

PYROLYSIS/MAGNETIC SEPARATION: A PROCESS FOR REDUCING THE SULPHUR CONTENT OF EASTERN CANADIAN COALS*

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Elements of a process are described, whereby the high sulphur coals of eastern Canada may be converted into a low sulphur product suitable for coal-slurry fuels. The process envisaged includes thermal/magnetic beneficiation followed by aggregative flotation. On a laboratory scale the optimum conditions for these steps include vacuum pyrolysis at 475°C, and wet magnetic separation at a field strength of $1.6 \times 10^{-5} \text{ A.m}^{-1}$. A favourable tar yield also occurred at about 475°C for chars exposed to vacuum pyrolysis.

Les étapes d'un processus par lequel les charbons en teneur élevé de soufre provenant de l'est du Canada peuvent être convertis en un combustible à teneur réduite de soufre sont décrites. Le processus envisagé inclut la beneficiation thermique/magnétique suivi d'une flotation agrégative. A l'échelle du laboratoire les conditions optimales pour ces étapes comprennent la pyrolyse sous vide à 475°C, et la séparation magnétique à une intensité de champ de $1.6 \times 10^{-5} \text{ A.m}^{-1}$. Un rendement favorable en goudron est aussi obtenu à 475°C pour les charbons soumis à la pyrolyse sous vide.

Introduction

Between 1981 and 1985¹ an advisory board, the Committee on Atlantic Coal, with representation from the users and suppliers of coal, and Federal and Provincial governments, consistently identified the reduction of the sulphur content of coal destined to be burned in eastern Canadian electric power stations as a priority target for research.

The literature on the reduction of sulphur in coal is voluminous; useful reviews are those of Moore (1982), and Attia (1985). When sulphur is removed before the coal is burned it may be by either physical or chemical means. Physical methods usually remove only that sulphur that is associated with the intrusive mineral matter of the coal; examples are the many processes generally named "coal washing." Chemical cleaning may in addition remove some or all of the sulphur which is associated with the carbonaceous matrix itself. This paper describes work carried out to investigate

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¹ During this time the National Research Council of Canada received funds from the National Energy Program which were mainly devoted to contract research in institutions in eastern Canada. Some of this work has been published in the Technical Report Series of the Atlantic Research Laboratory. Copies of these reports may be obtained from the Librarian of the Laboratory.

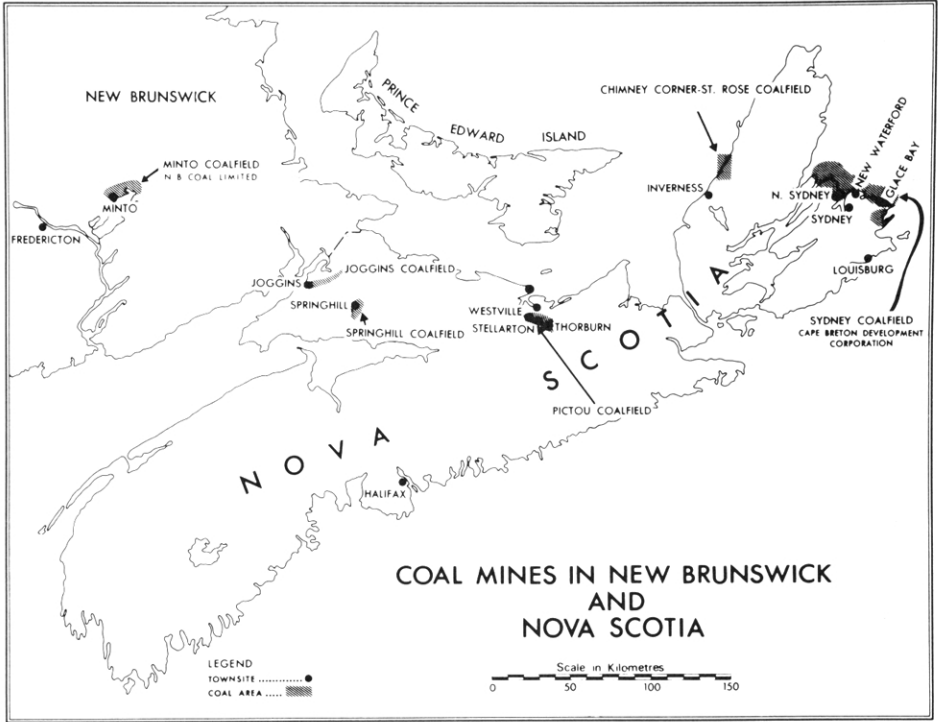


Fig 1 Coal mines in New Brunswick and Nova Scotia.

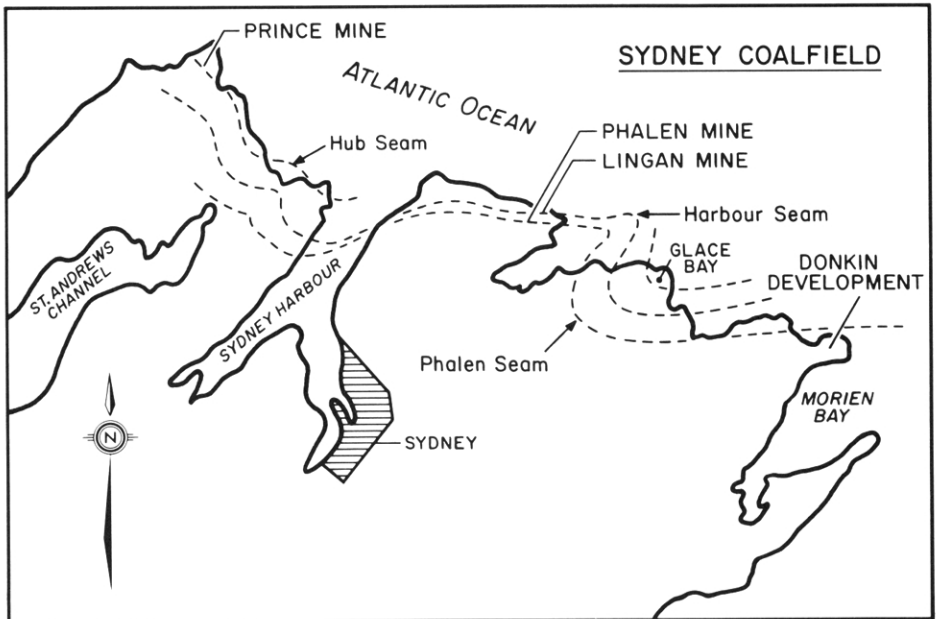


Fig 2 Map of Sydney coal field, showing outcrops and mines.

aspects of a method to remove sulphur before the coal is burned, having elements of both physical and chemical cleaning. It was based on the fact that mild pyrolysis of coal is known to change pyritic sulphur to a strongly magnetic form (Liu and Lin 1976) amenable to removal by a magnetic process. New results on magnetic beneficiation are given, and they are put in context by including some of the results of peripheral investigations.

In eastern Canada coal is found in the provinces of New Brunswick and Nova Scotia, as shown in Fig 1 and Fig 2. Currently the most active mining sites are the Minto coalfield in New Brunswick and the Sydney coalfield in Nova Scotia.

In New Brunswick the coal is high in ash and sulphur (Bonnell, Janke and Romaniuk 1983). In the Sydney coalfield (Fig 2) the bulk of the 2 billion tonnes of thermal coal potentially available can be divided loosely into two groups — about two-thirds having 3.9% sulphur and one-third containing 5.3% sulphur. This sulphur is present in three forms: organic, pyrite and sulphate. Organic sulphur (about 33% in high-sulphur coal) occurs as an integral part of the carbonaceous matrix and cannot be removed by physical means. Pyritic sulphur (about 66%) is found mainly as iron pyrite (FeS_2) outside of the carbon matrix; sulphate (trace) also occurs in this intrusive mineral fraction.

Stirling (1984) has studied the mineralogy of coals from the Sydney, Westville and Minto coalfields and concluded that the maturity of crystallization of pyrite increased in the order Sydney → Westville → Minto. The presence of the allotrope marcasite in the Sydney region coincided with this immaturity of crystallization. The grain size of pyrite particles in typical eastern coals also was reported in this study. For the Prince Colliery coal of the Sydney coalfield, 60% of the pyrite occurs in grains under 100μ , and 20% is smaller than 20μ .

Physical beneficiation of these coals for sulphur, using conventional float-sink washing methods based on the relative densities of coal and pyrite is not efficient. Coal from the Prince Colliery, with about 4% sulphur, 65% of which was pyrite, was processed through the coal cleaning test facility of the Electric Power Research Institute at Homer City, PA. Whereas sulphur reduction was achieved it was at the expense of carbon recovery. For example, when the specific gravity of the separation fluid was adjusted to 1.67 the energy recovery was 89%, but the sulphur had been reduced only from 4% to 3.8%. When the specific gravity was lowered to 1.3 the sulphur was reduced to 1.8%, but the energy recovery fell to only 60% (Mikhlin 1987).

The beneficiation of coal containing finely dispersed sulphur requires fine grinding of the coal, the carbon being recovered by some method which depends upon its

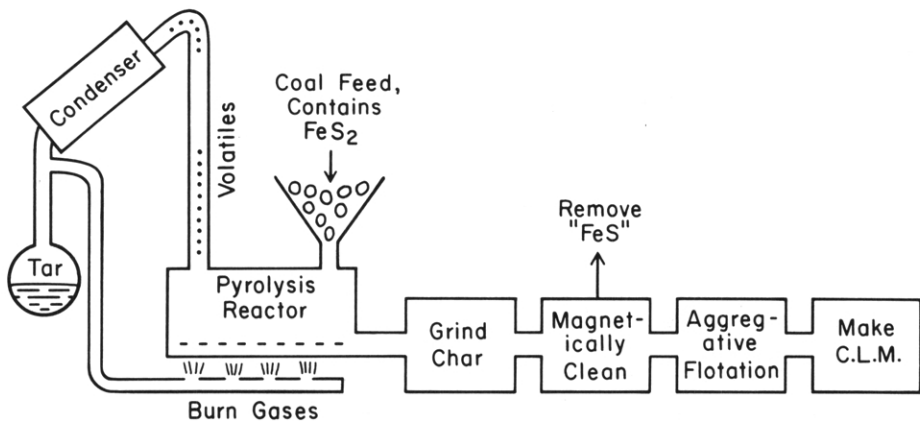


Fig 3 Conceptual process combining pyrolysis, beneficiation, coal-water mixtures.

hydrophobic nature. In the oil agglomeration method sulphur is not rejected efficiently from the carbon because pyrite is not strongly hydrophilic. A process developed to alter the nature of the surface of pyrite by adsorbing on it a hydrophilic layer of *Thiobacillus ferrooxidans* bacteria (McCready 1984) worked well for Minto coal, with good pyrite rejection at acceptable carbon recoveries, but the same was not true of Prince coal from the Sydney coalfield.

The work presented here is based on the premise that some method other than conventional washing will be required to remove the pyrite from eastern thermal coals. Magnetic separation is one such method. Coal is weakly diamagnetic while pyrite is weakly paramagnetic, and separation of these two requires high magnetic field gradients. However, when coal is heated to a temperature variously reported as being between 440 and 580°C, its pyrite decomposes to a pyrrhotite of composition near Fe_7S_8 (Jagadeesh and Seehra 1981). Depending upon the stoichiometry, this pyrrhotite may have a magnetic susceptibility about 7200 times that of pyrite. With such a change a separation based upon a magnetic process should be efficient.

A conceptual process sharing some of the features proposed by Fine, Lowry, Power and Geiger (1976) is shown in Fig 3. Coal is pyrolysed in a reactor to the correct temperature for formation of the most magnetic species of pyrrhotite. A vacuum process is envisaged because separate work (Roy and deCaumia 1984) showed that the quality of the coal tars produced is enhanced. The gases emitted would be used to fuel the process, and the tar liquids recovered for sale. The char is ground and the pyrrhotite removed magnetically, probably by a wet process. The char slurry would then be beneficiated for ash by aggregative oil flotation (AlTaweel and Wojcik 1983) possibly using some of the pyrolysis liquids as the collecting agent, and finally would be made into a clean coal-water-oil liquid fuel. Some parts of this conceptual process have been investigated and will be discussed.

Experimental

Pyrolysis experiments were carried out in a 1 kg capacity stirred tank reactor, equipped with temperature programming, and capable of being operated at pressures from 50 torr to atmospheric. All the gas was collected and analysed for amount and composition, the liquids were trapped and weighed, and the char was weighed and analysed. A complete description of this reactor, and associated analytical methods, has been given previously (Hirajima, Chan, Whiteway, Stefanski and Stewart 1985). Other methods used and described in previous publications are scanning electron microscopy (Cleyle, Caley, Stewart and Whiteway 1984) and Mössbauer spectroscopy (Stewart, Whiteway, Cleyle and Caley 1986).

The magnetic beneficiation of the above chars has been studied using a susceptibility balance and an isodynamic separator arranged for wet operation.

Results and Discussion

A typical plot of the emission of H_2S from 2% sulphur coal of the Sydney field, pyrolysed at atmospheric pressure, is shown in Fig 4 (curve B) (Whiteway and Galvez 1978). The maximum emission rate at 475°C is due to decomposition of FeS_2 . The smaller emission at 425°C is probably decomposition of organic sulphur. Added pyrite of size 200 microns, mixed with the coal, did not decompose below 560°C (Fig 4, curve A). Thus we might expect to see some variation in the decomposition temperature of pyrite depending upon the size of individual grains and their intimacy of admixture with the carbon matrix.

Fig 5 shows a microprobe analysis of actual grains of sulphide in a coal of 4% sulphur pyrolysed at different temperatures (Cleyle, Caley, Stewart and Whiteway

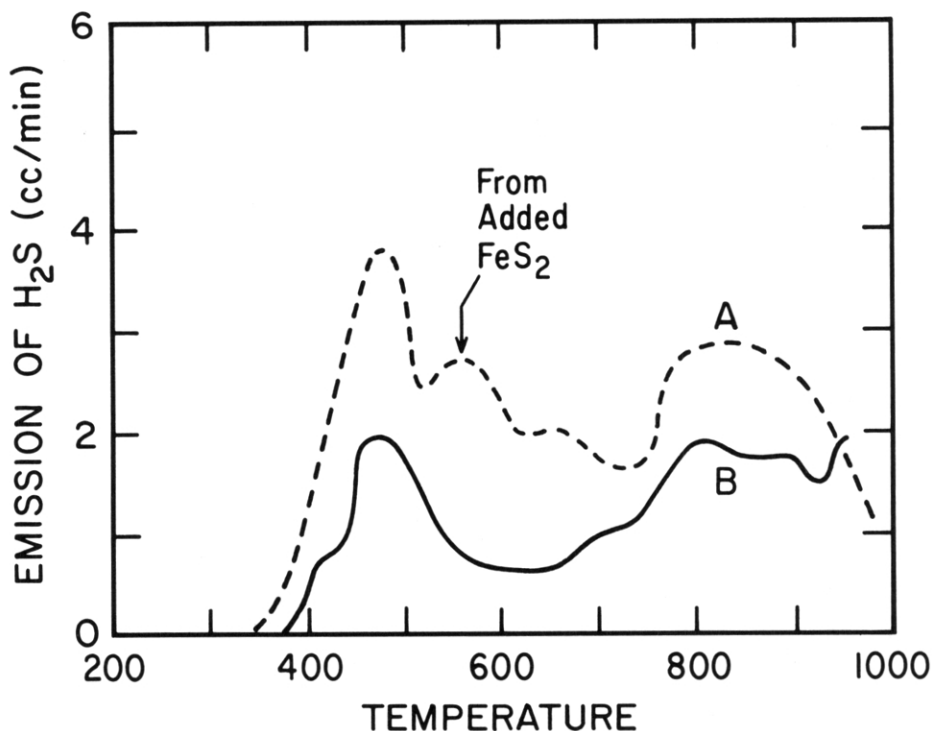


Fig 4 Emission spectra of H₂S from coal from Harbour Seam. (A) with extra FeS₂ added. (B) normal coal (Whiteway and Galvez 1978).

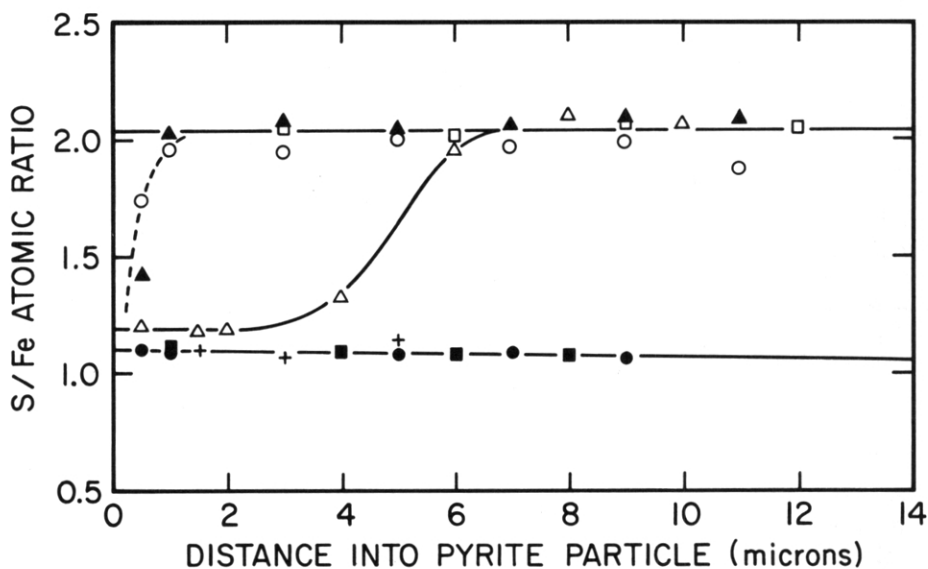


Fig 5 Plot of S/Fe atomic ratios versus distance from the coal/pyrite interface, moving into the centre of the pyrite particle, for a number of pyrolysis temperatures. Pyrolysis times 15-20 hours. □, untreated coal; O, 400°C; ▲, 500°C; △, 550°C; ●, 600°C; ■, 650°C; +, 700°C. (From Cleyle, Caley, Stewart and Whiteway 1984).

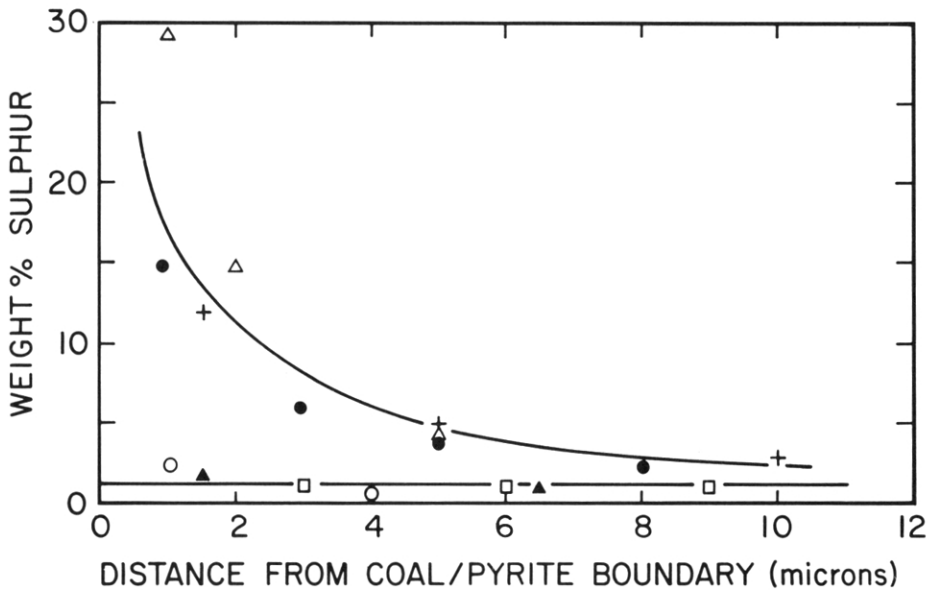


Fig 6 Plot of weight % sulphur in the carbonaceous matrix around the pyrite particles versus distance from the coal/pyrite interface, moving into the matrix. Pyrolysis time 15-20 hours. \square , untreated coal; \circ , 400°C; \blacktriangle , 500°C; \triangle , 550°C; \bullet , 600°C; +, 700°C. (From Cleyle, Caley, Stewart and Whitley 1984).

1984). The grains were about 20μ in diameter. No decomposition was seen at 500°C, while at 600°C and above all the original pyrite had changed to pyrrhotite of non-stoichiometric composition, with slightly more sulphur than iron. At a temperature of 550°C a grain was found that had partially decomposed, the non-stoichiometric sulphide at the surface appeared to have a higher S/Fe ratio than that of the completely decomposed grains. Fig 6 shows the sulphur content in the coal matrix just around grains of sulphide. Until the decomposition temperature for pyrite had been reached the sulphur content was low, and presumably represented the organic sulphur. After the pyrite had decomposed the coal matrix showed a considerably higher sulphur content close to the pyrrhotite. It is evident that considerable sulphur can be trapped in this manner by the coal; other work suggests that it becomes strongly bound to the carbon matrix as a high-temperature organic form (Attar 1978).

Several points may be made from this work bearing upon the possibility of magnetic beneficiation of chars. The extent to which individual grains of pyrite decompose to pyrrhotite will depend upon the temperature and time of pyrolysis, but at a given temperature may also depend upon the grain size and the exact chemical nature of the coal. In addition the stoichiometry and the magnetic susceptibility may depend upon the extent of decomposition. It may not be necessary for grains to be completely decomposed to achieve a useful level of susceptibility. A very magnetic shell of pyrrhotite may be able to carry with it an unreacted core of pyrite. In addition the trapping of sulphur as "organic sulphur" in the coal matrix may not be deleterious if this portion of the coal, upon grinding, is attached to the magnetic sulphide.

The following pyrolysis results are typical for coal from the Prince Colliery of the Sydney coalfield, of 30% volatile matter, 15% ash, and 4.8% sulphur (the latter 0.6 sulphate, 2.7 pyritic and 1.5 organic).

Table I Distribution of Products From Pyrolysis of Prince Coal

T (°C)	P (torr)	CHAR	GAS (weight fraction)	TAR
392	50	0.854	0.019	0.127
386	500	0.862	0.016	0.122
470	50	0.766	0.038	0.196
474	500	0.772	0.054	0.174
580	50	0.692	0.077	0.231
565	500	0.730	0.081	0.189

Table II Characteristics of Chars From Prince Coal

T (°C)	P (torr)	Ash	V.M. (dry basis weight %)	F.C.	Total S (%)
392	50	17.0	20.5	62.5	5.49
386	500	16.8	21.2	62.1	5.53
470	50	18.6	14.9	66.5	4.97
474	500	18.7	12.9	68.4	4.54
580	50	19.5	8.5	72.0	3.76
565	500	19.0	8.4	72.6	3.97
ROM Coal	15.0	30.3	54.7	4.78	

Table III Forms of Sulphur of Chars from Prince Coal

T (°C)	P (torr)	Total	Gms Sulphur/100 Gms original Coal			Organic
			SO ₄	Pyritic	Sulfide	
ROM Coal	4.78	.56	2.68	-	1.54	
392	50	4.69	.26	2.68	-	1.75
386	500	4.77	.24	2.78	-	1.74
470	50	4.00	.18	2.18	.29	1.36
474	500	3.50	.19	0.79	1.08	1.45
580	50	2.60	.03	.03	1.51	1.02
565	500	2.90	.05	.03	1.51	1.30

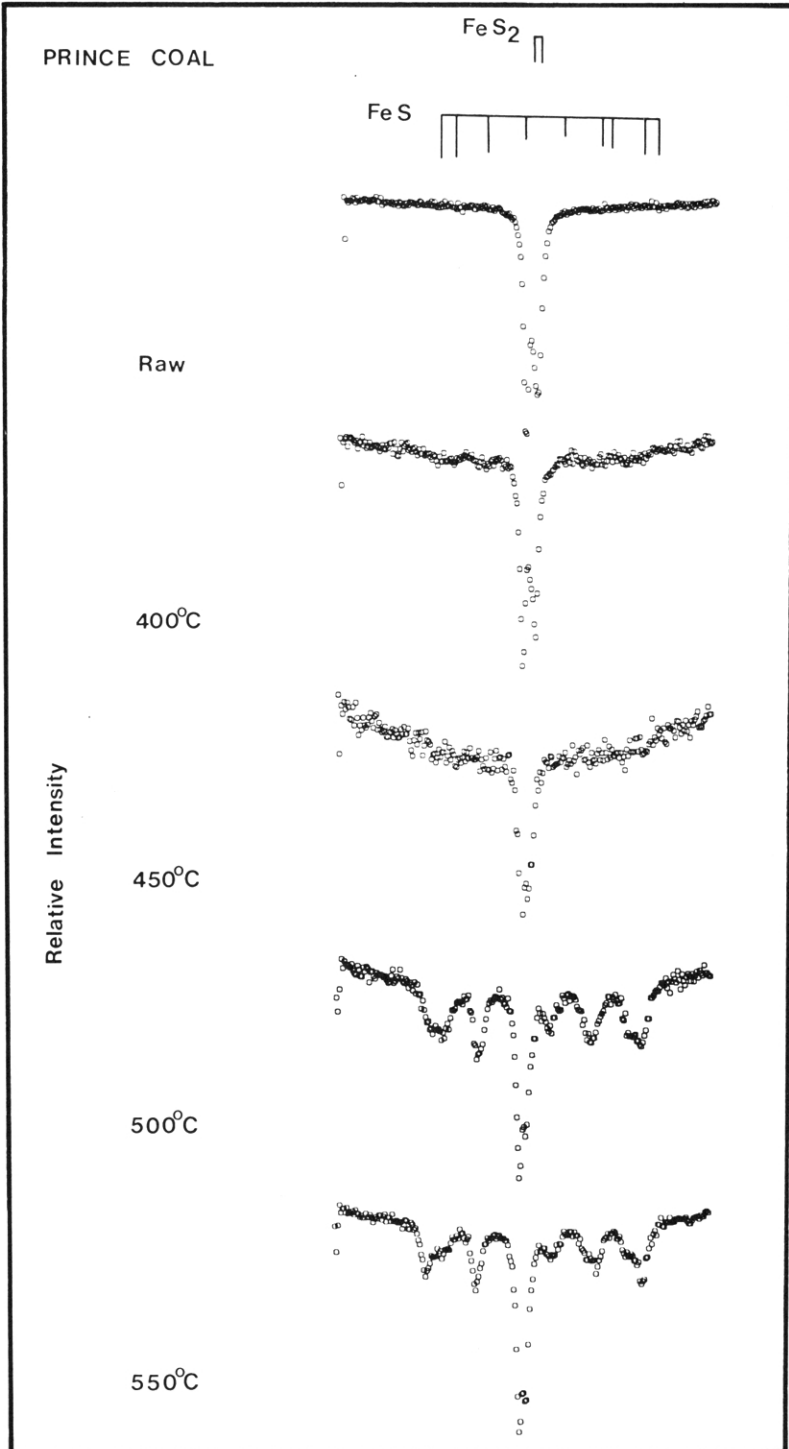


Fig 7 Mössbauer spectra of coal as it is pyrolysed. (From Stewart, Whiteway, Cleyle and Caley 1986).

Table I gives the distribution of the three products: char, liquid and gas. The extent of devolatilization goes up as the temperature is increased, and the ratio of liquids to gases increases as the pressure is decreased. Table II gives some of the characteristics of these chars. Chars made at 470°C still retain 13-15% volatile matter, and so should be readily combustible. Table III gives the distribution of the forms of sulphur in the chars (in g sulphur/100 g coal). For this analysis the sulphide was inferred from the drop in pyrite, assuming that the sulphide formed was Fe_7S_8 . It was also assumed that the sulphate was reduced to sulphite, not sulphide, during the pyrolysis. These results show that the sulphate was reduced, the pyrite disappeared, pyrrhotite was produced, and there was a loss of organic sulphur. The runs at 470°C show that the decomposition temperature for pyrite was affected by pressure; apparently under vacuum the reactive gases were removed more rapidly from the coal matrix and were not as available for reaction with pyrite.

Fig 7 shows Mössbauer spectra for Prince coal pyrolysed in the temperature range 400-550°C (Stewart, Whiteway, Cleyle and Caley 1986). The decomposition of pyrite to yield pyrrhotite is clearly shown by the relative amounts of the species FeS_2 and FeS

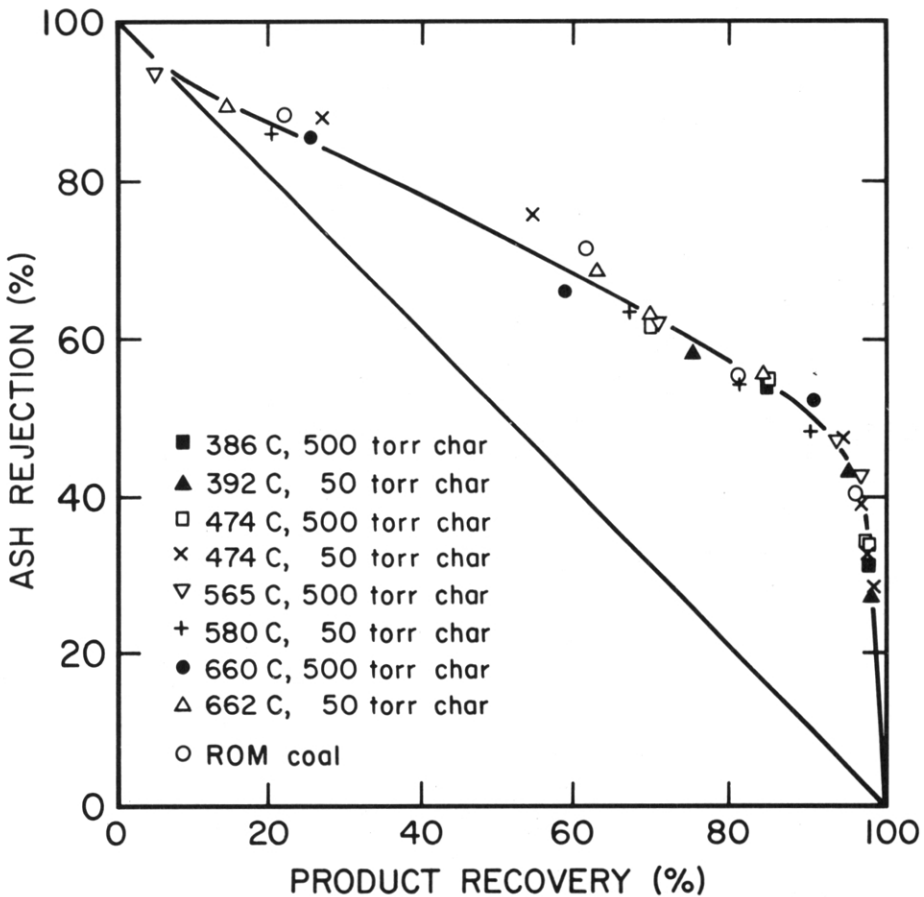


Fig 8 Beneficiation of char for ash by agglomerative flotation. (From Hirajima, Chan, Whiteway, Stefanski and Stewart 1987).

as the temperature was increased. However, there was a wide temperature range over which the two forms coexisted; for example, some pyrrhotite had already formed at 400°C, while pyrrhotite was still present at 500°C. Recent work (Caley, Whiteway and Stewart 1988) largely explains this wide range, by showing that the morphology of pyrite inclusions is an important factor in their decomposition temperature.

While the overall conceptual process would have an additional magnetic cleaning step for sulphur, we have examined the chars for washability with an agglomerative flotation column, using kerosene as an agglomerating agent and methyl isobutyl carbinol as frothing agent (Hirajima, Chan, Whiteway and Stefanski 1985). Fig 8 shows the ash rejection for vacuum and atmospheric pressure chars, and Fig 9 shows the sulphur rejection for vacuum chars. There was little difference in the ash rejection characteristics of all the chars and the parent coal. In terms of sulphur rejection the higher temperature chars showed little beneficiation.

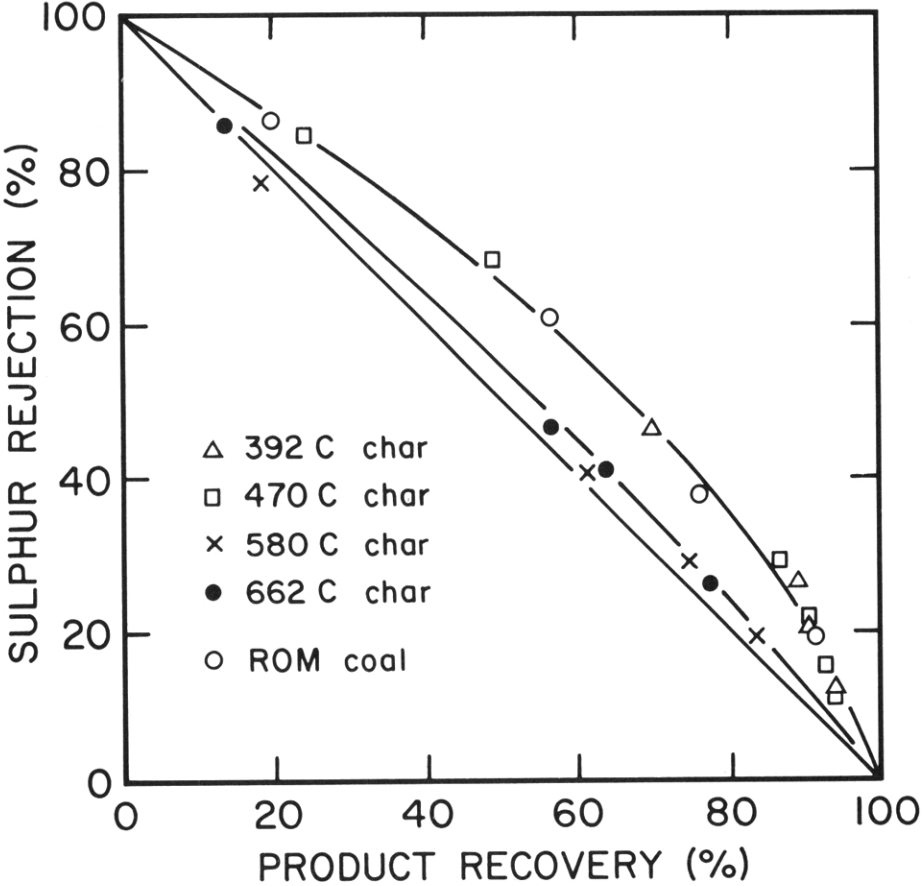


Fig 9 Beneficiation of char for sulphur by agglomerative flotation. (From Hirajima, Chan, Whiteway, Stefanski and Stewart 1987).

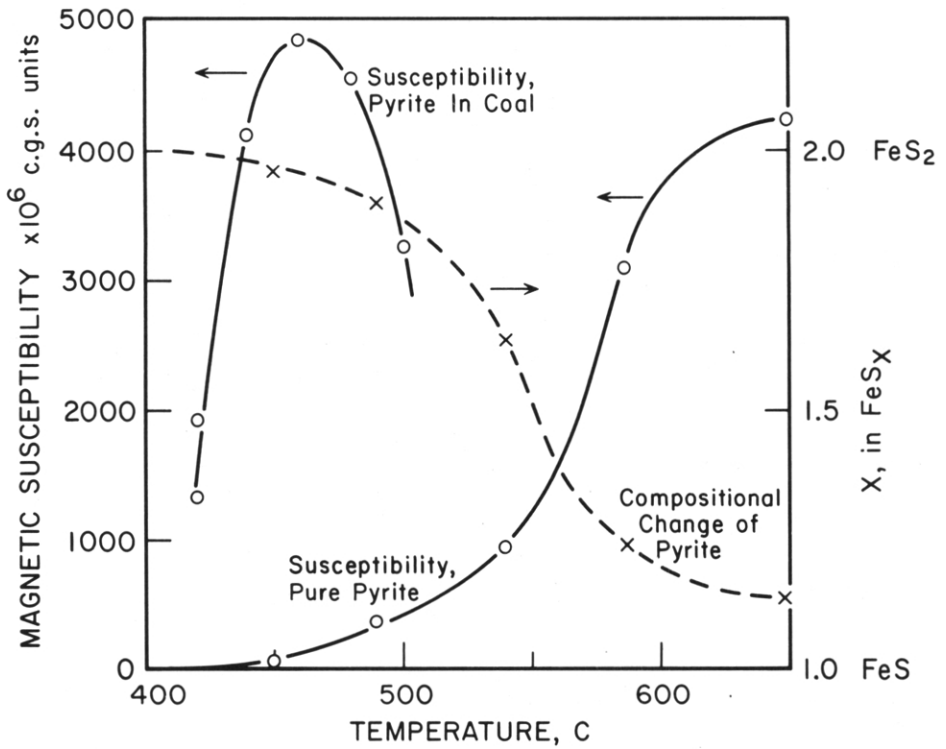


Fig 10 Magnetic susceptibility of pyrite, field strength 2000 Oersted.

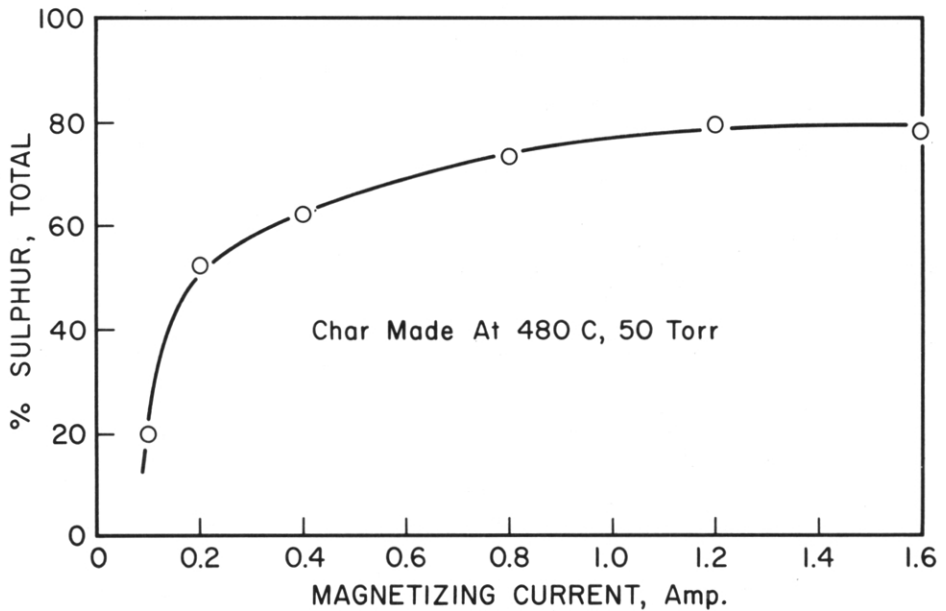


Fig 11 Percentage of original char sulphur in the magnetic fraction, as a function of magnetizing current.

Fig 10 shows how the magnetic susceptibility of pure pyrite increases as it decomposes to pyrrhotite, coming to a maximum at around 650°C. By comparison the susceptibility of finely ground pyrite added to coal (2 gm FeS₂ in 10 gms coal) peaked at about 470°.

Chars made at 480°C and 50 torr were ground and put through the magnetic separator. The sulphur collected in the magnetic fraction varied with the field strength, Fig 11. Some carbon was lost to the magnetic fraction. Fig 12 shows the recovery of carbonaceous product in the non-magnetic fraction, on an ash-free basis, as a function of magnet current. Fig 13 shows the effect of pyrolysis temperature over a range of pressures, on the fraction of total sulphur that was collected in the magnetic fraction. These results indicate that a current of 0.4 amps and a pyrolysis temperature of 475°C gave both a high sulphur rejection and a good product recovery. Of added benefit is the fact that this temperature is in the range already recommended (Roy and deColumbia 1984) from the standpoint of optimization of yield of coal tars.

The economic feasibility of the process envisaged has not been studied. In 1988, at a time of low world oil prices, capital investment in coal projects is not at a high level. In time, the acid rain problem will become greatly reduced with the introduction of

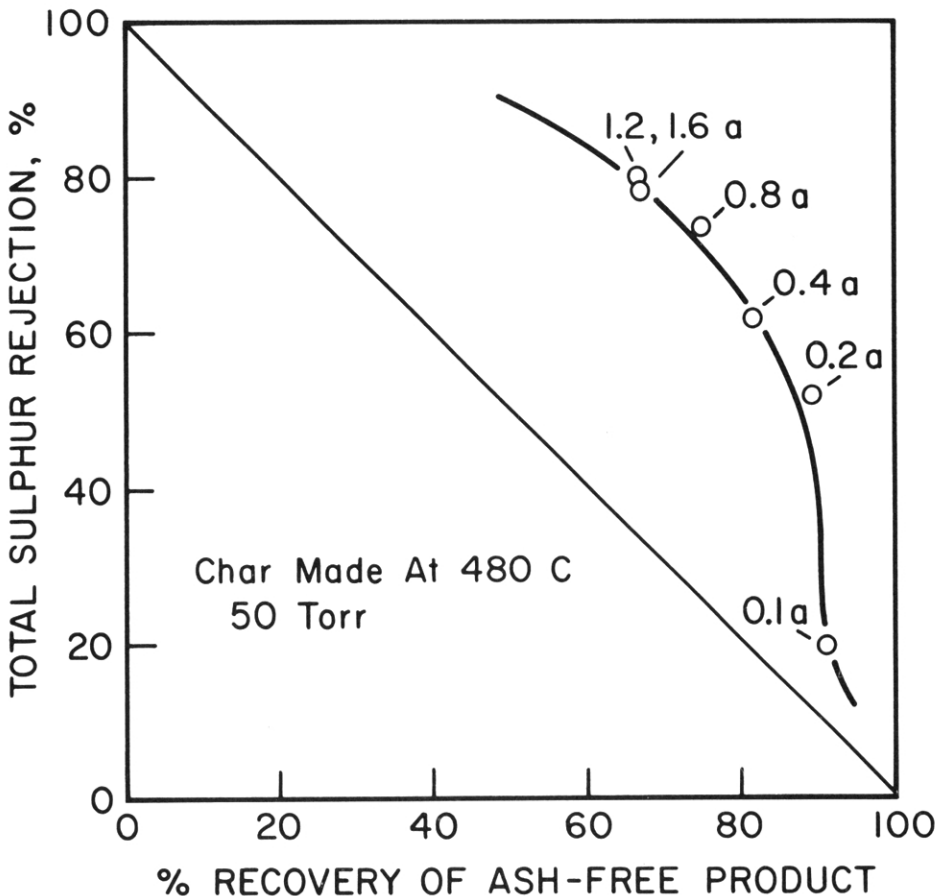


Fig 12 Beneficiation of char for sulphur: effect of magnetizing current.

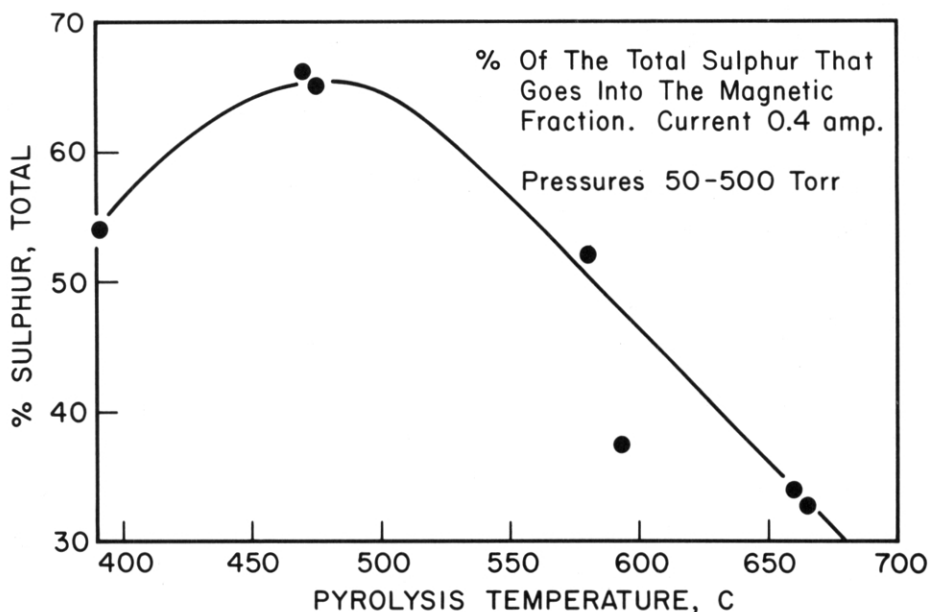


Fig 13 Percentage of original char sulphur in the magnetic fraction, as a function of temperature of pyrolysis.

advanced recirculating fluid-bed combustors. Therefore the process discussed here may be more relevant to the production of oil-like fuels, the coal-water slurries. It is notable that the liquid hydrocarbons given off in the pyrolysis step can be used in the oil-agglomeration step, leading to economies in the process, and reintroducing a volatile component which will aid combustion. Coal-water slurries should find a continuing market with small industrial users who are not in a position to handle bulk coal.

Acknowledgements

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