Microwave embrittlement and desulphurisation of coal

S.Marland [1], B.Han [1], N.A.Rowson [1], A.J.Merchant [1]

Mikrovlnné žiarenie frekvencie 2,45 GHz bolo použité na vzorkách uhlia z rôznych anglických lokalít, na ich tepelnú predúpravu pred rozpojovaním. Získané údaje poukazujú na vplyv mikrovlnnej tepelnej úpravy na relatívnu meliteľnosť uhlia. Výrazná redukcia (20 –40 %) relatívnej energie mletia bola zaznamenaná už po pomerne krátkom čase pôsobenia mikrovlnného žiarenia (3 –8 min). Vplyv mikrovlnnej predúpravy na fyzikálnu a chemickú štruktúru uhlia, ako aj na odsírenie uhlia, bol tiež analyzovaný.

Key words: Microwave radiation, Embrittlement, Desulphurisation, Grindability, Coal.

Introduction

Some ash minerals within coal readily heat within an applied electric field, (pyrite has an average heating rate of 1.0°C/s when exposed to a microwave field at a power of 650W and frequency of 2.45GHz) whilst others appear transparent to the radiation (quartz has an average heating rate of 0.08°C/s when exposed to a microwave field at a power of 650W and frequency of 2.45GHz) (Walkiewicz, 1988) (Chen, 1984) (McGill, 1988).

Whilst the organic components of coals are relatively poor absorbers of microwave energy, (Chironis, 1986) coals naturally contain water to varying degrees depending upon rank, microstructure and geological location. Water is considered a good absorber of microwave energy, at a frequency of 2.45GHz, and at an applied power of 650W coal's average heating rate has been calculated at 0.52°C/s. Water molecules are polar, when exposed to an alternating electric field; the molecules position themselves in the direction and at the same frequency to that of the applied field (Hulls, 1992) (Figure 1). This movement produces frictional heating. When a coal is exposed to microwave energy; water will heat, change phase and expand creating internal pressures within the coal matrix. Further embrittlement would be expected due to the differential expansion rates of gangue minerals found in coals (Chen, 1984). The extent to what this happens depends on the minerals dielectric constant, the quantity of mineral, and the position within the coals structure. Scanning electron micrograph images of irradiated Kiverton coal show fractures occurs (Figure 2). Similar fractures could not be found on untreated samples within this study.

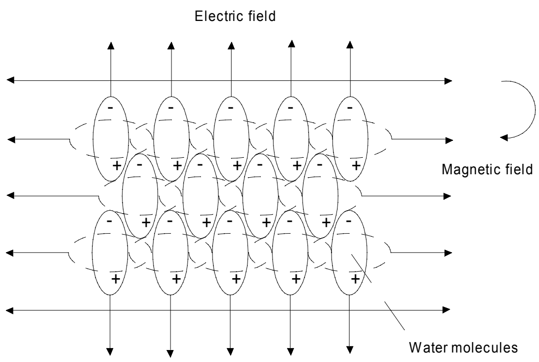

Figure 1 Realignment of polar molecules in an electric field giving rapid heating

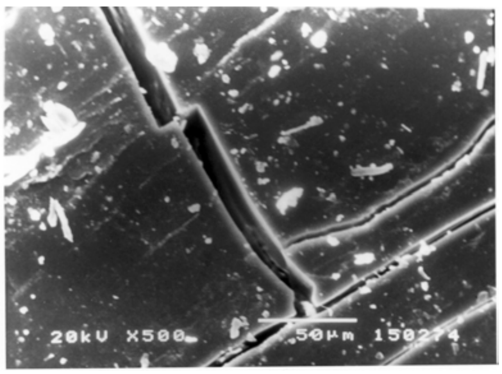

Figure 2 Electron micrograph of Kiverton coal, exposed to 2.45GHz, 650W for 5 minutes

[1]School of Chemical Engineering, The University of Birmingham, Edgbaston, Birmingham, B15 2TT, England

Experimental procedure

Experimental studies involved milling non-treated and microwave treated samples of coal, this was necessary to investigate any possible improvement in grindability after heat treatment. For the basis of these experiments, the dimension of the mill, type and number of mill medium, speed of rotation, and time of grinding remain constant. A mild steel rod mill of internal dimensions: 155mm diameter and 280mm length, was used. Mill medium consisted of seven steel rods of dimensions: 25mm diameter and 270mm length. Mill conditions were chosen to enable correlation with previous studies (Harrison et al, 1996, 1997). Rotational speed was set to 100rpm (the theoretical critical speed for this mill is calculated to be 117rpm (Wills, 1988).

The required size distribution of coal used as fuel in pulverised fuel (PF) power generation is 80% passing 75μm (Couch, 1995). Approximately 90 minutes of grinding was required to reduce untreated representative sub-samples of approximately 500g to this size. To study effects of heat treatment on grindability and to correlate with previous studies, size distributions (using sieve apertures in accordance to BS410) were determined before milling and after 5,20,45 and 90 minutes of milling.

Corresponding representative sub-samples of Rossington, Kiverton and Daw Mill coals were exposed to microwave radiation at a power of 650W and a frequency of 2.45GHz for times of 1,3,5 and 8 minutes. Size distributions for the milling tests were determined. The approximate maximum temperature attained by treated samples was measured. The maximum temperature reached for each coal type studied was used as the basis of a conventional heating experiment. A representative sample was heated for 1 hour and relative grindability determined.

Results and discussions

The Hardgrove Grindability Index for the untreated coals was experimentally determined in accordance to BS1016 part 112; results are shown in Table 1. The Hardgrove Index relates increased surface area to grindability due to the attrition grinding action of a captive ring ball mill. The Hardgrove test is the accepted method of measurement in the coal industry, however it is only used to rank coal on a relative grindability scale, and is not used to calculate required comminution energy. A correlation between the Bond Work Index and Hardgrove Grindability Index has been proposed by F.C.Bond (Bond, 1961). McIntyre and Plitt (McIntyre et al, 1980) reviewed this correlation in 1980 and suggested a supposedly more accurate correlation, however due to the differences between the tests, these correlations are deemed unjustified by other authors (Prasher, 1988).

Table 1 Hardgrove Grindability indices of reference coals

	15%Ash Daw Mill	**Kiverton**	**Rossington**
Hardgrove Index	58	59	53

The data from the size distribution graphs was converted into comparative Work indices and appear in Table 2. The Berry and Bruce (Berry et al, 1966) comparative test (Equation 1) gives a method of comparing grindability between heat treated and non-treated materials, and was derived from the Bond Work Index test (Bond, 1961).

$$RWI = \left(\frac{10}{\sqrt{\mathrm{Pr}}} - \frac{10}{\sqrt{\mathrm{Fr}}} \right) \Bigg/ \left(\frac{10}{\sqrt{\mathrm{Pt}}} - \frac{10}{\sqrt{\mathrm{Ft}}} \right) \qquad (1)$$

RWI – Relative Work Index
F - 80% passing size of feed (μm)
P - 80% passing size of milled product (μm)
r - non-heated coal (reference coal)
t - test, heat treated coal

Table 2 Relative Work Index of coals after microwave irradiation at 650W

	Relative Work Index, ground for:			
15%Ash Daw Mill	**(5 min)**	**(20 min)**	**(45 min)**	**Moisture %**
Non-treated	100%	100%	100%	4.09
Exposure 1 min	99%	94%	94%	3.72
Exposure 3 min	88%	92%	94%	3.45
Exposure 5 min	-	-	-	3.24
Exposure 8 min	82%	90%	92%	2.55
Kiverton	**(5 min)**	**(20 min)**	**(45 min)**	**Moisture %**
Non-treated	100%	100%	100%	4.70
Exposure 1 min	100%	100%	100%	4.05
Exposure 3 min	58%	80%	80%	2.98
Exposure 5 min	56%	72%	49%	2.98
Exposure 8 min	55%	70%	49%	2.26
Furnace 250^{0}C	65%	92%	81%	1.47
Rossington	**(5 min)**	**(20 min)**	**(45 min)**	**Moisture %**
Non-treated	100%	100%	100%	4.42
Exposure 1 min	85%	93%	92%	4.36
Exposure 3 min	80%	85%	89%	4.14
Exposure 5 min	77%	89%	90%	3.95
Exposure 8 min	71%	-	43%	2.32
Furnace 200^{0}C	77%	71%	54%	1.46

Data presented in Table 2 indicates there is a noticeable improvement in grindability (i.e. reduction in Relative Work Index), furthermore grindability improves with increasing microwave exposure times. Exposure to microwave radiation for 1 minute has had little effect. At 5 and 8 minutes, Relative Work indices are similar, indicating a natural cut off point for the heat treatment program. This apparent trend is a possible indication of the moisture super-heating within the microstructure of the coal, propagating cracks. Further fracture and embrittlement would be expected due to different ash minerals expanding at different rates during microwave heating. Ultimate analysis and ash composition analysis on these particular coals indicated that the majority of the mineral matter consists of poor absorbers of microwave energy, this suggests the importance of the water content for microwave embrittlement of coal. Results also indicate that the resistance to grinding could be reduced further by microwave exposure than with conventional heating.

Table 3 Proximate Analysis of reference and heat treated coals

Proximate Analysis	**15%Ash Daw Mill (%)**	**Kiverton (%)**	**Rossington (%)**
Moisture	4.09	4.70	4.42
Ash	13.54	16.30	13.45
Volatile Matter (VM)	34.08	30.73	32.25
Fixed Carbon (FC)	48.29	48.31	49.88
$Ash_{Dry\ Basis}$	14.12	17.10	14.07
$FC_{Dry\ Basis}$	50.35	50.68	52.18
$VM_{Dry,Ash\ free\ Basis}$	41.37	38.86	39.27
Proximate analysis for samples exposed to 650W, 2.45GHz for 8 minutes			
Moisture	2.55	2.26	2.32
Ash	10.74	16.08	15.20
Volatile Matter (VM)	34.61	28.53	30.78
Fixed Carbon (FC)	52.10	53.13	51.70
$Ash_{Dry\ Basis}$	11.02	16.45	15.56
$FC_{Dry\ Basis}$	53.47	54.36	52.93
$VM_{Dry,Ash\ free\ Basis}$	39.91	34.93	36.53

Microwave heating trials were terminated after 8 minutes and 9 minutes due to localised hot spots igniting the coals and therefore reducing the Calorific Value of the coal.

Differences in comparative grindability between coals depends upon initial size distribution, moisture content, ash content, microstructure, size range and location of the mineral phases that have high dielectric heating rates (e.g. pyrite).

Table 3 gives the proximate analysis for the three coals used in this study. Coal is a heterogeneous material, thus efficiency in sampling coal is reduced as the particle size increases. Mineral content can vary significantly within the same seam, however for the purpose of this study, smalls and singles have been used to determine grindability. The percentage changes for ash, volatile matter and fixed carbon are therefore within expected limits, indicating that no significant changes have occurred. Moisture content has significantly reduced (49% for Kiverton) corresponding with theories on induced fracture produced by super-heated steam. Furthermore results indicate moisture reduces as exposure increases (Table 2).

Microwave radiation may also be used to desulphurise coal. Dielectric data for selected coal components (Figure 3) indicate a high degree of selective heating is possible for pyrite within the coal matrix. Typical average heating rates of 1.0°C/s are achieved compared to 0.2°C/s for coals irradiated at a power of 650W and a frequency of 2.45GHz (Figure 4).

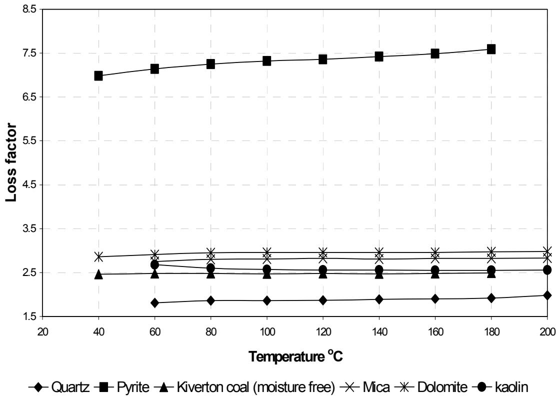

Figure 3 Loss factors of selected coal components over temperature range (40°C-200°C) (frequency 2.216GHz)

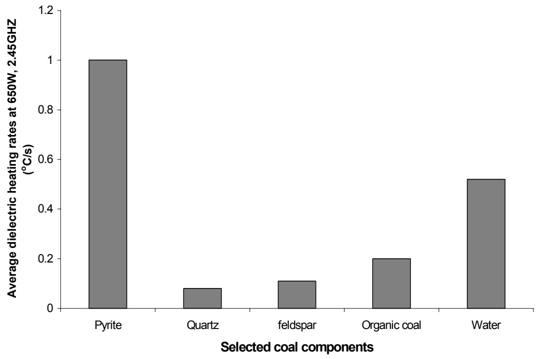

Figure 4 Measured average dielectric heating rates of selected coal components, (frequency 2.45GHz) (power 650W)

This selective heating allows the pyrite to heat to 250°C-300°C, facilitating a phase change from pyrite (FeS_2) to pyrrhotite (FeS). The selective nature of microwave treatment means that the bulk temperature of the coal does not exceed 150°C, thereby there is no significant loss in Calorific Value of the coal. Pyrrhotite is a highly magnetic mineral which can be easily removed from the coal via a low intensity magnetic separation stage.

Initial results indicate that this process may prove a possible method of physically desulphurising coal prior to combustion at power stations.

Conclusion

Initial studies have shown it is possible to reduce the resistance to grinding of some coals by up to 20-40%. Work has also suggested the possible mechanisms for fracture propagation. As part of this ECSC funded research, future studies will involve the microwave embrittlement of coals at higher powers of radiation, microwave exposure within an inert atmosphere (to prevent combustion), a full economical assessment after pilot scale trials is to be considered. Microwave technology will also be used to investigate any other beneficial effects, for example reducing the sulphur content prior to combustion and improving the flow characteristics of coals.

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