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MICROWAVE PRETREATMENT OF COAL PRIOR TO MAGNETIC SEPARATION

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Abstract: New methods to reduce the total sulphur content of coals are being developed since the introduction of legislation requiring cuts in sulphur emissions to the atmosphere. It is known that weakly paramagnetic pyrite (FeS_2) particles are difficult to remove from clean coal by standard magnetic separation techniques. Data is presented here comparing standard magnetic separation tests to results achieved when the coal is subjected to a caustic microwave leach pretreatment, prior to conventional dry magnetic separation. A significant increase in the removal of total sulphur is observed when this pretreatment is applied to the coal.

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INTRODUCTION

Microwaves are a ultra high frequency radiation with a wavelength between approximately 1 m and 1 cm [1]. Microwave radiation polarises the water molecules present within a material placed within the electric field generated. The water molecules are polarised and tend to align themselves with the electric field of the radio wave. As the field changes direction at an extremely high frequency the molecules flip over backwards and forwards, rubbing against each other and thereby producing heat. Thus microwave treatment is a very fast method of heating as it does not totally rely on thermal conduction.

As previous reports [2] have suggested it is very difficult to remove crystalline pyrite from coal by direct magnetic separation. This is due to the small difference in magnetic susceptibility between coal and pyrite. However, by changing all or even a small part of the pyrite particle to a more magnetic mineral (e.g. pyrrhotite, FeS) the economic and technical feasibility of magnetic separation of pyrite from coal would be greatly improved.

Many studies have shown that the magnetic susceptibility of pyrite can be significantly improved by heating to temperatures in the region of 300° C [3]. The application of conventional heating techniques will result in this effect, but heating consequently causes the pyrolysis of the coal matrix. Microwave radiation potentially avoids this problem, with the pyrite absorbing more electromagnetic energy than coal (due to differences in coal and pyrites dielectric properties) and thus heating up faster than coal.

The magnetic susceptibility of pyrite improves on heating due to the conversion of FeS_2 to FeS, a strongly magnetic material. This reaction occurs at a lower temperature (e.g. 250° C) in coal–derived pyrite than mineralogical pyrite [4]. The magnetic susceptibility of a pyrite particle can be improved by two orders of magnitude by converting 1% of the particle to pyrrhotite (FeS) [1].

Researchers [3] claim that pyrite will heat up under microwave radiation due to molecular vibration, whilst the coal matrix will remain relatively transparent to the energy (apart from the polar molecules present as inherent water). The degree of selective dielectric heating obtained will be a function of the power absorbed by the pyrite and the conduction of heat away to the surrounding coal matrix.

It must be noted that the frequency of the microwaves will affect the dielectric heating properties of the pyrite. Data [5, 6, 7] has been published without any conclusive guide to which frequencies are most suitable for this application. A majority of work [3, 5, 8] has been carried out using 2.45 GHz at various power levels; there is some data suggesting that higher frequencies may give increased heating [6].

It has been reported [3, 8] that microwave frequencies suitable for such treatment vary from 2.45 GHz to 10 GHz and the power range is given as 500 W to 1000 W. Published data from the USA [5] using US coals in the General Electric microwave unit utilised a frequency of 2.45 GHz at a power of 1000 W. Coal samples in the General Electric unit heated up to a bulk temperature of 200 – 300° C after 30 seconds (thus it may be assumed that pyrite within the coal reached considerably higher temperatures). Heating to this temperature causes the liberation of sulphur–containing gases as well as the conversion of a proportion of the pyrite to pyrrhotite, thus pyrite particles become susceptible to low gradient magnetic separation.

From a run–of–mine coal containing 4.1% total sulphur an initial product containing 2.3% sulphur was achieved. After density separation at a specific gravity of 1.6 and low–gradient magnetic separation a product of 1.52% total sulphur was produced. Subsequent work carried out in the UK [1] attempted to repeat this work on a UK coal using a frequency of 2.45 GHz at a power level of 500 W. This work was unsuccessful in producing heating rates high enough to liberate sulphur from the coal or to produce a magnetically enhanced pyrite which would be susceptible to low–gradient magnetic separation.

It has been reported [1, 5] that a very significant increase in heating rates can be achieved when coal was mixed with aqueous NaOH solutions. This resulted in the leaching of organic and pyritic sulphur from the coal and also the increase in magnetic susceptibility of the remaining pyritic particles within the sample. Behaviour characteristics of a ferromagnetic or a strongly paramagnetic material were observed for the magnetically separated fraction after NaOH microwave leaching. A small proportion of the weakly paramagnetic pyrite was altered to a more magnetic form. Heating rate experiments showed that caustic/pyrite mixture tended to heat up faster than caustic/coal mixtures, thus a magnetic product could be removed containing increased amounts of sulphur.

EXPERIMENTAL PROCEDURE

(i) Magnetic Separation

Samples of various size fractions of Silverdale coal (a middlings fraction) were passed over a high–intensity Magnaroll separator (Figure 1) to obtain the baseline data for this project.

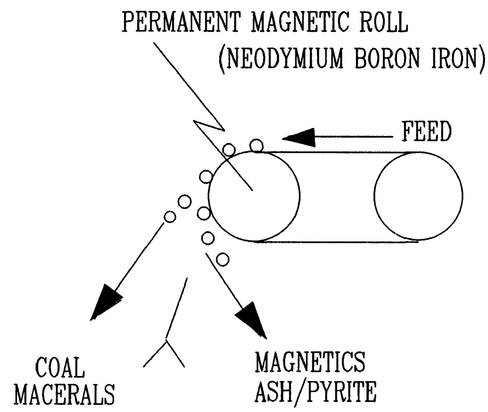

Fig. 1 Operation of Magnaroll

(ii) Microwave Pretreatment

Initial pretreatment involved heating the coal samples in 2.45 GHz, 650 W microwave heater for 30, 60, 90 and 120 seconds before magnetic separation.

(iv) Microwave NaOH Pretreatment

Coal samples were mixed with a 300g/litre NaOH solution prior to microwave exposure. After radiation the coal samples were washed to remove water–soluble sulphur compounds and filtered and dried prior to processing over the Magnaroll separator under identical conditions to the non–treated coal samples.

RESULTS

(1) No Pretreatment

Table 1 shows the percentage ash and sulphur reductions for Silverdale coal. Ash reductions up to 33.5%, for the –1000 + 500 μm size fraction, were achieved, from a feed ash content of 33.57% to a non–magnetic fraction of ash content 22.32%, with a loss in calorific value of 14.68%. The sulphur was concentrated in the non–magnetic (i.e. product fraction).

Table 1 Ash analysis, total sulphur, reduction figures and loss in calorific value for Silverdale coal, with no pretreatment prior to separation over the Magnaroll (dry basis)

SIZE RANGE microns		Feed	Magnetics (mags.)	Non-mags.	Overall Reduction	C.V. Loss %	Reduction in Emission Value %
.-3000+2000	Ash (%)	39.09	53.58	35.49	9.19		
	Sulphur (%)	6.59	5.57	7.70	-16.77	26.34	-9.02
.-2000+1000	Ash (%)	37.81	50.55	29.69	21.47		
	Sulphur (%)	6.20	5.44	6.63	-6.95	23.08	7.53
.-1000+500	Ash (%)	33.57	52.28	22.32	33.51		
	Sulphur (%)	6.41	7.00	6.39	0.29	14.68	16.94
.-500+300	Ash (%)	30.47	49.93	24.92	18.24		
	Sulphur (%)	6.79	6.51	6.88	-1.39	18.17	7.31
.-300+90	Ash (%)	28.40	39.35	24.00	15.50		
	Sulphur (%)	7.42	6.90	8.19	-10.37	32.84	-2.97

(2) Dry Microwave Pretreatment

Table 2 shows the results for coal pretreated by heating in the microwave for 60 seconds over size fractions from − 3000 to + 90 μm. Figures presented include the original feed analysis, prior to pretreatment, and pretreated feed analysis, prior to magnetic separation. The maximum ash reduction achieved was 21.12% for the −500+300 μm size fraction at a loss in calorific value of 16.73%. Sulphur was again concentrated in the product (non–magnetic) fraction.

(3) NaOH Pretreatment

Coal pretreatment by microwave heating with sodium hydroxide (NaOH) was carried out on size fractions below 2000 μm. Table 3 shows the results for the −2000+1000 μm size fraction after pretreatment in the microwave with NaOH for 60, 90 and 120 seconds. It can be observed that increased pretreatment times above 90 seconds (i.e. to 120 seconds) do not give any increased ash or sulphur reductions; in fact a slight fall in reduction may be observed. Ash reductions are fairly low, ranging from 5.7% to 10.8%. Sulphur reductions, however, are good, ranging from 26.7%, for a pretreatment time of 60 seconds, to 30.6% (from 6.20% to 4.30%) for a pretreatment time of 90 seconds. These results were achieved at a loss in calorific value in the order of 25%. For a pretreatment time of 90 seconds a reduction in sulphur emission value of 35.7% was achieved (from 3074.06 gS/GJ to 1977.82 gS/GJ).

Table 2 Ash analysis, total sulphur, reduction figures and loss in calorific value for Silverdale coal heated in microwave for 60 seconds prior to separation over the Magnaroll unit (dry basis)

SIZE RANGE microns		Orig. Feed	Pre. Feed	Mags.	Non-mags.	Overall Reduction %	C.V. Loss %	Reduction in Emission Value %
.-3000+2000	Ash (%)	39.09	39.23	53.44	34.08	12.81		
	Sulphur (%)	6.59	6.44	5.80	8.49	-28.71	25.16	-17.11
.-1000+500	Ash (%)	33.57	33.98	57.74	30.34	9.62		
	Sulphur (%)	6.41	6.28	7.09	8.50	-32.56	17.23	-25.34
.-500+300	Ash (%)	30.47	30.56	49.79	24.01	21.20		
	Sulphur (%)	6.79	6.52	6.46	6.93	-2.17	16.73	7.88
.-300+90	Ash (%)	28.40	28.32	34.40	22.98	19.10		
	Sulphur (%)	7.42	6.98	7.73	8.51	-14.73	45.40	-5.40

Table 3 Ash analysis, total sulphur, reduction figures and loss in calorific value for the –2000+1000 μm size fraction of Silverdale coal heated in microwave with NaOH prior to separation over the Magnaroll unit (dry basis)

PRETREAT. TIME seconds		Orig. Feed	Pre. Feed	Mags.	Non-mags.	Overall Reduction %	C.V. Loss %	Reduction in Emission Value %
60	Ash (%)	37.81	37.62	45.27	35.67	5.65		
	Sulphur (%)	6.20	6.41	10.03	4.54	26.72	26.52	29.62
90	Ash (%)	37.81	35.86	46.69	33.73	10.79		
	Sulphur (%)	6.20	6.01	9.88	4.30	30.60	25.86	35.66
120	Ash (%)	37.81	36.63	44.80	34.02	10.03		
	Sulphur (%)	6.20	6.06	9.81	4.41	28.84	22.49	33.69

Results for the –1000+500 μm size fraction are represented in Table 4. Similar figures are achieved for the –2000+1000 μm size fraction may be seen, although ash reduction is only attained with a pretreatment of 30 seconds (13.8%). Sulphur reductions are again high, ranging from 29.8% to 34.0% for losses in calorific value ranging from 27.39% to 22.24%, respectively. A peak reduction in sulphur emission value is obtained for a pretreatment time of 30 seconds, 39.0%.

Table 4 Ash analysis, total sulphur, reduction figures and loss in calorific value for the $-1000+500$ μm size fraction of Silverdale coal heated in microwave with NaOH prior to separation over the Magnaroll unit (dry basis)

PRETREAT. TIME seconds		Orig. Feed	Pre. Feed	Mags. Mags.	Non-mags.	Overall Reduction %	C.V. Loss %	Reduction in Emission Value %
30	Ash (%)	33.57	34.61	39.92	28.95	13.75		
	Sulphur (%)	6.41	6.53	10.95	4.23	34.02	22.24	39.03
60	Ash (%)	33.57	24.00	49.36	34.11	-1.62		
	Sulphur (%)	6.41	6.42	13.21	4.46	30.37	25.79	29.69
90	Ash (%)	33.57	35.28	40.03	34.06	-1.47		
	Sulphur (%)	6.41	6.86	13.46	4.50	29.81	27.39	29.18

Table 5 Ash analysis, total sulphur, reduction figures and loss of calorific value for the $-500+300$ μm size fraction of Silverdale coal heated in microwave with NaOH prior to separation over the Magnaroll unit (dry basis)

PRETREAT. TIME seconds		Orig. Feed	Pre. Feed	Mags. Mags.	Non-mags.	Overall Reduction %	C.V. Loss %	Reduction in Emission Value %
30	Ash (%)	30.47		38.88	21.58	29.18		
	Sulphur (%)	6.79	6.51	9.19	4.40	35.22	43.29	43.69
60	Ash (%)	30.47	30.80	37.83	25.57	16.07		
	Sulphur (%)	6.79	6.43	10.93	4.35	35.88	35.25	40.78
90	Ash (%)	30.47	30.33	38.32	26.73	12.27		
	Sulphur (%)	6.79	6.42	11.33	4.52	33.34	32.12	37.30

Table 5 shows the $-500+300$ μm size fraction results and displays an even higher reduction in sulphur emission value, reaching 43.7% for a 30 second pretreatment time. The sulphur emission value was brought down from 2949.68 gS/GJ to 1661.09 gS/GJ. This test also yielded an ash reduction of 29.2% and a sulphur reduction of 35.2%, at a loss in calorific value of 43.29%. It should be noted that this high loss in calorific value would be justified for a middlings fraction such as the sample treated. For a pretreatment time of 90 seconds the reduction in sulphur emission value drops by 14.6% to (a still significant) 37.3%. The loss in the calorific value is lowered by 25.8% to 32.84%. Sulphur reduction is also high at

33.3%, ash reduction is lower, at 12.3%. reduction in sulphur is not significantly altered by increased pretreatment time, but differences in the calorific value losses and sulphur emission values can be observed.

Table 6 completes the size fractions treated showing the results from the –300+90 μm size fraction. The highest reduction in sulphur emission value over all the size fractions for all pretreatments may be found, a reduction of 54.4%. This result is, however, attained with a calorific value loss of 68.42%, this being unacceptably high. Total sulphur content was reduced from 7.42% to 3.81%, a reduction of 48.7%. Ash reduction was 26.9%. At pretreatment times of 30 to 60 seconds an acceptable loss in calorific value was sustained, 45.90%, and 43.70% respectively. Reductions in sulphur emission value were good, both over 40%. Total sulphur reductions were in the order of 38%, with corresponding ash reductions in the order of 14%.

Table 6 Ash analysis, total sulphur, reduction figures and loss in calorific value for the –300+90 μm size fraction of Silverdale coal heated in microwave with NaOH prior to separation over the Magnaroll unit (dry basis)

PRETREAT. TIME seconds		Orig. Feed	Pre. Feed	Mags.	Non-mags.	Overall Reduction %	C.V. Loss %	Reduction in Emission Value %
30	Ash (%)	28.40	28.37	32.28	24.20	14.80		
	Sulphur (%)	7.42	6.86	9.52	4.53	38.99	45.90	42.91
60	Ash (%)	28.40	28.82	33.09	24.51	13.71		
	Sulphur (%)	7.42	7.11	10.77	4.66	37.23	43.70	40.98
90	Ash (%)	28.40	28.43	31.68	20.76	26.90		
	Sulphur (%)	7.42	6.57	8.40	3.81	48.70	68.42	54.39

CONCLUSIONS

For tests carried out on non–pretreated samples, ash reduction was achieved, but little or no reduction of total sulphur was attained. In a majority of cases the sulphur was concentrated in the product (non–magnetic) fraction; any small reduction can be explained by experimental error. Thus it can be assumed that the pyritic sulphur presents remains unaffected by the magnetic field through which it passes, and thus as some ash is removed the percentage of total sulphur present in the product effectively rises. This causes the result of negative reductions in total sulphur.

Similar conclusions can be drawn from samples pretreated by the microwave heating of coal alone. Some ash reduction was obtained, but total sulphur is again concentrated (in majority of cases) in the product fraction. Minimal reduction in sulphur emission value is reported for some tests. It appears that these pretreatments do not facilitate any increase in ash or sulphur reduction compared with the tests carried out without pretreatment.

For tests carried out on coal pretreated by heating with NaOH in a microwave considerable success was achieved. Reductions in total sulphur were between 26.7% and 48.7% for losses of calorific value between 22.24% and 68.42%. Significant reductions in sulphur (37%) were made for reasonable losses in calorific value (40%). These encouraging results were achieved for all size fractions. Ash reduction was low, a majority of tests achieving a reduction in the order of 14%. With the high reductions in total sulphur corresponding high reductions in sulphur emission value were obtained, in the order of 30–40%.

Tables 4, 5 and 6 show the comparison of ash and total sulphur content for tests using the NaOH pretreated coal, over the various size fractions tested. It can be observed that sulphur reduction is of similar magnitude for all size fractions, allowing for the fact that the lower size fractions contain a higher total sulphur content. Ash reduction, however, appears to increase as the size fraction decreases. This may be explained as a consequence of the higher losses in calorific value incurred in these fractions.

In conclusion, it can be deduced that the pretreatment of microwave heating of the feed coal with sodium hydroxide solution is successful in enhancing the magnetic susceptibility of the pyritic sulphur present. This is partly due to NaOH being an excellent microwave absorber and also its ability to leach out some sulphur in the pretreatment process. The caustic microwave treatment also facilitates the production of a magnetic pyrite product [9]. Previous investigators [10, 11] have reported the presence of a magnetic layer of γ–Fe_2O_3 and Fe_3O_4 after the more conventional autoclave alkali leaching of pyrite. Both of these studies were carried out under oxidising conditions whereas conditions are likely to have been strongly reducing in the present case.

Investigators [9] were unable to positively identify the magnetic product achieved, although the magnetic susceptibility did increase significantly so as to allow magnetic separation. In this case a magnetic pyrite fraction is produced as there is an increase of percentage total sulphur present in the magnetic fraction, of the samples which were subjected to caustic microwave treatment prior to magnetic separation in the Magnaroll. It is thought that this is mainly due to the coating of Fe_2O_3 on the surface of the FeS_2. Other pretreatments fail to improve the reduction of sulphur from the sample tested.

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