

PROCESS FOR PRODUCING LOW-ASH, LOW-SULFUR COAL

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Introduction

Previous work has shown that ash-forming mineral matter, including iron pyrites, can be removed from coal by leaching fine-size coal with a hot caustic solution under pressure followed by washing with a dilute mineral acid (1-4). Recently, similar results have been achieved by leaching fine-size coal with hot sodium carbonate solutions. In both cases much of the mineral matter reacts with alkali to form acid-soluble compounds. Since sodium carbonate is readily available, low in cost, and much less corrosive than sodium hydroxide, it could be used advantageously. Unfortunately, iron pyrites are not leached as readily by sodium carbonate solutions as by caustic solutions. However, this difficulty can be circumvented by employing a multistep process in which the coal is first leached under oxydesulfurization conditions at 120-150°C to extract pyritic sulfur and then leached at higher temperature in the same alkaline solution but under non-oxidizing conditions to convert other minerals to acid-soluble materials. Pyrites readily react with oxygen dissolved in hot alkaline solutions to form water-soluble sulfur species (5,6). But if oxydesulfurization is conducted at the higher temperatures (250°C and above) required for the reaction of other minerals with alkali, coal losses will be excessive because of oxidation. Therefore a two-step leaching process is needed. The results of applying such a process to several bituminous coals are presented below.

Experimental Methods

Bituminous coals from several sources were used for the leaching experiments (Table 1). These coals were first ground to pass either a 200 or 400 mesh screen (U.S. standard). For some leaching experiments the coals were precleaned by a physical separation process which reduced both the ash and total sulfur contents. Precleaning involved mixing the ground coal with perchloroethylene and water, allowing the suspension to settle, and separating the two liquid layers as prescribed by Vivian (7). The coal macerals tended to concentrate in the

Table 1. Bituminous coals used in leaching experiments

Coal Seam	Location	Coal Form	Size, mesh	Ash ^a , wt. %	Tot. S ^b , wt. %
Illinois No. 6	Trivoli, IL	Raw	-200	12.75	3.71
Illinois No. 6	Trivoli, IL	Precleaned	-200	4.92	2.83
Pittsburgh No. 8	Moundsville, PA	Raw	-400	37.11	6.55
Pittsburgh No. 8	Moundsville, PA	Precleaned	-400	6.20	3.67
Lower Kittanning	Armstrong Co., PA	Raw	-200	17.87	10.61

^aDry basis

^bDry, ash-free basis

perchloroethylene layer whereas the minerals tended to concentrate in the water layer. This procedure was repeated five times with each coal which was pre-cleaned. Approximately 87% of the Illinois No. 6 coal and 78% of the Pittsburgh No. 8 coal were recovered during precleaning. These values are expressed on an ash-free basis.

For most leaching experiments, 15g. of coal and 120 ml. of a 1.0 M sodium carbonate solution were placed in a 300-ml. stirred reactor made of type 316 stainless steel. The first leaching step involved reaction with oxygen dissolved in the solution under a partial pressure of 13.6 atm. at 150°C for 1 hr. (5, 8). During this step gas was bled from the reactor to avoid any build-up of gaseous reaction products in the system. Following the first step, the system was purged with nitrogen and the temperature of the system was raised to 250°C, whereupon the second leaching step was conducted for an additional 1 hr. under an inert atmosphere. After this treatment, the reactor was cooled quickly and the coal recovered by filtration. The filter cake was washed with water, dried for 4 hr. in an oven at 95°C, weighed, and sampled for chemical analysis. A portion of the leached coal was washed with a mineral acid (2M) by stirring the mixture in a flask for 30 min. After the acid treatment, the coal was recovered by filtration and the cake was washed with water, dried, weighed, and sampled for chemical analysis. These washing steps were conducted at either room temperature (25°C) or at the boiling point (100°C). In some cases, the regular washing step was extended by mixing the acid-treated coal with boiling water for 30 min., filtering, and then washing with more boiling water. Ash and total sulfur contents of the coal were determined by standard ASTM procedures (9).

Experimental Results

An initial set of experiments was conducted to see how effective the second leaching step was by itself when not preceded by the oxydesulfurization step. For this set of experiments raw coals were leached with a 1.0 M sodium carbonate solution at 250°C and then washed with 2M hydrochloric acid or sulfuric acid. When hydrochloric acid was employed, the acid washing step was always conducted at the boiling point and the final water washing step at room temperature. However, when sulfuric acid was used, the washing steps were conducted at various temperatures to see whether the temperature of the acid or the water had any effect.

The results of the first set of experiments presented in Table 2 indicate that the ash and total sulfur contents of the coals were reduced substantially by the treatment while the product recovery or yield was high. The results seemed to be affected by the source of the coal and the washing temperature, but it was not clear whether they were affected by the type of acid. The largest percentage reduction in either ash content or total sulfur content was achieved with Illinois No. 6 coal. In run 3 the ash content of Illinois No. 6 coal was reduced by 83% and the total sulfur content by 39%. The leached coal was washed with hot sulfuric acid in this run. Somewhat poorer results were realized when cold sulfuric acid was used. Also, extended washing with hot water had little effect when cold acid was employed.

The raw Pittsburgh No. 8 coal had a very high ash content which was reduced about one-third by the single-step leaching and washing treatment (Table 2). The total sulfur content was reduced 18-23% by this treatment. It seemed to make little difference which acid was applied to the leached coal.

The results achieved with Lower Kittanning coal were intermediate between those achieved with the other coals. Thus, the ash content was reduced 44-47% and the total sulfur content 25-27% when this coal was leached with an alkaline solution and washed with either of the hot acids. When the leached coal was

Table 2. Results of leaching raw coals with a hot alkaline solution followed by washing.

Run No.	Coal Seam	Acid Washing		Water Washing		Product %		
		Acid	Temp., °C	Type	Temp., °C	Yield ^a	Ash ^b	Tot. S ^a
1	Ill. 6	HCL	100	Regular	25	94	2.61	2.40
2	Ill. 6	H ₂ SO ₄	25	Regular	25	94	3.40	2.72
3	Ill. 6	H ₂ SO ₄	100	Regular	100	94	2.21	2.25
4	Ill. 6	H ₂ SO ₄	25	Extended	100	94	3.97	2.67
5	Pitts. 8	HCL	100	Regular	25	96	24.8	5.03
6	Pitts. 8	H ₂ SO ₄	25	Regular	25	96	24.5	5.34
7	Low Kit.	HCL	100	Regular	25	89	9.44	7.70
8	Low Kit.	H ₂ SO ₄	25	Regular	25	89	13.34	7.73
9	Low Kit.	H ₂ SO ₄	100	Regular	100	89	10.05	8.01

^aDry, ash-free basis

^bDry basis

washed with cold sulfuric acid, the ash content was reduced slightly less.

A second set of experiments was conducted in which the raw coals were leached first under oxydesulfurization conditions and then under nonoxidizing conditions at higher temperature (250°C). As the results shown in Table 3 indicate, this approach resulted in significantly greater sulfur removal. Under the best conditions, the total sulfur content of Illinois No. 6 coal was reduced 56%, Pittsburgh No. 8 coal 63%, and Lower Kittanning coal 86%. The total sulfur content seemed to be reduced by about the amount of inorganic sulfur present in the raw coal.

In most cases the two-step leaching method produced a lower ash content than the single-step leaching method. This result was probably due to the more complete removal of iron pyrites by the two-step approach. Also when two leaching steps were used, a cleaner product was obtained by washing with hydrochloric acid than by washing with sulfuric acid. However, when washing with hot sulfuric acid was followed by extended washing with hot water, the results approached those achieved by washing with hydrochloric acid. This effect can be seen in the case of Illinois No. 6 coal by comparing the results of run 14 with those of run 10 and in the case of Lower Kittanning coal by comparing the results of run 20 with those of run 16.

The coal recovery on a dry, ash-free basis was slightly lower for two leaching steps than for one leaching step. It seems likely that the lower recovery was due to coal oxidation in the first step. Although the coal loss was small, previous work (8) suggests that the loss could be reduced to an even lower level by decreasing the temperature in the first step.

In the final set of experiments, precleaned coals were leached by the one-step and two-step methods utilized before with the raw coals. The leached coals

Table 3. Results of two-step leaching of raw coals followed by washing.

Run No.	Coal Seam	Acid Washing		Water Washing		Product %		
		Acid	Temp., °C	Type	Temp., °C	Yield ^a	Ash ^b	Tot. S ^a
10	Ill. 6	HCL	100	Regular	25	91	1.82	1.63
11	Ill. 6	H ₂ SO ₄	25	Regular	25	91	4.07	1.81
12	Ill. 6	H ₂ SO ₄	100	Regular	100	91	2.97	1.84
13	Ill. 6	H ₂ SO ₄	25	Extended	100	91	3.31	1.65
14	Ill. 6	H ₂ SO ₄	100	Extended	100	91	2.43	1.62
15	Pitts. 8	HCL	100	Regular	25	92	17.3	2.41
16	Low Kit.	HCL	100	Regular	25	85	2.38	1.49
17	Low Kit.	H ₂ SO ₄	25	Regular	25	85	5.69	1.93
18	Low Kit.	H ₂ SO ₄	100	Regular	100	85	3.21	1.96
19	Low Kit.	H ₂ SO ₄	25	Extended	100	85	5.20	1.60
20	Low Kit.	H ₂ SO ₄	100	Extended	100	85	2.74	1.55

^aDry, ash-free basis

^bDry basis

were washed with hot hydrochloric acid, followed by water washing at room temperature. By using precleaned coals, very low ash contents were achieved with either the one-step or two-step leaching methods. As Table 4 indicates, the ash content of Illinois No. 6 coal was reduced to less than 0.5% and that of Pittsburgh No. 8 coal to less than 0.9% by either method. Thus by using a combination of physical and chemical cleaning the ash content of Illinois No. 6 coal was reduced 96% and the ash content at Pittsburgh No. 8 coal 98%. The combination of physical and chemical cleaning was particularly effective in the case of Pittsburgh No. 8 coal, since even the two-step leaching process by itself reduced the ash content of this coal only by one-half.

Combined physical and chemical cleaning also achieved lower total sulfur contents than was achieved by either method alone (Table 4). Physical precleaning made more of a difference when it was followed by the one-step leaching process than by the two-step process. However, the lowest sulfur contents were achieved when the two-step leaching process was applied to precleaned coals. Application of this combination reduced the total sulfur content by more than 60% in the case of either Illinois No. 6 coal or Pittsburgh No. 8 coal.

Conclusions

A coal leaching process for removing ash-forming mineral matter has been demonstrated. This process involves leaching fine-size coal with a hot, dilute sodium carbonate solution followed by washing with a dilute mineral acid and water. While much of the mineral matter reacts with the alkali at 250°C to form acid-soluble compounds, iron pyrites are incompletely reacted by the hot alkali alone. This difficulty can be overcome by using a two-step leaching process in which oxygen is introduced under pressure in the first step to convert the pyritic sulfur to water-soluble species. The temperature of the first step should be limited to 150°C

Table 4. Effect of coal precleaning on results of leaching experiments.

Run No.	Coal Seam	Coal Form	Leaching Steps ^a	Washed Product, %		
				Yield ^b	Ash ^c	Tot. S ^b
21 1	Ill. 6	Precleaned	II only	95	0.49	1.81
	Ill. 6	Raw	II only	94	2.61	2.40
22 10	Ill. 6	Precleaned	I & II	92	0.41	1.35
	Ill. 6	Raw	I & II	91	1.82	1.63
23 5	Pitts. 8	Precleaned	II only	95	0.88	2.55
	Pitts. 8	Raw	II only	96	24.8	5.03
24 15	Pitts. 8	Precleaned	I & II	93	0.76	1.92
	Pitts. 8	Raw	I & II	92	17.3	2.41

^aStep I: 150°C, 13.6 atm. O₂ pressure.

Step II: 250°C, inert atmosphere

^bDry, ash-free basis

^cDry basis

to minimize coal oxidation. The leaching process can be combined advantageously with physical precleaning in produce coal with less than 1% ash and markedly reduced sulfur content.

Literature Cited

1. Crawford, A., The de-ashing of coal by combined jig washing, froth flotation, and extraction with caustic soda, BIOS Final Report No. 522, Item No. 30, Feb. 19, 1946, British Intelligence Objectives Sub-Committee, London, (A.T.I.-118668, Central Air Documents Office, Wright-Patterson Air Force Base, Dayton, Ohio).
2. Reggel, L., Raymond, R., Wender, I., and Blaustein, B.D., Preparation of ash-free, pyrite-free coal by mild chemical treatment, Am. Chem. Soc. Div. of Fuel Chem. Preprints 17 (1):44-48 (1972).
3. Stambaugh, E.P., Hydrothermal coal process, in: Coal Desulfurization: Chemical and Physical Methods (T. D. Wheelock, ed.), ACS Symposium Series 64, Am. Chem. Soc., Washington, D. C., 1977, pp. 198-205.
4. Das, S. K., and Yang, R. T., Coal cleaning using sodium hydroxide and acid solutions, presented at 109th AIME meeting, Las Vegas, NV, Feb. 26, 1980.
5. Chuang, K.-C., Chen, M.-C., Greer, R. T., Markuszewski, R., Sun, Y., and Wheelock, T. D., Pyrite desulfurization by wet oxidation in alkaline solutions, Chem. Eng. Commun. 7 (1-3):79-94 (1980).
6. Stephenson, M. D., Wheelock, T. D., and Markuszewski, R., Sulfur species leached from pyrite during oxidative desulfurization of coal in alkaline solutions, Proceedings 1983 International Conference on Coal Science, Pittsburgh, PA, Aug. 15-19, 1983, pp. 252-255.

7. Vivian, T. A., presented at Chemical Engineering Department Seminar, Iowa State University. Ames, IA, April 9, 1980.
8. Wheelock, T. D., Oxydesulfurization of coal in alkaline solutions, Chem. Eng. Commun. 12(1-3): 137-160 (1981).
9. American Society for Testing and Materials, Annual Book of ASTM Standards, Part 26 (Methods D 3174 and D 3177), Philadelphia, PA, 1975.