Some Interactions Between Coal and Water Which Change Water Quality

Robert D. Reese* and Harold L. Lovell

The Pennsylvania State University
Department of Mineral Preparation
University Park, Pa.

The investigation (1), of which this discussion is a part, was primarily concerned with the use of coal as a reactant in a potential process to remove soluble pollutants from coal mine drainage. When water and coal come in contact, changes occur in each substance which may have considerable significance. The data developed are conceived to have influence in such coal preparation processes as froth flotation, flocculation and agglomeration as applied to solid-fluid separations, and in the control of water quality in the preparation plant as well as for subsequent discharge. The changes which occur in the coal itself may have some effect upon its utilization in specific instances or upon its handling in cold weather.

It does not seem to be unrealistic to seek an improvement in water quality from such a phenomena despite the occurrence of pyrites in coal strata and the role pyrites play in the origin of pollutants in coal mine drainage. Anthracite coal is successfully used as a filter media and may have characteristics of molecular sieves(2). Sulfonated bituminous coals have ion exchange properties(3). Some coals will react with sulfuric acid under mild conditions(4). Coagulants have been prepared from coal (5) and coal ash(6), which are claimed to be effective in creating flocculation in water treatment processes. Research is currently in progress considering the use of coal for an absorbent-type of response to remove organic contaminants from sewage effluents(7,8,9). Some improvement in water quality is indicated where mine water has been used as makeup water in coal preparation plants(10).

Preliminary studies established that coals will react with coal mine drainage to increase pH, decrease acidity, and remove iron. The extent of the phenomena was found to vary widely, although some response was measured in each of a number of different coals of varying rank and origin which were examined. The data presented in this discussion result from an attempt to explain the nature of this observed response as a base to optimize the effect.

The studies described were carried out on a run-of-mine sample of a Pittsburgh seam, high volatile bituminous coal originating in Southwestern Pennsylvania. The particle size of the coal employed was varied, although most of the studies were made with the minus 200 mesh fraction since it was found to be the most reactive. Limited data were measured using various specific gravity fractions of the coal. The waters considered were: freshly-boiled, distilled water; a municipal tap water; .0155 N sulfuric acid; two synthetic coal mine drainage solutions containing sulfuric acid - one with ferrous iron, the other with ferric iron; and naturally-occurring coal mine drainage in which all the iron present was in the ferric form.

The basic experimental data were acquired by agitating 10 grams of the coal fraction in 100 ml of a given water for 15 minutes at room temperature. The slurry was filtered. The original water and the filtrate were analyzed for pH, dissolved solids, acidity-alkalinity, calcium, sulfate, and in some cases ferrous and ferric iron. The residue from the dissolved solids determinations as well as the ash of the original and reacted coals, were analyzed for silica, alumina, iron, sodium, and potassium by spectrochemical procedures. The main variables considered were reaction time and coal concentration.

The effluent from distilled water had developed a pH in excess of 8 (Table 1) and acquired substantial concentrations of dissolved solids including calcium, sodium and sulfate. Although there is not a great difference in the level of soluble material between the 150 by 200 mesh fraction and the minus 200 mesh fraction, a much lower solubility existed in the larger size fractions. This is undoubtedly related

* Present address: Kennicott Copper Company, Salt Lake City, Utah.

to the more highly liberated mineral particles in the smaller sizes although they did have a higher ash content. The presence of soluble ions in the tap water resulted in a solution which was lower in pH, dissolved solids (including calcium and sulfate concentrations), but higher in alkalinity. A more detailed analyses of the dissolved solids for the minus 200 mesh fractions is described in Table 2 along with the analyses of the ash of the original coal and that of the residual coal ash.

These data show that various soluble minerals are leached from the coal, presumably from the dissolution of calcium sulfate or gypsum. This calcium sulfate leached from the coal represented 58 percent of the total solubles with distilled water. These concentrations indicate the leached liquor to be essentially saturated with respect to calcium sulfate. There is some sulfate ions in excess of that stoichiometrically related to the calcium sulfate present. Since sodium is the only other ion solubilized to any significant extent, at least part of the sodium is assumed to have been associated with the excess sulfate ion. There is, however, insufficient sulfate to relate to the total calcium and sodium ions present. The observed pH suggests these cations are present primarily as salts rather than associated with free hydroxyl ions. There is no significant amount of iron solubilized from the coal. The amount of potassium solubilized is small in respect to the sodium, despite the occurrence in nearly equal amounts in the original coal.

The calcium and sulfate found in solution from the distilled water-minus 200 mesh coal test achieved an overall concentration of 102 parts per million calcium sulfate from each gram of coal. The calcium solubilized corresponds to 29.8 percent of that available in the original coal fraction. The relative amount of sodium from the coal which was solubilized is even higher - 70 percent. It seems probable that most of the remaining calcium in the coal is present as calcium carbonate. The 0.87 percent carbon dioxide present in the original minus 200 mesh coal fraction would correspond to 0.1960 grams of calcium carbonate in the 10 grams coal system studied. The calcium found in the original coal sample but not solubilized, would correspond to 0.1955 grams of calcium carbonate showing a reasonably acceptable balance. The solubilization of calcium and sodium is in agreement with ash analyses of the original and residual coal.

With the 0.0193 N sulfuric acid reaction, rather drastic changes resulted in the water quality as detailed in Table 1. Definite reactions had occurred beyond the leaching of the soluble salts as observed with distilled and with tap water. Here also the level of reactivity was less for the larger sizes although the 1/4-inch by 48 mesh size coal fraction achieved a dissolved solids level of 910 mg/l, almost 500 percent of that observed to be soluble in distilled water. The most significant change in the water quality for the purposes under consideration was the change in pH, going from 2.72 to a value of 6.15. The acidity level of the solution dropped from 705 for the original sulfuric acid to 14 ppm $CaCO_3$ after the coal reaction.

In comparing the acid reaction with coal solubilities found in distilled water, the dissolved solids increased by 457 mg/l or by 25 percent. The soluble sulfate concentration increased 548 mg/l or nearly 75 percent over the sulfuric acid; however, the sulfate concentration was actually less by 252 ppm than that solubilized by the distilled water plus that contained in the sulfuric acid. The acidity decreased by 691 ppm $CaCO_3$ or 98.1 percent of that present. If one considers the 43 ppm alkalinity developed in the distilled water test to be related primarily with the solubilized sodium ion, thus in the coal-sulfuric acid reaction 648 ppm $CaCO_3$ acidity or 94 percent must be related to reaction with calcite or with the coal substance. The calcium found in the effluent increased by 425 ppm (as CaO) or 756 ppm (as $CaCO_3$) over that solubilized with distilled water. There appears to be distinct evidence that a major change in an acid water quality is related to calcium carbonate minerals in the raw coal and that little if any association can be related to the organic coal phases.

In tests with the synthetic solutions containing iron as well as sulfuric acid, major changes were also observed including an increase in pH, a decrease in acidity, a slight decrease in total dissolved solids, and an increase in the calcium sulfate concentrations in the solutions. In the experiment which dealt predominantly with ferrous ion, only a very small percentage of the iron was oxidized or removed.

TABLE 1

ANALYSES OF THE EFFLUENTS FROM REACTION OF PITTSBURGH SEAM COAL

Coal Size		pH Change		Dissolved Solids	Alkalinity	$SO_4^{=}$	CaO	Iron		
								Fe^{+2}	Fe^{+3}	Total
'assed	Retained	Initial	Final	mg/l	ppm $CaCO_3$	ppm	ppm	ppm	ppm	ppm
				Boiled Distilled Water						
/4"	48 mesh	7.3	8.50	142.	71.0	41.	15.	-	-	-
150 m	200 m	7.3	8.05	1562.	84.0	583.	350.	-	-	-
200 m	-	7.3	8.10	1818.	42.6	800.	425.	-	-	-
				Tap Water - With Minus 200 Mesh Coal						
'riginal Solution		8.21	-	170 .	195.	119.	90.	-	-	-
'roduct Effluent		8.21	7.68	1650.	107.	462.	320.	-	-	-
				0.0193 N SULFURIC ACID - WITH MINUS 200 MESH COAL						
'riginal Solution		2.72	-	-	705.*	735.	3.	-	-	-
'roduct Effluent		2.72	6.15	3010	14.*	1283.	850.	-	-	-
				Ferrous Synthetic Solution - With Minus 200 Mesh Coal						
'riginal Solution		2.92	-	3260.	1690.*	1765.	5.	446.	0.	446.
'roduct Effluent		2.92	5.05	4170.	820.*	1890.	473.	403.	3.	406.
				Ferric Synthetic Solution - With Minus 200 Mesh Coal						
'riginal Solution		2.91	-	3260.	1690.*	1765.	5.	0.	446.	446.
'roduct Effluent		2.91	5.65	3500.	423.*	2082.	1060.	14.	2.	16.
'Acidity										

TABLE 2

ANALYSES OF SOLID PRODUCTS FROM REACTION OF MINUS 200 MESH PITTSBURGH SEAM COAL

Sample	Weight % Ash	S** %	SiO_2 %	Al_2O_3 %	MgO %	CaO %	Fe_2O_3 %	Na_2O %	K_2O %
'riginal Coal Ash*	23.24	3.88	42.	17.1	1.2	6.5	18.0	2.15	1.73
'esidual Coal Ash 'rom dist. water	21.52	3.58	42.	18.1	1.16	5.2	17.6	0.71	1.61
'esidual Coal Ash 'rom tap water	22.04	3.76	42.	17.6	1.00	5.1	17.3	0.82	1.68
'issolved solids 'n dist. water	-	-	1.2	0.6	0.90	26.2	0.4	21.0	0.36
'oal Ash from 'errous Soln. Test	21.98	3.83	44.	18.6	1.10	3.7	19.3	0.82	1.68
'oal Ash from 'erric Soln. Test	21.81	3.78	45.	17.9	1.05	2.8	20.8	0.63	1.68

* Original Coal contains 0.87% CO_2

** Coal analysis, not on ash

However, in the synthetic solution which was all ferric iron, nearly all of the iron was removed. Most of the residual iron in the ferric effluent was present as ferrous ion. It is not obvious whether this small ferrous concentration detected resulted from a solubilization of a ferrous mineral in the coal or a reduction of some ferric iron in solution. Thus, if the iron is to be removed, it must be oxidized to the ferric state prior to or during the coal reaction. It should be noted that the air oxidation of ferrous to ferric iron proceeds rapidly under pH conditions which will allow the precipitation of ferric hydroxide. Thus it is assumed that the almost complete removal of iron from the test solution resulted from the precipitation of ferric hydroxide which remained with the coal upon solid-fluid separation. This is confirmed by the increase in iron content in the residual coal ash.

The results of studies made utilizing a naturally-occurring coal mine drainage sample are shown in Figure 1. The plot illustrates the actual reduction of acidity iron concentrations and increase in pH of the filtrate as a function of time. The reactions obviously occurred very rapidly. The continuing slower reaction can be related to the substantially decreased reactant concentrations and to various physical phenomena which would assist in favoring a continuing reaction. In addition, this drainage sample contained 3700 mg/l dissolved solids, 2130 ppm sulfate, 228 ppm CaO, and 115 ppm MgO. All the iron was present in the ferric state. After reaction for 60 minutes, the dissolved solids had increased to 4480 ppm (26 percent), the sulfate to 2221 ppm (4 percent), and the calcium to 1090 ppm (380 percent). The relative completeness of these reactions and the extent to which they might be expected to proceed is shown in Figure 2 in which the coal sample which had been allowed to react with the coal mine drainage for 60 minutes was filtered, dried in air for 20 hours, and retreated for 10 minutes with another sample of the coal mine drainage. This procedure was repeated three times after which the coal response was negligible. An additional series of tests were carried out in which the coal concentration was varied. The results of these reactions are shown in Figure 3. The data developed from the various gravity fractions of this coal with coal mine drainage established that a much higher level of reactivity resulted from the most dense mineral-containing fraction and that a negligible reaction occurred with the low gravity, low mineral content fractions.

These data show that various soluble minerals are leached from coal including calcium sulfate and some alkaline materials (sodium) with water which can change the water quality. The response found, evaluated and discussed here can result in an improvement in water quality as regards the most serious coal mine drainage pollutants, pH, acidity, and iron contents. It does leave the water with a large dissolved salt contents (primarily calcium and sulfate ions), which can be detrimental in some situations. The reaction found was related primarily to the calcium carbonate content of the raw coal and to its degree of liberation. Consequently any practical application implied from these results will vary with the individual coal and can limit its significance - especially due to the large amounts of coal required to treat a given volume of water. Commercial plant application has been carried out and found to be practical. However, in the course of these studies, other phenomena more related to those originally sought, were observed which show potential of much more significant effects. Further research is being pursued.

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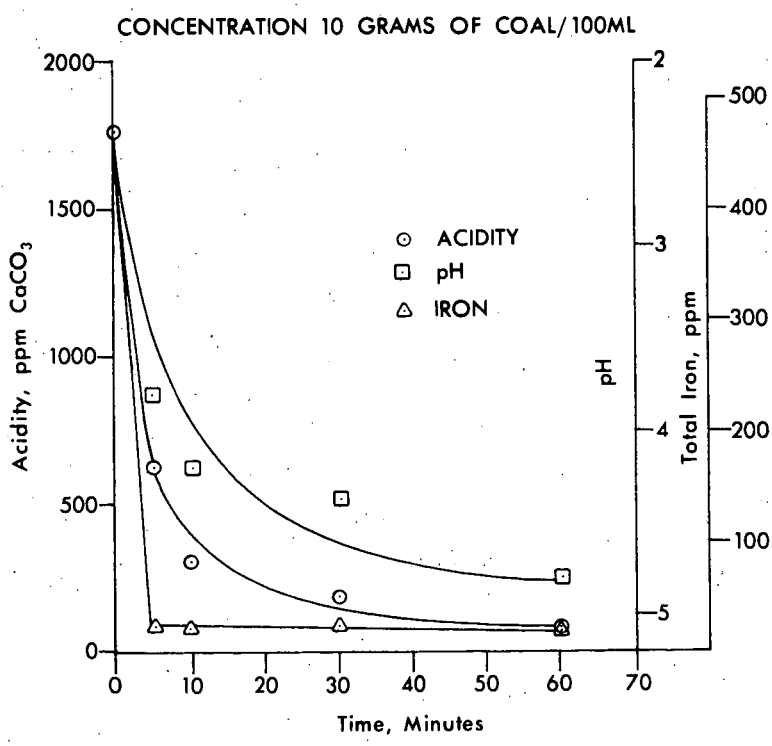

Figure 1
CHANGE OF WATER QUALITY WITH TIME

Minus 200 Mesh Pittsburgh Seam Coal - Coal Mine Drainage

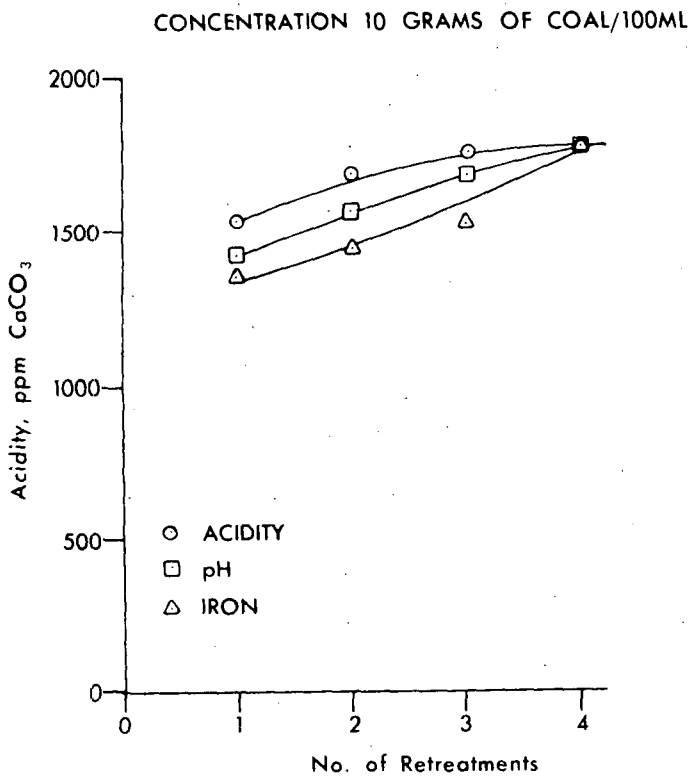

Figure 2

WATER QUALITY VARIATION WITH RETREATMENT OF SAME COAL SAMPLE

Minus 200 Mesh Pittsburgh Seam Coal - Coal Mine Drainage

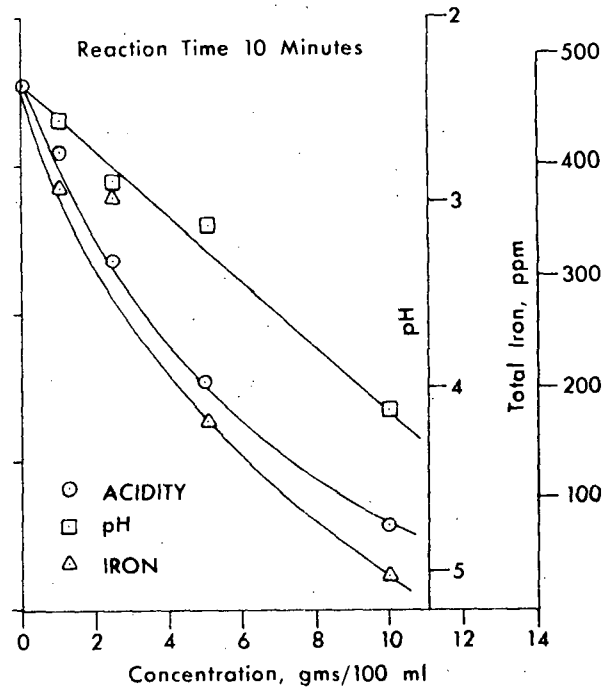

Figure 3

WATER QUALITY VARIATIONS WITH COAL CONCENTRATIONS

Minus 200 Mesh Pittsburgh Seam Coal - Coal Mine Drainage