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A new thermogravimetric method to quantify SO_2 absorption capacity by limestone

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ABSTRACT

A commercial limestone was used in aqueous suspension to capture SO_2 from coal combustion gases in a bench scale system. To evaluate the limestone absorption capacity during the applied process, a new method was developed by thermogravimetry (TG), which quantifies the absorbed SO_2, from the gypsum content formed in the residual sulphated limestone after absorption, on the limestone initial mass basis. With the new method the thermogravimetric analyses data needed for the calculations can be obtained in equipment which operate only up to 1000 °C and in a faster way than the methods used previously, which need analyses performed up to 1350 °C, to obtain, after the total anidrous calcium suphate decomposition, the conversion factors of the TG curves to limestone initial mass basis. The new method also allows one to reuse the sample alumina crucible, which is not possible in the previous methods because there was partial melting of the residual oxides when heated up to 1350 °C, which during cooling, adhere on the alumina crucible. A comparative analysis shows that the obtained results with the new method are practically the same of those obtained by the previous methods, applied to the same samples, with a relative error lower than 3%, which shows the importance and much better cost/benefit applicability. The new method is also more cost effective environmentally, because it avoids the release of SO_3 during the analysis of the residual sulphated limestone, which needed a banch scale SO_2 absorption system, from the gases leaving from the TG equipment, during the analysis.

1. Introduction

Coal-fired power plants account for 41% of the world's electricity generation [1]. Among the several environmental problems caused by the coal combustion, one of the main problems is the release of SO_2, usually formed during the combustion of the pyrite present in the coal [2–4]. Sulfur dioxide (SO_2) is a toxic and polluting gas, and therefore there are maximum emission limits in the atmosphere established worldwide.

In this context, many technologies to remove SO_2 from the combustion gases of coal were developed so far. One of these, uses limestone in aqueous solution [5], which captures SO_2 to form a solid residue containing gypsum and the unreacted calcium carbonate, when an excess of air is used. For this purpose, a bench scale system was set up to burn a Brazilian coal, in which, the combustion gases, after being cooled, were sent to an absorption column containing an aqueous suspension of limestone.

During the absorption of SO_2 by limestone in an oxidizing environment promoted by an excess of air, which is the case of the present study, the reactions that occur can be represented by Eq. (R-1) [6].

$$CaCO_3 + SO_2 + ½ O_2 \rightarrow CaSO_4 + CO_2 \qquad \text{(R-1)}$$

As the reaction occurs in aqueous solution, the $CaSO_4$ hydration reaction forms the correspondent dihydrate [6]:

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

Thermal analysis has been an important tool in research and development programs in many branches of technology, particularly fuels (fossil, synthetic and nuclear). It is versatile and cost-effective, capable of obtaining fundamental data and of simulating many aspects of a commercial process, quickly and with relatively little manpower [7].

TG has been a major research tool in study of limestone sulphation. For example, Wieczorek-Ciurowa [8] presented comparative data on the absorption rate and capacity for SO_2 capture by a natural Polish

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limestone with and without sodium chloride additive. Two sets of thermogravimetric experiments were carried out, under dry and wet conditions during limestone calcination and sulphation, to investigate the absorbent reactivity. In another work, Wieczorek-Ciurowa [9] studied limestone sulphation by contrasting examples of applications of thermoanalytical techniques using variable conditions. Their examples deal with the programmed thermal analysis using different gas sequences, the influence the calcination and sulphation conditions on the capture of SO_2, the effect of catalysts on limestone sulphation and the $CaSO_3$ thermal stability. Two proposed mechanisms were supported by the phase identification of the solid products. Souza and Bragança [10] used thermogravimetric analysis of limestones with different contents of MgO to investigate marble calcination in TGA/DTA, using air and an atmosphere similar to oxy-combustion.

TG is also a suitable laboratory method which enables reliable prediction of sorbent behavior. The use of several sets of programmed TG analyses with variable conditions allows identifying several factors, which influence the mechanism and kinetics of reactions with the $CaCO_3/CaO\text{-}SO_2/SO_3$-air system. Using thermoanalytical methods, with systematic changes of the experimental conditions (only changing a single parameter each time), one can draw conclusions as to the effect of a particular parameter, which can be independent [11].

Thermal analysis methods can predict the behavior of the potential sorbents towards SO_2/SO_3 in a larger scale installation. The thermal stability of the compounds from the Ca-S-O system and the influence of additives on sulphation have been found useful in elucidation of the limestone sulphation mechanisms. Usually these investigations must be supplemented by independent complementary techniques such as X-ray diffraction, scanning electron microscopy with backscattered electron image followed by quantitative energy dispersive X-ray microanalysis [12].

One of the most important uses of TG in this field is to obtain the desulfurization yield, which indicates the best adsorbent or the best operating conditions. Garea et al. [13] reported the thermogravimetric characterization of the solid products resulting from the low temperature reaction between SO_2 and mixed solids containing hydrated mixtures of calcium hydroxide and fly-ashes. Snyder et al. [14] used two methods to predict desulfurization performance of a specific limestone in fluidized-bed combustors at a specific Ca/S ratio. Li et al. [15] studied the calcination characteristics, sulphation conversion, sulphation kinetics, and microstructure of the residual white mud from paper manufacture, at the fluidized bed combustion temperatures. Frazier et al. [16] developed an analytical way to estimate the absorption capacity from TG curve data of the original and sulphated limestones.

All the previous cited cases used TG curve data obtained by default, on respective sample initial mass basis, which needs time consuming calculations, because the TG curve data of different initial composition samples cannot be compared directly, because a same percentual change of initial mass loss or a same residual percentual mass of the initial mass represent, respectively, differently composed changes or products [17].

To overcome this problem, Dweck has developed a method to convert thermal analysis curves of differently composed sample initial mass basis on a same composition calcined mass basis, or on a same initial mass basis of different samples common component. Applications where already done to study the effect of Pozzolanic materials in cement hydration [18–21], to compare different solid adsorbents having a common oxide component or organophilic bentonites prepared from a same natural bentonite [22,23], different coke samples formed by pyrolisis of a same raw material [24,25], to caracterize residual catalysts as aggregates of a same cement [25,26], on hydration kinetics of a same cement [27], on CO_2 sequestration study by a same type of cement [28], to determinate gypsum contents of commercial cements [29], to study pyrolysis products of biodiesel filtration cake having a common stable component [30], to compare differently aged hydrated pastes obtained from a same cement [31] and differently recycled materials obtained from a same initial commercial gypsum [32].

Therefore, the main objective of this work is to show and to apply different methods developed for the calculation of the SO_2 content absorbed by limestone in aqueous suspension, from the thermal analysis data of the limestone, before and after its use in the capturing process.

Table 1
Immediate analysis of Candiota coal.

Reference	Humidity (m%)	Volatile (m%)	Fixed carbon (m%)	Ashes (m%)
33	16.4	23.1	27.2	49.7
34	8.2	24.5	21.0	54.5
35	8.2	17.7	27.5	46.7

2. Materials and methods

The coal used in this work is from Candiota/RS, Brazil, extracted from Riograndense Mining Company (CRM) mine. Table 1 shows its immediate analyis performed by Pires and Querol [33], Lunkes [34] and Valle [35]. It must be noted that the coal used in the present experiments was sampled from the same lot than Valle. Pires and Querol [33] also report that the main mineral phases present in Candiota coal are quartz, kaolinite, illite, Kfeldspar and pyrite and that its sulfur content is 0.96 m%. As can be seen, this coal has a very high ash content and its combustion gases are mainly CO_2, H_2O and SO_2, the last of which is formed from pyrite combustion, which is the only gas component that can be chemically sorbed by calcium carbonate absorbent. Water vapors are also formed from kaolinite dehydroxilation, which occurs during coal combustion. FRX data are shown in Table 2, from which it can be estimated by stoichiometry that the sulfur content of the coal was 1.05 m%.

The limestone was produced by Carbomil S.A. Mining and Industry Company, located in Fortaleza, Ceará. Both raw materials were donated by respective Brazilian Companies.

The SO_2 capture experiments were performed in a prototype, which consisted of a split cilindrical furnace, in which coal samples of about 50 g were disposed on a ceramic longitudinal crucible into a vitreous horizontal cylindrical quartz reactor. The coal was burned using controlled air flow entring from the left side of the reactor. The combustion gases, which were beingreleased from the opposite exit of the reactor, where passed through a washer bottle containing the limestone aqueous suspension for SO_2 absorption. After about 3 h, when practically coal combustion was completed, the residual sulphated limestone suspension in the washer bottle was vacuum filtered, the retained sulphated limestone particles were dried at 40 °C up to constant mass and stored until their analysis.

Table 3 shows the main operating conditions of the combustion coal

Table 2
X-ray fluorescence chemical analysis of Candiota coal.

Oxide	SiO_2	Al_2O_3	Fe_2O_3	SO_3	K_2O	CaO	LOI	Total
m%	32.55	10.57	3.02	2.63	1.53	1.45	48.25	100.00

Table 3
Operating Conditions of coal combustion runs.

Run	E1	E2	E3	E4	E5	E6
Air flow ($L.\ min^{-1}$)	3	3	3	6	6	6
Heating rate (ºC. min^{-1})	5	7	10	5	5	5
Firing temperature (ºC)	700	700	700	700	600	500