



## Nanomineralogy in the real world: A perspective on nanoparticles in the environmental impacts of coal 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 gendered soil utilization in cement industry.
- The multi-analytical methodology has been applied to investigate elements occurrence in ultra-fine and nano-particles.

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### ABSTRACT

Detailed geochemistry similarities between the burning coal cleaning rejects (BCCRs) and non-anthropogenic geological environments are outlined here. While no visible flames were detected, this research revealed that auto-combustion existed in the studied area for many years. The occurrence of several amorphous phases, mullite, hematite and many other Al/Fe-minerals formed by high temperature was found. 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 work using multi-analytical techniques were performed to provide an improved understanding of the complex processes related with sulphide-rich coal waste oxidation, spontaneous combustion and new mineral creation. It recording huge numbers of rare minerals with alunite, montmorillonite, szmolnockite, halotrichite, coquimbite and copiapite at the BCCRs. The information presented 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 potential hazardous elements (PHEs), such as Cu, Cr, Hf, Hg, Mo, Ni, Se, Pb, Th, U, Zr, and others. Most of the nano-particles 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 impact to environment and subsequently animal and human health.

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### 1. Introduction

Coal seam fires and burning coal cleaning rejects (BCCR) have been observed in several parts of the world for millions of years. (McIntosh et al., 1994; 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). In summary, those fires are the result of heat accumulation in oxidation processes, set off when coal is exposed to atmospheric oxygen.

While 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. This marvel in itself represents a hazardous economic setback, particularly when occurring in underground mine systems, because it also impairs worker safety and often caused mining costs spiralling (UNESCO, 2010).

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This work is part of an attempt to investigate the distributions of mineral matter and hazardous elements (eg. As, Cd, Cr, Cu, Pb, and U) occurrence in ultra-fine/nano-minerals coming from an area directly impacted by coal fires.

## 2. Study area

The main geological material in Brazilian coal fires areas are amorphous materials, clays, sulphides, sulphates Fe-hidro/oxides, and residual carbonaceous materials, often constituting over 85% of all reject (Dias et al., 2014).

The study zone presented here, is really a deposition zone where burning refuse materials from coal mining were accrued. Precisely for about thirty years there has been about 5–10 acres of BCCR (Fig. 1) and for many years different waste materials. Coal wastes are mixture of materials coming from the cleaning process of coal, and usually these materials tend to burn forming the BCCR. Coal cleaning rejects (CCRs) heaps are complex structures, made up of a mixture of materials with different reactivity toward oxygen and different particle size distributions. Through big particles air flux can easily dissipate heat, but in ultra-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 disbursed.

## 3. Sampling and analytical methods

To clarify the modes of occurrence of nano-minerals and theirs hazardous elements, to underpin the processes of their environmental fate and behaviour, and to extrapolate the results between ultra-fine/nano-minerals, it is necessary to characterize the particles and minerals that are exposed in the different researched zones.

In the present study priority was given to 19 mineral samples from a Brazilian BCCRs abandoned zone located in the Urussanga city (Fig. 1). All samples were collected along various coal seams in CCRs fire zones, at essentially the same time and under similar weather conditions so as to minimize the atmospheric effects.

Some of the obtained samples provided enough condensate for preparation of thin sections amenable to examination of

mineralogical, textural, and morphological features, as well as quantitative compositional analysis (Dias et al., 2014). Special precautions were taken in sample preparation to account for the salt crystals' brittleness and high solubility, which, for instance, precluded water use.

BCCRs were powdered (<212  $\mu\text{m}$ ) and the mineralogy of each Low Temperature Ash (LTA) was evaluated by X-ray powder diffraction (DRX) using a Phillips PW1830 diffractometer with  $\text{Cu K}\alpha$  radiation. Quantitative analyses of the mineral phases of each LTA were made using Siroquant™, commercial interpretation software (Taylor, 1991), based on the Rietveld (1974) XRD analysis technique.

Sampled BCCRs were ashed at 815  $^{\circ}\text{C}$ . The resultant ashes, in addition to the powdered portions of each BCCRs sample, were calcined at 1050  $^{\circ}\text{C}$  and then fused into borosilicate disks following the methods described by Norrish and Hutton (1969). The loss on ignition (LOI) at 1050  $^{\circ}\text{C}$  was also determined for each sample as part of the planning procedure. The major element oxides in each ash sample were determined by X-ray fluorescence (XRF) spectrometry techniques using a Philips PW2400 spectrometer scheme.

The ICP-MS analysis and sample microwave digestion program related to coal and coal-related samples are outlined by Dai et al. (2011). For ICP-MS analysis, samples were digested using an UltraClave Microwave High Pressure Reactor (Milestone). The reagents digestion for each 50 mg sample was 2 ml 65%  $\text{HNO}_3$  and 5 ml 40% HF. Multi-element standards (Inorganic Ventures: CCS-1, CCS-4, CCS-5, and CCS-6) were used for calibration of trace element concentrations. Arsenic and Se were determined by ICP-MS, using collision cell technology (CCT) in order to avoid disturbance of polyatomic ions (Li et al., 2014).

The total sulphur for each sample was determined directly by means of LECO AMA 254 gold-amalgam atomic absorption spectrometer.

## 4. Results

Obtained BCCRs change the physico-chemical properties of disposed soil and reduced biodiversity of the Urussanga coal burning zone. BCCRs contain remnants of coal and coexisting sedimentary rocks discarded as mining waste. Researched Brazilian

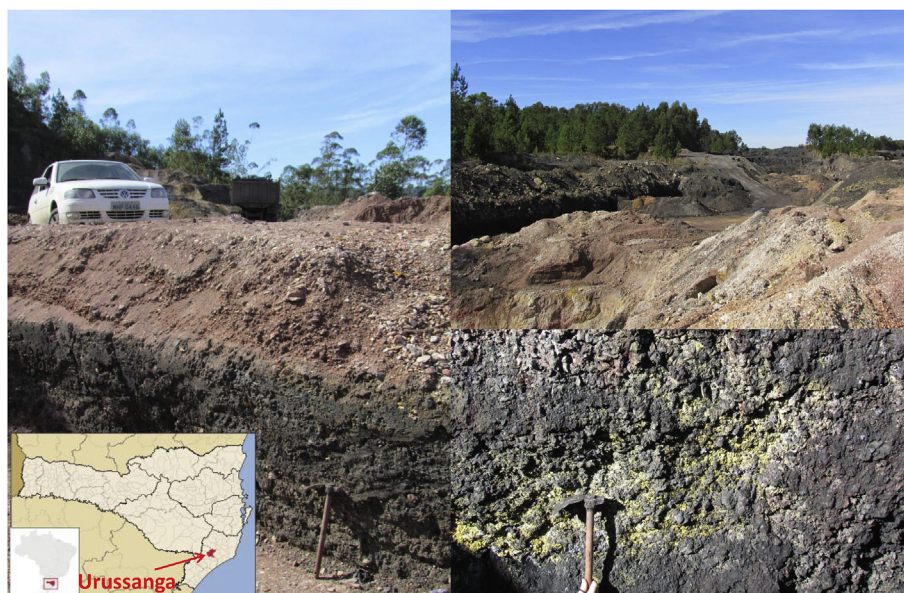


Fig. 1. Studied area and images of the BCCR sampling sites in Brazil.

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