

ION EXCHANGE PROPERTIES OF WYODAK PREMIUM COAL SAMPLES

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ABSTRACT:

Low rank coals (lignite and subbituminous) contain exchangeable cations. A sample of -20+200 mesh Argonne Premium Wyodak coal was washed with nitric acid in a burette fitted with a coarse glass frit at the base of the graduations to remove the exchangeable cations from the system. The eluent was passed to a flow-through pH electrode and a titration curve was obtained on a computer file. A series of electrodes (pH, calcium, sodium and potassium) were used in separate experiments to follow the elution from the coal. Some implications for coal structure are also indicated.

INTRODUCTION:

The abundant reserves of low rank coals in the United States are potentially useful for the production of synthetic liquid fuels. In addition the structure of these coals is becoming better understood but significant additional information is needed to optimize this use.

The coal structure involves polymers of molecules derived from the lignin in the original plants. This structure is known to contain several reactive functional group types including carboxylate and phenolic. The carboxylates are known to be able to act as ion-exchange materials. The functional groups are frequently linked to a variety of alkali and alkaline earth cations. The inorganic cations can be detrimental due to fouling of boilers during operation or reducing yields for liquefaction.

The latter deleterious effects of calcium in the coal (and any other exchangeable cations) can be overcome by removal of these species. A number of studies have indicated that low rank coals can be treated with acids to exchange the cation species with hydrogen ions (1-3). The cations can then be washed away from the coal to minimize their effect.

Cations with a single charge can be attached to a single carboxylate group. Calcium may be present in either or both of two forms. In one case the doubly charged cation can be bound to one hydroxyl and one carboxylate group. This represents a more easily removed form. The second case involves simultaneous bonding to two nearby carboxylate groups. Removal of this calcium involves release from one carboxylate, and later from the second. This process is more difficult and would appear more slowly.

EXPERIMENTAL:

The coal sample was the Argonne Premium Wyodak subbituminous (4). This coal contains (dry basis) 8.7% mineral matter from low temperature ashing. The 8.7% is made up of: 2.0% quartz, 0.1% pyrite, 0.4% calcite and 6.2 % clays which may be kaolinite (5). The -20 mesh samples were dry screened to -20+200 mesh. Weighed

amounts (about 30 grams) of the screened samples were slurried with deionized water. Fines (still -200 mesh) were decanted away from the slurry using about 200-600 ml of water. The slurry was washed into a special 50 ml burette. The burette had been fitted with a coarse fritted glass disk at the 50 ml mark to retain the coal but allow solutions to pass. Fine coal particles had to be removed to avoid pluggage of the frit. A peristaltic pump provided a uniform flow of 0.1 N HNO₃ to the sample. Acid flow rates were typically about 1-3 ml/minute and were set according to the ability of the solution to pass through the coal bed. Following the treatment with the acid, the samples were washed with distilled water fed by the peristaltic pump, and the record of pH and ion concentration was obtained in a manner similar to that for the acid treatment. The burette tip was fitted with tubing to connect a flow-through pH electrode from Cole-Parmer, or from Microelectrodes, Inc (Londonderry, NH). For some of the later experiments the pH electrodes were augmented with ion-selective electrodes for Ca²⁺, and Na⁺. The electrodes with used with an Orion EA940 pH meter. The pH meter in turn was connected to an IBM model AT computer for data acquisition. A schematic diagram of the equipment is given in Figure 1. A program was written which allowed data points to be acquired at specific intervals in the range of 10-18 seconds. The data files were then manipulated with a word processor and Lotus 123 macros to permit plots to be drawn of the data.

The pH electrodes were calibrated with Cole Parmer standard buffers of pH 4 and 7. The ion selective electrodes were calibrated with standard solutions made up of a series of analyzed reagents salts diluted to give 0.1, 0.01 and 0.001 M solutions for each of the cations. Calibrations were checked at the end of the runs.

This arrangement does give a different approach to an endpoint than a simple titration since the exchanged cations are removed from the system.

RESULTS AND DISCUSSION:

The results for the Wyodak sample with the pH and sodium electrode are shown in Figure 2. A number of features are evident. The pH changes for the Wyodak coal titrated with 0.1 N nitric acid indicate an initial period in which the water in contact with the coal was displaced by the acid (pH about 6.5 to 5). During this time the soluble species were released and contributed to a near neutral state. This period was followed by an extensive period in which the pH was steady at about 5. During this time the other cations associated with carboxylate groups were exchanging with hydrogen ions and being eluted. At the end of this phase a pair of inflections was exhibited before reaching the pH of the input acid.

The Na electrode indicated that the Na was eluted early in the exchange process, and tailed off slowly. The increase near the end of the acid addition is associated with a change in sensitivity with pH and is not associated with an increase in Na concentration. The most readily released species was released first. The pH remained high after the sodium release indicating that other species were reacting with the acid.

Figure 3 shows the effect of washing the coal with acid and monitoring the calcium ion concentration as well as the pH. A number of features can be seen. The initial pH for this solution is higher than for the sodium, believed to be due to the use of a smaller amount of water to decant the fines, and more of the soluble species were retained in the slurry and eluted in this stage. These species are alkaline as the pH exceeds 7. As the water is displaced from the coal by the acid the pH drops to about 6. During this period an initial calcium species is eluted. There is a slight increase to about pH 6.2 and a long period of very slow decrease to pH 6.1. During this period there is a rapid rise of the calcium concentration (dissolution of calcite is at least partially responsible) and then a slow and consistent increase to a maximum. Just before the maximum calcium concentration the pH drops from about 6.1 to about 4. During this period there is a rapid decrease in the calcium concentration. This is followed by an even more rapid decrease in pH to about 1.15, accompanied by a very rapid decrease in the calcium ion concentration. An instrumental problem caused the discontinuity in the pH curve and compressed the time during that period. The scatter in values for the calcium values at higher concentrations is attributed to the electrode stability.

Figure 4 shows the effects of rinsing the acid washed coal with deionized water. It should be noted that the coal changes character in the process and the rate of passage of the deionized water decreased. Initially the acid was washed out of the column at pH 1.15. A period followed during which the pH changed from 1.15 to about 1.9 with a linear slope. The pH changed more rapidly and then asymptotically approached a value of about 3.3. The shape of the latter part of the curve approached that of a parabola. The initial linear portion is assumed to be due to the mixing of the acid in the space between the particles with the incoming water flow and discharge from the burette. The latter more parabolic shaped curve is believed to be due to diffusional processes from the pores of the particles.

One characteristic of the water washing step is the release of some calcium near the intersection of the linear and the non-linear parts of the pH curves. This is seen in Figure 4 and is reproducible through several stages of acid washing and water rinsing. The shape of the curve is consistent through 3 wash and rinse sequences. In each case the calcium is rinsed out near the intersection of the two segments of the pH versus time plots. The calcium is also washed out in successive acid washes in the same pH range.

The cause of the release of calcium in both the acid wash and water rinse near the same pH is not yet clear. It may be that the physical structure of form of the external surface changes at a certain pH. If that were so, then any calcium which had been freed from internal linkages to carboxylate or other groups might be released in the rearrangement step during the transition between the structures.

A small amount of cloudy material was seen in the supernatant water after the treated coal was removed from the burette. The cloudy material was decanted and allowed to settle. The clear supernatant was discarded. A grey solid was recovered and analyzed with FTIR.

FTIR indicated the presence of clay type minerals. Apparently the acid form of the coal is active and can release very finely divided clay material.

An analysis of the the acid solution which was passed over the coal in the burette for the experiment with the sodium electrode, and the rinse water, was made. The results are given in Table 1.

Table 1. Concentrations of Cationic Species in Wyodak Solutions in ppm (ug/ml)

Cation	Acid Soln	Rinse
Al	56.6	6.80
B	1.04	<.10
Ba	7.94	.37
Ca	908.	14.6
Fe	35.7	4.73
Mg	212.	1.26
Mn	1.21	.04
Ni	.21	<.05
Si	.55	<.30
Sr	16.5	.22
Ti	.07	.04
V	.13	<.10
Zn	.42	.05
K	4.91	<.20
Na	49.8	.19

The estimated accuracy of the ICP AES analysis is +/- 10%.

Be, Cd, Co, Cr, Cu, Mo, Pb, Sn, and Zr were all below the limits of determination.

The release of clay during the acid washing and subsequent water rinsing may indicate that the clay is attracted to negative groups such as the carboxylate in the coal structure. The clay has a number of cations bound in its layer structure. The rinse water following the acid wash contained some additional calcium, indicating the release of this cation during the duration of the contact with the water. It is possible that the coal structure includes coal-matter-to-clay bonds. Acid washing can rupture some of these linkages, permitting the liberation of the clay. The structure of the coal particle would then be weakened. This weakening would limit the useful life of low rank coals for uses such as ion exchange resins.

CONCLUSIONS:

1. some of the ion exchange properties of low rank coals can be understood by titrating with the burette system described.

2. Alkali cations are removed early in the titration, and alkaline earth cations are removed throughout the acid treatment.
3. More acid is consumed in the titration than the equivalent amount of cations which are recovered.
4. Some aluminum is solubilized.
5. Clay is released following the acid treatment. This clay is probably associated with the exchanged cations.

FUTURE WORK:

The potential of application of small amounts of catalysts which can still be useful needs to be explored. The ion exchange capabilities of the low rank coals presents an opportunity to add catalytically active species such as Fe^{+2} , Co^{+2} , Ni^{+2} . Other useful metal species, such as MOO_4^{-2} , can be added by adsorption techniques.

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REFERENCES:

1. C. Lafferty and M. Hobday, *Fuel*, 69, 78-83 (1990)
2. C. Lafferty and M. Hobday, *Fuel*, 69, 84-87 (1990)
3. J. T. Joseph and T. R. Forrai, *Fuel*, 71, 75-80 (1992)
4. K. S. Vorres, *Energy Fuels*, 4, 420-426 (1990).
5. R. D. Harvey, *Ill. State Geol. Survey*, 1988.

FIGURE 1.
 DIAGRAM OF EQUIPMENT FOR ACID LEACHING OF COAL SAMPLES

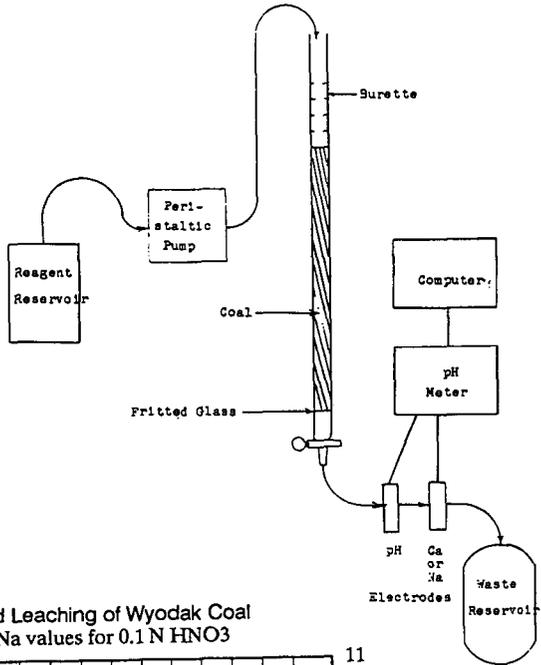
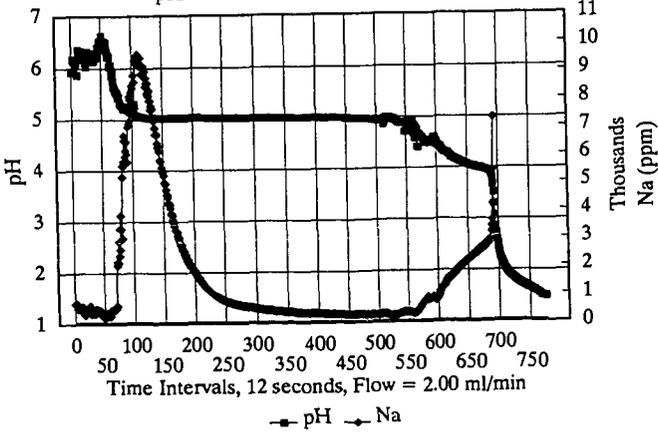
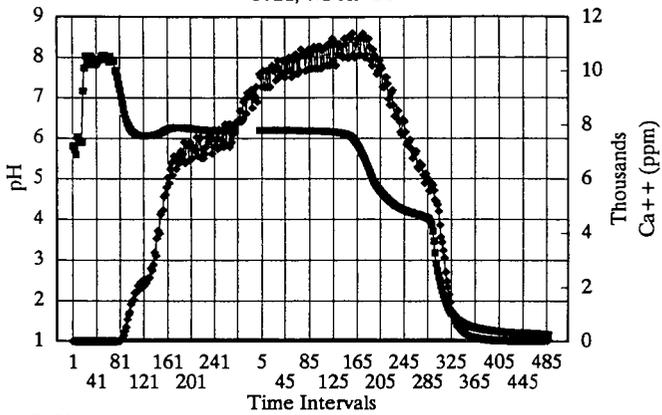


Fig. 2. Acid Leaching of Wyodak Coal
 pH and Na values for 0.1 N HNO₃



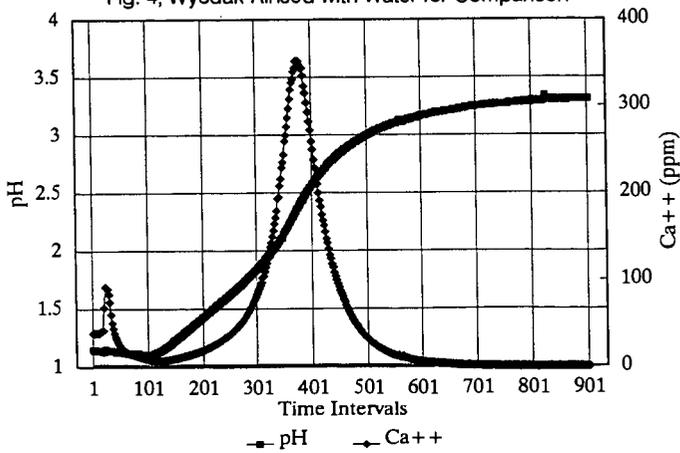
WY427S.wk3

Fig. 3, Wyodak Acid Washed for Comparison
WY521, 0.1 HNO₃



WY521 composite

Fig. 4, Wyodak Rinsed with Water for Comparison



WY521B