale (Cosca *et al.*, 1989). However, some field and petrographic observations combined with analytical data can help to deduce the relative importance of these factors. Moreover, the natural clinker should be studied not only in relation to its origin but also to its potential use as an indicator of coal resources. Therefore, future studies should consider benefits obtained by using mine tailings as natural clinker based on knowledge of their petrographic, structural, physical and chemical properties.

In general, natural clinker is a mineralogical and chemically complex mixture in which the amount of each mineral phase present depends on the original composition of the protolith from which it was formed by pyrometamorphism, the mixture characteristics, the burning conditions, and the thermal history of the material, among others (Jones *et al.*, 1984; Cosca *et al*., 1989, Coates & Heffern, 1999; Heffern *et al.*, 1993). Although a geological study was not carried out on the protolith from which natural clinker has been generated, we can deduct some mineralogical changes suffered in particular clay strata after burning by spontaneous combustion of coal beds. It can be inferred that the increase in temperature caused by spontaneous combustion evidently produced the dehydration and vitrification of clay minerals, the dissolution of carbonates and the formation of aluminosilicates. Therefore, mineralogical and textural changes observed probably occurred on a system with disequilibrium on a small scale, with the development of high-temperature metamorphic reactions (pyrometamorphism).

Petrographic studies on glass-bearing burned rocks reveal the occurrence solid solution series as magnetite-hercynite ($FeAl_2O_4$), ulvöspinel ($Fe_2TiO_4$), hematite-ilmenite ($FeTiO_3$), y magnesiumferrite along the spinel ($MgAl_2O_4$)-magnesiumferrite ($MgFe_2O_4$) join of $Sp_{80}Mf_{20}$ and along the magnesioferrita-hematita join of $Mf_{60}Hm_{40}$ (Cosca *et al.*, 1989). Typical high temperature non magnetic minerals found in pyrometamorphic rocks associated with

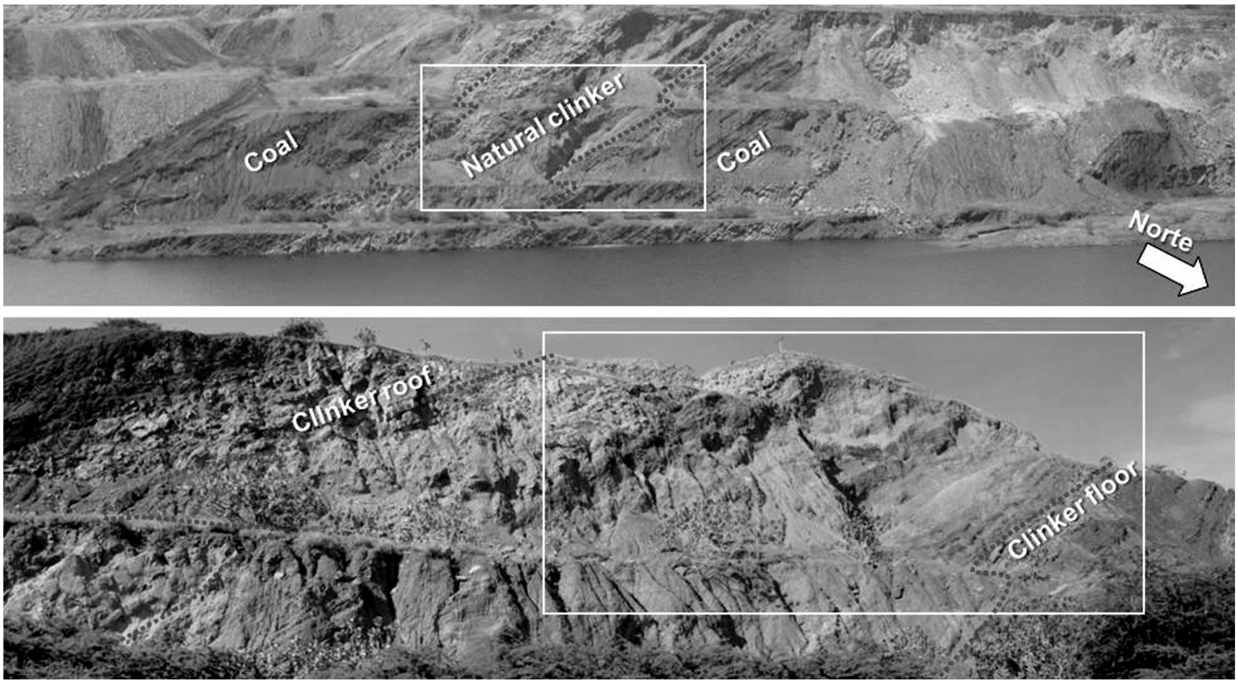


**Figure 1.** Photographs at outcrop scale of natural clinker associated with spontaneous combustion of coal beds, highlighting not only its geometry but also the various shades that present this geologic material.

coal combustion appear to include several Fe and Al rich clinopyroxene, melilita, cristobalite, tridymite, mullite, cordierite and fayalite solid solutions, as well as glass (Foit *et al.*, 1987; Cosca *et al.*, 1989; Râdan & Râdan, 1998). Glass compositions have been used by Cosca *et al.* (1989) to estimate the minimum temperatures of formation of natural clinker, which vary between 1020 and 1400 $^{o}$C. These authors suggest that different degrees of melting, mixing, crystallization, volatilization and liquid immiscibility in conditions of disequilibrium may be involved in the formation of such pyrometamorphic rocks. However, it is important to establish the type and amount of these magnetic phases in natural clinker, which affect its properties and, therefore, is necessary to identify and quantify them.

The determination of mineral phases and chemical composition of natural clinker is vital in resolving problems concerning their genesis, correlation of coal beds, characterization of the protolith and assessment of potential environmental impacts of coal combustion. Natural clinker is one of the contributing materials that could affect the environment, especially water chemistry, as important variables like the original composition of the protolith from which this geomaterial comes, burning conditions that generated it, and its particle size and mineralogy, influence the distribution and mobility of trace elements. Therefore, in response to environmental problems that occur as a result of the disposal of solid waste from coal mining, within which natural clinker lies, it is important to undertake studies to establish the environmental impacts of using this byproduct of coal in the field of materials science, based on its variability in quality and environmental impacts and human health.

The bulk chemical composition similarity of natural clinker with the volcanic materials from which the natural zeolites are originated by post-magmatic hydrothermal activity has motivated attempts of making zeolite from this geomaterial by Ríos and co-workers (Ríos & Williams, 2008; Ríos *et al.*, 2008a, 2008b, 2008c; Sandoval *et al.* 2009), justifying the development of future investigations in the field of the synthesis of new materials with potential industrial applications. According to them, zeolitic materials, such as Na-phillipsite, hydroxysodalite, hydroxycancrinite, K-chabazite, zeolite K-F, faujasite and zeolite Linde Type A can be synthesized by alkaline activation of natural clinker.

Recently, Sandoval *et al.* (2009) synthesized almost pure analcime with a high degree of crystallinity from natural clinker, optimizing the experimental conditions used by the pioneering work of Ríos & Williams (2008). Although its potential application might consume only a small part of the natural clinker produced by coal combustion, end products could reach a much higher added value than that currently presenting this geomaterial in the coal industry of Colombia.

The quantitative analysis using the Rietveld method has gained popularity in recent years as a rapid and accurate quantitative technique (O'Connor & Raven, 1988, Taylor & Matulis, 1991; Bish & Post, 1993; Weidler *et al.*, 1998; Raudsepp *et al.*, 1999; Gualtieri, 2000; de la Torre *et al.*, 2001). Quantitative analysis by the Rietveld method (Rietveld, 1969; Young, 1993) has huge advantages over traditional methods using integrated intensities of a small set of reflections in limited angular intervals, since the overlap of the lines of a pattern of powder diffraction, especially in mineralogically complex samples such as the natural clinker, make it virtually impossible to carry out a rigorous analysis by conventional methods. The analytical procedure using the Rietveld method is based on the relationship between the refined scale factor for each phase and its weight fraction in the multiphase mixture (Hill & Howard, 1987; Bish & Howard, 1988). This method makes efficient use of all information contained in the diffraction pattern and converts it into an effective analysis procedure without the use of standards, because it can be done on the diffraction data collected without the addition of an internal standard and without the need for calibration curves.

The only requirement to consider is that there must be a reliable isostructural model of each of phases to be quantified. On the other hand, if the process of quantitative analysis by the Rietveld method is successful on high quality diffraction data, the method can be used to quantify crystalline phases whose weight percentage are below 1.0%, and still can be used to determine the amount of amorphous material present in the multiphase mixture. In the last case, it requires adding a known amount of an internal standard to the sample and thus properly quantifies the material (Gualtieri, 2000).

The purpose of this study was to conduct a petrographic characterization of the natural clinker produced by spontaneous combustion of coal beds Cerrejón Formation and to apply the Rietveld method to the quantitative phase analysis of this geological material. Therefore, the implementation of the proposed methodology could be very important to quality control of geological materials for industrial use.

## Materials and methods

Petrographic analysis of different samples of natural clinker were carried out to establish their textural and structural features as well as their mineralogy, using the following analytical techniques: transmitted light microscopy (Nikon triocular microscope, model Labophot2-POL) of the School of Geology and image analyzer Leica of the School of Metallurgical Engineering and Materials Science at the Universidad Industrial de Santander, and scanning electron microscope ZEISS EVO50 of the Research Center of Applied Sciences at the University of Wolverhampton (analytical conditions: EHT = 20.00 kV, beam current 100 uA, Signal A = SE1, WD = 8.0mm).

The preparation and assembly of natural clinker samples for X-ray diffraction (XRD) was carried out at the Laboratory of Structural Chemistry of the School of Chemistry at the Universidad Industrial de Santander. Samples were homogenized in an agate mortar, and then mounted on an aluminum specimen holder using the technique of lateral filling (McMurdie, 1986). The process of disintegration and separation of clays (about 2μm) involved the separation of minerals by particle size using the Stokes' Law. Chemical and thermal treatments were conducted as follows: saturation with $K^+$ and $Mg^{2+}$ ions, calcinations at 350 and 550 °C and solvation with ethylene glycol. XRD patterns of the natural clinker were recorded with a RIGAKU D/MAX IIIB diffractometer operating in Bragg-Brentano geometry with Cu-$\alpha$1 radiation (k = 1.5406 Å) at 40 kV and 20 mA and graphite monochromation. The scan parameters were step size 0.02°, dwell time 2 s and 2θ range 2-70°. Phase identification was performed through the process of comparison search (Search/Match) using the crystallographic database Powder Diffraction File (PDF-2) from International Centre for Diffraction Data (ICDD). Full-pattern Rietveld refinement using RIQAS versión 4.0 (MDI, Rietveld Quantitative Análisis and Whole Pattern Fitting, 2006) was performed to quantify the amounts of phases in the natural clinker using a 20% by weight of aluminum oxide as internal standard.

## Results and discussion

### *Outcropping clinker*

One of the most remarkable features in the areas of Cerrejón coal mining complex is the occurrence of natural clinker as an indicator of ancient fires produced by spontaneous combustion of coal seams (Candela & Quintero, 2004; Quintero *et al.*, 2009). Natural clinker includes a variety of thermally affected rocks, which are easily recognizable on the field thanks to their mainly red color in a variety of intensities. Figure 1 illustrates a typical natural clinker outcrop, showing the reddening intensity due to the rock's alteration degree. However, it can also display several tones of black, gray, green and cream or even white, easily contrasting with the grayish hue of coal. It is a fine-grained particle size, compact and highly fractured rock, mainly reddish brown to red in colour due to the presence of hematite. These rocks represent a complex mixture of various amorphous and crystalline inorganic constituents and contain remaining inorganic materials derived from shales, sandy mudstones and grey sandstones originally associated with coal. In general, it is constituted by rocks of mainly clay texture but it could also be sandy. Natural clinker also retains much of the original rock characteristics as relict sedimentary structures and even fossil plant remains within layered sandstone and mudstone survive. The occurrence and distribution of natural clinker is described in more detail by Quintero et al. (2009). Evidence supports the fact that claystones, siltstones and sandstones adjacent to coal beds were metamorphosed by the spontaneous combustion of coal, recording continuous mineralogical and textural changes from relatively unaltered rocks to molten material (vesicular slag) during pyrometamorphism.

### *Petrography*

Natural clinker includes a variety of pyrometamorphic rocks, which vary in their degree of thermal alteration, according to their texture and structure, original composition and position on the burning area. These rocks are characterized by fine-grained particle size and usually red color in different shades, although black, gray, green, cream or white varieties also occur. It is relatively hard and compact but disintegrates at the touch, and it can show a sugary and slight brecciate vesicular appearance. General macroscopic characteristics of natural clinker varieties of the Cerrejón Formation are shown in Figure 2. Natural clinker usually shows cooked sandy and clay textures (Figures 2a and 2b), the last of them similar to a common building brick, which is characterized by its reddish-orange color, shiny fracture rather than opaque similar to jasper and intense oxidation, which has been accompanied by a hardening of the rock through the transformation of clay minerals in hematite. This variety sometimes exhibits very specific characteristics, taking into account that relics of the original sedimentary structure are preserved, which are still recognized by the millimeter scale “tigerstripe" pattern of its color (Figure 2c), with orange-red, locally purple, areas and light gray areas, the latter as relics of the original claystone with scalloped and parallel edges to the stratification surface. Orange-red areas present red edges, due to the formation of hematite, which tends to permeate the rock, producing relatively hard cement. Light gray areas are darker toward the contact with red-orange areas, due to the presence of black magnetite. Figure 2d illustrates an example of a natural clinker similar to a vesicular slag with a characteristic spongy texture. The distinguishing characteristics of this variety are shown in Figure 3. A glassy material of gray to grayish brown color occurs filling vesicles or along fractures that are arranged perpendicular or diagonal and, in some cases, parallel to the stratification surface (Figure 3, top). A microphotography captured in an image analyzer (Figure 3, bottom) illustrates the vesicular slag and sponge appearance of this variety. Under transmitted light microscopy, it is completely isotropic, except for tiny particles of quartz. Rogers (1918) interprets this variety as the result of hot gases (350°C) which escaped from the zone of spontaneous combustion of coal beds and affected the adjacent rock to the molten state, which then hardens into a vesicular glass.

Nevertheless, faulting locally generates breccia zones that clearly demonstrate that spontaneous combustion existed before the last fault’s activity period since it contains mixed fragments of natural clinker, fresh rock and coal (Figure 2e). Quintero *et al.* (2009) reported that calcareous rocks of the Cogollo Formation in the hanging wall of the Cerrejón thrust fault, and immediately over this tectonic discontinuity, are thermally affected and present reddish, cream and pink to purple colours, preserving already all of the original characteristics including fossil fragments (Figure 2f).

Figure 4 illustrates images of scanning electron microscopy (SEM) of natural clinker particles, which are characterized by their fragmentation and blocky morphology, with blocky, angular fragments with or without vesicles, occasionally exhibit stepped fractures.

### *X-ray difraction*

Figure 5 shows the XRD patterns of natural clinker in the range of 2θ from 2-40°, using Cu-α1 radiation, in which sharp reflections are observed corresponding to high intensities of quartz (PDF No. 010-46-1045). Similarly, there are broad bands with low relative intensity which correspond to hematite (PDF No. 010-73-2234), anatase (PDF No. 010-72-7058) and minerals of smectite and mica groups. Taking into account that the peak intensity corresponding to quartz is larger than those from other mineral phases, it was necessary to carry out the separation of the clay fraction in order to obtain separated XRD patterns (not shown here) for the aluminosilicates. The saturation with $Mg^{2+}$ and subsequent glycosylation of natural clinker samples (tigerstripe type, NC-1, and highly oxidized type, NC-2) produced displacements of the reflection (001) of the band corresponding

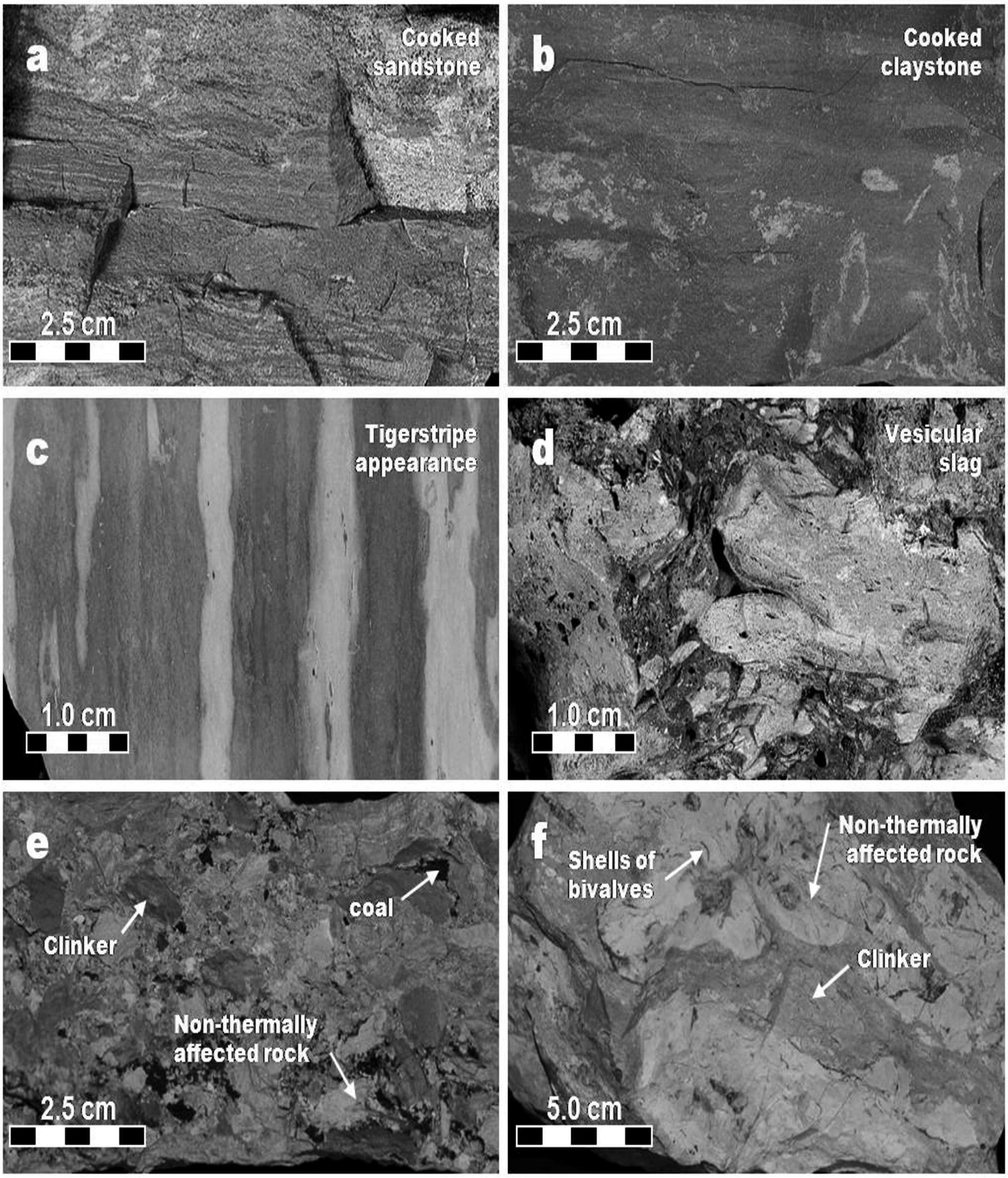


**Figure 2.** Photographs of hand specimens of natural clinker showing varieties, and textural and structural features.

to the smectite group from 15.07 to 17.38 Å for sample NC-1 and from 15.17 to 17.52 Å for sample NC-2. Additionally, strong reflections were observed, indicating the presence of montmorillonite and discarding the presence of vermiculite in both samples with predominance of interchangeable ion $Mg^{+2}$ principally in sample NC-2 in which it looks a greater

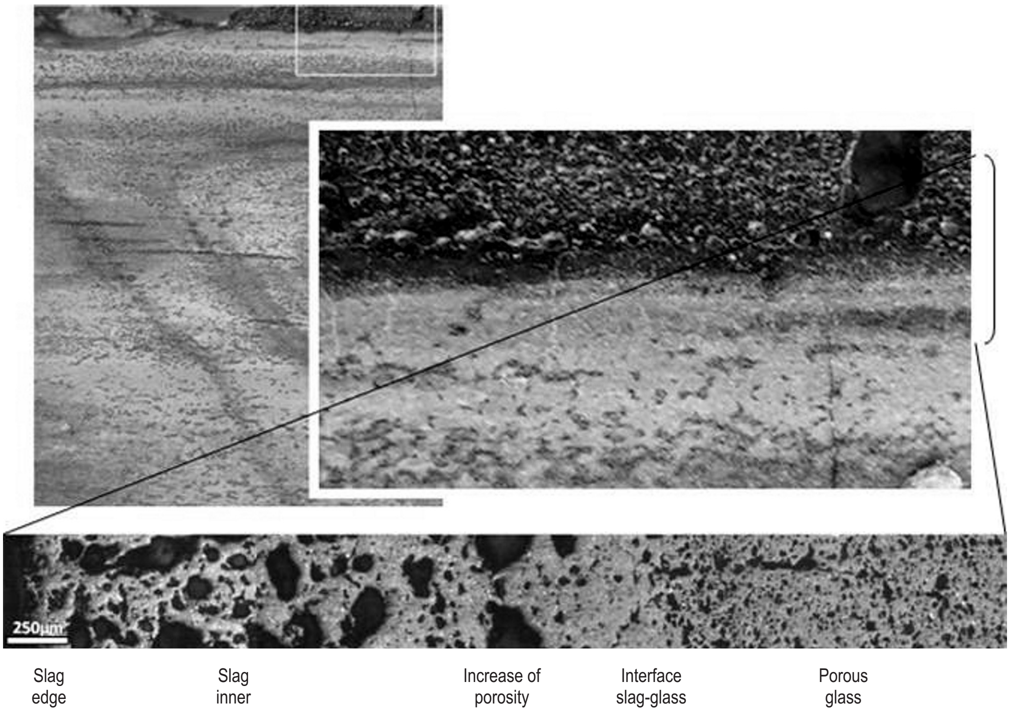


**Figure 3**. Above, photographs of a hand specimen of natural clinker, displaying a vesicular slag appearance. Below, micrograph of the upper left part of the detail shown above. Note the spongy texture and vesicular slag appearance.

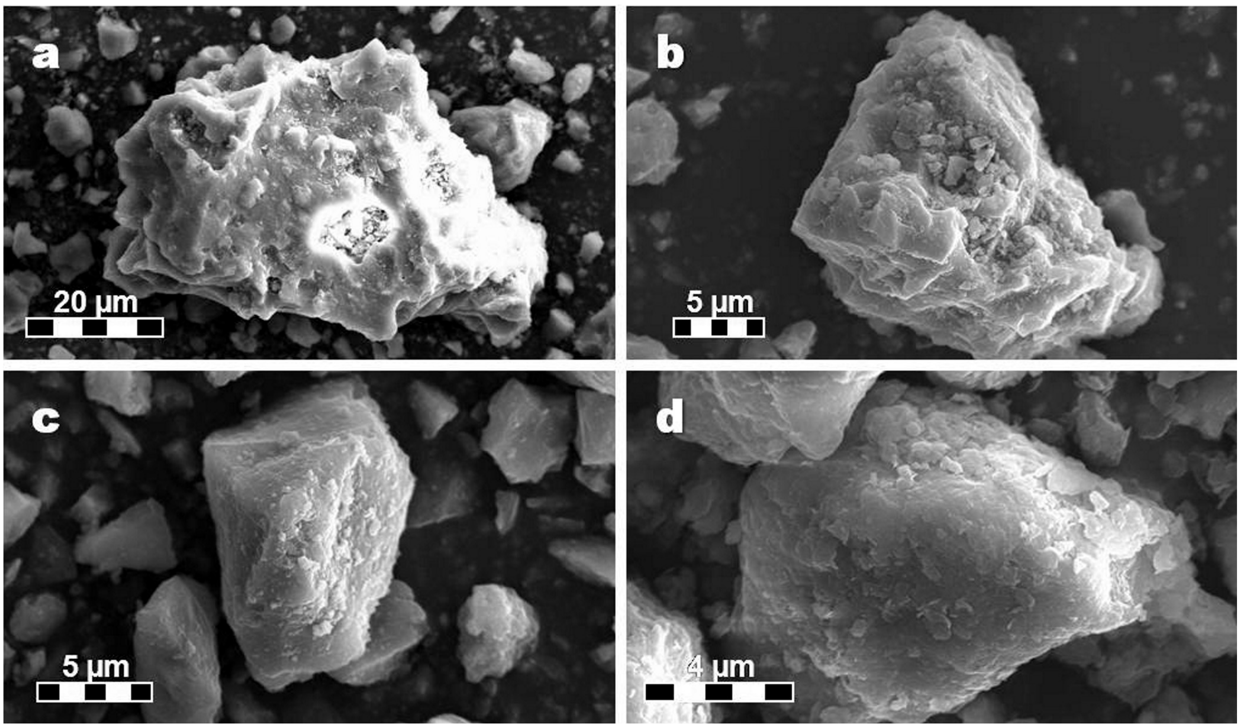


**Figure 4.** SEM images of natural clinker particles.

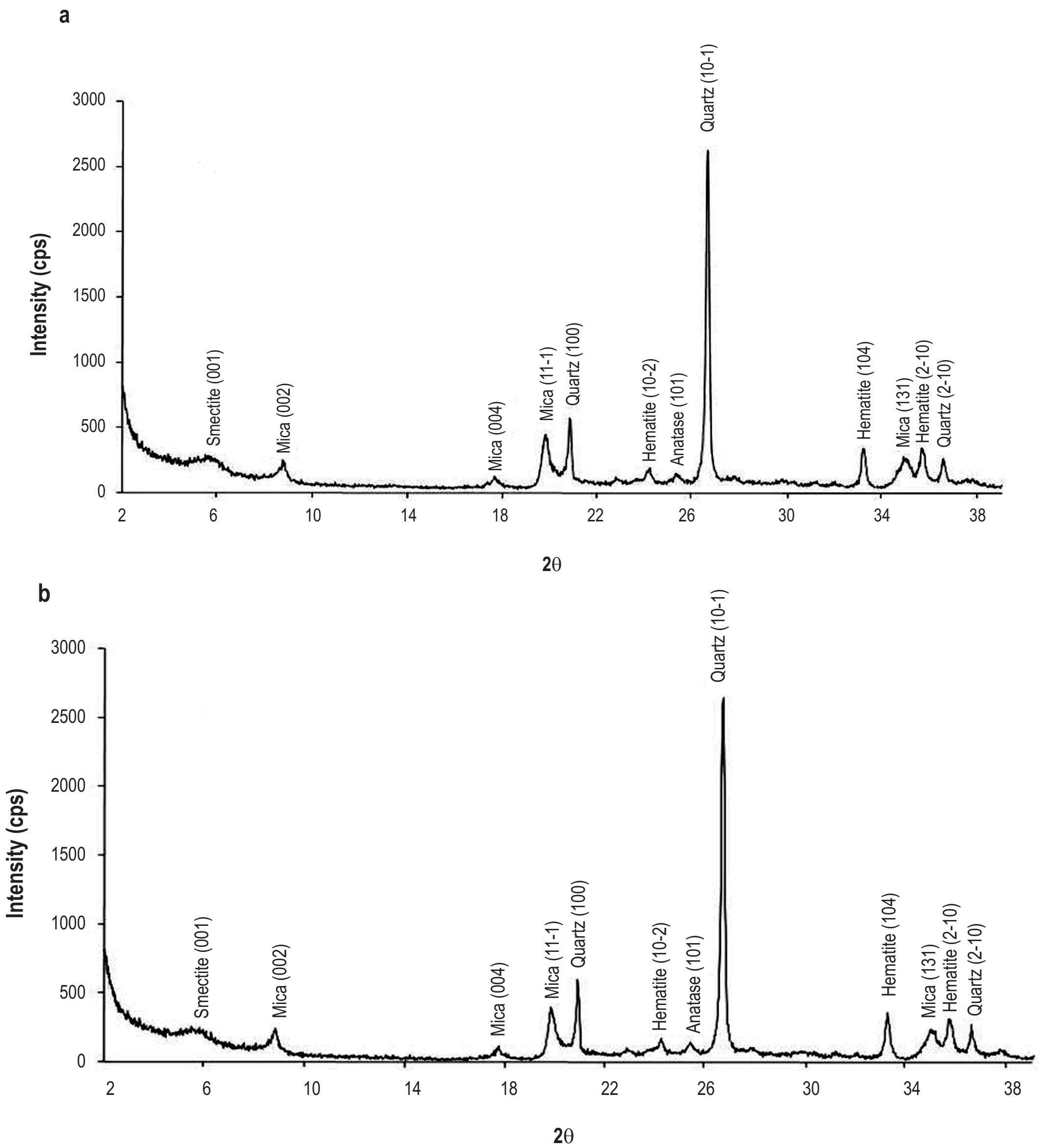


**Figure 5**. XRD patterns of samples NC-1 (a) and NC-2 (b) in the 2θ range of 2-40°, using Cu-$\alpha$1 radiation.

degree of swelling. In the region between 7.14 and 7.20 Å, there is a wide band of very low intensity which disappears by thermal treatment at 550 ºC. This behavior is characteristic of kaolinite which collapses at this temperature and is transformed into metakaolin (amorphous phase). Kaolinite was not detected in the qualitative and quantitative analysis because it is below the detection level, but it was identified after the thermal treatment of the clay fraction. Similarly, the presence of illite (interplanar spacings at 9.93-9.97 Å, 4.98-5.00 Å and 3.32-3.34 Å for sample NC-1 and 9.7-10.04 Å, 5.00 Å and 3.32-3.33 Å for sample NC-2) was confirmed, which remains stable after thermal treatments. XRD profiles of the original (untreated) and treated (saturated with ethylene glycol and heated to 550 °C) clay are shown in Figure 6.

Figure 7 shows the observed and calculated XRD patterns and their differences after refinement by the Rietveld method, where it can be observed the good fit of data, indicating that isostructural models chosen for each phase were appropriate. The models used for illite, hematite, quartz and anatase were taken from the Inorganic Database (ICSD, 2007 / I). The montmorillonite model was taken from the literature (Viani *et al.*, 2002), assuming a montmorillonite with some degree of disorder and interchangeable $Ca^{+2}$ and $Na^{+2}$ ions.

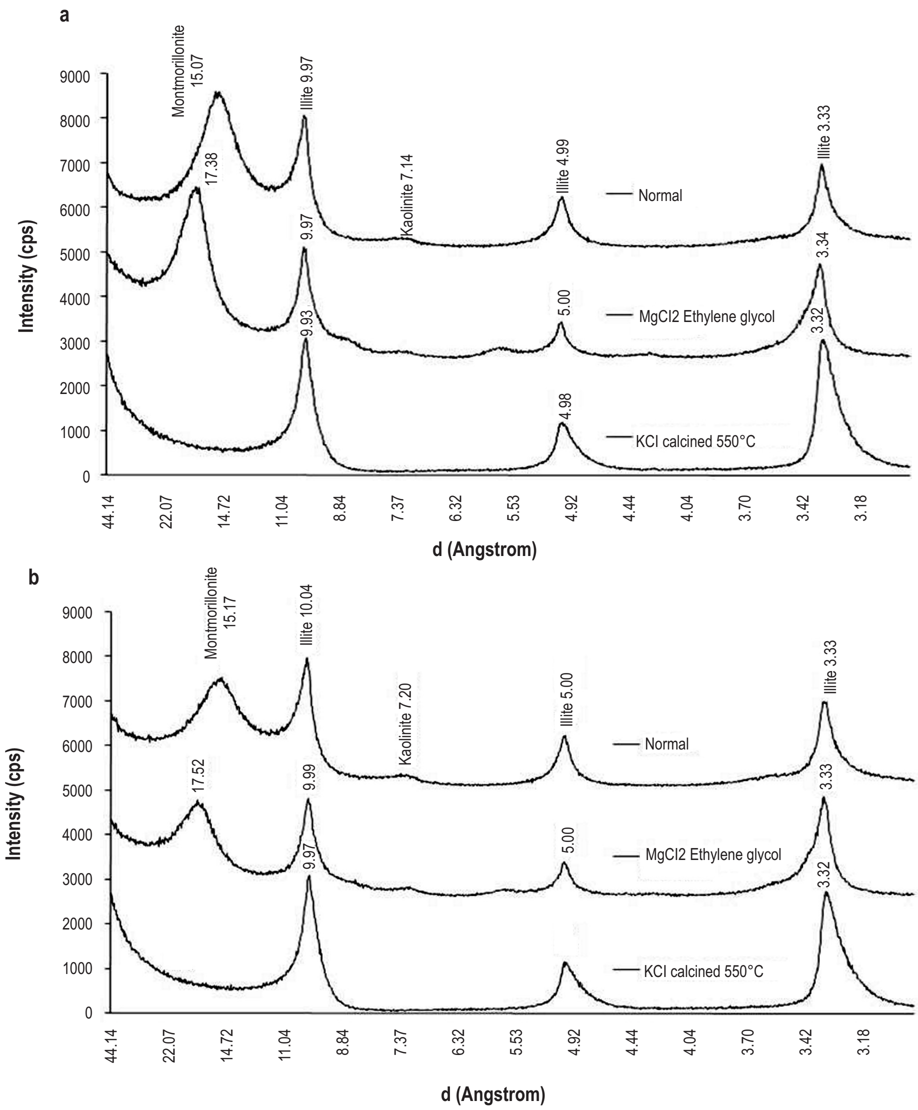


**Figure 6.** XRD patterns of the clay fraction in samples NC-1 (a) and NC-2 (b).

For illite, hematite, quartz and anatase structure factors were calculated using the atomic scattering factors. The background noise was fitted with a polynomial function and the peak profile was modeled using the Lorentzian function of Pearson VII. The cell constants, scale factor and coefficients corresponding to sample displacement and asymmetry were also refined. For the refinement of montmorillonite, the same previously described factors were calculated, except atomic positions, which were left fixed. This strategy avoided overestimating the content of this phase in natural clinker samples. Similarly, during the refinement of the illite some degree of preferential orientation for the reflection (11-1) was observed. This aspect, which is one of the most serious problems in quantitative analysis, was largely corrected using the March function (Dollase, 1986).

Table 1 shows the residual values defined by RIQAS, $R_{wp}$ y $R_{Bragg}$, for final refinements by least squares together with the percentages of the phases. $R_{wp}$ values (20.33% and 20.25% for samples NC-1 and NC-2, respectively) indicate that the refinement as a whole has been satisfactory if we consider that natural clinker samples consist of a mixture of minerals which hinders the achievement of lower refining indicators. Low values of $R_{Bragg}$ (5.05-10.26% and 3.99-12.28% for samples NC-1 and NC-2, respectively) achieved in each phase indicate that the structural model selected was appropriate. However, for the montmorillonite

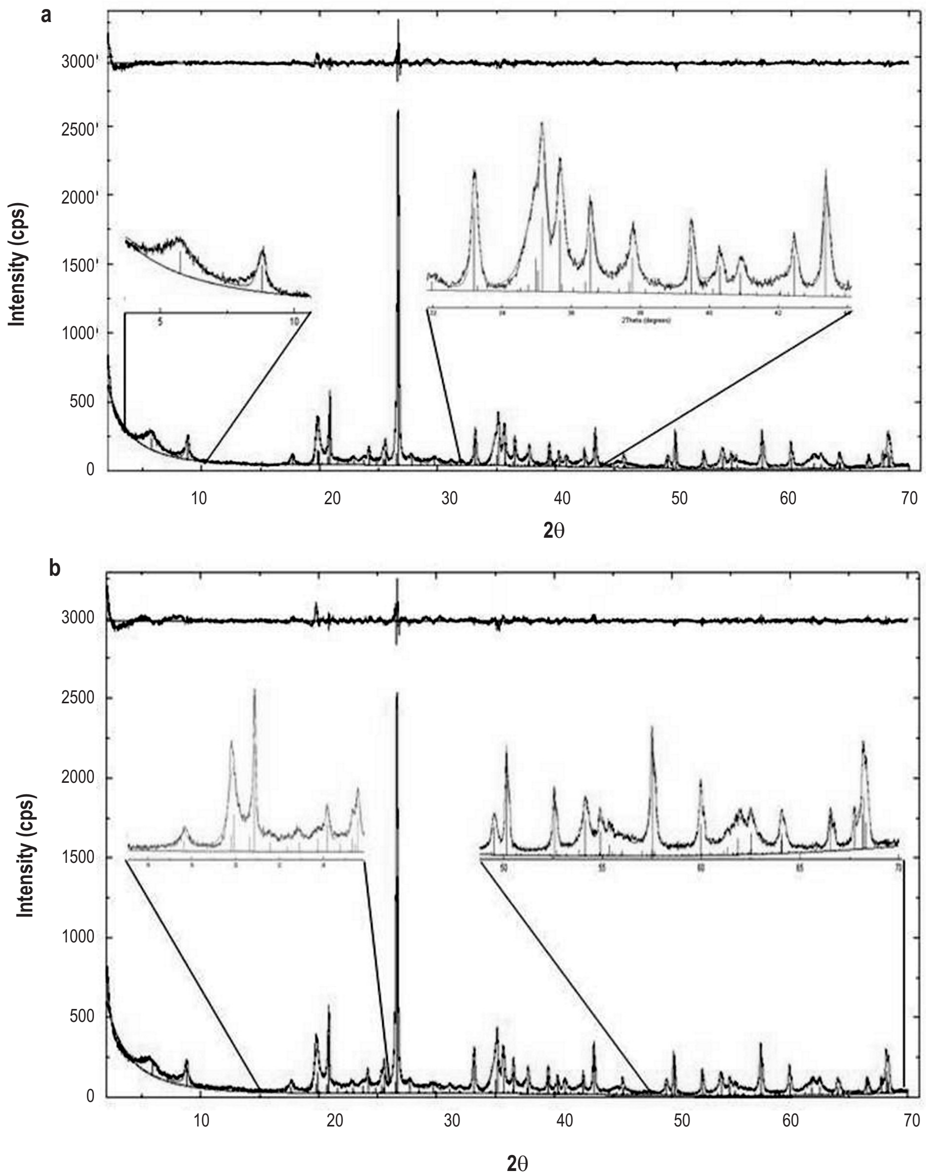


**Figure 7.** XRD profiles refined by the Rietveld method (observed profile in black; calculated profile in red and difference between the observed and calculated profiles in the upper part) from samples NC-1 (a) and NC-2 (b).

slightly higher values (12.51% and 14.32%) were observed, indicating that some reflections have been completely unadjusted. Moreover, we can notice that despite performing the correction for the preferred orientation of the reflection (11-1) of illite, the standard deviation of quantification is the highest (±0.4 and ±0.5 for samples NC-1 and NC-2, respectively), but this value is below the average standard deviations for mineral phases (Gualtieri, 2000). In general, very small deviations in the quantitative analysis of the identificated crystalline phases were observed. In accordance, the higher content of amorphous material that could be associated with NC-2 sample was exposed to a higher temperature during spontaneous combustion, which may be related to a possible conversion of quartz to amorphous silica.

Residual values of $R_{wp}$ and $R_{Bragg}$ as a whole indicate that the refinement has been satisfactory and that the structural models used were appropriate. The presence of amorphous material (2.7% for sample NC-1 and 3.3% for sample NC-2) is not an impediment to identify and quantify the mineralogy of the natural clinker.

**Table 1.** Crystallographic data and refinement details by the Rietveld method for the natural clinker phases

| | Hematite | | Quartz | | Illite | | Montmorillonite | | Anatase | |
|---|---|---|---|---|---|---|---|---|---|---|
| ***Crystallographic data*** | | | | | | | | | | |
| Chemical formulae | $Fe_2O_3$ | | $SiO_2$ | | $K(Al_4Si_2O_9(OH)_3)$ | | $(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2nH_2O$ | | $TiO_2$ | |
| M (g/mol) | 159,697 | | 60,084 | | 398,204 | | 549,07 | | 79,88 | |
| Crystalline system | Hexagonal | | Hexagonal | | Monoclinic | | Triclinic | | Tetragonal | |
| Space group | R-3c [No.167] | | P 3221 [No.154] | | C2/c [No.15] | | P1 [No.1] | | I41/a [No.141] | |
| | **NC-M1** | **NC-M2** | **NC-M1** | **NC-M2** | **NC-M1** | **NC-M2** | **NC-M1** | **NC-M2** | **NC-M1** | **NC-M2** |
| a (Å) | 5.0291 (1) | 5.0297 (2) | 4.9116 (1) | 4.9106 (1) | 5.181 (1) | 5.1928 (7) | 5.11 (7) | 5.12 (7) | 3.7816 (9) | 3.7856 (4) |
| b (Å) | 5.0291 (1) | 5.0297 (2) | 4.9116 (1) | 4.9106 (1) | 9.038 (2) | 9.010 (2) | 8.80 (9) | 8.42 (9) | 3.7816 (9) | 3.7856 (4) |
| c (Å) | 13.733 (1) | 13.739 (1) | 5.4025 (3) | 5.4008 (3) | 20.200 (3) | 20.206 (4) | 15.26 (3) | 15.16 (4) | 9.50 (1) | 9.42 (1) |
| α (º) | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 |
| β (º) | 90 | 90 | 90 | 90 | 95.67 (1) | 95.57 (1) | 90 | 90 | 90 | 90 |
| γ (º) | 120 | 120 | 120 | 120 | 90 | 90 | 90 | 90 | 90 | 90 |
| V ($Å^3$) | 300.81 (3) | 301.00 (3) | 112.87 (1) | 112.78 (8) | 941.3(3) | 940.6 (3) | 686.39 (12) | 653.88 (11) | 135.9 (2) | 134.9 (6) |
| ρ ($g/cm^3$) | 5.289 (1) | 5.286 (1) | 2.652 (1) | 2.654 (1) | 2.789(1) | 2.791 (1) | 1.93(6) | 2.02 (6) | 3.905 (1) | 3.933 (3) |
| Z | 6 | 6 | 3 | 3 | 4 | 4 | 1 | 1 | 4 | 4 |
| ***Refinement details*** | | | | | | | | | | |
| | **NC-M1** | **NC-M2** | **NC-M1** | **NC-M2** | **NC-M1** | **NC-M2** | **NC-M1** | **NC-M2** | **NC-M1** | **NC-M2** |
| No. refined variables | | | | | | | | | | |
| $R_{B\,(\%)}$ | 7,43 | 7,78 | 5,05 | 3,99 | 7,23 | 6,83 | 12,51 | 14,32 | 10,26 | 12,28 |
| R (%) | 13,52 | 13,38 | 13,52 | 13,38 | 13,52 | 13,38 | 13,52 | 13,38 | 13,52 | 13,38 |
| $R_{wp\,(\%)}$ | 20,33 | 20,25 | 20,33 | 20,25 | 20,33 | 20,25 | 20,33 | 20,25 | 20,33 | 20,25 |
| XRD (%) | 9.4± 0.1 | 9.1± 0.1 | 39.3± 0.3 | 35.2± 0.3 | 42.4± 0.4 | 46.3± 0.5 | 6.3± 0.2 | 5.4± 0.2 | 0.4± 0.1 | 0.7± 0.1 |
| Amorphous (%) | 2,7 | 3,3 | 2,7 | 3,3 | 2,7 | 3,3 | 2,7 | 3,3 | 2,7 | 3,3 |

NC, natural clinker

A significant amount of amorphous material appears to reduce the crystalline signals. Many of these signals contain a large number of reflections which overlap with those of the other phases. Quantitative analysis of amorphous material also looked at all the factors that could affect the results. It is evident that natural clinker contains amorphous material, which cannot be detected directly by XRD, although it is important to understand the thermal history of natural clinker. To quantify the amorphous material by using the program RIQAS a crystalline standard (free amorphous) was added to the natural clinker in a known percentage. However, the higher content of amorphous material was observed in the natural clinker with glass material.

## Conclusions

In the present work, the structural information on natural clinker associated to spontaneous combustion of coal of the Cerrejón Formation was obtained from high-quality powder diffraction patterns. The obtained crystallographic data were determined by Rietveld analysis.

Rietveld analysis of natural clinker reveals that it contains a large number of crystalline phases, many apparently present in small amounts that could be part of a series of solid solutions as a result of the thermal alteration process.

The results obtained in this study indicate that natural clinker is a complex chemical and mineralogical material. Nevertheless, it has been shown that quantitative analysis by the Rietveld method is appropriate to study the mineralogy and crystallochemistry of phases present in this geomaterial producing reliable results.

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