

CALORIMETRIC EVIDENCE FOR THE WATER VAPOUR/COAL INTERACTION AT LOW TEMPERATURE

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Calorimetric study shows that at 423 and 523 K, the water vapour/oxidised coal interaction is an exothermic process. It results in the superimposition of a rapid reversible adsorption (also encountered with unoxidised coal) on an irreversible and slow reaction. This later is correlated with a CO₂ formation. The enthalpy of the reaction is independent of the amount of CO₂ formed. Calorimetry clearly demonstrates that the water vapour reaction proceeds via a true hydrolysis mechanism rather than a catalytic one.

Keywords: calorimetry, coal, low-temperature oxidation

Introduction

The study of the low temperature oxidation of coal has clearly shown that water vapour is often the main gaseous product of the reaction [1, 2]. However, at 423 K, no influence on the rate of oxidation could be evidenced, even, when saturated water vapour was added. At higher temperature (523 K) water vapour behaves as an inhibitor [3] whereas at lower temperature (<373 K) according to Maloney *et al.* [4] water vapour accelerates the rate of oxidation playing a promotor or a catalytic role. At present the role of water vapour remains nonclear although it is now certain that moisture plays a key role in the weathering of coal [5-7]. This latter phenomenon has important economic implications as the loss of calorific value for plain coal and the loss of coking ability for coking coal.

For a better understanding of the role of water vapour the study has been limited in this preliminary work to the comparison of the behaviour of the two simplified systems: water vapour/oxidised coal (where free oxygen has been eliminated because of its probable overshadowing role) and water vapour/unoxidised coal. Calorimetry has been used with the purpose to

facilitate the discrimination of the reversible and irreversible part of water vapour interaction and shed light on the mechanism.

Experimental

The experimental device has been previously described [1, 2, 8]. In short, it consists of a Tian Calvet calorimeter using Platinel II thermocouples as detectors able to work from R.T. to 1273 K; the sensitivity was 10^{-2} V/W at 423 K. A volumetric device was connected to the calorimeter allowing the introduction, the measurement (with a micromanometer) and the sampling of the total amount of gases, which were then analyzed by GPC (O_2 , N_2 , CO , CO_2). Water vapour introductions and measurements were made according to a procedure especially designed for a previous work [1, 2].

The first experiments were carried out with small samples (1 g) of a high rank coal (semi-anthracite Escarpelle) containing very small oxygen quantities and being difficult to oxidise. In order to obtain characteristic thermal effects, the sample size was increased (3 g) and their nature also changed. They consisted of low rank coal samples (Vouters which is a high volatile subbituminous B coal able to fix large oxygen quantities) and, for comparison purposes carbon black (FW200 Degussa) before which contains before outgassing a large oxygen content (see Table 1).

Table 1 Composition of carbonaceous materials

	Ultimate analysis (w%)				
	C	H	O	N	S
FW200 (carbon black)	83.0	1.1	15.0	0.6	0.3
Vouters (coal)	82.8	4.9	10.4	0.5	1.3
Escarpelle (coal)	91.1	3.4	2.9	1.0	1.4

Results and discussion

Qualitative behaviour

Figure 1 shows the trend of the thermal curves obtained when water vapour was successively reacted at 523 K with a sample of oxidised coal (Escarpelle) for 4 h, then trapped with a dry-ice-acetone mixture for 3 h. It appears that the exothermic thermogram is larger than that of the endothermic one. Moreover, no return to the base line was achieved, pointing to the oc-

current of a slow reaction superimposed on the rapid and reversible process. The removal of the trapping mixture allowed the cycle adsorption – desorption to be recommenced (with, however, an increase of the time of contact until 16 h, the other conditions remained the same). The reversible part dramatically decreased and it is interesting to note that the shape also changed whereas the irreversible part was less affected. The decrease in reversible adsorption is likely to result in the irreversible process causing not only a dramatic decrease of water vapour pressure, but also, possibly, a reduction of the number of sites available for the reversible adsorption. At 423 K the same general behaviour was observed with oxidised coal and, as expected, the reversible adsorption increased whereas the irreversible reaction decreased.

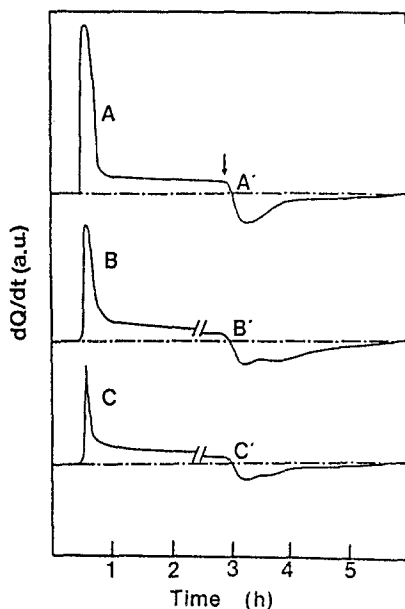


Fig. 1 Thermal curves obtained at 523 K when an oxidised Escarpelle sample was subjected to different water vapour exposures: 4 h (A), 16 h (B), 16 h (C). Each water exposure was followed by a 3 h trapping period allowing the desorptions A', B', C' to be measured

With unoxidised coal and coal outgassed for a long time at 523 K, the adsorption at 423 K was rapid with a return to the baseline over an hour and was almost completely reversible (Fig. 2).

The data clearly show the different behaviour exhibited by unoxidised and oxidised coal towards water vapour: unoxidised coal does not chemically interact with water vapour whereas oxidised coal reacts slowly. It points

out the role played by oxygen groups in the water/vapour interaction. Calorimetric results showed, since the reaction is exothermic, the water vapour interaction is not a catalytic decomposition of preexisting oxygenated groups (expected endothermic) but rather a true hydrolysis reaction. At 313, 423 and 523 K the water vapour interaction with an oxidised Escarpelle sample releases, after the removal of water vapour, significant amount of gas. Their CPG analysis showed that they mainly consisted of CO_2 , CO appearing as a minor product of the reaction [9]. This result is interesting because it is well known that, in contrast, the oxidation and pyrolysis of coal yield mixtures containing higher CO proportions. In consequence, the study of the changes in the CO_2/CO ratios ought to allow the characterization and the discrimination of the different treatments (out-gassing, oxidation, pyrolysis) from the water vapour reaction.

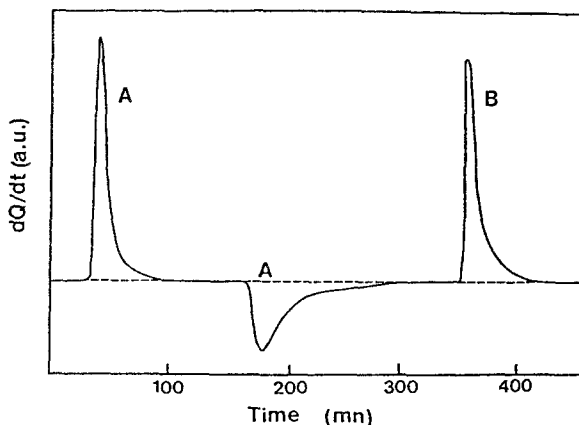


Fig. 2 Thermal curves obtained with an unoxidised Escarpelle sample

It is interesting to note, since GPC analysis has failed to find significant amounts of molecular hydrogen – only several hundred ppm hydrogen were detected by MS in the residual gases, in agreement with the work of Grossman *et al.* [10] – hydrogen released by water must remain attached on the coal surface either as hydroxyl or hydrid groups.

Quantitative study

Figure 3 shows the cumulative amounts of evolved CO_2 against the time for a Vouters sample which was successively heated from ambient to 523 K (region I), then at 423 K reacted with saturated water vapour (region II), treated with oxygen (region III), pyrolyzed, again reacted with water vapour

and finally again pyrolysed. It appears that, whereas no important change in the amount of evolved CO_2 was observed when water vapour was reacted with unoxidised coal (region II), a distinct increase of the amount of evolved CO_2 (in the 10^{-5} mole/g range) was evidenced with oxidised coal (region V).

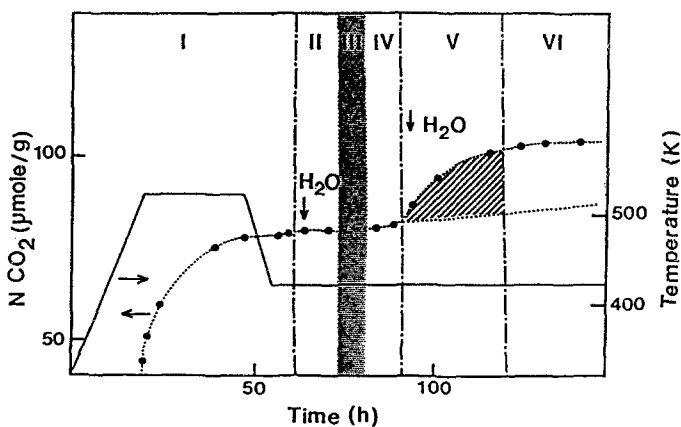


Fig. 3 Cumulative amounts of evolved CO_2 (left ordinate) against the time when an Escarpelle sample was subjected to different treatments: regions I, IV or VI pyrolysis; region III oxidation and regions II or V water vapour reaction. Temperature profile (right ordinate) against the time

At 423 K Fig. 4 shows the evolution of the CO_2/CO ratios against the time for the same Escarpelle sample. A drastic increase of the CO_2/CO ratio was observed in region V (oxidised sample) whereas no change was observed with unoxidised coal in region II.

Figure 5 illustrates the behaviour of a carbon black sample (FW200) successively outgassed and reacted with water vapour at 523 K (without any oxygen treatment). It is interesting to note that the oxygen untreated FW200 sample behaves as an oxidised coal because it initially contains large oxygen quantities (see Table 1). The high reactivity revealed by carbon black toward water vapour shows since this material has a low ash content, that the water vapour reaction involves rather the organic part of carbon black than the mineral matter. This is in agreement with previous experiments with an oxidised soot of pure gas (free of mineral matter) which exhibited a larger reactivity than the coal [8]. At 523 K the evolution of the CO_2/CO ratios against the time for the FW200 sample (oxygen untreated) was qualitatively similar to the behaviour of a Vouters oxidised sample i.e. a drastic increase of the CO_2/CO ratios was observed when water vapour was reacted.

Figure 6 illustrates the thermal curves obtained with a Vouters sample previously oxidised and treated with micromole doses of water vapour. After

the removal of the reversible process a strong pressure dependence of the water vapour reaction is visible.

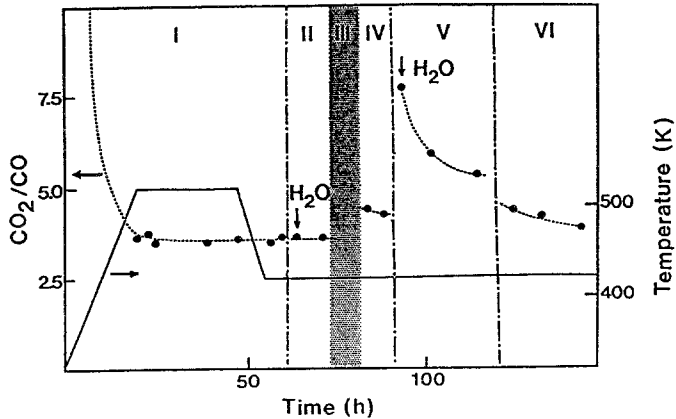


Fig. 4 Changes in the CO_2/CO ratio against the time for the same experiment as in Fig. 3

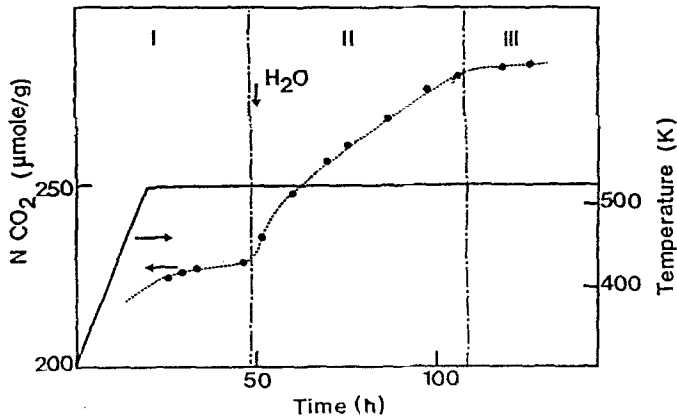


Fig. 5 Cumulative amounts of evolved CO_2 for a FW200 sample successively pyrolysed and reacted with water vapour at 523 K

Table 2 shows the enthalpy of water vapour reaction measured (by taking the difference between exothermic and endothermic contributions) at 423 and 523 K (for both Vouters and FW200 samples) quoted in KJ/mole of CO_2 . Measured carbon dioxide was corrected for the contribution due to the pyrolysis which is superimposed on the water vapour contribution (Fig. 3). The water vapour consumption is difficult to measure by difference between water vapour admitted and water vapour remaining at the end of the reaction since a significant part of water vapour may be held in the micropores.

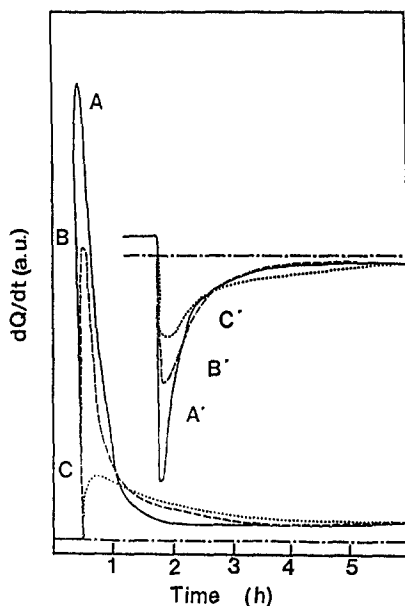


Fig. 6 Thermal curves obtained when micromole doses of water vapour were successively reacted with a Vouters sample and then desorbed A: 111 μ moles; B: 266 μ moles and C: 555 μ moles

These results give a clear indication that according to the temperature and the nature of material different oxygenated groups are involved in the hydrolysis reaction. Further discussion is not meanful before new data become available by FTIR.

Table 2 Enthalpy of the water vapour reaction

Sample	Oxygen treatment	$-\Delta H / \text{kJ} \cdot \text{mol}^{-1} \text{CO}_2$	
		423 K	523 K
Vouters	Yes	235 \pm 11	207 \pm 10
FW200	No	74 \pm 3	184 \pm 9
FW200	Yes	109 \pm 6	ND

Application to the weathering of coal

If the assumption that the water vapour/oxidised coal is correct, i.e. the reaction finally leads to the substitution of oxygenated groups for hydrid groups (i.e. partially regenerates surface groups present before oxidation) it is possible to tentatively reexamine the role of water vapour in the weathering of coal.

At room temperature the oxygen reaction (if natural moisture is absent and no water vapour is formed) must be stopped as soon as the coal surface is fully covered with oxygenated groups since the pyrolysis does not work at this temperature to regenerate active species toward oxidation. In contrast, the presence of water vapour allows the formation of hydrid groups and the oxidation to be continued; water vapour acts in this case as a promotor of oxidation and as the driving force of weathering.

At higher temperature ($T > 323$ K) the pyrolysis, for instance with the destruction of acid groups accompanied by CO_2 release, leads to the formation of reactive hydrid groups allowing the oxidation reaction to be continued. In this case the rate of the water vapour reaction is expected to be lower than the rate of formation of reactive species coming from the pyrolysis and consequently water vapour appears to have either no influence on the kinetic of the oxidation reaction or occasionally to have an inhibitor role (water vapour behaves as a diluent). In the same way, the protective role sometimes attributed to water and especially to liquid water is easy to understand if the coal is unoxidised: adsorbed water prevent oxygen diffusion [11] and this behaviour has been used to preserve coal samples from oxidation. However as coal is always partially oxidised even when subjected to a short oxygen exposure, water chemically interacts in changing the nature of the surface groups. This demonstrates that even the preservation of coal samples under inert gas is not sufficient to stop the slow reaction of moisture with oxygenated groups and an outgassing is recommended to mitigate this deleterious influence. Of course the degassing treatment causes not only the elimination of reversibly adsorbed water but also a change in the oxygenated groups if the temperature is increased (thermolysis). Nevertheless, the evolution due to water vapour must be drastically decreased. In the same way, the use of wet treatments as demineralization and washing are likely to induce important modifications of the surface groups of partially oxidised coal.

Conclusion

The hydrolysis reaction of oxidised coal has important consequences for understanding the mechanism of the weathering, the preservation of coal samples and the wet treatment of coal. Moreover, it provides new outlooks for the interpretation of the CO_2/CO ratios. Finally water vapour reaction appears as a very sensitive process able to detect, with the CO_2 measurement, trace of coal oxidation and of oxidation of carbonaceous materials.

References

- 1 J. C. Petit, *Fuel*, 69 (1990) 861.
- 2 J. C. Petit and Z. X. Cheng, *Advanced Methodology for Coal Characterization*, Elsevier, Amsterdam 1990, p. 259.
- 3 O. P. Mahajan, M. Komatsu and P. L. Walker Jr., *Fuel*, 58 (1980) 30.
- 4 D. J. Maloney, R. G. Jenkins and P. L. Walker Jr., *Fuel*, 61 (1982) 175.
- 5 R. M. Davidson, *Natural Oxidation of Coal*, I. E. A. Research, London 1990.
- 6 C. R. Nelson, *Chemistry of Coal Weathering*, Elsevier, Amsterdam 1989.
- 7 R. Klein and R. Wellek, *Sample Selection, Ageing, and reactivity of Coal*, John Wiley, N.Y. 1989.
- 8 J. C. Petit, *Fuel* 70 (1991) 1053.
- 9 J. C. Petit, Proc. 1991 International Conference on Coal Science, Newcastle U.K. Sept. 1991, p.186.
- 10 S. L. Grosman, S. David and H. Cohen, *Fuel*, 70 (1991) 897.
- 11 N. P. Panaseiko, *Solid Fuel Chem.*, 8 (1974) 21.

Zusammenfassung — Kalorimetrische Untersuchungen zeigen, daß die Wechselwirkung zwischen Wasserdampf und oxidiertes Kohle bei 423 und 523 K ein exothermer Prozeß ist. Er ergibt sich aus der Überlagerung schneller reversibler Adsorptionsvorgänge (auch bei unoxidiertes Kohle) und einer irreversiblen, langsamen Reaktion. Letztere steht für die Bildung von CO₂. Die Reaktionsenthalpie ist unabhängig von der Menge des gebildeten CO₂. Kalorimetrie zeigt deutlich, daß die Wasserdampfreaktion über echte Hydrolysemechanismen verläuft und weniger über katalytische.