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# SPONTANEOUS COMBUSTION RELATED FIRE RATIOS

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## ABSTRACT

For explaining the situation arising from spontaneous combustion, there is a necessity for quick and accurate analysis of the gaseous products of combustion. It is also very important to interpret these data correctly. This interpretation provides information prominence to mine rescue crew and the mine management concerning the withdrawal or continuity of rescue team in a rescue and recovery operation before an explosion takes place. Additionally, it is also of utmost importance to see whether the fire combating techniques are effective or the fire is under control ensuring the security of workers and equipment during and after the sealing works. Therefore, the indices related with spontaneous combustion which are still commonly in use are summarised in this work.

**Key Words :** Spontaneous combustion, Fire ratios, Liability to heating

## KENDİLİĞİNDEN YANMA İLE İLGİLİ YANGIN İNDEKSLERİ

## ÖZET

Yeraltı ocaklarında kendiliğinden yanmadan kaynaklanan durumun açıklanmasında, yangına ait gaz ürünlerinin çabuk ve hassas analizine gereksinim vardır. Ayrıca, bu verilerin doğru olarak yorumlanması da çok önemlidir. Bu değerlendirme, herhangi bir yangın kaynaklı patlamanın oluşmasından evvel tahlisiye ekibinin içinde bulunduğu kurtarma çalışmalarına devam etmeleri veya geri çekilmeleri konusunda, ocak idaresine bilgi akışı sağlar. İlave olarak, yangınla mücadele tekniklerinin ne kadar etkili olduğu veya barajlama sırasında veya sonrasında işçilerin emniyeti açısından yangının kontrol altında olup/olmadığının bilinmesi son derece önemlidir. Bu nedenle, günümüzde halen yaygın olarak kullanılan kendiliğinden yanmaya ait indeksler bu makalede topluca verilmiştir.

**Anahtar Kelimeler :** Kendiliğinden yanma, Yangın indeksleri, Kendiliğinden yanmaya yatkınlık

## 1. INTRODUCTION

As deeply mentioned in the related literature, the observation of the build up of combustion gases alone may be risky in order to determine the spontaneous combustion. Some researchers, given throughout this work, therefore suggested the use of fire ratios. The reliability of these ratios has always been and even today being questioned. These ratios are supposed to assist in the detection of heating as early as possible and to state the progress most accurately. To be effective, the gas analysis used by these ratios must be rapid, accurate and precise. It should also be noted that the valid interpretation of the gas analysis results is at least as consequential as the results themselves.

## 2. FIRE RATIOS

If the temperature has already increased too much and can no way be stopped by localising or inerting, then it has to be relinquished by sealing off. In order to observe the outgrowths behind the seal, the gas samples are regularly, if not continuously, taken through the pipes already installed into the seal. Since the evaluation of these gases differs from the analysis of ventilating air, the fire ratios should be realised in two different assemblies (Saraç, 1992; Şensöğüt, 1997) :

a - Fire ratios for ventilating air and
b - Fire ratios for air behind seals.

## 2. 1. Fire Ratios for Ventilating Air

### 2. 1. 1. Graham's Ratio

The carbon monoxide/oxygen deficiency ratio has been generally accepted since the early 1920's as a scale for the presence of a heating or a fire. This ratio is also called Graham Index, Graham Ratio or Carbon Monoxide Index. The concentration of carbon monoxide analysed from the mine air progresses depending not only on the heating but on the function of air quantity. Therefore it should be stated that the observation of carbon monoxide make alone gives an erroneous results as the air quantity where the carbon monoxide measurement is conducted changes by time. In order to compensate this circumstance, the ratio suggested by Graham compares the rate of production of carbon monoxide with that of the oxygen consumed by the oxidised material. Since it has an independency of the amount of material oxidised, it provides a valuable tool for the intensity of the oxidising mass (Coward, 1957; Chamberlain et all., 1970; Gill and Browning, 1971; Morris, 1988; Banerjee et all., 1990; Mackenzie-wood and Strang, 1990).

This ratio is usually multiplied by 100 to give a convenient number. The method of calculation is simply based on the following equations:

$$GR = \frac{100 * CO}{\frac{20,93 * N_2}{79,04} - O_2} \qquad (1)$$

$$GR = \frac{100 \; * \; CO}{0,265 \; * \; N_2 - O_2} \qquad (2)$$

Where CO, $N_2$ and $O_2$ are the percentages of gases present at any given time in a sample of air coming from the area of heating in a mine.

In order to make a difference between a fire and a heating, Graham's ratio can be utilised as follows (Lama and Vutukuri, 1986):

| Graham's Ratio | Comments |
|---|---|
| 0.4 or less | - Normal value |
| 0.5 | - Necessity for a through check |
| 1.0 | - Heating almost certain |
| 2.0 | - Heating is serious |
| 3.0 | - Open fire |

The normal value of this index is usually 0.4 or less. In German hard coal mines, values upto 30 with incipient fires and upto 90 with open fires have been obtained (Ramlu, 1991). It was also reported that the rise of carbon monoxide/oxygen deficiency to a value of greater than 0.5 may be supposed as indicating serious heating prior to the development of an open fire (Willett, 1961-62; Chamberlain et all., 1970).

It is of paramount importance to establish a particular normal value for a colliery or panel return, as it is for the production of carbon monoxide, so that any increase occurred above this significance should stimulate suspicion.

### 2. 1. 2. The Ratio $CO_2$/CO

This ratio was also suggested firstly by Rhead and Wheeler in 1910 (Morris, 1988) followed by many others to evaluate the progress of heating. The main advantage of the ratio is that as the change of air quantity affects the numerator and denominator equally, the ratio is not influenced by the changes in the air quantity. In Figure 1, the influence of temperature on the ratio is shown (Morris, 1988)

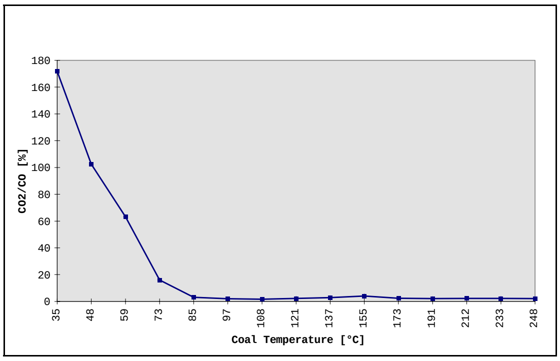


Figure 1. Changes in $CO_2$/CO with temperature (Morris, 1988)

It is merely seen from Figure 1 that initially the ratio $CO_2$/CO decreases sharply. After around 108 °C this ratio remains constant with an average value of 2.539 (Chamberlain et all., 1970; Morris, 1988) coinciding very much with the work of Nakata (1980). The plot of his results also confirms the previous conclusions that at lower temperatures (for his work up to about 225 °C), the ratio decreases rapidly with an increased rate at the temperature, but that as the temperature continuous to rise, the ratio seems to reach at an equilibrium (Figure 2).

It may be concluded that this ratio can be utilised at the onset of heating to indicate the rise in temperature. The main drawbacks of the ratio may be given as follows (Banerjee et all., 1990).

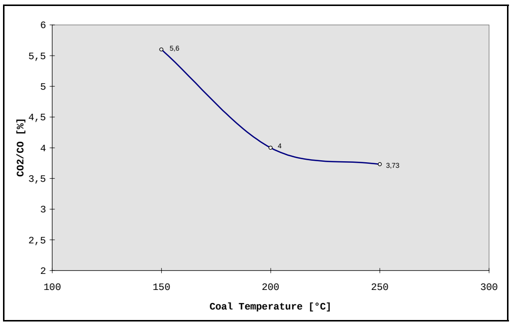


Figure 2. Changes in $CO_2/CO$ with temperature (Morris, 1988)

- After a certain level of temperature, it remains constant,
- The tendency of carbon dioxide to appear from various sources and
- Its dissolution in water.

### 2. 1. 3. Trickett's Ratio

Trickett's ratio is purely based on the principle that in fire molecules of each kind of matter consumed will have a proportion to the volumes of gases formed. This ratio is also used as a fire interpreter and expressed by the following formula (Trickett and Jones, 1954).

$$TR = \frac{\%\,CO_2 + 0{,}75\,\%\,CO - 0{,}25\,\%\,H_2}{0{,}265\,\%\,N_2 - \%\,O_2} \qquad (3)$$

It is mostly used to evaluate the suitability of samples and to determine the type of the fire. In the utilisation of Trickett's ratio, it should be born in mind that (Mackenzie-wood and Strang, 1990).

- The ratio will be erroneous if the intake air is oxygen deficient,
- It is not affected by fresh air dilution of the fire products,
- If the ratio is lower than 0.4, there is no fire and the gases are the residual then active and
- If the ratio has a greater value than 1.6 then there is an error in the analysis of sample.

These remarks can be summarised as follows (Mitchell and Burns, 1979).

| Trickett's Ratio | Comments |
|---|---|
| Greater than 1.6 | - Error in sampling or in analysis |
| 0.8 - 1.6 | - Timber fire |
| 1.0 | - Coal, oil or belt conveyor fire |

### 2. 1. 4. Carbon Monoxide Make

By using the actual build up of carbon monoxide from a suspected area, it may be possible to identify a heating and observe its progress. In case the carbon monoxide concentration and the air quantity is already determined, it may be stated that carbon monoxide formation of 10 L/min requires examinations and more than 20 L/min of production points out a considerable danger (Mackenzie-wood and Strang, 1990). It is worth to punctuate that this prediction method can be useful when Graham's Ratio is ineffective due to the inertisation of nitrogen.

### 2. 1. 5. The Ratio $N_2/(CO+CO_2)$

This ratio has also been used to predict the temperature of heating. It was stated by Partington (1919) that the ratio $N_2$/oxides of carbon increases together with an increase in temperature. However, the results of Chamberlain and his co-workers (1970) partly contradict and disprove Partington's work. It may be deduced from Figure 3 that the ratio $N_2$/oxides of carbon increases rapidly up to a temperature of around 200°C and then decreases sharply (Morris, 1988; Mackenzie-wood and Strang, 1990).

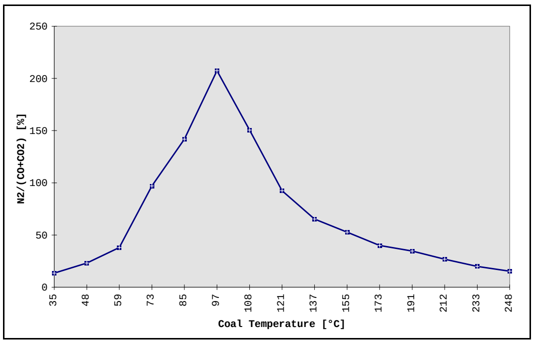


Figure 3. Changes in $N_2/(CO+CO_2)$ with Temperature (Morris, 1988)

### 2. 1. 6. The Ratio Carbon Monoxide or Carbon Dioxide/Methane

If the produced methane is fairly constant for a particular district, the ratios of the concentrations of carbon monoxide or carbon dioxide to that of methane would be useful in observing the oxidation process during the inertisation of nitrogen (Mackenzie-wood and Strang, 1990).

### 2. 2. Fire Ratios for Air Behind Seals

In case a fire has already progressed so far that it can not be stopped by localising, then the work of sealing off has to be commenced. In order to get an access behind the seal for recovering the equipment or to re-start coal extraction, the heating has to be completely stopped. It is therefore necessary to analysis of the gases taken behind the seal through the pipes inserted during the construction of sealing.

The ratios used to evaluate the fire incident behind the sealing differs from the ones used for the ventilating air as there is an intensive heating with no air income behind the seal. Under normal circumstances for the active heating, it may be commented on that the fire has deceased when the oxygen level falls below 12 %. However, the combustion at moderate levels may continue until the concentration of oxygen is lower than 2 % due to the combined effect of carbon monoxide and carbon monoxide. A conclusion of paramount may be drawn from this which is that the seal should be constructed in such a way that it is air tight.

Since there is not a single ratio alone in determining the status behind the seal, it may be necessary to check out with all the ratios known to have a mutual concern of the circumstance.

### 2. 2. 1. The Ratio CO/Oxygen Deficiency

This ratio is one of the most proven way used in sensing and assessing the state of combustion in sealed of areas (Chamberlain et all.,1970; Banerjee et all.,1990). However, it does not give any information on the amount of coal involved i. e. the extent of the combustion.

The major advantage of the ratio in concern that it has an independency of dilution of air or methane as both numerator and denominator are affected in in a similar manner by the introduction of additional air. Furthermore, the rise in the level of carbon monoxide and increase in carbon monoxide/oxygen deficiency is a definite test of commenting on the presence of heating and of evaluating its degree as carbon monoxide does not have any other extraneous originated source than heating by fire although transient appearance of carbon monoxide may be observed by fumes from diesel engines and during shotfiring (Mackenzie-wood and Strang, 1990; Banerjee et all., 1990). However, there are some limitations bound to this ratio which are:

- Only the average value is given, and therefore the maximum degree of heating in a sealed area is frequently under estimated (Willett, 1961-62).
- The ratio would also become invalid if nitrogen or oxygen deficient atmosphere passes over the heating (Mackenzie-wood and Strang, 1990; Banerjee et all., 1990).
- Oxygen deficiencies of less than 0.2 % would introduce intolerable errors (Mackenzie-wood and Strang, 1990; Banerjee et all., 1990).
- Carbon monoxide produced during the progress of heating usually decreases as the fire cools down. But, in cases when the disappearance of carbon monoxide may not comply with the decay of the fire and it may disappear even when the fire is not fully extinguished, particularly in wet mines (Banerjee et all., 1990).

### 2. 3. The Ratio $CO_2$/Oxygen Deficiency

In order to obtain evidences about the state of heating, the normal build up of carbon dioxide should be known in priority. This ratio may be used in the same manner as the carbon monoxide/oxygen deficiency index. In the further stages of fires, the production of carbon dioxide becomes superior thus causing this index to be essentially advantageous (Banerjee et all., 1990). However, as it is formed by other sources of irrelevant and due to its solubility, it has limited use. The evaluation of $CO_2$/oxygen deficiency presents similarity to the assessment of CO/oxygen deficiency.

This ratio can be used as follows

| $CO_2/O_2$ def. Ratio | Comments |
|---|---|
| > 25 | - Indication of a slight heating |
| < 50 | -It should be supported by other indices to decide on the presence of high intensive fire |

### 2. 4. Oxygen Consumption

It is a very well known fact that despite open fire being extinguished below an oxygen level of 12.4 %, coal can still keep heating for a great deal of time even at the 1-2 % oxygen level. If the temperature of the coal mass is not decreased to an ambient level, it will re-ignite due to re-introduction of air (Banerjee et all., 1990). According to Mason and Tideswell (1933-34), a mine fire is supposed to be extinguished, only in case of admission of air in the sealed off area, it does not become active again during the time which is required for the recovery of the area.

### 2. 5. Desorbed Hydrocarbon Index

It is principally based on the desorption of hydrocarbons from coal with an increase in temperature. Desorbed gas encountered at the ambient temperature is primarily methane while other hydrocarbons are also evolved with an increase in temperature.

The concentration ratio RI is defined as:

$$RI = \frac{1{,}01 * THC - CH_4}{THC + C} * 1000 \qquad (4)$$

Where;

THC : concentration of total hydrocarbons (ppm)
$CH_4$ : concentration of methane (ppm),
C : constant (0.01)

The concentration ratio decreases with cooling of the coal and increases with heating depending on the coal type. For bituminous coal, the index of RI is as follows

| The Index RI | Comments |
|---|---|
| 0-50 | - Normal temperature |
| 50-100 | - Possible source of heating |
| >100 | - Hot zone |

## 2. 6. Carbon Monoxide-Residual Gas Relationship

This ratio is primarily based on the rate of the variation of the amount of carbon monoxide in residual gas. The investigations carried out in the laboratory and through the in-situ works showed that a balanced value of the R index exists at normal temperature ($R_{eq}$). The value of the index in concern also increases with increasing temperature ($R_{act}$). Therefore, The ratio $R_{act}/R_{eq}$ would give the status of a sealed area on approaching deviation from normal temperature.

Calculation of the ratio $R_{act}/R_{eq}$ from compositional analysis is carried out as follows (Banerjee et all., 1990):

$$\frac{R_{act}}{R_{eq}} = \frac{1}{3}CO * R_g^{-\frac{3}{2}} * O_2^{-\frac{1}{2}} \tag{5}$$

Where;

$R_g$: residual gas content (100 - 4,77$O_2$ - $CH_4$ - $C_2H_6$)
CO: concentration of carbon monoxide (ppm)

The evaluation of the index is as follows

| The Ratio $R_{act}/R_{eq}$ | Comments |
|---|---|
| > 1 | - Higher temperature |
| < 1 | - Normal temperature |

This ratio is proved to be useful in predicting whether a sealed area has a normal temperature. It has such drawbacks that the ratio is not sufficient for gassy mines with high concentration of firedamp and oxygen percentage is less than 1 % and that due to bacterial activity etc. there is a great deal of instances where zero carbon monoxide is not indicative of heating.

## 2. 7. The Ratio Carbon/Hydrogen

The extent to which the carbon and hydrogen part of a fuel will burn is determined by temperature. It has been proven that hydrogen may burn completely at low temperature while unburned carbon tends to deposit as soot thus causing a reduction in the carbon/hydrogen value of the combustion products (Ghosh and Banerjee, 1967; Banerjee and Chakravorty, 1972; Banerjee et all., 1990).

The overall reaction of combustion may be explained as:

$$\underset{(Coal)}{C_xH_yO_z} + \underset{(Air)}{O_2 + 3{,}78 * N_2} \rightarrow CO_2 + CO + \text{hydrocarbons} + H_2 + N_2 + H_2O + O_2$$

From this, the Carbon/Hydrogen ratio of the combustion products may be found by:

$$\frac{C}{H} = \frac{6*(CO_2 + CO + CH_4 + 2*C_2H_4)}{2*\left(N_2 * \frac{20{,}93}{79{,}04} - O_2 - CO_2 + C_2H_4 + CH_4\right) + H_2 - CO} \tag{6}$$

This ratio can state the degree and extent of a fire in case it is used in conjunction with oxygen consumption data. It gives a better approach for the characterisation of a fire when the large sweep of values obtained for the C/H ratio compared to the ratio $CO/O_2$ deficiency. The C/H values obtained from burning of pure wood, cloth etc. is likely to be very high in view of the insignificant denominator.

The limitation of this method is that unlike the ratio $CO/O_2$ deficiency, it depends on the firedamp emitted from strata. The above ratio may also be affected by the dissolution of the gases in water and also from the non-uniform mixing of the products of combustion. It may give ambiguous results in cases of low oxygen deficiency values.

## 2. 8. The $N_2/(CO+CO_2)$ Index

This index may be practised in conjunction to state behind the seal although it was proved to be not suitable to examine the ventilating air. When the fire is put out, the value of ratio tends to decline. Furthermore, it shows a constant trend in case the fire is completely extinguished. Figure 4 shows the tendency in $N_2/(CO+CO_2)$ after the area of fire is sealed off. It can be deduced from this figure that the intensity of fire is reduced due to sealing (sharp fall from approx. 12 % to 4.5 %), however, a rise was then detected from approx.

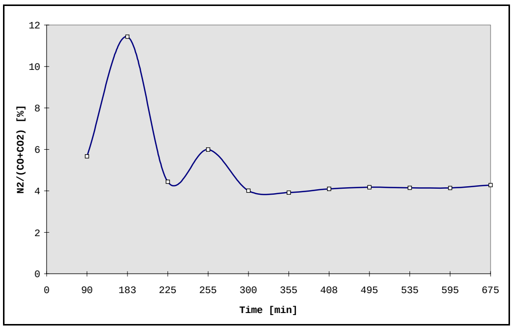


Figure 4. Changes in $N_2/(CO+CO_2)$ with time (Morris, 1988)

4.5 % to 6 % because of leakage as reported by Morris (1988). After sealing properly, it dropped and kept in constant proving that the fire is extinguished.

Although it is a proven index for sealed areas, it may not be utilised when inertising with nitrogen and in case of carbon dioxide income from irrelevant sources.

### 2. 9. The Dry Ash-Free (DAF) Oxygen Index

After a serial laboratory works carried out on South African coals by Gouws (1993), a predictive formula given below was proposed to outlay the propensity of coals to self-heat.

$$\text{DAF Oxygen Index} : e^{(0.907 + 0.126 * \text{daf oxygen})} \qquad (7)$$

The evaluation of the index is as follows

| The DAF Oxygen Index | Comments |
|---|---|
| > 10 | - High risk |
| 5 -10 | - Medium risk |
| < 5 | - Low risk |

## 3. CONCLUSIONS

As the result of spontaneous combustion, hazardous gases causing severe fatalities, loss of equipment worthing some millions of money – often exceeding $2.0 million (Singh et all., 1984) and loss of an exceptional amount of coal reserves may unfortunately be faced. Therefore, it should be the prime aim of the research team in every underground coal mines to determine the spontaneous combustion as early as possible. The ratios given in the text may well be utilised for this purpose.

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