

Desulfurizing Coal with Alkaline Solutions Containing Dissolved Oxygen

C. Y. TAI,* G. V. GRAVES, and T. D. WHEELOCK

Iowa State University, Department of Chemical Engineering and Nuclear Engineering, Energy and Mineral Resources Research Institute, Ames, IA 50011

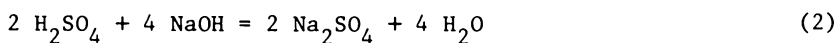
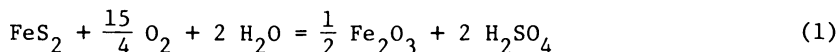
The extraction of pyritic sulfur from coal by leaching the comminuted material with hot aqueous solutions containing dissolved oxygen has been demonstrated in numerous laboratory experiments (1-6). Although acidic solutions have generally been used for such experiments, basic solutions appear to offer several important advantages. Thus Majima and Peters (7) showed that the rate of extraction of sulfur from relatively pure pyrite is much greater in basic solutions containing dissolved oxygen than in neutral solutions. Moreover it has been shown recently that basic solutions containing ammonium hydroxide and oxygen can extract a significant portion of the organic sulfur as well as most of the inorganic sulfur from coal at relatively moderate temperatures (e.g., 130°C) (4,5) whereas higher temperatures (150°-200°C) seem to be required with acidic solutions to remove organic sulfur (6). Furthermore some types of basic solutions are much less corrosive towards the common materials of construction than acidic solutions.

Although the chemical kinetics and mechanism of pyrite reaction with an oxygen-bearing caustic solution have been studied, they are not completely defined. Stenhouse and Armstrong (8) found sulfate ions and iron oxides to be the final products of reaction. Both Fe_2O_3 and Fe_3O_4 were identified in the residue. It appeared to these investigators that the iron oxides formed a stable layer around the unreacted pyrite. As a result of a later investigation, Burkin and Edward (9) concluded that the final oxidation product of iron is maghemite ($\gamma\text{Fe}_2\text{O}_3$) which is formed through a series of topotactic transformations. These investigators observed that the rate of attack was more rapid along grain boundaries and cracks in impure and imperfect pyrite crystals, with the result that these particles were leached more rapidly than particles containing few imperfections and impurities,

*Present address: Chung-Shen Institute of Science and Technology, Taiwan, R.O.C.

even though the insoluble oxidation product adhered to the imperfect crystals but not to the perfect ones. As a result of the intergranular attack by the leach solution, the smaller crystals within particles composed of different-sized crystals were desulfurized before the larger crystals. The reaction rate increased with temperature according to the Arrhenius equation with an activation energy of 9 kcal/mol. Also the reaction rate was controlled by the oxygen concentration at the mineral-solution interface so the rate increased with the oxygen partial pressure. In addition, the rate increased with increasing concentration of sodium hydroxide up to 2 wt %. Higher concentrations reduced the rate slightly.

In a solution of some base such as sodium hydroxide, the stoichiometry of the reaction of pyrite with oxygen and the subsequent neutralization of the acid produced can probably be represented by the following equations:



Although these equations suggest that the main purpose of the alkali is to neutralize the acid and to drive the first reaction to completion, the actual reaction mechanism is probably more complex with the alkali playing a more subtle role as well as the obvious one.

An investigation by McKay and Halpern (10) of the reaction of pyrite with oxygen in acidic solutions showed that the product distribution, and therefore the reaction mechanism, is quite different from that noted above for basic solutions. Thus pyrite was converted to soluble ferrous and ferric sulfate, sulfuric acid, and elemental sulfur when leached with oxygen-bearing acidic solutions at 100°-130°C. The product distribution depended on temperature and acidity, with a lower temperature and higher acidity favoring the production of elemental sulfur and a higher temperature and lower acidity favoring the production of sulfuric acid and soluble sulfates. Also at moderate pH (but not at low pH), the ferric hydroxide hydrolyzed, and ferric oxide precipitated. The Arrhenius activation energy was determined to be 13 kcal/mol, which, being significantly larger than that noted above for the reaction of pyrite in a caustic solution, indicates a greater energy barrier for the reaction in an acidic medium.

The present investigation was undertaken to evaluate the technical feasibility of extracting sulfur from coal with hot oxygen-bearing solutions. Since it was soon confirmed that alkaline or basic solutions resulted in a much greater rate of extraction than acidic solutions, considerable emphasis was placed on determining the effectiveness of different alkalis and alkali concentrations. Several high-sulfur bituminous coals, as well as

pyrite which had been isolated from one of these coals, were leached in a small stirred reactor under a variety of experimental conditions. In addition the over-all effectiveness of chemical leaching in combination with physical beneficiation was investigated.

Experimental

Leaching experiments were carried out in a 1-L, stainless steel autoclave equipped with a removable nickel liner and an agitator consisting of two pitched blade turbine impellers (7.3 cm diameter) mounted on a shaft driven by a compressed air motor. The autoclave was also equipped with a pressure gauge, temperature indicator, and electric heating jacket.

A suspension of coal or pyrite particles in an alkaline solution of a specific concentration was placed in the reactor which was then sealed and heated to a specific operating temperature. After the system attained this temperature, oxygen was introduced from a high-pressure cylinder equipped with a combination pressure-reducing valve and regulator. During the succeeding operation, the system pressure was kept constant by supplying oxygen on demand. Also a small amount of gas was bled continuously from the reactor to avoid any build-up of gaseous reaction products in the system. Reaction conditions were kept constant for a specific time while the material was leached. At the end of the reaction period, the flow of oxygen into the system was stopped, and the system was cooled. Throughout the operation the agitator was kept running at a constant speed which was usually in the range of 250-350 rpm. After a run the leached solids were recovered, dried, and weighed. Coal samples were analyzed by the standard ASTM methods of analysis (11). When pyrite alone was leached, the amount of sulfur extracted was determined by measuring the sulfate content of the spent leachant using the sulfate titration method of Fritz and Yamamura (12).

Coal samples from the Big Ben, ICO, and ISU Demonstration Mine No. 1, all located in Southeastern Iowa, were leached. The rank of the coal from these mines is high volatile C bituminous coal; typical compositions are shown in Table I. Since the coal from these mines is very heterogeneous, various batches used for specific sets of experiments were re-analyzed and the composition reported along with other experimental results.

A handpicked sample of iron pyrites was obtained from the coal deposit at ISU Demonstration Mine No. 1. This material was very impure and seemed to contain about 74% FeS_2 . Nevertheless, it was ground and screened into various sized fractions which were used subsequently for various leaching experiments. The sulfur content of the different size fractions is shown in Table II. In addition to pyritic sulfur, the material contained some sulfur in the form of sulfates and some in a form which was neither pyritic nor sulfate.

Table I. Proximate Analysis of Iowa Coals

Source of Coal	Proximate Analysis (wt %)			
	Volatile Matter	Fixed Carbon	Moisture	Ash
Big Ben mine	37.5	48.8	1.2	12.5
ICO mine	44.0	42.0	4.5	9.5
ISU mine	38.1	44.2	2.2	15.5

Table II. Composition of Iron Pyrites

Size Fraction (U.S. Series Mesh)	Composition (wt %)				
	Iron	Pyritic Sulfur	Sulfate Sulfur	Total Sulfur	Other
-60/+80				41.7	
-120/+140	42.5	39.2	0.5	40.9	16.6
-200/+230		36.4	0.7	40.3	
-230/+270		36.3	0.7	39.4	

Pyrite Leaching Experiments

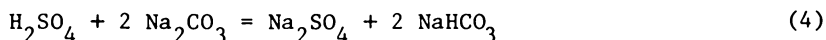
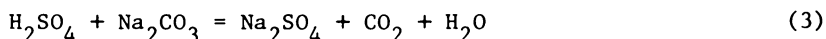
A series of leaching experiments was carried out to determine the effect of various system parameters on the extraction of sulfur from impure pyrite. For each experiment a suspension consisting of 2.0 g of pyrite particles and 500 ml of an aqueous solution was treated in the stirred autoclave at 150°C with oxygen dissolved under a partial pressure of 3.27 atm. Since the vapor pressure of water at this temperature is 4.56 atm, the total system pressure was 7.8 atm. Unless indicated otherwise, the leaching operation under oxygen pressure at the specified temperature was conducted for 1 hr. The conversion of all forms of sulfur in the particles to soluble sulfate was determined by analyzing the spent leachant.

The results presented in Figure 1 indicate that among the various alkalis tested, sodium carbonate was the most effective. Essentially all of the sulfur was extracted from -200/+230 mesh

pyrite particles in 1.0 hr by an oxygenated solution containing 1.5 wt % sodium carbonate. The best results obtained with either sodium hydroxide or sodium phosphate were slightly less favorable and with ammonium carbonate much less favorable. The ammonium carbonate solutions were noticeably less basic than the other solutions and this factor probably accounted for the poorer results obtained with them. However, the ammonium carbonate solutions, as well as the other alkaline solutions, all gave better results than water and oxygen alone. Thus only 27% of the sulfur was extracted from the pyrite during a run made without any alkali.

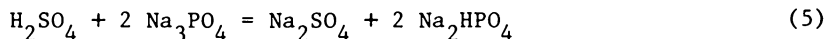
The effectiveness of all of the alkalis increased with initial concentration up to some optimum value and then decreased. For sodium hydroxide the optimum initial concentration was about 1 wt %, for sodium carbonate 1.5 wt %, for sodium phosphate 3 wt %, and for ammonium carbonate 4 wt %. The sharp increase in conversion for initial concentrations at the low end of the concentration scale seems to be related to the amount of alkali required to neutralize all of the acid produced in oxidizing the pyrite. Thus if it is assumed that all of the sulfur in the solids was converted into sulfuric acid during the leaching operation, it would have required an initial sodium hydroxide concentration of 0.40 wt % to neutralize all of the acid produced. Interestingly enough, the data presented in Figure 1 show that the conversion fell off sharply when less than 0.40 wt % caustic was used.

The amount of sodium carbonate required to neutralize the acid depends on the final products of neutralization. Two possibilities are shown below.



The first reaction would have required an initial sodium carbonate concentration of 0.53 wt % to neutralize all of the sulfuric acid whereas the second reaction would have required an initial concentration of 1.1 wt %. The experimental results (Figure 1) indicate that the conversion fell off sharply when less than about 1 wt % sodium carbonate was used.

In the case of sodium phosphate an initial concentration of 1.65 wt % would have been required to neutralize all of the possible sulfuric acid according to the following reaction:



Although the experimental results shown in Figure 1 indicate that the conversion fell off sharply between 2 and 3 wt %, the sparsity of the data leave considerable doubt as to the exact critical

concentration.

Why the conversion declined at higher alkali concentrations which exceeded the optimum levels can not be explained with certainty. A similar decline was observed by Burkin and Edwards (9) when pyrite was leached with caustic solutions, and they attributed the decline to the reduced solubility of oxygen in these solutions. Also similar behavior was observed in leaching both galena and molybdenite with caustic solutions containing dissolved oxygen (13,14). In the case of both minerals, a decline in reaction rate with increasing alkali concentration was attributed to the decreasing solubility of oxygen.

The results of leaching different sized fractions of pyrite with sodium carbonate solutions of different concentrations are presented in Figure 2. Clearly the effect of particle size on conversion was very pronounced with the conversion increasing in an almost exponential manner as the size was reduced (Figure 2). Particles smaller than 60 μm in diameter were completely desulfurized in 1.0 hr by solutions containing 2-5 wt % sodium carbonate for the conditions shown in Figure 2. On the other hand, particles larger than 210 μm in diameter were only about half desulfurized under these conditions. Figure 2 also shows the advantage of using an alkaline solution. The lower curve in this diagram represented the conversion obtained when no alkali was added to the system. Even with the smallest particles of pyrite, only 35% of the sulfur was extracted in the absence of an alkali.

Several runs were made using longer reaction times to see how the conversion would change with time (Figure 3). The results indicate that the reaction rate decreased as the batch leaching operation proceeded. The declining rate could have been caused by the decreasing availability of unreacted pyrite, increasing resistance to diffusion of reactants within particles, increasing concentration of some rate-inhibiting reaction product in the leach solution, or a combination of these factors.

Coal Leaching Experiments

A series of leaching experiments was carried out to determine the effects of various alkalis and alkali concentrations on the desulfurization of coal from the ISU Demonstration Mine No. 1. The raw coal was pulverized so that 90% was finer than 200 mesh. For each experiment 50 g of coal and 500 ml of water or alkaline solution were placed in the stirred autoclave. The chemical treatment was carried out for 2 hr at 150°C with oxygen dissolved under a partial pressure of 3.27 atm and using a total system pressure of 7.8 atm. The treated coal was recovered, dried, weighed, and analyzed to determine the effectiveness of the treatment.

The best overall results were obtained with sodium carbonate among the following alkalis which were tested in various concentrations: sodium carbonate, sodium hydroxide, sodium phosphate,

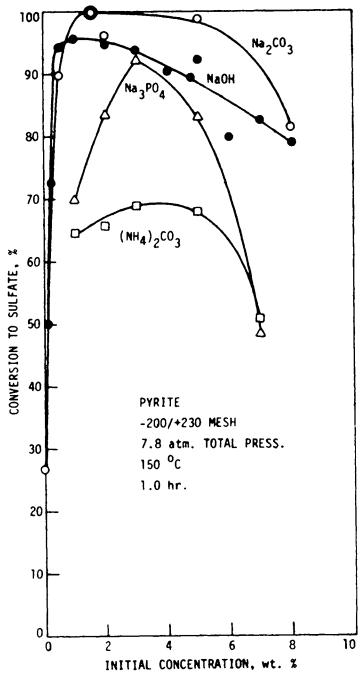


Figure 1. The effect of different alkalis and alkali concentrations on the extraction of sulfur from pyrite

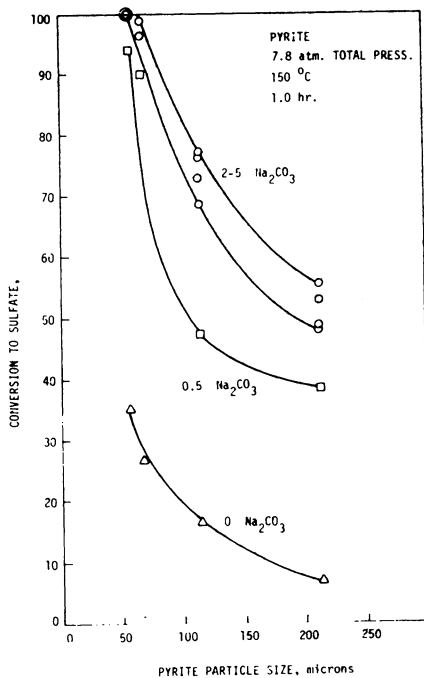


Figure 2. The effect of particle size on the extraction of sulfur from pyrite

calcium carbonate, calcium hydroxide, and ammonium carbonate. The only alkali which approached sodium carbonate in effectiveness was sodium phosphate. However, it required a 7 wt % initial concentration of sodium phosphate to produce coal with a sulfur content comparable to that obtained with a 1.4 wt % initial concentration of sodium carbonate. Moreover, the Btu recovery was lower and the ash content of the product higher when sodium phosphate was used to obtain comparable desulfurization.

The initial concentration of sodium carbonate had a very pronounced effect on the extent of desulfurization and the resulting sulfur content of the treated coal (Table III, Figure 4). The best results were obtained with an initial concentration of 1.4 wt % and using either lower or higher concentrations resulted in less desulfurization. The treatment with the optimum concentration reduced the pyritic sulfur content of the coal by two-thirds. A similar effect of concentration was observed when sodium hydroxide was used with the optimum initial concentration being about 1 wt %. Hence, the effect of alkali concentration was like that experienced in leaching pyrite (Figure 1).

Under the mild leaching conditions used in this work, mainly inorganic sulfur was extracted from the coal. Essentially all of the sulfate form of sulfur was extracted and a good share of the pyritic sulfur. Unfortunately the results reported in Table III for organic sulfur are so erratic that it is not possible to discern whether organic sulfur was removed or not.

For the experiments involving sodium carbonate, the yield of dry coal was 93-94%, and the Btu recovery was 88-92%. These values could have been higher with the exercise of greater care in conducting the experiments. Since the heating value of the treated coal on a moisture and ash free (maf) basis was nearly the same as that of the untreated coal, it does not appear that the coal was significantly degraded by the treatment. Also the oxygen content of the coal, as determined by ultimate chemical analysis, did not appear to be significantly different from that of the untreated coal. These results contrast markedly with those reported by Sareen et al. (3,4) for treatments using much higher oxygen partial pressures which resulted in noticeable oxygen uptake by Illinois No. 6 coal.

As a result of the alkali treatment, the sodium and ash content of the coal increased measurably (Table III, Figure 5). The increase in ash content was directly proportional to the increase in sodium content and seemed caused almost entirely by the adsorption of sodium. Most of the increase in sodium or ash content took place at lower alkali concentrations, and more than 2 wt % sodium carbonate in the leachant generally produced little additional increase. In other words, the coal seemed to become saturated when the leach solution contained 2 wt % sodium carbonate or more. On the other hand, the coal retained very little sodium when the leach solution initially contained 0.8 wt % sodium carbonate or less because the solution became acidic by the

Table III. Results of Leaching ISU Coal with Different Concentrations of Alkali

Treatment	Na ₂ CO ₃ Conc. (wt %)	Wt Yield (%)	Btu Recov. (%)	Heat Value (Btu/lb)		Ash (wt.%)	Na (wt %)	Sulfur Distrib. (lb/10 ⁶ Btu)			
				as recvd.	maf			Pyritic Sulfate	Organic Total		
none	--	--	--	11,240	13,660	15.5	0.05	3.22	0.60	1.81	5.63
wash	--	--	--	11,577	13,970	15.3	0.03	3.21	0.17	2.25	5.63
chemical	0	95	88	10,440	--	17.5	--	2.28	0.11	2.89	5.29
chemical	0.8	94	92	10,950	13,430	16.2	0.10	1.62	0.05	1.80	3.47
chemical	0.8	94	90	10,740	--	16.3	0.10	1.89	0.03	2.32	4.23
chemical	1.0	93	91	11,010	--	16.4	0.33	1.46	0.05	2.39	3.90
chemical	1.4	93	89	10,780	13,520	17.7	0.80	1.11	0.06	1.81	2.99
chemical	2.0	93	88	10,580	13,520	17.8	1.14	1.23	0.07	1.85	3.15
chemical	5.0	93	90	10,880	13,800	18.5	1.29	1.75	0.11	1.80	3.66
chemical	8.0	94	89	10,590	--	19.4	--	1.76	0.09	2.39	4.24
chemical	10.0	94	92	10,950	--	19.7	1.90	1.63	0.11	2.28	4.02
chemical	15.0	94	91	10,940	--	18.2	1.52	2.34	0.18	2.65	5.17

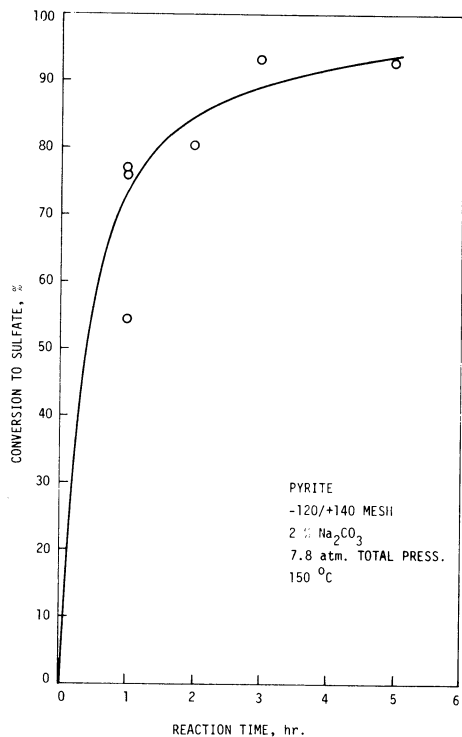


Figure 3. The effect of reaction time on the extraction of sulfur from pyrite

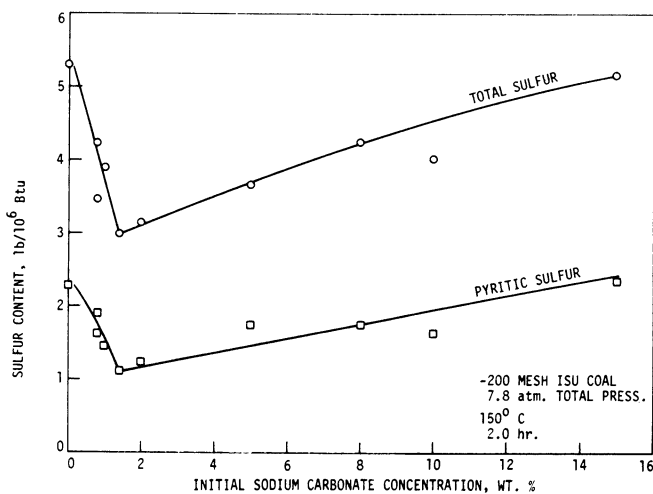


Figure 4. Sulfur content of ISU coal after leaching

end of a run. Washing with water did not remove sodium from the treated coal, but washing with dilute acid (0.1N hydrochloric acid) did remove it.

Another series of experiments was conducted to see what effect reducing the size of the coal would have on desulfurization by chemical leaching. ISU coal was first pulverized to -35 mesh (about 50% below 200 mesh) with a Mikro-Samplmill (Pulverizing Machinery Division, American-Marietta Co.). The coal was then wet-ground in a ceramic jar mill for different time periods. The particle size distribution of the coal after grinding for 2, 4, 8, and 20 hr is shown in Figure 6. After grinding for 2 hr, 97% of the coal was finer than 400 mesh (38 μ m) size. The pulverized or ground coal was then leached in the stirred autoclave for 2 hr at 140°C with a 2.0 wt % solution of sodium carbonate containing oxygen dissolved under a partial pressure of 2.4 atm and with a total system pressure of 5.8 atm. For each leaching run 25 g of coal was mixed with 500 ml of solution. The results presented in Table IV show that more sulfur was extracted from coal which had been ground in the ball mill than from coal which had only been pulverized with the Mikro-Samplmill. Thus the pyritic sulfur content of the ball-milled coal was reduced 87% whereas the pyritic sulfur content of the pulverized coal was reduced only 71%. However, grinding the coal for more than 2 hr did not produce any additional benefit.

Combined Physical and Chemical Cleaning

A final set of experiments involved combined physical and chemical cleaning of several Iowa coals. Each coal was crushed to 6 mm x 0 size with a double roll crusher and then cleaned by gravity separation in an organic liquid having a specific gravity of 1.60. The cleaned float fraction was recovered, dried, and pulverized with the Mikro-Samplmill. The pulverized coal was wet-ground next in the ceramic jar mill for 20 hr and finally leached in the stirred autoclave for 2.0 hr with a 2.0 wt % sodium carbonate solution. The effects of different leaching temperatures and oxygen partial pressures were studied.

The results presented in Table V show that gravity separation removed a substantial part of the pyritic sulfur from each coal and that chemical leaching removed most of the remaining inorganic sulfur, both pyritic and sulfate. Thus through the combined treatment, the inorganic sulfur content of each of the three coals was reduced 93-95%. The treated ICO coal came close to meeting the federal new source performance standard of 0.6 lb S/10⁶ Btu.

For the physically cleaned and finely ground coal, it did not seem to make any difference what leaching temperature in the range of 120°-150°C or what oxygen partial pressure in the range of 2.4-5.2 atm was used because essentially all of the inorganic sulfur was removed even under the mildest treatment conditions.

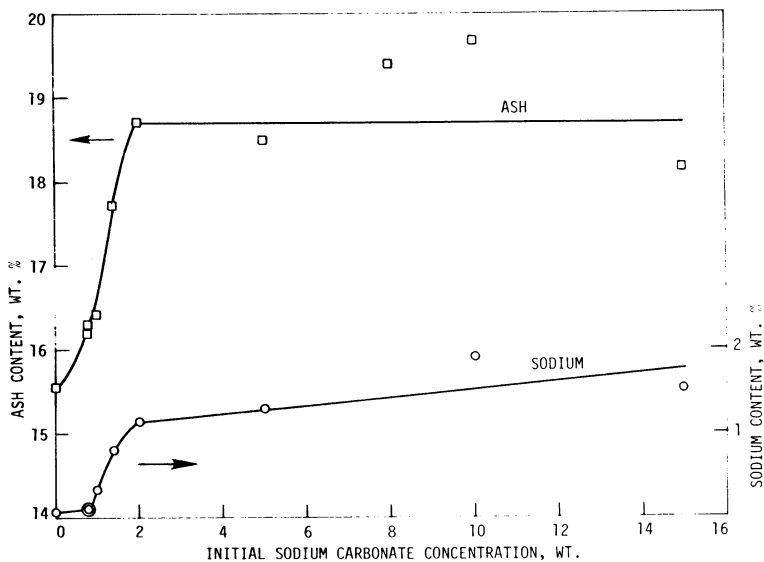


Figure 5. Ash and sodium content of ISU coal after leaching

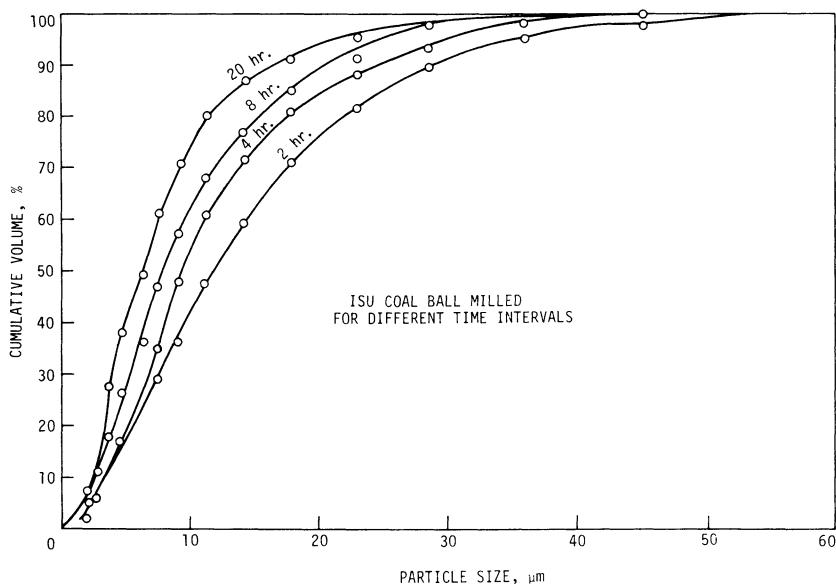


Figure 6. Cumulative volume of particles smaller than the indicated size

Table IV. Results of Treating Different Grinds of ISU Coal

Run No.	Treatment	Grind	H.V. (Btu/lb)	Ash (wt %)	Sulfur Distribution (lb/10 ⁶ Btu)			
					Pyritic	Sulfate	Organic Total	
	none	pulverized	11,040	12.0	2.31	0.54	2.19	5.04
3-108-5	chemical	pulverized	11,360	15.8	0.67	0.05	2.32	3.05
3-108-7	chemical	b.mill (2 hr)	11,500	14.7	0.29	0.04	2.10	2.43
3-108-6	chemical	b.mill (4 hr)	11,070	16.6	0.30	0.05	2.17	2.51
3-108-8	chemical	b.mill (8 hr)	11,237	16.2	0.34	0.05	2.06	2.46

Table V. Results of Combined Physical and Chemical Treatment

Coal Source	Coal Amt. (g)	Treatment	Temp. (°C)	Pressure (atm.)		H.V. (Btu/lb)	Ash (wt %)	Sulfur Distrib. (lb/10 ⁶ Btu)			
				O ₂	Total			Pyritic	Sulfate	Organic	Total
ISU	--	none	--	--	--	10,990	--	3.96	0.33	2.53	6.81
ISU	--	float/sink	--	--	--	12,990	--	1.38	0.23	2.41	4.02
ISU	40	chemical	120	2.4	4.4	11,650	12.2	0.13	0.06	2.34	2.53
ISU	40	chemical	135	2.7	5.8	11,490	12.1	0.18	0.07	2.32	2.57
ISU	20	chemical	150	2.4	6.9	10,770	24.0	0.21	0.04	2.04	2.29
ICO	--	none	--	--	--	12,040	--	1.66	0.25	0.61	2.52
ICO	--	float/sink	--	--	--	12,690	--	0.70	0.20	0.62	1.53
ICO	40	chemical	120	2.7	4.7	11,630	11.6	0.10	0.02	0.64	0.76
ICO	40	chemical	120	3.7	5.8	11,480	11.6	0.15	0.02	0.58	0.75
ICO	40	chemical	120	5.2	7.3	11,640	10.8	0.09	0.02	0.64	0.74
ICO	25	chemical	150	3.2	7.8	11,220	14.1	0.14	0.03	0.60	0.77
ICO	25	chemical	150	3.2	7.8	11,740	13.2	0.11	0.04	0.56	0.71
Big Ben	--	none	--	--	--	11,800	--	1.37	0.37	0.61	2.36
Big Ben	--	float/sink	--	--	--	12,790	--	0.42	0.28	0.81	1.47
Big Ben	25	chemical	132	2.9	5.8	10,950	10.6	0.09	0.03	0.89	1.00
Big Ben	25	chemical	150	3.2	7.8	11,680	10.0	0.16	0.04	0.81	1.01

Therefore, it should have been possible to obtain as good results even with milder treatment conditions or a shorter reaction time.

Conclusions

Dilute alkaline solutions containing oxygen dissolved under pressure were very effective at elevated temperatures for extracting the inorganic sulfur from coal. Of various alkalis tested, sodium carbonate gave the best results. This material also has the advantages of being readily available, low in cost, and relatively noncorrosive in aqueous solution towards steel and other common materials of construction. Although sufficient alkali should be used to neutralize all of the acid which is produced through oxidation of the coal sulfur, an excessive concentration of alkali seems to slow the rate of desulfurization. On the other hand, the rate of desulfurization can be increased by reducing the size of the coal and/or pyrite particles. Leaching coal fines with dilute sodium carbonate solutions at temperatures up to 150°C and with oxygen partial pressures up to 5 atm for up to 2 hr does not seem to degrade high volatile bituminous coal. However, the coal does adsorb sodium from the leach solution which can be removed subsequently by washing with dilute acid. Chemical leaching can be combined advantageously with physical cleaning since the latter is more adept at removing coarser particles of pyrite while the former is more adept at removing the microscopic particles.

Acknowledgement

This work was sponsored by the Iowa Coal Project and conducted in the Energy and Mineral Resources Research Institute at Iowa State University.

Literature Cited

1. Nelson, H. W., Snow, R. D., Keyes, D. B., *Ind. Eng. Chem.* (1933) 25, 1355.
2. Agarwal, J. C., Giberti, R. A., Irminger, P. F., Petrovic, L. J., Sareen, S. S., *Min. Congr. J.* (1975) 61 (3), 40.
3. Sareen, S. S., Giberti, R. A., Irminger, P. F., Petrovic, L. J., Preprint 50c, 80th National Meeting AIChE, (Sep. 7-10, 1975), Boston.
4. Agarwal, J. C., Giberti, R. A., Petrovic, L. J., U.S. Patent No. 3,960,513, 1976.
5. Sareen, S. S., This volume, in press.
6. Friedman, S., LaCount, R. B., Warzinski, R. P., This volume, in press.
7. Majima, H., Peters, E., *Trans. Metall. Soc. AIME* (1966) 1409.
8. Stenhouse, J. E., Armstrong, W. M., *Can. Min. Metall. Bull.* (1952) 45, 49.

9. Burkin, A. R., Edwards, A. M., in "Mineral Processing," (A. Roberts, Ed.), pp. 159-169, Pergamon, Oxford, 1965. (Proceeding of the Sixth International Congress held at Cannes, May 26-June 2, 1963.)
10. McKay, D. R., Halpern, J., Trans. Metall. Soc. AIME (1958) 301.
11. Book ASTM Stand., Part 26, "Gaseous Fuels; Coal and Coke; Atmospheric Analysis," Methods D2015-66, D2492-68, D3174-73, D3177-75, 1976.
12. Fritz, J. S., Yamamura, S. S., Anal. Chem. (1955) 27, 1461.
13. Anderson, J. E., Halpern, J., Samis, C. S., J. Met. (1953) 5, 554.
14. Dresher, W. H., Wadsworth, M. E., Fassell, W., Jr., J. Met. (1956) 8, 794.