ATTEMPTED DEVELOPMENT OF A "WEATHERING INDEX" FOR ARGONNE PCSP COALS

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INTRODUCTION

It is well known that weathering has a profound effect on many important coal properties such as coking characteristics, slurry pH, flotability, tar yield, extractability, etc., as well as on coal utilization processes such as combustion, pyrolysis, gasification and liquefaction. However, since coal is a very heterogeneous material and its properties differ according to rank and seam, it is very difficult to define reliable standard values for the degree of weathering. Therefore, most methods for determining the degree of weathering provide relative values and have practical usefulness only if measured values can be calibrated against coal samples weathered under carefully standardized conditions. Since fresh samples from several standard coals are now available from the Argonne Premium Coal Sample Program (PCSP) systematic studies of the weathering behavior of these coals have become practical as well as timely.

In the past, many different attempts have been made to measure the degree of weathering of a given coal sample. One of the more obvious approaches is perhaps to determine the oxygen content by oxidative (1,2), reductive (3,4), or pyrolytic methods (5). Alternatively, oxygen content can be measured directly by neutron activation analysis (6). However, the uptake of oxygen by a given coal can be offset to a significant degree by the concomittant loss of CO_2, CO and H_2O (7), thus making the net increase in oxygen content far from easily predictable. Moreover, most oxygen measurement techniques are notoriously time-consuming and unreliable.

Workers in the coke producing industry have known for a long time that caking properties of coal change dramatically upon weathering. Consequently, they have tried to develop simple and practical methods for determining the degree of weathering. Gray et al. (8) suggested an alkali-extraction method as one of several candidates. Lowenhaupt and Gray (9) applied this alkali-extraction method using light transmittance as an index of weathering for high to low volatile bituminous coals. The fact that coal swelling properties change dramatically when a caking coal is weathered presents many potential opportunities for determining the weathering status. Swelling properties of coal can be measured by means of Free Swelling Index (FSI), dilatation, Gieseler fluidity or gas flow resistance tests (10,11). For strongly caking coals FSI is not as sensitive as dilatation or Gieseler fluidity (12,13). In the early stage of weathering, Gieseler fluidity appears to be the most sensitive of the three methods. However, Gieseler values tend to drop to zero after some oxidation time. Under moderate and severe weathering conditions, however, FSI is a good index of weathering, especially in the FSI range between 1 and 4 (14).

Fourier Transform Infrared Spectroscopy is known to show an increase in carbonylic, carboxylic and phenolic groups as well as a decrease of aromatic and aliphatic moieties. Huggins et al. (15) proposed the ratio of reflectance in the carbonyl band region to that in the region of the aromatic and aliphatic C-H stretch bands as a possible weathering index.

Thermal analysis methods, e.g., thermogravimetry (TG), as well as analytical pyrolysis techniques (e.g., pyrolysis MS (Py-MS)) also show a strong response to weathering. Izuhara et al. (16) used the change of maximum weight loss rate in TG as a weathering parameter, whereas Jakab et al. (17) used time-resolved Py-MS to show that the evolution profiles of several components (carboxylic acids, naphthalenes, methanol, water, etc.) were quite different when coal was weathered.

The Zeta potential of coal particle suspensions in H_2O can also be a good indicator of weathering. Since weathered coal shows poor flotation characteristics, several studies were undertaken to understand this phenomenon in more detail (18-20). In general, weathered coal shows lower Zeta potential values than fresh coal.

Another important feature of weathered coal is its acidic character. Thus, Gray et al. (8) suggested coal slurry pH measurement method as one of several candidate techniques for determinating weathering status. They reported slurry pH changes from 7.1 to 5.5 for fresh and severely weathered Pocahontas #3 coal, respectively. Hill et al. (21) applied this idea to subbituminous (Adaville #6) coal, but added 0.01 wt% surfactant to the slurry in order to enhance the wetting of coal with water. For fresh and moderately weathered (1 to 6 days at 100° C)coals, they reported pH changes from 7.2 to 5.0 and applied this result to coal samples obtained from coal storage piles in order to estimate concomittant btu losses. When coal is exposed to air, oxygen, hydrogen peroxide, nitric acid, potassium permanganate, and other oxidizing agents, mixtures of water soluble acids are formed. For bituminous coal, chromatographic and mass spectrometric studies show that these acids consist mainly of benzoic, phthalic, mellitic and trimellitic acids and their isomers (22). Py-MS results also show an increase of short chain carboxylic acids, e.g., acetic acid, during weathering (23). Moreover, in some cases phthalic anhydrides can be detected by FTIR (24,25) as well as by time-resolved Py-MS (26). If these phthalic anhydrides formed due to weathering can be hydrated to the free acid form, then simple slurry pH measurements can be used as a method of detecting the degree of weathering, as will be shown in this presentation.

Even though some success was reported with the use of slurry pH as an index of weathering, its practical use appeared to be limited to severely weathered coals and some low rank coals. Here we report a modified and improved sample preparation titration method which overcomes these limitations.

EXPERIMENTAL

One to two pound aliquots of 2-4" sized PCSP coals were obtained submersed under water in sealed metal cans. Coals were dried with Drierite in a nitrogen atmosphere overnight and then ground to -60 mesh in a ball mill under nitrogen. Ground coals were transferred to 25 ml polyethylene vials in a glove box filled with nitrogen and stored at -90°C.

Twenty gram aliquots (-60 mesh) of all eight PCSP coals were exposed to a dry air flow (10 ml/min) in a 100 ml glass reactor, at 100°C for 8 days. The Blind Canyon seam coal was weathered for 2, 4, 6 and 8 days in separate glass reactors at 100°C and the Pittsburgh #8 seam coal was weathered at 150°C for 1 and 3 days in order to determine the effects of weathering time and temperature, respectively.

Weathered coal samples were then transferred to a Parr 4745 general purpose digestion bomb. 2.0 g of coal were mixed with 20 ml deionized water and was put in a 23 ml Teflon container and heated to 150°C for 2 hours. Subsequently, the bomb was cooled under tap water for 10 minutes. Next the coal slurry was transferred to a polystyrene beaker for pH measurements. 20 ml of deionized water were used to rinse remaining coal from the teflon container. Resistivity of the deionized water used was more than 16 Meg ohms-cm. pH titrations were performed with a Mettler DL40RC titrator using a 20 ml burette with 0.01 ml titrant (0.01N NaOH) increments.

RESULTS AND DISCUSSION

In earlier weathering studies involving a subbituminous Adaville coal (21), direct pH titration at ambient temperature showed a marked increase in acidity by more than 2 pH units after exposure of the coal sample to air at 100°C for 6 days. However, subsequent pH titration experiments with coals of different rank, including Wyodak (subbit/lignite), Hiawatha (hvBb) and Freeport (mvb) coals gave negative or ambiguous results under the same weathering conditions. Nevertheless, Py-MS analyses of the same coals showed a distinct increase in carboxylic and carbonylic functional groups (23). In subsequent Py-MS studies of the weathering behavior of individual macerals (26), strong signals were noted which appeared attributable to anhydrides of phthalic acid and/or other aromatic acids. This provided us with a possible clue to the observed lack of strong pH changes since anhydride formation would effectively remove the acidic protons. Therefore, an attempt was made to re-hydrate the weathered coal samples before carrying out pH titrations. As described under Experimental, rehydration was carried out at 150°C in teflon-lined Parr bombs. As shown in Figure 1 and subsequent figures this procedure was found to be very simple as well as effective in "restoring" the acidity of all weathered coals investigated thus far. Py-MS analysis of the solution extracted during the rehydration procedure, however, indicated that CO_2^+ fragment from acids and acetic acid were the main products, not phthalic acid. Thus more detailed studies are needed to clarify the chemistry behind this method. Figure 1 further suggests that the initial pH can also be a good weathering index for Utah Blind Canyon coal.

Figure 2 shows the effect of weathering duration on pH and repeatability of the method. Clearly, as coal is weathered, more acidic products are dissolved out and therefore lower pH values are obtained. The small differences between repeat analyses on the same weathered coal may be due to temperature variations of the solution. More precise standardization of the method is planned to overcome this problem.

Figure 3 shows the effect of different coal rank, viz. low volatile bituminous (lvb) to lignite. As expected, lower rank coals produce more acidic products during weathering. The difference in the amount of titrant needed to reach pH 8 between fresh and weathered coals reveals even more clearly the effect of rank. Difference spectra obtained by Py-MS analysis of coals of different rank confirmed this observation by showing that structural changes in mvb Upper Freeport coal were only about 30% of those observed in subbituminous Wyodak coal when weathered at 100°C (23).

Possible depositional effects for four coals of similar rank (hvb) are shown in Figure 4. Profound differences in terms of the initial pH as well as the slope of the titration curve are found. Lewiston - Stockton coal has the highest initial pH. This is thought to be due to major differences in depositional environments. Although Lewiston-Stockton coal and Pittsburgh #8 coal show very similar titration curves the difference of the initial pH is most noticeable. In contrast to these coals, Illinois #6 coal produces the most acidic solution. This may be due to its higher sulfur content (and/or higher surface area) than other coals.

The effect of weathering temperature is shown in Figure 5. Note the dramatic pH difference after only 1 day at 150°C as contrasted to up to 8 days weathering at 100°C. This suggests that the weathering temperature may be the most important variable in weathering.

In conclusion, a simple pH titration method based on rehydrating coal slurries with water at 150°C was proved to be a successful way of monitoring weathering effects in all 8 ANL-PCSP coals. For LVB and higher rank coals, however, slurry concentrations should perhaps be increased to compensate for the decreased susceptibility to low temperature weathering. Further work is underway to elucidate the structural moieties responsible for the observed differences in the shape of the titration curves. Moreover, detailed characterization of the low MW components extracted by the rehydration procedure is expected to yield important information on the underlying mechanisms of the weathering process.

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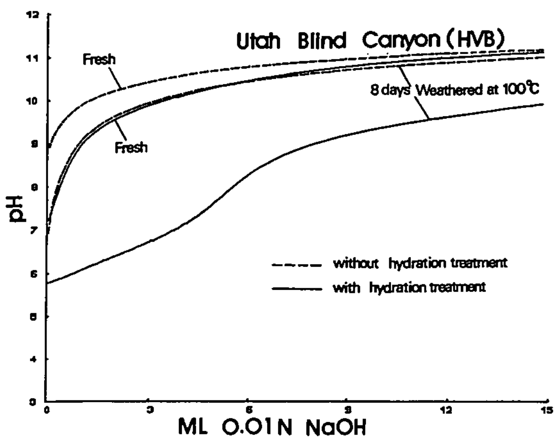

Figure 1. Effect of hydration treatment at 150°C on titration curve.

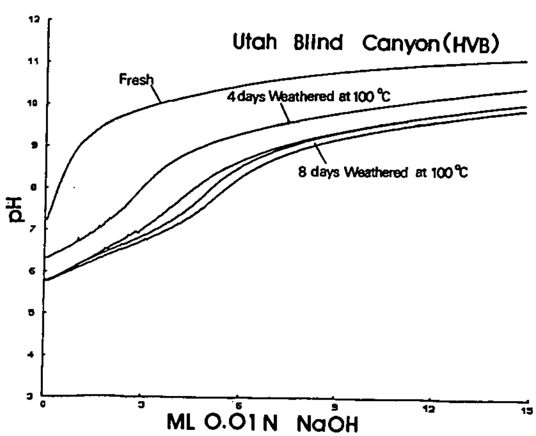

Figure 2. Effect of weathering duration on titration curves. Lower three curves show repeatibility for 8 days weathered coal at 100°C.

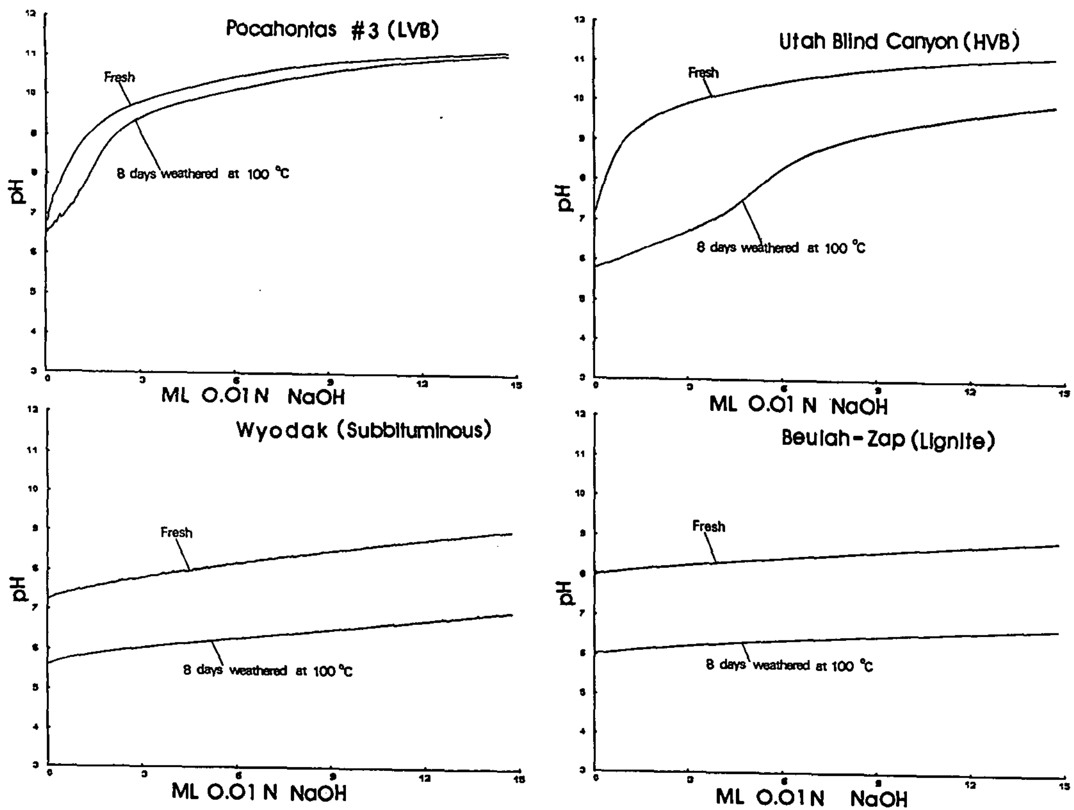

Figure 3. Effect of rank on titration curves.

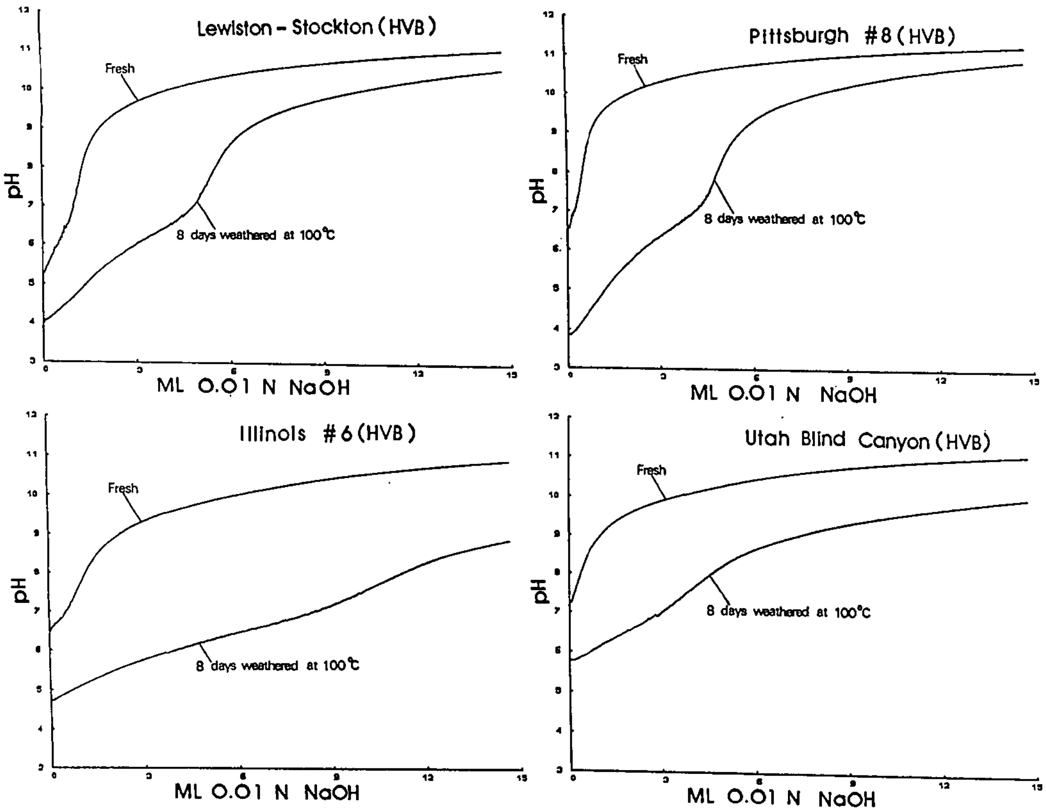

Figure 4. Effect of deposition on titration curves.

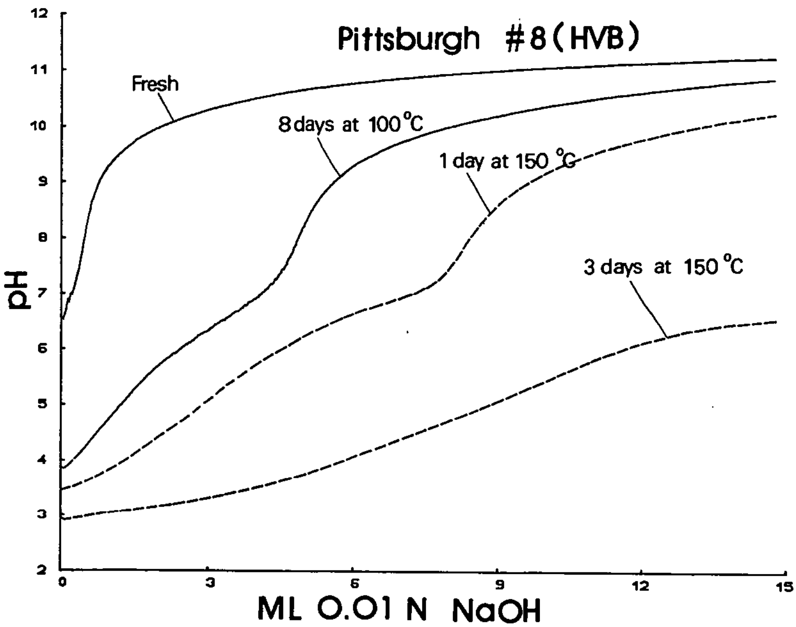

Figure 5. Effect of weathering temperature on titration curves for Pittsburgh #8 coal.