Sulphur Removal Potential of American Coals as a Determinant of Sulphur Dioxide Emissions from Coal-Fired Power Plants [and Discussion]

S. Ergun, N. D. Parkyns and M. M. Hirschler

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APPLIED COAL TECHNOLOGY

Sulphur removal potential of American coals as a determinant of sulphur dioxide emissions from coal-fired power plants

By S. Ergun

Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, *U.S.A.*

The presence of sulphur in coals is a major obstacle to their use in coal-fired power plants because of the restrictions placed on sulphur dioxide emitted from such plants. In this study, it has been found that the recently imposed sulphur dioxide emission standards in the United States are unrealistic because they are not consonant with the reserve base of U.S. coals by total and pyritic sulphur contents, and with factors influencing the removal of pyrite by physical methods. Since cleaning of coal by physical means is inexpensive compared with converting coals into clean-burning fuels before burning them in the boilers or reverting to stack-gas clean-up, and since direct firing of coal conserves the coal if the end product is electricity, it is recommended that the standards to be imposed should be consonant with the reserve base and the potential of physical methods.

Coal as a source of electricity

The electricity used in the United States would require roughly 1 Gt of coal or about 4×10^9 barrels (6.4×10^8 m^3; *ca.* 0.5 Gt) of oil annually if it were generated entirely in coal-fired or oil-fired power plants respectively. In reality, however, less than half of the electricity generated comes from coal. In that known reserves of coal in the United States are huge compared with known reserves of the indigenous crude oil, the importance of increased coal utilization for electricity generation requires no elaboration.

It is also well recognized that coal deposits, like other fossil fuel and mineral deposits, are not inexhaustible and that technologies have to be developed to rely on solar and other forms of energy that can be derived from renewable resources. In the interim, however, coal has to be used as a raw material for synthetic liquid and gaseous fuels.

Air quality standards for sulphur dioxide emissions

The Air Quality Act of 1963 necessitated a concerted effort by federal and local governments to regulate and monitor the quantity of hazardous substances contained in effluent streams. One of the commonly recognized pollutants is the sulphur dioxide produced in the combustion of fossil fuels. In 1975, for example, electric utilities burned about 400 Mt of coal with an average sulphur content of 2.2%. The initial regulations effective until 1979 permitted the release of 1.2 lb of SO_2 per 10^6 Btu (*ca.* 0.52 kg/GJ) heat generated in the combustion chambers. This corresponds roughly to a permissible sulphur content of 0.8% in the coal burnt. The current regulations reduce the permissible level to 0.5 lb/10^6 Btu (*ca.* 0.21 kg/GJ) or removal o 85% of the sulphur present in coal, provided SO_2 released does not exceed the earlier, pre-1980, limit.

If the reduction of permissible sulphur contents of coals to levels of 0.3 % precludes direct combustion of coal, there are obvious adverse consequences. The first is economic. Conversion of coal to clean burning fuels raises the cost of combustible boiler fuel from a level of about $1/$10^6$ Btu ($0.95/GJ) to about $6/$10^6$ Btu ($5.70/GJ). This will be reflected in the cost of electricity delivered. Likewise, desulphurization of stack gases does not appear to be very inexpensive compared with conversion of coal to oil. The economic advantages of producing electricity at low costs need no elaboration.

A second adverse consequence of converting coal to oil or gas for combustion in utility boilers would be the depletion of coal reserves at a faster rate. The expected thermal efficiency of the known conversion technology is about 67 %; thus a coal deposit that could last 75 years in direct fired boilers would be consumed in 50 years. If coal is consumed faster, the rate of carbon dioxide release into the atmosphere will be likewise increased. This will not be comforting to those concerned with the so-called greenhouse effects.

Obviously, concern over environment and health played a major role in the low levels of permissible SO_2 releases. Even in this respect there seems to be some scepticism as revealed in the following quotation from a recent textbook on sulphur (Meyer 1977, p. 2):

> During the dynamic 1960's, when all progress and values were reexamined, the public suddenly became aware that involuntary release of sulfur dioxide from coal burning power plants...equaled the international world sulfur production. The public became fearful of the enormous quantities of efferent sulfur because it did not realize that the total sulfur involved in all of man's recorded activities is smaller than the sulfur dioxide emission resulting from any of the large volcanic eruptions of Mt. Katmai in Alaska in 1912, Mt. Hekla in Iceland in 1947, or Mt. Agnug in Bali in 1963.

The important factors neglected

The above quotation implies that the ability of the Earth to take care of the sulphur dioxide emitted has not been fully explored. Another major factor neglected in the adoption of sulphur dioxide emission standards is the sulphur reduction potential of American coals. If we assume that 1 Gt of coal must be mined annually for electricity generation and that low-sulphur coals could be allocated for this purpose, we may then properly ask to what levels of sulphur content these coals can be cleaned by the conventional physical means. This paper primarily deals with the sulphur reduction potential of American coals.

Reserve base of U.S. coals by total and organic sulphur content

Sulphur in coals occurs mainly as pyrite and as a part of the coal matrix referred to as organic sulphur. The distinction between organic and pyritic sulphur is important in assessing the cleanability of coal seams. Since pyrite is much heavier than coal, it can, in principle, be separated from coal by gravimetric methods. The coal reserve base in the United States by total sulphur content was compiled by Thomson & York (1975) for the eastern United States and by Hamilton *et al.* (1975) for the western states. Those reserves in the eastern states containing less than 0.3 % sulphur are insignificant. The fraction of the eastern coal reserves that contains less than 0.8 % total sulphur ranged from a high of 70 % in Virginia to a low of only 3 % in Illinois. The total reserve of coals in the eastern states that contains less than 0.8 % sulphur can be estimated to be about 20 Gt, roughly 10 % of the total reserves. The western coals are of lower rank and contain less sulphur, except those that are found in Iowa and

Missouri. On the other hand, the Alaska coals were found to be nearly free of sulphur. The total reserves in the western states containing less than 0.8% sulphur can be estimated to be about 90 Gt, nearly 40% of the total reserves.

Unfortunately, the data collected by the Bureau of Mines researchers cited above do not contain information about the pyritic and organic sulphur forms. Such data are needed to provide estimates of coal reserves that would meet specified sulphur emission standards if the pyrite present in them could be removed by physical methods. The organic and pyritic sulphur contents of approximately 3000 samples that include most of the coal beds in the United States were compiled earlier by Walker & Hartner (1966) of the Bureau of Mines. However, the data lacked information about the calorific value and estimates of reserves. The former deficiency was overcome by deriving an empirical relation between the calorific value and moisture content (Ergun 1979). The question as to whether or not the sulphur data reported by Walker & Hartner reflected a state-wide reserve distribution proved to be more difficult to resolve for some states largely because an insufficient number of samples were analysed. The criterion used in this regard was a comparison of total sulphur distribution (state-wide) in the samples analysed by Walker & Hartner with those compiled by Thomson & Hamilton on the basis of reserve estimates. Such a comparison is illustrated in figure 1 for the Colorado coals. The open circles show the percentages of total bituminous coal reserves with sulphur contents less than those indicated by the abscissa; the closed circles show the percentages of the total number of chemical analyses compiled with sulphur contents less than the percentages shown in the abscissa. The agreement is good.

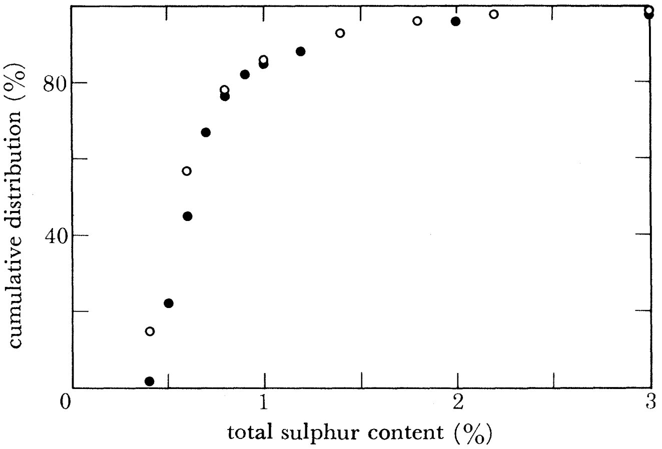

Figure 1. Distribution of Colorado coals by total sulphur content: circles represent reserve base data (Hamilton *et al.* 1975); closed circles represent random sampling (Walker & Hartner 1966).

An analysis of the data of Walker & Hartner reveals that in the eastern states the amount of coals containing organic sulphur less than 0.8% may be as high as 80 Gt (i.e. about 40% of the total reserves), and that in the western states, the reserves of coals containing less than 0.8% organic sulphur may be as high as 170 Gt, over half of which have a total sulphur content less than 0.8%. On the basis of these observations, it is obvious that coal cleaning has to be selective to be effective and this certainly deserves attention.

Distribution of organic and pyritic sulphur

Figure 2 shows the frequency of organic sulphur distribution in Colorado, Pennsylvania and Illinois coals. Both Colorado and Pennsylvania coals indicate a monomodal distribution, the mean values being about 0.5 and 0.6% for the respective states. The Illinois coals show, at least, a bimodal distribution and have excessive organic sulphur. Figure 3 shows the distribution of pyritic sulphur in the coals of the same states. In this respect Pennsylvania and Illinois coals show a similarity, but Colorado coals are distinctly different.

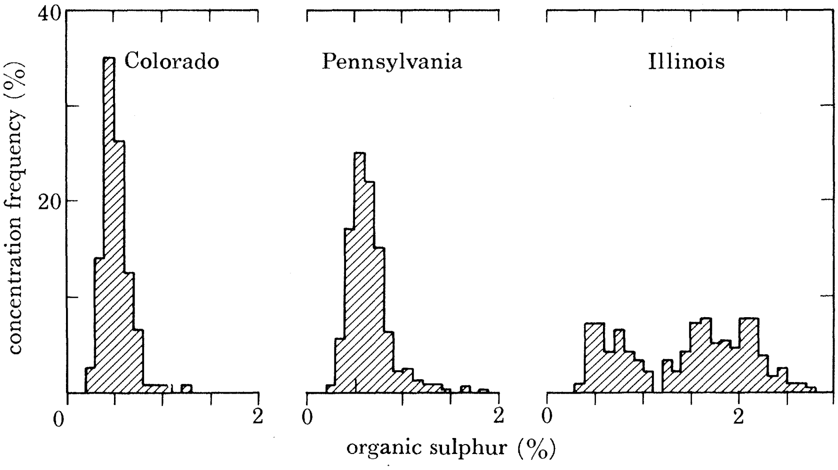

FIGURE 2. Frequency of organic sulphur concentrations in Colorado, Pennsylvania and Illinois coals.

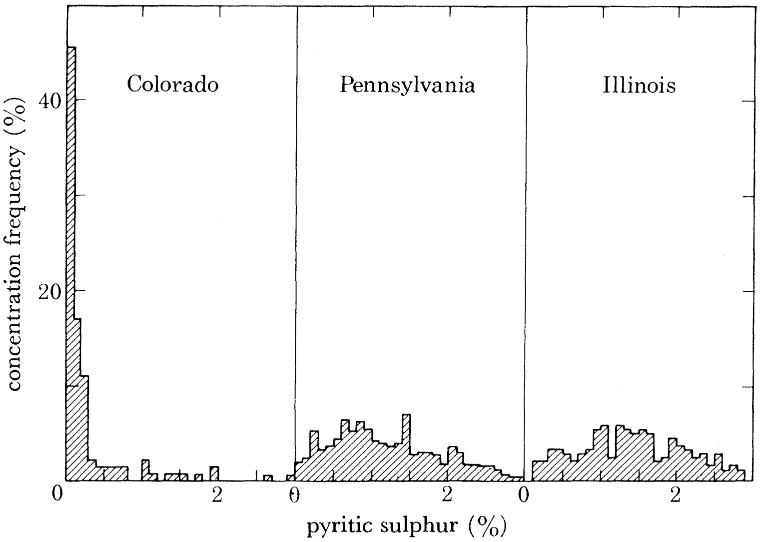

FIGURE 3. Frequency of pyritic sulphur concentrations in Colorado, Pennsylvania and Illinois coals.

The origin of both the organic sulphur and pyrite in coals has been the concern of many geologists or geochemists. Figure 4 shows the organic sulphur contents of coals from Pennsylvania, Alabama and Colorado against the pyritic sulphur contents of the respective coals. That there is a trend is undeniable. It is likely that there exists a better correlation between the organic sulphur contents of coal seams and the pyrite finally dispersed in the seams.

Mode of occurrence and size distribution of pyrite in coals

Pyrite is extremely variable in its occurrence in coals, both in amount and form. Figure 4 shows the ranges of pyritic sulphur contents of coals of Alabama, Colorada and Pennsylvania. Pyrite may occur as horizontal layers in a coal bed, or as fillings in the vertical cleats, or as minute aggregates scattered irregularly throughout the various lithologic ingredients of the coals, especially within vitrain bands. Pyrite is found in coal in particles from microscopic sizes up to large masses or boulders. Although difficult, a distinction must be made between free or nearly free (segregated) pyrite and that dispersed in the organic coal matrix. It is the latter kind that is hard to liberate, a step required for separation. Anticipating that the difficulties associated with the separation of pyrite from coals may be predicted from or related to the size distribution of pyrite in coals, McCartney *et al.* (1969) first tried to develop techniques for such determinations. The problem is beset with many difficulties because a microscopic technique must be used to observe the finely distributed pyrite. Another major difficulty lies in sampling. The necessity of using microscopes limited the top size of the particles used to a few millimetres. There is always the concern about the probability of reduction in the size of pyrite particles in the course of crushing coal to 2 mm top size. The extent of pyrite size reduction depends upon

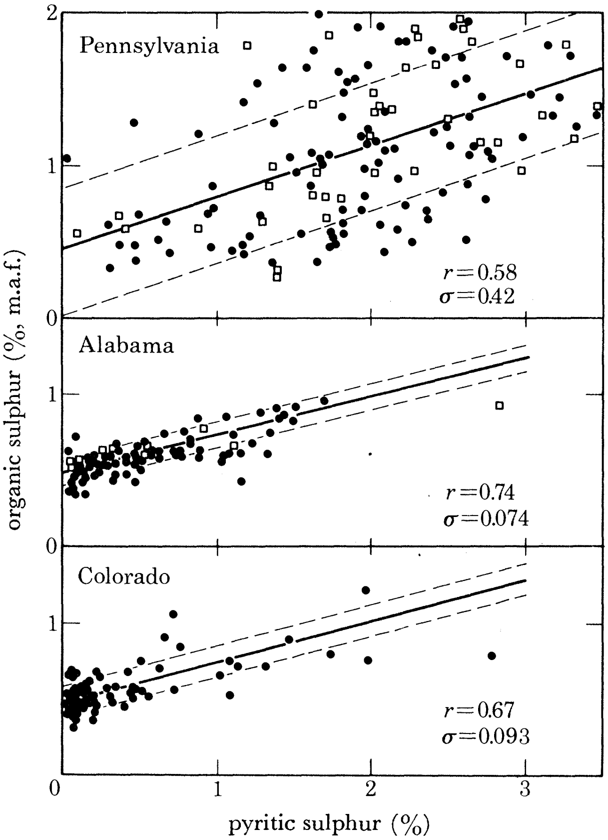

FIGURE 4. Relation between organic and pyritic sulphur contents of some American coals.

its size distribution in the coal seam, which is unknown. However, if the pyrite sizes in the coal smaller than 2 mm are smaller by an order of magnitude, or more, than the sizes of coal particles, appreciable reduction in pyrite size may not be expected. Based on this premise, McCartney *et al.* studied pyrite size distribution in 120 steam coals used by the electric utilities.

Figure 5 shows the pyrite size distribution in three steam coals containing relatively fine, medium and coarse pyrite on Rosin–Rammler coordinates (Herdan 1953, p. 12). The conformity of size distribution of pyrite found in 120 coals to Rosin–Rammler statistics is significant to note. What the conformity signifies is not yet very clear. From a practical point of view, the results obtained made it clear that pyrite size distribution in coals varies a great deal and that mean sizes are very small compared with top sizes of coal used in normal washing operations. For example, figure 5 shows that about 56 % of pyrite in Meigs Creek coal is smaller than 20 μm, and about 90 % is smaller than 50 μm. In contrast, only about 7 % of the pyrite in Lower Kittanning coal is smaller than 20 μm, and about 18 % is smaller than 50 μm. The mean pyrite size in 120 steam coals ranged from under 20 to near 800 μm; however, in relatively few coals, the mean size exceeded 200 μm.

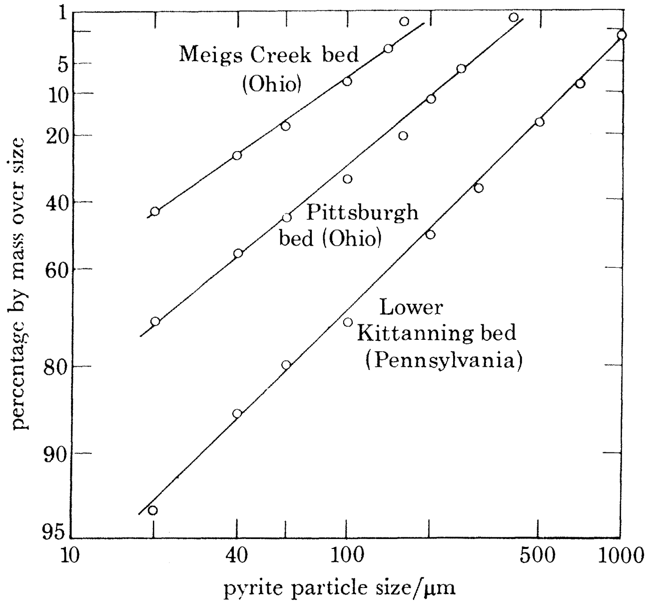

FIGURE 5. Apparent size distribution of pyrite in samples (< 1.2 mm) of three steam coals, containing relativel fine, medium and coarse pyrite.

Factors influencing removal of pyrite by physical methods

Differences in the specific gravities of the coal substance and those of the associated mineral impurities are large enough to effect the isolation of coal by float–sink techniques. Flotation is a well established technology and is widely practised. Pyrite is slightly paramagnetic and coal is slightly diamagnetic. Thus it is possible to separate pyrite from coal by using magnetic separators. The main advantage of this technique lies in the fact that it is a dry process. Its disadvantages stem from the low paramagnetic susceptibility of pyrite. The possibility of converting pyrite, at least partly, into iron–sulphur compounds (e.g. pyrrhotite), with larger susceptibilities, has not been overlooked (Ergun & Bean 1968).

Influence of pyrite particle size

For the pyrite to be separated from the coal physically, it must first be liberated from the coal substance. It is most likely that pyrite occurring as more or less distinct horizontal layers in the coal bed, as fillings in the vertical cleats or as large chunks will be liberated when coal is crushed to top sizes used in industrial practice, e.g. 10 mm. McCartney *et al.* first investigated the influence of mean pyrite particle size on the efficiency of pyrite removal by float–sink from the 120 coal samples examined. In all of the float-sink tests, the samples were crushed to pass through a 14-mesh screen (1.2 mm) and the relative density used was 1.60. Some of the results obtained are shown in figure 6, in which the reduction in pyritic sulphur content upon flotation is plotted against the mean size of the pyrite found in the coals. The correlation coefficient for the 60 samples plotted in the figure was 0.89, and 0.91 for the 120 samples. The figure clearly demonstrates that the efficiency of separation of pyrite by float–sink depends upon the size distribution of pyrite in the coal floated.

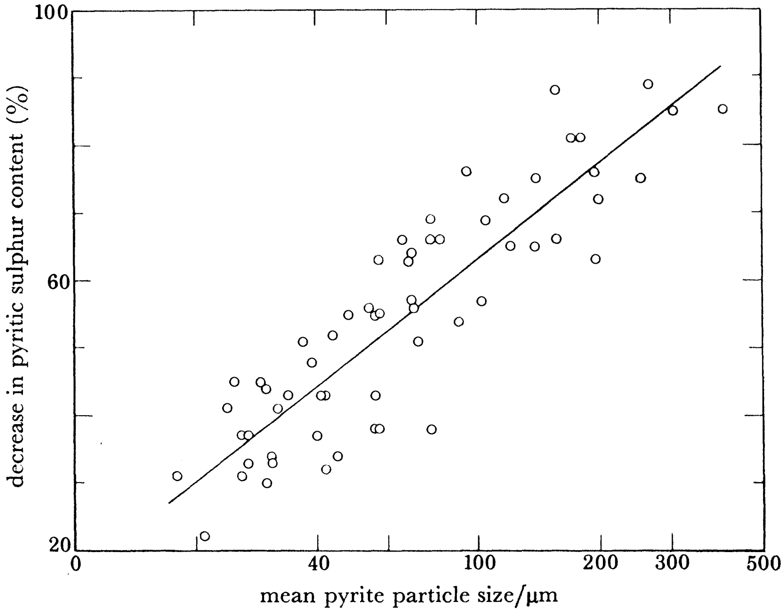

FIGURE 6. Relation of decrease in pyritic sulphur by float–sink tests of coal (< 1.2 mm) at 1.60 relative density to mean pyrite particle size. Correlation coefficient: 0.89.

Influence of pyritic–coal association

McCartney *et al.* also examined the effect of coal–pyrite association on the efficiency of pyrite removal by float–sink. They found that the reduction in pyritic sulphur content was linearly related to proportions of pyrite in individual coal particles containing more than 50 % pyrite by volume. The results obtained are shown in figure 7. Although 59 % cut-off level is arbitrary, the influence of proportion of pyrite in individual particles to the separation efficiency is clearly demonstrated.

Influence of top size of coal

McCartney *et al.* also conducted float–sink experiments on these coals with the use of samples crushed to 9.5 and 38 mm top size in addition to 1.8 mm used in pyrite size determinations.

Their study showed only a marginal increase in pyrite removal with a drop in top size, in spite of the fact that the top size was reduced considerably, i.e., by factors of 4 and 21. Moreover, they observed that pyrite removal efficiency did not improve at all with reduction in coal size for samples containing pyrite less than 100 µm. This fact, of course, was not unexpected. They concluded that coals must be crushed to top sizes approaching those of pyrites embedded in them if pyrite is to be liberated.

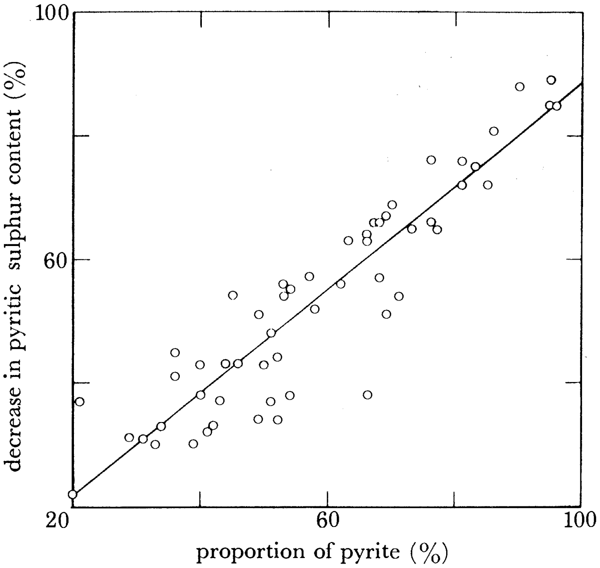

Figure 7. Relation of decrease in pyritic sulphur by float–sink tests of Coal (<1.2 mm) at 1.60 relative density to proportion of pyrite in coal particles containing more than 50% pyrite (from microscopic estimates of area). Correlation coefficient: 0.92.

Influence of relative density of flotation mediums

The influence of specific gravity of the flotation medium was investigated by Cavallaro *et al.* (1976). Since pyrite is denser than coal, particles containing more pyrite (by mass) will have a relative density greater than those containing less pyrite and will sink if the relative density of the flotation is slightly less. On this basis it is reasonable to expect that cleaner coal will be obtained as a float with lesser coal recovery as the relative density of the flotation medium is reduced. A verification of this expectation, of course, was not the intent of the study. Its purpose was to provide data on the cleanability potential of coals from a large number of coal seams (227) in the United States. A spin-off of this effect would have been a correlation with another parameter that would permit the prediction of the yield and the pyritic sulphur content of the floats as a function of the float relative density. The property most likely to shed light is the particle size distribution of pyrite. Unfortunately, this was overlooked in the study cited.

CONCLUSIONS

Estimates of reserve base of U.S. coals by total sulphur content reveal that no significant reserves exist in the industrial regions of the United States that would meet the standards of sulphur dioxide emissions recently imposed for combustion, i.e., 0.5 lb $SO_2/10^6$ Btu (*ca.* 0.21 kg/GJ) heat content.

Estimates of reserve base by pyritic and organic sulphur indicate that the number of coal seams in which the fraction of the pyritic sulphur is equal to or greater than 0.85 are very few. This fact rules out coal cleaning by physical methods as an effective means to meet the current requirements of 85% sulphur removal.

On the other hand, a reasonable fraction (25% or more) of the coals located in the industrial northeastern states and a much larger fraction of the reserves in the western states appear to be amenable to cleaning by conventional physical methods to meet the sulphur dioxide emission standards in effect until 1980, i.e. 1.2 lb $SO_2/10^6$ Btu (*ca.* 0.52 kg/GJ).

In view of the fact that sulphur dioxide emissions from the existing coal-fired electric utility power plants are about 3.3 lb $SO_2/10^6$ Btu (1.4 kg/GJ), a reduction to the 1980 level translates into a reduction of about 64% in the sulphur dioxide discharged. The tolerance of much higher levels of SO_2 emissions from existing plants obviously stems from realistic and practical considerations.

It is reasonable to expect that the price of coal that could meet the more liberal standards would rise and more or less wipe out the economic advantages of direct firings. However, this can be circumvented by legislation, i.e. by allocating low-sulphur coals for electricity generation and for metallurgical use (if suitable). After all, the current regulations requiring 85% sulphur removal obviously seek parity between high-sulphur and low-sulphur coals.

If the current regulations are not relaxed, electric utilities will compete for the capital available for the construction of coal liquefaction facilities and delay the day of energy independence. If coal reserves are to be used effectively and efficiently, sulphur distribution in coal must be a determinant of its end use.

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Discussion

N. D. PARKYNS (*British Gas Corporation, London Research Station, London, U.K.*) We have had some practical interest within British Gas in Pittsburgh no. 8 coal which we are told is typical of many eastern U.S. coals in being high in sulphur and iron. It is moreover a highly caking and swelling coal; all these features are likely to inhibit its widespread use. However, in a number of trials at our Westfield Development Centre, it has been successfully gasified in the British Gas–Lurgi slagging gasifier whereby most of the sulphur is converted to H_2S, which is easily removed from the make gas. I think that Dr Ergun would agree that from an environmental point of view, this is the best way of using such a coal.

The pyritic nature of the sulphur in Pittsburgh no. 8 was brought home to us by an interesting laboratory observation. We had a sample of the coal at the London Research Station for proximate and ultimate analysis. The unused remnant was then left in a glass bottle in a cupboard. When I went to look at it after about a year, I found that some of the lumps had turned completely white. Closer examination showed that the whiteness was due to whiskery deposits concentrated in bands in the lumps of coal. Moreover, the lump coal had exfoliated in a very similar way to that shown by graphite/potassium lamellar compounds after they are exposed to air.

The white crystals were identified by X-ray diffraction as $FeSO_4 . H_2O$ and were clearly the result of oxidation of iron pyrites in the coal on standing in slightly moist air. In view of the timescale of the oxidation, it would not seem to be a practical method of desulphurizing coal, but our observations do underline some of Dr Ergun's remarks.

M. M. Hirschler (*Department of Chemistry*, *The City University*, *London*, *U.K.*). Dr Ergun quoted in his paper some information on sulphur emissions and compared those due to some major volcanic eruptions with those due to man's activities. To put this into perspective, it should be noted that the total emission of sulphur dioxide by volcanoes over the past 400 years has been estimated at *ca.* 6×10^{14} g, i.e. 1.5 Tg/year (Kellogg *et al.* 1972). Although this value may be rather low and could possibly be increased to *ca.* 10 Tg year (Stoiber & Jepsen 1973; Cullis & Hirschler 1979), even this figure is dwarfed by comparison with emissions of sulphur dioxide due to man: 187 Tg in 1974 (Cullis & Hirschler 1979) and 207 Tg in 1976 (Cullis & Hirschler 1980).

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