12th U.S./North American Mine Ventilation Symposium 2008 – Wallace (ed)
ISBN 978-0-615-20009-5

A study of the gases produced by the oxidation of bulk coal under laboratory conditions

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ABSTRACT: Hydrogen is regarded as being a high temperature indicator of spontaneous combustion. It is currently used in underground coal mines to detect advanced heating's. Previous work has mostly consisted of small scale tests with high air flow to mass ratios. A large-scale test rig has been used to investigate the gas indicators of coal self-heating. In particular, the relationship of gas evolution, the location of its evolution and the temperature at which it is evolved has been examined. It has been found that there are two distinct zones of hydrogen production: one at the hot spot and the other in an oxygen deficient moist zone downstream from the hot spot which is at a relatively low temperature of approximately 100°C. This has implications for the interpretation of mine atmospheres.

1 Introduction

Coal self-heating leading to spontaneous combustion continues to pose a significant hazard during the mining of coal. A recent example of this is Southland Colliery in December 2003, where a heating progressed to open fire forcing the mine to be closed. Another example is the spontaneous combustion event at Newstan Colliery 2005-06, that spanned over twelve months and cost many millions of dollars to control. Unfortunately, the heterogeneous nature of coal and the contributing factors that control whether heat is gained or lost from the coal/oxygen system make it difficult to predict the onset of a heating with any confidence.

As part of the management strategy for spontaneous combustion at all Australian underground coal mines, there is a requirement to have in place trigger action response plans (TARPS) which rely heavily on gas monitoring and analysis of the mine atmosphere. These plans make use of gas indicators such as CO make, Graham's ratio, hydrogen production etc (Cliff, Rowlands and Sleeman, 1996), which act as guides to the stage that a coal self-heating may have reached. In particular, the detection of significant amounts of hydrogen is regarded as indicating an advanced heating.

The use of these indicators has been developed from research on evolved gas studies, in particular the work by Pursall and Ghosh (1965) and Chamberlain, Hall and Thirlaway (1970). More recent studies have been conducted by Street, Smalley and Cunningham (1975), Hurst and Jones (1985) and Wang, Dlugogorski and Kennedy (2002). All of these studies have used test methods involving grams of pulverised coal and air flow rates in the order of mL/min, resulting in high airflow to mass ratio conditions. However, these are not the conditions that are encountered in the mine environment.

Bulk coal self-heating tests have been limited due to the expense and time taken to obtain results. Some success has been obtained with various column-testing arrangements (Li and Skinner, 1986; Stott and Chen, 1992; Akgun and Arisoy, 1994; Arief, 1997), but the equipment used has not gained wide acceptance. A laboratory has been established within the School of Engineering at The University of Queensland (UQ) that uses a two-metre column to conduct a practical test capable of providing reliable gas evolution and temperature data on coal self-heating. The column allows not only the gas evolution at the hot spot location to be examined, as small-scale tests do, but also the examination of gas evolution downstream from the hot spot.

This paper presents some of the gas results from a test on a high volatile bituminous coal from the Bowen Basin using the two-metre column.

2 Column Self-Heating

2.1 Equipment

Beamish et al. (2002) describe the basic operation of the

UQ two-metre column, which has a 62L capacity, equating to 40 – 70 kg of coal depending upon the packing density and particle size used for testing.

The coal self-heating is monitored using eight evenly spaced thermocouples along the length of the column that are inserted into the centre of the column. A port for gas extraction is located adjacent to each thermocouple. Eight independent heaters correspond to each of these thermocouples and are set to switch on and off according to balancing equations which ensure that heat losses are minimised and semi-adiabatic conditions are maintained radially. Figure 1 shows a schematic of the UQ column.

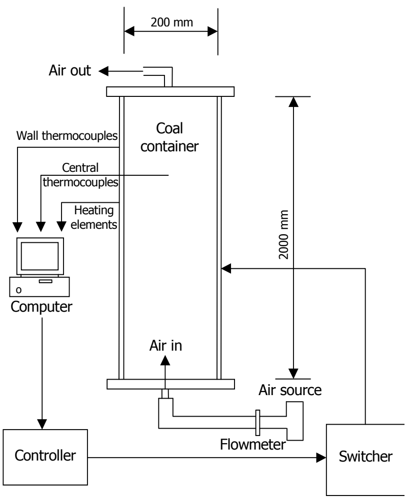

Figure 1. Schematic of UQ two-metre column.

2.2 Sample Preparation

A coal sample was obtained from a Hunter Valley mining operation for testing in the UQ two-metre column. The coal was crushed to less than 37.5 mm. This facilitated easy handling of the sample, particularly with regards to loading the column and insertion of the coal thermocouples. Three samples were taken at this stage to obtain data on the as-received moisture content of the coal, which was determined to be 3.4%.

2.3 Test Procedure

The coal was loaded into the column with three 20L plastic buckets. A total of 68kg of coal was loaded. The lid was then secured and air flushed through the column at 0.5L/min and the heaters used to set the starting coal temperature, which in this case was initially 40°C. Once the coal temperature had stabilised heaters were set to balance the coal temperature. A computer recorded all the data at ten-minute increments. Gas profiles of the column were taken at various stages of the heating. When the temperature of the hot spot exceeded 200°C and the hot spot was near the air inlet the coal was inerted with nitrogen. Another column gas profile was taken four hours afterwards. The heaters were then switched off and the column allowed to cool before being unloaded. During the unloading process, samples were taken for moisture analysis. The column has several safety devices including computer-controlled trips on the external heaters. These were set to ensure maximum safety during operation of the column.

3 Results of Column Testing

3.1 Gas Evolution in Response to Coal Oxidation and Hot Spot Development

Gas profiles of the column were taken at various stages. The gas bag samples were analysed by SIMTARS using standard gas analysis techniques, which are also used in coal mines across Australia. The gases detected are hydrogen, oxygen, nitrogen, methane, carbon monoxide, carbon dioxide, ethylene, ethane and argon by difference. In this paper two gas profiles are presented in detail: Gas Profile 1 which was taken approximately 32 days after the test start and 17 hours before the column was inerted with nitrogen and Gas Profile 2 which was taken approximately four hours after the column was inerted.

By comparing Figures 2 and 6 it can be seen that the temperature profiles are almost identical. When Figures 3-5 are compared with Figures 7-9, it can be seen that the nitrogen inertisation process has the expected effect of decreasing the gas evolution with the notable exception of hydrogen, which continues to be evolved in significant quantities.

Closer examination of Figures 2 and 3 reveals that there are three distinct zones in the column when a significant hot spot has developed. Zone 1 is defined from the air inlet to where the hot spot peaks. It has decreasing oxygen content due to the coal self-heating stripping it out of the airstream and has a dramatic rise in temperature across it. Zone 2 is defined as oxygen depleted and is at an elevated temperature that is above 100°C. Zone 3 is defined as being where the coal temperature plateaus at approximately 100°C and once again is oxygen depleted. The temperature of this zone suggests that moisture is retarding the coal temperature and this is confirmed by the moisture profile in Figure 10.

It can be seen that the majority of the gas is evolved at the hot spot front in Zone 1. It is here that the carbon monoxide, carbon dioxide and ethylene are generated, as shown by Figures 4, 5, 8 and 9. Hydrogen is also produced in Zone 1 and is not produced in Zone 2. Large amounts of hydrogen are produced in Zone 3, however. This zone is deficient in oxygen and is at a relatively low temperature of 100°C. Therefore this hydrogen is not being generated by pyrolysis. The fact that the hydrogen is not being generated by pyrolysis is confirmed by Zone 2 which is at approximately 200°C but does not generate hydrogen. Also, if hydrogen were a product of pyrolysis one would expect to detect other hydrocarbon fragments being

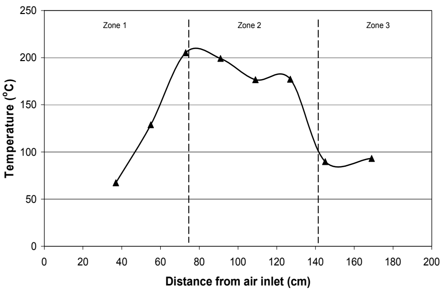

Figure 2. Hot spot temperature profile 17 hours before inertisation corresponding to gas profile 1

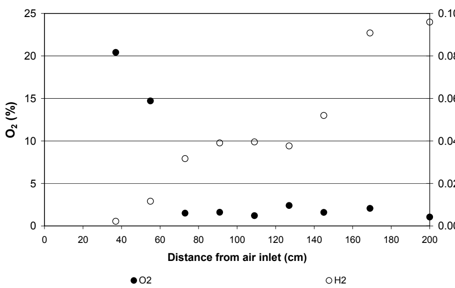

Figure 3. Gas Profile 1 showing oxygen and hydrogen concentrations

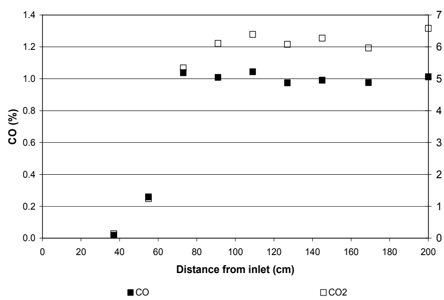

Figure 4. Gas Profile 1 showing carbon monoxide and carbon dioxide concentrations

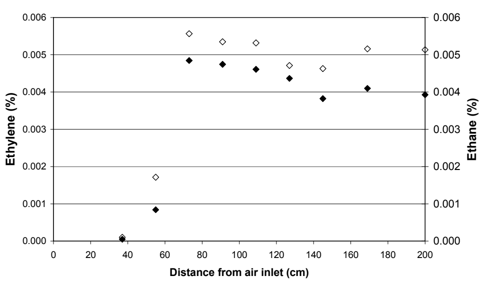

Figure 5. Gas Profile 1 showing ethylene and ethane concentrations

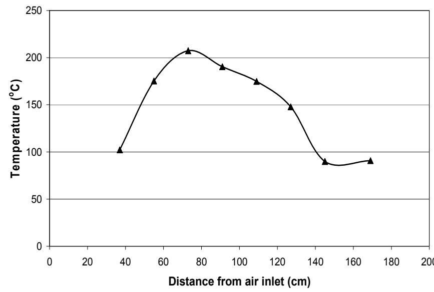

Figure 6. Hot spot temperature profile 4 hours after inertisation corresponding to gas profile 2

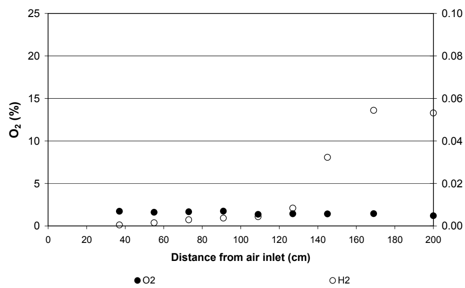

Figure 7. Gas Profile 2 showing oxygen and hydrogen concentrations

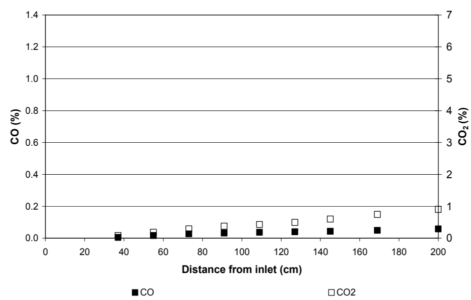

Figure 8. Gas Profile 2 showing carbon monoxide and carbon dioxide concentrations

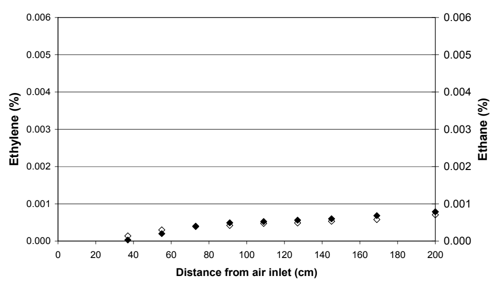

Figure 9. Gas Profile 2 showing ethylene and ethane concentrations

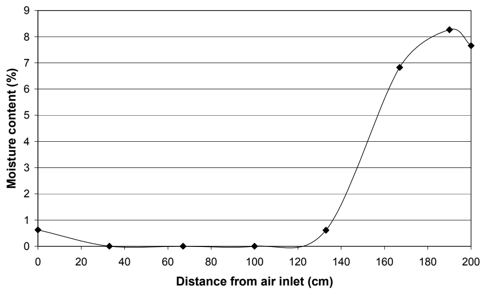

Figure 10. Final moisture profile of the column

generated in this region such as ethane and ethylene, however, this is not the case.

When Figure 3 is examined in detail it can be seen that approximately 0.04% hydrogen is generated in Zone 1 and another 0.05% is generated in Zone 3. When Figure 7 is examined it can be seen that even under nitrogen there is still approximately 0.05% hydrogen being generated in Zone 3. Hydrogen is not being generated anywhere else in the column under nitrogen even though Zone 2 is approximately 100°C higher in temperature than Zone 3.

Small-scale tests on Bowen Basin coals conducted by SIMTARS show that hydrogen is only produced in significant amounts once the temperature range of 250°C - 325°C is reached (Cliff, Bell and O'Beirne 1991). Tests under nitrogen indicated that this hydrogen production was from the pyrolysis of the coal. Low levels of hydrogen were detected at lower temperatures under oxidising conditions. Small concentrations of hydrogen were detected at temperatures in excess of 100°C. The SIMTARS tests had an air flow to coal mass ratio ranging between 0.035 mL/min/g to 1 mL/min/g. Street, Smalley and Cunningham (1975) showed that, depending on rank and air flow to coal mass ratio, the temperature at which hydrogen was first detected could be below 100°C but could be as high as 250°C. For these studies the air flow to mass ratios ranged between 1.79 mL/min/g and 0.75 mL/min/g. It was observed that the lower the air flow to coal mass ratio the higher the appearance temperature of the hydrogen.

The work completed by Chamberlain, Hall and Thirlaway (1970) with an air flow to coal mass ratio of 1.6 mL/min/g showed hydrogen being initially produced at 70°C and then ramping up from 100°C onwards. This is consistent with Street, Smalley and Cunningham (1975). The column has an air flow to coal mass ratio of 0.009 mL/min/g which indicates that based on the small-scale research that hydrogen should not be detected in significant quantities until temperatures in excess of 300°C are reached. The results obtained from the two-metre column contradict this, generating the highest hydrogen concentrations of any laboratory test. Further, these column results suggest that in a bulk coal situation, the majority of the hydrogen is in fact produced downstream of the hot spot where the coal is relatively cool i.e. around 100°C, not in the active oxidation zone. This implies the majority of hydrogen production in a mining situation is not necessarily related to the temperature or intensity of the hot spot oxidation but is in fact more dependent on the amount of hot/warm moist coal located downstream from the hot spot.

Small-scale tests have shown that coal does not produce significant amounts of hydrogen at these temperatures under pyrolysis conditions. The key difference between Zone 2 and Zone 3 is the moisture content of the coal. As Zone 3 is quite moist it would seem that the moisture is either acting as a catalyst or is the source of the hydrogen.

Work completed by Nehemia, Davidi and Cohen (1999) has shown that formaldehyde may be the precursor organic volatile that produces hydrogen with the coal acting as a catalyst as per equation 1.

$$2CH_2O + O_2 \xrightarrow{coal} 2CO_2 + 2H_2 \quad (1)$$

Small scale tests conducted by Nehemia, Davidi and Cohen (1999) resulted in a 100% yield for CO_2 but only a 15% - 30% yield for hydrogen. When Figure 8 is examined it can be seen that CO_2 is indeed produced in Zone 3 whilst the column is being inerted with nitrogen. It should be noted, however, that it is also produced in the first two zones of the column as well and is therefore not necessarily a confirmation of the suggested decomposition of formaldehyde.

Fourier Transform Infrared (FTIR) analysis of coal has shown that aldehyde functional groups are part of the coal structure (Tognotti et al., 1991). Chamberlain, Barrass and Thirlaway (1976) (Chamberlain, Barrass and Thirlaway, 1976) showed that dry, crushed coal provided that sufficient oxygen was present would amongst other gases, produce acetaldehyde. Production reached a plateau at approximately 70°C, however, a second increase occurred above 130°C. This suggests that aldehyde groups may be precursors for hydrogen production and as such experiments will be conducted to examine this.

Previous testing by Golding (2001) used isotopic studies in an effort to determine the source of hydrogen generation in an underground mine environment. It was found that hydrogen generated by mine water and coal could be differentiated. Further studies are planned to be conducted on the gas samples taken from the column to determine the source of the hydrogen.

4 Conclusions

Significant quantities of hydrogen production from bulk-coal self-heating have been recorded. The majority of the hydrogen is not generated at the hot spot but in the oxygen depleted downstream region. Figures 3 and 7 show that the hydrogen production is not necessarily related to the temperature of the hot spot, but is related to how much moist coal is downstream from the hot spot which is at approximately 100°C. Considering significant increased hydrogen production in an underground atmosphere is regarded as indicating advanced oxidation this research has important implications for how mine atmospheres should be interpreted. Further work will be carried out to determine the source of the hydrogen as well as studies to determine the effect of aldehyde groups on the hydrogen production.

Acknowledgements

The authors would like to thank UniQuest Pty Limited for granting permission to publish this research.

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