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The use of differential scanning calorimetry to identify coals susceptible to spontaneous combustion

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Abstract

Non-isothermal oxidation enthalpies have been measured for three Colombian coals which have been weathered under ambient conditions for period up to 105 days. It was found that although the total oxidation enthalpies decreased with increasing oxidation the decrease was not systematic. It was thought that the random behaviour was due to weight losses during the course of the experiments. It was noted that the onset temperature of oxidation increased with oxidation in a more systematic way and also increased with increasing coal rank. It was therefore proposed that the onset temperatures was a better indicator of the propensity of the coals to oxidation. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Differential scanning calorimetry; Coal; Spontaneous combustion; Weathering

1. Introduction

The high reactivity of certain coals to molecular oxygen is one of the major problems faced by the coal industry during mining, storage and transportation. Oxidation causes a reduction in the calorific value, a loss of coking properties, a reduction in liquefaction yield, self-heating and occasionally spontaneous combustion [1]. The changes induced by weathering depend on exposure time and how fast the reaction proceeds. The latter increases very rapidly with temperature. This phenomenon is common to other materials such as cellulose, grains, cotton, etc, and it is caused by exothermic reactions involving oxygen and the production of water. If chemical reaction is adiabatic or quasi-adiabatic, then the heat generated is higher than that which can be taken away by convection inside the coal pile and the temperature rise will augment the rate of oxidation and consequently the evolution of heat.

The problems in understanding and predicting spontaneous combustion are compounded because there is no simple test for the identification of coals liable to spontaneous combustion. Geologically similar coals from the same deposit vary considerably in this respect. Conventional characterisation such as petrographic, ultimate or proximate analysis are of little value. The experience of the Colombian mining industry, and in a number of different parts of the world, has shown that the susceptibility to spontaneous combustion may even vary within individual mines. This has lead to otherwise productive mines being closed as well as having important safety con-

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siderations. It is desirable to develop a straightforward test for rapid evaluation of the susceptibility of coals to spontaneously combustion.

The oxidation chemistry of low rank coals is complex and partly determined by mass transfer considerations. In general, the initial stage of the oxidation of coal at low temperatures involves the attack of molecular oxygen on hydrogen atoms located in the α position to an aromatic nucleus or groups OR to produce peroxides or hydroperoxides. These are reactive species and produce carbonyl and carboxylic groups [2–4]. The decomposition of these functionalities differ according to the presence of other functional groups [5].

Along with the chemical changes mentioned above, there are changes in the physical structure, for e.g., changes in the macromolecular structure, of coal. These can be observed from changes in the crosslink density [6,7] caused by secondary interactions of the functional groups, which affects the swelling ratios [8] of coal in solvents as well as their solubility in solvents [9,10].

Another property of coal which has been claimed to be affected by low temperature oxidation is surface area [11–13]. This effect is specially marked in low rank coals where up to 30% reduction of the area measured with CO_2 has been observed after oxidation at 35°C [11]. This reduction has been explained as caused by the blocking of the pores by the oxygen adsorbed which limits the diffusion of the CO_2 into some of the micropore system. However, such interpretation of changes to the gas adsorption of coals in terms of the pore structure may need corrections because gas adsorption must be performed on dry samples. For many coals, particularly low rank coals, the pore structure changes during drying. Recently, Larsen et al. [14] have argued that many coals do not possess a connected micropore system. If this model is accepted then the reduction in the amount of CO_2 which can be absorbed can equally be explained by increased crosslink densities induced by oxidation which reduces CO_2 diffusion through the macromolecular structure.

Most research into coal self-heating has been carried out using isothermal methods. Recently, a non-isothermal method has been used to study the reactivity of coal towards oxygen [15,16]. It was found that the exothermic peak in differential thermal analysis could be related to the self-heating process of coal. No systematic evaluation of the oxidation process was presented since the samples were oxidised at relatively high temperatures, 200°C. Although such temperatures are encountered in the centre of coal piles during spontaneous combustion, they are not relevant to the crucial initial stages.

The objective of the present paper is to determine whether non-isothermal DSC can be used as an indicator to determine the susceptibility of coals to self-heating or spontaneous combustion. The problem is that there is no universally accepted criterion for susceptibility toward spontaneous combustion and the differences in coal structure that determine this are quite subtle. Consequently, it is difficult to interpret DSC data in such a way as to correlate with any ranking of coals in this respect. The tactic adopted here has been to work with three geologically similar coals (which experience from their mining operations has shown to be varying in their susceptibility towards self-heating) and to alter their structure in some way which deliberately reduced this susceptibility. This has been achieved by low temperature oxidation under ambient conditions over extended periods. The task was then to determine which features of the non-isothermal oxidation enthalpies varied systematically with the oxidation and which also reflected the previous experience in the use of these coals. As a separate issue, this is also a study of the effects of low temperature oxidation on the susceptibility of coal to spontaneous combustion.

2. Experimental

Three low rank coals were used in the experiments. Samples were collected directly from the mine and stored in plastic containers with de-aerated water. Two of the samples, Venecia and Amaga, are known to exhibit strong tendencies to spontaneous combustion. Titiribi coal, which belongs to the same coal basin as the other two is more stable to reaction with oxygen at ambient conditions. Their elemental analyses are shown in Table 1. The ash content of the three samples was similar. The elemental analysis are given in Table 1 were obtained from ROM samples. The samples were ground to less 100 Tyler mesh under a high purity nitrogen atmosphere.

Table 1
Analytical data of the coal samples expressed on a dry ash free basis

Coal sample	C (%)	H (%)	N (%)	S (%)	O_{diff} (%)
Venecia	74.2	5.3	1.5	0.8	18.2
Amaga	76.4	5.1	1.8	0.4	16.3
Titiribi	82.5	5.6	1.9	0.6	9.4

The weathering of the samples was carried out in acrylic boxes designed to reproduce oxidation conditions as close as possible to those found during natural weathering, is, i.e., the samples were exposed to rain, wind and solar heating. During the 105 days of oxidation the samples were periodically mixed to ensure more uniform oxidation. The unoxidised coals were used as a reference. In order to follow the effect of the oxidation time on the coals, samples were taken from the acrylic boxes after 15, 30, 45, 75 and 105 days of weathering.

Comparative analyses were carried out using a thermogravimetric analyser, TA instruments 2950, and elemental analysis using a Leco CHN 600 apparatus. The enthalpies of oxidation were determined in a differential scanning calorimeter (DSC), TA instruments 2910. The philosophy of the DSC experiments was to maximise heat transfer from the oxidised coals while at the same time ensuring that these were no external diffusional limits for oxygen to reach the surface of the coal. About 10 mg of sample was placed in the sample pan, covered with a lid and sealed with pressure. Pinholes were made in the lid. The coal was in a monolayer at the base of the pan to ensure that the entire sample made good thermal contact with the bottom part of the pan and therefore good heat transfer with the sensors of the equipment.

The way in which the oxygen diffused into the sample holders and oxidised the sample was crucial. At the opposite extremes of lid opening, no exotherms could be detected. Obviously, oxygen cannot diffuse into a completely sealed pan and any heat evolved during oxidation was removed by the carrier gas flow using open pans. If the pinholes were too small oxygen diffused into the pans too slowly and this process determined the rate of oxidation, rather than diffusion into the pore structure of the coal itself. Hall and coworkers [17] used two pin holes of roughly 1 mm diameter each and reported no mass transfer limitations. In this study four pinholes were opened in the lid to allow the exchange of gas with the interior of the pan. Initially, the sample was dried under nitrogen flow by heating the sample at 10°C min^{-1} to 110°C and holding at this temperature for 5 min. The sample was then cooled to 50°C, the gas changed for high purity oxygen (20 ml min^{-1}), then heated at 10°C min^{-1} up to 600°C. Control experiments were carried out using nitrogen to evaluate the balance between the devolatilisation and condensation reactions that take place during pyrolysis. The data was recorded as heat flow in mW. Each analysis was carried out at least twice to test for reproducibility.

3. Results and discussion

The samples used in the present research are low rank coals and therefore their oxygen content is relatively high, as shown in Table 1. This oxygen is mainly in the form of hydroxyl, carboxyl, ether and carbonyl groups. The ash content of the three samples was 3.0%.

The oxidation enthalpy profiles of the non-isothermal oxidation reactions are shown in Figs. 1–3. The output curves are not corrected for weight changes during the oxidation reaction for reasons that will be discussed shortly. The shape of the profiles varies according to the type of coal. It was observed that for Venecia and Amaga coals there were three main thermal events that took place during the oxidation, which could be clearly differentiated by DSC. The main regions are identified as ***a***, ***b***, and ***c*** in the figures.

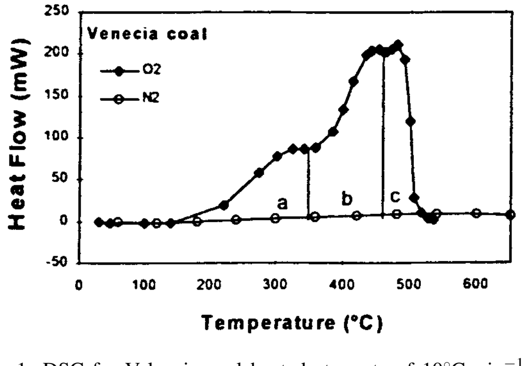

Fig. 1. DSC for Valencia coal heated at a rate of 10°C min^{-1} in nitrogen and oxygen.

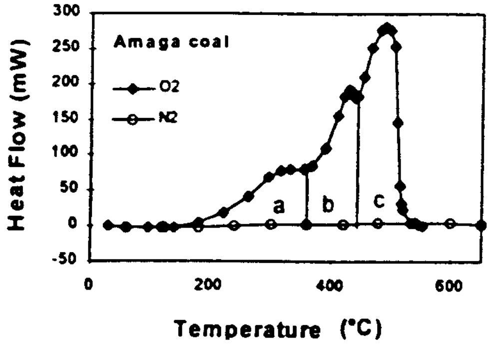

Fig. 2. DSC for Amaga coal heated at a rate of 10°C min^{-1} in nitrogen and oxygen.

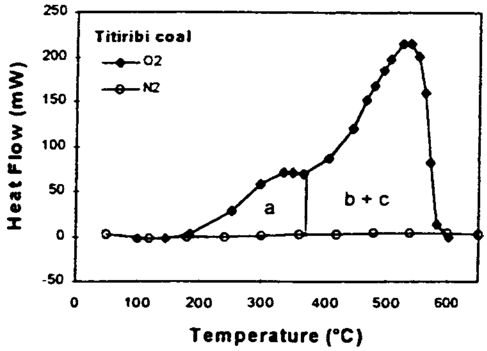

Fig. 3. DSC for Titiribi coal heated at a rate of 10°C min^{-1} in nitrogen and oxygen.

In the higher rank coal, region ***b*** and ***c*** are not clearly distinguished.

The onset of the exotherms will be discussed shortly. The exotherms reach a plateau around 360°C and this value is more or less constant for all the samples. At this temperature, the burn off of the sample, under oxygen, is less than 10%. Under a nitrogen atmosphere, pyrolysis, the weight loss of the sample at 360°C is less than 5%, which means that oxygen accelerates the weight loss by about 50% up to this temperature. In region *a*, the enthalpy of oxidation is mainly age result of the low temperature reaction of molecular oxygen with the most reactive coal structures such as hydroaromatic and oxygenated functional groups [5]. Therefore, in this low temperature region, the enthalpy profile is sensitive to minor changes in the nature of the coal sample. Particularly, in this region the most relevant process is oxygen chemisorption on the surface, which is a partly reversible. Due to the biradical nature of the oxygen molecule it readily couples with the free radicals of the coal structure producing peroxy radicals which can decompose at higher temperatures to produce different oxygenated species. At higher temperatures the effect of massive pyrolysis of the sample as well as higher rates of oxidation make it difficult to use this information to evaluate the tendency for the coal to spontaneous combustion.

A number of features of the exotherms were considered as possible parameters to characterise susceptibility to spontaneous combustion but only two are discussed here: the integrated oxidation enthalpy and the onset temperature of the exotherm.

It was observed that increasing oxidation progressively decreased the values of the integrated oxidation enthalpies, see Fig. 4. In the case of Venecia coal after 45 days of weathering, the enthalpy of oxidation does not change in any significant way. This information is presented in Table 2, normalised for the weight of the initial sample in the DSC. The data show the average variation of the enthalpy of oxidation with of time as well as the average per day for the whole duration of the experiment (0–105 days). The information presented in Table 2 clearly shows that a severe deterioration of the coal samples took place during the first 15 days of weathering. This initial oxidation of the coal samples has a passivating effect, which reduces the "average" rate of evolution of heat during the

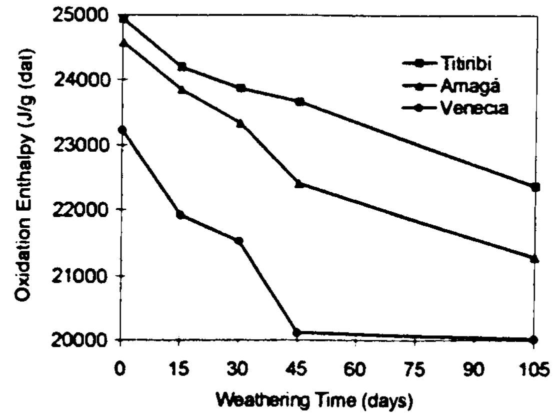

Fig. 4. Oxidation enthalpy of samples weathered at ambient conditions. The enthalpy values are normalised by the initial weight of the sample. Heating rate 10°C min^{-1} in nitrogen.

Table 2
Average decrease in the enthalpy of oxidation per day during the weathering per gram of initially loaded sample in the dsc pan

Coal sample	Period (days)				
	0–15	15–30	30–45	45–105	0–105
Venecia (J/g/day (daf))	87	29	94	1	32
Amaga (J/g/day (daf))	48	34	63	18	31
Titiribi (J/g/day (daf))	50	22	14	21	25

Table 3
Variation of the onset temperature T_o of the evolution of heat with the weathering time of the samples

Weathering time (days)	Onset temperature T_o (°C)		
	Venecia	Amaga	Titiribi
0	189	203	204
15	198	207	209
30	199	209	209
45	205	211	210
75	205	213	210
105	212	214	211

subsequent days of weathering. However, the trend is not uniform and, for example, the average decrease in enthalpy for Venecia between 30 and 45 days is larger than for the 15–30 and 0–15 day periods. Also, there is no clear relationship between the rank of the coal and the loss of enthalpy. The reasons for this non-systematic behaviour are not clear but may be related to the fact that the exotherms cease at temperatures over 500°C. As discussed above, over this temperature range there is a large amount of weight loss due to pyrolysis and, for greater accuracy the DSC results must be corrected for this effect. The amount of weight loss depends on the rank of the coal and also the oxidation state of the coal. All of these effects introduce large uncertainty and variability into the evaluation of the integrals. Potentially they could be corrected by the use of TGA but this additional complexity makes exotherm integrals unsuitable as an easy measure of oxidation stability.

The onset temperature of region ***a*** is another possibility of the measure of the susceptibility of coals towards spontaneous combustion. This has a number of potential advantages. Firstly, the overall weight change at this temperature is negligible, thus avoiding the problems inherent in exotherm integration. Also, as discussed above, the early stages of oxidation are more sensitive to the state of the sample. Hall et al. [18] have shown that heat evolved during the early stages is crucial to subsequent oxidation by inducing relaxation in the coal structure which enhance the mass transfer of oxygen.

Coal is a very reactive material towards molecular oxygen, isothermal experiments at 0°C show that there is O_2 chemisorption at this temperature, previously, the authors [18] have detected exotherms for the isothermal oxidation of pristine North Dakota Lignite from the Argonne programme at 60°C. Non-isothermally, any exothermic activity at such temperatures is undetectable due to noise. Therefore, it is important to have a rigorous and consistently applied definition of the onset temperature for the non-isothermal experiments. The onset temperature of the net exothermic heat flow was defined as the interception with the *x*-axis of the tangent to the enthalpy profile at 290°C. These values are tabulated for the fresh and weathered coals in Table 3. The estimated error in these values is ±2°C. Of course it is possible to define other methods but, as will be argued shortly, the above method gives values that can be rationalised with coal rank can changes to the coal structure.

There are a number of features of interest in Table 3. Three observations drawn from these data which suggest that the so-defined onset temperature, T_o, is a promising candidate for characterising the propensity of a coal towards spontaneous combustion:

1. T_o increases with time of weathering for all of the coals, subject to experimental error. This is entirely in agreement with the idea that the coals become more stable with increasing amounts of mild oxidation.
2. Although it is not reliable to draw conclusions about rank behaviour on the basis of three coals, it is nevertheless noted that T_o increases with rank. Again, this is consistent with the general idea of higher rank coals having a lower propensity to spontaneous combustion.
3. The values of the change in T_o between the pristine and 105 days weathered samples are also consistent with rank and the expected oxidative stability of the coals. Venecia, the coal with the highest propensity

exhibited an increase in T_o from 189°C to 212°C, an increase of 23°C. Titiribi only exhibited and increase of 7°C, again consistent with its known stability towards oxidation. Amaga exhibited an increase of 11°C.

T_o is therefore proposed as a new parameter to indicate the propensity of a coal towards spontaneous combustion.

The results also show the utility of mild oxidation in being able to stabilise coals. Indeed T_o may provide a useful quantification in being able to predict how much oxidation is necessary to stabilise coals.

4. Conclusions

Differential scanning calorimetry is a useful technique to investigate the early stages of the oxidation of coal. A new parameter based on the onset temperature of the profile of the enthalpy of oxidation is proposed and it was found that this parameter agreed with the rank of the coals investigated and increased with time of oxidative weathering. This parameter allowed the differentiation of subtle changes caused by the weathering of coal, which are otherwise very difficult to observe. It was found that coal is severely affected during the first days of exposition to ambient conditions. It is proposed that a mild controlled oxidation of coal can be used as a method to reduce the reactivity of coal towards molecular oxygen at low temperatures.

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