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directly by investigating the effects of particle size on tar yields and characteristics. Within the particle size range employed in this investigation for a HVA bituminous coal, intraphase transport considerations appear to have a second-order effect on tar yields and properties relative to interphase considerations. Of course, changes in maceral composition^{44,47} with particle size must be considered. A more extensive investigation is being conducted to affirm this phenomenology and to test its applicability to the range of coals investigated in this investigation.

The questions of similarity in kinetic parameters among a range of coal types and whether chemical or transport phenomena dominate a stage of tar-evolution processes require a multireactor approach in which the phases of tar

formation and evolution can be deconvoluted.

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Effect of Acid Treatment Atmosphere on the Thermoplasticity of a Low-Volatile Bituminous Coal

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A strongly caking low-volatile bituminous coal was treated with HCl and HF under air and N₂ atmospheres. The thermoplastic properties of the raw and treated coals were examined in N₂ (1 atm) by use of a microdilator. It was found that coals treated with the acids in air exhibited the lowest maximum swelling parameter (V_s , vol %) and weight loss during the dilatometry measurements. The above measured values were significantly restored for the coal acid treated under N₂. The results indicate that acid treatment of this coal in air promotes low-temperature air oxidation of the coal, consequently reducing its thermoplastic properties. It is shown that the acids may be important in catalyzing low-temperature coal oxidation. The significance of the acid treatment atmosphere and its implication for the reaction behavior of acid-treated coals are also discussed.

Introduction

An enormous body of literature has clearly indicated that the presence of mineral matter can have profound influences on almost all aspects of coal utilization and experimentation. It is beyond the scope of this paper to review the literature, but it suffices to say that mineral matter has been implicated in the catalysis of pyrolysis, gasification, liquefaction, and carbonization reactions. Treatment of coals with hydrochloric (HCl) and hydrofluoric (HF) acids is the method most commonly employed for the removal of mineral matter from coals for studying the effect of mineral matter on the reaction chemistry of coal and coal chars. This paper examines the thermoplastic properties of a highly caking bituminous coal demineralized under air and N₂ atmospheres.

Extraction of coal with concentrated hydrofluoric acid removes major minerals in coal quantitatively. Additional extraction with hydrochloric acid before and after hydrofluoric acid extraction is used to obviate the formation of insoluble calcium fluoride. Treatment of coals with HCl and HF can have a profound influence on the reaction behavior of the treated coals. Significant reduction in the

dilatometric properties of caking Polish coals resulted from demineralization using hydrochloric and hydrofluoric acids has been reported.¹ Coal demineralization is usually carried out in air. It should be noted that the possibility of oxidation during acid treatment was ruled out by Bishop and Ward.² Their conclusion was drawn based on a finding that the carbon and hydrogen contents for a low rank vitrain treated with HCl and HF under inert and air atmospheres were essentially the same. On the basis of this conclusion Wachowska et al.¹ also suggested that it is unlikely that the reduction observed in thermoplasticity of acid-treated coals is caused by oxidation. However, enhanced air oxidation of coal caused by acid demineralization was reported by Kister et al.³ They observed, by FT-IR and UV fluorescence, that both air oxidation and demineralization of a French subbituminous coal resulted in the loss of aliphatic groups attached to polycyclic aromatics with three or four rings and the appearance of oxygenated groups, mainly carbonyls and carboxylic acids. The loss of aliphatic carbon during air oxidation and acid demineralization of coal was also observed by high-resolution solid-state ¹³C NMR.⁴

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(1) Wachowska, H.; Pawlak, W.; Andrzejak, A. *Fuel* 1983, 62, 85-88.

(2) Bishop, M.; Ward, D. L. *Fuel* 1958, 37, 191-200.

(3) Kister, J.; Guillino, M.; Mille, G.; Dou, H. *Fuel* 1988, 67, 1076-1082.

Table I. Proximate and Ultimate Analyses of Low-Volatile Coal (PSOC-1133)

	moisture		ash		VM	fixed carbon
proximate anal., wt %, as received	0.9		19.0		19.0	61.1
	C	H	N	Cl	S (organic)	O (by diff)
ultimate anal., wt %, daf	87.6	5.2	1.4	0.1	2.0	3.8

In the present study the effects of the gas atmosphere during acid treatment on the thermoplasticity of a highly caking bituminous coal are reported. The swelling behavior of the coal demineralized under air and N₂ atmospheres was measured by a microdilatometer. It has been demonstrated previously that microdilatometry is an extremely sensitive technique for revealing changes in the thermoplasticity of coal brought about by air oxidation.⁵ The objective of the present study is to examine the acid treatment atmosphere during demineralization on the thermoplasticity of the treated coals. Results from the present study can lead to a better understanding of changes in the organic matter in coal when treated with HCl and HF in the presence of oxygen. This is important because the reaction behavior of demineralized coal can be significantly influenced by such changes.

Experimental Section

A highly caking bituminous coal (lvb), PSOC-1133, from the Lower Kittanning seam in Pennsylvania was examined in this study. The proximate and ultimate analyses of the coal are given in Table I. The sample was collected fresh and then ground (<25 mm) and immediately stored in sealed containers under N₂. Two size fractions of the coal, 100 × 140 mesh (125 μm, nominal mean particle size) and 200 × 270 mesh (62 μm, nominal mean particle size) were prepared for use by grinding and sieving in a glovebox under N₂.

Demineralization of the coal under N₂ was conducted by use of a technique similar to that described by Bishop and Ward² with minor modifications. For every 6 g of size-graded coal, 40 mL of 5 N HCl (J. T. Baker Chemical Co.) was added into a plastic bottle (200 mL) containing the coal. The bottle was sealed, and N₂ gas (99.999% purity) was bubbled through the acid/coal mixture for 10 min before the bottle was placed in a hot water bath maintained at a temperature of 330–335 K. After the acid treatment had proceeded for 1 h, the bottle was cooled to room temperature. The N₂ gas flow was stopped, and the treated coal was then filtered and mixed with 40 mL of full-strength (29 N) HF (J. T. Baker Chemical Co.). This mixture was also heated for 1 h at 330–335 K following the procedure already described. The coal was again filtered and mixed with full-strength (12 N) HCl for a third 1-h treatment at the same temperature. Finally the coal was filtered and washed with warm distilled water until no chloride ions were detected in the filtrate (using 0.1 M AgNO₃ solution). The treated coal was dried under vacuum at 110 °C. The multistep HCl/HF/HCl treatment described above is referred to as demineralization. When the coal was demineralized under air, no gas was bubbled through the coal/acid mixture and the contents of the open reaction bottle were magnetically stirred. Several acid treatments of coal were performed using only HCl or HF, full-strength acid solutions being used for all these stages of treatment in such cases. Treatment of the coal was also performed using distilled water and 12 N NaCl solution under air atmosphere.

A microdilatometer capable of being operated at high pressure, which has been utilized in several previous investigations,^{6–13} was

Table II. ASTM Ash and Volatile Matter Contents of Low-Volatile Coal (PSOC-1133) Treated under Different Conditions

sample treatment	ash, wt %, dry	VM, wt %, daf
raw coal	19.2	23.7
demineralized in N ₂	1.2	18.5
demineralized in air	1.8	18.8
HCl-treated in N ₂	5.7	20.2
HCl-treated in air	7.1	21.4
HF-treated in N ₂	0.6	20.2
HF-treated in air	0.7	19.9
H ₂ O-treated in air	16.7	22.8
NaCl-treated in air	18.1	25.7

Table III. Maximum Swelling Parameters (V_s) and Softening Temperatures (T_s) of Treated Coals Measured at 25 K/min Heating Rate

sample treatment	V _s , vol %	T _s , K
raw coal	196	736
demineralized in N ₂	160	744
demineralized in air	109	768
HCl-treated in N ₂	131	735
HCl-treated in air	110	748
HF-treated in N ₂	140	733
HF-treated in air	103	748
H ₂ O-treated in air	200	739
NaCl-treated in air	198	738

used to determine the thermoplastic properties of raw and treated coals in this study. Detailed descriptions of the apparatus, together with the parameters measured, are provided elsewhere.⁶ The maximum swelling parameter (V_s), expressed as a percentage of the initial volume of the coal sample, and the softening temperature (T_s) were measured by the dilatometer. The weight loss during pyrolysis was determined for selected experiments by weighing the samples before and after the dilatometry runs. The reproducibility of V_s for the raw and treated coal was found to be ±6%, and the weight-loss measurements can be reproduced to within ±0.2%. Temperature measurements can be resolved to within ±6 K. All measurements were conducted under atmospheric-pressure N₂, at an applied mechanical load of 9.8 kPa.

Results and Discussion

Two samples of the larger sized coal (125-μm mean size) were demineralized under N₂ and air atmospheres. Additionally, four coal samples were treated with HCl and HF alone under the two different gas atmospheres. Treatment of the coal samples with distilled water and with a NaCl solution under air atmosphere was also performed. Measurements obtained from the coal treated with distilled water served as a blank for comparison with those that were demineralized and acid treated. The coal treated with NaCl solution was used for studying the effect of chloride ion on the thermoplasticity of the treated coal. The ash and volatile matter (VM) contents of the demineralized coals and treated coals were measured by standard ASTM proximate analysis. Results are presented in Table II. It can be seen that the ash contents of the coals demineralized by using HCl/HF in air and in N₂ atmospheres are below 2%. The VM content decreases significantly from about 24% for the raw coal to 19% for the demineralized coal. When the coal was treated with HCl only, the ash content decreases to between 5 and 7% compared to about 0.6–0.7% ash content for the coal treated with HF. Evidently, the higher ash content of the

(4) Tekely, P.; Nicole, D.; Delpuech, J. J.; Totino, E.; Muller, J. F. *Fuel Process. Technol.* 1987, 15, 225–231.

(5) Maloney, D. J.; Jenkins, R. G.; Walker, P. L., Jr. *Fuel* 1982, 61, 175–181.

(6) Khan, M. R.; Jenkins, R. G. *Fuel* 1984, 63, 109–115.

(7) Khan, M. R.; Jenkins, R. G. *Fuel Process. Technol.* 1984, 8, 307–311.

(8) Khan, M. R.; Jenkins, R. G. *Fuel* 1985, 64, 189–192.

(9) Khan, M. R.; Jenkins, R. G. *Fuel* 1985, 64, 1618–1622.

(10) Khan, M. R.; Jenkins, R. G. *Fuel* 1986, 65, 1203–1208.

(11) Khan, M. R.; Jenkins, R. G. *Fuel* 1986, 65, 1291–1299.

(12) Khan, M. R.; Lee, C. W.; Jenkins, R. G. *Fuel Process. Technol.* 1987, 17, 63–71.

(13) Khan, M. R.; Jenkins, R. G. *Fuel* 1988, 67, 693–699.

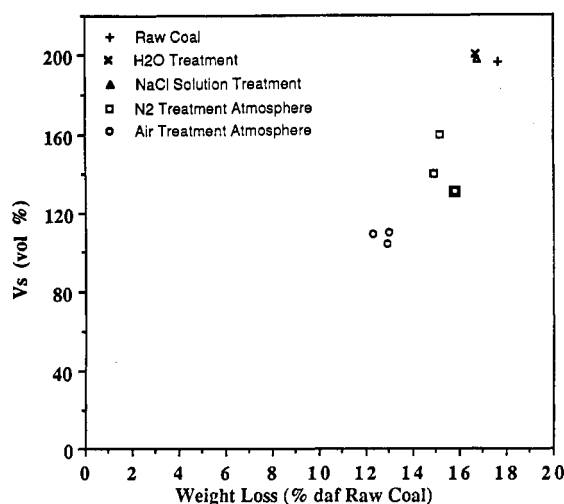


Figure 1. Relationship between V_s and weight loss of treated coals measured at 25 K/min heating rate.

HCl-treated coal indicates that relatively large amounts of minerals, e.g., silica and clays, are insoluble in HCl. Treatment of coal with distilled water and NaCl solution produced little change in the ash and VM contents of the treated coals.

Dilatometric measurements on the samples were performed at a heating rate of 25 K/min. Results of the maximum swelling parameter (V_s , vol %) and softening temperature (T_s , K) of the raw and treated coals are shown in Table III. Demineralization by HCl/HF under air reduces V_s from 196 to 109%, but the V_s is reduced to only 160% for the coal demineralized under N₂. Similar behavior is observed for coal treated with HCl or HF alone under the two different atmospheres (see Table III). It is also shown that treatment of coal with HF under air atmosphere reduces the V_s to its lowest value. Treatment of coal with distilled water and NaCl solution produced little change in its plastic behavior. This observation is consistent with the unchanged ash and VM contents. Results of the softening temperature suggest that coal demineralized under air has a higher softening temperature (768 K) than that of the coal demineralized under N₂ (744 K). Higher softening temperatures are also observed for coals treated with HCl or HF alone in air compared to coals treated with the same acid in N₂. This indicates that coals demineralized or treated with acids in the presence of air are more difficult to soften, possibly due to more cross-linked structures produced during pyrolysis.

An interesting correlation between swelling and weight loss during dilatometry is evident from Figure 1. A general trend that higher V_s value occurs together with greater weight loss can be seen. As expected, these data show that V_s and weight loss of the treated coals are strongly dependent on the treatment atmosphere. Treatment of coal with distilled water or NaCl resulted in V_s and weight loss being as high as those of the raw coal, but coals demineralized or treated with HCl and HF under air have the lowest V_s and weight-loss values, and those treated under a N₂ atmosphere have intermediate V_s and weight-loss values. The lower weight loss coupled with reduced swelling observed for those coal samples demineralized or acid treated under air indicate that the smaller amounts of volatiles released while the pyrolyzing coal particles were in the plastic state resulted in decreased swelling. The reduced weight loss provides further evidence that coal treated with HCl and HF in air leads to more cross-linked structures produced during pyrolysis, which prevent volatiles' escape.

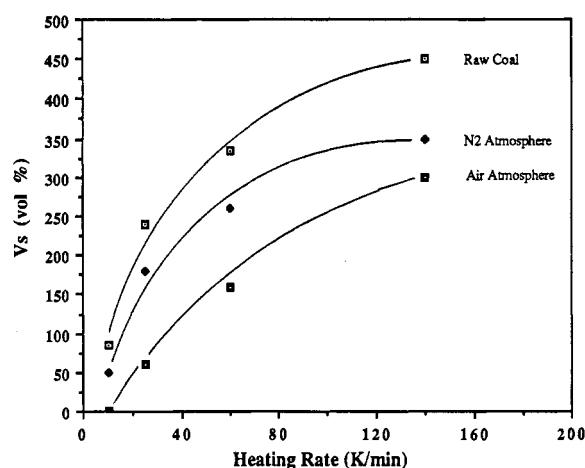


Figure 2. Effect of demineralization gas atmosphere on V_s of the demineralized coal measured at different heating rates.

Two samples of smaller sized coal (62 μ m) were demineralized (HCl/HF) under air and N₂. Dilatometric measurements on the demineralized coals were performed at heating rates of 10, 25, 60, and 140 K/min. Results are shown in Figure 2. It is well-known that the heating rate is an important experimental parameter that influences the swelling of coal particles.^{6,14} As seen in Figure 2, such heating rate dependent behavior is observed for both the raw coal and demineralized coals. Swelling of the coal that was demineralized under N₂ was always significantly greater than that of the coal demineralized under air atmosphere. This again indicates that demineralization in the presence of air brings about more chemical changes resulting in a greater loss of thermoplasticity of the coal.

It has been shown that demineralization by acid treatment reduces the thermoplasticity of the demineralized coals. The extent of reduction in thermoplasticity depends strongly on the gas atmosphere employed during demineralization. When demineralization was performed under N₂ to minimize the possibility of oxidation, the swelling of the demineralized coal was still significantly lower than that of the untreated coal. The reduction in thermoplasticity may result from retention of acids used in demineralization. It has been suggested¹⁵ that chloride ions could associate with molecules of coal to form amine hydrochlorides, on the basis that coals contain basic nitrogen. Evidence of hydrochloric acid being strongly held within demineralized coal was supported by the observation that HCl was still leaching out very slowly after 2 weeks of washing the demineralized coals with distilled water. The reduction in thermoplasticity of demineralized coals has been attributed to polymerization catalyzed by the acids retained after demineralization.¹ It is more difficult for the demineralized coals to transform into the plastic state during pyrolysis due to the cross-linked structures formed by polymerization.

The larger reductions observed in both swelling and weight loss for coals acid treated under air atmosphere compared to those treated under N₂ suggest that mild oxidation of the coal occurred when the treatment was conducted under air atmosphere. Oxidation of the coals treated under air atmosphere is believed to contribute to the observed additional reductions in the swelling param-

(14) Loison, R.; Peytavy, A.; Boyer, A. F.; Grillot, R. *Chemistry of Coal Utilization*; Lowry, H. H., Ed.; Wiley: New York, 1963; Suppl. Vol., p 150.

(15) Given, P. H.; Yarzab, R. F. *Analytical Methods for Coal and Coal Products*; Karr, C., Jr., Ed.; Academic Press: New York, 1978; Vol. II, p 3.

eter. It is well-known that low-temperature oxidation results in increased viscosity of the pyrolyzing coal particles and consequently changes the thermoplastic properties of the particles, and that such changes require only very small amounts of oxygen.^{5,14} The solubility of oxygen in concentrated acids such as HCl has been found to be significant at elevated temperatures, although this solubility decreases with increasing acid concentration.¹⁶ For example, oxygen solubility in HCl reduces by ~30% as acid concentration increases from 0 to 5 M. The oxygen concentration in concentrated HCl and HF acids can be sufficient to cause coal oxidation. Oxygen dissolved in aqueous electrolyte solutions have been employed as an oxidant to oxidize ores in many hydrometallurgical processes.¹⁶

It has been observed in this study that treatment of the coal with distilled water or NaCl solution alone under air atmosphere produced little change in thermoplastic properties of the coals. These observations indicate that, under conditions similar to those for demineralization, oxidation of the coal could not occur in the absence of acid. The role of the acid may be as a catalyst to promote the low-temperature oxidation of coal during demineralization. Another possibility is that acid plays an indirect role by dissolving minerals to provide ionic species which catalyze coal oxidation. The influence of acid and dissolved ionic species from coal minerals on the reactions of the organic portion of coal can not be separated during demineralization. Cross-linked structures produced by oxidized coals during pyrolysis can eliminate the thermoplasticity in coals. Higher softening temperatures and lower weight losses measured for those coals demineralized or acid treated under air atmosphere provide further evidence that more cross-linked structures were formed, which increase the resistance for these coals to transform into the plastic

state. It has been shown that this low-volatile bituminous coal (PSOC-1133) has very low fluidity as measured by Gieseler plastometry, in a previous oxidation study.⁵ The development of thermoplasticity in a coal that has an inherently low fluidity may be more sensitive to the formation of cross-linked structures during pyrolysis. Consequently, a small extent of oxidation resulting from demineralization can produce significant changes in thermoplastic behavior.

Conclusions

This study was concerned with the effect of acid treatment gas atmosphere on the thermoplasticity of the treated coals. Results of this study demonstrated that a low-volatile bituminous coal demineralized under air and N₂ atmospheres developed significantly different thermoplastic properties. It has been shown that demineralization under air atmosphere produces coal that swells less and releases a smaller amount of volatiles during pyrolysis compared to coals demineralized under N₂ atmosphere. The evidence presented indicates that demineralization in the presence of oxygen promotes low-temperature oxidation of the coal. Such reactions are catalyzed by either the HCl and HF present or by the ionic species produced by the dissolution of minerals during demineralization. The gas atmosphere used during acid treatment of coal can be a significant experimental parameter influencing the thermoplastic properties of the treated coal. Coals having low fluidity are particularly susceptible to changes in thermoplasticity caused by mild oxidation. When such coals are acid treated, the possibility of low-temperature oxidation of the coals leading to significant changes in their reaction behavior must be carefully considered.

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Registry No. HCl, 7647-01-0; HF, 7664-39-3.

(16) Narita, E.; Lawson, F.; Han, K. N. *Hydrometallurgy* 1983, 10, 21-37.