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The Ability of Current Gas Monitoring Techniques to Adequately Detect Spontaneous Combustion

D Cliff¹

ABSTRACT

This paper investigates the adequacy of current gas monitoring techniques to adequately detect spontaneous combustion in underground coalmines. Despite being in the 21st century spontaneous combustion continues to occur in underground coalmines sometimes being detected only at a very advanced stage. Control of the incident is often then very expensive and time consuming.

The adequacy needs to be assessed not only from the point of view of the analysis technique be it tube bundle, gas chromatograph or real time sensor but also the number, location and sampling frequency of the monitoring locations.

Recommendations are made to optimise monitoring processes and recognise limitations of current techniques.

INTRODUCTION

There are three key questions that need to be addressed when designing a mine environment monitoring system:

- What are you trying to monitor?
- Where are you going to monitor? and
- How are you going to monitor?

Determining the answer to the first question will define the boundary conditions for defining the answers to the second and third questions.

WHAT TO MONITOR?

The focus of this paper is monitoring for the detection of spontaneous combustion, however mines are required to monitor for a range of situations including, safe working conditions for the workers, outburst prevention, equipment fires and statutory monitoring requirements, eg ERZ in Queensland.

Classically monitoring for the detection of spontaneous combustion has focussed on gas monitoring and exceeding of predetermined maximum allowable values for gas concentrations (eg carbon monoxide) or derived indicators such as Graham's ratio. Most of these indicators have been derived based upon either laboratory testing or events in underground coalmines that occurred many years ago. Often the conditions in these mines bore no similarity to modern underground coalmines. Historically for example, spontaneous combustion events would often occur in the pillars of roadways and were detected by smell or a rise in CO make. Now the majority of incidents occur in the goaf some distance behind the longwall where there is no externally defined ventilation circuit. Thus it is unreasonable to expect that textbook definitions of indicators can be routinely applied without significant modification and testing for relevance.

Events in the recent past such as at Southland, North Goonyella and Dartbrook indicate that this detection process is less than perfect. This is due to the size of the area to be monitored and the inability to sample within goafs. The lack of defined airflows also hampers early detection. Indeed due to the difficulties of monitoring for the presence of heatings in the goafs of modern longwall mines there needs to be a shift from detection of a heating to detection to prevent a heating. In each of these cases a heating developed in the goaf of a longwall panel some distance behind the face. The heating was detected when gas samples were taken through a seal into the goaf that revealed abnormal CO and H_2 concentrations. Initially there was little indication of the location of the actual heating.

In two of the cases the application of inert gas into the goaf controlled the heating. Unfortunately in the third case the heating developed so rapidly that it became a raging fire and sealing at the surface was the only option, after inertisation was tried.

The gestation period of the heating in each case is unknown except that a maximum value can be established from the time the goaf was established. In two cases there was no indication of a worsening situation, in part due to the absence of regular gas monitoring through the seals. Local conditions, such as water blocking access to the seal prevented sampling in one case.

In one case it was only after sampling from a line of seals that it was determined that the heating was remote to the original detection point, indeed on the opposite side of the goaf, fed by air from the face. The treatment of the heating was protracted and it is likely that several lesser intensity oxidation occurrences initiated subsequent to the original heating.

For another case after sampling along the gate road into the goaf at various seal locations, the seat of the heating was determined to be close to a particular gate-road seal, and a surface borehole was able to intersect the heating allowing the application of inert gas directly onto it.

In the third case there is still today no definite evidence to locate the source of the heating. In each case however there is no way of knowing the genesis of the heatings in terms of what caused that particular area of goaf coal to abnormally oxidise and not the millions of tonnes of other coal in the goaf all around it. Circumstances at that point must just have been right for it to propagate. The initiation of the event in each case probably occurred months beforehand and the oxidation stewed away until conditions favoured acceleration. In two of the cases this was caused by sudden influx of additional air due to seal failures. In the third case it was probably simply a case of the longwall had been stationary for a number of weeks and air was able to continually flow to the heating site, under conditions that favoured abnormal oxidation.

Spontaneous combustion is a complex process and the chemistry of the process is still not well characterised. Laboratory experiments at SIMTARS (see for example Cliff *et al*, 2000) and UQ (Beamish, Barakat and St George, 2001) clearly show the complexity involved when coal reacts with air. Figure 1 depicts a 'typical' bituminous coal molecule. Coal is of course not a simple molecule rather it is a complex mixture of a range of large organic molecules containing carbon, oxygen, hydrogen, nitrogen and sulfur. Add to this impurities such as carbonates, pyrites and salts, stir in seam gases (methane and/or carbon dioxide) and water and you get coal as we know it. Some parts of the coal are far more reactive than others.

For example when methane is oxidised to carbon dioxide it goes through a series of intermediate compounds – methanol to formaldehyde to formic acid to carbon dioxide.

$CH_4 - CH_3OH - HCHO - HCOOH - CO_2$

The hardest step to achieve is the first step; methane is very unreactive and needs a lot of help (energy and catalysis) to begin

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FIG 1 - Example of molecular structure of coal (Shinn, 1984).

the process. The further to the right the process proceeds the easier it becomes. Thus acid functional groups are very reactive and alkyl functional groups are not. In Figure 1, the bits around the molecule labelled – CHx are thus unreactive whereas those containing oxygen are more reactive. Not surprisingly low rank coals contain more of the oxygenated species than high rank coals and hence have a higher inherent reactivity.

Of course being a mixture of many chemical components it means that the oxidation chemistry is also complex. Figure 2 below indicates a simplified model of the oxidation process. Even in this model each reaction step has its own temperature dependence as well as individual dependence on the concentration of the reactants. Coal reacts as a solid and thus the effective surface area available for reaction is an important factor. If oxygen cannot get into the coal to reach the reactive components of the coal then reaction cannot occur. In other words the presence of water and seam gas within the pores of the coal reduces the effective surface area of the coal available to react and hence the potential for the coal to heat up and proceed to spontaneous combustion is also reduced.

Similarly if the most reactive components of the coal macromolecule have already reacted, then the rate of oxidation is substantially reduced, ie if a coal has been exposed to air for a long time, the reactive components will have reacted and the heat will have dissipated to the atmosphere, the residual 'weathered' coal will be unreactive. A more detailed description of the chemistry of coal oxidation can be found in Cliff and Bofinger (1998).

Figure 3 illustrates two tests carried out on Dartbrook coal samples in the large-scale (16 tonne) reactor at SIMTARS (Cliff *et al*, 2000). It can clearly be seen that the coal apparently lies

dormant for many days and then suddenly the oxidation process accelerates out of control in a few hours. This translates to negligible gas concentrations and ratios suddenly becoming huge. In the case of the run of mine test, the CO make went from less than 1 L/min to over 100 L/min in less than 24 hours.

This is consistent with the laboratory observation that for every ten degrees increase in reaction temperature there is a doubling in the nett reaction rate and thus gas evolution rate. The dormant period appears to align with the dehydration of the coal and thus the energy being generated by the oxidation process is being absorbed by the energy requirements to volatilise the water out of the coal. Once this process is complete then the energy is channelled instead into heating the coal.

What this all means is that given the difficulty in detecting an active heating we should focus on preventing a heating from occurring. Monitoring strategies defined by an early response should be triggered by such things as:

- The detection of oxygen in areas of the goaf where it should not be. This does not immediately cause trouble but it will be the catalyst if this condition remains in place for any length of time. Remedial action to reduce the oxygen supply can avert a heating. Such action could include proactive inertisation, tightening of seals and reducing the pressure difference across the face of the longwall.
- The ability of oxygen to pass into areas of particular coal in the goaf for longer than normal, eg if the longwall stops for any length of time or is reduced to slow production rates.
- Pressure differences across seals that are not what is expected this of course presumes that you know what to expect. Abnormal pressures differences often indicate leaking seals and air ingress into goaf areas.

$$Coal-CH_2-Coal \xrightarrow{R^*} Coal-CH-Coal + RH$$
(1)

$$\begin{array}{ccc} \text{Coal-CH-Coal} & \underbrace{O_2}_{l} \text{Coal-CH-Coal} & (2) \\ & & & | \end{array}$$

0-0

$$\begin{array}{ccc} \text{Coal-CH-Coal} & \xrightarrow{\text{RH}} \text{Coal-CH-Coal} + \text{R}^{\bullet} & (3) \\ & & & & \\ & & & & \\ & & & & \\ & & & O - O \text{H} \end{array}$$

$$\begin{array}{ccc} \text{Coal-CH-Coal} & \longrightarrow \text{Coal-CH-Coal} + \text{OH} & (4) \\ & & & | \\ & & | \\ & \text{O-OH} & & \text{O}^{\bullet} \end{array}$$

$$Coal-CH-Coal \longrightarrow Coal-CH+Coal^{(5)}$$

$$\begin{array}{c} \text{Coal-CH} + \text{O}\dot{\text{H}} & \longrightarrow \text{Coal-}\dot{\text{C}} + \text{H}_2\text{O} \\ \\ \parallel & \parallel \\ \text{O} & \parallel \\ \end{array} \tag{6}$$

$$\begin{array}{c} \text{Coal-C} + O_2 \xrightarrow{+ \text{RH}} \text{Coal-C} - \text{OOH} \xrightarrow{+ \text{Coal-CHO}} 2\text{Coal-C} - \text{OH} \\ \downarrow & \downarrow & \downarrow \\ O & O & O \end{array}$$

$$\begin{array}{c} \text{Coal-C} \rightarrow \text{Coal} + \text{CO} \\ \parallel \\ \text{O} \end{array}$$
(8)

FIG 2 - Coal oxidation reaction scheme (Wells and Smoot, 1991).

- The detection of unusual trends in gas behaviour particularly carbon monoxide. For example, generally as the longwall retreats away from a gate road seal, the oxidation behaviour of the coal goes through a maximum and tails away, due to the reduced availability of oxygen and the weathering of the coal. A peak in CO is typically seen one or two cut throughs behind the face. If a peak is found further back or the smooth trend behaviour from seal to seal is not observed then something unusual is happening.
- Knowing the temperature profile across the face and around the goaf so that abnormal temperatures can be identified early. Temperature is very important as it affects the reaction rates as discussed above.

In the past too much reliance has been placed on small-scale laboratory testing such as R70 determinations, or in gas evolution testing. These have limited application to the real world, as the laboratory conditions bear no resemblance to those conditions found in a longwall goaf. R70 tests for example are carried out on small samples of dried crushed coal, which has been degassed. Often the tests are carried out under conditions where the airflow through the sample is much higher than would be found in the goaf. This means that the balance of reaction mechanisms depicted in Figure 2 above will differ from that in the goaf and hence give different gas evolution behaviour.

Medium and large-scale testing using run of mine coal and more realistic airflows often give very different results. For example the two-metre column work of Beamish *et al* (2002 and 2003), has been able to demonstrate that significant levels of hydrogen can be generated at temperatures much less than 100°C. These results are consistent with an oxidation pathway where coal reacts with air in the presence of water vapour, and internally rearranges itself to generate carbon dioxide and hydrogen. A separate oxidation pathway appears to generate a mixture of carbon monoxide and carbon dioxide.

WHERE TO MONITOR?

Monitoring needs to be undertaken to ensure that normal behaviour can be characterised and that abnormality can be detected as soon as possible. Too often mines collect inadequate



Dartbrook Self Heatings

FIG 3 - Temperature time plots for large-scale oxidation tests (Cliff et al, 2000).

amounts of data from far too few monitoring locations. This means that when something abnormal is detected, the situation is often serious and evacuation of the mine is the only option. Typical goaf seal behaviour needs to be determined including:

- pressure differentials across seals and around goafs as a function of distance from the face and other factors such as the change in the pressure difference across the face;
- gas evolution and derived indicators as a function of distance from the face, this is especially important where factors such as goaf drainage and or back by ventilation is used to reduce seam gas impacts on the face; and
- longwall return concentrations and derived indicators such as CO make as a function of operating parameters including size of goaf, rate of retreat, etc.

Monitoring is a multi-tier process. Initially characterisation of normal goaf and return roadway behaviour will be an intensive campaign until sufficient data has been gathered to give the mine confidence that it knows what to expect. Once this initial characterisation is complete then the monitoring can be tailored to check that the expected behaviour is occurring.

HOW TO MONITOR?

Frequency and complexity of sampling will depend on what is being monitored. Continuous monitoring of panel returns is required by regulation. Seal sampling can be undertaken by a mix of tube bundle sampling with analysis by a bank of infrared analysers for CO, CO₂ and CH₄, paramagnetic for O₂, and bag samples with analysis by gas chromatograph for the seals immediately inbye the face and perhaps just bag samples taken on a regular basis for those seals toward the rear of the panel or if there is spare tube bundle capacity, these tubes could be sampled less frequently than the more important (more likely to change) tubes. It may not be necessary to sample every seal if there is no indication of abnormality in terms of pressure differentials or oxygen presence. Gas chromatography gives the opportunity to directly analyse for the presence of hydrogen and higher hydrocarbons as well as check the accuracy of the tube bundle system. The older the coal the harder in general it is to resuscitate it for abnormal oxidation.

DETECTION

Much has been written about the use of indicators for detecting spontaneous combustion. There is only one real law for spontaneous combustion monitoring – *there is no universal indicator.*

There are many indicators that have been used to detect spontaneous combustion including:

- Carbon monoxide concentration. This is very unreliable in isolation as CO is produced at all temperatures by coal oxidation and extensive oxidation over a long time may well produce the same concentration as a small much more intensive oxidation event.
- Hydrogen concentration. This is also unreliable in isolation as the work of Beamish *et al* (2003) and Nehemia, Davidi and Cohen (1999) have demonstrated.
- Ethane. Ethane is most commonly present as a minor seam gas typically between 1/100 and 1/1000 of the methane present. *Do not use it as an indicator of spontaneous combustion.*
- Ethylene concentration. At high temperatures (> 200°C) the coal will pyrolyse and produce a raft of unsaturated and saturated hydrocarbons. The presence of significant concentrations of ethylene (>10 ppm) is a reliable indication that abnormal oxidation has occurred. Typically by the time this occurs the CO and hydrogen concentrations are orders of magnitude higher than this and rising.

- CO make. This is only valid in roadways with defined, known ventilation. Absolute numbers only have meaning when they are calibrated against the actual mine performance and operating conditions (see above). Real time air velocity/air quantity sensors are readily available and allow for real time monitoring of the ventilation flows as well as determining makes.
- Graham's ratio. This ratio can be a useful indicator of advanced oxidation however it is possible that effects of a small intense heating will be hidden in the effects of a large-scale low-level oxidation. This will cause Graham's ratio to underestimate the intensity of any oxidation process. It is thus important to set triggers based on normal behaviour at the mine rather than textbook values.
- CO/CO₂ ratio. This ratio suffers from the same problems as Graham's ratio and also interference from any CO₂ that is present in the seam gas.

There are many other indicators that have been suggested but none of them offer anything significant to the above, as they suffer from the same problems (Cliff, Hester and Bofinger, 1999) and may only serve to confuse the diagnosis. Some indicators such as CH_4 to CO_2 can be used to help identify anomalies and locate leaking seals or abnormal ventilation circuits in goafs.

Care needs to be taken when using inertisation techniques as they upset the parameters on which a number of computer programs calculate ratios as they use preset factors for such things as the ratio of oxygen to nitrogen in inlet air. This in turn will invalidate oxygen deficiency calculations and distort Graham's ratio, artificially reducing it. Equally importantly introducing additional flows into goafs can cause existing flow paths to alter and direct different gas atmospheres to monitoring locations with consequent effects on the interpretation.

Trigger action response plans (TARPS) for spontaneous combustion should be established to initiate when something abnormal is detected, hopefully indicating a precursor to advanced oxidation rather than actual advanced oxidation. This allows preventive action to be initiated without impacting on the production of the mine. TARPS should not simply be for evacuation or major concern, they should initially be advisory and necessitate action by perhaps just the ventilation officer and his support crew. The response to a trigger should be appropriate to the risk the trigger reflects. Why evacuate the mine when CO exceeds 100 ppm in the goaf? Is there a flammable atmosphere there? What is the source of the CO - is it extensive oxidation or intensive? These are questions that would modify the response to the trigger. In this modern era there is no need to use simple triggers relying on the measurement of one gas. Mine environment monitoring systems are capable of providing a lot of information and it should be utilised to assist in the decision making process.

CONCLUSION

In summary, prevention is better than cure, especially where there is no guarantee that a heating can be detected at a stage early enough to control it quickly and easily.

Comprehensive monitoring systems need to be established to establish normal mine environment behaviour and understand the factors that can affect gas concentrations in all areas of the mine, including monitoring pressure differences around the mine, air flows and temperatures. Proper maintenance and personnel skilled in understanding mine monitoring systems and interpretation of mine atmospheres must support these systems.

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