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The effect of sulphide and moisture content on steel corrosion during transport of fine wet coal

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Abstract In the present investigation the influence of compaction pressure (stress) on the corrosivity of wet coal was investigated. Two coal samples, one high in sulphur content (3 %) and the other low in sulphur content (0.6 %) were used to determine the influence of compaction stress on the corrosion rates of steel samples in contact with compacted coal. It was found that the pressure exerted on finely divided wet coal is an important factor in determining its water content and corrosivity towards mild steel. Corrosion of the steel was typically in the form of pitting and the sulphur content of the coal was an important factor in determining the corrosivity of the coal. The corrosion rate of the high sulphur content coal was higher than that of the low sulphur coal. Mössbauer spectroscopy showed that a FeS species developed on the steel surface.

Keywords Wet coal · Corrosion · Compaction

1 Introduction

South Africa is the 5th largest exporter of coal in the world with Asia importing about 80 % of the South African export market of coal [1]. The bulk of the coal is mined and then transported over distances of more than 500 km to the coastal ports in railroad cars. During the journey the water-containing fine coal typically separates out to the top of the load in the railroad cart and significant corrosion can occur at the interface between the steel and the coal. Furthermore coal compaction occurs, resulting from the vibration during transport and leads to sticking and various problems during unloading.

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Gupta and Gupta [2] studied the critical soil moisture content in the underground corrosion of mild steel. They found that in all soils, the corrosivity reaches its maximum value at 65 % of their water holding capacity (WHC). Using the ASTM 01412 and ISO 1018 Standards, Flores et al. [3] found linear relationships between the WHC and the total moisture content of a wide range of lignite and sub-bituminous coals.

Gardiner and Melchers [4] investigated the variation of the corrosion rate of mild steel as a function of the quantity of water in two types of black coal, sieved to three different size fractions. The experimental evidence from this study (and others, such as [2]) suggests that the corrosion rate is maximised at a range of moisture contents common to all samples, which is 60–80 % of the maximum WHC (MWHC). Therefore, to assess the corrosivity of fine-particle coal it is beneficial to express the moisture as a percentage of its maximum water holding capacity. The MWHC is dependent on the inherent moisture content defined by the moist bound within the particles, and also the porosity of the media. Furthermore the MWHC increases in proportion to the porosity and thus the maximum corrosion rate of loosely packed, highly porous samples of fine-particle coal will occur at a higher value of moisture compared to a more tightly packed sample. The corrosion rate of mild steel covered by pH-neutral coal and iron ore was found to be highly dependent on the quantity of moisture and the corrosion rate of the coal samples increased with smaller particle size distributions. It is suggested that the quantity of moisture is the primary factor influencing the corrosion rate of coal in contact with iron. The influence of chloride and sulphate concentration, and to a lesser extent particle size, is dependent on the quantity of moisture. The laboratory experiments yielded similar corrosion rates to those measured within a bulk carrier (ship) cargo hold. Based on this, and the porous texture and dustiness of coal and iron ore cargo, it is proposed that the corrosion rate of mild steel in contact with coal or iron ore cargo is dominated by the fine-particle material that is deposited from the larger particles.

In a subsequent investigation, Gardiner and Melchers [5] investigated corrosion processes in large-particle porous media, in particular reference to corrosion in bulk carriers (ships) and it was proposed that the corrosion process is dominated by finer particles which co-exist with the larger particles. The analysis indicated that to minimise corrosion it is desirable to maintain the moisture content of porous media in contact with mild steel either to less than 50 % or to more than 80 %, of the MWHC of the media. This is consistent with published experimental results for these materials as well as for sand and soil. For pH-neutral porous media, continuity of the fluid phase determines the relative influence of the electrical conductivity and oxygen diffusivity on the corrosion process. At low moisture the electrical conductivity of the porous medium dominates the corrosion rate whilst the effective diffusivity of oxygen is dominating for high moisture content.

In the present investigation the influence of compaction pressure (stress) on the corrosivity of wet coal was determined. The compaction pressure determines the WHC of the coal, which will elucidate some aspects of the corrosion processes associated with the transport of wet fine-particle coal.

2 Experimental

The coal used in this investigation was obtained from the Landau coal mine, South Africa. Two grades, differing in sulphur content were studied. In South African coals

Table 1 Proximate analysis of the original coal samples [6]

Sample	Calorific value MJ/kg	Moisture %	Ash %	Vol. matter %	Fixed carbon %	Total S wt%
1	27.86	2.8	14.2	23.8	59.2	3.0
2	27.86	2.8	14.7	23.8	58.8	0.6

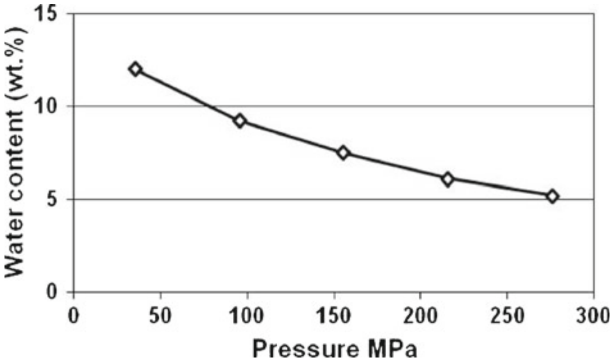

Fig. 1 Variation of the water content of the coal containing 0.6 wt% sulphur for various compaction pressures

the sulphur is mainly associated in the mineral pyrite. The coal was ball-milled, sieved and the 250–600 μm fraction was used in this study. The proximate analyses of the two coal samples are given in Table 1.

2.1 Determination of water content after compaction

Fifty gram samples of the coal were weighed off and 5 ml distilled water added to each coal sample before placing it in a 39 mm diameter hardened steel die. A hydraulic press was used to compact the samples at pressures ranging from 35 MPa to 280 MPa to form briquettes, 45 mm high and 39 mm in diameter. The briquettes were then sealed into glass jars and held at a constant temperature of 20 °C for a week in order to equilibrate. The water content of the coal was established by heating the finely ground briquettes at 110 °C in vacuum (SABS Method 923 [7]), followed by cooling in a desiccator. The results are depicted in Fig. 1.

2.2 Corrosion rate determination and identification of corrosion product

Duplicate steel coupons measuring 20 × 20 × 1 mm were metallographically polished and weighed. The weighed steel samples were embedded in the fine coal/water mixture before applying a pressure of 35 MPa to the die. The water content was assumed to be that obtained in the preceding experiments at the same. This pressure was determined from the above mentioned experiment. The coal briquettes were then sealed in glass jars and held at 20 °C for a predetermined time. They were then broken up, the steel samples recovered, ultrasonically cleaned, chemically derusted using Clark's solution, and weighed. It should be noted that Clark's solution removes mainly iron oxide species formed during corrosion, but in conjunction with the ultrasonic cleaning of the samples, all traces of possible contaminants on the steel substrate, were removed.

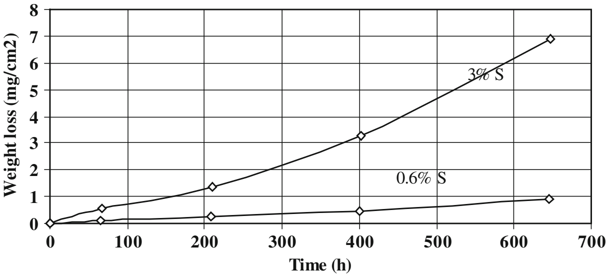

Fig. 2 Corrosion rate of mild steel in coal briquettes with different sulphur contents at 35 MPa compaction pressure

Conversion electron Mössbauer spectra for all the samples were measured at 295 K with the aid of a Halder Mössbauer spectrometer capable of operating in conventional constant acceleration mode using a backscatter-type gas flow detector and a 50 mCi ^{57}Co(Rh) source. The velocity scale was calibrated against the α-Fe spectrum and the spectra were stored in a multichannel analyzer and analyzed by a least-squares computer program by superimposing Lorentzian line shapes. Isomer shifts were determined with reference to the centroid of the spectrum of the standard α-Fe foil at 295 K. The corrosion product species were identified on the basis of their quadrupole and isomer shifts with reference to the values available in the literature [8].

3 Results and discussion

The results obtained for the preliminary test conducted to determine the water content of the coal at various compaction pressures showed that the amount of water contained in the coal declined by a factor of about two as compaction pressures increased from an initial pressure of 35 MPa to a final pressure of 280 MPa (see Fig. 1).

The coal containing 3.0 % S contained 8.3 % water and the coal containing 0.6 % S contained 11.8 % water after application of a pressure of 35 MPa and it was decided to apply this pressure to the samples intended for the investigation of the corrosion behaviour. It was found that the sulphur content of the coal was an important factor in determining the corrosivity of the coal, as shown in Fig. 2.

Corrosion of the steel was typically in the form of pitting, which makes the reporting of corrosion rates, based on weight loss measurements, rather difficult. An attempt was however made to determine the weight loss for the experiments conducted, using the two different sulphur containing coal samples. Clear differences in the corrosion rates were observed between the samples subjected to the different amounts of sulphur present (see Fig. 2).

In the first few hundred hours of the corrosion experiment the formation of the oxyhydroxides was visible and only after a test duration of 400 h the Mössbauer spectroscopy of the corroded surfaces of the mild steel imbedded in the high sulphur containing coal showed apart from pyrite and iron hydroxides, the presence of FeS, formed as a result of the reaction of pyrite (FeS_2) with the steel surface, possibly according to the reaction:

$$FeS_2 + Fe \rightarrow 2FeS \tag{1}$$

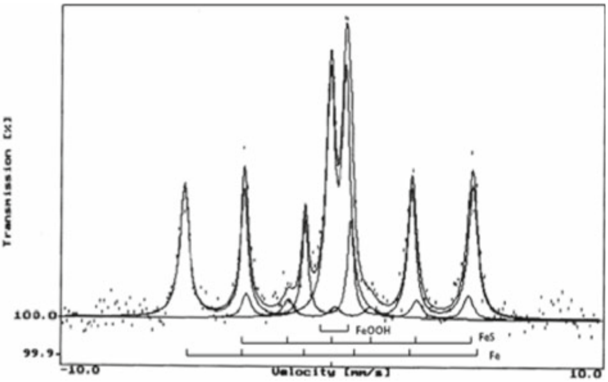

Fig. 3 Mössbauer spectrum of the corroded mild steel surface, subjected to the coal containing 3 wt.% sulphur

Table 2 Mössbauer parameters of Fe-components found in this investigation for the steel imbedded in the coal containing 3 wt.% S

Corrosion product	IS mms^{-1} (±0.02)	QS mms^{-1} (±0.02)	H Tesla (±0.3)	Relative intensity (%)
Steel substrate	−0.018	0.010	33.04	54
FeS	0.977	0.184	25.36	10
Pyrite and oxyhydroxides	0.338	0.580	–	36

IS Isomer shift relative to α-Fe, *QS* Quadrupole splitting and *H* Hyperfine magnetic field strength

The occurrence of FeS is rather surprising (Fig. 3) and merits further investigation. Other corrosion products possibly belong to the family of oxyhydroxides, but were not investigated due to the lack of low temperature analyses. Although the FeS component is partly masked by the peaks from the steel substrate a best fit was obtained when this component was added to the least squares fit program. The Mössbauer parameters of the different Fe-components are shown in Table 2 and are in accordance with literature [8].

4 Conclusions

It was found that the pressure exerted on finely divided wet coal is an important factor in determining its water content and corrosivity towards mild steel.

The results show that the sulphur content of finely divided wet coal has a major influence on the corrosion behaviour of mild steel.

Mössbauer spectra indicated the formation of FeS (derived from pyrite) on mild steel surfaces after exposure to compacted finely divided wet coal.

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