Mineralogical and Leaching Characteristics of Beneficiated Coals

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Abstract

Petrographic, mineralogical and geochemical studies have been carried out on beneficiated coal products from mines and preparation plants in the Santa Catarina Basin, southern Brazil, to investigate the range of characteristics exhibited by the materials and the potential impact of their stockpiling and storage on the environment. The coals contain varying proportions of vitrinite and inertinite macerals, and have vitrinite reflectance values ranging from 0.44 to 1.38%. With the exception of one material blended with peat from an external source, they have relatively high percentages of ash (30–58%) and mineral matter (36–66%). The mineral matter consists mainly of clay minerals (kaolinite, illite and illite/smectite), together with 15–25% quartz, up to 10% feldspar, up to 5% calcite and/or dolomite and up to 5% pyrite, and around 1% anatase and/or rutile. Most of the trace elements in most of the coals have higher concentrations than average values for world coals generally, probably due to the relatively high mineral matter content. A lower-ash product representing a blend of coal and peat has similar to lower concentrations of most elements, but higher concentrations of B, Ba, Be, Cd, Ge and Mn, which may be associated with the peat component. Interaction of relatively fresh coals with water in laboratory tests produces leachates with near-neutral to mildly acid pH values, but leaching of oxidized, jarosite-bearing coal produces a strongly acid leachate, with higher concentrations of Cd, Co, Cu, Ni and Zn. Leachates derived from coals in which the pyrite has been oxidized during storage would thus be expected to have a more adverse environmental impact than leachates derived from coals in which such oxidation has not had an opportunity to develop.

Keywords: Coal petrology, Mineral matter, Trace elements, Leaching, Environmental impact

1. Introduction

Coal has been used in Brazil as solid fuel for thermoelectric generation for nearly 80 years (Pires and Querol, 2004; Silva et al., 2009a,b), and has provided great support to national development. The southern part of Santa Catarina State, Brazil, is a well-established coal mining region, supplying the largest electric power plant in South America, the Jorge Lacerda Power Station, as well as fuel for ceramic production, cement manufacture, chemical factories, and a former fertilizer plant (Da Silva et al., 2010; Levandowski and Kalkreuth, 2009; Oliveira and Kalkreuth, 2010).

According to local coal industry data, the average run-of-mine coal production for Santa Catarina state is around 6 Mt/year (ABCM-Associação Brasileira do Carvão Mineral), 2011); (SIECESC-Sindicato da Indústria de Extração de Carvão do Estado de Santa, 2011). Of this, some 3.5 Mt/year are rejected from preparation plants and disposed of in landfills (Marcello et al., 2008), leaving a balance of 2.5 Mt/

year of saleable coal production.

The washing techniques generally used in Santa Catarina state include jigging (the most widely used method), dense medium separation and cyclones. Although such stockpiles may be designed to prevent escape of water to the adjacent surface runoff or to the groundwater beneath, leachates from the stockpile may still be released to the ground or surface water in a variety of ways. This study therefore aims to investigate the nature of the mineral matter in the coals produced in the Santa Catarina Basin, including the concentrations of a range of trace elements, and also the extent to which different major and trace elements might be mobilized from the coal when exposed to water under laboratory leaching test conditions.

2. Methods

2.1 Sampling program

Twenty samples of mined and (in most cases) beneficiated products from the main seams in the Permian sequence were collected from 12 localities (Fig. 1). An Etrex® geographical positioning system unit (GPS) was used to determine the geographic coordinates (latitude/longitude) of the sampling points. Fresh samples were collected at each location immediately after the coal cleaning process. In some cases, however the samples were collected from product stockpiles that had been exposed for approximately 18 months before sampling took place.
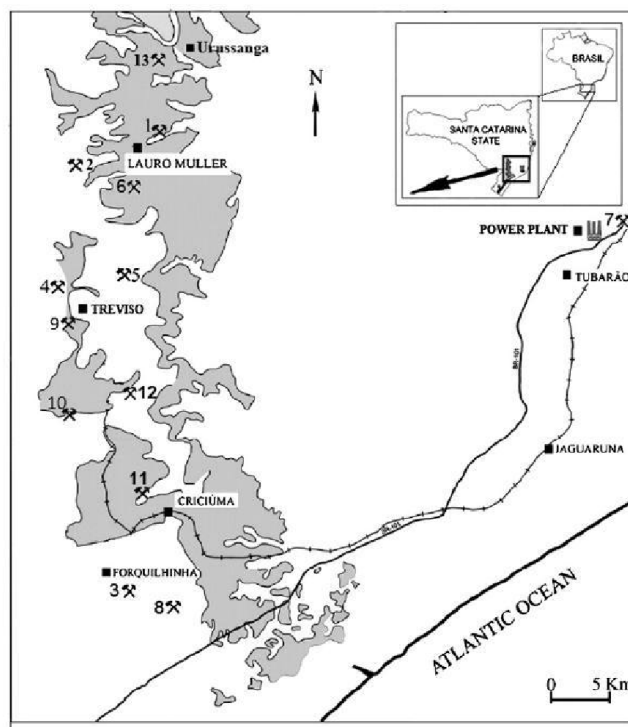

Fig. 1. Location of sampling sites in Santa Catarina.

The samples were quartered and individually homogenized in the field according to ASTM D2797 (1991), reduced in size by hand and finally milled in the laboratory to provide a representative sample of approximately 0.5 kg for the analytical program. The samples were dried in a furnace (40 °C, 16 h), homogenized and sieved through a 450 μm screen.

2.3 Analytical methods

Epoxy-bound particulate pellets of each coal sample (finer than 20-mesh) were prepared to a final 0.05-μm polish. Microscopic examination was carried out on a Leitz Orthoplan microscope, using

reflected light optics and a 50× oil-immersion objective. Maceral identifications for the coal samples followed the nomenclature of ICCP (1998, 2001). Mean maximum vitrinite reflectance was measured from 50 points per coal, using polarized light and a 546-nm filter.

The mineralogy of each LTA was evaluated by X-ray powder diffraction, using a Phillips X'pert MPD diffractometer equipped with a Pixcel multi-channel detector, Cu Kα radiation, and a scan range from 2 to 60°2θ. Quantitative analyses of the mineral phases in each LTA were made using Siroquant™, commercial interpretation software (Taylor, 1991), based on the Rietveld (1969) XRD analysis technique.

A LEO-435VP scanning electron microscope (SEM), fitted with an Oxford energy-dispersive X-ray spectrometer (EDS), having a resolution better than 133 eV, was used for chemical analyses of individual particles exposed on natural and/or polished surfaces of selected coal samples. The unit was equipped with a motorized stage and a four-quadrant back-scatter detector, using an accelerating voltage of 20 kV and a beam current of $10-10$ A.

Coal samples were ashed at 815 °C. The resultant ashes were then calcined at 1050 °C, mixed with lithium borate, and fused into borosilicate disks following the methods described by Norrish and Hutton (1969). The major element oxides in each ash sample were determined by X-ray fluorescence (XRF) spectrometry techniques using a Philips PW2400 spectrometer system.

The coal samples were acid digested following a two-step digestion method devised to retain volatile elements (Querol et al., 1997). The resulting solution was then analyzed by inductively coupled plasma atomic-emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) to determine the trace element concentrations. In order to study the leaching of elements from the coal samples, compliance leaching tests described by the European Committee for Standardisation (2002) (EN 12457–2: 2002) were carried out at the Institute of Environmental Assessment and Water Research.

3. Results and discussions

On a minerals included basis the coals contain from 17 to 60% vitrinite, mainly in the form of collotelinite, and 17 to 60% inertinite, mainly fusinite and semifusinite (Fig. 2A, C). Samples with high inertinite contents have low proportions of vitrinite and vice-versa. The coals also contain up to 9% liptinite, mostly sporinite, although most samples contain between 2 and 5% liptinite.
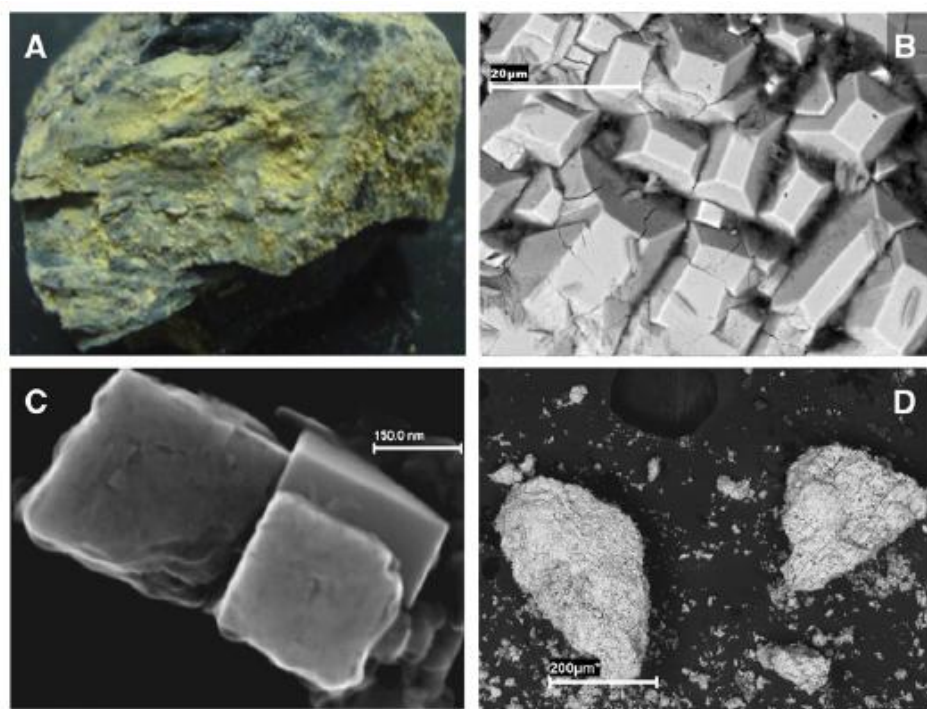
Fig. 2. (A) Pseudomorphs of jarosite (yellow to light brown) after pyrite in a coal fragment (CR-50); (B) Cubic pyrite crystals on a natural surface under the SEM; (C) Replacement of cubic pyrite crystals by jarosite; (D) Hematite typically also present in samples containing jarosite

Mean maximum vitrinite reflectance for the samples ranges from 0.44% to around 1.4%, indicating a rank range from sub-bituminous to medium volatile bituminous coal. The mineralogy of the LTAs isolated from the coals is given in Table 1. Clay minerals, especially illite and mixed-layer illite/smectite (I/S), are the dominant components of the LTA isolated from the coal samples. Comparison with other Gondwana coals (e.g. Ward, 1989) suggests that the illite and I/S are probably mainly of detrital origin, while the kaolinite, especially the well-ordered material, may be at least partly authigenic, formed as precipitates within the pores of the maceral components.

Table 1. Mineralogy of coal LTAs from XRD and Siroquant (wt. %).

	CR-02	CR-06	CR-10	CR-16	CR-18	CR-22	CR-24	CR-29	CR-36	CR-37
LTA yield	39,9	55,4	44,4	43,1	41,9	43,9	49,9	48,0	36,4	37,9
Quartz	15,3	24,7	12,1	26,5	11,4	20,9	26,1	25,7	15,6	17,0
Kaolinite	30,3	11,2	20,7	5,9	27,5	56,1	8,1	8,4	29,1	31,1
Illite	19,3	17,6	11,4	24,4	13,1	11,9	22,3	20,4	28,6	30,3
I/S	30,5	32,5	45,8	28,4	31,6		33,0	35,0	21,5	18,4
Feldspar		10,3	2,7	6,8	0,3		4,5	5,4	0,2	
Pirite	1,9	1,5	1,1	1,7	2,4	2,4	3,4	3,2	1,2	1,2
Calcite			2,8	1,6	2,4	1,7	2,6	0,4	2,4	1,6
Dolomite					6,1					
Siderite					0,7					
Apatite						0,8				
Anatase			1,2	0,7	1,5			0,4	0,8	
Rutile			1,2	0,9	0,3				0,2	
Bassanite	2,8	2,3	1,0	3,1	2,7	1,7		1,0	0,5	0,4
Gypsum						4,6				

	CR-41	CR-43	CR-44	CR-49	CR-50	CR-58	CR-59	CR-65	CR-66.1	CR-66.2
LTA yield	37,8	49,5	37,5	37,4	66,1	51,9	52,0	54,7	46,6	21,7
Quartz	15,5	19,1	15,7	22,2	20,3	19,1	17,4	16,4	22,0	40,7
Kaolinite	17,3	20,9	16,7	43,6	28,4	29,8	30,3	26,8	37,4	35,5
Illite	20,2	15,8	25,8	13,5	20,8	14,8	16,1	14,1	14,1	7,2
I/S	43,5	41,7	34,2	9,9	25,0	31,9	22,7	33,1	28,7	10,6
Feldspar						1,0	0,9	0,7		
Pirite	0,6	0,5	1,6	0,8		0,1	0,4	2,1	1,0	2,7
Jarosite			1,1		3,3	1,6	6,3	3,9	3,5	1,7
Calcite	0,8	0,3	1,7	4,2						
Dolomite				0,9						
Anatase	1,1	0,9	1,4		1,3	1,4	1,5	1,2	1,3	
Rutile				2,1	0,1	0,1	2,3	0,7		
Bassanite	1,0	0,7	1,6	2,7	0,8	0,3	2,1	1,0	2,1	1,8

Quartz makes up between 10 and 25% of the LTA for most of the coal samples. Pyrite is a minor but significant constituent of the LTA isolated from almost all of the coal samples, making up to around 3.5% of the mineral matter. Calcite is present in the LTA of some of the coal samples, although again only in minor proportions (less than 5%). Dolomite is also noted in two of the samples, and possible traces of siderite and apatite in other LTA residues. Anatase and rutile are also present as minor to trace components of the mineral matter for most of the coal samples. Bassanite ($CaSO_4 \cdot \frac{1}{2}H_2O$) is present in all but one of the LTAs, along in one case (CR-22) with gypsum.

As might be expected from the LTA percentages in Table 1, almost all the coals have relatively high 815 °C ash yields. The ashes also contain low percentages of Na_2O but 1 to 3% K_2O, consistent with the abundance of illite and I/S in the mineral matter. The ashes contain 4.5 to 9% Fe_2O_3, suggesting that, as well as occurring in pyrite and jarosite.

The proportion of CaO in the coal ashes varies from 0.1 to 5%. The proportion of sulfur (as SO_3) retained in the ash varies over a similar range (0.5 to 5.4%). The ash of sample CR-18, the LTA of which contains 6% dolomite (Table 1), has the highest proportion of CaO (and MgO), and the highest proportion of retained SO_3 among the samples studied.

Although all of the samples, with the exception of sample CR-66.2, have similar overall proportions of the individual major and trace elements. The concentrations of Al, Fe, and S, as well as those of Cd, Co, Cu, Ni and Zn, are significantly higher in the leachates from the acid-generating coals than from the other coal samples. Although only low concentrations are involved, the leachates from the acid-generating coals also have higher concentrations of Ga, Gd, La, Nd and Y.

4. Conclusions

The mineral matter in most of the coals is made up mainly of kaolinite, illite, and interstratified illite/smectite, together with 10 to 25% quartz and minor proportions (up to 5%) of calcite and pyrite. Pyrite in coals that have been exposed for a significant period typically shows alteration to jarosite. Small proportions of feldspar (up to 10%), and in individual cases dolomite, siderite and apatite, may also be present. Anatase and/or rutile are found at trace levels (1–2%) in the mineral matter of most coal samples, and bassanite, probably derived mainly from interaction of organically-associated Ca and S, typically makes up to around 2.5% of the LTA residues.

Most of the trace elements in the coals have somewhat higher concentrations than the same elements in world coals generally. Higher concentrations of several elements of potential environmental significance, including Cd, Co, Cu, Ni and Zn, are found in leachates from the oxidized coal samples. This suggests that fresh Santa Catarina coals, such as those in operating power station stockpiles, may be expected to produce leachates with neutral to slightly acid pH levels, but coals in which the pyrite has been oxidized, such as stored and reprocessed rejects or materials from longer-standing stockpiles, may produce quite acid leachates containing greater concentrations of several

environmentally-significant elements.

References

American Society for Testing and Materials (ASTM), 1991. D2797: standard practice for preparing coal samples for microscopical analysis by reflected light. Annual Book of ASTM Standards, Section 5, Petroleum Products, Lubricants and Fossil Fuels: Gaseous Fuels, Coal and Coke, vol. 05.05, pp. 308–310.

DaSilva, R., Pires, M., Azevedo, C.M.N., Fagundes, L., Garavaglia, L., Gomes, C.J.B., 2010. Monitoring light hydrocarbons in Brazilian coal mines and in confined coal samples. International Journal of Coal Geology 84, 269–275.

Levandowski, J.H., Kalkreuth, W., 2009. Chemical and petrographical characterization of feed coal, fly ash and bottom ash from the Figueira Power Plant, Paraná, Brazil. International Journal of Coal Geology 77, 269–281.

Marcello, R.R., Galatob, S., Petersona, M., Riellac, H.G., Bernardin, A.M., 2008. Inorganic pigments made from the recycling of coal mine drainage treatment sludge. Journal of Environmental Management 88, 1280–1284.

Norrish, K., Hutton, J.T., 1969. An accurate X-ray spectrographic method for the analysis of a wide range of geological samples. Geochimica et Cosmochimica Acta 33, 431–453.

Oliveira, J.S., Kalkreuth, W., 2010. Sequence stratigraphy, organic petrology and chemistry applied to the upper and lower coal seams in the Candiota coalfield, Paraná Basin, RS, Brazil. International Journal of Coal Geology 84, 258–268.

Pires, M., Querol, X., 2004. Characterization of Candiota (South Brazil) coal and combustion by-product. International Journal of Coal Geology 60, 57–72.

Querol, X., Whateley, M.K.G., Fernandez-Turiel, J.L., Tuncali, E., 1997. Geological controls on the mineralogy and geochemistry of the Beypazari lignite, central Anatolia, Turkey. International Journal of Coal Geology 33, 255–271.

Silva, L.F.O., Oliveira, M.L.S., da Boit, K.M., Finkelman, R.B., 2009a. Characterization of Santa Catarina (Brazil) coal with respect to human health and environmental concerns. Environmental Geochemistry and Health 31, 475–485.

Silva, L.F.O.,Moreno, T., Querol, X., 2009b. An introductory TEM study of Fe-nanominerals within coal fly ash. Science of the Total Environment 407, 4972–4974.

Ward, C.R., 1989. Minerals in bituminous coals of the Sydney Basin (Australia) and the Illinois Basin (U.S.A.). International Journal of Coal Geology 13, 455–479.