THE BEHAVIOR OF HEAVY METALS IN THE PROCESS OF DESULFURIZATION OF BRAZILIAN COAL COMBUSTION GASES BY THE ADDITION OF LIMESTONE

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Abstract - The concentrations of heavy metals in two kinds of Brazilian coals at 100° C (acid digestion) and at 850° C were studied (ashes the obtained in muffle furnace with and without addition of limestone). Data were analyzed by flame atomic absorption, using the air acetylene flame. For Pb, Zn, Ni, Mn and Cu the metal concentration obtained the acid digestion were higher than metal concentration were obtained in tests in the muffle furnace. This behavior observed in the muffle furnace occurs because these metals are fixed in stable sulfated compounds in the ashes, which are difficult to dissociate at flame temperature, and also due to the volatile character of the metals, mainly Pb and Zn. There was a constant concentration in the ashes in of Cr the acid digestion and muffle furnace tests. Results from tests using an XRD apparatus indicated, he formation of sulfated compounds in the ashes for both. coals. The analysis using microprobe electronic showed retention of metals like Ni, Mn, Cu, Fe, Ti and Ca. For both coals, the low mobility of most of the metals studied occured due to the alkaline pH of sulfated ashes. These metals in the ash from coal combustion in fluidized bed reactor were also studied and showed similar results, enabling a scale-up to pilot scale.

Keywords: desulfurization, ash, heavy metals, coal combustion.

INTRODUCTION

The study of heavy metals and the characterization of ash from coal combustion depend mainly on the chemical composition and the inorganic fraction of the coal as well as on combustion technology (Chincón et al.,1991).Temperature and also the time of exposure of the sample. The products obtained make possible retention in the mineral phases, fixing contamination elements that would be emitted to the atmosphere.

Chincón et al. (1991) studied the forms of sulfur from sub-betuminous coal (from the District of Turuel). They pointed out that sulfur is found in coal as

1)sulfide sulfur, mainly as pyrite and marcasite;
2)sulfate, chiefly gypsum anhydrite, with small proportions of hematite and melanterite;
3)organic sulfur (sulfide and sulfate, sulfur incorporated into the structure of organic molecules);

The inorganic fractions of the coal are made up mainly of the sulfides and sulfates, clay minerals (kaolinite, illite) and a smaller proportion of calcite.

Metals are found as ZnS, NiS, PbS and $FeCuS_2$. Goldschmidt (1937) showed the litophilic character of Cr ($FeCr_2O_4$) and the strong calcophilic character of Mn (MnS). Studying coal from the Leão Coal Mine located in the state of Rio Grande do Sul, Brazil, Azambuja (1977) found Mn associated with carbonates. Studying British coal, Raask (1985), attributed the presence of Mn to the mineral form ankerite ($FeCO_3$, $CaCO_3$ and $MnCO_3$). Azambuja (1977) pointed that Cr in the coal (Leão Coal Mine) is related to carbonaceous materials and clay minerals, but not to sulfides.

It is well known the sulfides in coal are responsible for pollution of the air, ground water, superficial water and soil. This pollution is also caused by heavy metals, released during coal combustion. Limestone added in the combustor to control SO_2 emission reduces metal emissions because of the pH of sulfated ash to 10, forming alkaline ash. In high alkalinity and salinity oxianions (B, As, Se) are mobile although, the most trace metals are not mobile. The alkaline ash formed can be disposed without problems of in refuse areas and soils because the heavy metals remain fixed in the ashes (Weinberg and Hemmings, 1995).

MATERIALS

The coals used in this study were from Butiá-Leste Mine and Candiota Mine, Rio Grande do Sul, Brazil. The limestone was from Candiota Mine.The coal and limestone were run of mine (ROM) without any wash treatment. Their chemical compositions are shown in Tables 1, 2 and 3.

Table 1: Proximate analysis of Butiá-Leste coal.

	BUTIÁ- LESTE (%)	ISO
Hygroscopic moisture (W_h)	4,0	589
Ash (A)	42,1	1171
Volatile material (VM)	28,9	562
Total sulfur (S_t) (b.s)	13,4	334
Fixed carbon (C_{fix})	29,0	CF=100-(VM+A+Wh)

Table 2: Chemical composition of Candiota limestone.

Components	Candiota Limestone
CaO	47,5
MgO	3,1
Al_2O_3	1,9
SiO_2	7,3
Fe_2O_3	0,86
K_2O	0,74
Na_2O	0,003
TiO_2	< 0,05
MnO	0,07
Cr_2O_3	< 0,003
S	0,093

Table 3: Proximate analysis of Candiota coal.

	Candiota (%)	ISO
Hygroscopic moisture (W_h)	1,3	589
Ash (A)	46,7	1171
Volatile material (VM)	25,7	562
Total sulfur (S_t) (b.s.)	1,2	334
Fixed carbon (C_{fix})	27,6	CF=100-(VM+A+Wh)

The coal ash without limestone from Candiota and Butiá-Leste was prepared by combustion in the muffle furnace at 850° C for 2 hours. The sulfated ash (samples of coal + limestone) was prepared using the same methodology (at molar ratios Ca/S = 1, 2 and 2.5).The materials were ground in a porcelain mortar and classified by sieving

(0.063 mm), using polyethylene meshes to avoid the contamination of the metals. For each sample 6g was used.

Sulfated ash was also obtained in the fluidized bed combustor (pilot scale) for the analysis of the heavy metals from the Candiota coal. This coal was burned at 850° C with the addition of Candiota limestone at molar ratio Ca/S = 2. The reactor belongs to the Fundação de Ciência e Tecnologia do Estado do Rio Grande do Sul (CIENTEC).

EXPERIMENTAL PROCEDURE

The concentrations of the heavy metals in the coal, coal ashes, sulfated ashes and ashes obtained from fluidized bed combustor were analyzed. The samples were obtained by acid digestion at 100ºC and by coal combustion in the muffle furnace at 850ºC. The coal combustion ashes were prepared with and without the addition of the limestone. The samples with addition of limestone were prepared and burned at different molar ratios Ca/S =1, Ca/S =2 and Ca/S = 2.5.

For acid digestion, the coals were submitted to chemical attack at 100° C, using a method proposed by Tessier et al. (1979). Metal concentrations were determined by acid digestion with H_2O_2, HNO_3, $HClO_4$ and HF, using HCl for further dissolution. A blank test was prepared to eliminate the interference caused by the chemical reagents. For the ashes, only the use of $HClO_4$/HF is needed.

The metal concentrations in samples obtained without the addition of limestone (Ca/S = 0), the sulfated ashes in muffle furnace (Ca/S = 1, 2 and 2.5), the sulfated ashes in fluidized bed and acid digestion (100° C) were determined by flame atomic absorption spectrometry (FAAS), using Varian model air/acetylene flame.

The pH measure by coal lixiviation and ash lixiviation (for coal by combustion with and without limestone).The pH of mixtures with 1g of the sample for 16 mL of deionized water was measured according to Brazilian standards (NBR 10005).

The mineral constituents of coal and coal ashes were studied by X-ray diffraction. For this purpose the content of organic matter in each sample had to be reduced to < 5%. This value was obtained by previous digestion with HNO_3/H_2O_2. The heavy metals retained in coal ashes and sulfated ashes were analyzed by the means of microprobe an electronic.

RESULTS AND DISCUSSIONS

In Tables 4 and 5, the metal concentrations in coal, coal ash and the sulfated ash for Butiá-Leste and Candiota coal, by flame atomic absorption spectrometry (FAAS) are shown. The addition of limestone leads to a decrease in the concentrations of metals such as Pb, Zn, Ni, Mn and Cu. At molar ratio Ca/S = 2.5, it was verified that metal concentrations show the highest decrease for the majority of the metals analyzed.. The formation of stable compounds like sulfates, in the ashes result from the oxidation of the

sulfides in the air (ustulation reactions). These sulfate compounds do not dissociate at the air acetylene flame temperature, used for analysis of the metals. Thus, the metals do not turn to the fundamental states (atomic states) which makes it impossible to detect them (or at the very least they decrease in show concentration in the flame). The decrease in metal concentrations is due to chemical interference in the flame, caused by the presence of sulfates, which was also observed by Slavin 1969 and Trescases 1984. It is very difficult to decompose the compounds fixed in the ashes with the air acetylene flame (atomic absorption apparatus) because of the small amount of free atoms (Me^0) in these compounds elemental Pb and Zn and their sulfates are volatiles so they are not retained in the ashes. Due to its lithophilic form ($FeCr_2O_4$) in coal, Cr was shown to be stable in the ashes.

Table 4: Concentration of heavy metals (g ton^{-1}) from Butiá Leste coal. Acid digestion (100°C), coal ash (Ca/S =0) and sulphated ashes (Ca/S 1, 2 and 2.5) at 850°C for Butiá-Leste Coal + Candiota limestone mixtures. Atomic absorption apparatus.

Coal Combustion	Ca/S=0	Ca/S =1	Ca/S=2	Ca/S=2.5	Acid Digestion
Pb (g ton^{-1})	40	23	5	3	200
Zn (g ton^{-1})	50	60	50	15	400
Ni (g ton^{-1})	100	35	20	23	200
Cr (g ton^{-1})	50	40	42	40	60
Mn (g ton^{-1})	160	110	90	80	200
Cu (g ton^{-1})	40	10	5	3	60

Table 5: Concentration of heavy metals (g ton^{-1}) in Candiota coal Acid digestion, (100°C), coal ash (Ca/S=0) and sulfated ashes (Ca/S 1, 2 e 2.5) at 850°C for Candiota + Candiota limestone mixtures. Atomic absorption apparatus.

Coal Combustion	Ca/S=0	Ca/S=1	Ca/S=2	Ca/S=2.5	Acid Digestion
Pb (g ton^{-1})	30	8	5	3	200
Zn (g ton^{-1})	40	25	8	5	100
Ni (g ton^{-1})	20	12	12	3	50
Cr (g ton^{-1})	50	45	45	45	55
Mn (g ton^{-1})	70	80	30	30	200
Cu (g ton^{-1})	30	10	10	10	50

In Table 6, it can be seen that the metal concentrations of metals are very similar both the for combustion in fluidized bed and the muffle furnace. This confirms the validity of results obtained under laboratory condition showing this to be a simple and fast method to study the behavior of metals during coal combustion with limestone as the

desulfurization agent. The results obtained in this study are probably appropriate for power stations on an industrial scale.

Table 6: Concentration of heavy metals (g ton^{-1}) in the ash from the combustion of Candiota coal with the addition of Candiota limestone Ca/S = 2 at 850 °C in the fluidized bed reactor or muffle furnace.

	Pb	Zn	Ni	Cr	Mn	Cu
Muffle furnace	5	8	12	45	45	10
Fluidized Bed	2	6	10	30	40	7

The pH results in Tables 7 and 8, for both coals studied, show that the increase in limestone in the mixtures with coal leads to an increase in the pH value. This is due to the increase in the alkalinity and salinity of the ashes, since the nonvolatile metals are fixed as stable compounds. This is in agree with the remarks of Weinberg and Hemmings (1995).Thus, according to Brazilian standards (NBR 10004), ashes resulting from the process of desulfurization with limestone (sulfated ash), can be classified as nontoxic for this pH level.

Table 7: pH measures for Butiá-Leste coal and coal ashes with and without the addition of limestone.

	COAL	Coal ash (without limestone)	Sulfated ash (with limestone Ca/S=2..5)
pH	2.8	10.2	12.2

Table 8: pH measures for Candiota coal and coal ashes with and without limestone.

	COAL	Coal ash (without limestone)	Sulfated ash (with limestone) Ca/S=2.5
pH	4.5	10.2	12.4

Analysis shows that the pH in the coal ash is similar for both coals. This indicates that the initial concentration of total sulfur in the coal did not influence the final pH of the ashes.

Using XRD, the compounds in the samples of the tests with acid digestion, coal ash and sulfated ashes can be seen. However, only the compounds with concentrations above 5% can be analyzed using this equipment (this equipment is not capable of detecting trace level). The results from XRD analysis of the Butiá-Leste coal are shown Figures 1,

2 and 3. In Figure 3, the presence of anhydrite, melanterite and iron sulfate indicates the formation of sulfate in the ashes. This was not noted in Figure 1, and only small quantities are shown in Figure 2 for the Butiá-Leste coal.
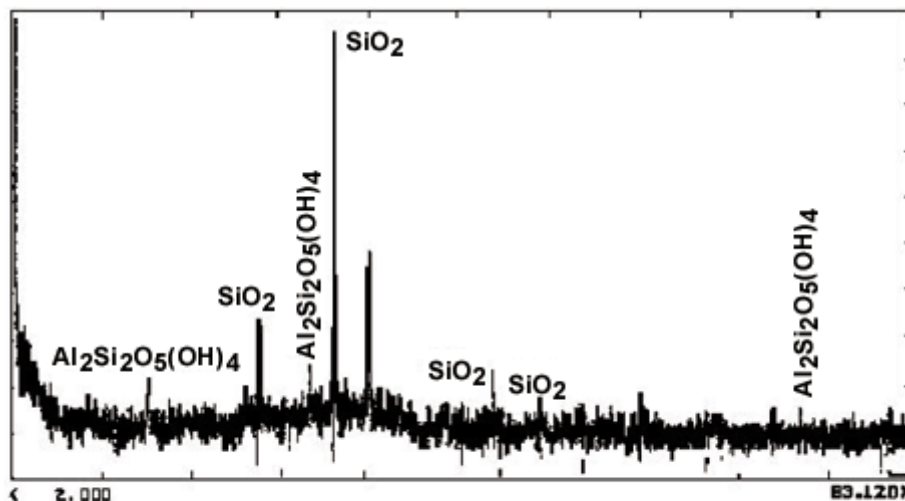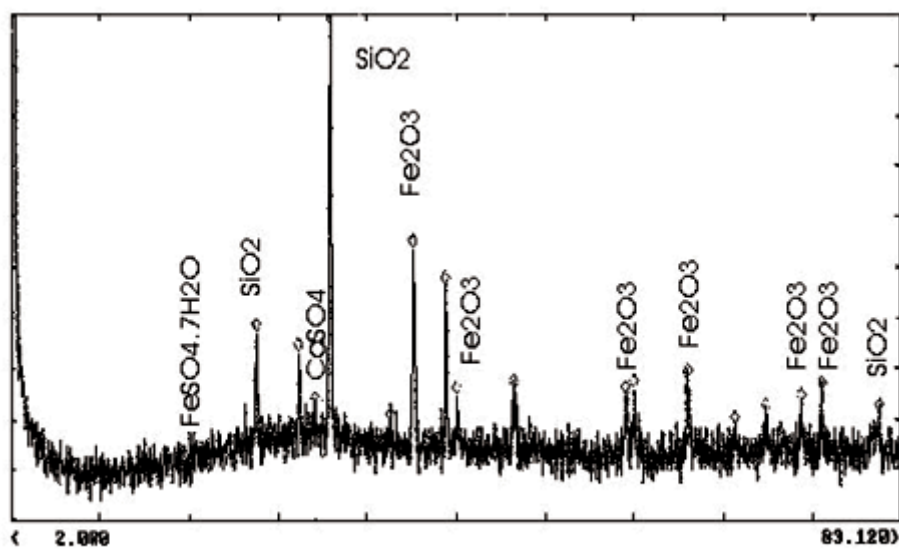
Figure 1: Butiá-Leste Coal.

Figure 2: Butiá-Leste coal (ash from combustion in muffle furnace 850°C).

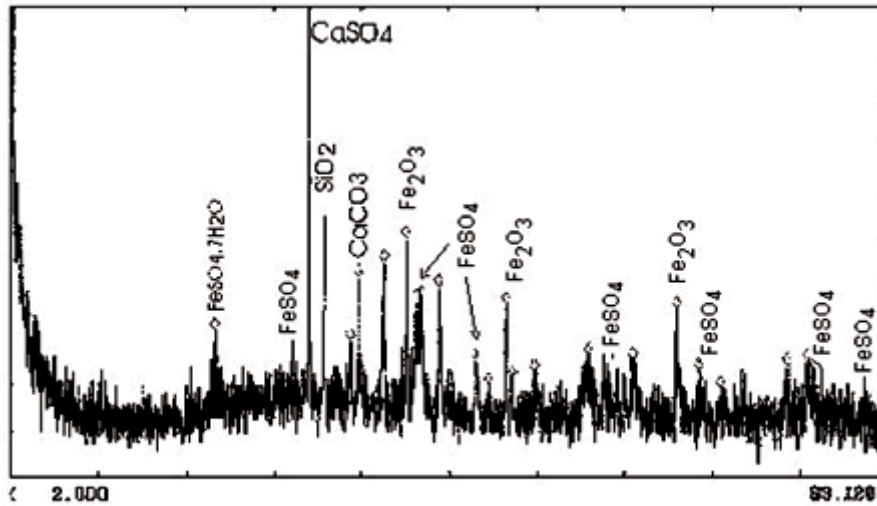**Figure 3:** Butiá-Leste (sulfated ash from coal combustion in muffle furnace (850°C) with addition of Candiota limestone (Ca/S=2.5).

The results of the tests with Candiota coal are shown in Figures 4, 5, and 6. Figures 5 and 6 show the presence of anhydrite in the ashes. In Figure 5, the anhydrite generated is probably from a "self-desulfurization" process (i.e., thermal decomposition of calcite and further reaction with the sulfur present in the coal, like pyrite or organic the compounds). In sulfated ashes (Figure 6), the level of anhydrite observed was higher than the level shown in Figure 5, due to the reaction of CaO (from the addition of limestone) with the sulfur in the coal. This illustrates the interation between Ca and sulfate, forming calcium-sulfate (anhydrite) with high quantities of limestone in the mixture (with an increase in molar ratio Ca/S). This also agrees with Chincón (1991).
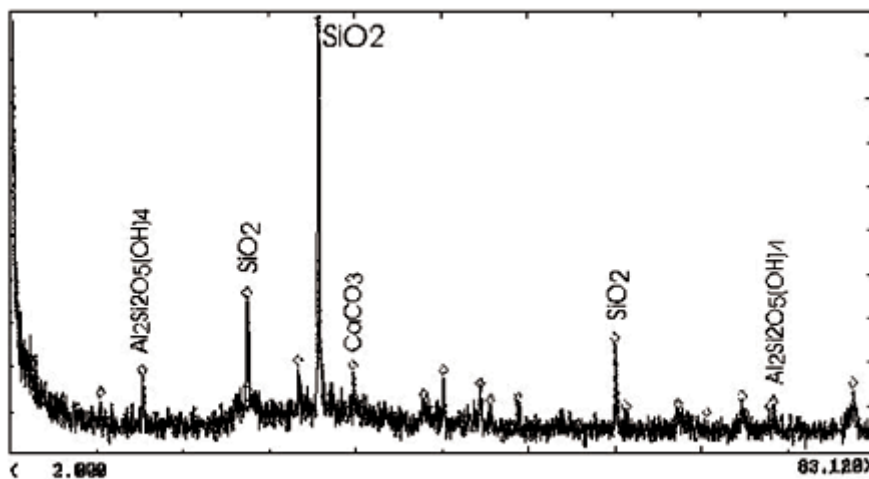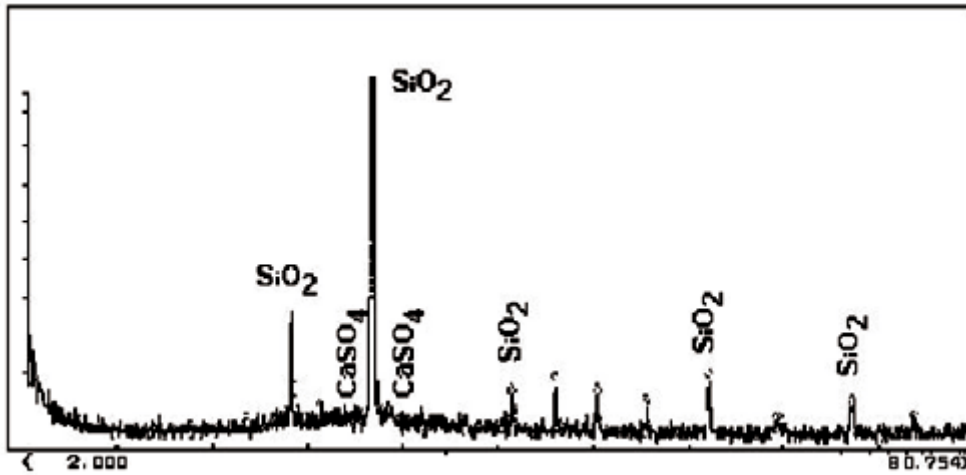

Figure 4: Candiota Coal

Figure 5: Candiota coal ash (combustion ash at 850ºC).
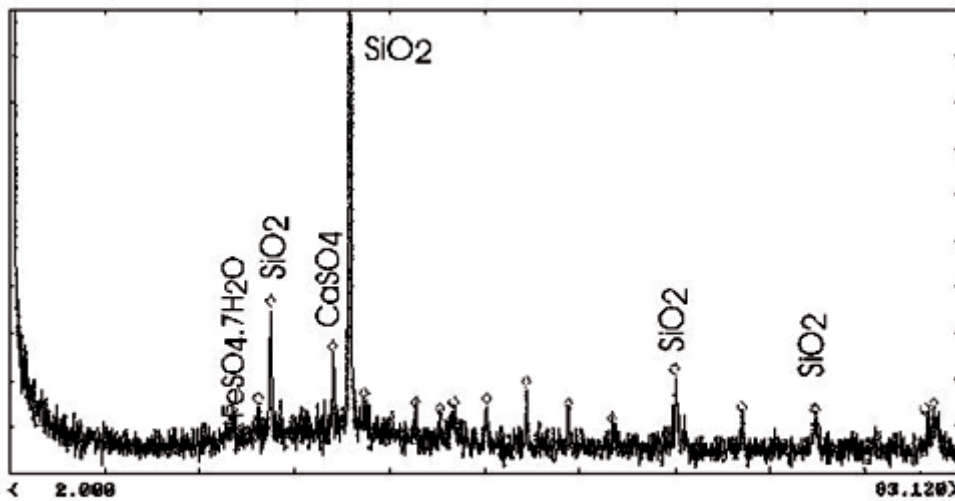

Figura 6: Candiota coal ash (sulfated ash from coal combustion in muffle furnace at 850°C with the addition of Candiota limestone (Ca/S 2.5)).

For coal acid digestion (100° C), only the presence of clay minerals, quartz and calcite are observed (Figure 4).

Figures 7 and 8 show the analysis with electronic microprobe. In Figure 7, Candiota coal ash without the addition of limestone, only Ca, Si, S, Al and Fe can be found.

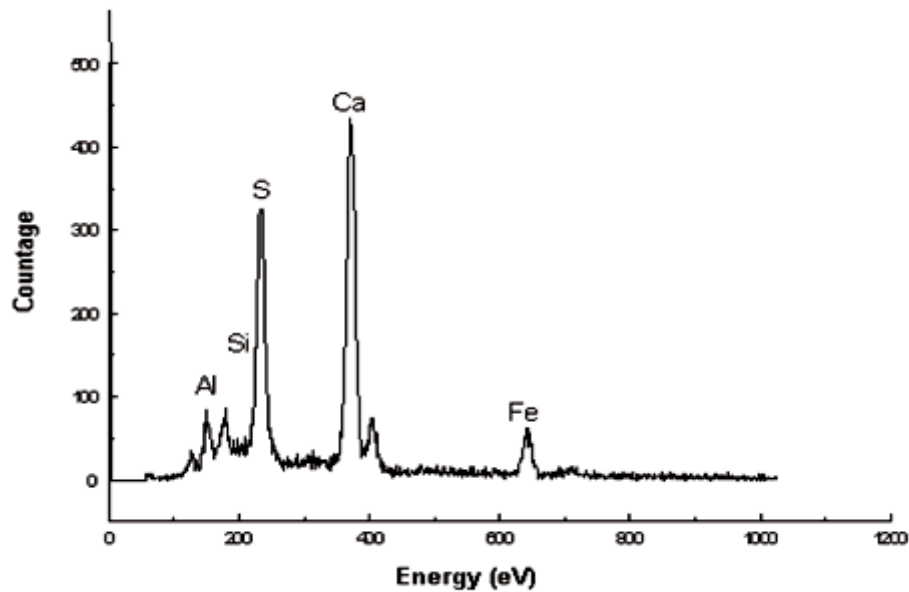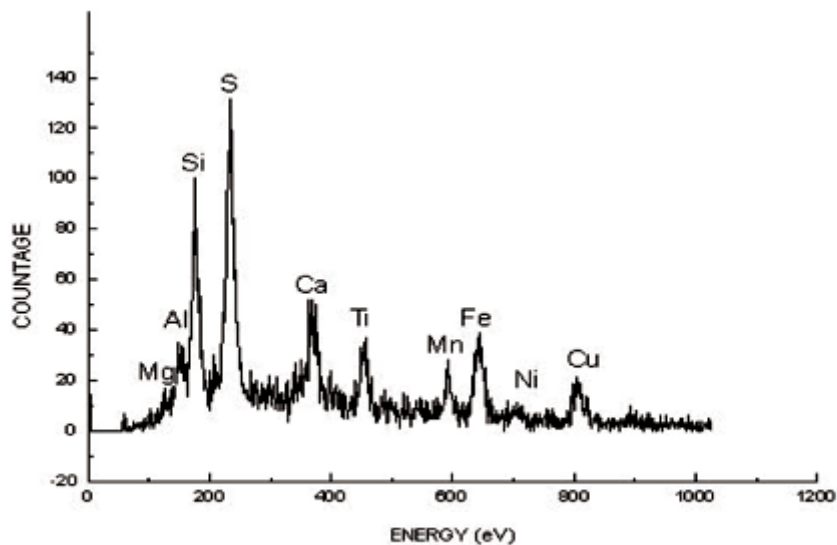**Figure 7:** Microprobe analysis of Candiota coal ash.

Figure 8: Microprobe analysis from sulfated ash from Candiota coal + Candiota limestone.

In Figure 8, Candiota sulfated ash, the presence of limestone leads to the retention of others metals, like Mn, Cu, Ti and Ni. On the other hand, it can be noted that Pb and Zn are not present. This is explained by the volatile behavior of these metals already in their elemental forms. Cu is only slightly volatile in elemental form as well as in sulfated forms remaining fixed in the ashes. Mn, Ni, and Ti are slightly volatile and they can be found in the sulfated ashes (Figure 8). Although not volatile, Cr is not present in the results of the analysis by microprobe electronic. This occurs due to the difficulty of detecting this element under the conditions employed in this work. However, the fact

that its concentration showed constant values in the ashes, with and without limestone, in the tests carried out in atomic absorption apparatus, indicates its retention. These results with are in agreement what was found by Rubin (1976) and Smith (1987), considering a decreasing order of volatilization as follows:

In the sulfate form:

As>Hg>Cd>Pb>Ag>Zn>Cu>Sn.

In the elemental form:

Hg>As>Cd>Pb>Zn>Sb>Ag>Sn>Cu>Ni>Cr>Mn.

CONCLUSIONS

The addition of limestone in coal combustion has been confirmed as an efficient alternative for reducing SO_x emissions. At the same time, the results obtained in this work also suggest that heavy metals can be retained in the ashes. The large amount of limestone used in the desulfurization process like resulted in retention of some metals, like Ca, Cu, Ni, Fe, Ti and Mn, in the ashes.

The microprobe analysis showed the presence of Ca, S, Mn, Ni, Ti, Fe and Cu in the sulfated ashes. The use of limestone mixed with coal shows that some elements can be retained as stable compounds in the ashes (nonvolatile elements). In the process of desulfurization using limestone as the sorbent agent, attained a high degree of volatilization (Pb as $PbSO_4$, and Zn as $ZnSO_4$), which might cause atmospheric pollution. Cr did not show significant changes in its concentration in the ashes in any of the tests carried out in this study (acid digestion of coal and coal combustion with or without limestone).

The XRD analysis confirmed the formation of sulfates instead of aluminate and phosphate. This is due to the temperature employed (850ºC).

The alkaline pH of the sulfated ashes from the Candiota and Butiá-Leste coals fixed the nonvolatile metals in the ashes. Thus the ashes are classified as nontoxic, according to Brazilian standards.

NOMENCLATURE

A	Ash
Ca/S	molar ratio Ca/S
C fix	Fixed carbon
FAAS	Flame atomic absortion spectrophotometry
St	Total sulphur
VM	Volatile material

| Wh | Hygroscope mixture |
| XRD | X- ray diffraction |

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