Reports

Desulfurization of Coal

Abstract. *Coal combustion is the largest single source of sulfur oxide pollution. Treatment of some major representative U.S. coals with aqueous ferric solution removes 40 to 75 percent of the sulfur content through near quantitative oxidation of the pyritic sulfur contained in the coal matrix. Elemental sulfur and iron sulfate are recovered as products of the reaction. Engineering assessment indicates that the system, when fully developed, offers high potential for the economic abatement of sulfur oxide pollution.*

Coal combustion is by far the largest single source of sulfur oxide pollution in the United States, with a preponderance of the total emissions concentrated in the geographical area east of the Mississippi River. Further, the amounts of sulfur oxide produced from the combustion of coal are expected to increase from 26×10^6 metric tons anually in 1966 (*1*) to 45 to 55×10^6 metric tons annually by 1990 (in the absence of controls). The sulfur content of coal, nearly all of which is emitted as sulfur oxide during combustion, is, on the average, about equally distributed between two chemical forms, inorganic (iron pyrites) and organic sulfur. However, the sulfur content of some major eastern U.S. coal reserves is mainly pyritic.

An unconventional approach for the removal of the pyritic sulfur content of coal, which has just entered bench-scale development, is presented below. Termed the Meyers process, its total effectiveness for sulfur reduction and its economic merit are currently being evaluated under the sponsorship of the Environmental Protection Agency.

The idea of the removal of pyrites from coal by chemical means has not heretofore been advanced as a solution to the sulfur oxide air pollution problem because iron pyrites are insoluble in any known liquids. For example, the acids hydrochloric, hydrofluoric, or sulfuric, or combinations of these, which dissolve many inorganic salts, have little or no effect on iron pyrites. On the other hand, pyrites may be oxidatively converted to sulfates, soluble in strong acid, by strong oxidizing agents such as nitric acid or hydrogen peroxide. In fact, these reagents have long been used for the analysis of the pyritic sulfur content of coal. However, the use of these reagents has never seriously been advanced as a method for lowering the sulfur content of coal, because hydrogen peroxide and nitric acid, which are strong enough to dissolve pyrite, also oxidize the coal matrix (nitric acid also nitrates the coal).

In order to provide an economically viable process for the chemical removal of pyrites from coal, it would be necessary to utilize an oxidizing agent (most likely aqueous) which is (i) highly selective to pyrite, not significantly reacting with the organic portion of the coal matrix; (ii) regenerable; (iii) highly soluble in both oxidizing and reduced forms; and (iv) inexpensive. We discovered that aqueous ferric salts (*2*) meet the above combination of requirements, and these reagents are the basis for the process which is described below. In this approach, aqueous ferric solution at 100°C selectively oxidizes the pyritic sulfur content (*3*) of coal to form free sulfur (with part of the sulfur content being oxidized to sulfate, which dissolves in the aqueous solution). The aqueous solution is separated from the coal, and the coal is washed to remove residual iron salts. The free sulfur may then be removed from the coal matrix by steam or vacuum vaporization (or solvent extraction with toluene or kerosene) (*4*), and the oxidizing agent may be regenerated [in any number of ways, including air oxidation [O] of ferrous ion to ferric ion (Eq. 3) (*5*)]. The resulting coal is basically pyrite-free and may be used as low-sulfur fuel. The chemistry is outlined in Eqs. 1 through 3.

$$2\mathrm{Fe}^{3+} + \mathrm{FeS}_2 \rightarrow 3\mathrm{Fe}^{2+} + 2\mathrm{S} \qquad (1)$$

$$\mathrm{S} \cdot \mathrm{coal} \rightarrow \mathrm{S} + \mathrm{coal} \qquad (2)$$

$$3\mathrm{Fe}^{2+} + 3/2[\mathrm{O}] \rightarrow 3\mathrm{Fe}^{3+} + 3/2[\mathrm{O}^{2-}] \qquad (3)$$

Since "iron is used to remove iron," on regeneration it is not necessary to separate the iron, which is extracted from the coal, from a metal oxidizing agent.

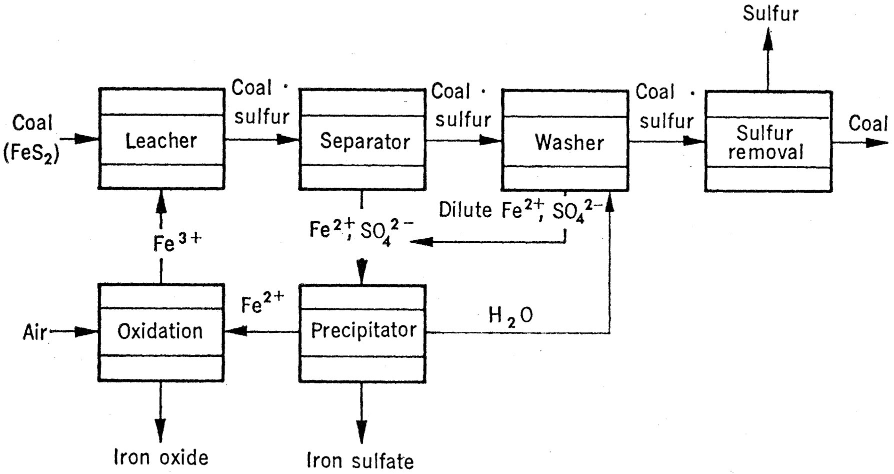

Fig. 1. Process flow chart: (i) the coal is treated with aqueous ferric solution in a batch or countercurrent leaching unit; (ii) the coal is separated from residual iron salts in a batch or countercurrent washing unit; (iii) the elemental sulfur formed is removed by vacuum flash distillation, inert gas vaporization, or solvent extraction to give desulfurized coal; (iv) the depleted ferric solution containing sulfate is cycled to remove iron sulfate, a product of the process; (v) the ferrous solution is air-oxidized, producing iron oxide; and (vi) the regenerated ferric solution is recycled to the leaching unit.

Table 1. Data on pyrite removal. All coals were washed prior to use. Each coal sample (100 g) was pulverized to − 100 mesh top size for accurate sampling (no decrease in the amount of sulfur that can be removed for larger particle sizes has been observed). Each coal sample was treated with four 1-hour leaches with 1*M* $FeCl_3$; Fe_2SO_4 gives almost the same results as $FeCl_3$. The elemental sulfur was removed with hot toluene after aqueous treatment.

Coal*	Sulfur content (% by weight) of: Coal as received†	Sulfur content (% by weight) of: Coal after treating†	Pyritic sulfur removed‡ (% by weight)	Total sulfur removed (% by weight)
Number 6	3.81	2.19	98	43
Number 5	3.49	2.02	94	42
Pittsburgh	1.77	0.77	84	57
Lower Kittanning	4.30	1.13	88	74

* Sources: number 6, Randolph County, Illinois; number 5, Fulton County, Illinois; Pittsburgh, Greene County, Pennsylvania; Lower Kittanning, Indiana County, Pennsylvania. † Total sulfur content and sulfur forms (dry basis) were determined by American Society for Testing Materials techniques at the Commercial Testing and Engineering Laboratories, Chicago, Illinois. ‡ We confirmed the values for the amounts of sulfur removed by analyzing the aqueous extract for its sulfate content and the toluene extract for its elemental sulfur content.

Some typical experimental results (average of duplicate runs) are shown in Table 1 for four major U.S. coals. It can be seen that for these four coals almost all of the pyritic sulfur is removed, while the decrease in the total amount of sulfur varies from 42 to 74 percent because of the varying organic sulfur content. The molar ratio of sulfate to sulfur formed as a result of the treatment with ferric salt varies from 0.2 to 2.5. The heat content of the coal increases and the ash content decreases as a result of pyrite removal.

These four coals were selected for evaluation because their distribution of sulfur forms is typical of coals east of the Mississippi River and because they represent major U.S. coal beds. The Pittsburgh bed has been described as the most valuable individual mineral deposit in the United States and perhaps in the world. Its production accounts for approximately 35 percent of the total cumulative production of the Appalachian bituminous coal basin up to 1 January 1965, and 21 percent of the total cumulative production of the United States to that date (*6*). The Lower Kittanning bed together with its correlative beds contain even larger reserves than the Pittsburgh seam. The number 5 bed is the most widespread and commercially valuable coal bed in the eastern interior coal basin. The Herrin number 6 bed is second in commercial importance only to the number 5 bed. Thus, the experimental results presented here indicate that the sulfur content of a significant portion of U.S. coal can be lowered by at least 40 to 75 percent if the coal is treated with aqueous ferric solution.

A block diagram of one preliminary process design utilizing the technical approach described above for the removal of pyritic sulfur from coal, together with an air oxidation regeneration scheme for the ferric leach solution, is shown in Fig. 1.

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References and Notes

1. "Air Quality Criteria for Sulfur Oxides" [U.S. Department of Health, Education, and Welfare National Air Pollution Control Administration Publication No. AP-50 (January 1969)].
2. We have found that ferric sulfate and ferric chloride are most effective.
3. The use of aqueous ferric salts to oxidize and dissolve copper sulfide ores is well known [for example, F. P. Haver and M. M. Wong, *J. Met.* **23** (No. 2), 25 (1971)]; however, Haver and Wong state (without direct proof) that iron pyrite in copper ore concentrates is not attacked in a period of hours at 100°C. In much earlier work, it was variously claimed (i) that ferric salts do not attack pyrite or (ii) that the reaction has a 60 to 80 percent level of completion [J. W. Mellor, Ed., *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Wiley, New York, 1961), vol. 14, pp. 231–232]. In contrast, we have found that treatment of − 200 mesh top size iron pyrite mineral with 1*M* aqueous ferric chloride solution at 100°C results in 49 percent dissolution after 2 hours, 96 percent after 8 hours, and 99.5 percent after 16 hours.
4. It was not obvious at the start of our work that elemental sulfur could be removed from the coal matrix; earlier reports had indicated that coal heated with elemental sulfur resulted in recombination and elimination of hydrogen sulfide [for example, B. K. Mazumdor, *Fuel* **41**, 121 (1962)].
5. The literature contains a number of references to the air oxidation of ferrous salts [for example, E. J. Sercombe and J. K. Gary, British Patent 1,143,139 (1969); V. V. Ermilov, Y. P. Romanteev, Yu. A. Shchurouskii, *Tr. Inst. Met. Obogashch. Akad. Nauk Kaz. SSR* **30**, 55 (1969); L. Liepina and B. Macejevskis, *Dokl. Akad. Nauk SSSR* **173** (No. 6), 1336 (1967)].
6. P. Averitt, *U.S. Geol. Surv. Bull. 1257* (January 1967).
7. We thank T. K. Janes, L. Lorenzi, and L. Cramer of the Environmental Protection Agency and J. Blumenthal, E. R. Boller, E. A. Burns, B. Dubrow, W. Krawitz, A. A. Lee, and L. J. Van Nice of TRW Systems for their encouragement. Presented in part by R.A.M. at the Symposium on the Desulfurization of Coal, 71st national meeting of the American Institute of Chemical Engineers, Dallas, Texas, 22 February 1972, and at the All-Union Session on Coal Conversion and the Environment, American Geophysical Union, Washington, D.C., 19 April 1972. Supported by the Environmental Protection Agency (after initial feasibility demonstration) under contract EHSD 71-7.

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Absence of Polymerase Protein in Virions of Alpha-Type Rous Sarcoma Virus

Abstract. *Noninfectious particles of a mutant of Rous sarcoma virus failed to exhibit DNA polymerase activity even with the use of the most sensitive synthetic template-primer complexes. A neutralization blocking test against antibody to DNA polymerase revealed that these mutants did not contain protein immunologically related to the DNA polymerase.*

A small fraction of clones of chicken cells transformed by the Bryan strain of Rous sarcoma virus (RSV) is known to produce only noninfectious virus particles, whereas the majority produce infectious RSV (*1*). The defect of this noninfectious virus, called RSVα, can be complemented by helper leukosis virus but not by the viral genome existing in normal chicken cells (*1, 2*). Characterization of the RSVα particles demonstrated that these are deficient in RNA-dependent DNA polymerase that is generally found in the virions of RNA-containing oncogenic viruses (*3*). Independent work by Robinson and Robinson (*4*), however, suggested that this type of RSV has an abnormal enzyme that is inactive with the endogenous viral RNA as template, but active with exogenous DNA templates. Moreover, since the original workers (*3*) did not use synthetic templates that can substantially heighten the sensitivity of the enzyme assay (*5, 6*), the existence of a low level of enzyme in RSVα could not be ruled out.

In this study, we first examined the enzyme activity in RSVα particles with the most sensitive assay systems available. Then we asked whether or not the enzyme protein is present in a functionally inactive form by examining possible reaction with a monospecific