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**Oxygen deficiency in Graham's Ratio evaluation**

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ABSTRACT: There are a number of indicators used to determine the level of coal oxidation in underground coal mines. The common indicator Graham’s ratio is the amount of carbon monoxide produced in proportion to the amount of oxygen consumed by the coal. The more carbon monoxide produced relative to the oxygen consumed (oxygen deficiency), the greater the intensity of the coal’s reaction. Graham’s ratio is often used as a trigger for Trigger Action Response Plans (TARPs) for the management of spontaneous combustion. This emphasises the importance of accurate measurement of oxygen deficiency and ability to successfully determine the status of underground atmosphere. Samples with a similar composition to air may return a negative or minuscule measured oxygen deficiency unsuitable for Graham’s ratio. The same problem is identified in samples diluted with seam gas or when there are inaccuracies in other measured components when nitrogen is calculated by difference.

If the oxygen deficiency is inadequate and insufficient, the Graham’s ratio result can be overestimated and trigger a TARP level. If the minimum oxygen deficiency is set to inadequate level, in order to avoid alarm “fatigue”, there is a concern that valid data may be excluded from interpretation. The optimal value which indicates the beginning of spontaneous combustion event is site specific. This paper will present the case studies where the oxygen deficiency minimum limit has been adjusted to suit the mine site actual real data and analysis technique.

INTRODUCTION

Australian legislation is processed based legislation where mines are encouraged to manage and monitor their own risks. The mining companies achieve this through internally developed systems and processes, which effectively reduce the risks to acceptable levels. Spontaneous combustion is regarded as principal hazard in Queensland mines. Mines Principal Hazard Management Plan (PHMP) must identify the risks associated with principal hazards. To enable this identification TARPs are established, which outline trigger points at which action must be taken to prevent any incident from escalating (Cliff, Watkinson and Brady, 2018). Graham’s ratio is often used as a trigger for TARPs for the management of spontaneous combustion. This emphasises the importance of accurate measurement of oxygen deficiency and ability to successfully determine the status of underground atmosphere. If the oxygen deficiency is inadequate and insufficient, the Graham’s ratio result can be overestimated and trigger a TARP level. If the number of these false alarms is large, it can affect Control Room Operator (CRO) fatigue and introduce another risk of missing important non-false alarms.

As mentioned in Muller, et al., (2017), raw carbon monoxide concentrations are not always indicative of the intensity of a heating due to dilutions or accumulation of gases. By comparing carbon monoxide generated to oxygen deficiency a more relative measurement can be made (Graham’s ratio). This measurement is independent of air flow and various forms of the equation account for dilution effects (Cliff, Hester and Bofinger, 1999). In order to incorporate
the initial gas readings, and to incorporate nitrogen by difference to include effects of dilution, the following equation is applicable:

In order to incorporate the initial gas readings, and to incorporate nitrogen by difference to include effects of dilution, the following equation 1 is applicable:

\[
Graham's \ Ratio = \frac{100 \times (carbon \ monoxide_{final})}{0.265 \times nitrogen_{final} - oxygen_{final}}
\]

\[\text{(1)}\]

Note that the constant 0.265 is simply the theoretical ratio of oxygen to nitrogen in air. In order to incorporate the initial gas readings, and to incorporate nitrogen by difference to include effects of dilution, the following equation is applicable:

\[
Graham's \ Ratio = \frac{100 \times (carbon \ monoxide_{final})}{0.265 \times nitrogen_{final} - oxygen_{final}}
\]

\[\text{(1)}\]

is commonly used to calculate GR on real time sensors underground. The assumptions in this instance are that the ratio between oxygen and nitrogen in the inlet stream is the same as in fresh air, and that inlet contains no carbon monoxide. This is not applicable for inlet stream that is depleted in oxygen, enriched in carbon monoxide or enriched in nitrogen.

It is very important for a mine to establish a database for its deposit individual conditions. Using a measured fresh air value and taking dilution into account is represented by equation 2;

\[
Graham's \ Ratio = \frac{100 \times (carbon \ monoxide_{final}) \times nitrogen_{final}}{oxygen_{initial} \times nitrogen_{initial} - oxygen_{final}}
\]

\[\text{(2)}\]

Equation 2 is a common equation used to calculate Graham’s ratio for tube bundle monitoring points in underground coal mines. The measured fresh air point is typically from a point on the surface at the tube bundle building, or from an intake roadway underground. More detailed explanations are presented in Muller, et al., (2017).

As oxygen cannot be generated underground, it is logical that final oxygen can never exceed initial oxygen. Analysing equipment has a typical tolerance of +/- 0.2 % and small error is expected, which occasionally could present higher final oxygen readings than initial oxygen readings. Negative oxygen readings will produce negative Graham’s ratio, which is impossible result.

Muller, et al., (2017) states that current practice in mines is to apply the minimal oxygen deficiency requirement of 0.3 %, which eliminates the majority of non-reliable data points. Brady (2007) stated that Graham’s ratio can be unreliable for oxygen deficiencies below 0.3 %. Strand and MacKenzie-Wood (1985) state that the calculation is subject to analytical limits and that oxygen deficiency of less than 0.2 % would introduce gross errors. As the technology advanced since 1985, it is now possible to investigate, with greater confidence, the threshold value for this equation.

Investigation performed in Muller, et al., (2017) indicated that an oxygen deficiency of less than 0.3 % may still be reliable in some situations and generate critical data for underground air monitoring.

**METHODOLOGY**

As per conditions set in Muller, et al., (2017), the minimum oxygen deficiency value selected was 0.05 %, as this value appears to be the lowest and most conservative value. Data in the form of tube bundle logs were obtained from gas monitoring software. These logs were obtained from two underground coal mines in Australia, all of which had previously experienced and
flagged invalid Graham’s ratio triggers in their alarm logs and had their filter threshold points were set to 0.05 %. The locations containing low oxygen deficiencies (around 0.5 % or less) were chosen for the study. Each relevant data log was extracted to a Comma Separated Values file (CSV) containing the following information:

- Date and time of measurement and monitoring point number (location)
- Methane, Carbon Monoxide, Oxygen and Carbon Dioxide concentrations (%)
- Carbon Monoxide Make (Litres per minute)
- Graham’s ratio - calculated.

As per Muller, et al., (2017), in addition to these gas components, the Graham’s ratio calculated from the gas monitoring software, as per industry standards, was extracted with each set of gas readings. The CO value correlating with each data measurement was also extracted. These extracted data logs were processed in order to calculate a theoretical oxygen deficiency and theoretical Graham’s ratio values based on fresh air as the initial readings for real time data, and fresh air point for tube bundle data. For several tube bundle locations the measured initial air values were used rather than the theoretical initial values. This allowed the Graham’s ratio calculation to be replicated as accurately as possible, reproducing the actual values calculated by the mine site monitoring system before extraction. Locations processed in this regard were compared to locations processed using theoretical air values, as a means to validate extrapolation of the theoretical data.

The calculated Graham’s ratio value for each measurement was categorised based on the following thresholds:

- Normal data was defined as any data with corresponding theoretical Graham’s ratio calculated at 0.2 or below. This range is often used as normal conditions for spontaneous combustion management TARPs in Queensland mines (Mines Rescue Gas Detection and Emergency Preparedness, 2014).
- Investigate data is defined in this testing as any data with theoretical GR’s calculated at 0.2 to 0.4. This range is often used as an ‘investigate’ trigger for spontaneous combustion management TARPs in Queensland mines (Mines Rescue Gas Detection and Emergency Preparedness, 2014).
- An invalid trigger is defined as any data with theoretical Graham’s ratio calculated at over 0.4 without a corresponding significant increase in carbon monoxide or CO make.
- A valid trigger is defined as any data where the theoretical Graham’s ratio is calculated at over 0.4 with a corresponding significant increase in raw carbon monoxide or CO make associated with the data. By definition any Graham’s ratios over 0.4 which are not valid triggers are considered invalid triggers.

Filtering of tube bundle and real time data sets were based on minimum oxygen deficiency set points. Overall data retention, retention of normal data, investigate data points removed, invalid data points eliminated and valid data points eliminated were evaluated for each filtered data set.

RESULTS AND DISCUSSION

Two mines presented data for a three month period. The locations investigated in this paper were selected based on feedback from each mine. The locations showed the need to adjust applied filters in order to reduce control room operator alarm fatigue.

In the real time data set presented in Figure , the mine experienced large quantity of RG alarms, as the filter applied in that location was $O_{2i} - O_{2f} \geq 0.3$ % filter, ($O_{2i}$ is oxygen initial and $O_{2f}$ is oxygen final). Around 20th January, (note dates have been adjusted for confidentiality
The GR values exceeded 1 and triggered TARPs at the mine. Figure presents the same data set pre and post time when oxygen deficiency filter 0.05 % was applied. This filter, although conservative, removed the majority of invalid triggers.

![Figure 1: Case study, mine 1, Graham’s ratio (no oxygen deficiency filter (a) logarithmic scale, (b) values between 0-1 GR)](image)

In Figure, various filters were applied to investigate the most appropriate filter for this situation. Although the normal data retention was 100 %, 0.05 % filter did not achieve the reduction of invalid triggers. With the application of 0.2 %, 0.25 % and 0.3 % filters in oxygen deficiency, all suspect invalid data points were removed, while the retention of normal data points was 99.9 % for 0.2 % filter and 74.6 % for 0.3 % filter. The 0.2 % filter achieved a 42.89 % reduction in suspected invalided triggers, while retaining 68.7 % of data points.

Similar to the mine 1 results, the tube bundle data set from mine 2 indicated that no filter application, if $O_2i - O_2f \geq 0.3$ %, would result in false trigger alarms as in Figure a. With the application of 0.05 % filter on oxygen deficiency, these false alarms would be removed as in Figure b (around 23/08/2017).
Figure 3: Case study, mine 1, Graham’s ratio (applied oxygen deficiency filter (%)
0.05 (a), 0.1 (b), 0.2 (c), 0.25 (d) and 0.3 (e)), with CO (%)

Figure 4: Case study, mine 2, Graham’s ratio ((a) O₂i - O₂f ≥0.3 % filter, (b) oxygen deficiency filter 0.05 %)
There will however remain few false alarms. If higher filters were applied (0.2 % and above) there would be no invalid triggers in the end of June period. The mine investigated this instance and confirmed that GR alarm values were invalid triggers, period around 23rd August 2017, and there were no corresponding significant increases in CO or CO Make. The mine then accepted the 0.05 % filter change for this location. Furthermore, in period between 15th and 23rd of September, over 30 GR alarms were noted. The 0.05 % filter included these values and the mine investigated the situation. In this case there was an increase in CO and CO make, confirming valid triggers in GR ratios. If higher filters were applied in this case there would have been the possibility of valid data loss. Filter 0.1 % would still remove 100 % of invalid data, and retain 89.20 % of valid triggers, while higher filters, 0.2 % and above, would remove 100 % of valid triggers from this period (Figure ). Reduction of suspected triggers “investigate” is optimised with a 0.1 % filter (85.79 %), while a 0.05 % filter only reduces 54.64 % of suspected “investigate” data points.

Figure 5: Case study, mine 2, Graham’s ratio (applied oxygen deficiency filter (%)
0.05 (a), 0.1 (b), 0.2 (c), 0.25 (d) and 0.3 (e)), with CO (%)

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CONCLUSIONS AND RECOMMENDATIONS

The optimal oxygen deficiency filter is most likely dependant on mine deposit, individual database and measurement technique (instruments). It is possible that different locations may require different filter points. CO and CO Make filter could be considered as addition to oxygen deficiency filter for GR ratio trigger alarm. These parameters could also be included in TARPs together with Graham’s ratio. It is clear, based on presented data that different measurement techniques had different optimal filter points. Further testing and investigation is required for optimal alarm threshold points. It is possible that a 0.05 % filter for tube bundle, as suggested previously, is too conservative for this application and that 0.1 % or higher values may be more appropriate. Based on presented data set, the threshold value of 0.05 % did not appear optimal. However, the number of false alarms was considerably reduced and no positive alarms were removed by using a 0.05 % filter.

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