

PREPARATION OF ASH-FREE, PYRITE-FREE COAL BY MILD CHEMICAL TREATMENT

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The major fraction of the electricity generated in the United States is produced by coal-fired power plants, and the demand for electricity is increasing rapidly. Low-sulfur coals meeting air pollution specifications for utility use are in short supply in the eastern part of the country. Low-sulfur fuel oils which are also used to generate electricity are limited in domestic supply, are costly, and usually must be obtained from foreign sources. Removal of sulfur from coal, either before, during, or after combustion (i.e., removal of sulfur oxides from stack gas), to meet air quality standards, is therefore one of the most pressing needs in the related fields of energy and clean environment. Numerous processes for sulfur removal are being actively investigated by many organizations, including the Bureau of Mines of the U. S. Department of the Interior.

Sulfur in coal occurs as sulfate; as pyrite, FeS_2 ; and as organic sulfur which is part of the coal structure. The sulfate is usually low. In experiments being carried out at the Pittsburgh Energy Research Center of the Bureau of Mines, almost all of the pyritic sulfur has been removed from some coals by treatment with aqueous alkali. For example, 30 g of -200 mesh Illinois No. 6 high volatile B bituminous coal is treated with a solution of 24 g of sodium hydroxide in 240 ml of water for 2 hr at 225° in a stirred autoclave, followed by acidification of the coal-aqueous alkali slurry with carbon dioxide. (The solution of sodium hydroxide used is referred to as "10% aqueous NaOH" in the tables.) In this treatment, the pyritic sulfur is removed, but the organic sulfur in the coal is not attacked by this procedure; for some coals, removal of pyritic sulfur would give a product that meets present specifications for sulfur content for use in power plants. The solid product obtained by this experimental procedure has a somewhat higher ash content than does the original coal. However, if the sodium hydroxide treatment is followed by acidification with dilute hydrochloric acid (instead of carbon dioxide), most of the mineral matter originally present is removed from the coal. The starting Illinois No. 6 coal contains 9.5% ash and 1.1% pyritic sulfur; the product contains 0.7% ash and 0.1% pyritic sulfur. The yield of coal is 91.5% (maf basis).

Table 1 gives the results of various experiments with Illinois No. 6 coal. The organic sulfur is reported on a moisture- and ash-free basis, since removal of ash and/or pyrite will concentrate the organic sulfur and make it seem to increase. It is noted that in some runs the organic sulfur does increase, even on an maf basis, and even allowing for the fact that the analysis is by difference and subject to an inherently large (but uncertain) error.¹

¹Organic sulfur in coal cannot be determined by any direct method. The standard procedure is to determine total sulfur, sulfate sulfur, and pyritic sulfur. The sulfate sulfur and the pyritic sulfur are subtracted from the total sulfur and the remainder is assumed to be organic sulfur. In an indirect method such as this, the probable error of the organic sulfur must be larger than the largest probable error of the three values from which it is derived.

TABLE 1. Illinois No. 6 (River King) hvbb coal: effect of 10% aqueous NaOH for 2 hr at 225°, followed by various acid workups, on ash and sulfur content (analyses on dry basis)

Run	Treatment	Workup	Ash	S total	S sulfate	S pyritic	S organic (diff., maf)
37	None	-	9.8	3.26	0.21	1.08	2.19
37A	NaOH	CO ₂	12.4	2.05	0.11	0.13	2.06
83A	NaOH	CO ₂	12.2	2.25	0.18	0.16	2.17
93	None	-	9.82	3.27	0.31	1.05	2.12
96	Ca(OH) ₂	HCl	8.16	3.04	0.04	1.04	2.14
97	NaOH	HCl	0.67	2.54	0.01	0.11	2.44
103	None	-	9.77	3.30	0.33	0.92	2.28
103A	NaOH	HCl	0.84	2.58	0.00	0.09	2.51
110	None	-	9.85	3.28	0.42	0.93	2.14
110A	H ₂ O	CO ₂	9.46	2.77	0.01	0.98	1.96
111A	H ₂ O	HCl	8.76	2.85	0.01	1.04	1.98
112	None	-	9.84	3.20	0.42	0.96	2.01
112A	NaOH	SO ₂	0.72	2.40	0.23	0.19	1.99
113A	NaOH	H ₂ SO ₄	0.52	2.75	0.24	0.19	2.33
133	None	-	12.58	3.69	0.09	1.39	2.53
133A	NaOH	Aspirate; H ₂ SO ₄ slowly	0.85	2.99	0.17	0.12	2.73
134	NaOH	Aspirate; H ₂ SO ₄ slowly	0.59	2.96	0.20	0.18	2.59
135	NaOH	Aspirate; H ₂ SO ₄ dropwise	0.91	2.82	0.09	0.16	2.59
136	30% NaOH	Aspirate; H ₂ SO ₄ dropwise	0.87	2.84	0.07	0.06	2.73

The erratic increase in organic sulfur mentioned above is puzzling. It is possible that elemental sulfur is precipitated either at some stage of the reaction, or during the workup of the product; free sulfur would be reported as organic sulfur in the standard analytical procedure for sulfur forms. (In a modification of the standard procedure, where the organic sulfur is determined by taking the residue from the pyrite determination and analyzing for sulfur, free sulfur would also be reported as organic sulfur.) An attempt was made to settle this question by extraction (Soxhlet) of a coal sample with ethanol, and analysis of the extract for sulfur by ultraviolet spectrometry; no sulfur was found. It is also possible that at some point in the procedure, free sulfur or polysulfide ion is formed and attacks the coal, giving an actual increase in organic sulfur.

One possible method of preventing an increase in organic sulfur would be to remove the sulfide-containing alkali solution from contact with the coal before any work-up is done. (This assumes that the troublesome sulfur material is in solution and is not already adsorbed on the coal surface.) This technique, using a filter stick, has been used on those runs which are marked (in the tables) as "aspirate." This aspiration procedure removes about 70-90% of the alkaline solution. Obviously, in any commercial procedure, filtration, centrifugation, or some other process would be used in order to recover caustic solution for re-use, to minimize the amount of acid needed, and also to recover minerals and sulfur dissolved in the alkali.

There is some evidence that the aspiration of the caustic results in less of an increase of organic sulfur (table 1, run 113A compared with runs 133A, 134, 135). There is also evidence that aspiration results in better removal of ash and pyrite (table 2, runs 119A and 121A).

TABLE 2. Elliot mine mvb coal: effect of 10% aqueous NaOH for 2 hr at 225°, followed by various workups, on ash and sulfur content (analyses on dry basis)

Run	Treatment	Workup	Ash	S total	S sulfate	S pyritic	S organic (diff., maf)
99	None	-	18.15	4.31	0.20	3.25	1.05
99A	NaOH	CO ₂	22.84	2.27	0.19	0.19	2.44
104	None	-	18.21	4.31	0.26	3.29	0.93
104A	NaOH	HCl	5.11	3.61	0.01	1.94	1.75
114	None	-	19.86	5.21	0.32	3.74	1.44
114A	NaOH	HCl (special)	4.06	4.06	0.01	2.39	1.73
115A	NaOH, 7 hr	HCl	5.84	3.88	0.10	2.08	1.81
116A	30% NaOH	HCl	3.03	3.16	0.03	0.75	2.45
117A	NaOH, 325°	HCl	8.43	2.77	0.04	0.48	2.46
119-1	None	-	19.68	5.23	0.35	3.85	1.28
119A	NaOH	H ₂ SO ₄	7.26	5.21	0.06	3.35	1.94
120A	NaOH	H ₂ SO ₄ (special)	4.56	4.38	0.14	2.46	1.85
121A	NaOH	Aspirate; H ₂ SO ₄	6.06	3.79	0.07	2.54	1.25
122A	NaOH	Aspirate; H ₂ SO ₄ (special)	4.07	3.52	0.19	1.97	1.41
126A	Double volume 10% NaOH	Aspirate; H ₂ SO ₄	5.24	3.49	0.13	1.86	1.58

The use of sulfur dioxide for the acidification step (table 1, run 112A) gave good results, suggesting that it might be possible to use sulfur oxides from stack gas for the process. It is noteworthy that sulfur dioxide is a strong enough acid to cause the deashing reaction to take place, but carbon dioxide is not effective for deashing.

The chemistry of the dissolution of pyrite in aqueous alkali is not known, but something can be suggested with regard to the deashing reaction. The following mechanistic scheme is based upon the reactions which take place in purification of alumina from bauxite ore. When a coal is treated with alkali, the clay minerals probably dissolve and then precipitate as a stable insoluble sodium aluminum silicate of composition $3\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$. This is not soluble in alkali but is soluble in strong acid. Thus, after acidification, the silica, alumina, and some other mineral matter of the coal should be found mostly in the acid fraction, with only a small amount in the alkaline fraction. Preliminary analytical data confirm this hypothesis.

In table 3, runs 124A and 125A give the results of alkali deashing-depyriting in the presence of hydrogen. The coal itself had a somewhat different behavior during workup; it tended to float during centrifugation. There was no uptake of gas and the results were similar to runs made under similar conditions in the absence of hydrogen (table 2). Further experiments are desirable, since the runs using

hydrogen gave relatively low ash and pyrite values. Run 128A was done in the presence of 1700 psi initial pressure of synthesis gas (0.9 H₂:1 CO). At the end of the reaction, the aqueous layer had a pH of about 5. It is obvious that the carbon monoxide reacted with the sodium hydroxide to give sodium formate. Analysis of the gases showed that 0.58 mole of carbon monoxide was used up, corresponding well to the 0.60 mole of sodium hydroxide initially present; the calculation also indicated the formation of 0.15 mole of hydrogen. Removal of pyrite is good (82% removed) but removal of ash is poor (only 49% removed). This suggests two possibilities. With neutralization of the sodium hydroxide via the formation of sodium formate, ash removal must be a relatively slow reaction or may require a fairly high alkali concentration, so that rate of mineral conversion becomes very slow after a short time. On the other hand, rate of pyrite reaction with sodium hydroxide must be fairly rapid, or else continues even in weak alkali, so that the final pyrite removal is still good. Another possibility, but a rather unlikely one, is that some of the pyrite is dissolved not by the alkali but by the formic acid. Pyrite is not soluble in dilute hydrochloric acid, but formic acid is a reducing agent, which may have some effect upon the pyrite.

TABLE 3. Effect of various gases in the presence of 10% aqueous NaOH, followed by acid workup, on the ash and sulfur of coal (dry basis)

Run	Coal	Treatment	Workup	Ash	S total	S sulfate	S pyritic	S organic (diff., maf)
119-1	Elliot	None	-	19.68	5.23	0.35	3.85	1.28
124A	Elliot	H ₂ , NaOH 250°	H ₂ SO ₄	3.72	2.48	0.08	0.64	1.84
125A	Elliot	H ₂ , NaOH, 250°	H ₂ SO ₄	3.39	2.26	0.02	0.29	2.02
128A	Elliot	H ₂ + CO, NaOH, 250°	Aspirate; H ₂ SO ₄	10.03	2.41	0.06	0.69	1.85
133	River King	None	-	12.58	3.69	0.09	1.39	2.53
137	River King	Air, NaOH, 225°, 1 hr	Aspirate; H ₂ SO ₄	14.27	2.10	0.05	0.21	2.16

Run 137 in table 3 shows the effect of air (760 psi at room temperature) upon the reaction of River King coal with sodium hydroxide. There was an uptake of oxygen. The aspirate had a pH of 5.5-6.0 (probably bicarbonate with dissolved carbon dioxide) and the oxygen content of the coal increased from 9.66 to 10.37%. Probably the oxygen and alkali oxidized some of the coal to "humic acids," using up the alkali in this reaction. The ash content increased, the pyritic sulfur decreased, but the sulfate was almost unchanged. The results suggest that the pyrite was rapidly attacked and converted to water-soluble sulfate; this is substantiated by the observation that during the acidification of the treated coal, there was no odor of either hydrogen sulfide or sulfur dioxide, though there was copious evolution of an odorless gas, presumably carbon dioxide. The organic sulfur (moisture- and ash-free basis) decreased from 2.53 to 2.16%. Since the increase in oxygen content of the coal would decrease the organic sulfur by dilution, these figures can be put on a moisture-, ash-, and oxygen-free basis; the change is then from 2.84 to 2.46% organic sulfur. This decrease in organic sulfur is small and probably subject to a fairly large analytical error; however, it does seem to be significant, in view of the fact that the organic sulfur tends to increase slightly in most other experiments.

One run (table 1, run 96) was made using aqueous calcium hydroxide, which would be a cheaper source of alkali than sodium hydroxide. The pyritic sulfur was not attacked; possibly this is because of the very limited solubility of calcium hydroxide, resulting in a very low concentration of hydroxide ion in solution.

Treatment of the coal with water at 225° (conditions used for the alkali treatment) did not have any effect; thus, there is no doubt that the deashing requires alkali and is not simply a result of a hydrothermal water treatment. This was shown to be true for both carbon dioxide workup and hydrochloric acid workup (runs 110A and 111A, table 1).

No further discussion of the results given in table 2 (Elliot mine mvb coal) and in table 4 (Indiana No. 5 hvbb coal) will be given here, except to point out that Indiana No. 5, like Illinois No. 6, has been converted to a low-ash, low-pyrite material.

TABLE 4. Indiana No. 5 hvbb coal: effect of 10% aqueous NaOH for 2 hr at 225°, followed by various acid workups, on ash and sulfur content (analyses on dry basis)

Run	Treatment	Workup	Ash	S total	S sulfate	S pyritic	S organic (diff., maf)
108	None	-	9.55	3.47	0.35	1.02	2.32
108A	NaOH	HCl	0.48	2.63	0.02	0.06	2.56
109A	NaOH	CO ₂	10.57	2.35	0.16	0.13	2.31
141	None	-	9.42	3.46	0.50	0.94	2.23
141A	NaOH	Aspirate; H ₂ SO ₄ with heating and stirring	0.72	2.56	0.20	0.15	2.23

The depyriting-deashing procedure usually increased the heating values of the coals somewhat, as would be expected. The free swelling index usually changed only slightly.

An ash-free, pyrite-free coal would have several important potential applications, which would depend on its cost and specific characteristics. Ash-free coal might simplify the process to produce synthetic high-Btu gas from coal. If it were cheap enough, ash-free, pyrite-free coal would be much preferred for combustion to generate electricity, either in conventional steam plants, gas turbines, or MHD generators. The use of ash-free, pyrite-free coal should extend the life of the catalyst used for the catalytic hydrodesulfurization of coal. An ash-free feed should simplify the process of converting coal to liquid fuels with the conventional coal hydrogenation catalysts, by eliminating the separation of oil from solid residues. Ash-free coal should also find uses as materials for the preparation of electrodes and other specialty carbon products.

Further studies of the many variables in this deashing-depyriting reaction are in progress, to develop technical and economic data required so that the applicability of the process for supplying low-sulfur fuel can be fully evaluated.