Changes of pyrite and pyrrhotite in coal upon microwave treatment

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Abstract. More stringent environmental regulations and the demand for higher quality final products require optimum sulphur removal from sulphur-containing ores. Microwave treatment is an emerging technique in minerals processing and may be used to reduce sulphur-containing minerals. In the present study two coal samples containing low and high amounts of sulphur, respectively, were subjected to microwave and caustic soda treatment with a view to desulphurization. In order to assess the microwave treatment, the same procedures were applied to a pyrite/pyrrhotite rock obtained from a coal mine. XRD and Mössbauer analyses were performed, before and after treatment in order to determine changes brought about in the structure and bonding. Following the treatment, both the low and high-sulphur coal samples showed a decrease in sulphur content of ≈ 40%, whilst the XRD and Mössbauer analyses did not detect the formation of new minerals or changes in structure. In the case of the pyrite/pyrrhotite rock sample the Mössbauer investigations showed the presence of pyrite (26%) and pyrrhotite (74%) After treatment the concentrations changed to 8% and 92% respectively, indicating a change in sulphur mineral composition during treatment, but no structural changes.

1. Introduction
Coal consists mainly of hydrocarbons and also contains inorganic constituents, which are mainly minerals, incorporated in various ways in the coal. The amounts of these minerals, which are the inert solid material, vary considerably in coals of diverse origin and remain behind in an altered form as ash after coal combustion or gasification [1]. Clays, quartz and carbonate minerals and the iron-containing minerals pyrite (FeS₂), jarosite (KFe₃(SO₄)₂(OH)₆), troilite and pyrrhotite (both FeS) and the non-sulphur-containing iron minerals ankerite (CaFe(CO₃)₂), illite (clay mineral) and siderite (FeCO₃) [2] can occur in varying amounts in South African coals. The pyritic, organic and sulphatic sulphur minerals in the coal are difficult, and sometimes impossible, to remove [3]. The sulphur content is of great concern owing to its harmful effect on boilers where sulphates cause corrosion, its lowering of the quality of metallurgical coal and atmospheric pollution. The removal of sulphur from coal prior to utilization has, therefore, become a primary concern to industry.

Microwave applications have been extensively used in minerals processing, due to its intense energy flow and penetration depth. The primary advantage of microwave processing is the specificity of microwave energy absorption, allowing volumetric heating of materials [4]. Desulphurization of coal using high power microwave energy was previously investigated [5-7]. The addition of strong solutions of NaOH or KOH, and repeated microwave irradiation, yielded high sulphur removal values [8-12].
In the present work, two South African coals containing different amounts of sulphur were desulphurized by exposure to a strong alkali solution. Subsequently the samples were subjected to both XRD and Mössbauer analyses.

2. Experimental
Two high-volatile bituminous coals, with sulphur contents of 0.5% and 3.6%, respectively, were used in this study. The as-received coal samples were in the form of large lumps, requiring crushing to a size fraction of > 212µm. Proximate analyses were performed and the calorific values were determined. Typically, 15g of coal was mixed with a 300g/L of NaOH solution, with a solid to liquid ratio of 25:75. The solution was then microwave-treated at a microwave energy input of 650W for 10 minutes. After treatment the mixture was filtered and washed until all traces of the alkali were removed (red litmus paper). The extent of desulphurization was determined by sulphur analysis using a Leco analyzer. The changes in structure and bonding were determined by means of XRD and Mössbauer analyses, before and after treatment.

A rock sample containing pyrite and pyrrhotite was also milled to a desirable size fraction and further investigated to be able to gauge the reaction to microwave processing after NaOH solution treatment. The possible changes in structure and bonding were determined by means of XRD and Mössbauer analyses.

3. Results and Discussion
The results for the coals, containing high or low amounts of sulphur, are discussed in with reference to the "pyrite / pyrrhotite" containing rock sample.

3.1. High-sulphur coal
Milling liberated the pyrite particles, which were found to occur randomly in the coal matrix as nodules with a size > 25µm. The sulphur in this sample was mainly (97%) in a pyritic form with the balance occurring in the organic form. Following microwave treatment and exposure to the NaOH solution, a decrease in the sulphur content of ≈ 40% (see Table 1) was found. XRD (see Figure 1) and Mössbauer analysis (see Table 2 and Figure 2) did not show the formation of new minerals or a change in the crystallographic structure following the NaOH treatment. After combustion, negligible changes were noted in the ash content. The volatile matter and calorific value of the treated coal decreased slightly; therefore, the benefit of lower sulphur content needs to be weighed against the loss of calorific value. The doublet fitted in the Mössbauer spectrum is indicative of the pyrite in the sample, with no formation of pyrrhotite visible. The parameters are presented in Table 2.

3.2. Low-sulphur coal
The low-sulphur coal contained predominantly fine nodules of pyrite embedded in the coal structure making this coal more difficult to desulphurize. A decrease in sulphur of ≈ 40% was possible after the NaOH treatment (see Table 1), even though the sulphur content of the coal was low initially. XRD and Mössbauer analyses did not show the formation of new minerals or a change in the crystallographic structure following the NaOH treatment. Again, only a doublet was fitted in the Mössbauer spectrum, indicative of the pyrite in the sample, with no formation of pyrrhotite visible (see Table 2).

3.3. Pyrite/pyrrhotite rock sample
In the case of the pyrite / pyrrhotite rock sample the Mössbauer investigations showed the occurrence of pyrite (26%) and pyrrhotite (74%) as the sulphur-containing minerals. After NaOH and microwave treatment the intensities changed to 8% and 92% respectively, indicating a change in sulphur mineral composition during treatment. The XRD and Mössbauer spectra (see Figure 2) did not show new mineral formation and only a decrease in the amounts of each constituent was observed.
Table 1. Analysis of the > 212µm coal particle samples before and after treatment

| Proximate Analysis (wt%) | Moisture | Ash | Volatile Matter | Fixed Carbon | Total Sulphur | Calorific Value (MJ/kg) |
|-------------------------|----------|-----|-----------------|--------------|---------------|-------------------------|
| Before treatment (High S = 3.3%) | 4.0 | 18.5 | 32.0 | 45.5 | 3.3 | 24.6 |
| After treatment (High S = 3.3%) | 7.8 | 17.9 | 27.6 | 46.6 | 1.8 | 22.4 |
| Before treatment (Low S = 0.5%) | 4.2 | 24.9 | 22.1 | 48.8 | 0.5 | 21.1 |
| After treatment (Low S = 0.5%) | 6.8 | 24.8 | 19.7 | 48.7 | 0.3 | 20.5 |

The Mössbauer parameters are presented in Table 2 and are in agreement with literature [13].

Table 2. Mössbauer parameters of Fe components found in the samples in this investigation

| Sample | Component | IS mms⁻¹ (±0.001) | QS mms⁻¹ (±0.001) | H Tesla (±0.3) | Relative intensity (%) |
|--------|-----------|-------------------|-------------------|----------------|------------------------|
| High S-coal untreated | Pyrite | 0.27 | 0.59 | - | 100 |
| High S-coal microwave and NaOH treated | Pyrite | 0.26 | 0.59 | - | 100 |
| Low S-coal untreated | Pyrite | 0.27 | 0.59 | - | 100 |
| Low S-coal microwave and NaOH treated | Pyrite | 0.26 | 0.59 | - | 100 |
| Pyrite / pyrrhotite untreated | Pyrite | 0.30 | 0.59 | - | 26 |
| Pyrrhotite | 0.68 | -0.07 | 30.6 | 25 |
| 0.72 | 0.15 | 23.8 | 49 |
| Pyrite / pyrrhotite microwave and NaOH | Pyrite | 0.27 | 0.60 | - | 8 |
| Pyrrhotite | 0.65 | -0.09 | 29.9 | 29 |
| 0.63 | 0.13 | 23.7 | 63 |

Note: IS = Isomer shift relative to α-Fe, QS = Quadrupole splitting, H = Magnetic hyperfine field

Figure 1: On the left the XRD scan of the >212µm particles before treatment and on the right the XRD scan after treatment
Figure 2. On the left is the Mössbauer spectrum of the pyrite in the coal, where the spectrum before and after treatment remained the same, whilst on the right the Mössbauer spectrum of the pyrite / pyrrhotite rock, after treatment, is shown. Only a decrease in the amounts of each constituent was observed.

4. Conclusion
The study was undertaken to determine whether desulphurization of two South African coals is possible using microwave power and an alkali solution treatment. It forms part of a larger investigation into the desulphurization methods of coals. Both the high and low-sulphur coals showed an approximate sulphur removal of 40%, with the volatile matter content decreasing by 14% and the calorific value decreasing slightly, impacting negatively on the coal quality. The uniform sulphur removal for the high and low-sulphur coals indicates that the form of pyrite in the coal does not affect desulphurization, as was also observed for the pyrite / pyrrhotite sample. Mössbauer spectroscopy showed no change in the Fe-S structure.

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