QUALITATIVE AND QUANTITATIVE CHARACTERIZATION OF A COAL POWER PLANT WASTE BY TG/DSC/MS, XRF AND XRD

JOSEFA FERNÁNDEZ[1*], FERNANDO GONZÁLEZ[1], CARMEN PESQUERA[1], ALEX NEVES JUNIOR[2], MARCELO MENDES VIANA[3] AND JO DWECK[3]

[1]*Department of Chemistry and Process and Resource Engineering, ETSIIyT, University of Cantabria, Santander, Spain*
[2]*Architecture, Engineering and Technology Faculty, Mato Grosso Federal University, Cuiabá, Brazil*
[3]*Department of Inorganic Processes, School of Chemistry, Federal University of Río de Janeiro, Rio de Janeiro, Brazil*

Abstract

SO_2 removal from coal-fired power plant flue gases can be done by dry, semi-dry or wet desulfurization processes, using limestone or lime containing products as sorbents. In a Brazilian coal power plant there is a dry desulfurization unit to capture SO_2 with hydrated lime from the combustion gases. A part of the flying ashes produced is mixed with the bottom coal ashes and the spent sulphated product generated after SO_2 capture. This residual solid blend is then buried in a non-productive area, from which coal was already extracted and is studied in this work. According to the authors experience in development and characterization of adsorbents for low temperature dry desulfurization processes and in Thermogravimetric Analysis, this paper shows and discusses a method which was developed to characterize qualitative and quantitatively the chemical and mineral composition of this waste by using Thermogravimetry coupled with mass spectrometry (TG/MS), X-ray fluorescence (XRF) and X-ray diffraction (XRD), to preview new potential industrial applications for this waste.

Key words

Coal power plant, dry desulfurization, hydrated lime, TG/MS, XRD, and XRF

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*****Corresponding author

Introduction

Sulphur dioxide is considered an indicator of atmospheric pollution, as it is a major contributor to contamination and environmental degradation, being anthropogenic sources through the combustion of fossil fuels that produce the 80% of this pollutant [1, 2]. Fossil fuels will still play a key role in the energy mix for the years to come, despite the different prospective frameworks that might be under consideration, and investment in clean fossil fuels technologies is mandatory for taking benefit from this relatively abundant source of energy [3]. In this sense, the reutilization of wastes and by-products and their proper management are important aspects for the sustainability of the processes and are promoted by legislation in some sectors, as is reflected in the Industrial Emissions Directive of the European Union (2010/75/EU).

The techniques for reducing SO_2 emissions can be divided in [4, 5]: (i) pre-combustion technologies, that include fuel desulfurization and coal gasification or liquefaction; (ii) during combustion technologies, that includes combustion of coal and limestone mixtures; (iii) post-combustion technologies or flue gas desulfurization (FGD), widely used, in which the flue gas from combustion is put into contact with an alkaline component.

SO_2 removal from coal-fired power plant flue gas by desulfurization processes can be done by dry, wet or semi-dry processes [6], using limestone or lime containing products as absorbents or adsorbents.

During the dry desulphurization with commercial hydrated lime the main reaction that occurs is R-1, during which $CaSO_3$ is formed [7], releasing water.

$$SO_2 + Ca(OH)_2 \rightarrow CaSO_3 + H_2O \qquad (R\text{-}1)$$

As the used commercial adsorbent contains calcium carbonate, SO_2 is also captured by reaction R-2 [7, 8]:

$$SO_2 + CaCO_3 \rightarrow CaSO_3 + CO_2 \qquad (R\text{-}2)$$

The presence of an excess of $Ca(OH)_2$ may adsorb the released CO_2, regenerating the calcium carbonate by reaction R-3 [7, 8]:

$$CO_2 + Ca(OH)_2 \rightarrow Ca\ CO_3 + H_2O \qquad (R\text{-}3)$$

Calcium sulphite may be hydrated and partially oxidized, forming the hydrated phases $CaSO_3.0.5H_2O$ and $CaSO_4.2H_20$, by reactions R-4 and R-5. Double calcium salts as $xCaSO_3.yCaSO_4.nH_20$ may be formed as well [9].

$$CaSO_3 + 0.5H_2O \rightarrow CaSO_3.\ 0.5H_2O \qquad (R\text{-}4)$$

$$CaSO_3 + 0.5O_2 + 2\ H_2O \rightarrow CaSO_4.2H_20 \qquad (R\text{-}5)$$

In a Brazilian coal power plant there is a dry desulfurization unit to capture SO_2 with dry solid hydrated lime from the combustion gases. A part of the flying ashes produced in the plant from coal combustion is commercialized and the rest is mixed with the bottom coal ashes and the spent sulphated product generated after SO_2 capture. This residual solid blend is then back destined to the coal reserve to be properly buried in a non-productive area, from which coal was already extracted. This is the waste that is studied in this work.

So in the case that will be shown and discussed in this paper, the compounds that may be present in the final processed hydrated lime (in the waste), depend on the other contaminants present in the commercial hydrated lime, on the particulate solids (fly ashes) carried by the combustion gases trapped by the adsorbing column or present in the bottom ash, as well as on hydrated and carbonated products that may be formed during storage at ambient conditions by humidity and / or carbon dioxide action.

Part of the authors have already developed typical adsorbents to study low temperature dry desulfurization processes [7, 10-12] and have experience in Thermogravimetric Analysis [7, 10, 13-15].

The present paper shows and discusses a method which was developed to characterize qualitative and quantitatively the chemical and mineral composition of this waste by thermogravimetry coupled with mass spectrometry (TG/MS), X-ray fluorescence (XRF) and X-ray diffraction (XRD), to preview new potential industrial applications for this waste.

Materials and Methods

A sample of the waste was taken in the second semester of 2014, directly from the coal reserve, near to the Brazilian coal power plant. The plant operates in three production units, and only one of them includes a dry desulfurization capture unit. The sample corresponds to a blend of the flying ashes produced in the plant from coal combustion that have not been commercialized, mixed with the bottom coal ashes and the spent sulphated product generated after SO_2 capture in the desulfurization unit.

The simultaneous TG-DSC-MS curves were obtained on a SETARAM thermal analyser, model SETSYS-1700. The samples of approximately 40 mg were heated in platinum crucibles in Nitrogen atmosphere, at a total flow rate of 100 ml min^{-1}, with a heating rate of 10 ºC min^{-1} and a final temperature of 1350 ºC. All the TG measurements were blank curve corrected. Each experiment was repeated to check for consistency. The TG instrument was coupled to a Balzers Thermostar / OmniStar mass spectrometer (Pfeiffer vacuum) for evolved gas analysis. Quadrupole mass spectrometer model was QMS 200. The number of m/z signals selected was: 18.03 (H_2O^+), 32.00 (O_2^+), 43.94 (CO_2^+), 63.96 (SO_2^+), 80 (SO_3^+). TG-MS analysis supplies in this work only qualitative information.

A representative sample was analysed by X-ray florescence (XRF) using an ARL-ADVANT-XP sequential spectrophotometer to elucidate major and minor elements, using a software UNIQUANT 5.0.

The crystalline components of the sample were identified by X-Ray diffraction using a Bruker Advance 8 diffractometer with a Cu anode as the X-ray source using Cu-Kα radiation (λ= 1.5418 Å), connected to a Difrac Plus program. Samples for X-Ray study were prepared by manual milling in a mortar of agate and placed on the sampler. The diffraction figures were compared to the pattern of all the possible crystalline components of the ashes or of the hydrated lime.

Results and discussion

Fig. 1 shows the X-ray diffraction pattern obtained, with the main crystalline compounds identified, that include Quartz (SiO_2), with the most intense peak at 2θ=27º, Portlandite ($Ca(OH)_2$), with the most intense peaks in order of intensity at 34.10º and 18.00º, Mullite ($Al_2O_3 \cdot 0.32\ SiO_2$), at 26.27º and 25.99º, Hydrotalcite ($6MgO \cdot Al_2O_3 \cdot CO_2 \cdot 12H_2O$), Brucite ($Mg(OH)_2$), at 37.98º and 18.58º, Gypsum ($CaSO_4 \cdot 2H_2O$), at 31.13º and 20.74º, Ettringite ($6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 32H_2O$), at 9.09º and 15.78º, Calcite ($CaCO_3$), at 29.36º and 47.31º, Magnesite ($MgCO_3$), at 33.15º and 43.04º, and calcium sulphite hemihydrate ($CaSO_3 \cdot 0.5H_2O$) at 29.05º and 35.33º. It can be also observed the characteristic pattern that is ascribed to amorphous compounds of fly ash at 2θ=15-40º, 2θ=40-45º and 2θ=45-53º.

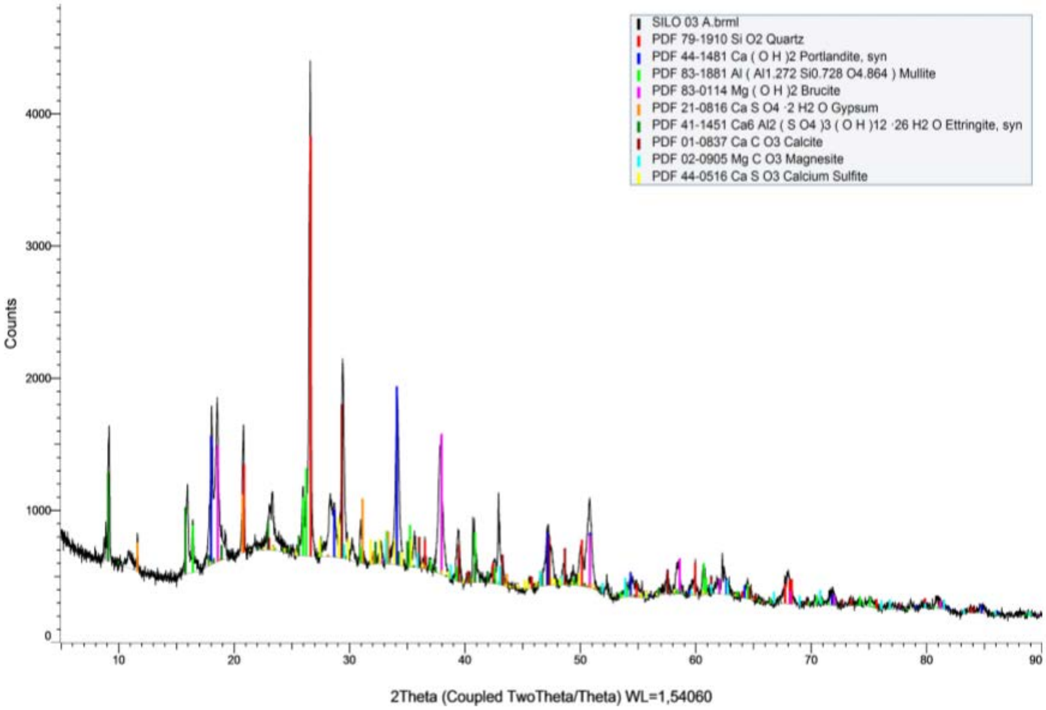

Fig. 1 X-ray diffraction pattern for the coal power plant waste.

As it has been introduced, Portlandite ($Ca(OH)_2$), Calcite ($CaCO_3$), Calcium Sulphite Hemihydrate and Gypsum come from the non-reacted hydrated lime, ambient hydration and carbonation action during storage and the desulphurization products, being present also Brucite ($Mg(OH)_2$), Magnesite ($MgCO_3$) and Hydrotalcite ($6MgO \cdot Al_2O_3 \cdot CO_2 \cdot 12H_2O$) in the commercial hydrated lime used. The rest of the crystalline compounds come from the fly ash.

Fig. 2 shows TG-DTG results obtained in 100% nitrogen atmosphere.

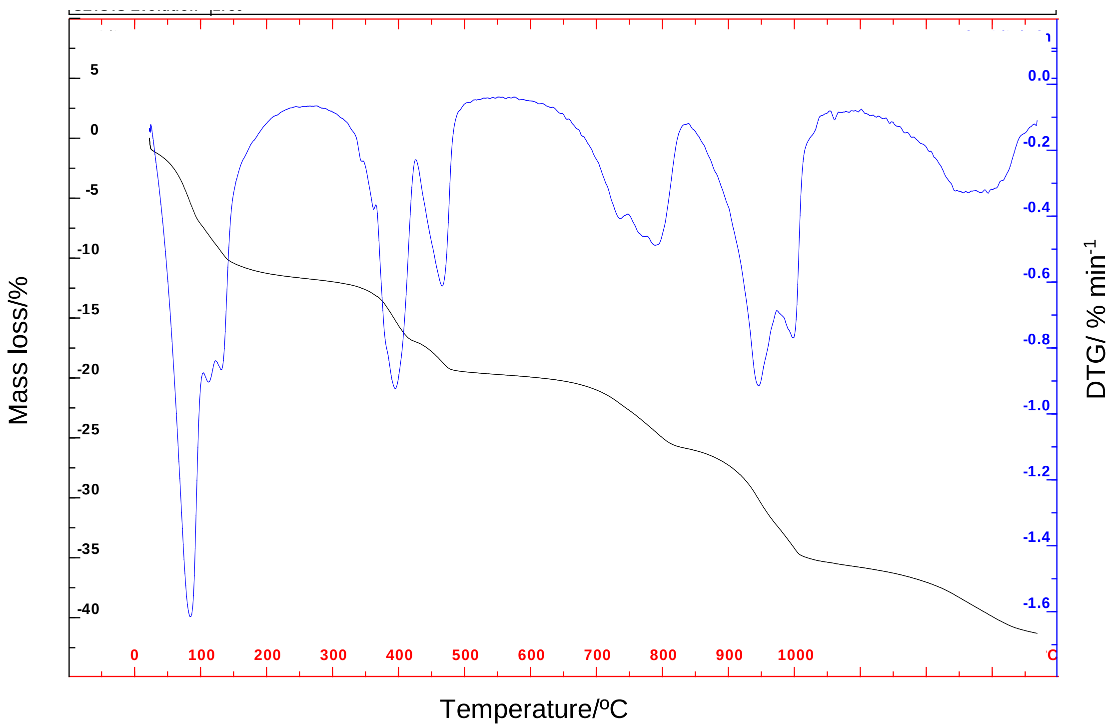

Fig. 2 TG and DTG of the coal power plant waste, using N_2 as the carrier gas, 10ºC/min and 100ml/min.

As it can be observed by DTG results, many stages are involved in each mass loss step observed in the TG curve. Because of that, the losses will be assigned in the next section "TG-MS results".

To help the interpretation of the complex thermal analysis curves that were obtained with many decomposing steps, a review of thermal decomposition properties of the products that were identified by X ray diffraction (XRD) was done, which main reactions are presented in the following items.

Calcium sulphite thermal decomposition

$CaSO_3{\cdot}0.5H_20$ is obtained in humid ambient and exists in three crystallographic structures, but concerning with the α (orthorhombic) form, the dehydration process are referred to take place at about 297-400ºC [16] or between 360 and 410ºC [17].

$$CaSO_3{\cdot}0.5H_20 \rightarrow CaSO_3 + 0.5\ H_2O \qquad \text{(R-6)}$$

Renedo et al [7], in their study of CO_2 and SO_2 sorption by calcium hydroxide using simultaneous thermogravimetry, differential scanning calorimetry and mass spectrometry (TG/DSC/MS), have shown that the dehydration of $CaSO_3.0.5H_2O$ occurs at 275-375ºC temperature range.

Ciurowa [18] studied the thermal decomposition of $CaSO_3$ in air and nitrogen ambient by TG, differential thermal analysis (DTA) and XRD. In air, $CaSO_3$ may be partially oxidized from 450ºC to $CaSO_4$, as shown in reaction R-7 but it also may suffer a disproportion reaction (R-8) from 600ºC, which also occurs in N_2 atmosphere, forming $CaSO_4$ and CaS, which is completed at 850ºC:

$$CaSO_3 + 0.5\ O_2 \rightarrow CaSO_4 \qquad \text{(R-7)}$$

$$4\ CaSO_3 \rightarrow 3\ CaSO_4 + CaS \qquad \text{(R-8)}$$

In nitrogen, above 900ºC, calcium sulphate and calcium sulphide react with each other forming calcium oxide and sulphurous oxide as per reaction R-9, also reported by Zhao et al [19] in a temperature range of 849-1119ºC:

$$3\ CaSO_4 + CaS \rightarrow 4\ CaO + 4SO_2 \qquad \text{(R-9)}$$

In oxidant atmosphere, CaS is oxidized to $CaSO_3$ from 450ºC and at higher temperatures, to $CaSO_4$ [18]. This oxidation steps were also reported by Dweck [20], when analyzing a solid residue containing calcium sulphide heated in air.

Calcium sulphate thermal decomposition

Thermal decomposition of Gypsum $CaSO_4.2H_2O$ occurs in two steps: in the first, Plaster of Paris ($CaSO_4.0.5H_2O$) is obtained by reaction R-10, and in the second one, γ-anhydrous calcium sulfate (γ $CaSO_4$) is produced by reaction R-11 [21-24]:

$$CaSO_4.2H_2O \rightarrow CaSO_4.0.5H_2O + 1.5H_2O \qquad \text{(R-10)}$$

$$CaSO_4.1/2H_2O \rightarrow CaSO_4 + 0.5H_2O \qquad \text{(R-11)}$$

At elevated heating rates R-10 and R-11 may occur simultaneously, which are equivalent to reaction R-12 [22, 25]:

$$CaSO_4.2H_2O \rightarrow CaSO_4 + 2H_2O \qquad \text{(R-12)}$$

According to this, dehydration of gypsum may take place within the 75–130ºC range [21], or apparently with a continuous water loss in the 63–106ºC range [22], between 150-250ºC [26] or at 156ºC and 184ºC [24].

Reaction R-10 may begin at 34ºC in dry air [27] and at higher temperatures when the water ambient vapor partial pressure (p_w) increases. Actually reactions R-10 to R-12 are reversible, but if anhydrous γ calcium sulphate is heated above 400ºC, rehydration is practically impossible, because a crystalline phase change occurs transforming it to β $CaSO_4$, which practically cannot be rehydrated [28].

Thermal decomposition of $CaSO_4$ in air occurs only at high temperatures (1200-1250ºC) by reaction R-13 [29]:

$$CaSO_4 \rightarrow CaO + SO_2 + \tfrac{1}{2}\ O_2 \qquad \text{(R-13)}$$

In inert or reducing atmosphere, thermal decomposition of metal sulfates occurs at lower temperatures than in oxidant atmosphere [30,31].

Thermal decomposition of other compounds present in the waste

The temperatures of dehydration of Portlandite (about 400-575ºC) and brucite (about 350-400ºC) and of the decomposition of calcite (DTG peak at 936ºC, but can be lower depending on the well crystallized variation) and Magnesite (620-650ºC) are widely found in literature and previous works [24, 26, 32, 33].

Hydrotalcites, also known as layered double hydroxides (LDH's) or ionic clays, are natural minerals (but also synthetic) based upon the brucite [$Mg(OH)_2$] structure in which some of the divalent cations are replaced by trivalent cations (e.g. Al or Fe) resulting in a layer charge. This layer charge is counterbalanced by anions such as carbonate or sulfate in the interlayer. For the carbonate intercalated hydrotalcite, dehydration takes place in three steps, between 29 and 235ºC [34] or up to 259ºC [35].

Alonso and Fernández [36] described by TG/DTA/DSC the endothermic peak at about 100ºC in that the ettringite disappears after heating and recovers after rehydration, also described in other works by Shimada and Young [37].

It must be noted that during thermal analyses, dry purge gases may accelerate dehydration reactions to much lower temperatures than those mentioned above, because they act decreasing significantly the vapour partial pressure above the decomposing sample. The same effect occurs with purge gases that do not have CO_2 in their composition, with respect to decarbonation reactions, because carrying away any CO_2 right after it is formed, they act on the equilibrium of those reactions enhancing a higher formation of $CO_{2,}$ decreasing significantly the temperature range of the decarbonation reactions [14].

TG-MS results

Fig. 3 shows the TG-MS obtained results, within the interval of temperature in which the peaks of H_20 (18.03), O_2 (32.00), CO_2 (43.94) and SO_2 (63.96) appear. The m/z signal 80 (SO_3^+) does not appear because at temperatures higher than 700ºC, SO_3 is unstable, decomposing to SO_2 and ½ O_2 and as shown in R-13 and as seen in Figure 3 due to the decomposition of some sulphate.

It can be observed that the loss of water takes place in a first complex interval until 250ºC, and in a second complex interval from this temperature up to 450ºC, being the loss of CO_2 found between 600 and 800ºC approximately.

As will be shown in Figure 3, all the water and carbon dioxide released from the thermal decomposition of the components present in the sample are eliminated before 900ºC, and sulphite or sulphate products are decomposed above that temperature. According to these results, the losses of CO_2 and SO_2 are not overlapped.

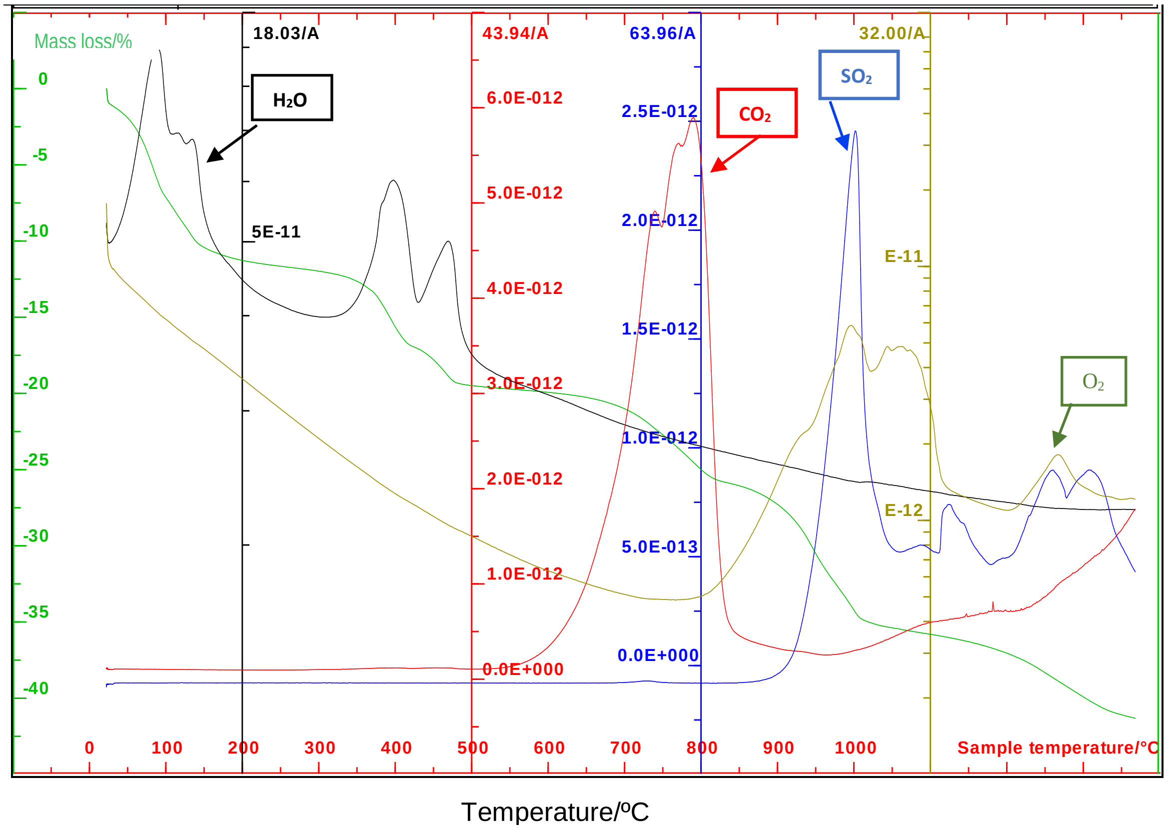

Fig. 3 TG-MS results of the coal power plant waste in nitrogen atmosphere, 10ºC/min, 100ml/min, showing the MS curves of H_20 (18.03), O_2 (32.00), CO_2 (43.94) and SO_2 (63.96) in arbitrary units (A)

The mass loss steps (TG signal, left-y axis) in Fig. 2, according also to Fig. 3, can be ascribed as water loss (< 320°C), that includes at least the free water and also, according to the revision carried out, combined water from hydrotalcite, ettringite and gypsum; the second complex dehydration process may comprise the dehydration of sulphite hemihydrate, $Mg(OH)_2$ dehydration (320-420°C) and $Ca(OH)_2$ dehydration (420-520ºC). A complex CO_2 release that includes that from $MgCO_3$ decomposition (550-750°C), hydrotalcite decarbonation (750-800°C) and $CaCO_3$ decarbonation (800-870 °C). Along with the mass loss steps, the MS signal in figure 3 (63.96/A) shows a SO_2 release from 870 °C, which can be attributed to the decomposition of calcium sulphite according to R-8 and R-9 or R-14 [7] and to calcium sulphate decomposition according to R-13 and also to reactions R-15 and R-16, as discussed below.

$$CaSO_3 \rightarrow CaO + SO_2 \qquad \text{(R-14)}$$

Marchal, in her study of $CaSO_4$ decomposition at elevated temperatures [38] and more recently Mihara et al [39] and Yan et al [40] reported that the presence of Fe_2O_3 or SiO_2 promotes $CaSO_4$ decomposition from about 900ºC, by reactions similar to R-15 and R-16, respectively:

$$CaSO_4 + Fe_2O_3 \rightarrow CaO.Fe_2O_3 + SO_2 + 1/2\ O_2 \qquad \text{(R-15)}$$

$$2\,CaSO_4 + SiO2 \rightarrow SiO_2.2CaO + 2SO_2 + O_2 \qquad \text{(R-16)}$$

These reactions may explain the many oxygen release peaks identified in the TG-MS curves of the waste in N_2 atmosphere in Figure 3, occurring simultaneously to the many SO_2 released peaks.

Mineral and chemical composition of the waste

The X-ray Fluorescence results obtained are showed in Table 1 as oxides in percentage. The results found considering the loss on ignition (LOI) value calculated from TG data until 900ºC in N_2 atmosphere are also shown, which correspond to the sum of the losses of water and CO_2.

Table 1 Composition of the waste according to XRF analysis and corrected XRF values considering the loss on ignition (LOI) determined by TG of the sample in N_2 up to 900ºC

Composition	XRF analysis / %	Corrected XRF with LOI from TG / %
MgO	10.378	7.570
Al_2O_3	6.496	4.738
SiO_2	15.740	11.481
SO_3	17.913	13.066
K_2O	0.700	0.511
CaO	45.759	33.378
TiO_2	0.311	0.227
Fe_2O_3	2.252	1.643
ScO_3	0.349	0.255
SrO	0.092	0.067
Rb_2O	0.009	0.007
Free water		1.018
1st comb H_2O set		10.721
2nd comb H_2O set		7.703
Total water content		19.438
CO_2		7.618
LOI		27.056

An excel program was designed to estimate the quantitative mineral composition of the waste, being the obtained results shown in Table 2. This table shows in the first two horizontal files the composition obtained from corrected XRF results in Table 1, obtained from XRF and TG-MS results. The first column in Table 2 shows the compounds identified by XRD and other oxides assigned according to corrected XRF results. This column represents the qualitative mineral composition of the studied waste.

Each column presents the distribution of each oxide in the different compounds identified by XRD (or in the form of oxides if their presence was not confirmed in XRD). The columns LOI H_2O and LOI CO_2 represent the percentage of water or CO_2 in each crystalline compound identified in XRD.

The dashed line cells values in Table 2 were obtained from respective TG curve mass loss graphically (from the partial mass loss of each DTG peak limit of each higher mass loss step), considering bibliographic data of the mass loss temperature interval; the other values were obtained stoichiometrically or by mass balance of each oxide, using the excel program for calculation. The excel program allows doing hypothesis analysis, being quickly the calculation when a change in one cell is proposed, and allowing the assignation of the different values obtained in the TG for combined water from hydrotalcite, ettringite and gypsum.

The second column in Table 2, obtained as the sum of each file, represents the quantitative estimated composition of the coal power plant waste. As can be seen at the end of the second column, practically 99% of the composition was estimated by using this methodology.

Table 2 Qualitative and quantitative composition of the coal power plant waste according to corrected XRF composition, compounds identified by XRD, TG-DTG losses data, stoichiometry and mass balance

Component / Oxide	m (%)	LOI H_2O	LOI CO_2	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	TiO_2	Fe_2O_3	Sc_2O_3	SrO	Rb_2O
free H_2O	1.02	1.02												
SiO_2 quartz	11.18					11.18								
Al_2O_3. $0.32SiO_2$	1.90				1.60	0.30								
$6CaO.Al_2O_3.3SO_3.32H_2O$	2.69	1.24			0.22		0.51		0.72					
$6MgO.Al_2O_3$ $CO_2.12.H_2O$	14.47	6.18	1.26	4.12	2.92									
$CaSO_4.2H_2O$	15.81	3.31					7.35		5.15					
$CaSO_3$. $0.5H_2O$	8.38	0.58					5.20		3.64					
$Mg(OH)_2$	1.68	0.41		1.28										
$Ca(OH)_2$	27.56	6.70							20.86					
$MgCO_3$	6.17		3.99	2.18										
$CaCO_3$	5.38		2.37						3.01					
TiO_2	0.23									0.23				
Fe_2O_3	1.64										1.64			
Sc_2O_3	0.25											0.25		
SrO	0.07												0.07	
K_2O	0.51							0.51						
Rb_2O	0.01													0.01
Total	98.95	19.44	7.62	7.57	4.74	11.48	13.07	0.51	33.38	0.23	1.64	0.25	0.07	0.01

According to XRF, XRD, TG-MS, and results from Table 2, the composition estimated for this waste presents a high ratio of dry spent desulfurization sorbent, being $Ca(OH)_2$ the major component of the waste (27.56%), that corresponds to the non-reacted hydrated lime (or CaO from fly ash hydrated, according to the atmospheric deposits), followed by gypsum as the main present product (15.81%) and hemihydrated calcium sulphite in lesser extent (8.38%). Very probably the higher gypsum content can be a consequence of the oxidation and hydration of the hemihydrated calcium sulphite formed in the SO_2 absorbing unit, during storage. It is also important the presence of hydrotalcite (14.47%) and quartz (11.18%), the first one from the commercial hydrated lime used in the adsorption tower, and the second from the fly ash, as in the case of the mullite (1.90%), being ettringite (2.69%) a product of desulphurization when fly ash is present. Calcite (5.38%) and Magnesite (6.17%) are also in important amounts from dolomite accompanying the commercial hydrated lime.

Taking into account the valorisation options found in the bibliography for dry FGD products [39, 41-43] and these results, the high percentage of hydrated lime and other basic compounds like magnesite or calcite can make advisable to explore the reuse of this waste in the same dry FGD unit, alone or after reactivation, its use in the CO_2 capture, or its use as a soil amendment for alkalized soil, added to the most common use in concrete admixture.

Conclusions

A method has been developed to characterize qualitative and quantitatively the chemical and mineral composition of a coal power plant waste with data obtained from thermogravimetry coupled with mass spectrometry (TG/MS), X-ray fluorescence (XRF) and X-ray diffraction (XRD) that allowed estimating its composition. The high percentage of hydrated lime and other basic compounds like magnesite or calcite, can make advisable the reuse of this waste in the same FGD unit, its use in the CO_2 capture, or as a soil amendment for alkalized soil, added to the most common use in concrete admixture.

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