Contents lists available at ScienceDirect



International Journal of Coal Geology



journal homepage: www.elsevier.com/locate/ijcoalgeo

Spontaneous combustion of the Upper Paleocene Cerrejón Formation coal and generation of clinker in La Guajira Peninsula (Caribbean Region of Colombia)

J.A. Quintero^a, S.A. Candela^b, C.A. Ríos^{c,*}, C. Montes^d, C. Uribe^e

^a Carbones del Cerrejón Limited., Cl. 100 No. 19-54 piso 12, Bogotá D.C., Colombia

^b ECOPETROL S.A. Edificio Principal Cr. 7 No. 37-65. Bogotá D.C., Colombia

^c Escuela de Geología, Universidad Industrial de Santander, Cr 27 Cl 9, Ciudad Universitaria, Bucaramanga, Colombia

^d Smithsonian Tropical Research Institute, Roosvelt Ave., Tupper Building – 401, Balboa, Ancón, Panamá, Panamá

^e Tubos Moore S.A. Cll 99 No. 57-74, Bogotá, Colombia

ARTICLE INFO

Article history: Received 22 July 2009 Received in revised form 26 September 2009 Accepted 26 September 2009 Aavailable online 5 November 2009

Keywords: Clinker Cerrejón Formation Spontaneous combustion Coal Geologic past

1. Introduction

Coal geologists refer as clinker the baked and fused sedimentary rocks associated to the subsurface spontaneous combustion of coal seams during the recent geologic past (since early Pliocene time), which are common geologic features that have been reported in different areas throughout the world (United States of America: Heffern et al., 1983, 1993, 2007: Cosca et al., 1989: Hoffman, 1996: Heffern and Coates, 1997, Lyman and Volkmer, 2001; India: Prakash et al., 1997; Rumania: Râdan and Râdan, 1998; Australia: Ellyett and Fleming, 1974; New Zealand: Lindqvist et al., 1985 and China: Zhang, 1998; De Boer et al., 2001). In some cases, these rocks have been the main factor that contributes to the formation of characteristic topographic features and geoforms in intermountain carboniferous basins (Coates and Heffern, 2000). Kuchta et al. (1980) considered that the rank of coal and geological structures are the most important characteristics that facilitate the natural self-heating of the coal. However, in addition to these factors, air flow, temperature and sulphide mineral content, also play an important role in the beginning of the combustion (Kim, 1977; Lyman and Volkmer, 2001). Sevenster (1961) determined that the amount of heat produced during the oxidation will mainly depend on the oxygen-coal interaction.

E-mail addresses: carios@uis.edu.co, carios123@hotmail.com (C.A. Ríos).

ABSTRACT

Clinker referred here as red and brick-looking burnt rocks found interbedded in the Upper Paleocene Cerrejón Formation is the result of spontaneous and natural combustion of coal seams in the recent geologic past. These rocks have been mapped, measured and characterized in the Cerrejón Coal Mine at La Guajira Peninsula (Colombia). These burnt rocks usually outcrop in irregular patterns as almost tabular bodies up to 100 m thick, thinning and pinching out below ground surface to depths up to 448 m. Mapping revealed that clinker is usually found near deformed zones, either faults or tight folds. Timing of spontaneous combustion seems to predate folding and faulting, but seems to postdate the development of the Cerrejón thrust fault and alluvial fan proceeding from the Perijá Range. Clinker covers an area of around $2.9 \times 10^6 \text{ m}^2$ with a volume of approximately $1.4 \times 10^8 \text{ m}^3$. The calculation of the amount of heat released through coal burning indicates that complete combustion of 6.4 Mt of $26.4 \times 10^6 \text{ J/kg}$ coal would yield 17×10^{13} J.

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According to Timko and Derick (1995), if the oxidation heat is not dissipated or removed from the environment, the coal will gradually continue warming up, leading to the spontaneous combustion. The chemical reactions that occur during the slow oxidation of the coal are very complex (Swan and Evans, 1979), however, the low-rank coals, especially those with a sub-bituminous characteristic, easily undergo selfheating (Litton and Page, 1994). Lyman and Volkmer (2001) indicated that the self-heating occurs due to low-temperature oxidation in combination with humidity adsorption, depending on whether coal was partial or totally dried. Paleomagnetic studies in rocks thermally affected by coal combustion indicate that they can be high-fidelity geomagnetic field recorders (Jones et al., 1984; Krsová et al., 1989). De Boer et al. (2001) reported magnetic properties of sedimentary rocks thermally metamorphosed by spontaneous combustion of coal in Xinjiang (NW China), which is of great importance to delineate the extension in surface and depth of penetration of extinct coal fires. Balachandran (1996) performed seismic wave tests in the Wyoming's Powder River Basin. The results support the concept that fractured zones may be identified by the strength of the converted shear waves, which may be a valuable and economical way to detect fractured reservoirs. Zhang (1998) and De Boer et al. (2001) demonstrated from remote sensing imagery that over 90% of the burnt rocks in Xinjiang (NW China) are associated with extinct coal fires, which have repeatedly occurred during the recent geologic past (mainly during the Pleistocene). Some studies (Heffern et al., 1983, 2007; Jones et al., 1984; Coates and Naeser, 1984; Reiners and Heffern, 2002) using modern techniques of dating determined the age of thermally altered rocks

^{*} Corresponding author. Tel./fax: +57 7 6343457.

^{0166-5162/\$ -} see front matter © 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.coal.2009.09.004

associated with ancient fires that happened on repeated occasions from the beginning of the Pliocene (4.0 ± 0.7 m.a.) to the recent geologic past (0.5 ± 0.3 m.a.). Jones et al. (1984) argued that combustion events could be correlated by fission-track dating on zircons that also would provide absolute ages for (part of) the thermal record. Reiners and Heffern (2002) determined ages (U–Th)/He from detrital zircons in clinker from the Powder River Basin to the NE of Wyoming, which are concordant but generally more precise with respect to the fission-track ages in zircon reported by Coates and Naeser (1984).

In Colombia, research concerning the Cerrejón carboniferous basin includes several geological studies mainly based on structural and stratigraphic aspects. Candela and Quintero (2004) carried out the first detailed geologic cartography of clinker cropping out in the Cerrejón Coal Mine, which in addition included its modelling and structural control in depth. However, the processes of spontaneous combustion of coal and generation of clinker barely have been studied. Álvarez and Gómez (1986) carried out a petrological study of the products obtained as a consequence of the intense heat to which the adjacent host rocks were exposed during the combustion of coal seams, which was high enough for partial melting of ashes and roofrocks producing paralavas of basaltic composition.

This paper concerns with the occurrence of clinker zones in the Cerrejón Coal Mine. The objectives of this study were to describe the occurrence of clinker, discuss the hypothesis related to its formation and age and estimate the volume and heat released through burning of coal during the recent geological past.

2. Methods

Field-mapping of the occurrences of clinker zones was performed along highwalls and endwalls of active and abandoned mine pits. This yield a map that shows detailed structural control of the distribution of surface clinker. The analysis and interpretation phases included the organization of the information, which were complemented with the revision of geophysical logs from boreholes to generate geological cross-sections to control the geometry of clinker bodies both on the surface and at depth. However, it is necessary to take into account that the thickness of clinker depends on such factors as the thickness of the coal bed that burned, the quality of the coal, and the thickness, porosity, and lithology of the surrounding rocks (Heffern and Coates, 2004). Estimation of how much coal has burned was performed using a very simple method of reducing the clinker bodies to a regular geometric form to easily calculate the volume. The three dimensional aspects of clinker bodies were measured with the aid of maps and geological cross-sections: (1) the height (average thickness, obtained between the minimum (at depth) and maximum (on the surface) thickness), (2) the width as the length in outcrop, and (3) the depth as the extension in the direction of dip divided by two, taking into account that clinker bodies tend to wedge out at depth. Calculation of burnt coal was easier, simply taking the area obtained in the previous step and multiplying it by the average thickness of the corresponding coal seam.

3. Geological setting

The Cerrejón Coal Mine is located within La Guajira Peninsula in the Caribbean Region of Colombia (Fig. 1). Carbones del Cerrejón Limited. is dedicated to the exploration, exploitation and marketing of high quality thermal coal, representing the largest opencast coal mine in the world. Colombia is the fourth largest coal exporting country in the world (International Energy Agency, 2008). The mining operation reached a coal production of 31.3 Mt during 2008, with approved expansion plans to increase production to 42 Mt in 2011. The main market for global coal consumption has been Germany, Holland, Denmark, North America and the United Kingdom. Fig. 2 illustrates a generalized geological map of the Cerrejón Coal Mine. It is a structurally complex deposit controlled by tectonic features associated to the Cerrejón and Ranchería thrust faults and Tabaco folding zone. This deposit is limited to the north by the Oca fault, to the southeast by the Cerrejón thrust fault and to the northwest by an abrupt topographic change due to the occurrence of calcareous rocks of the Manantial Formation. In addition, there are strike-slip faults, which split the deposit into blocks, maintaining its stratigraphic continuity. The Cesar-Ranchería Basin mainly consists of a sedimentary succession of Paleocene age (Bayona et al., 2004) and unconsolidated recent deposits. The Cerrejón Formation (Upper Paleocene) is approximately 900 m in thickness and forms part of the Triassic to mid-Miocene sequence of sediments that filled a regional basin in the northern part of South America (extending eastwards to Los Llanos Basin in Venezuela). The coal-bearing sequence forms part of this sedimentary unit, which consists of shales, sandy mudstones, grey sandstones and coal, with notable absence of a conglomeratic siliciclastic succession (Jaramillo et al. 2007). Coal seams of economic interest are actually in exploitation, being more or less regularly distributed and present variable thickness. The Cerrejón Formation has been divided into three groups (lower, middle, and upper) based on the thickness and distribution of the coal beds. Overall coal bed thickness averages 3 m and ranges from 0.7 to 10 m (Weaver, 1993), although the thickest coal beds (1.4 to 10 m) is in the upper part of this sedimentary sequence. A palynological study of the Cerrejon Formation was conducted by Jaramillo et al. (2007) to date the formation and understand the floristic composition and diversity of a Paleocene tropical site. Palynomorph assemblages indicate that the age of the Cerrejon Formation is Middle to Late Paleocene (ca. 60-58 Ma). There is an angular unconformity of approximately 15° between the Cerrejón Formation and the overlying Tabaco Formation of Upper Paleocene age, which includes grey and yellow sandstones and conglomeratic sandstones with thin intercalations of sandy mudstones. The base of the Cerrejón Formation rests transitionally on the Manantial Formation of Paleocene age, which consists of intercalations of sandy limestones (on the base), mudstones and muddy sandstones (on the top) (Jaramillo et al. 2007). Fig. 3 illustrates a simplified lithostratigraphic column of the Cerrejón Formation. It is exposed in the mining area throughout a simple monocline shallowly dipping towards the SE and in structural continuity with the Santa Marta Massif. This belt is locally segmented and partially repeated due to tectonic features, such as the Ranchería fault towards the south of the mining area and folded and faulted towards the north in the Tabaco folding zone, where it is also displaced by strike faults (Cerrejón geology team, 2005). The Cerrejón Formation rocks were deposited in a transitional to continental environment of subaerial deltaic type marked by rapid subsidence (Durán et al., 1981), with sedimentary structures of facial association typical of this environment, accompanied by an originally passive tectonics that controlled subsidence, contribution of detritus and interment speed of sediments (Bayona et al., 2004). Lithofacies associations and floral composition indicate deposition fluctuating from an estuarine-influenced coastal plain at the base to a fluvialinfluenced coastal plain at the top (Jaramillo et al., 2007).

4. Coal and clinker composition

4.1. Coal composition

The coal gangue is characterized by high proportions of quartz (54.2%) and minor proportions of kaolinite (16.9%), pyrite (12.9%), illite (9.4%), coquimbite (3.5%) and bassanite (3.2%). Petrographical analysis of coal reveals that it is characterized by a high vitrinite content (75–78.4%) of tellinite and desmocollinite type, inertite (18–20%) of fusinite and semifusinite type, liptinite (2–6%) of esporinite, cutinite and resinite types. Fusinite confers a high microporosity to the coal (Gómez et al., 2007). Pyrite occurs as fine-grained



Fig. 1. Geographic localization of the Cerrejón Coal Mine in La Guajira Peninsula (Caribbean Region of Colombia).

disseminations, as anhedral grains, as framboids and framboidal aggregates with carbonate and fragmental vitrinite, as fine-grained aggregates in vitrinite and filling microfractures (Carmona and Ward, 2008). Sub-angular to rounded quartz grains are also present, possibly of detrital origin, but most other minerals, including clay minerals, occur mainly as aggregates consisting of intimately admixed mineral and maceral constituents. According to Barranco (2001), the coal in the study area is a low-moisture (8.3-12.0%, ad), low-sulphur (0.4-0.85%, db) and low-ash (4.5-11.5%, db) coal. The C content is 82.4-84.23% daf and the calorific value reaches 26.9-28.5 MJ/kg (maf). The N, H and O contents are 1.3-1.85, 5.53-5.9 and 7.73-9.5% db, respectively. The volatile matter content (31.5-37.0% daf) suggests a bituminous rank. The low-sulphur content is typical of the coal of the Upper Paleocene Cerrejón Formation. A representative chemical composition of the coal ash of the Cerrejón Formation was determined by Karlsen et al. (2006) and Carmona and Ward (2008). It can be expressed as SiO₂ (41.2-73.0%), Al₂O₃ (14.73-42.6%), CaO (0.94-1.97%), MgO (0.92-2.22%), Na₂O (1.2-2.1%), K₂O (0.03-0.57%), Fe₂O₃ (2.7-11.9%), TiO₂ (3.0-3.3%), P₂O₅ (0.12-0.22%), SO₃ (2.1-2.7%). Chemical data from coal are characterized by relatively very low concentrations of As (0.078-23.91 mg/kg), Tl (0.003-0.004 mg/kg), Fe (0.009-0.188 mg/kg), Th (0.060-1.11 mg/kg), Cd (0.012-1.41 mg/ kg), Hg (0.004–0.187 mg/kg), Pb (0.30–4.66 mg/kg), Se (0.97–6.4 mg/ kg), except by As that can reach markedly high concentrations, and relatively moderate contents of Zr (2.37-28.4 mg/kg), Zn (1.01-5.02 mg/kg), Ni (0.446-5.6 mg/kg), Li (0.656-5.74 mg/kg), Mn (2.01-8.77 mg/kg), Cu (1.49-9.78 mg/kg), V (0.67-12.5 mg/kg), and Sr (1.79–20.6 mg/kg), when compared with the average values of the Shanxi coal in China reported by Dai et al. (2008). In general, the concentration of trace elements do not follow a specific pattern with regards to ash content, because their occurrence is related to characteristic mineral species and organic associations (Morales and



Fig. 2. Generalized geological map of the Cerrejón Coal Mine within La Guajira Peninsula.

Carmona, 2007). As and Hg are the trace elements that present the best correlations with total sulphur, which indicates their close association with coal minerals (e.g., pyrite). On the other hand, Pb is

the unique trace element that presents a high positive correlation with the ash content, showing its association with coal minerals such as galena or some silicates or phosphates.



Fig. 3. Simplified lithostratigraphic column of the Cerrejón (modified after Carbones del Cerrejón, 2003; Ramos, 1990) and Manantial (modified after Haught et al., 1944) formations. Taken from Bayona et al. (2004).

4.2. Clinker composition

The mineral phases in clinker are dependent on many physical and chemical variables including the original sediment bulk composition, temperature, degree of melting, and degree of oxidation or reduction achieved during burning (Cosca et al., 1989). Recently, Sandoval et al. (2009) carried out a study on its mineralogy and chemical composition. X-ray diffraction data revealed acute reflections with high intensity of quartz (in different crystalline polymorphs), as well as wide reflections with low intensity that reflects the presence of traces of different mineral phases like cordierite, cristobalite, hematite, kaolinite, montmorillonite, mullite, quartz and tridymite. However, clinker is a geomaterial with a complex mineralogy, with overlapping of peaks corresponding to different mineral phases. The elemental composition of clinker calculated from the quantitative analysis of the EDXS spectra and expressed as weight percentages displays variations of up to 15 wt.% among its major oxides (SiO₂, Al₂O₃, K₂O and CaO), which probably reflects local heterogeneity related to small changes in the original sedimentary rock (Ríos and Williams, 2008). Clinker is mainly composed of several polymorphs of SiO₂ (22.8-34.4%). However, this coal by-product contains other crystalline phases like mullite (14.2%), montmorillonite (4%), hematite (1.7–2.4%) and traces of rutile, ilmenite and anatase. Therefore, clinker colours could be explained by its mineralogical concentrations. For example, the increase in the opaque minerals concentrations (magnetite) of metallic shine define the black stripes, while the reddish colour zones are associated to greater oxidation and to the high content of hematite.

5. Spontaneous combustion of coal

Coal mine-related fires represent worldwide catastrophe (Stracher and Taylor, 2004; Stracher, 2004, 2007a,b) and can be ignited by (1) mine-related activities such as cutting and welding, explosives and electrical work and smoking, which may ignite gases such as methane and hydrogen (Mine Safety and Health Administration, 1996), (2) surface fires transmitted to culm banks or coal seams by lightning, forest or bush fires and burning trash (Dekok, 1986; Geissinger, 1990), and (3) spontaneous combustion induced either by coal fines, oilsoaked rags, lumber, hay or manure in culm banks or by exothermic oxidation reactions catalyzed by oxygen circulating through coal seam joints (Anthony et al., 1977; International Institute for Geo-Information Science and Earth Observation, 2003). Centralia, a small town in Columbia County in the anthracite region of eastern Pennsylvania, is an example of a worst-case scenario for the effect of a coal fire on a community (Nolter and Vice, 2004).

Spontaneous combustion of coal is an important problem in its mining, long distance transportation, and storage, in terms of both safety and economics (Chakravorty and Kolada, 1988; Kaymakçi and Didari, 2002; Arisoy et al., 2006). According to Querol et al. (2008), although most studies point to oxidation of organic matter as the main cause of coal self-ignition, other factors could also favour or hinder spontaneous combustion. The exact mechanism of the reaction is still not well understood. The main reason for the difficulties in understanding the mechanism of spontaneous combustion is the presence of many internal and external factors affecting the initiation and development of the phenomenon (Kaymakçi and Didari, 2002). It occurs when the rate of heat generated by the oxidation of organic matter exceeds the rate of heat dissipation (Misra and Singh, 1994). Coal requires a heat source to promote spontaneous combustion. The heat mainly results from coal-oxygen interaction, drying and rewetting processes and latent heat of water vapour (Moxon and Richardson, 1985). However, heat generated by oxidation of inorganic coal-bearing phases as pyrite can represent a key factor in attaining the necessary heat for self-ignition.

Coal reacts with atmospheric oxygen even at ambient temperatures by exothermic reaction. If the heat liberated during this process is allowed to accumulate, the rate of reaction increases exponentially and there is a further rise in temperature. When the ignition temperature of coal is reached, it starts to burn by spontaneous combustion (Timko and Derick, 1995; Gervet, 2007). The temperature at which the coal oxidation reaction becomes self-sustaining and spontaneous combustion occurs generally depends on the type of coal and surrounding conditions of heat dissipation (Gervet, 2007). In poor quality coal, the fire may start burning at temperatures as low as 303-313 K. According to Lyman and Volkmer (2001), low-rank coals, due to their high content of humidity and reactive macerals, have a greater tendency to self-heating, which means that coal increases dramatically its temperature while it absorbs humidity, as it provides coal the required amount of oxygen to start oxidation reaction. Although some authors found a relationship between maceral composition and the potential for spontaneous combustion of coal, a general rule is not clear (Querol et al., 2008). The coal oxidizes and self-heating is accelerated until the combustion occurs. With decreasing in coal rank, the tendency to the spontaneous combustion increases. For example, lignites and sub-bituminous coals can begin their spontaneous combustion at 573 K, whereas bituminous coals as those of the Cerrejón Coal Mine at 873 K. Apparently, the presence of dispersed pyrite in coal that oxidizes can increase significantly the potential for the spontaneous combustion (Eichhubl et al., 1999). Coal oxidation is a very complex process due to its diverse composition and heterogeneous nature.

According to De Boer et al. (2001), the maximum temperatures will be reached in the proximities to a burning coal seam and especially close to the fractures on overburden rocks (supply of fresh oxygen). Kim (1977) demonstrated that during drying, an endothermic process takes place, decreasing its temperature. On the other hand, an exothermic reaction occurs, when humidity increases, releasing heat and therefore accelerating the spontaneous heating of coal. But not only the humidity and oxidation are the main factors to initialize the spontaneous combustion, there are other factors that can contribute to the occurrence of this phenomenon: (1) Air flow provides the necessary oxygen during the oxidation is also a form to dissipate the heat generated. (2) A low coalification rank favours spontaneous combustion due to the faster transport of oxygen across the coal enhanced by higher porosity, moisture and volatile matter (Misra and Singh, 1994). Sub-bituminous coals have a high percentage of reactive macerals that increase the tendency to the heating. (3) Higher temperatures act as a promoting factor in the oxygen-coal reaction. (4) The presence of pyrite and other minerals in coal may catalyze oxidation reactions (Carras and Young, 1994). Furthermore, in a humid atmosphere, pyrite undergoes an exothermal oxidation that accelerates the coal self-heating (Banerjee, 1985). This phenomenon considerably favours spontaneous combustion when pyrite occurs as fine-grained disseminations in the coal matrix and its content is relatively high (Ghosh, 1986). Other minerals such as siderite (Misra and Singh, 1994) and calcite (Sujanti and Zhang, 1999) have also been found to facilitate spontaneous combustion. The concentration of sulphide minerals must be >1-2% so that they have a significant effect. However, Cerrejón coals have very low sulphide mineral content (0.4–0.7%) to be a determining factor. (5) Spontaneous combustion may also be triggered by geologic factors such as tectonic influence (increasing porosity and enabling underground water to come into contact with coal seams), igneous intrusive episodes reaching coal seams, blasting and mining effects in worked seams, lightning strikes and forest fires (Heffern and Coates, 1997). Rocks are poor conductors of heat. However, the faults and fractures can facilitate the entrance and flow of water and air within the coal seams, with oxygen influx, which was the main factor that promoted the occurrence of self-heating followed by spontaneous combustion in the Cerrejón Coal Mine. Therefore, there are other factors that do not apply in the present study since they are associated to the mining activity, being the main causes of the recent and artificial combustion of coal.

The heat arising from dry oxidation of coal is often insignificant for self-ignition (Misra and Singh, 1994).

Spontaneous combustion generally occurs at high (>873 K) to ultra-high (>1273 K) temperatures and low pressures (\leq 100 MPa) (De Boer et al., 2001). However, near burning coal seams and especially near vents and cracks in the overlying rocks extreme temperatures up to 1773–2373 K can be reached (Bentor et al., 1981), which produce partial fusion of the host rocks. On the other hand, within 20–30 m of the burning zone, the adjacent rocks reach a temperature of 623 K, but only when they reach 873 K it will undergo remarkable thermal alterations (Eichhubl et al., 1999; De Boer et al., 2001).

6. Results and discussion

6.1. Occurrence and distribution of clinker

Clinker outcrops cover extensive areas of sedimentary basins and represent natural burning of tens of billions of tons of coal throughout the past few million years. The degree of thermal alteration produced by burning coal beds is variable and a single outcrop may contain altered rock ranging from slightly baked (clinker) to entirely fused (paralava) as reported by Heffern (2006). This author considers that rock types in the clinker reflect the rock types in the overburden and have varying degrees of hardness depending on the degree of heating. At the base of the clinker there is a thin layer of light tan ash and glassy, greenish scoria, formed by uncombusted minerals left over from the original coal bed. Clinker, hardened by heating, forms resistant reddish layers that cap plateaus, hilltops and escarpments in the landscape. It is highly fractured, which allows rainfall and snowmelt to infiltrate rather than run off the surface and erode the outcrop. The unbaked overlying and underlying rocks are eroded more rapidly, leaving clinker standing in relief (Coates and Heffern, 2000). Therefore, clinker refers to rocks that vary with respect to thermal alteration, texture, structure, original bulk-composition, and position within the burning area. Clinker hinders mining operations since they generate geotechnical instability zones.

Candela and Quintero (2004) carried out the first detailed geologic mapping of clinker zones accompanied by its modelling and structural control at depth in the Cerrejón Coal Mine. The Cerrejón Coal Mine is administratively divided in three zones (Fig. 2): Cerrejón Northern Zone – CNZ (Fig. 4), Cerrejón Central Zone – CCZ and Cerrejón Southern Zone – CSZ (Fig. 5). They represent the coal exploitation and extraction fronts developed through 18 open pits. According to Barranco (2001), the northern zone covers an area of 380 km² with about 55 seams and the central zone extends over 100 km² with 38 seams. These zones contain high-volatile B bituminous rank coal according to the ASTM coal classification system. The southern zone covers an area of 200 km² with at least 15 seams and it is the least explored of the three zones. Mapping revealed that clinker is usually



Fig. 4. Detailed geological map showing the distribution of the burnt Cerrejón Formation rocks – Tpcc (square area A in Fig. 2) in the Cerrejón North Zone (CNZ). CC indicates clinker from a specific coal seam.



Fig. 5. Detailed geological map showing the distribution of the burnt Cerrejón Formation rocks – Tpcc (square area B in Fig. 2) in the Cerrejón Central and South zones (CCZ–CSZ). CC indicates clinker from a specific coal seam.

found near deformed zones, either faults or tight folds, and usually outcrop in irregular patterns as almost tabular bodies up to 100 m thick, pinching out to depths of up to 448 m (Candela and Quintero, 2004). The main clinker bodies identified in these zones are illustrated in Figs. 4 and 5. Clinker appears in structurally complex zones and reaches its maximum expression next to Ranchería fault. Nevertheless, there is no definitive evidence that allow establishing a direct cause-effect relation between tectonic discontinuities and the origin and development of spontaneous combustion. Clinker shows varying thickness (from 5-65 m at depth to 9-100 m on the surface), with penetration depths of up to 448 m downward direction along the dip of the coal seam. Clinker covers an area of $2.9 \times 10^6 \text{ m}^2$ and its volume is $1.4 \times 10^8 \text{ m}^3$. It is spread out over the Palotal 10, Tipiala, 100, Patilla, Tabaco High Dip, Tabaco Extension and La Puente pits, forming finger-like bodies. Table 1 summarizes the location of clinker bodies, their associated coal seams, thickness at depth and on the surface, penetration depths, area (m^2) and volume (m^3) , and volume of burnt coal by seam.

6.1.1. Northern Zone

Clinker covers an area of $2.7 \times 10^5 \text{ m}^2$ (9.4% of the total area covered by clinker) and its volume is $1.3 \times 10^7 \text{ m}^3$ (9.1% of the total volume of clinker). Eight clinker bodies were identified, which are associated to the combustion of seams 170, 155, 145 and sometimes 150. In general, they have an elongated character, with varying thickness (from 10 m at depth to 50 m on the surface). Clinker associated to seam 155 is observed in the southern part of the Tabaco Extension pit (with approximately 1500 m long) and in the Tabaco High Dip pit (with approximately 1200 m long). Clinker associated with seams 145 and sometimes 150 also occurs in two bodies. The first one is observed in the Tabaco Extension pit, with a surface length of 500 m approximately. The second one is observed in the Tabaco High Dip pit (with approximately 1800 m long), which gets thinner towards the north. Fig. 6a illustrates a typical clinker outcrop associated to seam 145 in the north end wall of Tabaco High Dip pit. The reddening intensity corresponds to the rock's alteration degree, which preserves the relict primary stratification. Here, clinker displays several colours such as red, orange, black and even white among others. In certain areas, rock fragments of varying sizes are embedded in random disposition, which represent unaltered relict rock within the clinker. Stripes of red or black colour reveal the occurrence of reconcentrated mineralization and/or residual ash from the original coal. Generalized stratigraphic columns of clinker in the Tabaco High

Dip pit are given in Fig. 7. Clinker associated to seam 170 occurs in two bodies. The first one is located in the Tabaco Extension pit (with shallow depths and approximately 900 m long). The second one is located between Tabaco High Dip and La Puente pits (with approximately 1700 m long). It has a lenticular geometry, getting thinner towards its ends.

6.1.2. Southern-Central Zone

Clinker covers an area of $2.6 \times 10^6 \text{m}^2$ (90.6% of the total area covered by clinker) and its volume is $1.3 \times 10^6 \text{m}^3$ (90.9% of the total volume of clinker). Clinker in the 100 pit outcrops as a rectangular body, getting thinner towards its ends. The biggest clinker body is located in the Palotal 10 and Tipiala pits. Here, spontaneous combustion was so deep that it included the burning of several seams (approximately 10 – seams from 175 to 120). This clinker body coincides with a tight structural inflexion point, where the stratification strike changes from NE to E. Another clinker body (approximately 1200 m long) shows a strike E–W being parallel to that previously described. It is associated to seam 75. Five clinker bodies where mapped to the south of the Patilla pit, near the Ranchería fault. The two main bodies are associated to seams 70, 71, 75, 80, 81 and 83, and 45–60, respectively. The last of the clinker bodies shows a lenticular geometry, which gets thinner towards the ends.

6.2. Outcropping clinker

Clinker is easily recognizable on the field thanks to its mainly red colour in a variety of intensities, although it can also display several tones of black, gray, green, cream or even white that easily contrast with the greyish hue of the Cerrejón Formation coals. It is a compact and highly fractured rock, mainly reddish brown to red in colour due to the presence of hematite. It is a complex mixture of various amorphous and crystalline inorganic constituents and contains remaining inorganic materials derived from shales, sandy mudstones and grey sandstones originally associated with coal. Clinker is constituted by rocks of mainly clayey texture but it could also be sandy. It also retains much of the original rock characteristics as relict sedimentary structures and even fossil plant remains survive. We have occasionally found plant traces and stems within layered sandstone and mudstone in clinker. Siderite can occur as stripes, even though it also appears as nodules in mudstones and as sideritelike lenses in sandstones. White ash is also found as layers of friable

Table 1

Summary of general aspects on spontaneous combustion of coal seams and occurrence of clinker in the Cerrejón Coal Mine.

Location of clinker (pit)	Coal seam	Width of clinker (m)		Penetration	Area	Volume	Burnt coal	
		(in deth)	(on surface)	depth of clinker (m)	(m²)	(m³)	m ³	Mt
Cerrejón Southern-Central Zone								
Palotal 10 and Tipiala	160	14.33	17.33	108	1.5×10^{6}	1.1×10^{8}	1.3×10^{6}	1.7000
Palotal 10 and Tipiala, to the SW	135-130-125-120	50	50	246				
	150	6	20	190				
	170	8	14	120				
	175	8	9	150				
	135	5	18	240				
Palotal 10 and Tipiala, to the E	145-150-155-160	46.5	91.5	434				
	75	28	34	146	1.3×10^{5}	3.3×10^{6}	4.7×10^{5}	0.6055
100	145-150	25.33	31	262.5	1.3×10^{5}	5.2×10^{6}	6.0×10^{5}	0.7747
Patilla	70-71-75-81-83	22.5	42.5	80	6.9×10^{5}	2.1×10^{6}		
	From 45 to 60	26	53	310	1.1×10^{5}	3.1×10^{6}		
	30–35	10	10	26.5	1.1×10^{4}	4.8×10^4		
	75	12	12	98	1.1×10^{4}	1.5×10^{5}	4.9×10^{4}	0.0631
Cerrejón Northern Zone								
Tabaco extension	170	5	10	45	5.1×10^{4}	1.3×10^{4}	9.4×10^{4}	0.1226
Tabaco High Dip — La Puente	170	4	10	275	6.7×10^{4}	6.1×10^{6}	1.5×10^{6}	1.9000
Tabaco extension	155	10	15	45	4.3×10^{4}	3.7×10^{5}	1.4×10^{5}	0.1856
Tabaco High Dip	155	12	45	100	4.1×10^{4}	1.5×10^{6}	2.5×10^{5}	0.3284
Tabaco Extension	145 and 150	10	12	35	2.2×10^{4}	1.1×10^{5}	3.4×10^{4}	0.0441
Tabaco High Dip	145 and 150	16.5	26	235	4.1×10^{4}	4.3×10^{6}	5.4×10^{5}	0.7053



Fig. 6. (a) Natural clinker displaying different colours and tonalities as evidence of ancient natural coal-bed fires in the north end wall of Tabaco High Dip pit (Cerrejón North Zone). (b) Highly brecciated rocks from the Saman zone fault, characterized by coarse, angular fragments of natural clinker, coal and non thermally affected rocks, which formed either by a crushing and natural cementing essentially in place or by the deposition of angular pieces that became consolidated. (c) Unusual highly brecciated rocks of the Cogollo Formation in the hanging wall of the Cerrejón thrust fault, characterized by coarse, sub-angular fragments of natural clinker and non thermally affected calcareous rocks, last of them preserving bivalve shells (open square).



Fig. 7. Generalized stratigraphic columns of the natural clinker, north end wall, Tabaco High Dip pit (Cerrejón North Zone).

material no more than 3 cm thick, which represents the residue of the original several meter-thick coal seam after combustion. Rocks within a clinker body may display from a uniform massive texture (with red colours) to other types of textures with planar-parallel internal stripes a few centimetres thick. Other layers shows several tenths of centimetres thick with no apparent structure, chaotic (brecciated), and with sintering black mudstone incrustations remaining from the original rock and unaltered or slightly affected rock fragments, of several sizes, and occasionally fragmented with a random disposition. Other rocks, less abundant, with brecciate structure and vesicular texture and with sacaroid appearance are present generally towards the surface. The thicker its original bedding texture, the greater its hardness and resistance weathering, making it initially a harder rock than the fresh rock.

6.3. Factors controlling clinker development

Clinker development is controlled by the presence and abundance of oxygen, since the heat generated and the increase of the temperature depend on its interaction with coal (Sevenster, 1961). Clinker reaches its maximum extension on the surface or near it due to the oxygen abundance and simultaneous spontaneous combustion of several coal seams, getting thinner in depth accompanied by decreasing oxygen supply. In effect, partially melted and frequently highly vesicular rocks that seem to be industrial or metallurgic furnaces residues are found on the surface but never with depth. Once ignition occurs in a specific point of the coal seam near surface, fire moves in opposite directions from the starting point, advancing without difficulty until the coal seam finds an obstacle such as faults or thinning of the coal seam, which impedes its continuity or isolates it from oxidation zones. Spontaneous combustion can only advance in depth if water is evacuated from the system and fractures contain atmospheric gases instead of water. In a carboniferous sequence where the phreatic level falls, coal suffers an endothermic reaction while losing superficial humidity in fractures. However, it suffers the contrary effect when water circulates along the coal seam; for example, when a recharge of the aquifer from the surface occurs. Anyway, spontaneous combustion may advance only up to the minimum level reached by the phreatic level. Spontaneous combustion process is auto-sustained since once a several meters thick coal seam is consumed by this process; its volume will be reduced to a few centimetres. This makes the fitting rock to collapse generating cracks, which propagate towards the surface acting as a chimney that promotes the exchange of gases and heat.

6.4. Estimation of burnt coal

In a very simplistic way and knowing the approximate volume of fitting rock converted to clinker and assuming some factors during the spontaneous combustion process, it is possible to obtain a calculation of the amount of heat needed to turn the original rocks into clinker. Thus, supposing that clinker was generated after spontaneous combustion of coal seams with similar thicknesses to those being exploited today in the Cerrejón Coal Mine, the calculated volume of coal consumed by spontaneous combustion was approximately 6.4 Mt. On the other hand, assuming an average calorific value of 26.4×10^{6} J/kg, spontaneous combustion of this calculated coal volume produced approximately 17×10^{13} J. To estimate how much heat was necessary to generate a volume of rock turned into clinker of approximately 1.4×10⁸m³ (Table 1), it was necessary to assume that: (1) the coal spontaneous combustion presented with oxygen deficit, supplying only the formation heat of CO (40% of the complete reaction); (2) the losses of heat contained in the gas escape (by convection) are only of 20%; (3) the surplus heat was conducted to the fitting rock with no gas contact, which favoured transporting heat by convection; and (4) the spontaneous combustion was slow and only reached 873 K in such manner

that all the surplus heat was transmitted to the fitting rock by conduction and the remaining heat was consumed during endothermic reactions of the fitting rock. The transformations that demand more heat in the fitting rock are the mechanically aggregated water evaporation and chemically linked water, as well as calcium carbonate dissolution. The cooling heat of the compound may approximate to 837.2 J/kg K, that is, 73.1×10^4 J/kg at 873 K. Therefore, a consumption of 62.8×10^4 J/kg of the Cerrejón Formation rocks during their transformation to clinker at such temperature was considered. If 1.4×10^8 m³ of this geologic unit were converted to clinker, and assuming that a density of 2×10^3 kg/m³, 276 Mt of mudstones and sandstones would have needed 17×10^{13} J, a figure that is in the same order of magnitude than the heat generated by the complete combustion of 6.4 Mt of 26.4×10^6 J/kg coal estimated $(17 \times 10^{13}$ J).

The calculated volume of burnt coal was approximately 6.4 Mt, of which 48% and 52% correspond to CSZ and CNZ, respectively, despite the fact that the clinker relation between CSZ and CNZ is 9 to 1. This demonstrates that the thermal alteration process in CSZ was much more effective than in CNZ. The reason for this is still unclear, but if we assume that the adjacent host rock along the coal deposit is in general the same one, the primarily factor to be considered would be the difference between CSZ and CNZ under a same spontaneous combustion involving simultaneously several coal seams, as occurring in Palotal 10 — Tipiala and South of Patilla pit, where five to eleven seams converged under a same fire, covering a greater combustion area and therefore affecting more rock volume, with approximately the same average calorific capability by seam in all the coal deposit.

6.5. Relative chronology to the spontaneous combustion

Field observations have allowed establishing the temporality related to the natural spontaneous combustion periods. Three areas were observed (Tabaco High Dip pit, proximities of pit 831 and Palomino stream), which show simple cut relationships that are useful to date in a relative way the spontaneous combustion age. In the Tabaco High Dip pit a tabular clinker zone is divided by the Samán fault zone. Nevertheless, the clinker at both sides of this fault corresponds to two different seams (155 to the south of the fault and 145 to the north of it). This fault locally generates a breccia zone that clearly demonstrates that spontaneous combustion existed before the last fault's activity period since it contains blocks of clinker, fresh rock and coal mixed (Fig. 6b). Due to its sinistral character, this fault cuts stratum dipping to the SE. Coal seams that generated clinker have never been affected by the activity of this fault. The Cerrejón thrust fault is exposed in the Palomino stream canyon to the south of the coal deposit. According to INGEOMINAS (1999), this fault affects calcareous rocks of the Cogollo Formation, which overly mudstones and sandstones of the Cerrejón Formation along a very low angle thrust fault approximately 7° SE (Fig. 8), with a fault zone of no more than 10 m thick. 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 (Fig. 6c). The Cerrejón Formation rocks, immediately below this fault present colour, texture and all other characteristics of clinker, clearly demonstrating that spontaneous combustion occurred after the latest activity of the Cerrejón thrust fault. On the other hand, the dissected alluviums exposed to the southeast of the 831 pit contain conglomerates with calcareous cants that were thermally affected, including a strongly cemented matrix, reddish to brown in colour, and abundant chalk veins cutting the alluvial deposit, which reveals that spontaneous combustion occurred after or during the accumulation of this alluvial deposit.

Spatial-temporal patterns of clinker ages may prove to be useful in deciphering the patterns of fluvial incision and excavation in this



Fig. 8. Geological map of the Palomino stream canyon to the south of the study area (square area C in Fig. 2). The Cerrejón thrust fault affects Mesozoic calcareous rocks, which overly the Cerrejón Formation. Rocks in the hanging wall of this fault were thermally affected by spontaneous combustion of coal seams, revealing an auto-combustion process posterior to the development of this fault.

carboniferous basin and in weighing the relative importance of uplift, variations in climate, and base-level change (Heffern et al., 2007).

Coal-bed fires ignited by spontaneous combustion thermally affected sedimentary rocks of the Cerrejón Formation to form clinker. Currently, there are no reports of active spontaneous combustion in the Cerrejón Coal Mine. From all the discussed factors, the only one that could vary regionally is the phreatic level. If this is the case, spontaneous combustion could be revealing a period in which the aquifer present along the coal seams registered extremely low levels (as much as 145 m below surface), and therefore an aridess climatic period than the current one. Given that the space distribution of clinker suggests a strong structural control, the authors infer that the oxygen was transported in depth along pre-existent structures such as faults or tight folding zones. Nevertheless the cut relationships indicate that spontaneous combustion sometimes took place after (e.g. the Cerrejón thrust fault) or before (e.g. the Samán thrust fault) deformation. Authors suppose that spontaneous combustion took place simultaneously along the Cesar-Ranchería valley as a result of an aridness climatic period (sudden fall of the phreatic level), and therefore, the development of the Cerrejón thrust fault can predate the folding and faulting of the Tabaco zone. In this case, spontaneous combustion would likely be independent of the occurrence of deformation and only in some cases could use pre-existing deformed zones as oxygen conducts. Thus, the main factor that could have favoured spontaneous combustion of coal seams was a phreatic level lower than the currently existent. Our results justify the development of future investigations in order to know the absolute age of the spontaneous combustion process that occurred in the Cerrejón Coal Mine, which would be very useful to determine whether the cutting relationships established in this study support or not a chronology of a simple deformation, with several periods of spontaneous combustion, or a complex one, with only a single period of spontaneous combustion. A determination and characterization of the magnetic mineral phases occurring in clinker for paleomagnetic studies would be of particular interest taking into account that the paleomagnetic potential of these rocks can be used to know with exactitude absolute chronologies of overburden removal by erosion, tectonic rotation and deformation.

7. Prevention and control of spontaneous combustion

Coal mine fires are mainly caused by spontaneous combustion, which is recognized as a major hazard in terms of safety and economics (Chakravorty and Kolada, 1988). The ignition of coal is a global concern and burning coal may cause significant environmental problems (Stracher and Taylor, 2004; Sheail, 2005; Chatterjee, 2006). One of the biggest concerns in the world with the use of coal is the environmental impact generated by some trace elements which, despite being in very low concentrations, are very harmful, particularly to human health. Recently, different authors (Zhao et al., 2008; Querol et al., 2008; Dai et al., 2008) characterized the trace elements in coals of different places in the world and wastes generated during the combustion and conversion processes. This is very important to directly contribute to the prevention of environmental pollution problems (Finkelman et al., 2002). As a coal by-product, clinker is one of the factors that affect the environment, particularly water chemistry, and it is very important to consider several variables such as composition of the protolith from which comes this coal byproduct, combustion conditions that generate it, and its particle size and mineralogy that influence the distribution and mobility of trace elements. Therefore, in response to environmental problems that occur as a result of the disposal of solid wastes during coal mining activities, it is necessary to undertake studies to establish the environmental impacts of using clinker in the field of materials science.

Based on the factors controlling the spontaneous combustion, coal mine operators can follow a management plan with coals suspected of being liable to self-heating to (1) prevent both additional spontaneous combustion of coals especially those being mined and hazardous underground coal fires that may affect mining operations (Chakravorty and Kolada, 1988), (2) detect spontaneous combustion fires fairly early in their development (Hornsby and Makower, 1983; Steer, 2009), and (3) control spontaneous combustion by use of a combination of several techniques (Qin et al., 2009). The first task is to evaluate the fire hazard in the mine workings so as to adopt the most rational and effective precautionary measures (Veselovskii et al., 1967). Spontaneous combustion is best prevented by carefully managing high carbon content material within the coal mine operation. It is important that the overall management plan for the mine include appropriate measures for dealing with spontaneous combustion and identify reactive and inert (including sealing properties) materials as guidelines to mine operators to assist them to reduce the risk of spontaneous combustion. There is no simple method of predicting whether a particular mining method applied to a specific coal seam will result in spontaneous combustion (Chakravorty and Kolada, 1988). However, monitoring combustion products during the early stage of heating is the most suitable method for detecting spontaneous combustion.

Clinker generates two main problems in the Cerrejón Coal Mine (1) uncertainty caused by disregarding the actual production of coal reserves, i.e. knowing precisely the extent of clinker for its deduction from the coal reserves, and (2) geotechnical instability zones, taking into account that clinker is an unstable material (it represent a natural aquifer) that offers no guarantees. Therefore, clinker is rapidly removed from the advancing front. As a last resort, on the fronts of abandoned mining but defined for future development, coal is coated with antioxidant paint and thus avoids its reaction with oxygen and therefore its heating and spontaneous combustion. However, we suggest evaluating suitable materials to be tested to determine a sealing method to be applicable to the Cerrejón Coal Mine, determining depletion of oxygen within a reactive material sealed by a layer of sealing material.

8. Conclusions

There is no doubt that spontaneous combustion has a negative impact in world coal deposits (such as the Cerrejón Coal Mine) on mining operations, coal beneficiation and safety, health and environment of the mine and surrounding communities. However, the management and control of this phenomenon can be sorted with mine planning, drilling, blasting and loading techniques, and transport and beneficiation techniques. Clinker as a by-product of the spontaneous combustion of coal seams generates two main problems (1) uncertainty caused by disregarding the actual production of coal reserves and (2) geotechnical instability zones.

The important contribution of this research showed spontaneous combustion of the Upper Paleocene Cerrejón Formation coal seams as influenced in some cases by pre-existing faults and folds as avenues for oxygen supply for combustion, lowering of groundwater table to dry the coal seams, and timing of this combustion especially through the relative movements of the faults that cut across the coal seams. Spontaneous combustion management is a complex process and should not be oversimplified. Despite the best efforts of researchers to try to understand this process, they are still not able to reliably predict the propensity for a coal seam to spontaneously combust. Therefore, more research and experimental work under controlled conditions is necessary to identify all the factors that can influence spontaneous combustion.

It may be possible to predict with some confidence if a coal has a propensity to combust spontaneously, thus dealing with a global scale problem that produce huge of greenhouse gas emissions and may contribute to climate change altering ecosystems and a range of human health problems. Therefore, we suggest the formulation of strategies to minimize the risk of spontaneous combustion such as sealing to reduce oxygen inflow, speeding up stacking rates to ensure stack faces be exposed for a minimum period, compacting the top layer of stacked material, avoiding uncontrolled segregation during stacking through modification of size distribution and stacking methods, and minimizing the probability of deep-seated combustion.

Acknowledgements

This research was carried out as a part of the undergraduate thesis of S.A. Candela and J.A. Quintero at the Universidad Industrial de Santander. We would like to express our gratefulness to Carbones del Cerrejón Limited. for the logistic support during the development of the geologic mapping of clinker in the Cerrejón Coal Mine. We would like to thank C. Jaramillo, W. Mendoza, S. Pardo and S. Socha for their valuable contributions to this research, and to the Cerrejón Geology Team for its assistance in selecting and obtaining field sites for the research.

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