

EPR STUDY OF THE CATALYTIC EFFECTS OF
MINERALS ON FREE RADICAL FORMATION DURING COAL PYROLYSIS

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A systematic *in situ* study of free radicals in Pittsburgh No. 8, acid treated coal (ATC) as a function of temperature and residence time has been carried out using the electron paramagnetic resonance (EPR) technique at temperatures up to 900 K. The catalytic effects of pyrite, pyrrhotite, calcite, and clays on free radical formation during pyrolysis have been examined.

INTRODUCTION

Various investigators have reported that the inherent mineral matter in coal may have a positive effect during conversion processes (1-3). Pyrite and pyrrhotite are of particular interest since pyrite, which is the major iron-sulfur compound in coal, is known to affect various stages in coal processing, and pyrrhotite, which is formed from pyrites under liquefaction conditions, has been found in one study (4) to influence conversion efficiency, although other work is in disagreement with this conclusion (5).

Since the formation of free radicals by the rupture of coal bonds during pyrolysis is believed to be an important step in liquefaction, the EPR technique has been used to advantage in studies on pyrolyzed and heat-treated coals (6,7). Recently Srinivasan and Seehra (8,9) have reported results of studies on the effects of pyrite and pyrrhotite on free radical formation in two West Virginia coals which were heated to ~900 K. Observing that the maximum increase in the number of free radicals occurred at ~800 K for coal samples containing 8% added pyrite, with a somewhat smaller increase for pyrrhotite, they concluded that both the conversion of pyrite to pyrrhotite and pyrrhotite itself contributed to the enhancement in the number of free radicals. An overall increase in the number of free radicals which was smaller on heating in H₂ than in vacuum, was interpreted as indicating that free radicals were stabilized by hydrogen.

An important point to note about the studies so far (8,9) on the effects of pyrite and pyrrhotite on free radical formation, is that the EPR measurements were carried out on coal samples which had been sealed in evacuated or gas-filled sample tubes, heated in a furnace, and then cooled. This procedure may preclude the observation of information on transient effects, which may be lost on cooling down the sample before EPR measurements are taken. A significant objective of the present work therefore, was to examine mineral effects on radical formation *in situ* during pyrolysis at temperatures up to 900 K. A step in this direction was recently reported by Seehra and coworkers (10) who carried out *in situ* measurements on samples of raw coal, and were able to de-

tect several distinct stages in pyrolysis based on the variation in spin concentration as the temperature increased during pyrolysis.

EXPERIMENTAL PROCEDURE

The coal samples used in this work were derived from a ground sample (C19825 in reference 14) from the Pittsburgh No. 8 seam, a high volatile bituminous coal, which has been the subject of several previous EPR investigations in this laboratory (11-13) and has been otherwise extensively characterized (14). Mineral samples used include pyrite from Custer, South Dakota, pyrrhotite from Falconbridge, Ontario, and calcite. Standard clay samples of well crystallized kaolinite (KCa-1), illite (IMT-1), and montmorillonite (SCa-2) were obtained from the Clay Minerals Society.

Small samples for EPR studies were prepared by thoroughly grinding mineral/coal mixtures so that the average particle size was much smaller than the microwave skin depth (15). The coal and mineral were dispersed in KBr in the ratio 1:100 (16), and then ground further in a ball grinder using plexiglass vials and balls to avoid metal contamination. Samples were placed in vacuum and usually used immediately following grinding; however, when necessary, they were stored for 24 h under nitrogen, with no observable deterioration in the EPR spectrum.

The low temperature ash fraction (14.5%) from the Pittsburgh No. 8 coal has been analyzed to contain 16% pyrite, 25% calcite, 8% quartz, with the remaining 54% composed of kaolinite, illite, expandable clays, and other minerals. For experiments designed to study the evolution of free radicals in the absence of the inherent mineral matter, acid treated samples were used. These were prepared by boiling raw coal with 5M HCl for 30 minutes, thoroughly washing with acetone and ethanol, and then drying at 375 K for 8 h. Subsequent preparation proceeded as already described for raw coal.

Prior to carrying out the EPR measurements, each coal sample was placed in a 4 mm o.d. quartz sample tube which was evacuated through a side arm. The sample tube was inserted into a double-walled quartz dewar inside the microwave cavity. Nitrogen gas heated by passage over a series of two chromel-alumel heater elements flowed through the dewar. By suitable adjustment of the gas temperature and flow rate, the sample temperature, as measured by a chromel-alumel thermocouple, could be raised to 900 K with a stability of ± 1 K. The Varian TE₁₀₂ mode cavity was maintained at room temperature by means of refrigerated water circulating inside a jacket which surrounded, and was in good thermal contact with the cavity. The signal intensity from a sample of DPPH fixed to the cavity wall was unchanged by heating the sample inside the dewar, confirming that the sensitivity of the cavity was not affected.

EPR measurements were made at ~ 9 GHz using a Varian V-4500 spectrometer equipped with 100 kHz field modulation. The arrangement for pyrolysis experiments has already been described; low temperature experiments on the acid following demineralization were done using a Varian variable temperature

accessory. Field measurements were made using a Harvey-Wells NMR gaussmeter and a Hewlett-Packard frequency counter. The spectrometer is interfaced to an IBM XT computer which is used for data acquisition, calibration, storage, and analysis.

RESULTS AND DISCUSSION

Figure 1 shows plots of the absolute temperature (T) versus the product of the temperature and the intensity of the EPR absorption obtained by numerical double integration of the observed line profile (IT). The results illustrated are for a sample of raw Pittsburgh No. 8 coal and for two other samples, coal + 8% pyrite and coal + 8% pyrrhotite, heated for 20 minutes at ~40 K intervals. In the case of raw coal there is no significant change in free radical concentration until ~600 K, after which it rises, but at a slower rate than the curves for the samples with mineral added. Both of the latter samples show evidence of an intermediate step in which a small increase in concentration is followed by a decrease, before the onset of the steep rise at ~600 K. The preliminary step is similar to that observed by Seehra *et al.* (10) for *in situ* measurements on three raw coals, but was not observed in their earlier study (8,9) on the effects of the addition of pyrite and pyrrhotite in which measurements were made after heating outside the cavity. The number of free radicals increases faster for added pyrrhotite than for pyrite until it reaches a peak at 800 K and then drops rapidly thereafter. The pyrolysis of the raw coal and coal + 8% pyrite continues to yield additional free radicals up to the cutoff in the data at 900 K. This continued enhancement of the free radical yield in coal + 8% pyrite samples contrasts with the earlier observations for samples pyrolyzed outside the cavity and recorded cold (8,9), where all three samples showed a decline in free radical concentration back to prepyrolysis levels, and suggests the importance of *in situ* observations in monitoring the dynamic process. The observation that at temperatures up to 800 K the coal + 8% pyrrhotite sample shows higher concentrations of free radicals than pyrite, which then continues to enhance free radical formation as the yield from pyrrhotite declines, suggests that the catalytic activity of the pyrrhotite has been depleted, while in the coal + 8% pyrite sample the pyrite continues to convert to pyrrhotite which then enhances the free radical yield. This tends to support the view that the conversion to pyrrhotite as well as the mineral itself are positive influences.

A significant question is the possible influence of the inherent mineral matter on radical yield. In an attempt to investigate this possibility samples of acid treated coal were studied. Figs. 2(a) and (b) show the EPR spectrum of the raw coal at room temperature (296 K) and after heating at 814 K, respectively. The room temperature spectrum shows evidence of Fe^{3+} at $g \approx 4.4$ which is probably contained in clays, and a broad weak signal underlying the free radical signal at $g \approx 2.0$, which may be from metallic iron. Pyrite, with Fe^{2+} , has no EPR spectrum; however, after heating, conversion of pyrite to pyrrhotite has occurred, and a strong ferromagnetic resonance signal is

observed at center field. The spectrum shown in Fig. 2(c) of ATC-1 at room temperature shows that the Fe^{3+} -bearing mineral has been removed, and Fig. 2 (d) recorded at 869 K shows no evidence of converted pyrrhotite. Finally, when 8% pyrite is added to ATC-1, heating to 871 K again reveals the presence of pyrrhotite as shown in Fig. 2 (e). The spectrum shown in Fig. 2 (f) of a glass of the HCl which was used in the demineralization, shows evidence of the iron extracted from the coal.

Figure 3 shows the IT versus T curves obtained for two samples of acid treated coal (ATC-1 and ATC-2) which were heated *in situ* for ~85 min at ~40 K intervals, compared to the curve for the same ground sample of raw coal before acid treatment which was heated for ~20 min at each interval. The consistently higher concentration of free radicals generated in the pyrolysis of the raw coal compared to the ATC supports the contention that the inherent mineral component contributes to the radical yield.

Prior to examining the influence on free radical yield of adding specific minerals to the ATC, a series of experiments was carried out to determine the effect of residence time. Figs. 4(a) - (e) show the time evolution of radical concentration for ATC with added pyrite, pyrrhotite, calcite, clays (4% kaolinite, 2% illite, 2% montmorillonite), and a mixture of calcite and pyrite. In each case the results were obtained by pre-heating the dewar in the cavity to ~830 K, inserting the sample tube, and beginning to record observations after 5 minutes residence. It is seen that the maximum in free radical concentration occurs for widely different residence times for the various coal/mineral combinations. In particular, the radical concentration for ATC-1 + 8% pyrrhotite reaches a maximum after only 10 min, while at least 50 min are required for ATC-1 + 8% pyrite. This again points to the importance of converted pyrrhotite. A mixture of 4% calcite + 4% pyrite added to ATC appears to be even more effective. Radical concentration increases rapidly in the first 5 minutes, and after 30 minutes has reached a maximum. By contrast, the addition of clays, pyrite, or calcite separately, appears to produce no dramatic increases.

Plots of the the relative concentration of free radicals as a function of temperature for ATC and ATC with the five minerals mentioned earlier are shown in Fig. 5. At temperatures up to ~825 K the number of free radicals produced is generally best for a mixture of calcite and pyrite. Pyrrhotite also enhances free radical yield, but only up to ~800 K. Pyrite appears to be much less effective when added to the ATC than it was when added to the raw coal. Pittsburgh No. 8 coal does, of course, contain calcite, and these results at least raise that this inherent calcite and the pyrite together play a role in the observed increase in free radical concentration shown in Fig. 1.

CONCLUSIONS

Several conclusions may be drawn from the results reported here. The increase in radical concentration observed on the addition of pyrrhotite to ATC in contrast to the relative ineffectiveness of pyrite supports the view

that the conversion of pyrite to pyrrhotite and pyrrhotite itself are responsible. Of interest, is the apparent positive influence of calcite on free radical yield. In studies on the pyrolysis of Pittsburgh No. 8 coal in helium and hydrogen at temperatures up to 1300 K Franklin *et al.* (17,18) found strong effects by calcium minerals. In particular, they concluded that CaCO_3 and its decomposition product during pyrolysis CaO , are especially active in cracking oxygen functional groups and aromatics. We note however, that the free radical yield shows substantial enhancement only when in the presence of pyrite.

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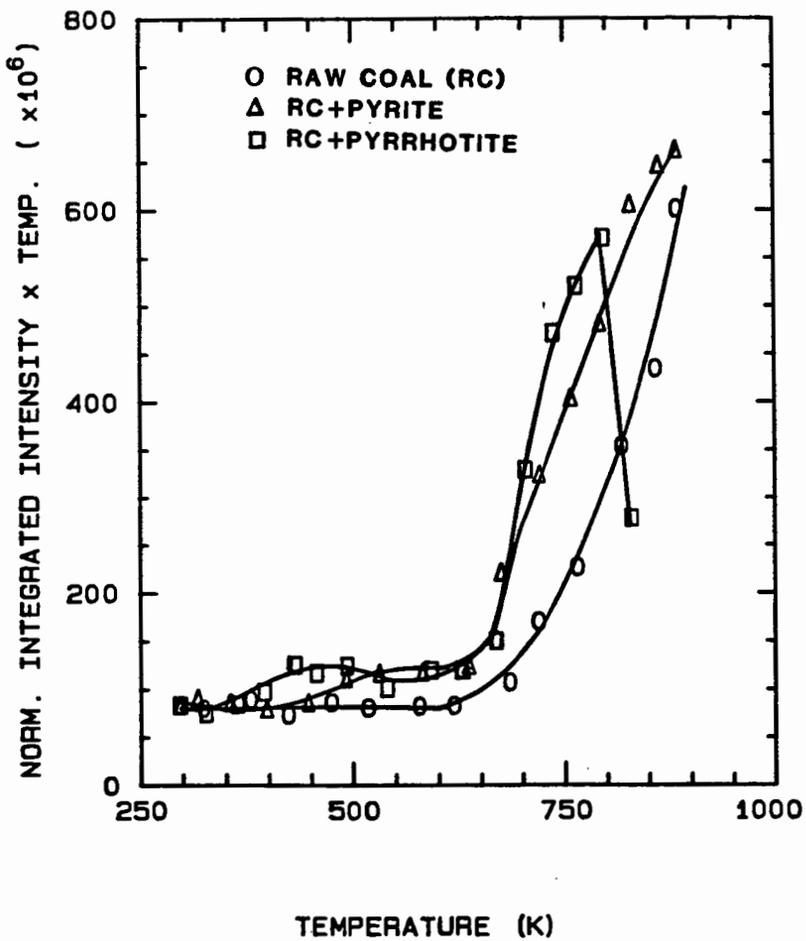


Fig. 1. Plot of IT versus T for raw coal, raw coal + 8% pyrite, and raw coal + 8% pyrrhotite.

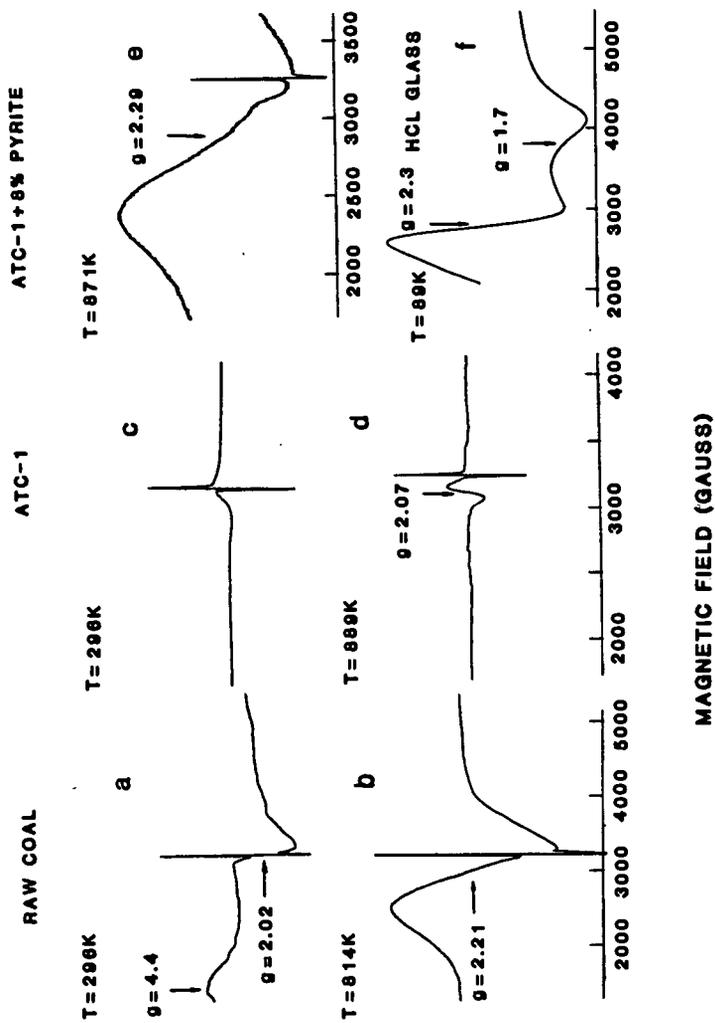


Fig. 2. EPR spectra of raw coal at (a) 296 K and (b) 814 K; ATC-1 at (c) 296K and (d) 869 K; (e) ATC-1 + 8% pyrite at 871 K; and (f) a glass at 89 K of the HCL extract from demineralization.

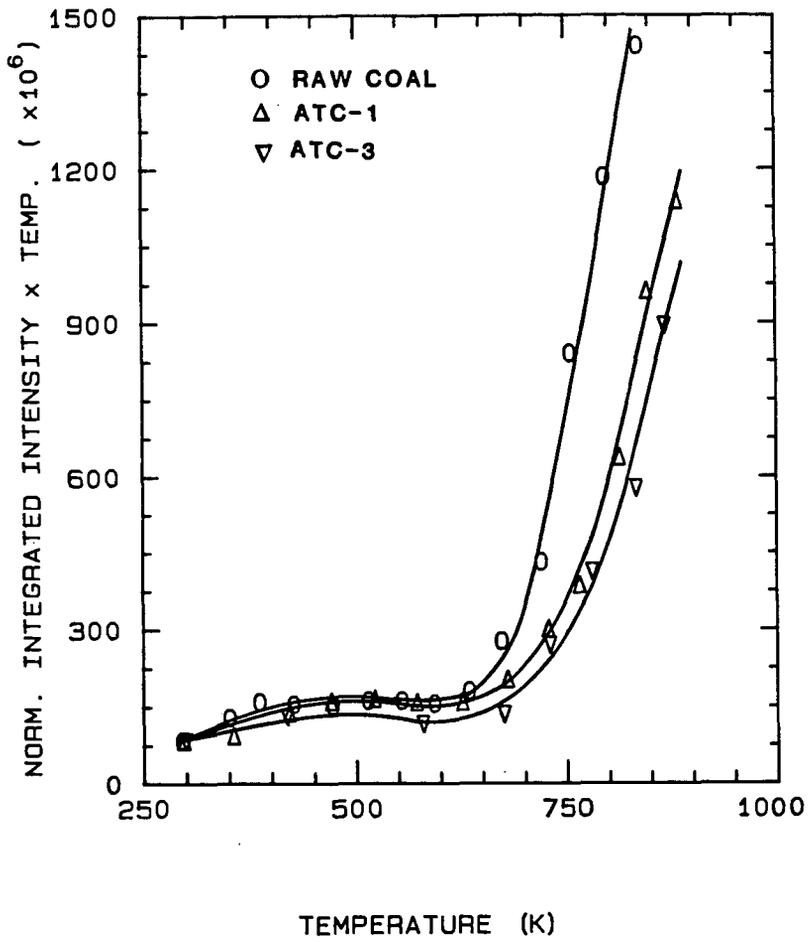


Fig. 3. Plot of IT vs. T for ATC-1, ATC-3, and raw coal.

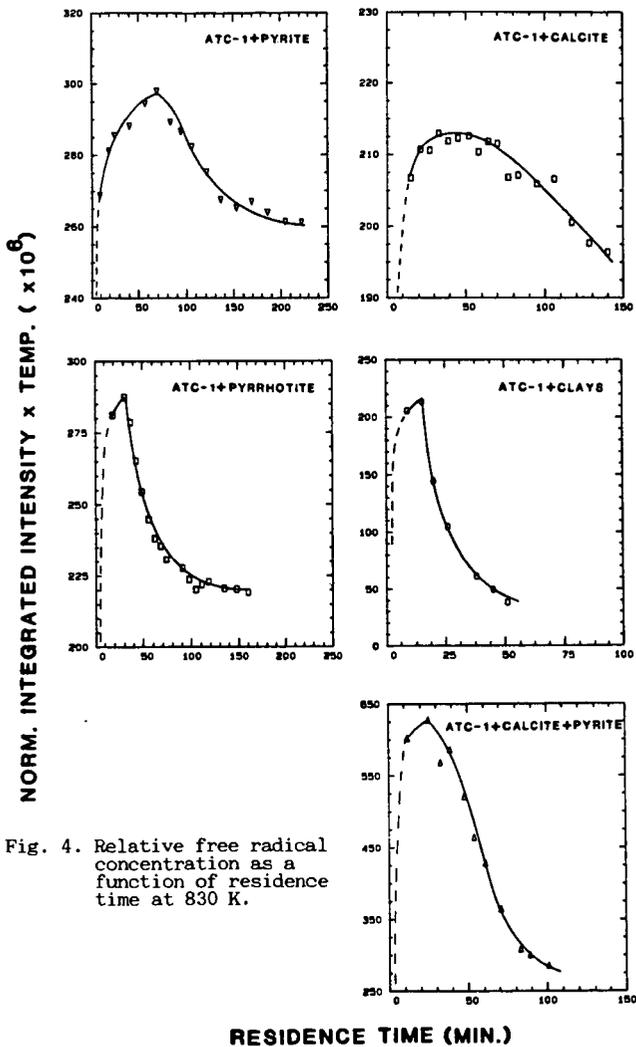


Fig. 4. Relative free radical concentration as a function of residence time at 830 K.

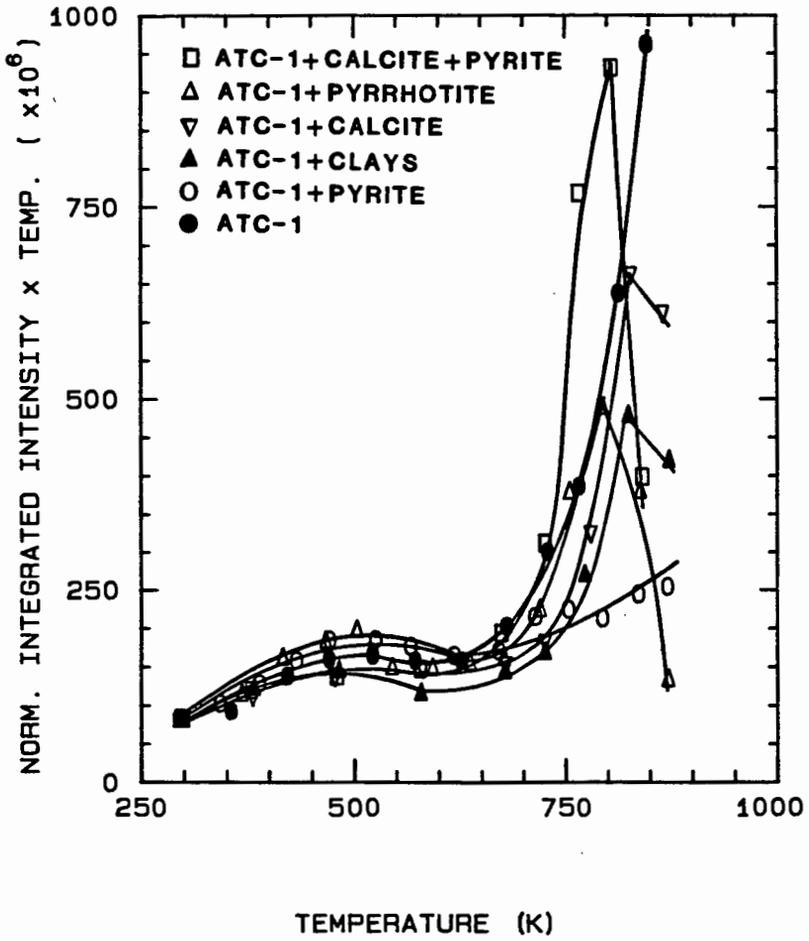


Fig. 5. Plot of IT vs. T for ATC-1 and ATC-1 + 8% various minerals.