Colorimetric studies of the reduction of Fe^{3+} by coal

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The reduction of Fe^{3+} by coal surfaces has been followed colorimetrically. The kinetics of the reaction in coals with a relatively high O/C ratio are sensitive to mild air oxidation, those having a low O/C ratio are relatively insensitive.

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On a fait appel à une méthode colorimétrique pour suivre la réduction du Fe^{3+} par des surfaces de charbon. Les cinétiques des réactions dans les charbons, avec un rapport relativement élevé de O/C, sont sensibles à une oxydation douce par l'air alors que celles avec un faible rapport O/C sont relativement insensibles.

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Introduction

Coal confronts chemists with formidable analytical problems. Defined as a rock consisting of more than 65% carbon by weight and constructed largely from plant material metamorphosed by time, temperature, and pressure in the earth's crust, it is essentially a non-repeating polymer of immense complexity. It remains a puzzle to organic and inorganic chemists alike since it is known to include in its structure virtually all the naturally occurring elements in the periodic table. It remains as the focus of intense study both because it is an interesting problem in its own right and because of its industrial importance. The value of coal increases significantly if it can be used to make coke for steel production. The coking properties of a given coal are usually inferred from optical reflectance data while thermal coal is usually valued on the basis of the degree of oxidation of the material. Both the coking and thermal properties of coal deteriorate more or less rapidly after mining for reasons that, while clearly related to air oxidation (so-called low-temperature oxidation), are poorly understood. The oxygen content is normally obtained from difference measurements and is generally regarded as being the least accurate value obtained in normal coal analysis. Surface-sensitive techniques usually yield O/C ratios that are higher than those obtained from bulk analysis. A simple chemical analysis that would be reflective of the O/C ratio would find wide utility in coal characterization.

Coal research is often frustrated by the variability of the parent material from mine to mine and often within a given coal seam. A series of coal samples representative of North American coal has been prepared as part of the Argonne Premium Coal Sample Program for use by researchers to insure a common set of starting materials. These samples, from which the coal samples used in this study were drawn, are described in detail elsewhere (1).

$Ba(OH)_2$ has been used as an indicator of ion-exchange sites, which could then be identified using scanning electron microscopy (2). Iron salts have been used to stain coal surfaces as an aid in optical and electron microscopy (3). We suggest that the development of blue colours on the coal surfaces following exposure to $Fe^{3+}/Fe(CN)_6{}^{3-}$ solutions results from oxidation of the coal surface by Fe^{3+} with the subsequent formation of a charge-transfer complex (prussian blue) $Fe^{2+}/Fe^{3+}(CN)_6{}^{3-}$. Since this complex absorbs strongly in the visible region the reaction can be followed by colorimetry of appropriate coal slurries. The kinetics of the Fe^{3+} reduction are a direct measure of the reactivity of individual coals with these reagents and may provide a means of predicting coal quality in specific industrial uses.

Experimental

Five 100 mesh Argonne Premium coal samples, Pocahontas, Stockton, Illinois no. 6, Wyodak, and North Dakota, chosen to give a wide range of O/C ratios (Table 1), were exposed with rapid stirring to 0.6 M $FeCl_3$ solutions having a pH of 2.6 at 30°C. The resulting slurry contained 3 g of coal per 100 mL. Approximately 1 mL of solution was withdrawn from the slurry at appropriate time intervals using a syringe fitted with a 0.8 μm filter. This solution was added to 10 mL 0.3 M $K_3Fe(CN)_6$, which served as an indicator due to the formation of $Fe^{2+}/Fe^{3+}(CN)_3{}^{3-}$ (prussian blue.) The progress of the reaction was followed by UV–VIS spectroscopy using the strong absorption line at 700 nm. The procedure was repeated with the same set of coal samples after they had been exposed to air at 105°C for 5 days, and with fresh coals that had been demineralized by soaking overnight in concentrated HCl.

A single sample was prepared by adding $K_3Fe(CN)_6$ directly to the coal–$FeCl_3$ slurry. The coal was withdrawn and the infrared spectrum of both fresh and exposed coal was obtained on KBr discs. In addition, X-ray photoelectron spectra (XPS) were obtained from coal surfaces after exposure to $FeCl_3$.

Results and discussion

The sample prepared by adding $K_3Fe(CN)_6$ directly to the coal–$FeCl_3$ slurry showed only minimal reduction of the Fe^{3+}. Since the $K_3Fe(CN)_6$ clearly acted as an inhibitor to the Fe(III) reduction we suggest that it adsorbed on the coal surface, blocking the reduction sites against further reaction. The IR

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TABLE 1. Fe^{3+} reduction rate 0–5 min

Coal	O/C	Rate fresh $\times 10^{-5}$ mol L^{-1} min^{-1}	Rate oxidized $\times 10^{-5}$ mol L^{-1} min^{-1}
Pocahontas (POC)	0.038	0.4	0.5
Stockton (WV)	0.10	1.3	0.73
Illinois no. 6 (IL)	0.14	4.3	3.9
Wyodak (WY)	0.26	5.3	2.6
North Dakota (ND)	0.29	8.0	0.9

TABLE 2. Fe^{3+} reduction rate 5–25 min

Coal	O/C	Rate fresh $\times 10^{-5}$ mol L^{-1} min^{-1}	Rate oxidized $\times 10^{-5}$ mol L^{-1} min^{-1}
Pocahontas (POC)	0.038	0.3	0.2
Stockton (WV)	0.10	0.3	0.2
Illinois no. 6 (IL)	0.14	0.9	0.6
Wyodak (WY)	0.26	1.0	Not observed
North Dakota (ND)	0.29	0	Not observed

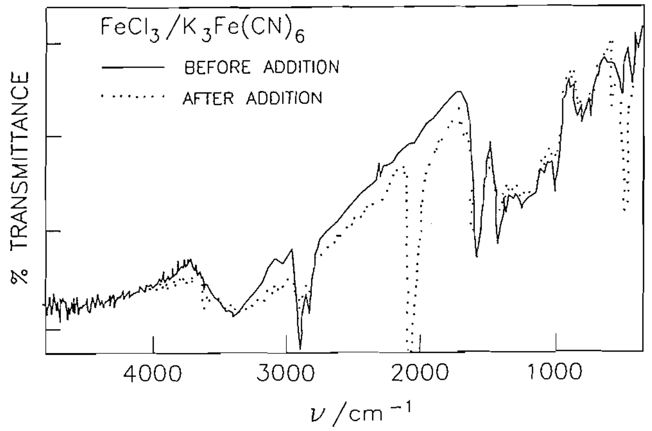

FIG. 1. IR spectrum of coal before and after exposure to $FeCl_3/K_3Fe(CN)_6$ solution.

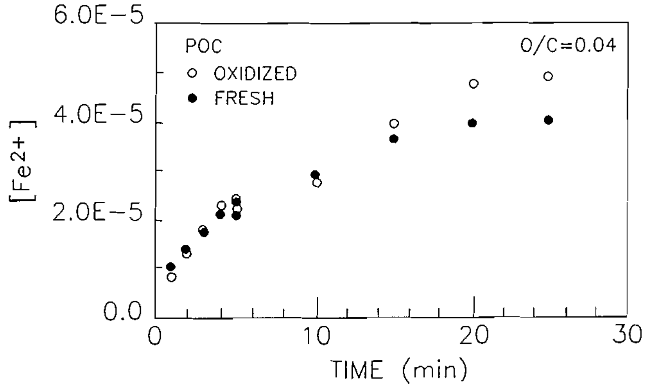

FIG. 2. $[Fe^{2+}]$ vs. time for Pocahontas coal before and after oxidation in air at 105°C.

spectra from this coal and untreated material are shown in Fig. 1. The intense absorption at around 2100 cm^{-1}, the C≡N vibration, in the treated sample that is resistant to reaction with Fe^{3+}, is consistent with the suggestion that CN^- adsorbs, possibly as $Fe(CN)^{3-}$, on active sites on the coal surface inhibiting reduction of Fe^{3+} species in the bulk slurry.

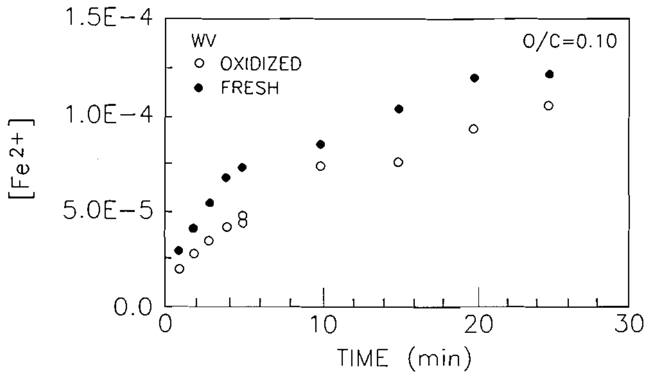

FIG. 3. $[Fe^{2+}]$ vs. time for Stockton coal before and after oxidation in air at 105°C.

The XPS spectrum shows several iron species including Fe_3O_4 (708.3 eV), Fe_2O_3 (711.1 eV), and FeO (709.5 eV). These results, coupled with the formation of prussian blue, would account for the suite of colours observed by Salehi and Hamilton (3).

The other results obtained are recorded in Tables 1 and 2 and are displayed in Figs. 2–6. The kinetics of Fe^{3+} reduction in this system cannot be fixed with certainty for several reasons. The first is purely mechanical: separation of the solution from the slurry requires rapid withdrawal of material through a fine mesh and therefore easily clogs the filter. Secondly, although a large excess of Fe^{3+} is used, thus ensuring pseudo-zero-order kinetics for iron, the nature and distribution of the reactive surface species (i.e., the concentration) is unknown and probably varies rapidly during the course of reaction. Finally, the possibility that Fe^{2+} is oxidized back to Fe^{3+} cannot be rigorously excluded. Nevertheless, the following analysis, which is meant to assess the relative reactivities of the coals studied, is internally consistent.

The two coals having the highest O/C ratios, Figs. 5 and

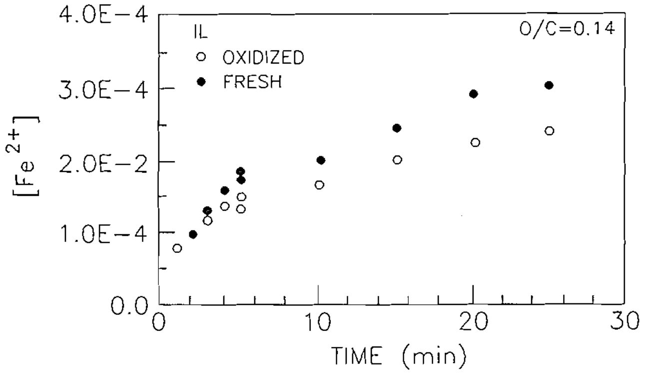

FIG. 4. $[Fe^{2+}]$ vs. time for Illinois no. 6 coal before and after oxidation in air at 105°C.

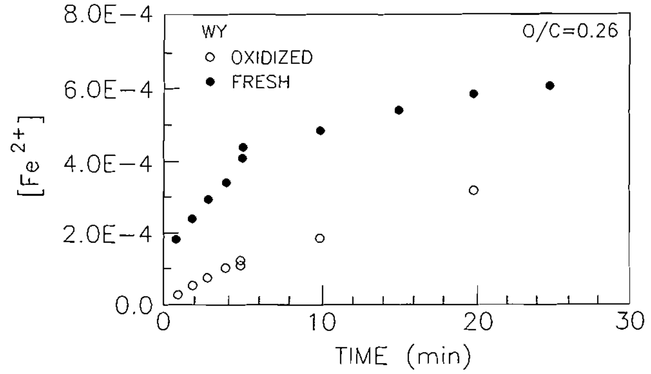

FIG. 5. $[Fe^{2+}]$ vs. time for Wyodak coal before and after oxidation in air at 105°C.

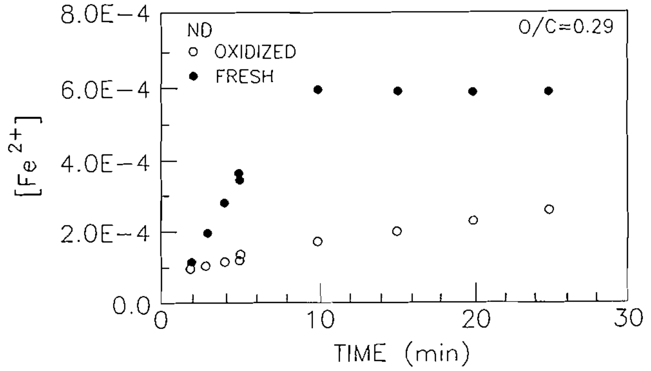

FIG. 6. $[Fe^{2+}]$ vs. time for North Dakota before and after oxidation in air at 105°C.

6, show two distinct reaction regimes, an initial fast reaction that appears to be close to completion after 5 min followed by a relatively slow reaction. These regions become progressively less distinct as the O/C ratio falls, Figs. 4, 3, and 2, and the fast reaction appears to be completely absent in the coal of lowest O/C, Pocahontas, Fig. 2. The fast reaction is probably due to reactive oxygen functional groups, which are more abundant in the coals of highest O/C ratio, while the slow reaction originates from less reactive oxygen species and (or) basic nitrogen groups (4). In an attempt to quantify these results, reaction rates (shown in Figs. 2–6) for the various coals were compared by taking the slope of the $[Fe^{2+}]$ vs. time plot between 2 and 4 min to avoid either forcing the data through the origin or biasing the results to later times in the reaction sequence. A second reaction rate was determined by taking the slope between 10 and 20 min. These data, together with the names and O/C ratios of the coals used are recorded in Tables 1 and 2. This relatively simple approach was chosen because a more sophisticated treatment is precluded by the scatter of the data and uncertainty about the concentration of the surface-reactive material, which can only be inferred from the O/C ratio. We refer to the two time regions as the fast and slow reactions, respectively, although this description is most appropriate for the North Dakota and Wyodak coals (Figs. 5 and 6). The lowest O/C coals, Pocahontas (Fig. 2), may well present a single continuous reaction while Stokton and Illinois (Figs. 3 and 4) appear to represent an intermediate case. The reaction rate for both regions is a clear function of the O/C ratio of the parent coal.

After air oxidation, the initial fast reaction is absent in the coals having the highest O/C ratio and appears to be much reduced in coals with intermediate O/C ratios (Figs. 2–6). There is little or no change in the initial reaction rate in the coal with the lowest O/C values. The slower reaction, i.e., that estimated from the slope after 10 min, appears to extend continuously into the "pre 5-min" region for the coals of highest O/C ratio after air oxidation (Figs. 5 and 6); for this reason we have chosen to describe this reaction simply as "not observed" in Table 2. The intermediate O/C coals (Figs. 3 and 4) still show a second process, while the lowest O/C material (Fig. 2) shows essentially one process. Thus the reactive sites may be divided into two classes, those sensitive to both air oxidation and oxidation by Fe^{3+} and those sensitive to oxidation by Fe^{3+} only. The standard reduction potential for the quinone/hydroquinone system is -0.7 V while that for Fe^{3+}/Fe^{2+} is 0.77; although the concentration of surface species is unknown, it is clear that oxygen-based organic functional groups are capable of reducing Fe^{3+} and that a continuous series of reactive sites having structures similar to the quinone system could be responsible for the behaviour we observe.

Mineral matter has been shown to be capable of reducing Fe^{3+}; however, there is no charge in kinetics after demineralization with concentrated HCl. Consequently, we do not believe that indwelling minerals play a significant role in iron reduction.

Conclusions

Fe^{3+} oxidizes coal and the reaction kinetics can be followed colorimetrically using $K_3Fe(CN)_6$ as an indicator. The formation of various iron oxides and $Fe^{2+}/Fe^{3+}(CN)_6^{3-}$ on the coal surface is responsible for the colours observed by Salehi and Hamilton (3) after treating coal with these reagents. Fresh coal having a relatively high O/C appears to exhibit two oxidation processes of differing kinetics. The differences between the two rates appear to be absent in coals having low O/C ratios and are more pronounced in coals with high O/C ratios. In any case the rates are a smooth function of the O/C ratio of the parent coal. Mild air oxidation effectively eliminates the first, more rapid, reaction, allowing the active species to be divided into two types, those oxidized by Fe^{3+} and air oxidation and those oxidized by Fe^{3+} only. The coal may thus be viewed as containing a series of functional groups of varying oxidation potential. The kinetics of Fe^{3+} oxidation of coal may provide a direct measure of coal quality in industrial applications.

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