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Coal emissions adverse human health effects associated with ultrafine/nano-particles role and resultant engineering controls

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ABSTRACT

There are multiple elements which enable coal geochemistry: (1) boiler and pollution control system design parameters, (2) temperature of flue gas at collection point, (3) feed coal and also other fuels like petroleum coke, tires and biomass geochemistry and (4) fuel feed particle size distribution homogeneity distribution, maintenance of pulverisers, etc. Even though there is a large number of hazardous element pollutants in the coal-processing industry, investigations on micrometer and nanometer-sized particles including their aqueous colloids formation reactions and their behaviour entering the environment are relatively few in numbers. X-ray diffraction (XRD), High Resolution-Transmission Electron microscopy (HR-TEM)/ (Energy Dispersive Spectroscopy) EDS/ (selected-area diffraction pattern) SAED, Field Emission-Scanning Electron Microscopy (FE-SEM)/EDS and granulometric distribution analysis were used as an integrated characterization techniques tool box to determine both geochemistry and nanomineralogy for coal fly ashes (CFAs) from Brazil´s largest coal power plant. Ultrafine/nano-particles size distribution from coal combustion emissions was estimated during the tests. In addition the iron and silicon content was determined as 54.6% of the total 390 different particles observed by electron bean, results aimed that these two particles represent major minerals in the environment particles normally. These data may help in future investigations to asses human health actions related with nano-particles.

1. Introduction

Over the several decades there have been many studies to evaluate risks associated with the by-products and co-products of coal combustion (Schneider et al., 2016). However, there is a small number of papers where nano-minerals present on coal fly ashes (CFAs) are considered (e.g.: Saikia et al., 2015; Wilcox et al., 2015; Martinello et al., 2014; Ribeiro et al., 2010). Thus there is a need to assess the potential impacts of nano-particle mobilization from coal combustion on human health. Previous research (Lu et al., 2014) have found that coal combustion by-products could be both carcinogenic and mutagenic often leading to lung cancer. In a global base case calculation, reports show that around 223,000 deaths could be linked to lung cancer from air pollution. There are also investigations (Lv et al., 2009; Saikia et al., 2015; Sanchís et al., 2015) of the influence of carbon sphere-like molecules carried by air streams, causing lung cancer. Pollution control systems in conjunction with boiler and electrostatic precipitator design and operating conditions and coal feed properties are the main variables affecting the properties of coal combustion products (Wilcox et al., 2015; Martinello et al., 2014). Coal fed into most Brazilian power plants is a blend from different coal mines but also different fuels (such as biomass). The feed stream is therefore not always well characterized and commonly has a wide spectrum of properties, which we need to understand in order to properly improve post-combustion facilities and process designs (Lu et al., 2016). The coal is not characterized on a daily base making it hard to predict the subsequent properties of the coal combustion by-products (Quispe et al., 2012). Coal's physical and chemical properties may substantially differ after its removal from its natural environment, because of blending and weathering. Because the coal composition varies, its ashes and co-products also varies in

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physical and chemical properties opening a window for new researches (Kronbauer et al., 2013; Oliveira et al., 2012a, 2012b; Ribeiro et al., 2010). Likewise, coal fly ash, which improper disposal may result in serious human health issues as well as economic and environmental challenges (Silva et al., 2009a, 2009b). As CFA's could be considered absorptive materials, they could contribute to the partitioning, transport and toxicity, of various compounds similar to the effect that black carbon has on suspended particulate materials, and colloids in river water (Martinello et al., 2014; Silva et al., 2011a, 2011b, 2011c). In Brazil electrostatic precipitation (ESP) are commonly used for particulate material control. However, their performance efficiency trends to decrease as particle size decreases and there are several studies that have found that short term (1–5 days) increases in PM2.5 could be linked with lung function reductions in both healthy people and those with preexisting pulmonary diseases, such as asthma or chronic obstructive pulmonary disorders (Rice et al., 2013). In coal power plants the outlet gas emissions can contain ultrafine/nano-particles and these emissions can be considered as one of the major contributors of nanoparticles in urban areas (Martinello et al., 2014).

Particulate pollution can be harmful to human health and the environment and is a major contributor to atmospheric pollution (Fenger, 2009; Morillas et al., 2016a, 2016b; Calparsoro et al., 2017). Previous studies have shown that CFA's could easily reach deeply into the lungs and they can carry a significant quantity of toxic compounds, such as hydrocarbons and hazardous elements, on their surfaces. Previous investigations have also shown that fine particles with an aerodynamic diameter less than 2.5 μm (PM2.5) tend to be richer hazardous elements and other pollutants because of the large surface area and strong surface activity (Li et al., 2009). The research described in this paper was driven by the motivation to obtain accurate data on morphological and geochemical characteristics of ultra-fine/nano-particles in Brazilian CFAs.

2. Experimental section

Samples used for this paper were collected from the largest coal power plant in South America located in Brazil. The power plant generates around 857 MW/h of electricity using a coal blend. The combustion temperature oscillates from 900 to 1500 °C and in the process coals with a medium sulphur content and their ash yield is as high as 40%. The power plant is fitted with low-NOx burners which include 7 pulverised fuel units, where the CFA samples were collected over a five-day period in order to complete a representative sample of around 15–20 kg of CFAs, following the ASTM (D 2234-89, 1991) standard. From one 10 kg was took 10 samples of approximately 1 kg that were stored in plastic bags and randomly selected for the research. The samples were stored in polypropylene bags inside a phosphorous pentoxide containing system to prevent moisture contamination. Detailed analytical methods are needed to properly evaluate the threat of ultrafine/nano-particles derived from coal power plant emissions resulting from the anthropogenic activities, and also to observe particles interactions with other materials and hazardous elements in the environment.

2.1. X-ray powder diffraction

To ensure that these interactions and hazardous elements are observed, the major crystalline mineralogy of CFA was determined by X-ray powder diffraction (XRD). The samples were homogenized and compacted on the sample holder so the surface required was uniform (Oliveira et al., 2012a, 2012b). During data collection samples were constantly agitated to get the best peak profile but also to mitigate the orientation effect. A Philips powder diffractometer equipped with a "PW1710" control unit, a Vertical Philips "PW1820/00" goniometer and FR590 EnrafNonius generator, was used to analyse the samples. This instrument was equipped with a graphite diffracted-beam monochromator and Cu-radiation source λ(Kα1) = 1.5406 Å, operating at 40 kV and 30 mA. The XRD pattern was collected by measuring the scintillation response to Cu Kα radiation versus the 2θ value over a 2θ range of 2 − 65°, with a step size of 0.02° and counting time of 3 s per step. Semi-quantification of individual crystalline phases (minerals) in each sample was determined using the program Match! (©2003–2011 CRYSTAL IMPACT, Bonn, Germany). Laboratory of Mineral Processing (LAPROM), Federal University of Rio Grande do Sul (UFRGS) executed all particle size analysis and for the finest material (particle size lower than 500 μm), a Silas laser diffraction granulometer was used.

2.2. Electron bean

The CFA micro-structures were observed by a FE-SEM electron beam (Zeiss Model ULTRA plus with charge compensation) and HR-TEM (200-keV JEOL-2010F; equipped with a scanning - STEM unit), electron beam allowed the study of the extent of sintering and/or agglomeration in the CFAs containing the nanominerals to be able to identify the possible presence of hazardous elements too (Cerqueira et al., 2012, 2011). Most typical dense particles have a rough surfaces. A large number of ultrafine/nano/micro-spheres, consisting of hematite, magnetite, or spinel crystals in the glassy matrix, adhered to the surface of magnetospheres. Individual particle compositions estimations were possible with the technology provided by the HR-TEM and FE-SEM with EDS, it was possible to look at the nanoparticle morphology as well and in order to keep track on the contents of Mo and Cu changes was used a silver grid in the HR-TEM.

Changes at Mo and Cu are caused by Mo-Cu-rich nanominerals and ultrafine particles. With the help of a microbeam diffraction model (MBD), selected-area diffraction pattern (SAED), and fast Fourier transformation (FFT) of the HR-TEM images we were capable to obtain data on nanominerals and hazardous volatile elements (HVEs) crystallinity and symmetry at ultrafine/nanoparticles. Crystalline phases identification was determined using the inorganic compound powder diffraction file (PDF) database comparing the *d*-spacing obtained with the International Centre for Diffraction Data sheets (ICDD, 2011). The detection limit of the EDS (coupled with FE-SEM and HR-TEM) analyses is ~1 wt%, making it a useful method for characterization of major elements (> 1%) in the detected individual ultrafine particles only (Arenas-Lago et al., 2013).

3. Results and discussion

In Table 1 the most common minerals and inorganic phases recognized in the CFA samples, are shown. On the samples we calculated that the largest composition include inert amorphous phases, silicates, oxides, and to a lesser extent (by electron beam) carbonates, sulphates, and hydroxides, which formed during heating. Thanks to unaltered minerals found in the CFAs we may have an idea of the origin of several elements, i.e. in which mineral and amorphous phases they were hosted in the coals and the formation steps for the inorganic morphotypes in the CFAs, which are a consequence of industrial supplementary volatilization of elements and induced alteration, decomposition,

Table 1
Mineralogy of CFAs samples by XRD (wt%).

	CFA 1	CFA 2	CFA 3	CFA 4	CFA 5	CFA 6	CFA 7
Amorphous	59.3	62.1	62.7	59.0	65.3	69.5	70.0
Anhydrite						0.5	0.4
Magnetite				0.1			
Maghemite	1.3	1.6	1.1	1.5	1.2	0.7	0.7
Mullite	23.6	21.5	22.8	25.1	22.4	22.2	22.3
Rutile				0.2		0.1	0.3
Quartz	15.7	14.7	13.4	14.1	11.0	7.1	6.3

Note: Amorphous material may include unburnt carbon, as well as aluminosilicate glass.