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The properties of the nano-minerals and hazardous elements: Potential environmental impacts of Brazilian coal waste fire

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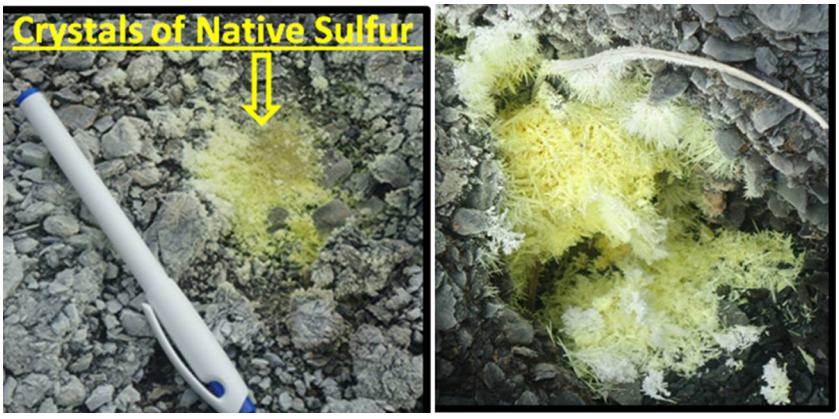
HIGHLIGHTS

- Evaluation of the environmental impact of abandoned Brazilian coal fires area was performed.
- Grave effort should be made to set clear restrictions of genered soil utilization in cement industry.
- The analytical methodology has been applied to investigate elements occurrence.

GRAPHICAL ABSTRACT



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ABSTRACT

Brazilian coal area (South Brazil) impacted the environment by means of a large number of coal waste piles emplaced over the old mine sites and the adjacent areas of the Criciúma, Urussanga, and Siderópolis cities. The area studied here was abandoned and after almost 30 years (smokeless visual) some companies use the actual minerals derived from burning coal cleaning rejects (BCCRs) complied in the mentioned area for industry tiles or refractory bricks. Mineralogical and geochemical similarities between the BCCRs and non-anthropogenic geological environments are outlined here. Although no visible flames were observed, this study revealed that auto-combustion existed in the studied area for many years. The presence of amorphous phases, mullite, hematite and other Fe-minerals formed by high temperature was found. There is also pyrite, Fe-sulphates (eg. jarosite) and unburnt coal present, which are useful for comparison purposes. Bad disposal of coal-dump wastes represents significant environmental concerns due to their potential influence on atmosphere, river sediments, soils and as well as on the surface and groundwater in the surroundings of these areas. The present study using advanced analytical techniques were performed to provide an improved understanding of the complex processes related with sulphide-rich coal waste oxidation, spontaneous combustion and mineral formation. It is reporting huge numbers of rare minerals with alunite, montmorillonite, szomolnokite, halotrichite, coquimbite and copiapite at the BCCRs. The data showed the presence of abundant amorphous Si–Al–Fe–Ti as (oxy-)hydroxides and Fe-hydro/oxides with goethite and hematite with various degrees of crystallinity, containing hazardous elements, such

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as Cu, Cr, Hf, Hg, Mo, Ni, Se, Pb, Th, U, Zr, and others. By Principal Component Analysis (PCA), the mineralogical composition was related with the range of elemental concentration of each sample. Most of the nano-minerals and ultra-fine particles found in the burned coal-dump wastes are the same as those commonly associated with coal cleaning rejects, in which oxidation of sulphides plays an important role to environment and human health.

1. Introduction

In general spontaneous coal seam fires and burning coal cleaning rejects (BCCRs) have been observed in different parts of the world for millions of years. They are indeed a global phenomenon and they have been thoroughly investigated (McIntosh et al., 1994; Chong and Chen, 1999; Gray et al., 2002; Carras et al., 2009; Engle et al., 2012; Finkelman, 2004a, 2004b; Hower et al., 2009, 2013; O'Keefe et al., 2010, 2011; Pone et al., 2007; Querol et al., 2008; Ribeiro et al., 2010; Zhao et al., 2008; Kok, 1981; Schmal, 1989; Rosema et al., 1999). Since prehistoric times the exposure to hazardous elements coming from these fires has resulted in serious human health problems (O'Keefe et al., 2010, 2011). These problems are still present, but few people are aware of the extent and the long-term effects of coal fires. This phenomenon, under certain conditions, is very common even in modern-day mining since coal can spontaneously ignite in an exothermic process which may be accelerated by catalytic compounds (e.g. water, pyrite, etc.). The hypothesis holds that if the active molecule sides of flammable materials are exposed to air, such as in porous coal, oxygen will be absorbed into the material. This fact could induce a series of heterogeneous surface reactions, whose rates rise exponentially with temperature as a function of oxygen content in the immediate vicinity of the coal deposits.

In summary, those fires are the result of heat accumulation in oxidation processes, set off when coal is exposed to atmospheric oxygen.

Although occurring all over the world, causing disasters on a large scale in mining areas of America, Africa, Europe, Asia, and Oceania have so far slipped public attention. Despite a host of dire economic and environmental consequences that, even at a global level, these occurrences go hardly unnoticed. This phenomenon in itself represents a serious economic setback, especially when occurring in underground mine systems, because it also impairs worker safety and often caused mining costs spiralling.

As a man-made hazard affecting limited natural resources in specific localities as much as the atmosphere, spontaneous coal seam fires are an interesting object of scientific research. Their very complex nature responds to a whole range of disciplines and necessitates that concert interdisciplinary and international effort for effective mitigation.

In general hazardous element contamination in soils is commonly assessed by comparison of the total concentrations of metals in bulk samples with soil quality standards and regulations (e.g., Ljung et al., 2005, 2006). However studies have shown that the concentrations of various metals in the soils increase with decreasing particle size (e.g., Al-Rajahi et al., 1996; Ljung et al., 2006; Hower et al., 2013). Fine and nanoparticles have a specific area that retains high amounts of elements (Wang et al., 2006). In addition, small particles are soluble and are more likely to traverse the gastric mucosa and be more efficiently adsorbed in human tissues than coarse fractions (Lin et al., 1998).

Other problem in coal fires areas is the coal tar, because it is a respiratory carcinogen identified by the International Cancer Research Institution of the World Health Organization. For example, As contained in coal fire discharge can cause chronic intoxication with after-effects such as pigment deficiency, over-pigmentation, keratosis, and skin cancer. Fluorine released from coal combustions can lead to fluorine osteopathy, and even impair people's ability to work (Finkelman, 2004a, 2004b; Dai et al., 2007; Nriagu, 1988). As a last resort, people have to be relocated to unaffected areas. The health risks are especially high for children because of their low tolerance to toxins as well as the inadvertent ingestion of significant quantities of dust or soils through hand-to-mouth pathways (Acosta et al., 2009).

The principal objective of the present study was to determine the distributions of mineral matter and hazardous element (e.g. As, Cd, Cr, Cu, Pb, and U) occurrence in ultra-fine and nano-minerals coming from an area directly affected by BCCRs.

Moreover it provides an answer to: *i*) the problems of nano-minerals generation during coal waste fire and the corresponding influence on environmental parameter son the self-ignition behaviour of coal waste; *ii*) show that nano-particles are associated with a burning coal waste deposit in southern Brazil; and *iii*) describe the wider-ranging mineralogical processes associated with that burning waste deposit as a whole. It also discusses the susceptibility of these coals to spontaneous combustion with respect to coal rank and pyrite content.

2. Study area

The study area is located in the city of Urussanga, in the coastal region of Santa Catarina (Brazil) (Fig. 1). Specifically, the work zone is located on the eastern edge of the Paraná Basin, a Paleozoic sedimentary basin which evolved over the South American platform. Deposition began about 450 Ma ago, in Ordovician time, and extended until the Tertiary.

Using lithostratigraphic criteria the Rio Bonito Formation has been subdivided into three major sedimentary packages with a hierarchy of members labelled from the base to the top: Triunfo (coastal and fluvial sandstones, minor coal development), Paraguaçu (marine mudstones and fine-grained sandstones) and Siderópolis near Urussanga city (coastal and fluvial sandstones, major coal development) (Kalkreuth et al., 2010). The predominant geological material in Brazilian coal waste fires areas are amorphous materials, clays, sulphides, sulphates Fe-hydro/oxides, and residual carbonaceous materials, often constituting over 85% of all waste (Dias et al., 2014).

The area of study presented here, is really a deposition zone where burning refuse materials from coal mining were accumulated. Specifically for about 30 years there has been about 5–10 acres of BCCR (see Fig. 1) and for many years different waste materials from … without any control. Coal Cleaning Rejects (CCRs) are a mixture of materials coming from the cleaning process of coal, and usually these materials tend to burn forming the BCCR. Spontaneous combustion of coal cleaning rejects is most likely to occur in loosely tipped and well aerated heaps with high carbonaceous and pyrite content. Coal waste heaps are complex structures, made up of a mixture of materials with different reactivity toward oxygen and different particle size distributions. Through large particles air flux can easily dissipate heat, but in fine materials, air stagnates and allows heat to build up gradually. However, stagnant air also means that fires caused by accumulative heating will stop as soon as the oxygen in the material is consumed. Waste distribution in the current BCCR heaps depends both on the layering of the mined soil as well as on the dumping method, each resulting in a different overall layering and mixing of materials in the heap. As a consequence of all these facts, the coal mining companies decided to cover the BCCR with about 1–3 m of soil (composed basically of quartz, albite, anorthite, kaolinite, rutile and illite/smectite) and rocks in the region throughout the area. The companies thought that this process would eliminate the spontaneous coal combustion, but they did not take into account the necessities of the modern industry, which require those materials for the