

COAL SLURRY pH STUDIES

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ABSTRACT

Coal slurry pH values can be used to characterize coals. pH values depend on the coal, time since slurry preparation, contact with gas atmosphere, particle size, and stirring. Measured values reflect a sequence of reactions probably including: carbon dioxide absorption by water from the air, wetting of the coal (pH may be affected by the elemental composition of the mineral matter), and further equilibration with species in the water. The pH initially drops as carbon dioxide is absorbed, then rapidly increases as the coal is wetted, and then slowly decreases as some reactions with species in the water take place.

INTRODUCTION

Coal slurry pH values are used to characterize samples. It has been suggested as a means to indicate the degree of oxidation or weathering. The measurement procedure is similar to that used for soil samples (1). The usual procedure calls for the addition of a weighed quantity of coal and water (1:2), stirring well, and measurement of the pH of the liquid above the settled coal after a time period of one half hour.

The stirring is intended to quickly wet the hydrophobic coal particles so that they will be suspended in the slurry rather than remain on the surface of the mixture. The waiting period before the measurement implies a dynamic situation and an approach to a steady state pH value. This paper is intended to describe some of the changes which take place during the course of the period from the beginning of the mixing to several hours afterward. Several reactions are apparent from the changes which have been observed.

The wetting involves an interaction with the surface of the coal particles. The effect on pH includes at least dissolution of soluble acidic or basic species, interaction with surface acidic or basic functional groups, interaction with acidic or basic surface sites or areas. Oxidation can change the surface of the mineral as well as the organic parts of the coal, and can be expected to affect the pH. Some of these potential effects may be deduced from changes in the progression of pH with time for a sample.

EXPERIMENTAL

An Orion Model EA940 pH meter was used with an Accumet pH electrode. The electrode was calibrated with standard buffers of pH 4, 7 and 10. A two point method was used depending on the range of pH values involved in the experiment. Typically calibration was done at pH 7 and 10. Distilled and de-ionized water was used.

The coal samples were taken from the Argonne Premium Coal Sample Program set. Both -100 and -20 mesh samples were used. Water/coal ratios of 2-32 to 1 were obtained by mixing an ampule of 5 grams of -100 or 10 grams of -20 mesh coal with varying amounts of water. For some experiments a polyethylene plug (machined to fit inside the pyrex beaker and center the electrode in a snug-fitting hole) was used to limit the access to the atmosphere. For deaerated water experiments, the water was prepared by bubbling a stream of nitrogen through the stirred water for a minimum of 30 minutes. In one experiment, nitrogen gas was passed over the coal-containing equipment in a plastic enclosure. A magnetic stirrer was used in a number of experiments.

Sealed ampules were opened at the beginning of the experiment, weighed, water added and weighed, and mixed with a glass stirring rod or magnetic stirrer. Data were recorded on a IBM microcomputer at 15-20 second intervals. The computer data were analyzed using Lotus 123.

RESULTS AND DISCUSSION

A typical result for a Pittsburgh high volatile bituminous coal is shown in Figure 1. Initially the pH decreases as the water is stirred and affected by the atmosphere. As the coal is added the pH increases to a maximum value and then slowly decreases again. This general behavior pattern has been observed for most of the coal samples.

The initial decrease is believed to be due to the dissolution of carbon dioxide from the air, formation of carbonic acid, and ionization to provide hydronium and bicarbonate ions. The increase on addition of coal involves an interaction with the surface accessible to the water. This interaction consumes hydronium ions. The final slow decrease in pH may be again due to interaction with the carbon dioxide in the air.

The initial reaction with coal gives a series of maximum values. The value of the maximum does not correlate with carbon content or others of the organic elemental composition.

A series of runs with Illinois #6 (IL) indicated the effects of several values and produced a range of values for the maximum pH. For the -100 mesh samples run in pyrex beakers, the maxima were in the range 9.75-9.80. If a stainless steel beaker was used instead (250 ml) the maxima were in the pH range 9.65-9.71. These results were obtained over a water/coal ratio range of 2/1 to 32/1. However, for the -20 mesh sample with a water/coal ratio of 4, the pH range was lower, 9.61-9.76, with a value of 9.53 for the stainless steel beaker. The high values were obtained when the magnetic stirrer was off in the early stages of the run. Stirring introduced a limitation to the maximum pH, probably due to the incorporation of carbon dioxide from the atmosphere. Aerating or de-aerating the water had little effect on the maximum pH as both gave 9.72. Interestingly, a sample which had no gas bubbled through gave pH 9.67.

The run with equipment blanketed with nitrogen and de-aerated water gave the pH 9.76 which was higher than other stirred runs.

The effect of stirring speed was notable at low coal concentrations. Apparently, more rapid stirring gives a higher maximum pH.

In an effort to understand the reason for the increase in pH on the addition of coal to water, a series of materials were stirred with water. It was apparent that graphite did not behave like the coal, unless it was assumed that the behavior was like an extremely high rank coal. However the addition of titanium dioxide, as an example, gave a behavior very reminiscent of the plot of pH versus time for the coal samples. This observation would indicate that the pH may be due to the effect of various mineral constituents in the sample.

CONCLUSIONS

The measured pH value of a given coal slurry will depend on the parameters of the experiment, including water/coal ratio, stirring speed, particle size, and coal rank.

The addition of coal to water produces a series of pH changes. Initially, the drop in pH corresponds to the addition of carbon dioxide to the slurry. A subsequent increase appears to be related to inorganic constituents in the coal. A long term decrease in pH is assumed due to continued interaction with carbon dioxide.

The maximum pH depends on the interaction of the concentration of carbon dioxide, and the concentration of the mineral matter in the slurry.

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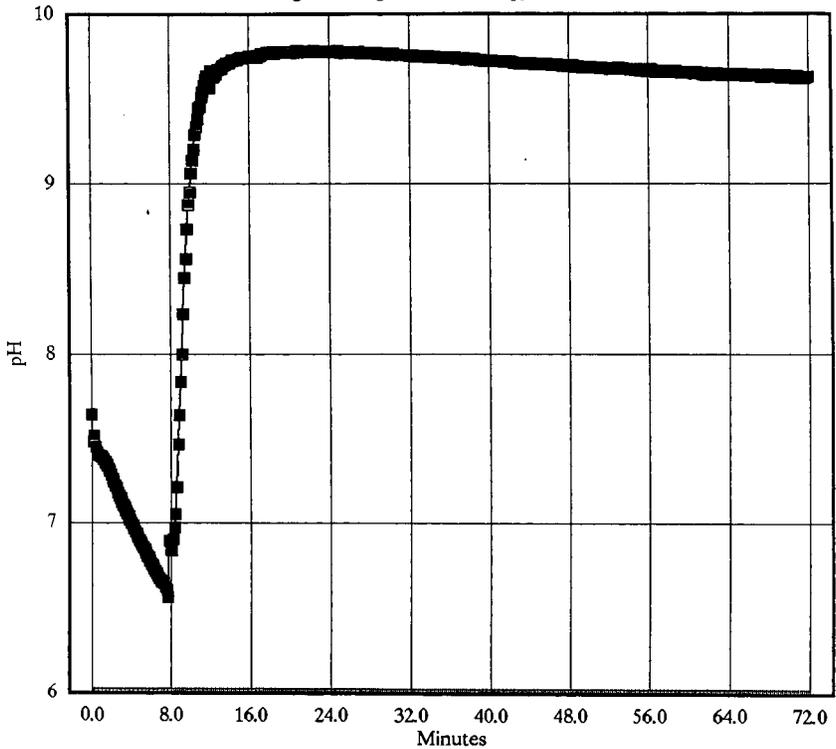
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Fig. 1, pH of PI-100 mesh Slurry

5 g coal, 35 g water in 50 ml pyrex beaker



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