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A STUDY OF THE FORMATION OF HYDROGEN PRODUCED DURING THE OXIDATION OF BULK COAL UNDER LABORATORY CONDITIONS

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ABSTRACT: A number of studies of the oxidation of coal using The University of Queensland's two- metre, 62L test rig have been carried out over the past few years. The rig simulates a semi-adiabatic environment radially and allows gas samples to be taken along its length and from the exhaust stream. This enables the generation of a gas and temperature profile across a coal self-heating zone. As the state of spontaneous combustion in underground coal mines is usually inferred from gas samples taken remote to the heatings these laboratory studies offer important insights into the mechanisms of gas formation during coal self-heating events. In particular much emphasis is placed upon the presence of and concentration of any hydrogen. This paper reports the preliminary findings from a test where such gas samples were taken. The bulk of the hydrogen appears to be generated downstream from the hot spot where the coal is at approximately 100°C and there is no free oxygen.

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, significant amounts of hydrogen are 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 allows 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 A bituminous coal from the Bowen Basin using the two-metre column.

COLUMN SELF-HEATING

Equipment

Beamish *et al.,* (2002) describe the basic operation of the UQ two-metre column, which has a 62 L capacity, equating to 40 – 70 kg of coal depending upon the packing density used. 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

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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.

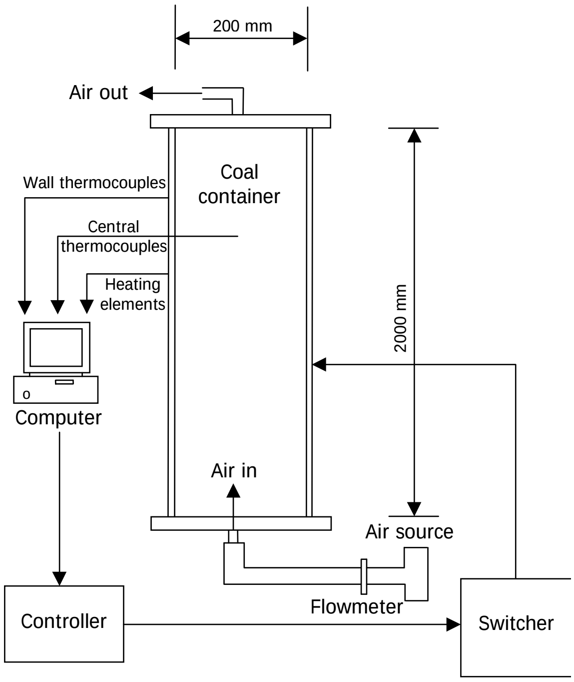

Figure 1 - Schematic of UQ two-metre column

Sample Preparation

A coal sample was obtained from a Bowen Basin coal mine for testing in the UQ two-metre column. The coal was crushed to an average particle size of less than 12.7 mm. This facilitated easy handling of the sample, particularly with regards to loading the column and insertion of the coal thermocouples. Three subsamples were taken at this stage to obtain data on the as-received moisture content of the coal, which was determined to be 6.7%. Samples were also taken at this stage to establish the R_{70} self-heating rate of the coal.

Test Procedure

The coal was loaded into the column with three 20 L plastic buckets. A total of 56kg of coal was loaded. The lid was then secured and nitrogen flushed through the column at 0.5 L/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 the nitrogen was switched off and air was then introduced to the coal at a flow rate of 0.5 L/min. A computer recorded all the data at ten-minute increments. 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.

As the column test progressed gasbag samples were collected from the exhaust and ports located along the length of the column. A peristaltic pump was used to suck samples from the ports. This pump had a low flow rate relative to the column so that sampling does not disturb the normal gas flow within the reactor and is designed such that there is no gas leakage. The gas samples were later analysed by Simtars using standard gas chromatography. In total there were four gas profiles completed throughout the test.

RESULTS OF R_{70} AND COLUMN TESTING

R_{70} value of the column sample

The R_{70} testing procedure is described by Beamish, Barakat and St George (2001). Essentially, a 150 g coal sample is crushed to less than 212 µm, dried under nitrogen at 110°C and then tested under oxygen in an adiabatic oven. The R_{70} value is a simply the average rate of heating of the coal between 70°C from a starting temperature of 40°C and is expressed in units of °C/h. Figure shows the self-heating curve obtained in the UQ adiabatic oven for the sample taken whilst loading the column. The R_{70} value determined from this test was 0.52°C/h. This places the coal on the borderline between the 'low' and 'medium' propensity to spontaneous combustion categories.

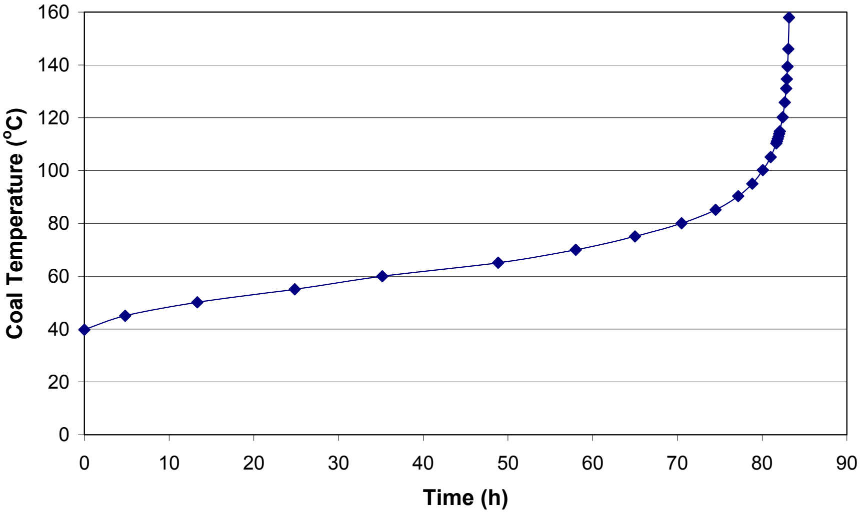

Figure 2 - Adiabatic self-heating curve for a Bowen Basin high volatile A bituminous coal

Column Testing

The hot spot initially developed at the downstream end of the column, before moving forwards towards the air source. This is typical of all column tests and is consistent with numerical modelling of spontaneous combustion. A total of four gas profiles were taken during the test. The temperature profiles of the column at the time of each gas profile are shown in Figure .

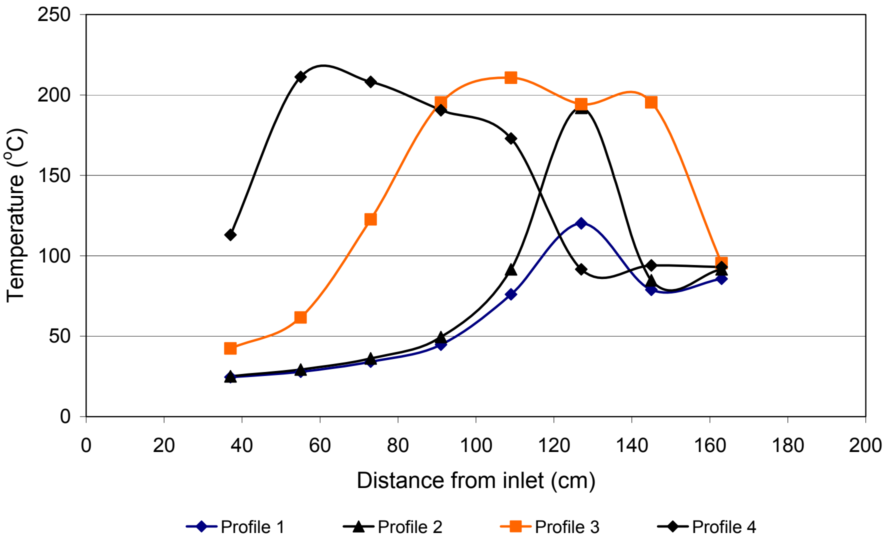

Figure 3 - Temperature profiles of the column for each gas sampling profile

Gas evolution in response to coal oxidation and hot spot development

Table 1 details which locations were sampled for each column profile. These were determined based on the location and severity of the hot spot at the time of sampling. It should be noted that the gas sample from each port is the sum of all the gas evolution that has occurred prior to the air stream reaching that point.

For purposes of clarity, only the data for gas profiles 2 and 4 is presented. Figures 4 and 5 and Figures 7 and 8 respectively show the temperature and oxygen profiles. It can be seen that the hot spot strips most of the oxygen from the airstream and that on the downstream side of the hot spot the atmosphere is very oxygen depleted. This is consistent with what has been observed in small-scale test work which indicates that once the hot spot reaches the temperature region of 150°C - 200°C it will strip most of the oxygen from the atmosphere (Chamberlain, Hall and Thirlaway 1970; Street, Smalley and Cunningham 1975; Hollins 1995; Cliff, Bell and O'Beirne 1991).

Table 1 - Table of gas sample locations

	Exhaust	*Port 9*	*Port 10*	*Port 11*	*Port 12*	*Port 13*	*Port 14*	*Port 15*	*Port 16*
Profile 1	yes	-	-	yes	-	yes	-	yes	-
Profile 2	yes	-	-	yes	-	yes	-	yes	-
Profile 3	yes	yes	-	yes	yes	yes	yes	yes	-
Profile 4	yes	yes	-	yes	-	yes	-	yes	-

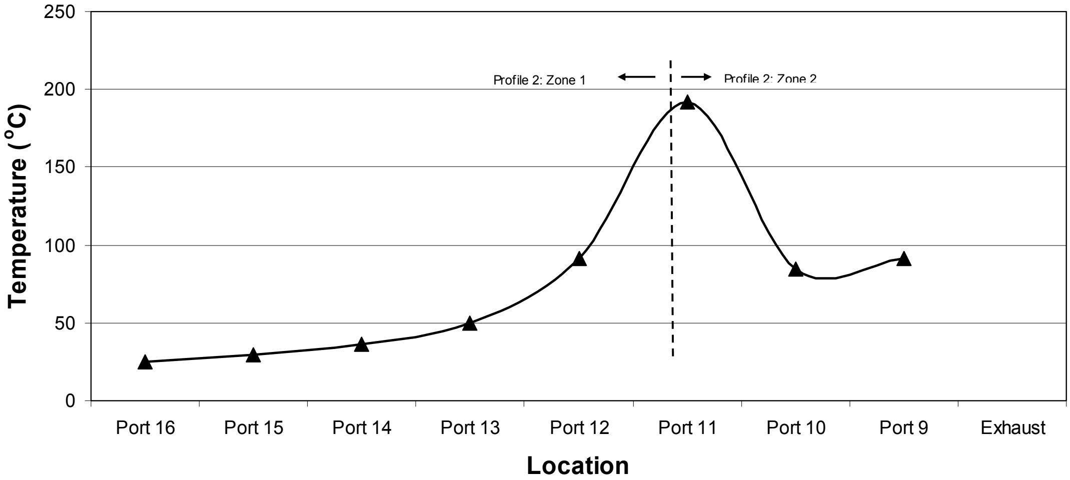

Figure 4 - Temperature profile 2 showing zones 1 and 2 based on hot spot location

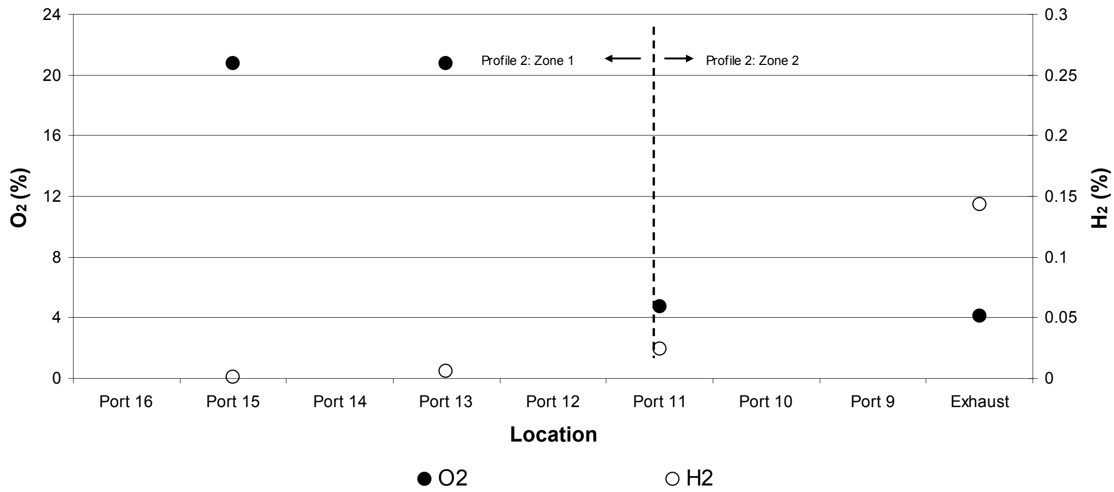

Figure 5 – Gas profile 2 showing oxygen and hydrogen concentrations

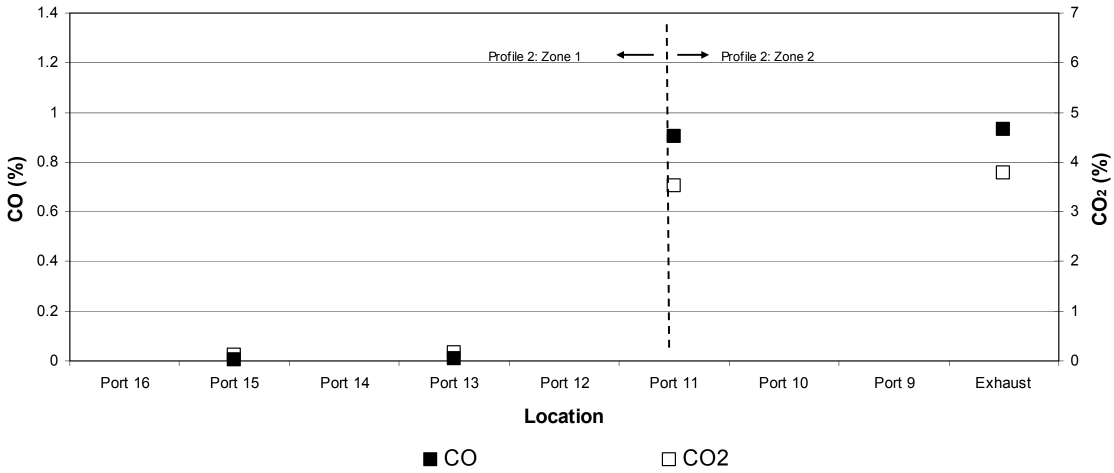

Figure 6 – Gas profile 2 showing CO and CO_2 concentrations

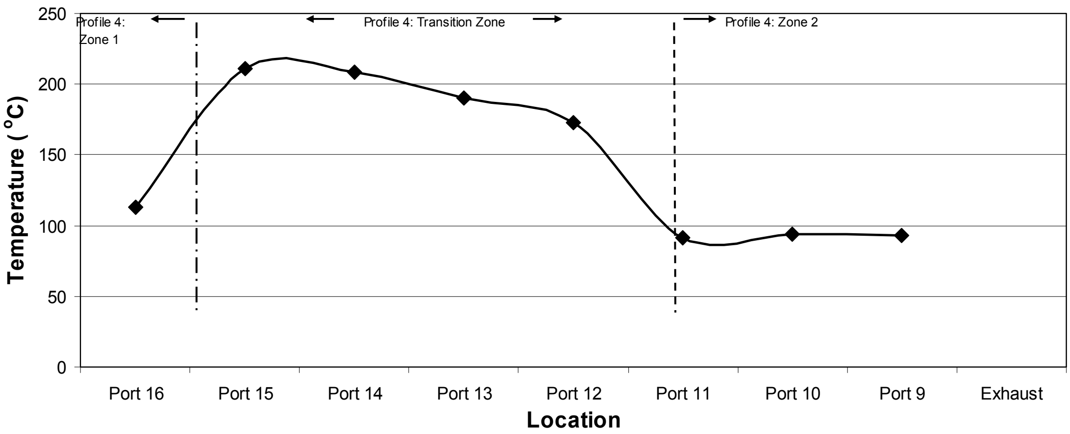

Figure 7 - Temperature profile 4 showing zones 1 and 2 based on hot spot location

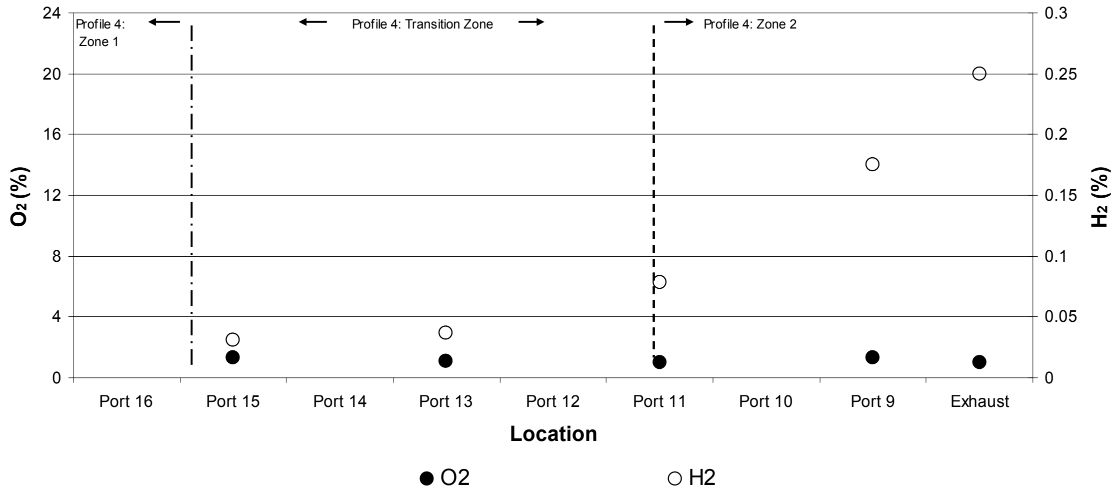

Figure 8 - Gas profile 4 showing oxygen and hydrogen concentrations

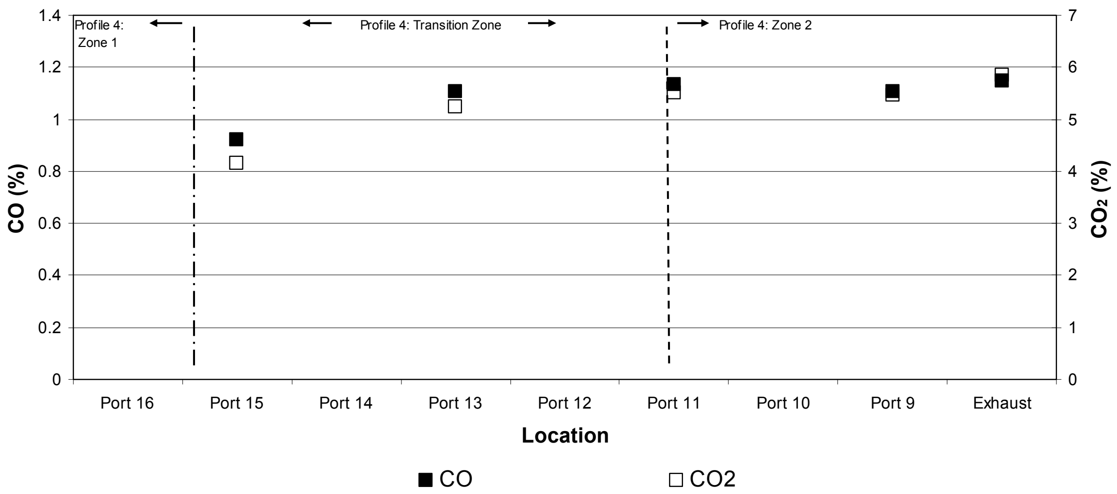

Figure 9 - Gas profile 4 showing CO and CO_2 concentrations

Figures 6 and 9 show the CO and CO_2 production for each profile. It is evident that these gases are produced by oxidation at the hot spot. Once again this is consistent with small-scale tests. Evidently, there are two distinct zones within the column. The first, Zone 1, is the region before and up to the hot spot which is undergoing oxidation reactions. This then transitions into Zone 2, which is located after the hot spot and is oxygen deficient. It should be noted that the oxygen depletion is not balanced by the production of oxides of carbon, i.e. there is a net oxygen absorption by the coal.

The hydrogen content in Figures 5 and 8 shows minimal amounts of hydrogen are produced in the Zone 1 region but there is significant hydrogen production throughout Zone 2. 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 whereupon the production rate ramps up significantly (Cliff, Bell and O'Beirne 1991). 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 produced (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. The temperature of the coal in this region suggests that the coal at this point is still evaporating moisture. 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. Therefore, there must be a catalyst involved in the production 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. 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) 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 should be conducted to examine this.

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 5 and 8 show that the hydrogen production is not necessarily related to the temperature of the hot spot, but is related to how much 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.

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