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THERMOCHEMICAL STUDIES OF HELIUM AND ARGON SORPTION BY OXIDATED COALS

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ABSTRACT

The influence of noble gases such as helium and argon on the structure of oxidated coals (sub-bituminous coal, high-volatile bituminous coal and anthracite) has been studied. It was found that the process of oxidation changed; essentially, helium induced modification of the coal structure. An attempt has been made to explain the phenomena observed.

INTRODUCTION

Coal is an extremely complex heterogeneous solid [1,2]. Knowledge and understanding of its structure are needed if full use is to be made of this fundamental material. It has already been reported that coal swells during the sorption of many liquids, their vapours, and gases [3–5]. This process is caused by strong interaction between the sorbed species and the macromolecular structure of coal.

Thermochemical investigations showed that the structure of coal may also be changed by sorption of noble gases [6,7]. These processes may not be described by the swelling model only. Recently, a qualitative description of sorption of helium by coal was proposed. In this model, the helium atoms are treated as a "molecular grease" which discharges the localized stress between graphite-like domains in the coal structure [7].

In the present work, helium and argon sorption by partially oxidated coals is investigated. In this case, the graphite-like domains are additionally

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connected by oxygen bridges, and the oxidated structure is more rigid than the non-oxidated one [8–10]. These characteristics influence the helium-induced structure modification caused by displacement of domains in the coal structure.

EXPERIMENTAL

Details of the three coals used, their origins and their analyses are given in Table 1. The coal samples were stored for 3.5 years at ambient temperature under a pressure of 2×10^4 Pa.

The helium and argon used were reagent grade. The enthalpies of adsorption of helium and argon on the coals were determined using a Tian–Calvet microcalorimeter operating at a constant temperature of 298 K. The microcalorimeter cell was calibrated electrically. Complete details of the experimental procedures have been reported elsewhere [11,12].

The coal samples (2.7–3.3 g) were placed in glass ampoules and outgassed [13,14]. The maximum temperature during this procedure was 393 K, and the pressure above the samples at the final temperature did not rise above 0.1 Pa. After outgassing, some coal samples were saturated with helium or argon under 5.4×10^4 Pa at 383 K for 10 h, and these samples were then outgassed at ambient temperature.

The pressure range for measurements was from 0.1 Pa to 2.7×10^4 Pa. The experiment was initiated by introducing the gas into the calorimetric vessel at a constant rate of 1.83×10^{-2} cm^3 (S.T.P.) min^{-1} for helium and 8.5×10^{-2} cm^3 (S.T.P.) min^{-1} for argon. The gases were introduced over a period of 120 min. Only for the helium experiments, in which an endothermic effect was observed, was the helium introduced over a period which extended to the end of that effect (a maximum of 10 h).

TABLE 1

Origins and analyses of coals used

Type	Origin	Moisture (wt.%)	Ash (wt.%)	Volatile (wt.%)	Carbon (wt.%) daf [a]	Hydrogen (wt.%) daf [a]	Sulphur (org. wt.%) daf [a]	Nitrogen + Oxygen (wt.%) daf [a]
Anthracite	Walbrzych	1.0	4.1	5.6	90.9	3.3	–	–
High-volatile bituminous	Pokoj	1.4	4.2	36.4	86.4	5.4	0.8	7.4
Sub-bituminous	Sosnowiec	8.2	2.9	39.3	79.4	4.4	0.4	15.8

[a] daf, Dry ash-free.

RESULTS

The results of calorimetric measurements of the argon sorption, as well as amounts of sorbed gas, are listed in Table 2. The enthalpies were calculated per mole of adsorbed argon. The mean error of the measured enthalpies was estimated to be less than 10%. In Fig. 1, thermograms of argon sorption on anthracite are given. The results of calorimetric experiments of helium sorption on the various samples, outgassed as well as helium- and argon-saturated, are presented in Figs. 2–4.

No attempt was made to calculate the values of enthalpies of helium sorption because the amounts of helium adsorbed were of the same order as the estimated error.

The endothermic heat effects recorded for helium sorption were: for anthracite 5×10^{-2} J, for high-volatile bituminous coal (h.v.b. coal) 1.75×10^{-1} J, and for sub-bituminous coal (s.b. coal) 3×10^{-2} J.

TABLE 2

Results of calorimetric measurement of adsorption of argon and amounts of gas at S.T.P. (enthalpies calculated for 1 mole of adsorbed gas)

	Outgassed only		Argon saturated		Helium saturated	
	(kJ mol^{-1})	(cm g^{-1})	(kJ mol^{-1})	(cm g^{-1})	(kJ mol^{-1})	(cm g^{-1})
Sub-bituminous	−4.1	0.216	−5.1	0.229	−5.0	0.258
High-volatile bituminous	−7.7	0.084	−8.0	0.063	−9.8	0.164
Anthracite	−10.7	0.275	−10.6	0.116	−5.2	0.300

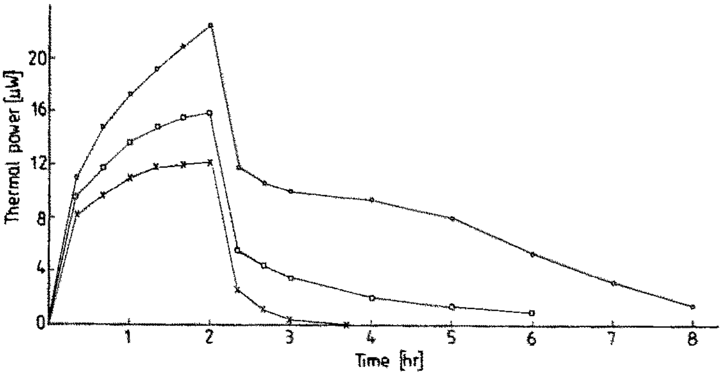

Fig. 1. Thermograms of adsorption of argon on anthracite. (A) ○, Outgassed sample; (B) □, argon-saturated sample; (C) ×, helium-saturated sample.

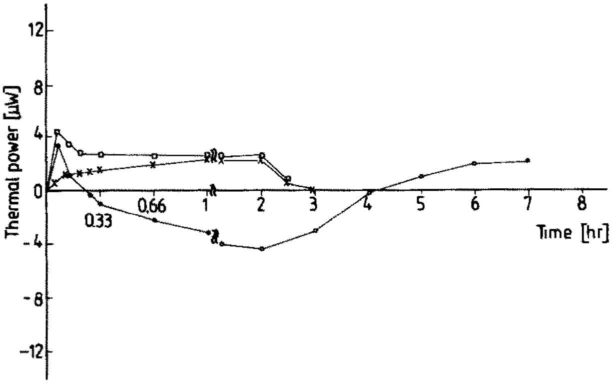

Fig. 2. Thermograms of adsorption of helium on sub-bituminous coal. (A) ○, Outgassed sample; (B) □, argon-saturated sample; (C) ×, helium-saturated sample.

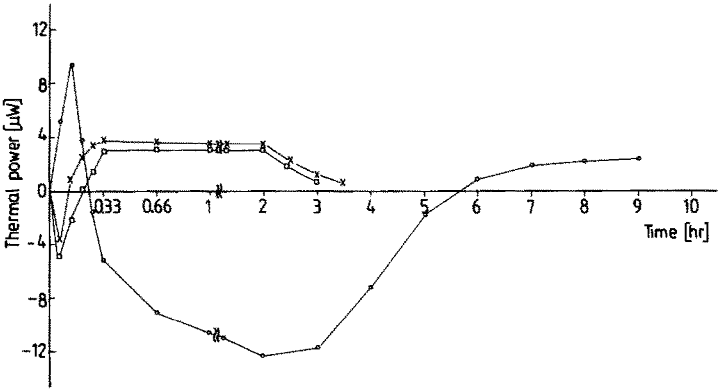

Fig. 3. Thermograms of adsorption of helium on high-volatile bituminous coal. (A) ○, Outgassed sample; (B) □, argon-saturated sample; (C) ×, helium-saturated sample.

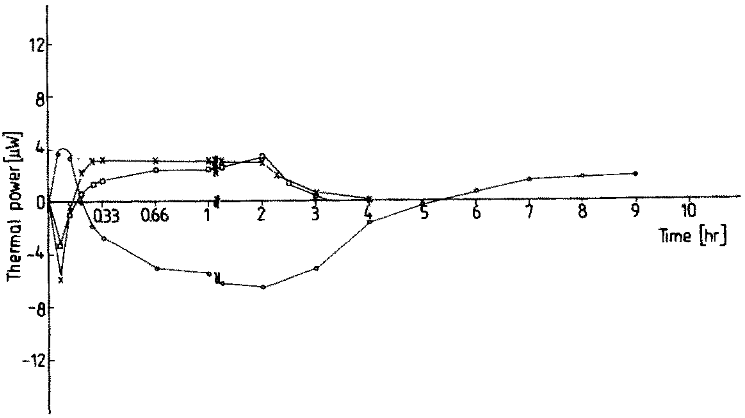

Fig. 4. Thermograms of adsorption of helium on anthracite. (A) o, Outgassed sample; (B) □, argon-saturated sample; (C) ×, helium-saturated sample.

DISCUSSION

Helium sorption

The thermograms for helium experiments show that partial oxidation of coals changes qualitatively the process of helium sorption. In the experiments, abnormally high enthalpies of sorption were not observed. After interruption of the gas inflow, constant pressure was reached immediately and the calorimetric signal returned to the base-line. This indicated that coal structure modification did not occur.

The suppression of this phenomenon may be explained by an increase in coal viscosity. The oxidated coal structure, with additional oxygen bridges, is more rigid, and the displacement of graphite-like domains is more limited. However, the experiments for samples outgassed only show an entirely new effect. These experiments are initiated by small exothermic effects (Figs. 2–4), which may be treated as a residual modification process lasting ca. 10–15 min. This effect is the highest for h.v.b. coal, which is consistent with differential scanning calorimetry (DSC) and thermogravimetry (TG) experiments [7]. This effect is followed by the endothermic effect, which occurs for all types of coals; again, the highest value of the effect is observed for the h.v.b. coal. Finally, these experiments end with a small constant exothermic effect ($3\text{–}5 \times 10^{-7}$ W).

We propose the following explanation of this phenomenon. The small, weakly interacting helium atoms easily penetrate the coal structure, and their presence gives the possibility of coal domains being more mobile (the helium atoms act as a "molecular grease"). The DSC experiments showed that helium-saturated coal has a heat capacity higher than that of non-saturated coal [7,15]. When the graphite-like domains become more mobile, some of the oxygen bridges may be broken. This process must be endothermic. However, the structure becomes more mobile (entropic effect) at the cost of partly broken bridges (energetic effect).

The simplest explanation for the final constant exothermic effect observed for all types of coal is physical adsorption on the microporous surface of the coal.

The shapes of thermograms for anthracite (Fig. 4) and h.v.b. coal (Fig. 3) initially saturated with helium or argon are different from those for samples which were not saturated. These experiments were carried out on saturated samples which were then stored under vacuum for a few days. In that time, a small fraction of the bridges broken during saturation were rejoined. In the first part of the thermograms, a small endothermic effect (lasting about 10 min) was observed. This is a consequence of rupture of the bonds rejoined when the coal was stored under vacuum. A small exothermic effect was then observed, as in the other experiments (physical adsorption on coal surface).

To confirm the proposed explanation of helium sorption processes on coals, the following additional experiments for the h.v.b. coal–helium system were carried out. The calorimetric experiment was repeated immediately after the experiment carried out on h.v.b. outgassed coal. The thermogram showed initially an exothermic effect typical of the end of the helium experiments. We may conclude that broken oxygen bridges were not restored and that the heat effect recorded was produced by physical adsorption only.

The calorimetric measurement was carried out in the same way as for the sample of h.v.b. coal stored under normal pressure for 3.5 years. In this case we did not observe an initial exothermic effect but only the endothermic effect, which was ten times smaller than that for the sample stored under reduced pressure. Increasing the temperature of preliminary outgassing to 500 K and increasing the rate of helium introduction into the calorimetric vessel by six times did not change the results of the calorimetric measurements [16].

The above additional experiments show the following.

(1) Oxidation of the coal structure eliminates the helium modification process and essentially reduces the possibility of oxygen bridge rupture induced by helium. The process of bridge rupture may be reversible.

(2) Absence of a relationship between helium pressure and the course of the thermograms shows that the thermal effect is mainly caused by coal structure modification induced already by small amounts of helium.

Argon sorption

The calorimetric results obtained for argon sorption are essentially different from those for the helium experiments. The enthalpy values and the shapes of the calorimetric curves are typical of physical adsorption [17]. The small values of sorption enthalpies for s.b. coal may be explained by geometrical factors. The structure of this type of coal is open; the diameters of pores are too large for argon atoms.

In Fig. 1, it is shown that presorption of argon or helium changes the conditions of argon sorption. Presorption of argon does not change the enthalpy values, but decreases the amount of sorbed gas for h.v.b. coal and anthracite (Table 2). Probably the presorbed argon atoms block some of the coal micropores.

The enthalpy value for argon sorption on helium-presorbed anthracite is about half that for the anthracite without helium presorption (Table 2). This enthalpy value and the shape of the thermogram (Fig. 1, curve C) demonstrate that changes in the coal structure are eliminated by helium presorption. In all cases, helium presorption caused an increase in the amount of sorbed argon.

The other processes, structure modification and bridge-breaking induced by argon atoms, were observed to only a small extent. For example, argon presorption eliminates the process of bridge-breaking during the helium sorption (Figs. 3 and 4).

CONCLUSION

Recapitulating, the interaction of inert gases such as helium with coal is very complex. We may distinguish the following processes: (1) physical adsorption on the microporous surface of coal (exothermic effect); (2) structural modification caused by helium atoms acting as "molecular grease"; this action results in ordering of the graphite-like domains (exothermic effect); and (3) rupture of oxygen bridges, caused by increase in the mobility of rigid domains, engendered by the presence of helium atoms in the coal structure (endothermic effect).

Effects (2) and (3) are especially strong for h.v.b. coal.

It seems that the explanation of the sorption process of inert gases by coal may be a combination of these three effects. Their relative importances in the process are dependent on the surface area, the degree of oxidation and the internal ordering of graphite-like domains.

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