COAL WEATHERING: CAUSES, EFFECTS AND IMPLICATIONS

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INTRODUCTION

If it is meaningful to single out one characteristic of coal as having unique importance, that designation would have to go to the dynamic nature of coal's chemical and physical properties. The chemical and physical properties of coal can and often do undergo substantial changes after removal of the coal from its natural environment. This phenomenon is known as weathering and can alter the coal's calorific value, beneficiation, coking, liquefication, and gasification characteristics. Weathering also influences standard tests and other experimental results, and thus has important implications with respect to fundamental research on the structure and properties of coal. This short review focuses on the incomplete state of our knowledge of the causes, effects and implications of coal weathering.

CAUSES AND EFFECTS OF COAL WEATHERING

Weathering commences once the coal is unearthed and/or removed from the coal seam unless precautions are taken to prevent its exposure to oxygen (air) and changes in temperature and humidity. The exposure of coal to and its subsequent reaction with the oxygen in air is recognized as the most important contributor to weathering. The reaction of the coal with oxygen occurs readily at ambient temperature, results primarily in oxidation of the coal's organic constitutents, and leads to an increase in the oxygen content and a decrease in the atomic hydrogen-to-carbon ratio of the coal (1-5).

The general outlines of the oxidation of coal's organic constituents by oxygen have been well characterized. Peroxides have been detected as transient intermediates in the early stages of coal oxidation (3,6,7), and it is generally thought that decomposition of the peroxides leads to creation of the new oxygen-containing functional groups (3,6-13). The formation of hydroxyl, carbonyl and carboxyl groups, and ether linkages have been detected or inferred from wet chemical and spectroscopic data (4,7,12-21). In general, the chemical structural changes that accompany coal's oxidation at low temperatures (from ambient to 200°C) by molecular oxygen are strongly dependent upon coal rank, particle size, oxygen partial pressure, moisture content, and temperature (1-5,17,22,23). Considerable uncertainty still exists, however, concerning the mechanisms whereby the peroxides are formed and subsequently decompose.

Perhaps the most elusive aspect of the reaction of coal with oxygen has been identification of the initiation reaction, the step by which the oxidation reaction gets started. Although the oxygen molecule has two unpaired electrons, one on each oxygen atom, and behaves as a diradical (•O-O•) it is too unreactive to be the species which actually oxidizes the coal. However, the fact that coal already contains substantial concentrations of carbon radicals (12,24-26) suggests the possibility that initiation may occur by reaction between molecular oxygen and a carbon radical in the coal to form a peroxy radical (Coal-OO•). The peroxy radical could then serve as the initiator for free radical chain reactions which lead to peroxides and their decomposition products. The evidence for free-radical chain processes for the decomposition of the peroxides, however, is not unequivocal. Since water, a protic solvent, is invariably present in coal and has been observed to facilitate the oxidation of coal by oxygen (2,3,5,22,23) the decomposition of the intermediate peroxides might also occur, at least in part, via ionic reaction mechanisms (27). Clearly, many of the mechanistic aspects of the oxidation of coal by oxygen remain unresolved and present challenging problems for further exploration.

The reaction of coal with oxygen is also notorious for its idiosyncrasies. One of these is that the thermoplastic properties of bituminous and subbituminous coals are often extensively altered long before changes can be detected in the coal's chemical composition (1,2,5,28,29). In general, exposure of the coal to oxygen at ambient temperature can result in a very rapid reduction in the fluidity that it exhibits when heated and a significant narrowing of its plastic temperature range (5,10,28-30). The loss of the coal's thermoplastic properties suggests that a more highly cross-linked macromolecular structure has been formed which will not easily melt and flow when heated. However, the exact nature of the changes that occur in the coal's macromolecular structure which adversely affect its thermoplastic properties remain points of considerable uncertainty and interest.

The weathering of coal's inorganic constituents, in sharp contrast to the situation with coal's organic constituents, is quite well understood. Except for the iron bearing mineral pyrite which is readily air-oxidized, the coal's inorganic constituents apparently remain unchanged by weathering (31-33). The pyrite in coal is oxidized initially to iron sulfates, which are then transformed to iron oxyhydroxide (33). Pyrite oxidation, as expected, is accelerated by increasing humidity, temperature, and oxygen partial pressure. Although oxidation of the coal's organic and inorganic constituents occur simultaneously, they are generally regarded as quite separate processes.

Another contributor to weathering is the stresses caused by cyclic sorption and desorption of moisture which produce fissures and cracks that mechanically weaken the coal (2,5,34). This decrepitation phenomenon is referred to as slackening. The thermal cycling of coal also contributes to slackening. Slackening is much more rapid and extensive for lignites and subbituminous coals than for higher rank coals (5,34). Slackening can also accelerate oxidation by increasing the exposed surface area of the coal to air. Although oxidation can be accelerated by slackening, its possible participation in and importance to slackening has not been stressed or studied. The oxidation of coal's organic constituents could participate in slackening through the creation of new hydrophilic sites which would promote moisture sorption.

TECHNOLOGICAL ASPECTS OF COAL WEATHERING

The changes in coal's chemical and physical properties produced by weathering may affect the suitability of the coal for existing and future technological uses. Coal's major domestic uses include: direct combustion for electricity generation and for industrial process heat, steam and power generation; and conversion to coke for steel production (35). Coal-based synthetic fuel (gas and liquid) and chemical technologies are currently under development. Coal-water and coal-oil slurries are also being investigated as potentially economical means of converting solid coal into a form suitable for transport through pipelines and use as a liquid-like fuel.

Oxidation reduces the calorific value of coal. Low rank coals will lose about 190 Btu-per-pound for each 1% increase in oxygen content while high rank coals will lose about 240 Btu-per-pound for each 1% increase in oxygen content (34). The oxygen content of freshly mined and crushed lignite coals can increase several percent in a matter of weeks when the coal is stored in air at ambient temperature. Such rapid oxidation can lead to spontaneous combustion of the coal under certain storage conditions (34,36).

Oxidation also converts coal to a more hydrophilic material which makes beneficiation more difficult. The purpose of beneficiation is to upgrade the quality of the coal so that it can meet specific end-use requirements. Beneficiation is primarily carried out to reduce the mineral matter (including pyrite) and clay content of the coal. Oxidation reduces the hydrophobicity-hydrophilicity differences between coal's organic constituents and mineral matter which, in turn, makes it more difficult to selectively separate mineral matter particles on the basis of their hydrophilic surface properties (37-39). This results in a reduction in the efficiency of beneficiation by flotation, agglomeration and flocculation processes.

The new oxygen-containing functional groups that are created when the coal is oxidized also increase its adsorptive affinity for polar molecules such as water as well as its water solubility (40-42). Hence, the dewatering and drying of coal becomes more energy intensive and less efficient as the coal's degree of oxidation increases. The stability and viscosity of coal-water and coal-oil slurries would also be affected by the more polar surface properties of particles of oxidized coal. Additionally, the peroxides produced during coal oxidation could potentially have a detrimental affect on the stability and viscosity of coal-oil slurries.

The detrimental effects of oxidation on a coal's suitability for producing high-quality metallurgical coke have been extensively studied (1,2,5,16,28,43) and are well understood from a practical viewpoint. The adverse effects include reduction in coke strength, coal bulk-density-control problems, overheated charges, carbon deposits leading to oven damage, coke handling problems, and reduced coke yields as a result of increased coke breeze, increased coke reactivity and decreased coking rate (1,2,5,16,43). One important effect of oxidation is to destroy the coal's thermoplastic properties which, in turn, prevents its organic components from adequately fusing and binding together during the coking process. This results in a reduction in coke strength and yield.

The effects of oxidation on coal's behavior during thermal processing can be predicted to be profound but have not been extensively investigated. The new oxygen-containing functional groups that are created when the coal is oxidized will lead to increased yields of carbon monoxide and carbon dioxide at the expense of tar and/or liquid yields during gasification, liquefaction, pyrolysis, and thermal depolymerization in non-hydrogen-donating solvents (1,2,4,43-47). The increased cross-linking of coal's macromolecular structure that accompanies oxidation will also reduce its swelling during heating, extractability by organic solvents, and tend to increase the molecular weight distribution of the extractable material and low-temperature pyrolysis tars (1,2,46,47). An enhancement of char surface area (by a factor of up to 10) and gasification reactivity (by a factor of up to 40) has also been observed as a consequence of the preoxidation of bituminous coals (48).

CONCLUSIONS

The changes brought about by weathering that affect the suitability of coal for existing and future technological uses have a very definite molecular basis. At a molecular level, however, we are for the most part at a very primitive level of understanding of the weathering process. In spite of the recent research interest that has been shown in this important phenomenon, insufficient definitive experimental data exist to permit a detailed mechanistic description to be written which accounts for this phenomenon's complexities and idiosyncrasies. The complexity of the coal itself contributes significantly to the experimental difficulties. Hence, progress in elucidating the mechanistic details of weathering will require a more aggressive approach and help from many disciplines.

REFERENCES

1. L. D. Schmidt, J. L. Elder, and J. D. Davis, Ind. & Eng. Chem., 32, 548 (1940).

2. L. D. Schmidt, in Chemistry of Coal Utilization, vol. 1, H. H. Lowry, ed., John Wiley & Sons, Inc., 627 (1945).

3. R. E. Jones and D.T.A. Townend, J. Soc. Chem. Ind., 68, 197 (1949).

4. J. D. Brooks and T. P. Maher, Fuel, 36, 51 (1957).

5. R. J. Gray, A. H. Rhoades, and D. T. King, Trans. ASME, AIME, 260, 334 (1976).

6. R. E. Jones and D.T.A. Townend, Nature, 155, 424 (1945).

7. R. Liotta, G. Brons, and J. Isaacs, Fuel, 62, 781 (1983).

8. H.A.W. Van deVries, C. Bokhoven, and K.N.M. Dormans, Brennstoff-Chemie, 50, 289 (1969).

9. G. Albers, L. Lenart, and H. Oelert, Fuel, 53, 47 (1974).

10. H. M. Wachowska, B. N. Nandi, and D. S. Montgomery, Fuel, 53, 212 (1974).

11. E.A.C. Chamberlain, G. Barrass, and J. T. Therlaway, Fuel, 55, 217 (1976).

12. T. Yokono, K. Miyazawa, Y. Sanada, and H. Marsh, Fuel, 60, 598 (1981).

13. J. C. Donini, S. A. LaCour, B. M. Lynch, and A. Simon, Proc. 64th CIC Coal Symp., 132 (1982).

14. M. G. Rockley and J. P. Devlin, Appl. Spectrosc., 34, 407 (1980).

15. P. C. Painter, M. M. Coleman, R. W. Snyder, O. Mahajan, M. Komatsu, and P. L. Walker, Jr., Appl. Spectrosc., 35, 106 (1981).

16. D. E. Lowenhaupt, P. R. Griffiths, M. P. Fuller, I. M. Hamadeh, Proc. Ironmaking Conf., 41, 39 (1982).

17. D. C. Cronauer, R. G. Ruberto, R. G. Jenkins, A. Davis, P. C. Painter, D. S. Hoover, M. E. Starsinic, and D. Schlyer, Fuel, 62, 1124 (1983).

18. P. B. Tooke and A. Grint, Fuel, 62, 1003 (1983).

19. J. R. Havens, J. L. Koening, D. Kuehn, C. Rhoads, A. Davis, and P. C. Painter, Fuel, 62, 936 (1983).

20. D. L. Perry and A. Grint, Fuel, 62, 1024 (1983).

21. A. Grint and D. L. Perry, Proc. Intl. Conf. Coal Sci., 655 (1983).

22. D. C. Cronauer, R. G. Ruberto, R. S. Silver, R. G. Jenkins, I.M.K. Ismail, and D. Schyler, Fuel, 62, 1116 (1983).

23. E. Beier, Proc. Intl. Conf. Coal Sci., 735 (1983).

24. H. Ohuchi, M. Shiotani, and J. Sohma, Fuel, 48, 187 (1969).

25. J. W. Larsen, J. Clardy, A. Davis, R. C. Neavel, H. L. Retcofsky, and H. W. Sternberg, in Scientific Problems in Coal Utilization, B. R. Cooper, ed., U.S. DOE Technical Information Center, 93 (1978).

26. A. G. Sharkey, Jr. and J. T. McCartney, in Chemistry of Coal Utilization, 2nd Supplemental Volume, M. A. Elliott, ed., Wiley-Interscience, 241 (1981).

27. R. Curci and J. O. Edwards, in Organic Peroxides, D. Swern, ed., Wiley-Interscience, 199 (1970).

28. B. S. Ignasiak, B. N. Nandi, and D. S. Montgomery, Fuel, 49, 214 (1970).

29. D. L. Marchioni, Intl., J. Coal Geol., 2, 231 (1983).

30. D. J. Maloney, R. G. Jenkins, and P. L. Walker, Jr., Fuel, 61, 175 (1982).

31. F. E. Huggins, G. P. Huffman, D. A. Kosmack, and D. E. Lowenhaupt, Intl. J. Coal Geol., 1, 75 (1980).

32. F. E. Huggins, G. P. Huffman, and R. J. Lee, Coal and Coal Products: Analytical Characterization Techniques, E. L. Fuller, Jr., ed., ACS Symp. Series No. 205, 239 (1982).

33. F. E. Huggins, G. P. Huffman, and M. C. Lin, Intl. J. Coal Geol., 3, 157 (1983).

34. J. F. Fryer and A. J. Szladow, in Storage of Coal Samples, Info. Series No. 66, Alberta Research Council, 1 (1973).

35. H. Perry, Science, 222, 377 (1983).

36. J. R. Herring and R. J. Rich, Intl. Conf. Coal Sci., 753 (1983).

37. H. A. Hamza, K. H. Michaelian, and N. E. Andersen, Intl. Conf. Coal Sci., 248 (1983).

38. H. B. Gala, S. H. Chiang, G. E. Klinzing, J. W. Tierney, and W. W. Wen, Intl. Conf. Coal Sci., 260 (1983).

39. B. C. J. Labuschange and J. G. Van der Watt, Intl. Conf. Coal Sci., 264 (1983).

40. S. Kelekek, T. Salman, and G. W. Smith, Proc. 64th CIC Coal Symp., 145 (1982).

41. A. Taweel, A.M.H.A. Farag, J. Kwak, H. A. Hamza, and M. Falk, Proc. 64th CIC Coal Symp., 125 (1982).

42. T. Murata, Fuel, 60, 744 (1981).

43. J. C. Crelling, R. H. Schrader, and L. G. Benedict, Fuel, 58, 542 (1979).

44. R. C. Neavel, in Coal Science, vol. 1, M. L. Gorbaty, J. W. Larsen, and I. Wender, eds., Academic Press, 1 (1982).

45. E. Furimsky, J. A. MacPhee, L. Vancea, L. A. Ciavaglia, and B. N. Nandi, Fuel, 62, 395 (1983).

46. B. S. Ignasiak, D. M. Clugston, and D. S. Montgomery, Fuel, 51, 76 (1972).

47. H. Wachowska and W. Pawlak, Fuel, 56, 342 (1977).

48. O. P. Mahajan, M. Komatsu, and P. L. Walker, Jr., Fuel, 59, 3 (1980).