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OSTI

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U.S. Dept. of Energy
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DOE/PC/90287-724

Dear Mr. Byrnes:

Please find enclosed a copy of the final report for the DOE Project No. DE-FG22-90PC90287, entitled "Oxidation of Coal and Coal Pyrite: Mechanisms and Influence on Surface Characteristics."

Sincerely yours,

Fiona M. Doyle

Fiona M. Doyle
Professor of Materials and Mineral Engineering

encls.

MASTER

**OXIDATION OF COAL AND COAL PYRITE
MECHANISMS AND INFLUENCE ON SURFACE CHARACTERISTICS
DE-FG22-90PC90287**

**Fiona M. Doyle
University of California at Berkeley
Dept. of Materials Science and Mineral Engineering**

FINAL REPORT

We have no objection from a patent
standpoint to the publication or
dissemination of this material.

RESEARCH OBJECTIVES

Mark P. Dvorsky 2-29-96
Office of Intellectual Property
Date

Coal oxidation has been studied extensively in previous work. However, there is still no general agreement concerning the mechanisms of oxidation. Moreover, the oxidation behavior of coal and mineral matter have generally been regarded as separate processes. There is appreciable evidence that the organic and inorganic oxidation process are actually coupled, consequently the changes in their surface properties induced by oxidation are notoriously difficult to predict. This makes the effectiveness of coal cleaning processes highly sensitive to the extent of weathering and oxidation that the coal has experienced. The objective of this research was to investigate the oxidation behavior of coal and coal pyrite, and to correlate the intrinsic physical and chemical properties of these minerals, along with changes resulting from oxidation, with those surface properties that would influence the behavior in physical cleaning processes.

RESEARCH SUMMARY

Fourteen coal samples of different rank, ranging from high to medium sulfur content, have been studied by dry oxidation tests at different temperatures and humidities, and by wet oxidation tests using different oxidizing agents. The coal samples were characterized extensively before and after oxidation. The surface areas of the coal samples were determined by CO₂ adsorption, followed by analysis using the Dubunin-Polanyi equation. The concentration of surface functional groups was determined by ion-exchange methods. The changes in the coal composition resulting from oxidation were analyzed spectroscopically. The wettability of coal and coal pyrite samples was assessed by film flotation tests. The electrokinetic behavior of different coal and coal pyrite samples was determined by electrophoresis. Different oxidation treatments induced significantly different changes on the coal surface. Possible oxidation mechanisms have been proposed to explain these changes.

Flotation tests were done on different coals under controlled pH and solution potential to investigate the effect of polarization on the flotation of coal, and the ability to separate pyrite from coal by selective flotation of either coal or pyrite. The results were related to selected rank parameters from the proximate, sulfur and oxygen group analysis, to identify any parameter that correlated well with flotation response, either positively or negatively.

The electrochemical behavior of two polished and etched coal pyrite samples was investigated from pH 1.0 to 10.5 by rest potential measurements and cyclic voltammetry. Additionally, the effect of the electrode potential on the wetting behavior of coal pyrite was investigated by contact angle measurements on polarized coal pyrite electrodes. The reliability and suitability of standard test methods for determining the pyrite content of coal and mineral samples,

and their propensity to release acidic drainage, were studied. The kinetics of coal pyrite dissolution in aqueous solutions of hydrogen peroxide and nitric acid were also investigated.

The ability of oxidized Upper Freeport coal to adsorb Cu^{2+} and Cd^{2+} ions from aqueous solutions was investigated as a means of characterizing the surface functional groups. The kinetics of metal uptake provided information on the relative pore sizes and tortuosities. The different oxidative treatments affected both the surface and pore structure of Upper Freeport coal. The large amount of carboxylic and phenolic functional groups remaining after equilibration with Cu^{2+} and Cd^{2+} indicated the low affinity of the surface acid groups for these cations. There was almost no metal ion adsorption at low solution pH's, reflecting the presence of acid groups in the undissociated form.

When the coal was oxidized by KMnO_4 , the Mn(VII) was reduced to Mn(IV) , and adsorbed on the coal surface, albeit as an amorphous oxide phase. This oxide was capable of adsorbing Cu^{2+} and Cd^{2+} from solution, but with characteristics quite different from the ion-exchange exhibited by surface acid groups on the coal. The overall ion-exchange capacity of coal, even when strongly oxidized, is too low for commercial applications to be attractive.

RESEARCH CONCLUSIONS

All of the research done under the five years of the existing grant has been reported in the twenty quarterly reports submitted to PETC. In addition, the work is reported, synthesized, and discussed in the doctoral dissertation of Miguel N. Herrera, and the M.S. thesis of Donna L. Bodine, both of which have been filed with PETC. Rather than reiterate these, it seems most appropriate to highlight the most significant findings of the study.

The coal samples studied were mostly obtained from the Pennsylvania State Coal Bank, and are listed in Table I, along with their proximate, sulfur and oxygen group analyses. A large supply of Upper Freeport coal was obtained from the Troutville #2 Mine, Clearfield County, Pennsylvania. The coal was stored under argon after mining to prevent oxidation, and after grinding, sized fractions were stored under argon for use in this work. The effects of specific oxidation treatments on various surface properties of coal samples have been studied systematically. The concentration of oxygen functional groups increased as the temperature, humidity and oxidation time were increased. During oxidation at 230°C , anthracite coals showed only a small increase in their oxygen functional group concentration. This is consistent with the predominantly aromatic structure of anthracite coal, and the fact that oxidation occurs preferentially on aliphatic groups. Conversely, sub-bituminous coals experienced severe oxidation, with significant increase in the oxygen functional group concentration. This is consistent with the fact that lower rank coals are generally considered to be more susceptible to oxidation than higher rank coals.

The wettability of as-received and thermally oxidized samples was studied by film flotation tests using a series of aqueous methanol solutions with different surface tensions. In general, coals showed wetting distribution curves that shifted towards higher surface tensions with increasing oxidation. This decrease in hydrophobicity, which would, of course, decrease the effectiveness of coal flotation or oil agglomeration, is attributed to the increase of functional groups that interact strongly with water and the evolution of volatile matter with oxidation. The decrease in hydrophobicity was most pronounced in bituminous coals, possibly due to more significant evolution of volatile matter.

Table I: Proximate, Sulfur, and Oxygen Group Analysis of Coal Samples Studied.

Sample	Origin	Rank	Proximate (As-rec'd, %)				Sulfur Forms (dry, %)		Wt% Phenolic oxygen, As-rec'd	Wt% Carboxyl oxygen, As-rec'd
			Ash	Volatile Matter	Fixed Carbon	Moisture	Pyritic	Total		
PSOC 1442	Darco Texas	Sub bituminous C	7.60	45.42	14.38	32.60	0.11	0.78	3.23	0.99
PSOC 1538	Bottom Texas	Sub bituminous C	11.07	33.18	25.75	30.00	0.11	0.99	5.30	0.66
PSOC 1486	Big Dirty Washing- ton	Sub bituminous B	15.45	34.47	29.94	20.13	0.29	0.94	9.02	1.52
PSOC 1487	Adaville #1 Wyoming	Sub bituminous A	4.55	34.67	41.78	18.99	0.03	1.31	1.42	0.35
PSOC 1539	Illinois #6 Illinois	HVC Bituminous	14.77	34.16	40.93	10.43	2.27	4.52	1.68	0.62
PSOC 1497	Illinois #2 Illinois	HVC Bituminous	10.13	35.70	40.74	13.44	3.51	5.93	1.38	1.02
PSOC 1494	Kentucky #9 Kentucky	HVB Bituminous	10.97	35.77	46.14	7.12	3.14	4.85	1.07	0.50
PSOC 1481	Upper Clarion Penn.	HVA Bituminous	8.76	38.73	50.79	1.73	3.20	4.82	2.84	0.81
DECS 12	Pittsburgh # 8 Penn.	HVA Bituminous	10.00	35.16	52.44	2.40	0.38	1.12	0.41	0.15
U.F.	Upper Freeport Penn.	MV Bituminous	17.59	27.05	55.35	1.50	0.66	1.12	0.68	1.01
PSOC 1527	Upper Freeport Penn.	MV Bituminous	30.30	23.14	46.10	0.46	1.63	2.02	1.22	0.25
PSOC 1516	Lower Kittann. Penn.	LV Bituminous	10.11	17.38	70.54	1.97	0.61	1.40	0.02	0.35
PSOC 1515	Penn. Anthracite Penn.	Semi Anthracite	28.46	8.23	60.87	2.44	0.10	0.58	0.42	0.11
PSOC 1461	Mammoth Penn.	Anthracite	23.44	3.89	69.61	3.06	0.36	0.74	1.47	0.11

With the exception of anthracite coal, electrokinetic tests on as-received and oxidized coals showed that oxidation decreased the zeta potential, and the PZC shifted to lower pH values. The shift became more pronounced as the coals became more oxidized. This is due to the formation of more oxygen functional groups that dissociate at low pH. The presence of significant amounts of ash minerals in the coal samples also affects the zeta potential. At strongly basic pH values, the zeta potential of coal samples became less negative, an initially unexpected result found to be due to the formation and dissolution of humic acids.

The dry thermal oxidation of coals was accompanied by a change in the concentration of various functional groups. The DRIFT spectra of different coals showed that the intensities of some specific absorption bands changed during oxidation. With the exception of anthracite coal, the intensity of the carboxylate peak increased with oxidation in most cases. The peaks corresponding to ester and anhydride functionalities also increased slightly, whereas the intensity

of the peaks corresponding to aliphatic configurations decreased dramatically. The latter confirms the fact that thermal oxidation at 230°C severely modified the aliphatic structure of coal.

The mechanisms of oxidation at 230°C were interpreted in terms of classical auto-oxidation reactions, in which the first step could be the formation of hydroperoxide compounds by the preferential oxidation of the aliphatic units present in coal. The loss of aliphatic structure detected by DRIFT measurements suggests that this would be the initial site of abstraction of hydrogen and subsequent hydroperoxide formation. Hydroperoxide compounds were not detected, but would not be expected to be detectable, because they are easily decomposed at the experimental oxidation temperature. Once hydroperoxide has decomposed and released further radicals into the system, the range of reaction possibilities becomes extensive, and choosing between them is somewhat speculative. However, the presence of carboxylic acids, phenolic groups, esters and anhydrides detected in this study has been consistently explained on the basis of coherent reaction sequences.

Wet oxidation studies using different oxidizing agents revealed that the extent of oxidation for the sub-bituminous C (PSOC-1442) and MV bituminous (PSOC-1527) coals is comparable to that observed after dry thermal oxidation at 230°C. The susceptibility to oxidation by a given oxidizing agent varied from sample to sample in no obviously systematic way. Wet oxidation also reduced the hydrophobicity of the coal, although to a lesser extent than dry thermal oxidation. Wet oxidation by hydrogen peroxide probably involved a Fenton reaction mechanism, by which pyrite catalyzed the oxidation process by reducing H_2O_2 to form $\text{OH}\cdot$ radicals that enhanced the oxidation of coal. Interaction between coal and nitric acid involved complex mechanisms characterized by a series of reactions such as oxidation of the organic and inorganic fractions of coal. In the oxidation of coal by ferric sulfate solution, there was a marked decrease in the concentration of total iron in solution during the initial stage of oxidation, although some pyrite was oxidized, which would be expected to increase the concentration of dissolved iron. The decrease in the concentration of dissolved ferric and ferrous is thought to be due to ion-exchange by the functional groups present in as-received coal and those generated by oxidation.

Although the inorganic and organic materials were altered simultaneously in coal exposed to the atmosphere, these processes have generally been regarded as independent. This study analyzed the role that the interaction of pyrite with water and oxygen might play in the oxidation of coal. Pyrite oxidation could promote and catalyze the oxidation of coal by the generation of sulfuric acid and dissolved iron. The role of sulfuric acid is very important because it participates in primary steps of coal oxidation, and it can leach trace toxic metals from ash minerals, promoting the alteration of minerals that might otherwise be stable. Dissolved iron can act as an "oxygen carrier", in which ferrous is oxidized by oxygen at solution-air interfaces to ferric iron, which in turn oxidizes pyrite and coal. The reduction of Fe^{3+} is much less strongly polarized than the reduction of O_2 , and hence can give much faster oxidation kinetics.

Oxidation of coal creates conditions for water sorption; water activates oxygen molecules that participate in the formation of free radicals, promoting the oxidation of the organic structure of coal, and also oxidize pyrite. These concurrent oxidation processes produce an autocatalytic effect, thereby making the process self-propagating.

The complex nature of coals means that definitive results on coal oxidation are difficult to obtain. The results of the present study indicate that the oxidation mechanism is probably similar in all coals, except, perhaps, for anthracite coal. The principal variations in oxidation are probably due to different relative proportions of the reactive species in different coals.

Bituminous coals exhibited the highest floatability, whereas sub-bituminous and anthracite coals were poorly floatable. No obvious reason could be found for the unexpectedly low flotation response of anthracite coals, however similar behavior has been observed by other authors. The

results of the oxidation, film flotation and salt flotation studies indicate that the presence of oxygen functional groups, high ash and moisture contents may be responsible for the mediocre flotation behavior of some coals.

The effect of the solution potential on the flotation of coal and coal pyrite was studied on high sulfur coals. An important conclusion drawn from these flotation tests is that, at reducing potentials, the functional groups present on the coal surface are reduced, and consequently the hydrophobic character of the coal surface is partially restored. Moreover, at these potentials, the pyrite surface was more hydrophilic, due to the formation of layers of sulfur-deficient (metal-rich) sulfides such as FeS or FeS_{2-x} . These concurrent effects contribute to potentially significant improvements in the separation of coal pyrite from coal, and should be considered in seeking more efficient conditions for flotation.

At oxidizing potentials, the flotation of coal decreased significantly due to the presence of highly oxidized functional groups on the coal surface, which decreased the hydrophobicity of coal. Moreover, at these oxidizing potentials, the surface of pyrite was less hydrophobic, due to the formation of a hydrophilic oxide layer on its surface. Therefore, it is clear that high potentials do not provide appropriate conditions for coal flotation.

This study showed that controlled experimental procedures can control the density of carboxylic, phenolic and other functional groups on coal surfaces. Such control would provide a way to control, for example, the wettability, solvent penetration, and ion-exchange capacity of coals. Thus, for example, control of the surface characteristics of coals may allow the selective chemistry more commonly attainable with catalysts to be achieved with coals.

An important contribution of this study has been the extensive use of electrochemical tests at different pH to study the effect of different solution conditions on the behavior of coal pyrite. Results of these tests are very important because they provide insight into the behavior of pyrite in flotation systems and in the formation of acid mine drainage. It has been observed that significant differences can be expected in the electrochemical behavior of coal pyrite samples, according to their prior history. For example, grinding can introduce damage or defects in the surface layers, and trace quantities of oxygen can readily oxidize their surface. These effects are particularly likely during idealized laboratory experiments.

The pyrite samples studied here were more susceptible to oxidation after a cathodic excursion, suggesting that the reducing environment provided by coal actually increased the susceptibility of freshly exposed pyrite to oxidation. This finding constitutes important additional evidence to explain the reported higher reactivity of coal pyrite in comparison with ore pyrite.

Coal pyrite undergoing weathering in coal mines and storage piles may develop solutions of low pH. The results of the present work suggest that such weathering at low pH would make the coal pyrite surface more hydrophobic, because of the formation of sulfur and polysulfides. This transformation would be undesirable, since cleaning methods such as flotation and oil agglomeration require the pyrite to be less hydrophobic than the coal. The problem would be compounded by concurrent oxidation of coal, which introduces hydrophilic carboxylate and phenolic groups. Oxides form when pyrite oxidizes under basic conditions, although the effect of this on the surface properties would depend on whether non-equilibrium polysulfides also appeared.

Another significant observation from this work is that the borate or phosphate buffer solutions used routinely in electrochemical studies actually interacted with pyrite electrodes. This observation should be crucial in the interpretation of previous electrochemical studies that have used borate and phosphate buffers as electrolytes. The compounds formed would not, of course,

be expected in a coal flotation circuit where pH would be regulated with inexpensive, readily available bases.

Thermal oxidation had no significant effect on the PZC of Pittsburgh coal pyrite, but caused the PZC of Upper Freeport coal pyrite to shift to more acidic pH values. Recalling that oxidation decreased the zeta potential of coal, the associated negative charge on the coal surface must then be determined mainly by the acidic groups present on the coal, rather than by the oxidation products of pyrite. The critical surface tension of both coal pyrite samples increased dramatically on oxidation, reflecting a decrease in the hydrophobicity with oxidation. This is undoubtedly due to the presence of hydrophilic iron oxide or hydroxide on the surface. Clearly, this change with oxidation would affect the performance of coal cleaning.

The reliability and suitability of standard tests methods used to determine the pyrite content of coal and mineral wastes, and their propensity to release acidic drainage, were studied. The hydrogen peroxide method prescribed by the U.S. Environmental Protection Agency was not reliable for materials containing coal, because of interference from the coal itself. The nitric acid oxidation-extraction method, described in ASTM D2492-84, was effective at dissolving coal pyrite. Coal pyrite oxidized faster than ore pyrite, and, therefore, differences in the reactivity of pyrite samples should be taken into account in any pre-mine prediction of post-mine drainage quality.

We have examined how oxidized Upper Freeport coal interacts with Cu^{2+} and Cd^{2+} ions in aqueous solutions, primarily to assess the complexing ability of functional groups generated by oxidation. The kinetics of metal uptake provided information on the relative pore sizes and tortuosities. The different oxidative treatments affected both the surface and pore structure of Upper Freeport coal. The large amount of carboxylic and phenolic functional groups remaining after equilibration with Cu^{2+} and Cd^{2+} indicated the low affinity of the surface acid groups for these cations. There was almost no metal ion adsorption at low solution pH's, reflecting the acid groups being present in the undissociated form. This work on the adsorption of metal ions also provides relevant information for situations in which pyrite in coal releases acid, which then mobilizes toxic metal ions into the resulting acid rock drainage. Further, this work might provide useful information for addressing the emission of potentially hazardous air pollutants during combustion of coal containing trace metals; it is quite likely that the coal could undergo an acid leach stage before combustion.

When the coal was oxidized by KMnO_4 , the Mn(VII) was reduced to Mn(IV), and adsorbed on the coal surface, albeit as an amorphous oxide phase. This oxide was capable of adsorbing Cu^{2+} and Cd^{2+} from solution, but with adsorption behavior quite different from the ion-exchange exhibited by surface acid groups on the coal.

The possibility that coal might be used as a reducing agent or metal sorbent for treating a wide variety of effluents and process streams that originate outside of the power industry was considered. Many process streams contain traces of toxic metal ions, and are particularly problematic if they also contain oxidizing agents. The discharge of such streams is highly regulated, but there is an urgent need for more cost-effective technology for achieving compliance.

The adsorption isotherms obtained in this study, along with the results for sequential contacting, indicate that although coal is capable of adsorbing ions, its capacity is too limited to warrant serious consideration as an economic or technically viable treatment option. Our metal uptake tests used one gram of coal to 10 ml of solution, which is equivalent to 100 kg coal/ m^3 solution. This coal would not only have to be transported to the treatment site, but it would also

require disposal. The only realistic disposal strategy would be combustion for the purpose of generating electrical power, and this strategy would require precautions to ensure that no additional metals were emitted in flue gases, and that all leachable metals were removed from the ash phase. Furthermore, the residual concentrations of metal ions in equilibrium with coal are too high for compliance with most water quality regulations.

Coal is more promising as an inexpensive reducing agent for oxidized species. Permanganate is particularly easy to treat because, using coal alone, it is easy to achieve an equilibrium potential and pH where a solid manganese-bearing species predominates. Cr(VI) is not quite as amenable to treatment, because it is reduced to a soluble species with coal alone. However coal might be used as a reducing agent, in conjunction with other reagents that could control pH to promote the formation of a solid Cr(III) species.

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- Donna L. Bodine, "Effect of Oxidation on the Removal of Cu^{2+} , Cd^{2+} and Mn(VII) from Dilute Aqueous Solutions by Upper Freeport Bituminous Coal", M.S. Thesis, University of California at Berkeley, June, 1995

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