

DECOMPOSITION OF PYRITE IN A COAL MATRIX
DURING PYROLYSIS OF COAL

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The high sulphur content of Eastern Canadian coals has led to a number of studies aimed at reducing these sulphur levels¹. In general about two thirds of the sulphur is pyritic, often occurring as small inclusions, and therefore difficult to remove by conventional beneficiation techniques.

In general when coal is pyrolysed the pyrite decomposes to pyrrhotite and H₂S is emitted. It has been reported² that not all of the sulphur from the pyrite/pyrrhotite transformation is emitted; some becomes trapped in the organic matrix as 'bound' sulphur. In ³ investigations of the pyrolysis of Nova Scotian coal, Brothers' noted that when 95% of the pyritic sulphur was removed prior to pyrolysis, the residual organic sulphur in the char decreased by about 50% in comparison to that of char formed from the raw coal.

The present study deals with the pyrolysis of coal from the Prince Colliery in Cape Breton Island, Nova Scotia (Table 1). This particular coal was chosen both because of its high sulphur content (~4 wt.% S) and because it is typical of much of the proven reserves of the field.

Experimental

The coal was crushed and sieved on Tyler screens to -8 + 16 mesh, (1-2.4 mm). Approximately 2 g of coal was placed in an alumina boat and pyrolysed under argon in a tube furnace at a variety of temperatures and times.

After pyrolysis pieces of the coal were mounted using Fisher Chemical Co. 'Quickmount' cold-mounting resin, and polished in preparation for scanning electron microscopy (SEM). Representative pyrite crystals about 20 μm in diameter, and not near macropores or other discontinuities, were selected for study.

A Jeol-35 SEM microprobe equipped with energy- and wavelength-dispersive spectrometers was used for elemental analysis. Point analyses were carried out; these covered approximately 0.5 μm for the

pyrite and 1 μm for the coal. The standard atomic number, absorption and fluorescence (ZAF) corrections were applied to all analysis, using counting times of 200 seconds, an accelerating voltage of 15 KV, and a pyrite crystal as standard.

Results

The extent of pyrite decomposition was followed by obtaining S/Fe atomic ratios at various points across selected pyritic inclusions. Figure 1 is a plot of this ratio vs. "distance from the edge of the inclusion" for seven particles pyrolysed at different temperatures. The duration of pyrolysis was 15 - 20 hours. It is apparent that the transformation from pyrite to pyrrhotite in Prince coal mainly occurs in the temperature range 500-550°.

Figure 2 is a plot of wt.% S as a function of distance from the inclusion/coal interface into the matrix. This demonstrates the constant background level of organic sulphur in the coal matrix surrounding undecomposed pyrite particles at 400 and 500°. In contrast, it is clear that the sulphur content is enhanced around pyrite particles that had been pyrolysed at 550, 600 and 700°C, and that sulphur transfer has occurred.

Figure 3 shows the effect of time on this sulphur transfer during pyrolysis at 600°C. It can be seen that the total amount of sulphur transferred remains approximately constant after 15.5 hours and that the depth of penetration of sulphur into the surrounding organic matrix does not increase with time of pyrolysis.

Discussion

A. Transformation Temperature

At 400°C and 500°C very little decomposition occurred, while at 600°C and 700°C transformation was virtually complete. At 550°C, however, the transformation was incomplete within the 20 hours given for pyrolysis, the results indicating a pyrite core surrounded by a pyrrhotite shell. These results indicate that pyrite in Prince coal begins to pyrolyse between 500 and 550°C; this is in general agreement with temperatures reported by other authors⁴.

B. Sulphur Transfer

The results of this study indicated that there was little transfer of sulphur from pyrite to the surrounding organic matrix of coal not heated beyond 500°C. This is similar to the findings of Raymond and Hagan⁵ who examined unreacted coal by SEM.

The extra sulphur observed around the decomposed pyrite in the present study therefore was formed as a result of the pyrolysis reactions. Radio-tracer work using ^{35}S -doped pyrite has shown that some of the sulphur released combines with the organic matrix with the formation of carbon-sulphur bonds⁶. It has been suggested⁷ that during pyrolysis sulphur migrates within the iron sulphide as S^- . At the surface of the FeS charge transfer, reaction and desorption would lead to a variety of compounds.

Considering the hydrogen-rich environment presented by the decomposing coal matrix, one important sulphur compound would be H_2S , which would begin to diffuse away from the FeS/coal interface through the pores of the matrix. Active carbon sites, that are being generated simultaneously by devolatilization of the coal matrix, also could react with the sulphur trapping it as newly formed and strongly bound "organic" sulphur. In the ^{35}S tracer work referred to above, 38% of the overall sulphur liberated in the decomposition of the pyrite became fixed as "organic" sulphur.

Figure 1 shows that at 600°C a typical pyrite grain has decomposed entirely to pyrrhotite within 15.5 hours. Referring to Fig. 3 it is significant that the depth of penetration did not increase with increasing time, which indicates that the trapped sulphur was not mobile. In addition, therefore, we may conclude that diffusion in the matrix is not an important mechanism for migration of sulphur from the pyrite/coal interface. The main transfer mechanism for the sulphur that does escape probably is pore-diffusion of H_2S .

The data of Fig. 2 can be used to estimate the amount of sulphur trapped in a spherical shell around a pyrite particle, and to compare it with the amount of sulphur known to be released by the pyrite/pyrrhotite decomposition. Within the uncertainties of this order-of-magnitude calculation we concluded that all the sulphur released from a small, well-embedded, pyrite particle in Prince coal becomes trapped in the coal matrix. However, it should be pointed out again that during the pyrolysis of macro amounts of coal a considerable amount of pyritic sulphur is released into the gas phase as H_2S ; presumably this originates with pyrite of a more massive nature or which is not so well embedded in the matrix.

Summary

The decomposition temperature of pyrite in Prince coal was found to be between 500 and 550°C as determined using a SEM-microprobe. In addition, some of the sulphur liberated in this decomposition became trapped in the coal matrix surrounding the pyrite crystals. For small crystals, well embedded in the coal matrix, all the sulphur released by the decomposing pyrite becomes trapped as "organic" sulphur.

References

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Table 1. Proximate Analysis and Sulphur Forms of Prince Coal

Constituent	Weight Percent (moisture free basis)
Moisture	5.5*
Volatiles	27.8
Ash	19.9
Carbon	52.4
Sulphur:	
Pyritic	3.33
Sulphatic	0.34
Organic	1.13
Total	4.80

* On "as received" basis

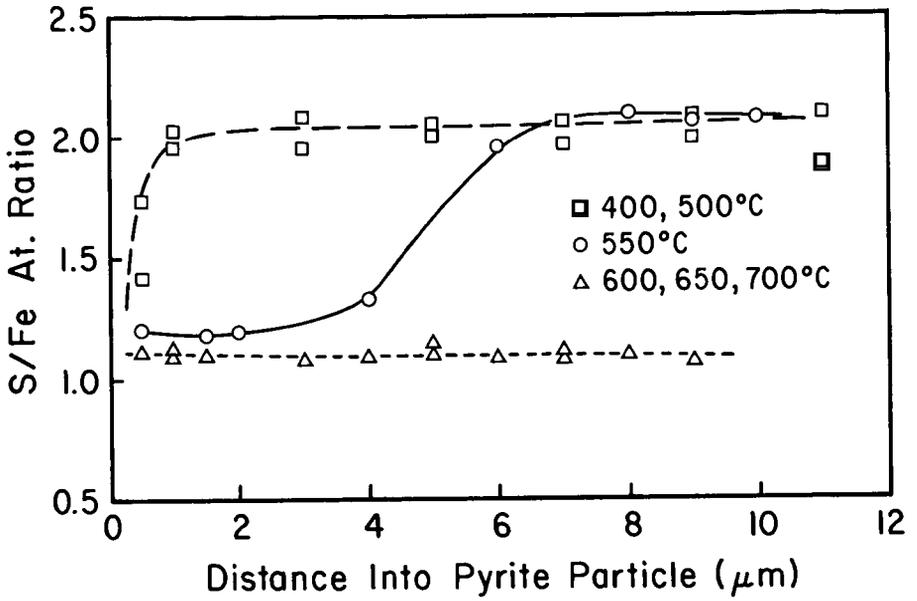


Fig.1 Decomposition of FeS_2 to FeS as coal is heated above 500° .

Fig.2 Sulphur from decomposed pyrite trapped in matrix of coal.

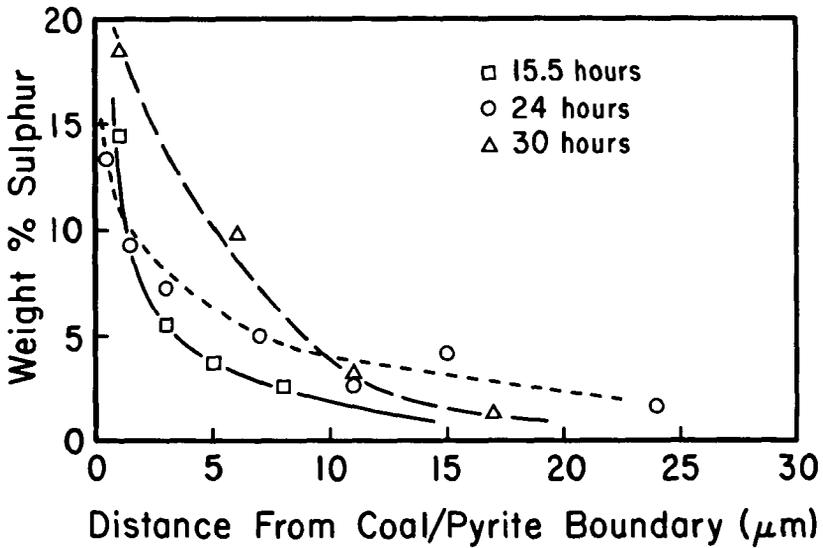
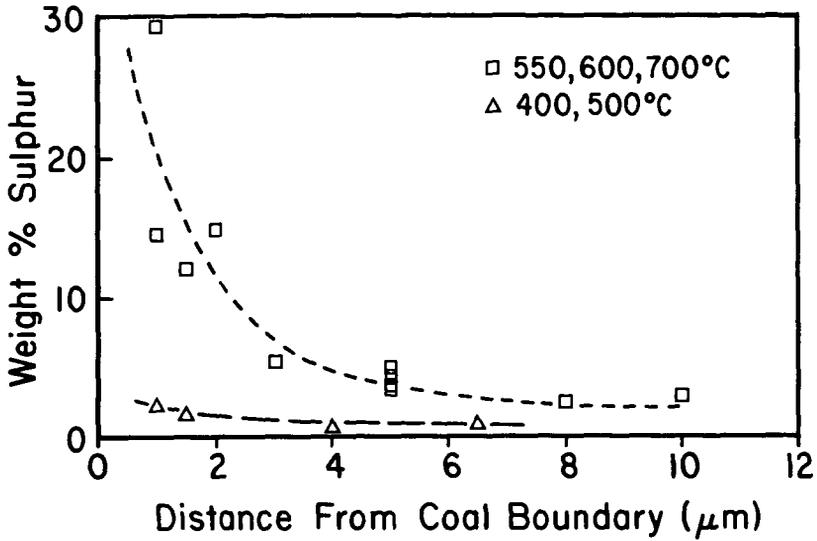


Fig.3 Stability with time of sulphur trapped in matrix of coal.