Ronald R. Martin, Jinjiang Li
Department of Chemistry, University of Western Ontario
London, Ontario, Canada, N6A 5B7
J. Anthony MacPhee
CANMET/ERL, 555 Booth Street
Ottawa, Ontario, Canada, K1A 0G1

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ABSTRACT

Solutions of $FeCl_3/K_3Fe(CN)_6$ have been used to stain coal macerals. In this paper the development of a blue color in coal slurries in contact with $Fe^{3+}/Fe(CN)_6^{3-}$ resulting from oxidation of the coal by Fe^{3+} is used as a measure of the reactivity of the coal surface.

INTRODUCTION

Salehi and Hamilton[1] have used iron salts to stain coal surfaces as an aid in optical and electron microscopy. The authors did not speculate on the chemistry involved in the staining process. We suggest that the development of blue colors 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) between $Fe^{2+}/Fe(CN)_6^{3-}$. 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 and may provide a means of predicting coal quality in specific industrial useage.

EXPERIMENTAL

Five of the coals used were obtained from the Argonne Premium Coal Sample Program while an additional two coals, P851 and P832 were mid volatile bituminous coals from Western Canada, supplied by CANMET, Ottawa, Canada. All samples were 100 mesh.

Coal slurries were maintained at 30°C and stirred with a magnetic stir bar for periods ranging from five to twenty minutes. The slurries were then filtered to remove all solid matter. The resulting solutions were subjected to colorimetric analysis at 700 nm. Coal slurries were prepared in two different ways: a) 0.30 g of coal were added to a solution prepared by mixing 20 ml of 0.60 M $FeCl_3$ with 10 ml of 0.30 M K_3FeCN_6 - this method did not yield satisfactory results and was used only for one sample; b) 0.30 g of coal were added to 20 ml of 0.60 M $FeCl_3$. This slurry was filtered after reaction with the coal and 10 ml of 0.30 M $K_3Fe(CN)_6$, which served as an indicator of the Fe^{3+}/coal interaction, was added after filtration was complete.

RESULTS AND DISCUSSION

The coal P851 was used to test the two procedures used in preparing the coal slurries. Figure 1 shows the results obtained by procedure a) while Figure 2 shows the results from procedure b). The first procedure leads to little measurable reaction while the second yields a well defined increase in the concentration of Fe^{2+} with time. These results suggest that K^+, $Fe(CN)_6^{3-}$ and/or the $Fe^{2+}/Fe(CN)_6^{3-}$ complex are strongly adsorbed on the coal surface and prevent further reaction of Fe^{3+} with the coal surface. The $Fe^{2+}/Fe(CN)_6^{3-}$ seems to be the most likely explanation since Salehi and Hamilton observed a blue stain on coal surfaces after rinsing and drying coal surfaces identical to those used in preparing the coal slurries in procedure a). Accordingly procedure b) was used throughout the remainder of this study.

Figures 3-7 show the increase with Fe^{2+} concentration with time as well as the reaction rate obtained from the slope of this plot. In the case of the North Dakota coal only the first two points were used since the graph shows an initial fast reaction followed by a plateau with little further reaction. Figure 8 shows a plot of reaction rate vs O/C ratio for each of the Argonne coals.

It is clear that each coal yields a reaction rate which is strongly correlated with O/C ratio. The North Dakota coal shows an initial fast reaction while the other coals have an apparent non-zero intercept for Fe^{2+} in the Fe^{2+} vs time plot. This result may be due to an initial rapid reaction or to Fe^{2+} present in the coal prior to reaction.

CONCLUSIONS

Fe^{3+}, from $FeCl_3$, in solution oxidizes coal surfaces and the resulting Fe^{2+}/Fe^{3+} charge transfer complex may be used as an indicator of the extent of reaction when Fe^{3+} is introduced as $Fe(CN)_6^{3-}$.

The $Fe^{2+}/Fe(CN)_6^{3-}$ is strongly adsorbed on the coal surface and inhibits further reaction. The kinetics of the Fe^{3+} reduction can be followed colorimetrically if $K_3Fe(CN)_6$ is added to solutions obtained from coal slurries in contact with $FeCl_3$.

The kinetics of Fe^{3+} reduction can be correlated with the O/C ratio in the coal.

REFERENCE

1. MORTAZA R. SALEHI and LLOYD H. HAMILTON. Surface-reaction of Australian coal macerals and coke by iron salts: an aid in microscopy. Fuel, 1988, 67, 296-297.

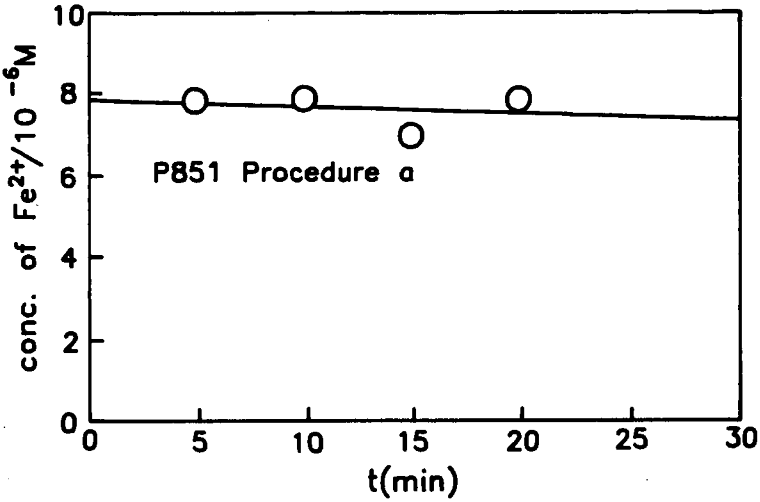
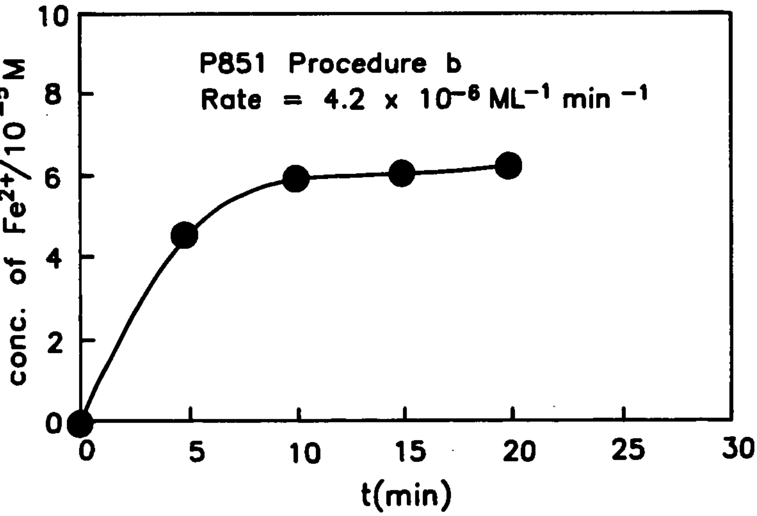


Figure 1



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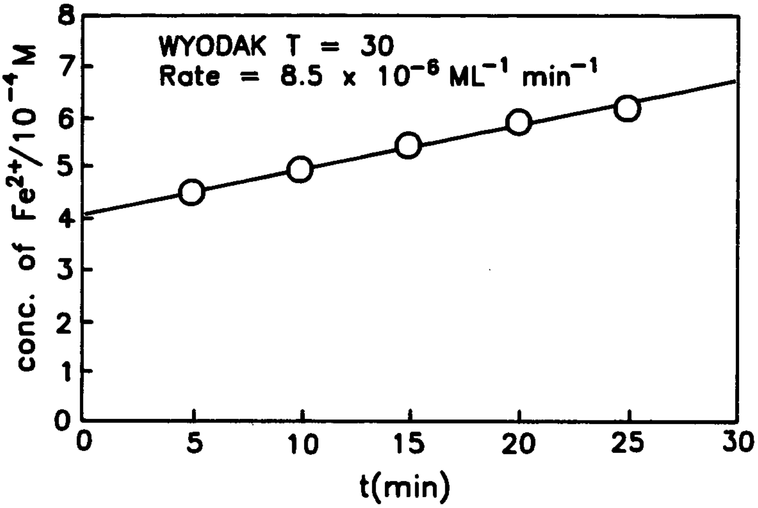

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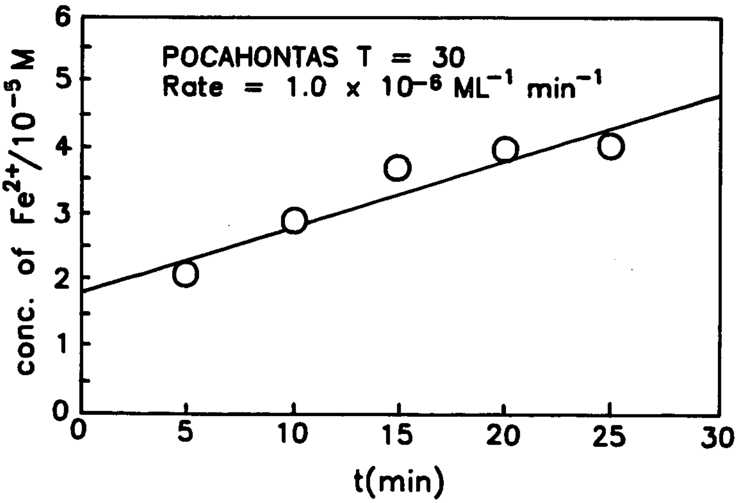

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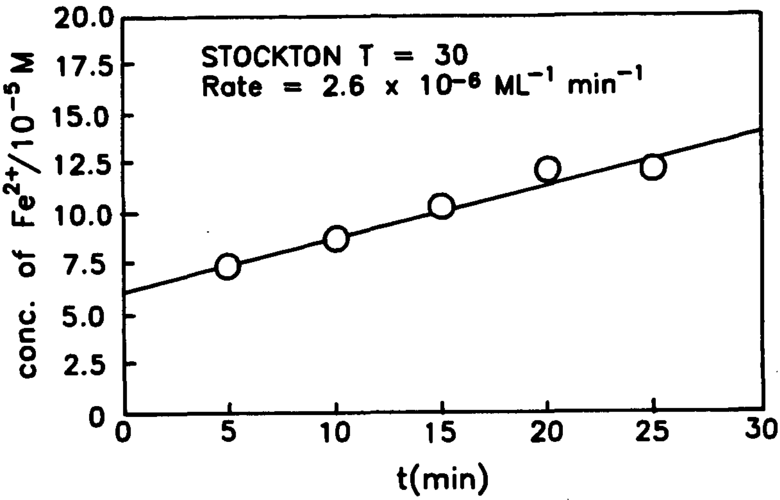

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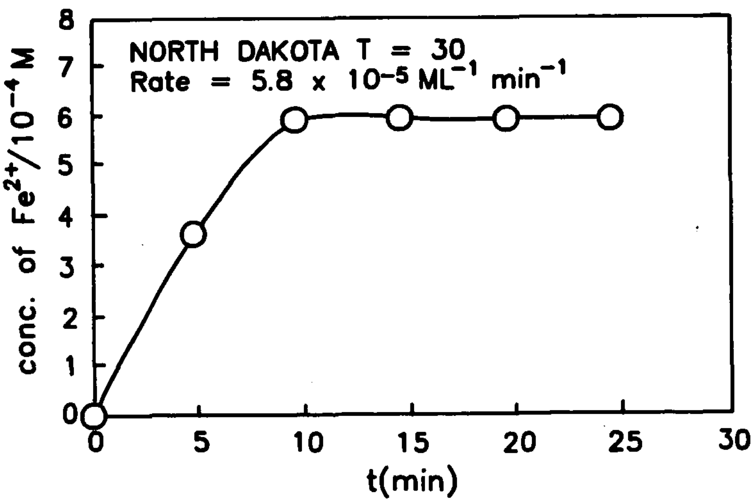

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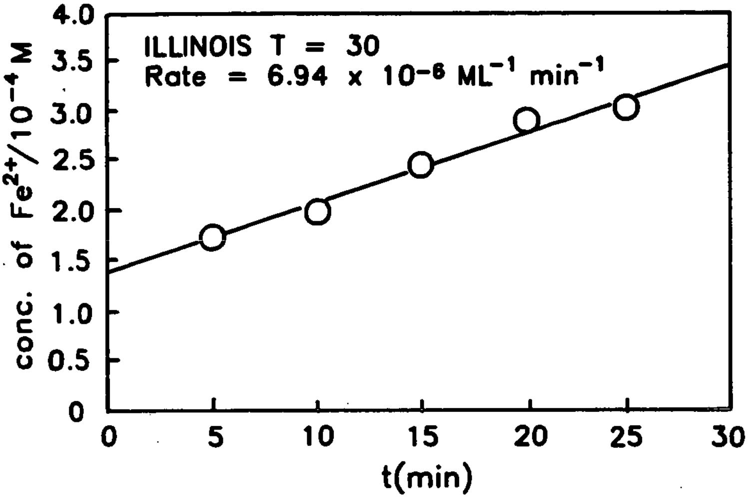

Figure 7

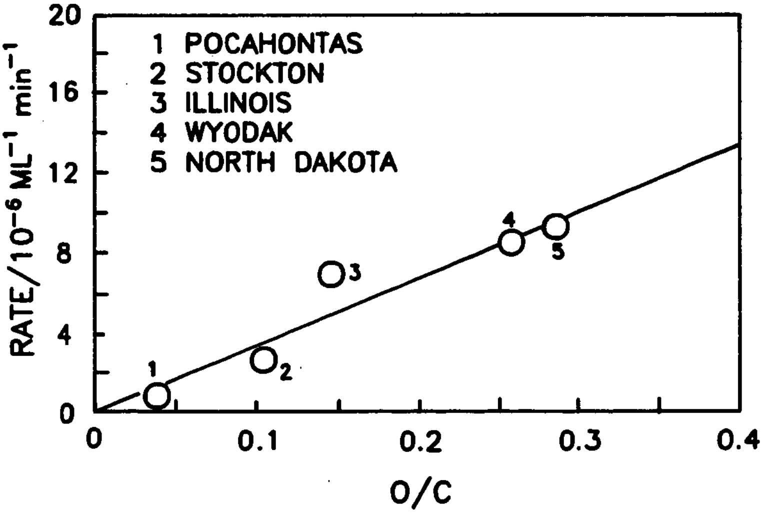

Figure 8