# ION EXCHANGE AND ADSORPTION ON LOW RANK COALS FOR LIQUEFACTION

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**OBJECTIVE:**

The objectives of this program involve the study of the catalysis of liquefaction of low rank coals. Ion exchange and adsorption techniques are being used or modified to incorporate catalytically active metals into coal samples. Relative oil yields will be determined by Sandia National Laboratory and PETC collaborators to establish the effectiveness of the catalyst incorporation techniques.

**INTRODUCTION:**

This report describes work done over the past 12 months of an ongoing project. A report describing earlier work was included in the Proceedings of the previous Contractors Meeting (1).

Ion Exchange and Adsorption

A number of techniques are being explored to place catalytically active materials on coal to facilitate direct liquefaction. Catalysts capable of liquefaction as small particles are being developed to permit maximum conversion at minimum cost. Additional motivation is due to a reduced need to recover active materials and the associated cost.

A variety of forms of iron catalysts are being developed in other research groups and are being reported at this meeting.

Other approaches have included the use of cation-exchanged catalysts. The hoped-for advantages include: close contact with the coal surface for good catalytic activity, more limited dosage required because of the close contact, and reduced need to recover the catalyst (particularly if it is an iron oxide).

A related technique is adsorption of anions. Some metals like molybdenum form oxy-salts such as molybdates. The active metal is present in the anion form and requires a different surface site than a cation for attachment to the coal surface. In addition the chemical nature of the metal is altered by surrounding it with oxide ions in the molybdate complex. A technique has been developed for reproducibly placing the molybdate ions on the surfaces of coal particles (2). An equivalent procedure has not been developed for iron and the success of various efforts to ion-exchange iron has not been uniform.

A part of this work has involved an effort to understand the environment around the coal particle in an aqueous system so that better ion-exchange procedures may follow. The environment can be characterized in terms of the slurry pH of the coal sample. The pH affects the feasibility of ion exchange. Sudden shifts to alkaline values would cause precipitation of hydroxides rather than the exchange with surface sites that is desired.

The coal slurry pH is one of several tests used to characterize coals. A recipe is generally used. The typical recipe (3,4) involves taking one gram of coal for each two grams of water, mixing well, letting the mixture stand for 30 minutes and measuring the pH. Several things are implied in this procedure. The ratio of coal to water is specified and gives a fairly thick material, but not as thick as used in slurry pipelines and feed to burners for boilers. The time period of 30 minutes before measurement implies some reaction(s) are taking place and that a steady state or equilibrium may be reached after the 30 minute period.

A part of this study will explore the changes around coal in an aqueous environment and establish pH ranges during reasonable time periods of value in commercial processing.

### Direct Liquefaction Studies

This project has used ion exchange and the related adsorption techniques to place catalytic materials on low rank coal samples. The samples have been sent to other laboratories for treatment to evaluate liquefaction potential. The efforts over time of Drs. Frances Stohl at Sandia National Laboratory, Christine Curtis at the University of Alabama and Anthony Cugini at PETC are much appreciated.

## EXPERIMENTAL APPROACH

### Ion Exchange - Slurry pH

An Orion Model EA940 pH meter was used with an Accumet pH electrode. The electrode was calibrated with standard commercial 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. Figure 1 is a schematic of the experimental apparatus.

At the beginning of a run, the pH electrode was placed in the weighed amount of water and data taking was initiated. Stirring was begun. Sealed ampules were opened, weighed, added to the water, and mixed with a glass stirring rod or magnetic stirrer. Stirring continued if the magnetic stirrer was used. Data were recorded on a IBM microcomputer at 15-20 second intervals. The computer data were analyzed using Lotus 123.

Several beaker materials and sizes were used to evaluate the effects of these parameters.

For comparison with the coal samples a series of oxide materials related to the mineral species in the coal, pyrite and graphite were also run.

A static measurement procedure is used for soil samples (3). 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.

## Liquefaction

The application of catalytic metals by ion exchange has been described in detail earlier (1). The technique involves the sieving of a -20 mesh sample to obtain -20+200 mesh material. This material is then rinsed with distilled water to remove adhering fine material. The moist slurry is transferred to a 50 ml burette equipped with a coarse fritted glass at the lower end of the markings. Initially a 0.10 N acid solution is used to elute the acid exchangeable material. The elution is followed with a series of pH and ion-selective electrodes for Ca, Na and K. The pH decreases and the eluted ion concentration decreases as the acid rinsing is near completion. A distilled water wash is used to remove the acid and provide a pH range of value for the ion exchange. Since some calcium was observed on the washing with water, the process is typically repeated through several cycles.

Following the coal preparation, the slurry is removed from the burette. A solution of known cation concentration is poured over the sample and allowed to stand for a period of several days. The solution is sampled and analyzed for the cation of interest. The change in concentration is related to the cation loading on the coal sample.

## CURRENT STATUS - RESULTS AND DISCUSSION

### Slurry pH

A typical result for a Wyodak subbituminous coal is shown in Figure 2. 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 maximum pH value could be used to characterize the samples.

Table 1 gives the maximum pH values for different coal samples with measurements taken in a pyrex beaker, and magnetically stirred at the same setting.

Table 1. Maximum pH Values for Argonne Premium Coal Samples

| Coal | Mesh | Max pH |
|---|---|---|
| ND | -100 | 9.626 |
| WY | -100 | 8.925 |
| IL | -100 | 9.752 |
| UT | -100 | 9.717 |
| WV | -20 | 7.735 |
| PI | -100 | 9.785 |
| UF | -100 | 9.298 |
| PO | -100 | 9.417 |

For static runs (recipe type) and 2/1 water/coal ratio, the shape of the pH vs time plot is that of a parabola on its side with an asymptotic approach up to a limiting pH. The parabolic shape implies a diffusion limited change through a growing barrier.

The diffusion appears to be related to dissolution of $CO_2$ in water and formation of bicarbonate ions as well as hydronium ions with consequent decrease in pH.

The observation in some cases of an increase in pH appears to be related to a reaction of some species, such as an inorganic oxide, with water at the surface. Hydronium ions may be attracted to the oxide surface, leaving hydroxide ions free to increase the pH.

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 of different coals of varying ranks gives a series of maximum pH values. The value of the maximum pH does not correlate with the coal carbon content or other organic elemental components.

## Effects of Variables

A series of runs with Illinois #6 (IL) indicated the effects of several variables and produced a range of values for the maximum pH. A number of variables were observed to determine if they were significant: container material, water/coal ratio, particle size, stirred/not stirred, aerated/deaerated water, and nitrogen environment.

### Container Material

For the -20 mesh sample run in 250 ml pyrex beakers, the maxima were in the range 9.79, the same as if a stainless steel beaker was used instead (250 ml). These results were obtained for a high stirring speed. If the stirring speed was reduced the pH values were reduced to 9.73-9.75.

### Particle Size

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.

### Water Aeration or Deaeration

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.

### Gas Environment

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

### Stirring Speed

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

### Mixture aging

Samples were set aside for several days after initial measurements. pH measurements were repeated with stirring. An IL-20 sample had been measured to peak at 8.98 and decline in pH to about 8.53 after 73 minutes. After 7 days the static pH measurement dropped to 7.61. On stirring as before, the pH again increased to a maximum value of 8.00 before decreasing to 7.94 over about 3 hours. The reaction that increases the pH appears to be aided by stirring. The attrition of particles and exposure of fresh surfaces, including minerals would be consistent with this observation. The fresh mineral surfaces could react with hydronium and release hydroxide to increase the pH. The slow and limited subsequent pH decline reflects the near saturation with $CO_2$ and equilibrium between $CO_2$, bicarbonate and other ions in the system. The suggested mechanism is also consistent with the earlier observation of the release of a suspension of clay material from a Wyodak sample after several cycles of acid and water washing. Perhaps chemical comminution by water develops cracks over time, which stirring propagates, leaving a tougher core after peeling off softer material. If so, then the overall rate might be combination of linear rate of exposing new surface from stirring and parabolic one from diffusion into particles. The observation of a slow decrease in pH over time with stirring implies that the addition of $CO_2$ with subsequent concentrations in the system has a greater effect on the pH than the particle attrition and interaction with new surface. However after standing for several days there is always some initial increase in pH with time after stirring.

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. 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.

## Other Materials - Inorganic Oxides, Graphite

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. These materials included a series of insoluble inorganic oxides related to those found in the mineral matter of coal: alumina, titania, silica, calcium carbonate and clay. In addition pyrite was examined. A non-inorganic oxide, graphite, was also studied because it was somewhat similar to the organic material in the coal.

All of the inorganic insoluble oxides gave a slurry pH profile similar to the coal. After the water was equilibrated and stirred, the oxide was added. The pH immediately rose sharply and then slowly declined. This implies that the observed coal slurry pH behavior could be due to the mineral matter alone. Figure 3 shows a typical slurry pH profile for $CaCO_3$.

The pyrite behavior, from a sample which had been in a reagent bottle for some time was quite different. The pH dropped sharply on addition of the pyrite to the water. This implies that the pyrite sample had aged. The outward appearance was typical of the material in a fresh state, and was free flowing. The acid evolution implied a surface oxidation of the sample. The coal samples apparently did not have significant amounts of oxidized pyrite in them. Figure 4 shows a slurry pH profile for pyrite.

It was apparent that graphite did not behave like the coal either, unless it was assumed that the behavior was like an extremely high rank coal. The pH dropped on addition of the graphite in a manner similar to the pyrite. Figure 5 shows a slurry pH profile for graphite.

These observations taken together would indicate that the pH may be due to the effect of various insoluble inorganic oxide mineral constituents in the sample.

## Liquefaction

Samples were prepared for a series of WY materials. These included:

WY Mo loaded 1.045 % on moist or 1.45 % on dry coal
WY Fe loaded 0.89 % on moist coal
WY acid and water washed, no catalyst loading for comparison
WY water washed, no catalyst loading for comparison
WY Mo + Fe loaded, 1.45% Mo + 0.053 % Fe on dry coal
WY + Fe loaded 0.71 % Fe on moist coal
WY + Mo loaded 0.126 % Mo on moist coal

These samples have been sent to Sandia National Laboratory for evaluation.

## ACCOMPLISHMENTS & CONCLUSIONS:

Application of molybdenum by anion exchange has been successful using the technique developed by Schroeder (2). The ability to apply iron depends on the pH of the system which in turn is affected by environmental variables which are being studied.

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 pH of a slurry of insoluble oxides gives a sharp increase on the addition of the oxide to water. Conversely, the addition of pyrite or graphite showed a decrease of pH on their addition to the water.

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.

## PLANS:

The results of liquefaction runs will be learned as they are completed at Sandia National Laboratory. The results with iron loaded samples will be of special interest because of the lower cost of this material and the lower environmental concern.

Alternate means of ion exchange of iron onto coal samples will be explored to optimize the application of this catalyst. Control of pH and exchange of other cations for calcium etc. before addition of iron are initial approaches for the application of iron.

## ACKNOWLEDGMENT:

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3. Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties, ed. C. A. Black, Amer. Soc. of Agronomy, Madison, WI 1965, pp. 915-920.

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# Figure 1- Apparatus Schematic

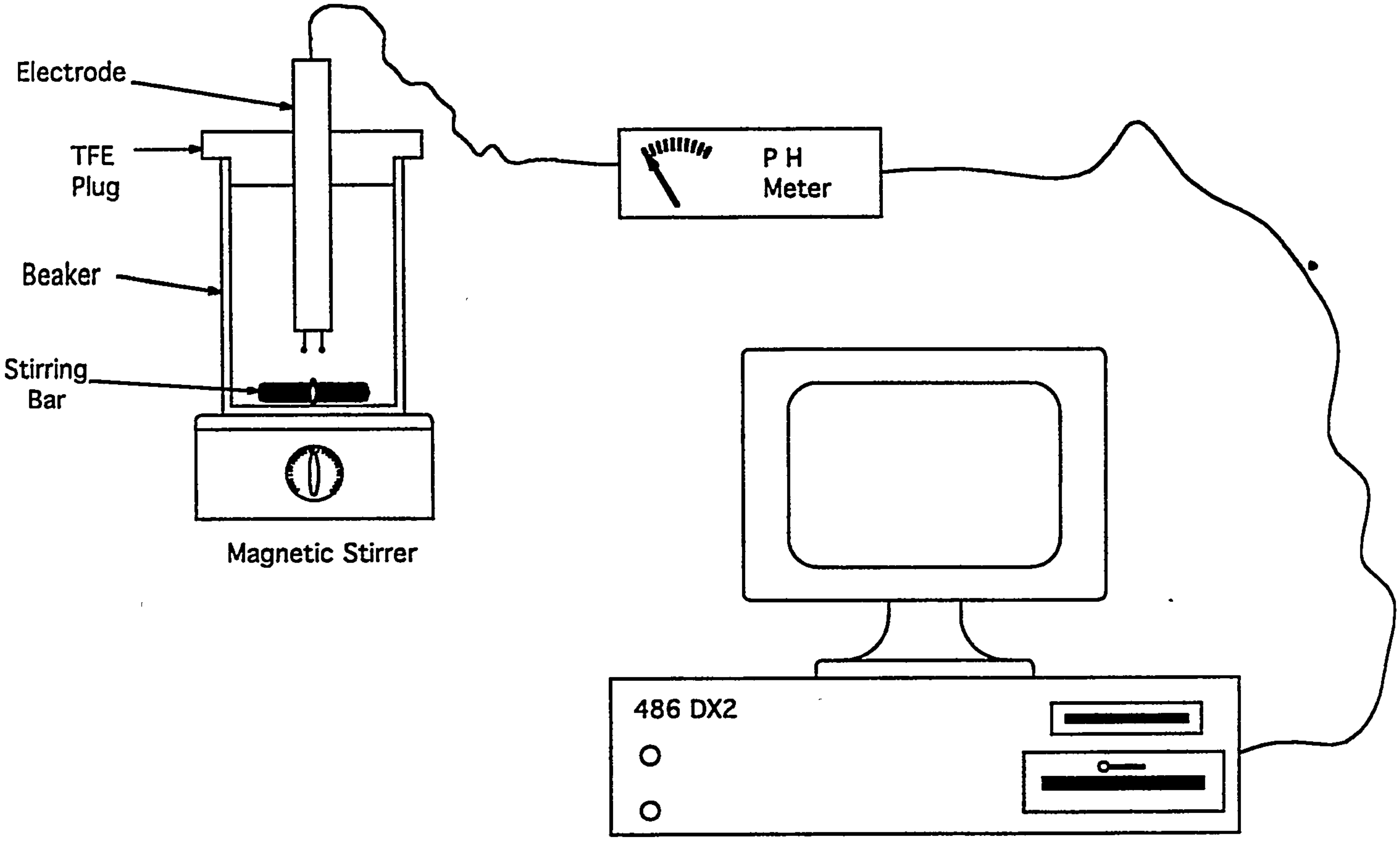
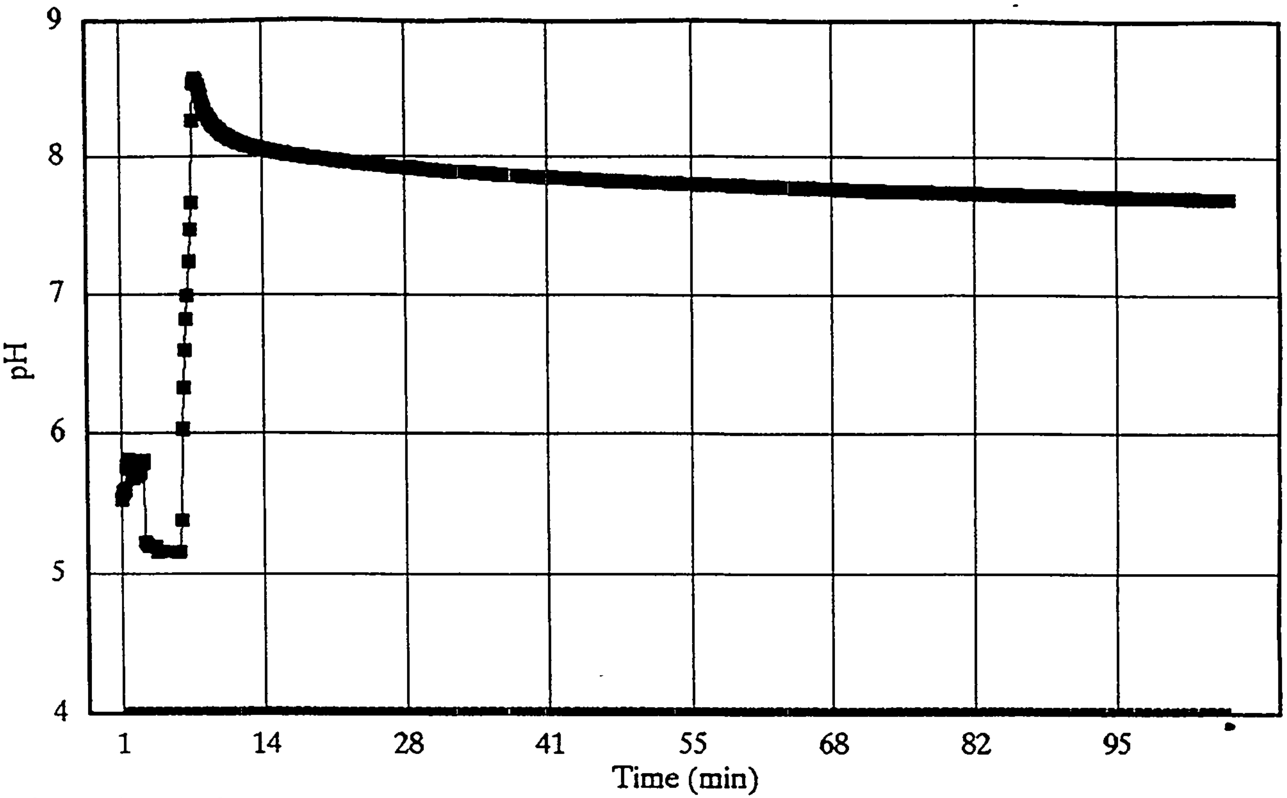


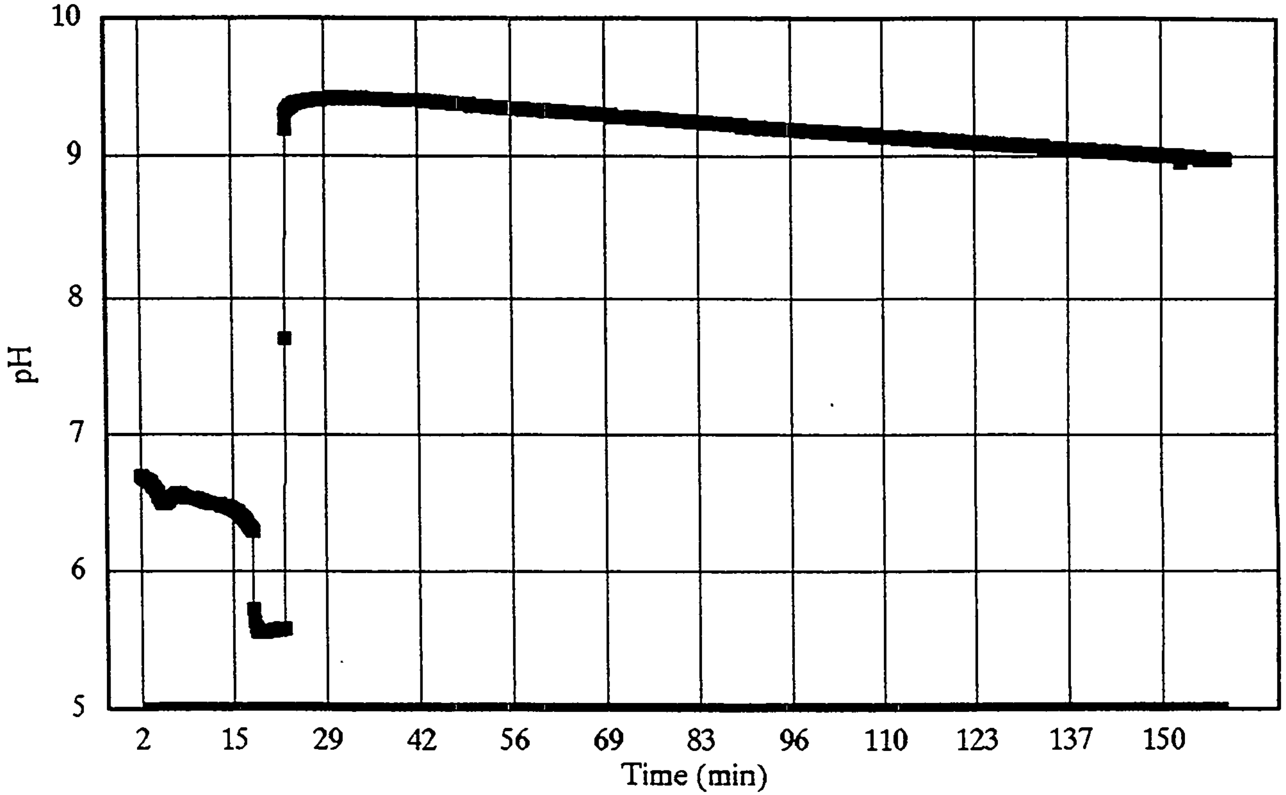
Fig. 2. Wyodak –20 mesh Slurry pH



5/31/95

WY2_5315.wk3
pH 2

Fig. 3 CaCO3 Slurry pH

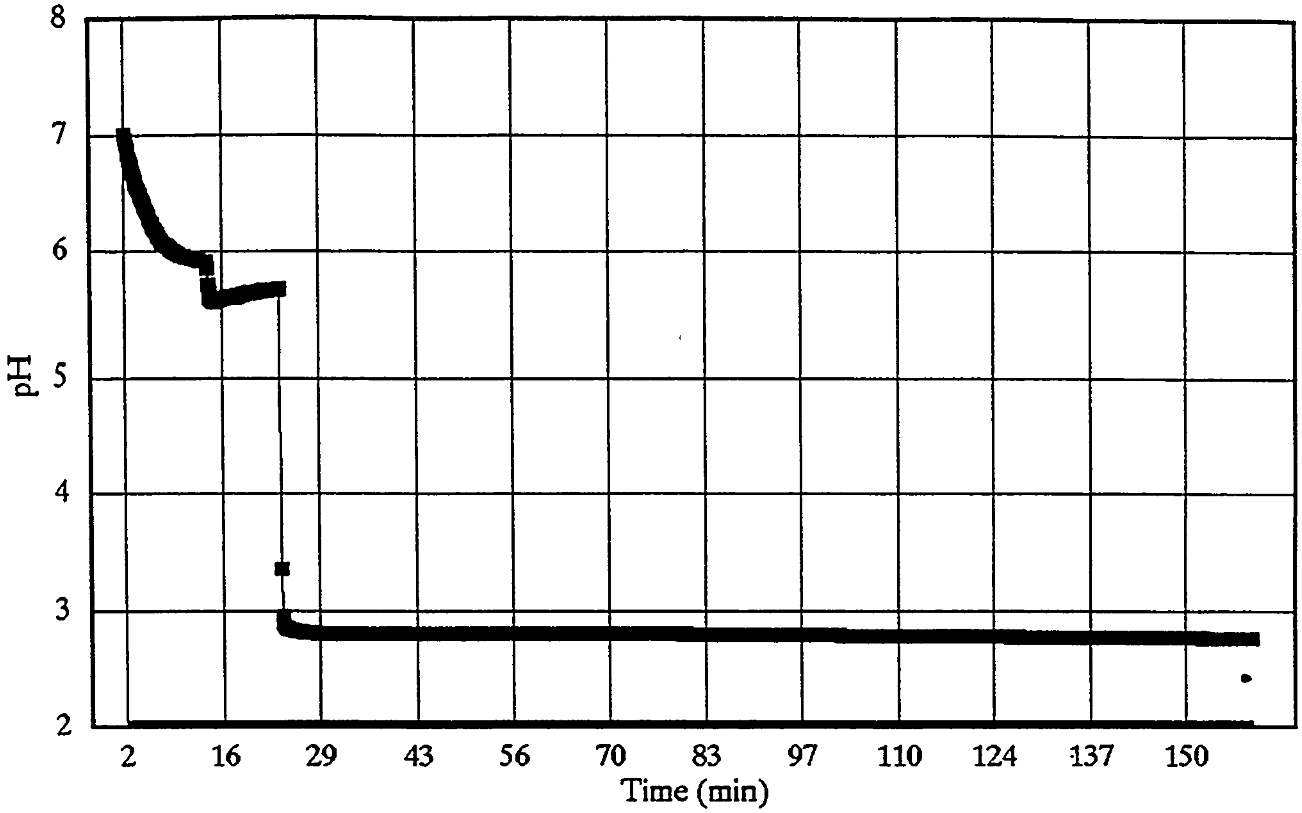


5/22/95

CA_5225.wk3
pH 2

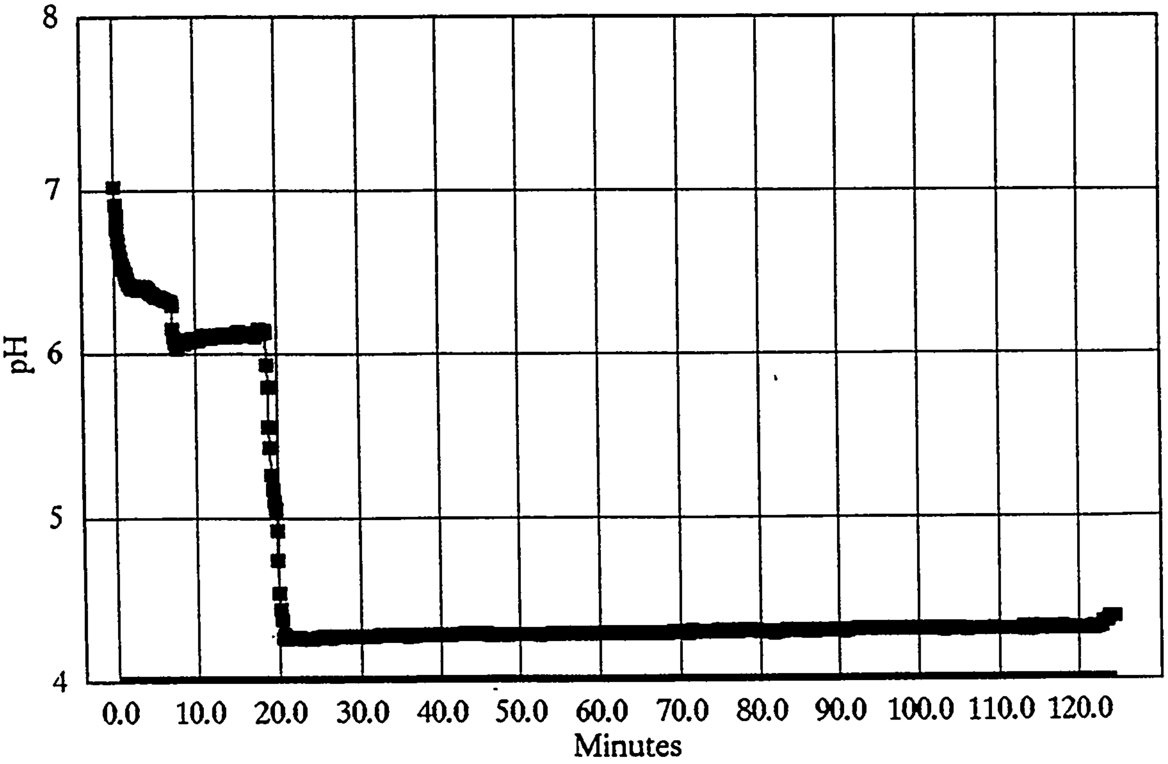
Fig. 4 Pyrite slurry pH

5/25/95



PY_5255.wk3
pH 4

Fig. 5 Graphite slurry pH



GR1025A4.wk3
pH 5