THE EFFECTS OF WEATHERING ON FLOTATION AND THERMOPLASTIC PROPERTIES OF COAL

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INTRODUCTION

Weathering can affect the behavior of coal in many production and end-use processes (1). Extensive laboratory research has been performed to determine the chemical nature of coal weathering. Most reported coal weathering simulation experiments have been conducted at temperatures greater than 100°C to accelerate the oxidation rate. Carboxyl, carbonyl, ether and phenolic groups have been reported to form upon coal oxidation (2,3). The oxidation mechanism is reportedly different at temperatures above and below about 70°C (4). In addition, recent studies indicate that the chemical nature of coal oxidation may be different at the lower temperatures more typical of natural coal weathering (≤80°C) (5). The work reported here is a systematic laboratory study of coal weathering at realistic conditions of temperature and time using different ranks of coal. The objectives of this study are 1) to determine the effects of weathering on coal properties with emphasis on froth flotation and thermoplastic properties, 2) to compare the abilities of various techniques to measure the degree of weathering, 3) to better define the chemical nature of low-temperature coal weathering. In this paper, weathering is defined as the progressive changes in coal properties that occur as coal is exposed to humid air at temperatures of 80°C or less.

Medium and high volatile bituminous coals were weathered at temperatures of 25°C, 50°C and 80°C in flowing humid air for as long as 369 days. Absolute humidity, which was constant for all experiments, was equal to 80% relative humidity at 20°C. Weathered coals were sampled periodically and characterized by a variety of relevant techniques, including ultimate and proximate analyses, forms of sulfur, Gieseler plastometer, free swelling index (FSI), Audibert-Arnu dilatometer, heat of combustion, slurry pH, alkaline extraction and petrography. The froth flotation performance of the fresh and weathered coals was measured as a function of weathering time at several collector dosages. The weathered coals were also characterized by Fourier Transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) to study the chemical nature of weathering.

Properties of laboratory weathered coals were compared with those of a naturally weathered coal.

EXPERIMENTAL

Weathering Unit. A schematic diagram of the weathering unit is shown in Figure 1. The coal (1.2 kg, -28 mesh) used in the study was dispersed in a fixed-bed reactor (3" ID) using 3/8" Intalox ceramic saddles (ca. 1.2 kg) to prevent air channeling. The temperature of the coal bed was controlled by circulating water from a thermostated bath through the reactor's outer jacket. The water circulator maintained the coal bed at temperatures up to 80°C to within 1°C. Two thermocouples were located at 1/3 and 2/3 of the coal bed height to monitor bed temperature. Air was introduced to the bottom plenum of the reactor at 1.7 SCFH. A third thermocouple was inserted in the reactor bottom to monitor the temperature of the incoming air. Air humidity (80% relative humidity at 20°C) was controlled by dividing the air into two controlled-flow parallel streams with one stream passing through two water saturators in series. Feed air and reactor off-gas, sampled several times for gas chromatographic analysis, showed no significant difference in oxygen composition, thus indicating that these reactors are being operated at differential conditions and that the air flow is sufficient for uniform coal weathering. Periodic samples were taken from the weathering units as follows. The entire reactor contents were emptied over a screen to remove the saddles. The entire coal sample was riffled ten times and sampled for analyses. The remaining coal was re-mixed with the saddles, then re-packed into the reactor. The reactor was tapped while being packed to settle the bed. Bed back-pressure, typically 0.5 psig, was monitored to ascertain the absence of channelling.

Coals. The high-volatile bituminous coal used in this study was freshly mined run-of-mine (ROM) Pittsburgh seam coal from West Virginia. The coal was ground to -28 mesh before use. The medium-volatile coal used was the natural -28 mesh portion of freshly mined ROM Horsepen seam coal from West Virginia. The mine from which the coal was obtained extracts both the upper and middle Horsepen seams. The "naturally weathered" medium-volatile bituminous coal used in this study was obtained from an adjacent mine that also extracts the Horsepen seam coal, except in this case the seams are very near the surface. The "naturally weathered" coal examined here was the natural -28 mesh portion of the coal. Analyses and properties of these coals are listed in Table 1.

Analyses. Gieseler plastometer and free swelling index (FSI) measurements followed ASTM procedures. Audibert-Arnu dilatometer measurements followed the ISO procedure. The alkaline extraction test was performed by the published procedure (6). Ultimate and proximate analyses, forms of sulfur and heat of combustion were measured by standard procedures. Fourier Transform infrared (FTIR) spectra were collected of the neat samples (not ground further after removal from weathering unit) using diffuse reflectance with a Nicolet Model 7199 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) was performed with a Perkin-Elmer PHI Model 560 ESCA/SAM spectrophotometer with a magnesium X-ray source.

Froth Flotation Tests. Froth flotation tests were made using a Denver Model D1 flotation cell. Coal slurry (5 wt % coal) was first charged to the cell and conditioned at 1500 rpm for three minutes to ensure thorough wetting of the coal. Collector (No. 2 fuel oil), when used, was added and conditioned for 15 seconds. Frother (methyl isobutyl carbinol) was then added and conditioned for 15 seconds. The air valve was opened and the froth was manually removed for two minutes. Froth concentrate and tails were filtered, dried, then analyzed.

RESULTS AND DISCUSSION

Medium-Volatile Bituminous Coal. Horsepen seam coal (-28 mesh) was weathered at 80°C. Only slight changes in chemical composition were observed upon weathering. For example, there was a small but significant decrease in heating value (14446 vs 14809 Btu/lb, dry), an increase in oxygen content (5.6% vs 3.0%, by difference) and a slight increase in sulfate sulfur content (0.06% vs 0.02%) as weathering time increased to 84 days. In contrast, the thermoplastic properties, i.e., Gieseler maximum fluidity and Audibert-Arnu dilatation, exhibited very rapid decreases with weathering time. These two properties, log Gieseler maximum fluidity and Audibert-Arnu dilatation, are plotted as fractions of their initial value and as a function of weathering time in Figure 2. After 30 to 40 days, % dilatation became negative, indicating that there was no dilatation, only contraction. After 50 to 60 days, log Gieseler maximum fluidity became negative, indicating Gieseler maximum fluidity was below 1 DDPM (essentially no fluidity). In contrast to these two thermoplastic properties, coal recovery (% MAF) in the froth flotation tests using frother (9.6 mg MIBC/L slurry, 0.38 lb MIBC/ton coal) but no collector showed a more gradual decrease with weathering time (Figure 2). Clearly, coking/caking properties are lost more rapidly than flotation recovery. Flotation recovery of the weathered coal can be restored to a large extent by use of small amounts of collector oil. For example, flotation recovery of the coal weathered for 84 days at 80°C increased from 14% (no collector) to 66% when collector (0.08 lb fuel oil/ton coal) was used.

Similar to flotation recovery, FSI decreased much less rapidly during early weathering than the Gieseler plastometer and Audibert-Arnu dilatometer measurements. At 80°C, FSI decreased from 8 1/2 to 5 1/2 after 44 days and to 2 1/2 after 84 days weathering. This decrease in FSI correlated fairly well with the loss in flotation recovery. FSI is obviously less responsive to early weathering than the Gieseler and Audibert-Arnu measurements. However, FSI may be a more meaningful measurement for the severely weathered coals because the plastometer and dilatometer values decreased to such low values with extensive weathering. FSI may show less responsiveness to early weathering partially as a result of the sample preparation required by the ASTM test. For FSI measurements, the coal must be ground to -60 mesh (as opposed to -35 mesh for the Gieseler), thus opening up fresh, less weathered surfaces. However, the Audibert-Arnu test, which requires a -100 mesh grind size, still shows excellent responsiveness to weathering.

The diffuse reflectance FTIR spectra (neat) of the fresh coal and coal weathered for 51 days are shown in Figure 3. The difference spectrum clearly indicates an increase in the carbonyl peak intensity at about 1700 cm^{-1} and a decrease in the C-H stretch intensity at about 2900 cm^{-1} upon weathering. The carbonyl peak can be assigned to carboxylic acids or ketones (7). An oxidation index developed by U.S. Steel (7), based on the FTIR spectra, is plotted as a function of weathering time in Figure 4. The index consists of the ratio of the integrated intensity of the carbonyl band (1635 cm^{-1} to 1850 cm^{-1}) to that of the aromatic and aliphatic C-H stretch band (2746 cm^{-1} to 3194 cm^{-1}). Since the index includes the C-H stretch band, it is sensitive to the loss of C-H intensity from weathering as well as to carbonyl production (7). Figure 4 indicates a fairly consistent increase from an index value of 0.45 for the fresh coal to 1.45 after 84 days weathering at 80°C. Others have attributed such changes to the oxidation of C-H groups to carbonyl groups (3,7).

The surface elemental compositions (C, total and organic O, S, N, Si, Al) by XPS of the coal weathered at 80°C for various times were obtained by XPS. Organic oxygen was calculated by subtracting inorganic oxygen from total oxygen, assuming that inorganic oxygen is associated with Si and Al in the oxide forms (2,8). The surface organic oxygen content increased from 4.8% to 8.5% after 84 days weathering. This increase is consistent with the carbonyl production determined by FTIR. The atomic ratio of organic oxygen to carbon (organic O/C ratio) obtained by XPS has been used as an indication of coal surface oxidation (8). The organic O/C ratios obtained by XPS (surface) and by ultimate analyses (bulk) along with the ratio of oxidized to unoxidized surface sulfur (by XPS) at various weathering times are shown below.

Weathering Time (Days at 80°C)	Organic O/C Surface	Organic O/C Bulk	Surface Sulfur (Oxidized/Unoxidized)
0	0.056	0.026	0.6
31	0.072	0.032	---
51	0.090	0.042	---
84	0.105	0.051	1.7

The surface organic O/C ratio increased more rapidly than the bulk organic O/C ratio, indicating the sensitivity of the coal surface to oxidation (weathering). The ratio of oxidized to unoxidized surface sulfur was calculated using the XPS S_{2p} peaks shown in Figure 5. Two distinct S_{2p} peaks were resolved, one at a low binding energy (164 eV) and one at a high binding energy (169 eV). The peak at

164 eV can be assigned to unoxidized sulfur species (pyritic sulfur and perhaps some organic sulfur) (9) and the peak at 169 eV can be assigned to oxidized sulfur species (sulfate) (9,10). The relative intensity (atomic percentage) of the S_{2p} peak at 169 eV to the S_{2p} peak at 164 eV increased after 84 days weathering at 80°C, indicating that surface pyritic sulfur was oxidized to sulfate.

High-Volatile Bituminous. Pittsburgh seam coal (-28 mesh) was weathered at 25°C, 50°C and 80°C for up to 369 days. As with the Horsepen seam coal, small decreases in heating value and small increases in oxygen and sulfate contents were observed with increased weathering time. For example, heating value decreased from 13335 to 12940 Btu/lb (dry), oxygen content (by difference) increased from 6.5 to 8.6% and sulfate sulfur content increased from 0.06 to 0.09% after 45 days weathering at 80°C. As shown in Figures 6 and 7, the rates of change with time (slopes) of both the Gieseler maximum fluidity and FSI are strongly dependent on weathering temperature. Similar changes in maximum fluidity and FSI with time and temperature have also been reported by others (7,13). Interestingly, the rate of change of maximum fluidity with time shows a first-order Arrhenius dependence on temperature. Using the Arrhenius expression, an energy of activation of about 40 kJ/mol is calculated. The exact physical significance of this result is unknown. However, observations of relationships between multiple parameters such as this should permit better understanding of the effects and mechanisms of weathering.

FTIR was used to characterize the chemical nature of weathering on Pittsburgh seam coal at 25, 50 and 80°C. The U.S. Steel oxidation index was used to represent the extent of organic matrix oxidation. At 80°C, the oxidation index increased from 0.72 (fresh coal) to 1.63 after 20 days and to 2.05 after 45 days. At 50°C, the oxidation index increased to 1.29 after 229 days and to 1.30 after 268 days. At 25°C, the oxidation index showed little change from the fresh coal, being 0.82 and 0.71 after weathering 268 days and 313 days, respectively. These data show that the rate of production of carbonyl groups and loss of C-H stretch intensity upon weathering is strongly temperature dependent, consistent with the temperature dependence of the change in maximum fluidity upon weathering (Figure 6).

Fresh and weathered coals were characterized by XPS. An asymmetric C_{1s} peak with a shoulder at high binding energy was observed after weathering at 80°C, indicating that some oxyhydrocarbon was generated. This is consistent with the FTIR results showing carbonyl production. As with the Horsepen Seam coal, two distinct S_{2p} peaks were resolved with binding energies of 164 eV and 169 eV. The relative intensity (atomic percentage) of the S_{2p} peak at 169 eV to the S_{2p} peak at 164 eV increased after 45 days weathering at 80°C, indicating that surface pyritic sulfur was oxidized to sulfate. Froth flotation performance depends on surface interactions (11). Flotation recovery is compared below to the ratio of oxidized/unoxidized sulfur and to the atomic ratios of organic O/C obtained by XPS. Organic oxygen was calculated as with the Horsepen seam coal.

Weathering Time (Days at 80°C)	Flotation Recovery (% MAF) Using 0.5 lb Fuel Oil/ Ton Coal	Surface Sulfur (Oxidized/ Unoxidized	Organic O/C Surface	Organic O/C Bulk
0	94.5	0.62	0.077	0.066
45	25.1	2.98	0.156	0.088

Flotation recovery decreased with increasing surface oxidation of both the organic matrix and the pyrite. The surface organic O/C ratio increased more rapidly than the bulk organic O/C ratio (obtained from ultimate analysis), indicating the sensitivity of the coal surface to oxidation (weathering). In contrast to the coal weathered at 80°C for 45 days, a symmetric C_{1s} peak, similar to that of fresh coal, was observed in XPS spectrum of the coal weathered at 25°C for 313 days, thus showing little oxyhydrocarbon production (2,8). This is also consistent with the FTIR results which show no evidence for significant carbonyl production at 25°C. Two distinct S_{2p} peaks were resolved (164 eV and 169 eV) for the coal weathered at both 80°C and 25°C, indicating surface pyritic sulfur was oxidized to sulfate at both temperatures. The ratio of oxidized to unoxidized sulfur for the coal weathered at 25°C for 313 days is 1.70. For this weathered coal, pyrite oxidation was evident but little organic oxidation was apparent. This may suggest that for the 25°C weathered coal, the loss of flotation recovery is primarily caused by pyrite oxidation instead of organic matrix oxidation (12). A similar conclusion was reached in an assessment of a stockpile sample of the same Pittsburgh seam coal which showed poor flotation performance (14).

The froth flotation results with this coal were qualitatively similar to those using the Horsepen seam coal. Coal recovery (% MAF) decreased with the extent of weathering (time and temperature) and could be significantly improved by increasing the collector dosage. Even for the coal most severely weathered at 80°C (45 days), flotation recovery was restored to over 90% by increasing the collector dosage from 0.5 to 2.0 lbs fuel oil/ton coal. Substantial losses in flotation recovery occurred only after very large decreases in fluidity had occurred; however, the relationship between fluidity and flotation recovery appears to be temperature dependent as shown below.

Weathering T (°C)	Weathering Time (days)	Flotation Recovery (% MAF)	Maximum Fluidity (DDPM)
Fresh	0	94.5	30,600
80	30.9	78.2	2.6
80	45	25.1	1.5
50	268	69.4	70.6
25	313	46.4	3,442

These flotation data were obtained using 0.5 lbs fuel oil/ton coal as collector. At each temperature, the degree of weathering that produced substantial loss of flotation recovery results in different reductions in maximum fluidity. This would suggest that the loss of flotation recovery and loss of fluidity result from different causes. Weathering temperature apparently affects not only the rate of weathering, but also the relative change of the different properties affected by weathering. Thus, it would appear that the use of high temperature, e.g., over 100°C, to accelerate weathering may produce coal with properties different from those produced at lower temperatures and longer times.

Naturally Weathered Coal. A "naturally weathered" Horsepen seam coal was characterized for comparison with the laboratory weathered coals. Properties of this coal, listed in Table 1, indicate that it is at least moderately weathered. The Gieseler maximum fluidity measurement was low at 30 DDPM, the % dilatation (Audibert-Arnu) was negative (-22%) and the alkaline extraction test gave a low transmittance of 13.8%. The flotation recovery (% MAF) was extremely low at 10.1% using frother (0.38 lb MIBC/ton coal) but no collector. FTIR and XPS indicated that there was mild oxidation of the organic matrix. The surface organic O/C ratio was extremely high at 0.29. This compares to a bulk ratio of 0.07 obtained by ultimate analysis. The relatively large surface organic O/C ratio occurring in the presence of only moderate carbonyl production suggests that chemisorbed oxygen may be present on the coal surface (probably peroxide)(4). XPS characterization showed a ratio of oxidized/unoxidized sulfur of 3.8, indicating that pyrite was highly oxidized. It appears that oxidation of both pyrite and the organic matrix is responsible for the poor froth flotation performance of this naturally weathered coal.

SUMMARY AND CONCLUSION

The Gieseler plastometer and Audibert-Arnu dilatometer are the most responsive tests to the early stage of weathering, thus demonstrating that relatively moderate weathering will destroy coal thermoplasticity. Other parameters measured are much less reponsive to weathering. FSI appears to be a useful indicator only for relatively severely weathered coal. Substantial loss in flotation recovery upon weathering occurred only after the Gieseler maximum fluidity was greatly reduced. The rate of decrease in Gieseler maximum fluidity with time shows an Arrhenius temperature dependence. FTIR shows production of carbonyl groups at 80°C (fast) and 50°C (slow), but carbonyl production is small or nonexistent even after 313 days at 25°C. XPS shows that the surface organic O/C ratio increased more rapidly than the bulk O/C ratio obtained by ultimate analysis, indicating the sensitivity of the coal surface to oxidation (weathering). Pyritic sulfur was also oxidized to sulfate on the coal surface. Froth flotation recovery of the weathered coals deteriorated with increasing degree of weathering and showed a different dependence on temperature than maximum fluidity. Flotation recovery can be largely restored by increasing the collector dosage used. The relative importance of the effects of organic matrix and pyrite oxidation on flotation recovery appear to be dependent on the weathering temperature. If this is the case, it would appear imperative to use realistically low temperatures to model natural weathering.

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TABLE 1

ANALYSES AND PROPERTIES OF HORSEPEN AND PITTSBURGH SEAM COALS

	Horsepen Seam	Pittsburgh Seam	Horsepen Seam "Naturally Weathered"
Proximate Analysis (wt % As Det.)			
Moisture	0.61	2.29	1.75
Volatile Matter	24.59	36.57	25.52
Ash	5.82	10.41	9.83
Fixed Carbon (By Difference)	68.98	50.73	62.90
Ultimate Analysis (wt % Dry Basis)			
Carbon	84.06	74.04	78.75
Hydrogen	4.69	4.93	4.28
Nitrogen	1.33	1.39	1.19
Sulfur, Total	1.11	2.54	0.98
Pyritic	0.41	1.37	0.15
Sulfate	0.02	0.06	0.15
Organic (By Difference)	0.68	1.11	0.68
Oxygen (By Difference)	2.96	6.48	4.79
Ash	5.86	10.66	10.01
Heating Value (Btu/lb, Dry)	14,809	13,335	13,790
Gieseler Plastometer			
Maximum Fluidity (DDPM)	1,836	30,600	30
Softening Temperature (°C)	387	348	398
Resolidification Temperature (°C)	511	481	498
Maximum Fluidity Temperature (°C)	472	434	440
Plastic Range (°C)	124	133	106
Free Swelling Index	8 1/2	7 1/2	7
Audibert-Arnu Dilatometer			
Contraction (%)	28	27	24
Dilatation (%)	191	103	-22
T_1, °C	377	334	384
T_2, °C	418	404	442
T_3, °C	496	454	475
T_2-T_3, °C	78	50	33
Alkaline Extraction (% Transmittance)	88.8	90.0	13.8
Flotation Recovery (% MAF)			
Without Collector	94.1	-	10.1
With Collector (0.5 lb Fuel Oil/ Ton Coal)	-	94.5	49.1
Wet Screen Analysis, wt %			
Tyler Mesh			
28 x 48 mesh	39.4	36.3	34.0
48 x 100 mesh	26.4	23.7	24.9
100 x 200 mesh	14.3	17.7	15.0
-200 mesh	19.9	22.3	26.1

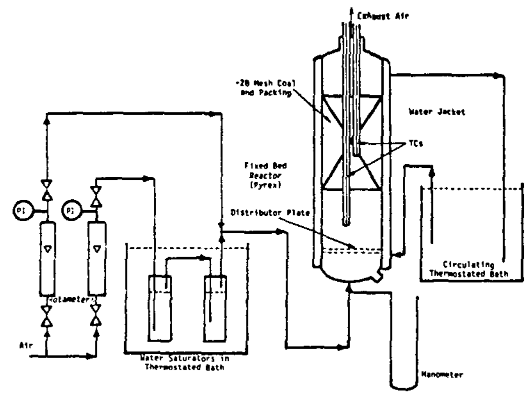

Figure 1. *Coal Weathering Unit.*

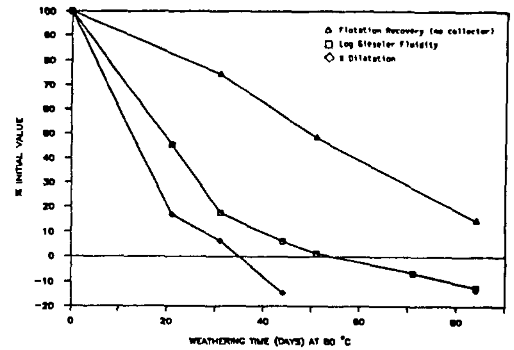

Figure 2. *Thermoplastic and Flotation Properties of Horsepen Seam Coal as a Function of Weathering Time at 80°C.*

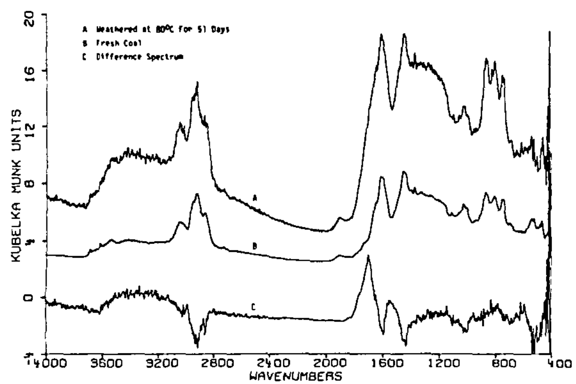

Figure 3. FTIR Spectra of Horsepen Seam Coal.

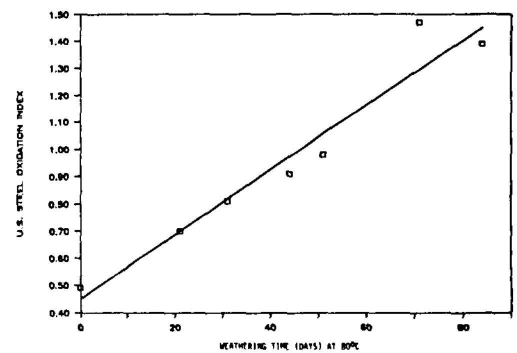

Figure 4. Oxidation Index of Horsepen Seam Coal as a Function of Weathering Time at 80°C.

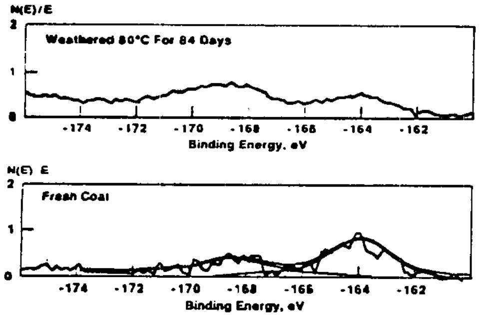

Figure 5. XPS S_{2p} Spectra of Horsepen Seam Coal.

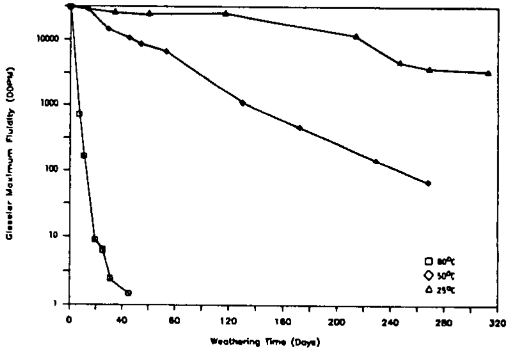

Figure 6. Gieseler Maximum Fluidity of Pittsburgh Seam Coal as a Function of Weathering Time and Temperature.

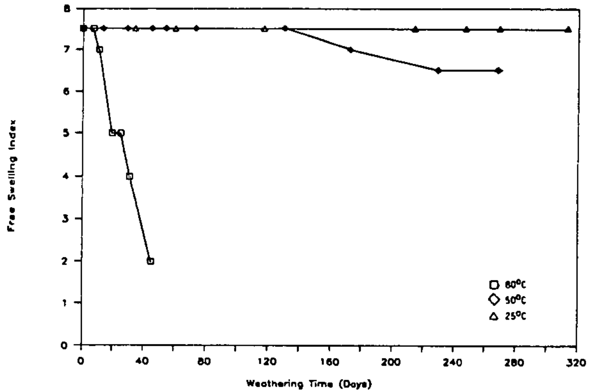

Figure 7. Free Swelling Index of Pittsburgh Seam Coal as a Function of Weathering Time and Temperature.