THIN SECTION MICROSCOPIC STUDIES OF THE DIFFUSION OF OXYGEN INTO COAL AT ELEVATED TEMPERATURES

D. Brenner

Corporate Research Science Laboratories
Exxon Research and Engineering Company
P.O. Box 45, Linden, N. J. 07036

Introduction

The oxidation of coal is important to a range of coal technologies. These include oxidation of lignites in storage piles, which can cause spontaneous combustion, the detrimental effect of oxidation on liquid yields in liquefaction and on the coking properties of metallurgical coal, and the use of oxidation to inhibit the swelling of coal in both liquefaction and gasification processes. Optical microscopy has been an important means of investigating oxidation in coal for many years. Such studies generally involve the observation of polished surfaces of coal using reflected light. Immersion oil is also normally used to increase the contrast between the various components of the coal. A number of studies of coal oxidation using reflectance microscopy have been reported. Peters and Jüntgen (1) observed oxidation borders around particles of coal exposed to oxygen at 230°C. They also developed mathematical equations to describe the rate of widening of these oxidation borders from the surface towards the center of a coal particle. Other reflectance studies on oxidized or weathered coals have been reported by Chandra (2), Benedict and Berry (3) and Goodarzi and Murchison (4).

Transmitted light optical microscopy employing thin section samples is also used in the study of coal. Because of the high light absorption of coal, these samples must be less than about 20 micrometers thick. Thin section microscopy of coal was common some 40 years ago. In particular, Thiessen (5) and other workers at the U.S. Bureau of Mines used this technique extensively. However, although some workers continue to use thin section techniques to study coal, since the 1950's reflected light microscopy of coal using polished surfaces and immersion oil has become predominant. Reasons for this include ease of preparation of the samples and the ability to readily obtain quantitative data from measurements of the reflectivity of the coal surface. There are a few references to the use of thin sections for the study of thermally metamorphized coals, such as the work by Marshall (6), but no references to the use of transmitted light microscopy for the study of coals oxidized at elevated temperatures have been found. In the present study it was discovered that transmitted light microscopy using thin section samples of coal was far more sensitive to the effects of oxidation than the conventional reflected light microscopy of coal. In the present investigation thin section samples are utilized to study the pathways for rapid penetration of oxygen into coal.

Experimental

Illinois #6 coal was ground and sieved to obtain a 20 X 30 U.S. mesh cut. This sample was washed of fines in distilled water and then dried overnight in vacuum at 120°C. It was then stored in nitrogen at room temperature. The samples were oxidized at atmospheric pressure in a Perkin-Elmer TGS-2 thermogravimetric analyzer. The gas consisted of 1 mole per cent oxygen in argon. The samples described in this study were heated at 160°C per minute to 365°C and held at that temperature for 15 minutes unless otherwise noted. They were then cooled rapidly.

The oxidized coal particles were embedded in epoxy, and thin section samples were prepared using procedures similar to those described by Ting (7). A Leitz Ortholux II-Pol BK microscope was used for observing the samples and a Wild photoautomat MPS 50 automatic 35 mm camera system was used for taking photomicrographs with Kodak High Speed Ektachrome ASA 400 daylight film. The color slides were converted to black and white prints for this paper.

Results and Discussion

A part of a thin section of an oxidized coal particle is shown in the transmitted light photomicrograph of Figure 1. This specimen, of relatively uniform vitrinite, has a thin oxidation border around its periphery. The border, which is about four micrometers thick, is unusally uniform; this is indicative of the homogeneity of this particular piece of coal. The narrowness of the border shows that the diffusion of the oxygen into the homogeneous vitrinite is quite slow.

An internal region of a sample of vitrinite, which was oxidized at 365°C for three minutes, is shown in Figure 2. The sample is permeated by a number of cracks and holes. The dark areas bordering these regions are oxidized. This shows that cracks and holes are pathways for rapid penetration of oxygen into the coal structure. Around some of these regions the oxidation borders are thin, much as they were at the surface of the particle in Figure 1. However, around most of the holes and cracks there are massive blackened areas. In these regions the vitrinite has become microporous permitting rapid penetration by the oxygen.

The darkened oxidation regions in these coal particles are not a consequence of localized heating of the coal or pyrolysis. There are several reasons why localized heating would not be a problem:

(a) The oxygen concentration in the surrounding gas is quite low, only 1.0 mole per cent,

(b) Oxidation occurs along deep cracks and at other spots deep within the coal, as well as at the surface. This indicates that the oxidation is not appreciably enhanced by temperature gradients from the surface to the interior of the particles,

(c) Many of the oxidation borders are quite narrow, so the temperature gradients across them must be quite small,

(d) When this coal is heated in the absence of oxygen to more than 20°C higher than the temperatures used in this experiment, no blackening effects such as those caused here by oxidation are observed,

(e) The temperature of the coal in this experiment was carefully controlled and the sample size was only about 20 mg,

(f) Finally, similar darkening effects due to oxidation were observed in coal which was oxidized at temperatures as low as 150°C.

In Figure 3 exactly the same region of the same particle as was shown in Figure 2 is again shown, except this time it is viewed in reflected light using immersion oil. Many of the oxidized areas are not readily evident. This shows that transmitted light microscopy of thin sections is a far more sensitive technique for studying the effects of oxidation of coal at elevated temperatures than is reflectance microscopy.

A section of coal containing a circular maceral is shown in Figure 4. This maceral, which is classified as a "resin rodlet" is a type of vitrinite. Resin rodlets appear to quite homogeneous and they apparently have very little porosity. This is illustrated in Figure 4 where almost the whole interface between the resin rodlet and the common type of vitrinite is darkened by oxidation; but although the oxidation extends well into the common vitrinite material, there is almost no penetration of the resin rodlet.

The overall sample in Figure 4 is somewhat heterogeneous as can be seen from the variations in the lightness of the material (apart from oxidation). This heterogeneity is probably the reason for the rather high degree of penetration of oxygen

into this particle (the blackened regions) both in interior regions and at the surface (for example, compare this particle with the one in Figure 1). Note that some parts of the surface of this particle have a very narrow oxidation border--such as just below the large crack--whereas around most of the surface there is substantial penetration. These variations are indicative of the heterogeniety of this particle. Also, note that the oxidation border along the large crack is narrow from its mouth up to about half way along its length, but the end region of the crack has a massive oxidized area around it. Large oxidized areas around the ends of cracks are quite common; they are probably a result of the fracture mechanism (or the termination of fracture propagation) in the coal. It is likely that a multitude of microfractures are formed at the tip of the propagating crack due to the stresses created in the fracture process. These microfractures broaden the region of stress concentration around the crack tip and thereby terminate crack propagation.

A sample of coal containing a considerable amount of liptinite material is shown in Figure 5. The liptinite is the lighter bands in the photomicrograph. Some of the liptinite is derived from spore walls and possibly some of it is resinous material. It is clear from this photomicrograph that the oxygen only penetrates the liptinite regions slowly (in the absence of cracks). The penetration appears to be no faster than for the adjacent vitrinite regions. Even where oxygen penetrated across one of the liptinite macerals at the top of the photomicrograph (probably along a crack), the further diffusion of oxygen into the maceral was slow. There is no indication of oxygen penetration at the interface between the liptinite and vitrinite bands. This indicates very intimate bonding between these macerals. However, there does appear to be penetration of oxygen (darkened diffuse lines) at the interfaces between some rectangular vitrinite macerals in the left-middle part of the figure and the larger bands of vitrinite in which they are contained.

Only a small fraction of the pieces of coal observed in this study at 365°C showed the formation of vacuoles (i.e. swelling). Figure 6 is a photomicrograph of one of the pieces containing a vacuole. The particle has a thin border of oxidized material at the surface but there is no trace of oxidation on the interior border of the vacuole. This indicates that either there were no sizable pathways to the surface of the coal particle, or if there were such pathways, gases escaping from the vacuole prevented significant counter diffusion of oxygen. With respect to this latter possibility, it should be noted that cracks in the coal which have an opening on the surface invariably have an oxidation border in spite of any gases being released from the coal--this even includes very long and very narrow microcracks. On the other hand, a vacuole has far more surface area to take up any oxygen which enters it than does a crack. It is interesting that in spite of the large vacuole in this particle, no distortion of the surface of the particle is evident. This suggests that the oxidation rim has a strong reinforcing and stabilizing effect on the surface of the particle.

A heterogeneous region of vitrinite material is shown in Figure 7. On the left side of this photomicrograph are some resin rodlets embedded in striated (thin bands) vitrinite. In this disrupted region of the coal, substantial penetration of oxygen (the black areas) is found. The oxidation tends to follow along the striations indicating poor contact or bonding at the interfaces between the different macerals. However, in many particles which have a relatively regular banding pattern, penetration of the coal structure has been observed to be slight.

A sample of relatively homogeneous vitrinite with several pieces of pyrite embedded in it is shown in Figure 8. This photomicrograph utilized a combination of transmitted light and reflected light on a thin section sample. The light spots in the coal are the pyrite, the diffuse dark regions are the oxidized areas. In transmitted light alone the pyrite would be black, so the pyrite could be distinguished from an oxidized region only by its shape or by its sharp border (as contrasted with the diffuse borders of oxidized regions). In Figure 8, however, the area around the pyrite has been oxidized so use of reflected light was necessary in order to see the interface between the pyrite and the oxidized regions of the vitrinite. In samples that contained particles of pyrite it was often found that the area around the pyrite was oxidized such as was seen in Figure 8--especially if the pyrite was near the surface of the particle. Apparently the interface between the pyrite and the vitrinite

is porous or perhaps the particles of pyrite have porous structures.

In addition to the studies of oxidation described above using an exposure temperature of 365°C, observations were made recently on samples oxidized at temperature as low as 150°C. Even at 150°C oxidized regions of the coal were readily observable in thin section samples as darkened areas. These results are in contrast to reflectance studies of coal oxidation where oxidation rims have not been observed for exposure temperatures below 170°C and where detection of oxidation is extremely difficult even for an exposure temperature of 200°C (8).

Conclusions

Transmitted light optical microscopy using thin section samples has been found to be substantially more sensitive to regions of coal oxidized at elevated temperatures than conventional reflected light coal microscopy. This higher sensitivity enables detection of mild oxidation which would go undetected in reflectance observations. It also allows study of the locations of oxidation in greater detail than is possible with reflectance microscopy. It was found that major pathways for rapid penetration of oxygen into coal particles included maceral interfaces, heterogeneous or disrupted microstructures, and mineral matter, as well as cracks and holes. Penetration of oxygen into coal was slow in homogeneous vitrinite and in the observed liptinite macerals. Penetration was particularly slow in resin rodlets. The pathways for penetration of coal by oxygen are probably also relevent to the penetration of coal by other gases, vapors, and even liquids.

Acknowledgements

The author acknowledges the excellent technical assistance of Mark S. Beam in carrying out the oxidation treatments and the preparation of samples.

References

1. Peters, Von W., and Jüntgen, H., Brennstoff-Chemie 46(2), 56 (1964).

2. Chandra, D., Econ. Geol., 53, 102-108 (1958).

3. Benedict, L. G., and Berry, W. F., Coal Sci., Adv. Chem. Ser. 55, 577-601 (1966). Published by Am. Chem. Soc., Washington, D. C. (1966).

4. Goodarzi, F., and Murchison, D. G., Fuel, 52, 164, (1973).

5. Thiessen, R., U.S. Bur. of Mines Tech. Paper 564 (1935).

6. Marshall, C. E., Fuel, 24, 120, (1945).

7. Ting, F. T. C., Analytical Methods for Coal and Coal Products, edited by C. Karr Jr., Volume I, Chpt. 1, (1978). Published by Academic Press, New York.

8. Chandra, D., Stach's Textbook of Coal Petrology, 164, (1975). Published by Gebrüder Borntraeger, Berlin, 1975.

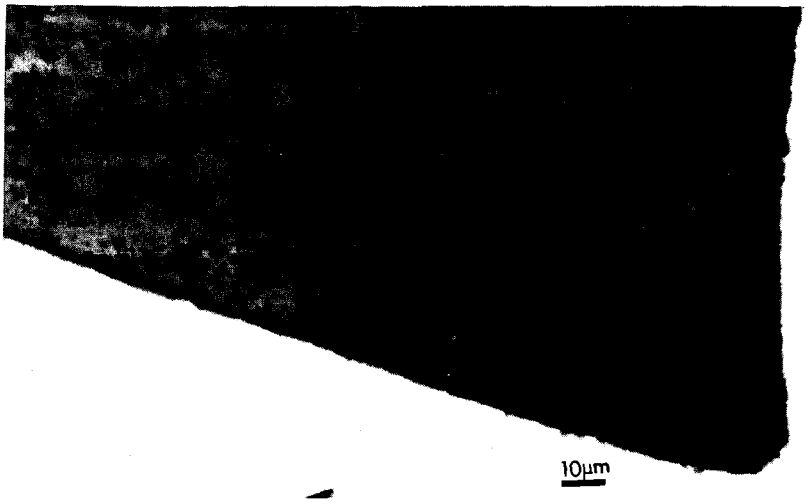

Fig. 1. Thin oxidation border around relatively homogeneous vitrinite

Fig. 2. Internal oxidation around cracks and holes and in micro-fissured regions

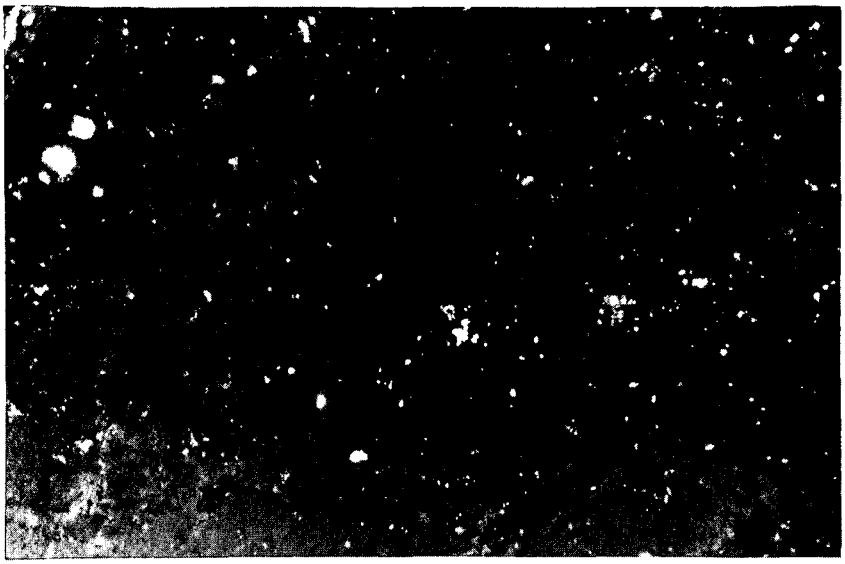

Fig. 3. Reflected light illumination using immersion oil of same area as was shown in Fig. 2

Fig. 4. Oxidation at a maceral interface, but with very little penetration of a resin rodlet

Fig. 5. Slow oxygen penetration into liptinite macerals with no observed penetration along the liptinite-vitrinite interface

Fig. 6. Vacuole with no oxidation along its interior surface

Fig. 7. Extensive oxidation in heterogeneous regions in a particle of coal

Fig. 8. Oxidation around pyrite granules as observed in combined transmitted and reflected light