Coals Industrial Beneficiation Processes from Santa Catarina, Brazil: Inorganic Components Geochemical

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Abstract

Comparative research of the mineral matter and trace elements in 12 pairs of run-of-mine (ROM) and clean-coal products from beneficiation plants in Santa Catarina, southern Brazil, have been developed out using low-temperature oxygen-plasma ashing, X-ray diffraction and chemical analysis techniques with the aim of estimate the effect of coal preparation on the mineralogy and chemical composition of the final coal products. The results showed that substantial reductions in mineral matter and ash levels are associated with beneficiation of coals mined from the different deposits. These reductions are accompanied by changes in the levels of Fe_2O_3 in the respective coal ashes, due to the reduction in the proportion of pyrite in the mineral matter, and also by a reduction in the level of Na_2O, possibly due to ion exchange within the clay minerals. The relative proportions of quartz, clay minerals, and minor phases such as calcite and feldspar (mainly albite) within the mineral matter are not, however, significantly changed by the beneficiation processes. The concentrations of most trace elements in the beneficiation products are similar to the respective concentrations in the relevant ROM materials, or are reduced to an extent similar to that of the total mineral matter level for the respective coal samples. This indicates an association mainly with the clay-rich mineral matter. The concentrations of As and Pb, however, are reduced to a greater extent for most samples by the beneficiation processes, in accordance with a pyrite association. Concentrations of Ge, U and Zr are higher in many of the clean coals than in the respective run-of-mine materials, indicating the possibility of preferential association, at least for some deposits, with the organic-rich fractions of the coals concerned. Comparison of ROM and clean coal products from Santa Catarina preparation plants shows significant reductions in ash, mineral matter and total sulphur percentages associated with beneficiation, and also in the relative proportions of pyrite within the mineral matter. With the exception of pyrite, the mineral matter of the clean coals, as determined by quantitative X-ray diffraction, is similar to that of the respective ROM materials, with abundant quartz, kaolinite, illite and interstratified illite/smectite, and minor proportions of calcite and other accessory phases, and appears to have been little changed by coal preparation.

Keywords: mineral matter, X-ray diffraction, coal preparation, pyrite, trace element

1. Introduction

In Brazil the principal coal deposits mined are of Early Permian age, and distributed in a lenticular belt across the SE part of the country that extends from the state of Paraná in the north to the state of Rio Grande do Sul in the south (Thomas, 2002; Kalkreuth et al., 2004). Brazil's total coal resources are in the order of 32×109 tonnes (Kalkreuth et al., 2006), the majority of which (89%) are located in Rio Grande do Sul. Most of the remainder (a little over 10%) are located in the adjoining state of Santa

Catarina (Fig. 1), and small amounts are located in Paraná and the adjacent state of São Paulo.

In Santa Catarina the most of the seams mined have marginal coking properties, but current production is almost entirely used for electricity generation at the Jorge Lacerda (Tractebel Suez) Power Station (875 MW), located near Tubarão city in the NE of the state (Fig. 1). A small amount of material, however, mainly fine coal from the preparation plants, is used in metallurgical foundry operations.
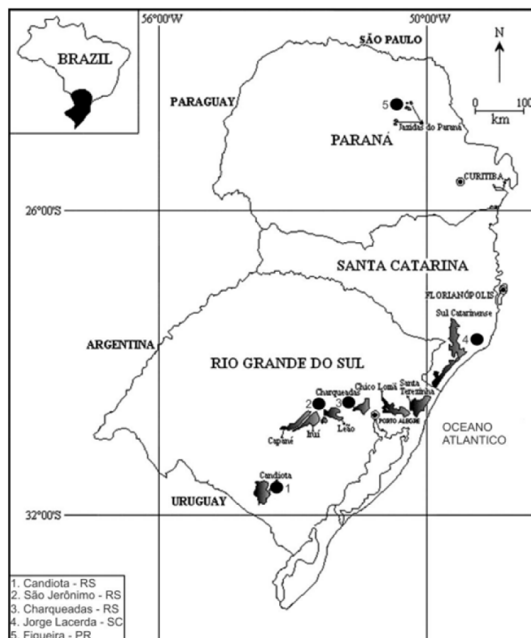

Fig. 1: Location of sample sources, and also of Jorge Lacerda (Tractebel-Suez) power station

1.1 Preparation characteristics of Brazilian coals

To provide products with low ash yields (about 30-35%), small top sizes should ideally be used. This would, however, cause a decrease in the efficiency of the beneficiation processes (Sampaio and Tavares, 2005), and also increase the moisture content of the products. Consequently, top sizes used in the preparation plants are not over 50 mm and rarely less than 30 mm.

Figure 2 show an example of the preparation characteristics of a Brazilian coal, which present Henry-Reinhardt liberation curves for a Candiota coal with a size range of 25.4 mm x 2 mm (de Souza, 2012; Feil et al., 2012). The first curve, the densimetric curve (Fig. 2A), illustrates the variation in the cumulative floats percentage as a function of separation density. In this case, for each density chosen (cut point) there is a proportion of the coal that floats (density less than the cut point) and there is a proportion of the coal that sinks (density higher than the cut point).
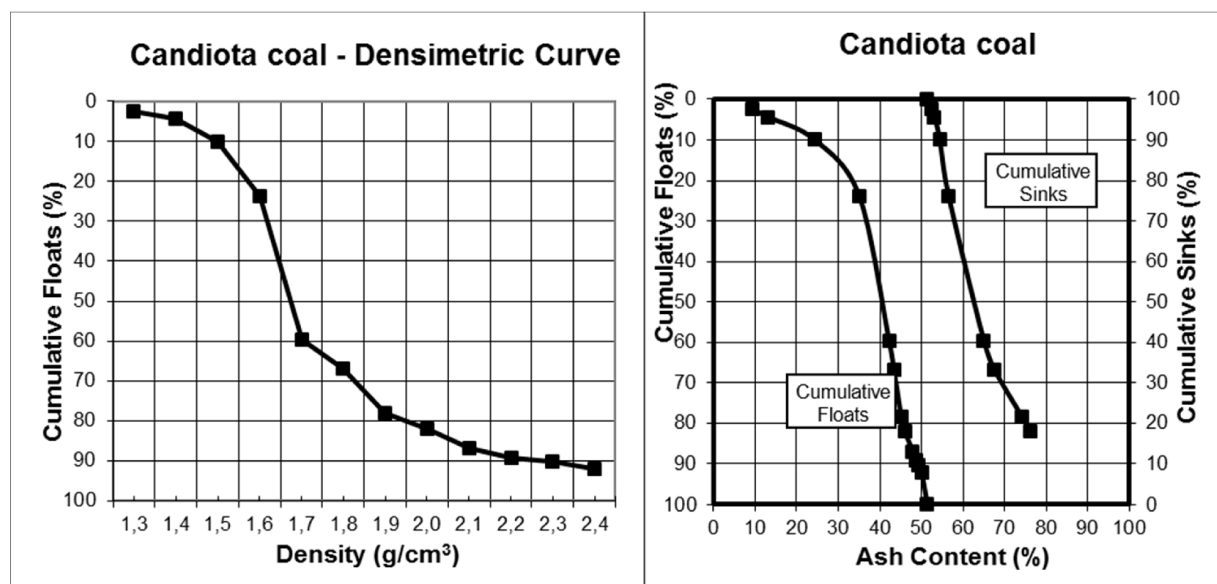
Fig. 2: Henry-Reihardt liberation curves for a coal from Candiota, Rio Grande do Sul, with particle size range 25.4 mm x 2 mm. A) Plot showing variation in cumulative floats percentage with separation density; B) Plot showing ash yield of cumulative floats and sink fractions for the same coal sample.

1.2 Objectives of the present study

Has been used in a number of studies the Separation of finely crushed coal samples into different density fractions (e.g. Gluskoter et al., 1977; Ward, 1980; Senior et al., 2000; Querol et al. 2001; Wagner and Tlotleng, 2012) as a basis for assessing the modes of occurrence of different trace elements. Such an approach is generally used to indicate whether particular elements are more strongly associated with the dense, mineral-matter rich fractions of the coal (i.e. have an inorganic affinity) or with the less-dense, maceral-rich fractions (i.e. have an organic affinity). Studies are commonly carried out on samples crushed to a relatively fine particle size, with greater liberation of mineral and organic components and more efficient separation than would typically be obtained under industrial processing conditions.

The intention of the present study is to compare the mineralogical and inorganic geochemical characteristics of ROM and beneficiated coals from the principal mines and preparation plants in Santa Catarina that contribute to the blend used in the Jorge Lacerda power station, in order to evaluate the partitioning of the minerals, major elements and trace elements associated with concentration of the organic matter by the beneficiation processes used. As well as providing a basis for comparison to similar mineralogical studies based on other deposits, the work is intended to help in designing new preparation plants and processes, to assist the design and operation of coal-fired power stations, and to increase the level of understanding in the development and use of Brazil's high-ash coal resources.

2. Methods

2.1 Sampling

Were collected (12 ROM and 12 beneficiated or clean coals), a total of 24 coal samples, from both large and small mines in the Paraná Basin of Santa Catarina (Fig. 1). Bulk samples of 100 kg were collected over a 5-day period from each site immediately after the mining and beneficiation processes, following American Society for Testing and Materials procedures (ASTM, 1996). The samples were reduced by cone and quartering; the quartered fractions were then homogenized in the laboratory following ASTM procedures (ASTM, 1991), and split to supply subsamples for further grinding and analysis.

2.2 Analytical procedures

Pulverized (<212-µm) subsamples prepared from the ROM and clean coals were oven-dried for 24 hours at 40 °C. Ultimate analysis was carried out on these samples using a LECO CNHS-932 elemental analyzer at the University of Rio Grande do Sul, providing data on the carbon, hydrogen, sulphur, nitrogen and oxygen contents of the dried coal samples.

Minerals of importance is selected coals were examined on natural coal surfaces using a LEO-435VP scanning electron microscope (SEM), fitted with an Oxford energy-dispersive X-ray spectrometer (EDS) with a resolution >133 eV (Silva et al., 2012). The accelerating voltage was 20 kV and the beam current was 10-10 A.

3. Results and Discussion

3.1 Ash and sulphur

Ultimate analysis data for the ROM and clean coal samples are presented in Table 1. The data in Table 1 represent values determined to a dry basis, so that the sum of the C, H, N, S and O percentages effectively represent the total proportion of organic matter. The difference between that value and 100%, also listed in Table 1, approximates the ash percentage (dry basis) for each sample. Ash yields range from 45 to 84% for the ROM samples (average 60.9%) and from 29 to 51% (average 40.4%) for the clean coal materials. Total sulphur ranges from 1.0 to 3.9 % for the ROM coals (average 2.26%) and 0.7 to 3.2% (average 1.57%) for the clean coal samples.

Table 1: Ultimate analysis (wt %, dry basis) of coal samples

Sample	Company / mine	Coal	C	H	N	S	O	Total	Ash *
CR 1	3G Plano II	Run-of-mine	37.34	2.96	0.76	2.25	9.31	52.62	47.38
CR 2	3G Plano II	Clean coal	52.76	3.69	1.01	1.44	8.59	67.49	32.51
CR 5	Bonito	Run-of-mine	21.50	1.64	0.29	1.78	5.03	30.24	69.76
CR 6	Bonito	Clean coal	38.99	2.28	0.49	1.55	5.55	48.86	51.14
CR 9	UM II-Verdinho	Run-of-mine	26.68	1.95	0.49	2.11	5.10	36.33	63.67
CR 10	UM II-Verdinho	Clean coal	51.65	3.56	0.96	1.66	4.75	62.58	37.42
CR 15	Fontanela	Run-of-mine	36.45	2.06	0.47	2.34	3.83	45.15	54.85
CR 16	Fontanela	Clean coal	50.97	2.92	0.69	1.53	3.74	59.85	40.15
CR 17	Esperança Leste	Run-of-mine	36.51	2.84	0.78	2.02	5.41	47.56	52.44
CR 18	Esperança Leste	Clean coal	51.80	3.53	1.05	1.37	5.66	63.41	36.59
CR 23	Barro Branco	Run-of-mine	36.41	2.32	0.71	2.72	3.93	46.09	53.91
CR 24	Barro Branco	Clean coal	46.21	3.26	0.91	2.70	3.95	57.03	42.97
CR 35	Mina 3	Run-of-mine	45.43	3.09	0.90	1.75	3.91	55.08	44.92
CR 36	Mina 3	Clean coal	60.84	3.95	1.17	1.12	3.48	70.56	29.44
CR 40	Morozino	Run-of-mine	41.72	2.69	0.90	2.65	3.35	51.31	48.69
CR 41	Morozino	Clean coal	56.55	3.40	1.18	1.40	3.09	65.62	34.38

CR 42	Cantao	Run-of-mine	35.10	2.44	0.77	2.44	3.39	44.14	55.86
CR 43	Cantao	Clean coal	49.02	2.81	0.99	1.37	3.05	57.24	42.76
CR 48	Morozin/Cantao	Run-of-mine	12.52	1.58	0.39	2.38	2.62	19.49	80.51
CR 49	Morozin/Cantao	Clean coal	47.17	3.38	0.78	0.74	8.02	60.09	39.91
CR 57	Gabriela	Run-of-mine	8.09	1.10	0.08	0.99	5.71	15.97	84.03
CR 58	Gabriela	Clean coal	44.32	3.29	0.89	0.90	4.55	53.95	46.05
CR 64	Car. Siderópolis	Run-of-mine	11.23	1.25	0.11	3.91	6.10	22.60	77.40
CR 65	Car. Siderópolis	Clean coal	39.31	3.09	0.82	3.21	6.27	52.70	47.30
	Average	Run-of-mine	29.08	2.16	0.55	2.28	4.81	38.88	61.12
	Average	Clean coal	49.13	3.26	0.91	1.58	5.06	59.95	40.05

Note: * ash percentage estimated by difference

3.2 Mineral matter in coal samples

The remaining three ROM samples (CR 48, CR 57 and CR 64) had a light grey colour in powdered form, indicating a low percentage of organic matter, and the mineralogy of these samples was assessed by XRD analysis of the raw coal without an intermediate plasma-ashing process.

According to Oliveira et al. (2012), the illite and I/S are primarily detrital in origin. The kaolinite, quartz and feldspar may also be mainly of detrital origin, although some of the kaolinite and quartz might also represent authigenic precipitates formed within the pores of the maceral components. The pyrite is commonly framboidal, and was probably formed mainly by bacterial reduction of sulphate in the original depositional environment; the jarosite was probably derived from oxidation of the pyrite with exposure and/or storage.

Again according to Oliveira et al. (2012), the bassanite and gypsum may represent artefacts of the plasma-ashing process (cf. Frazer and Belcher, 1973), although interaction of calcite in the coals with acids produced by pyrite oxidation (cf. Rao and Gluskoter, 1973), or precipitation following evaporation of Ca-bearing pore waters in the samples (cf. Koukouzas et al., 2010), may also be involved. The occurrence of bassanite and gypsum in the ROM samples that had not been subjected to low-temperature ashing suggests that precipitation from solution was probably dominant, at least for those particular materials. Any such gypsum would, however, probably be removed from the ROM coal during preparation, so that the bassanite in the clean coal LTAs probably represents artefact material derived mainly from Ca and S in the organic matter.

3.3 Chemical composition of coal ashes

According to expected from the mineralogy of the LTA residues, the dominant oxides in the ashes are SiO_2 and Al_2O_3. Although some variation exists among the individual samples, these make up, on average, around 58% and 27% respectively of the coal ashes for both the ROM and clean coal materials. The remainder of the ash constituents are represented by Fe_2O_3, CaO, K_2O and SO_3, with lesser but still significant proportions of TiO_2, MgO, and Na_2O, and a very minor proportion of P_2O_5.

The contents of most of these oxides are similar in the respective ashes of both the ROM and clean coal samples. However, for reasons discussed in Section 3.5 (below), the average percentages of both Fe_2O_3 and Na_2O are lower in the clean coal ashes than in the ashes of the ROM materials.

3.4 Changes in mineral matter with beneficiation

One of the main objects of this study was to assess whether the overall reduction in the percentages of ash associated with beneficiation of the ROM coals (Table 1) has been accompanied by any changes in the nature of the mineral matter. Averages for siderite (20%), anatase (70%) and rutile (240%) lie well outside this range, but these phases, where present, each make up less than 2% of the mineral matter in the samples, and significant levels of scatter are associated with the individual determinations.

3.5 Minerals and major elements as fractions of whole-coal samples

When considered on a whole-coal basis, the average proportions of quartz, kaolinite, illite + I/S and bassanite + gypsum in the clean coals are between 55 and 80% of the average proportions of quartz, kaolinite, illite + I/S and bassanite + gypsum in the clean coals are between 55 and 80% of the average proportions of the same minerals in the ROM samples. This is similar to the change in the average proportion of LTA in the two groups of materials, and confirms that the relative abundance of these components in the mineral matter is not significantly affected by the preparation processes.

On the contrary, the average percentages of pyrite, jarosite and pyrite + jarosite in the clean coals, when considered on a whole-coal basis, represent only 45%, 12% and 25%, respectively, of the average percentages in the ROM materials; this confirms the selective removal of these components from the coal during beneficiation. Similar comparisons for other minerals, such as feldspar, dolomite, calcite, anatase and rutile, are unreliable due to the low percentages of these components in the coals; indeed, the percentages of these minerals in many ROM and clean-coal samples are below the relevant detection limits.

The average content of Na_2O in the clean coals is only around 25% of the average for the ROM samples. As discussed above, this is also apparent in the chemistry of the coal ashes, and may represent the result of cation exchange in the clay minerals associated with the beneficiation processes.

3.6 Elements with concentrations reduced by beneficiation

The concentrations of number of elements in the clean coals, such as Ba, Cs, Mn, Nb, Rb, Sr, Ta, Ti, Tl and W, are between 60 and 80% of the respective average concentrations in the ROM samples. Since the average ash yield or mineral matter content of the clean coals is around 66% of the average for the ROM coals, and the average percentages of major components in the clean coals (SiO_2, Al_2O_3, CaO, K_2O) on a whole-coal basis are also between 60 and 80% of the average percentages in the ROM materials, the difference in concentration of these trace elements between the two groups may be related to the overall reduction in mineral matter or ash produced by the beneficiation processes. These trace elements may therefore be associated with the main minerals in the coals, which in this case are the clay mineral components. Many are lithophile elements, and have been shown in other studies (e.g. Ward et al., 1999; Dai et al., 2012) to be associated with clays and other aluminosilicate phases.

3.7 Elements with concentrations increased by beneficiation

For three of the elements, Ge, U and Zr, the average concentrations in the clean coals are significantly higher than in the ROM materials (i.e. >120% of the average ROM values). In these cases the element might be associated in some way with the organic matter, which would give rise to an increase in concentration as the proportion of mineral material is reduced.

Though the mode of Zr occurrence in the coals requires additional investigation, the averages for the majority of the sample pairs, suggest a relatively even partitioning of such crystals between the mineral-rich and organic-rich fractions for most of the sites studied.

3.8 Elements with concentrations unaffected by beneficiation

For the remainder of the trace elements, the average concentrations in the clean coal are similar to the averages in the ROM materials, with average concentrations in the clean coals representing between

80 and 110% of the averages in the ROM samples. These elements, moreover, represent the great bulk of the trace elements analyzed for the study. Despite the general reduction in the proportion of mineral matter, and also variation in some cases on a site-by-site basis, the average concentrations of these elements do not appear to have been significantly changed by the beneficiation processes. They are probably partitioned, at least at the particle sizes used in commercial preparation, more or less evenly between the mineral-rich and organic-rich components.

4. Conclusions

Comparison of ROM and clean coal products from Santa Catarina preparation plants shows significant reductions in ash, mineral matter and total sulphur percentages associated with beneficiation, and also in the relative proportions of pyrite within the mineral matter. With the exception of pyrite, the mineral matter of the clean coals, as determined by quantitative X-ray diffraction, is similar to that of the respective ROM materials, with abundant quartz, kaolinite, illite and interstratified illite/smectite, and minor proportions of calcite and other accessory phases, and appears to have been little changed by coal preparation. The concentrations of As and Pb are reduced to a greater extent, consistent with the reduction in pyrite associated with beneficiation, and plots of their concentration against pyrite on a whole-coal basis confirms that these elements are associated with the pyrite in the ROM materials. The concentration of B also decreases substantially with beneficiation in some of the sample pairs, possibly indicating an association with tourmaline in the relevant ROM materials, but in other most cases is similar in the respective ROM and clean-coal samples.

Some elements, such as Ge, U, and possibly Zr, have higher average concentrations in the clean coals than in the ROM materials, suggesting an association, at least in part, with the organic matter. This does not necessarily mean that the elements are incorporated within the organic material; they may occur in mineral phases that are more intimately admixed with the maceral components. The relation to ash percentage suggests that the association for these elements in the different coal deposits may be split between the organic-rich and the mineral-rich components, at least at the particle sizes used in the beneficiation processes.

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