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SOME INVESTIGATIONS INTO THE EXPLOSIBILITY OF MINE DUST LADEN ATMOSPHERES

A. D. S. Gillies and S. Jackson

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CONTACT: Dr Stewart Gillies, Department of Mining, Minerals and Materials Engineering,
University of Queensland, Brisbane Queensland 4072
Phone 07 33653738, Fax 07 33653888, email gillies@minmet.uq.oz.au

AUTHORS' AFFILIATIONS:

Dr Stewart Gillies, Reader in Mining Engineering,
Department of Mining, Minerals and Materials Engineering,
University of Queensland, Brisbane Queensland 4072
Phone 07 33653738, Fax 07 33653888, email gillies@minmet.uq.oz.au

Steven Jackson, Mining Engineer
Girilambone Copper Company, PO Box 12 Girilambone
New South Wales 2831
Phone 068 331091, Fax 068 331049

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ABSTRACT

An investigation into different aspects of importance in the understanding of explosibility of hybrid mixtures of coal dust, air and gases potentially found within mine workings through a comprehensive laboratory program of explosibility tests was conducted. Plotting of test results revealed that conditions of potential explosibility could be described using two dimensional flammability limit surfaces for coal dust/oxygen; methane/oxygen; and coal dust/methane mixtures. From these plots, the three dimensional flammability envelopes defining the explosibility of the coal dust/methane/oxygen mixtures can be defined and illustrated for a coal sample. The surfaces of the three dimensional envelope describe limits which separate inert mixtures of coal dust and methane at varying oxygen levels from those concentrations which are ignitable under defined conditions. It is considered appropriate to generalise that the geometric shapes of these limit regions are applicable to all type classifications of coal dust. There are practical applications of these results to the underground environment.

The action of free radical initiators in the propagation of a methane gas explosion was examined for its applicability to the flammability of coal dust/gas/air mixtures. The oxides of nitrogen or NO_x radicals have influence upon the lean limits of flammability of hybrid mixtures and this is illustrated by use of three dimensional coordinate geometry. Gases can be introduced to the underground environment through the exhaust gases of diesel equipment. It is concluded that radical species can substantially increase the flammability of gas and dust flames and as a consequence raise risk of mine atmosphere explosibility.

INTRODUCTION

Explosions are a continuing threat to the safety of operations in underground coal mines. Although each incident differs in structural details from others, one can nevertheless determine a typical scenario from the evidence of post disaster investigations (Hertzberg, et al., 1982). The usual sequence of events is for an initial

ignition in a methane/air mixture to raise and disperse clouds of coal dust from the mine floor and ribs, thereby creating an atmosphere capable of sustaining a rapid deflagration.

Many environmental and mechanical factors contribute to the explosion phenomenon. Modern mining methods and machinery are capable of high production rates from a single coal face resulting in the presence of increased levels of methane and coal dust which increase the risk of ignitions or explosions (Landman and Phillips, 1993). The production of coal dust quantities throughout the working sections of a mine is a byproduct of the cutting, loading and transporting operations conducted underground. Ventilation airflows carry the finer size fractions for some distances before being deposited onto floor, roof and ribs. In addition, high production rates in gassy mines can lead to the liberation of significant volumes of methane simultaneously with the formation of coal dust.

The lineal advances obtainable with modern mining equipment in high output workings in bituminous coal mines cannot always be fully utilised because of an inability to maintain methane concentrations below acceptable limits (usually 1.0 to 2.0 per cent by volume as enforced by mining regulations). Future development trends are towards greater face production output. This may lead to demands for changes in approaches to explosion suppression, improved ventilation and gas control measures.

From a safety point of view the question arises as to whether increasing the limiting gas concentration (assuming homogeneous mixing) involves an increase in the risk of explosion. This question cannot be answered simply, for an increased methane concentration may affect not only the development of an explosion but also the incendivity of the airborne dust (Reeh, 1980). Dust concentrations that are currently of no practical importance with regard to explosion potential may, in combination with significant methane levels, present a hazard. High energy sparks which may ignite methane at very low concentrations can lead to a propagating explosion. It is therefore of interest to determine how high energy ignition sources interact with coal dust/methane/air mixtures ("hybrid mixtures"). The primary objective of this study can broadly be defined as an investigation into the ranges of explosibility of a Queensland coal dust in mixture with methane under varying oxygen levels.

Diesel equipment finds wide use within the underground coal mining industry for the transport of personnel and equipment. As a result the composition of diesel exhaust gases has been widely studied in an effort to reduce the health hazards posed by toxic gases such as carbon monoxide and the various oxides of nitrogen. However recent work has established that some exhaust gases can ultimately increase the explosibility of mine atmospheres containing both coal dust and methane.

The action of free radical initiators in the propagation of a methane gas explosion has been examined for its applicability to the flammability of coal dust/gas/air mixtures. The influences of the oxides of nitrogen or NO_x radicals upon the lean limits of flammability of hybrid mixtures have been investigated and some results are illustrated by use of three dimensional coordinate geometry.

BACKGROUND

The flammability of a system is describable as some form of limiting geometric surface that delineates a domain of flame propagation within from a region outside of that surface where flame propagation is not normally possible. That mathematical surface, the flammability limit surface, describes a discontinuity in the real combustion behaviour of any system. Its exact size and shape in space are of basic significance in evaluating the practical hazards involved in the use of fuels, refined substances, and synthetic chemicals.

In the case of the explosibility of coal dust, work has been conducted upon the two dimensional explosibility surface for coal dust with respect to oxygen concentration. European researchers (Deguingand and Galant, 1981; Krzystolik and Sliz, 1988; Bartknecht, 1989; Wolanski, 1992) have hypothesised that while the lean limit concentration of dust is not greatly influenced by a reduction in oxygen concentration the rich limit concentration is significantly affected (figure 1).

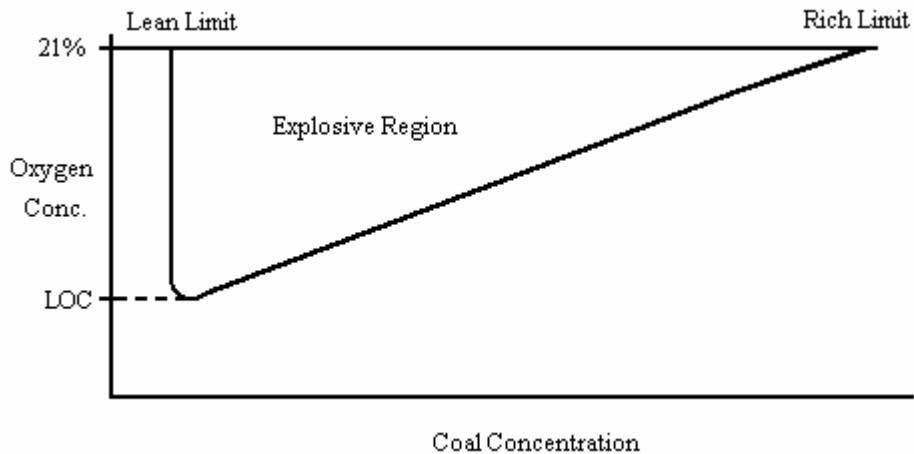


Figure 1 The surface of explosibility for coal dust and oxygen (after Bartknecht 1989).

This surface is broadly definable by three points, namely the lean limit, rich limit and limiting oxygen concentration (LOC). The minimum suspended dust concentration in air that can sustain flame propagation is referred to as the lean flammability limit. There is a potential for a dust/air explosion in any environment in which the concentration of dust in air is above the lean flammability limit given an adequate ignition source.

These findings suggest that an approximate value for the rich limit can be determined by extrapolation of limiting oxygen concentrations at two or more dust levels to determine the intercept at 21 per cent oxygen and so the corresponding dust concentration.

The limits used to define the explosibility of a coal dust are the same as those defined for methane mixtures (figure 2). Coward (1929) derived the methane/oxygen relationship from empirical data that depicted whether mixtures of methane and oxygen in mine air were potentially explosive under certain conditions. Coward's triangle indicates that methane gas is explosive between approximately 5 and 15 per cent by volume when mixed with air. Each of these diagrams represents a two dimensional mathematical surface of compatible dimension defining the explosibility of the respective reactive fuel in the presence of a variable oxygen concentration.

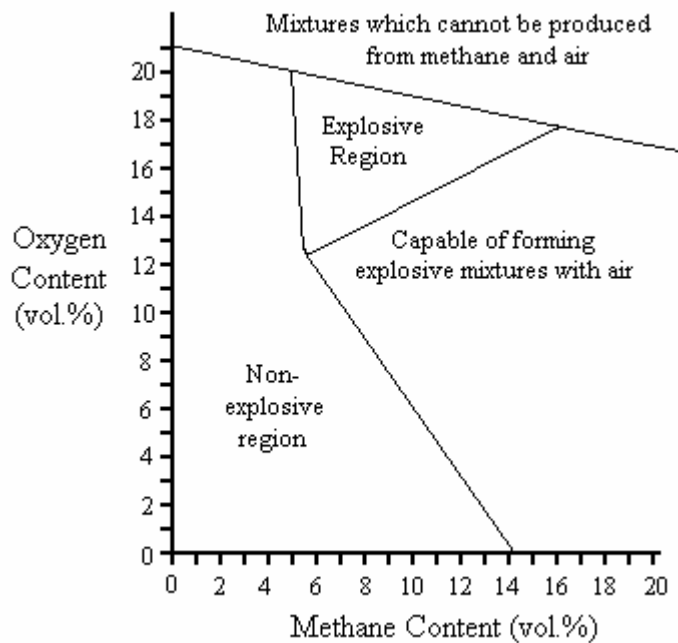


Figure 2 Coward's Triangle for methane (after Coward, 1929).

The methane/oxygen explosibility diagram is especially significant as methane is the most frequent constituent involved in mine explosions. However, major mine disasters caused by explosions invariably, in addition, involve coal dust. It therefore follows that these two diagrams could be utilised to draw a three dimensional envelope representing hybrid explosible mixtures. The dimensions for the envelope would be defined by the explosion limits of the coal dust, the methane and the limiting oxygen concentrations for both the dust and gas.

Foniok (1985) defined a hybrid dispersive mixture as flammable dust in air with a small addition of flammable gas. This mixture has lower lean limits of explosibility than either of the flammable constituents.

Further, a reduction in the minimum ignition energy to ignite the mixture and a reduction in the most explosive concentration of dust is apparent.

Le Chatelier's law can predict the decrease in the lean flammability limit with methane admixture (McPherson, 1993). Le Chatelier proposed a linear relationship that weighs the lean limit for each of the two components (methane and coal dust) according to the percentage of each in the hybrid mixture.

The three dimensional geometric surface defining the explosibility of hybrid mixtures of coal dust and methane gas under varying oxygen concentrations will be defined according to the explosion limits of the fuel. The concept of the three dimensional geometric surface has been described by Gillies and Jensen (1994). The size and shape of the explosibility envelope is defined by the explosion limits of the respective coal samples (Lebecki, 1991) as methane can be considered to be a constant fuel source.

The oxides of nitrogen (NO_x) are a common product found within diesel exhaust gases. Several oxides of nitrogen are usually found together and are collectively known as nitrous fumes (Le Roux, 1990). Nitrous fumes, being a mixture of NO , NO_2 , N_2O_4 and perhaps some N_2O_3 , are within the mine environment present in the exhaust gases of diesel engines and are produced in small quantities by both oxyacetylene welding and arc welding. Of particular interest with regard to nitrous fumes is the characteristic that in the presence of high energy sources the fumes can act as a radical initiator. The result of this action is the formation of NO and NO_2 radical ions. A radical can be defined as an atom or group of atoms with an unpaired electron and includes such species as triphenylmethyl, chlorine atoms, sodium atoms and nitrogen dioxide (Nonhebel and Walton, 1974). Many free radical reactions are brought about by the addition of radical initiators to the reaction system. These initiators break down to form the free radicals.

A large body of work (Sosnovsky, 1964; Peters, 1991; Leffler, 1993) confirms that nitrogen dioxide free radicals will enhance the reactions of hydrocarbons through a nitration process. The ease with which gas-phase nitration occurs depends upon the nature of the hydrocarbon. The hydrocarbons that more readily yield radicals are usually the ones that are most easily nitrated. For example, methane is more difficult to nitrate than ethane as higher hydrocarbons can more easily disperse the methyl free radical.

There are only a small number of publications referring to the temperature depression effects of NO_x gases on methane ignition and related aspects under circumstances found within the mining industry. Coward (1934) described "concentric tube" ignition experiments undertaken by Dixon. He found that retention of

traces of NO_x dramatically reduced the ignition temperature of many combustible gases with a maximum depression of ignition temperature for methane/air mixtures of 122°C in the presence of 7000 ppm NO_x. The Twentieth Annual Report of the British Safety in Mines Research Board (1941) reported that the presence of 2000 ppm NO_x in a gaseous explosive mixture of air and hydrocarbons of 16 per cent ethane in methane was found to have its ignition temperature depressed from 732 to 550 °C. Later Annual Reports (1942/43/44) from the same organisation reported that a powdered explosive (70 per cent ammonium nitrate and 10 per cent nitroglycerine) introduced into air as fine particles depressed ignition temperature of methane/air mixtures from 700 to 370°C.

Fairhall (1993) in a study at The University of Queensland confirmed the earlier findings of Dixon. He found that the introduction of chemically produced laboratory NO_x gases into a methane/air mixture gave a 106°C ignition temperature depression at an introduced gas concentration of 1600 ppm.

Diesel engines are in widespread use in modern underground coal mines. To achieve safe operating conditions, regular engine maintenance is required and maximum power output may have to be reduced and engine derating undertaken when operating at altitude by reducing the fuel injector setting to account for decreased atmospheric pressure. Australian state mining regulations set maximum NO_x exhaust limits of 1000 to 2000 ppm. Fairhall (1993) reported some diesel emission data from a survey of working equipment in an Australian coal mine. He found that raw exhaust gas tests of five diesel machines using "Draeger" gas analysis stain tubes reported NO_x emissions generally within the range of 300 to 400 ppm. One machine produced readings of 800 and 1000 ppm over two tests. Exhaust oxygen levels were generally less than seven per cent and carbon dioxide in excess of ten per cent. Within the general body of mine air the maximum NO_x concentration recorded was 2.5 ppm in an air split with more than one unit of equipment in use. Examination of raw exhaust readings from another mine with 20 units of diesel equipment in use revealed NO_x emission levels across the range 20 to 600 ppm.

LABORATORY MEASUREMENTS

A series of experimental determinations of the combustion behaviour of both coal dust and gas mixtures was conducted within a standard 20 litre explosion chamber sphere. Siwek (1982) described the design and standard method of operation of this chamber for the laboratory determination of dust and gas explosibility. A homogeneous dust cloud can be formed within the chamber through evacuation of the chamber followed by pneumatic dispersion of the pulverised dust. Methane and any other gases are added with a syringe. An

ignition source comprising two chemical igniters is used to provide ignition energy of 10 kJ. Controls placed upon the system ensured that all tests were conducted with standardisation for both atmospheric temperature and pressure. Undertaking three identical tests at each concentration and five tests at each limit concentration tested repeatability of results. Details of the experimental approach are described in Jackson, Gillies and Gollidge (1997).

Although use of the 20 litre explosion test sphere has gained international acceptance for the laboratory evaluation of dust and gas ignitions, there exist two standard methods for defining an explosion. The principal difference between these is the ignition energy to be used. The standard set by the American Society for Testing and Materials (ASTM E1226-88, 1994; ASTM E1515-93, 1994) recommends the use of a low energy ignition system with energy level no higher than 2.5 kJ. On the other hand, the International Standards Organisation (ISO 6184/1,2,3, 1995) recommends the use of a 10 kJ ignition energy for the testing of combustible dusts and a 10 J ignition energy for the testing of combustible gases.

These recommendations also carry over to the testing of hybrid dust/gas flames where the ISO recommends use of the 10 kJ energy due to the presence of dust. However, by virtue of the reaction mechanism, gas flames and therefore hybrid flames are vulnerable to being overdriven by high ignition energy. As a result a discontinuity exists between the lean limit result for the high energy tested hybrid mixtures and the lean limit result for the low energy tested gas mixtures under ISO conditions. The ISO therefore recommends that when gas results are to be juxtaposed with hybrid results, the 10 kJ energy must be used (Siwek, 1982). As a result the lean limit values determined for methane using the ISO standard are significantly less than the accepted result of 5.0 per cent by volume predicted by the ASTM standard.

For this investigation, results have been obtained and evaluated using both standards. It can be concluded that the explosion limits predicted by the ISO standard encompass dust and gas mixtures that will ignite but not propagate unless the shock wave produced by the ignition can subsequently raise dust into the atmosphere thereby creating a dust concentration within the ASTM explosive region. Those mixtures defined as explosive under ASTM conditions have properties to propagate a flame so long as neither the airborne dust or gas concentrations decrease.

COAL DUST EXPLOSIBILITY

Proximate analysis for the test coal sample is shown in table 1.

Table 1 Proximate analysis result, %, for coal sample.

Moisture	2.0
Ash	23.1
Volatile Matter	22.2
Fixed Carbon	52.7

The lean and rich limit explosion data determined using the 20 litre testing chamber are shown in table 2. The testing of rich limits is inherently difficult due to the high dust concentrations involved, and as such, the rich limit data can only be taken as indicative of the real behaviour.

Table 2 Lean and rich limit data, g/m^3 , for the coal dust sample.

Standard	ISO	ASTM
Lean Limit	40	60
Rich Limit	5500	5000

In addition to these results, the experimental series investigated the limiting oxygen concentration for the coal sample. In this case, the gaseous agent used to reduce the oxygen concentration within the vessel was nitrogen gas. It would be expected that if carbon dioxide were used as an inerting agent it would give results that vary slightly from those presented here. The results from the 20 litre chamber at reduced oxygen concentrations are shown in table 3.

Table 3 Limiting oxygen concentration (LOC) data for coal sample.

	Oxygen(vol %)	ISO	ASTM
LOC (20 l) %		7.0	8.5
Lean Limits (20 l) g/m³	21	40	60
	15	50	80
	10	60	130
	9	70	150
Rich Limits (20 l), at 8.5 vol % oxygen, g/m³	8.5	230	200

METHANE EXPLOSIBILITY

Coward's triangular shape for the limit surface of flammable gases has been widely applied to a variety of gases over an extensive range of ignition energies and explosion chamber types. The results obtained under ISO standards increased the range of explosive concentrations beyond those normally accepted. Siwek (1982) and Bartknecht (1989) have shown that increased ignition energies will reduce the lean limit value for methane ignitability and that high energy igniters (of the rating used) do not over drive the resulting explosion. The explosion limits for methane in air are illustrated in table 4.

Table 4 Lean limits, vol%, for the flammability of methane gas in air.

	ISO	ASTM
Lean Limit	2	4.5
Rich Limit	27	16
Nose Limit		
Methane	4	6
Oxygen	12	12

The limits resulting from the ASTM criteria mirror those results that are generally accepted for methane gas explosibility. The ISO data has expanded explosion limits results for all but the limiting oxygen

concentration of 12 per cent oxygen. The explosion curves produced by the gas ignitions indicate that energies greater than 10 kJ have a significant effect upon the rate of gas ignition. This increase results in a subsequent increase in the explosion pressure produced by the gas ignition. It is unlikely that these increases caused by the high ignition energy will result in a propagating explosion. However, the possibility exists that the increased explosion pressure could raise mine dust into the atmosphere (Siwek, 1982). The ISO standard has been formulated to include these possibilities.

HYBRID MIXTURES EXPLOSIBILITY

Lean limit data at normal atmospheric oxygen concentrations for the coal dust sample in admixture with methane gas are illustrated in figure 3 which presents limit data over the range of gas concentrations for which explosions could be initiated. The data has been plotted to present an explosion profile with the coal dust concentrations on the vertical axis and the gas concentrations on the horizontal axis. The values determined for the lean limits of the methane gas in table 6 are taken as the first point of each curve on the horizontal axis. The vertical axis intercepts are taken from the limit data for the coal dust samples. All points between these two represent the measured values for lean limit concentrations at various methane concentrations.

The resulting curves for each sample divide the graphs into three regions. Dust/gas mixtures with concentrations higher than the lean ASTM standard curve are capable of propagating a flame away from the ignition source without the necessity of added fuel. Concentrations falling within the region between the two standards represent those mixtures that cannot be guaranteed to propagate a flame. However these concentrations are capable of producing a shock wave of sufficient intensity to raise dust into the atmosphere, thereby creating a hybrid potentially explosive mixture. The lower region indicates mixtures that were found to be non-explosive under the ignition conditions within the explosion chamber. The ISO curves follow the trends predicted by Le Chatelier's law with a generally direct linear relationship. However the ASTM curve shows a trend toward a curve where the adsorbed methane alters the behaviour of coal insofar as its explosibility is concerned, even increasing the magnitude of the explosion to a greater extent than the alterations caused by the presence of methane in the atmosphere together with coal dust. This effect has been found in previous work (Torrent and Arevalo, 1993).

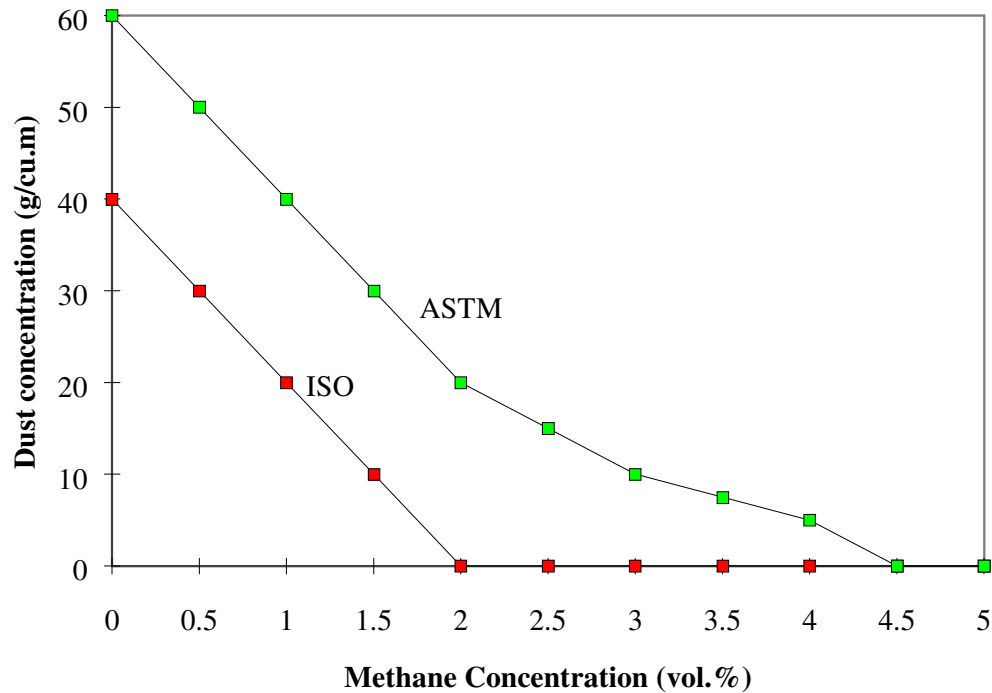


Figure 3 Lean limit data for the coal sample.

The results obtained for the rich limit curve cannot be considered as reliable as those for lean limit. The laboratory testing of rich limits is inherently difficult due to the size of the equipment and the volume of dust required. It therefore becomes difficult to maintain a stable homogeneous dust cloud at the required concentration. Nevertheless, rich limit concentrations were determined although due to the reduction in accuracy for concentrations above 1 kg/m³, testing increments of 200 g/m³ were used. The rich limit data are shown in figure 4. The curves again portray three regions akin to the situation with lean limit curves. Both the ISO and ASTM curves follow the same trend with a near straight line relationship below 10 per cent by volume methane. However above 10 per cent methane, the coal dust rich limit concentration becomes more dependent on the methane concentration under ASTM conditions than under the ISO conditions.

The rich limit curve for the hybrid mixture is determined mainly by the limiting oxygen concentrations (LOC) of the dust and gas. The LOC for the hybrid mixture is taken to be the lowest value of either the LOC (dust) or LOC (gas). In most cases, the LOC of the dust is the lowest value and therefore becomes the LOC value for the hybrid. As shown in figure 5, the LOC for the dust (and therefore the hybrid) occurs at dust concentrations between 50 and 100 g/m³. At this dust concentration the limiting effect from the displacement of oxygen by methane is at its most pronounced.

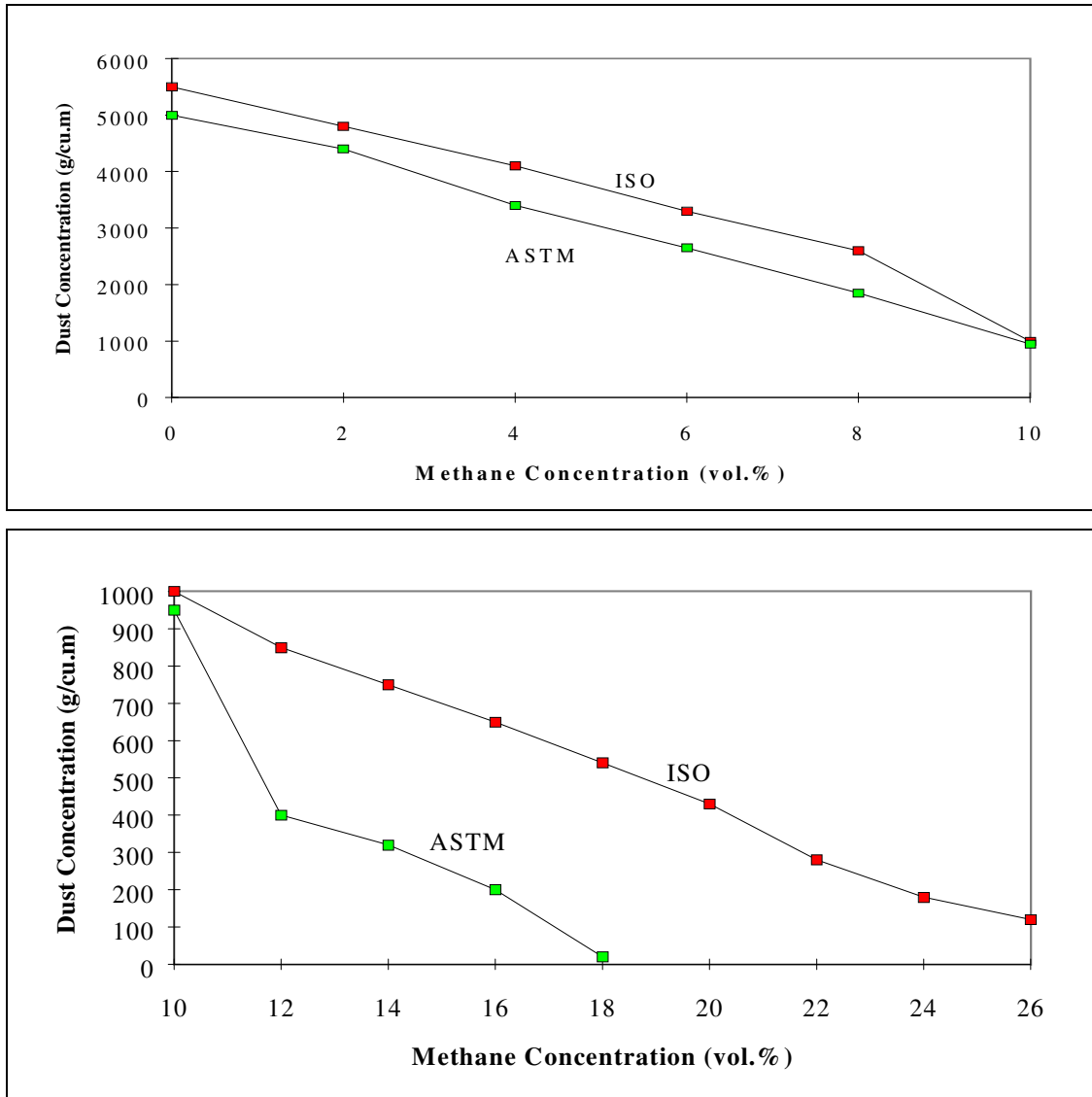


Figure 4 Rich limit data for the coal sample

It is possible to speculate on the reasons for this behaviour with the ISO curve used as an example. The experimental series did not continue beyond 30 per cent by volume methane due to the inaccuracies in gas mixing at such high concentrations and therefore the rich limit curve could not be continued. However, by using the LOC for 30 g/m³ of 11 percent by volume oxygen and assuming that methane has the same effect as nitrogen, a rich limit value of 47 percent by volume methane is obtained. The rich limit action of methane is not simply explained by inertisation of the atmosphere through oxygen depletion. Methane in this reaction undergoes a slow combustion under which more energy is consumed than is produced. While there may be sufficient oxygen to allow an initial ignition to occur, it does not progress as the released energy by combustion is less than the ignition energy required for propagation of the explosion within the surrounding atmosphere.

LIMITING FLAMMABILITY SURFACE FOR THE HYBRID MIXTURE SYSTEM

Data discussed to this point has been two dimensional in nature, presenting information on the behaviour of dust/oxygen, methane/oxygen, or dust/methane mixtures. Gillies and Jensen (1994) have shown that these two dimensional explosibility surfaces can be brought together to form a three dimensional mathematical surface describing the flammability limits of dust/methane/oxygen mixtures potentially found within the underground environment. This envelope, the flammability limit surface, has been defined for the coal sample under both ISO and ASTM conditions in figure 5. As explained previously, the ASTM region includes mixtures that are capable of propagating a flame out from the ignition source. The ISO region poses a marginally lower hazard, as the mixtures cannot propagate a flame on their own. These mixtures require the addition of more dust or gas, or a slightly higher oxygen concentration to allow an explosion to occur. However the power of the initial ignition produced by these mixtures is sufficient to raise dust into the general body of air. Such an event could lead to a propagating explosion.

It is therefore evident that the ignition source and the ignition energy will significantly alter the size and shape of the flammability envelope with respect to both the coal dust and the methane gas. For the methane gas in particular, both the ASTM and ISO standards produced lean and rich limit data at variance to generally accepted results. Under the ISO standard at high ignition energy the lean limit for the methane was found to be as low as 2.0 per cent by volume. The experiments indicated that increased ignition energy would expand the explosion limits of methane gas. Far from overdriving the gas flame within the laboratory chamber, the increased energy simply allowed the gas to burn at a faster rate. Bartknecht (1989) has determined that this laboratory simulated effect will extrapolate to the real environment.

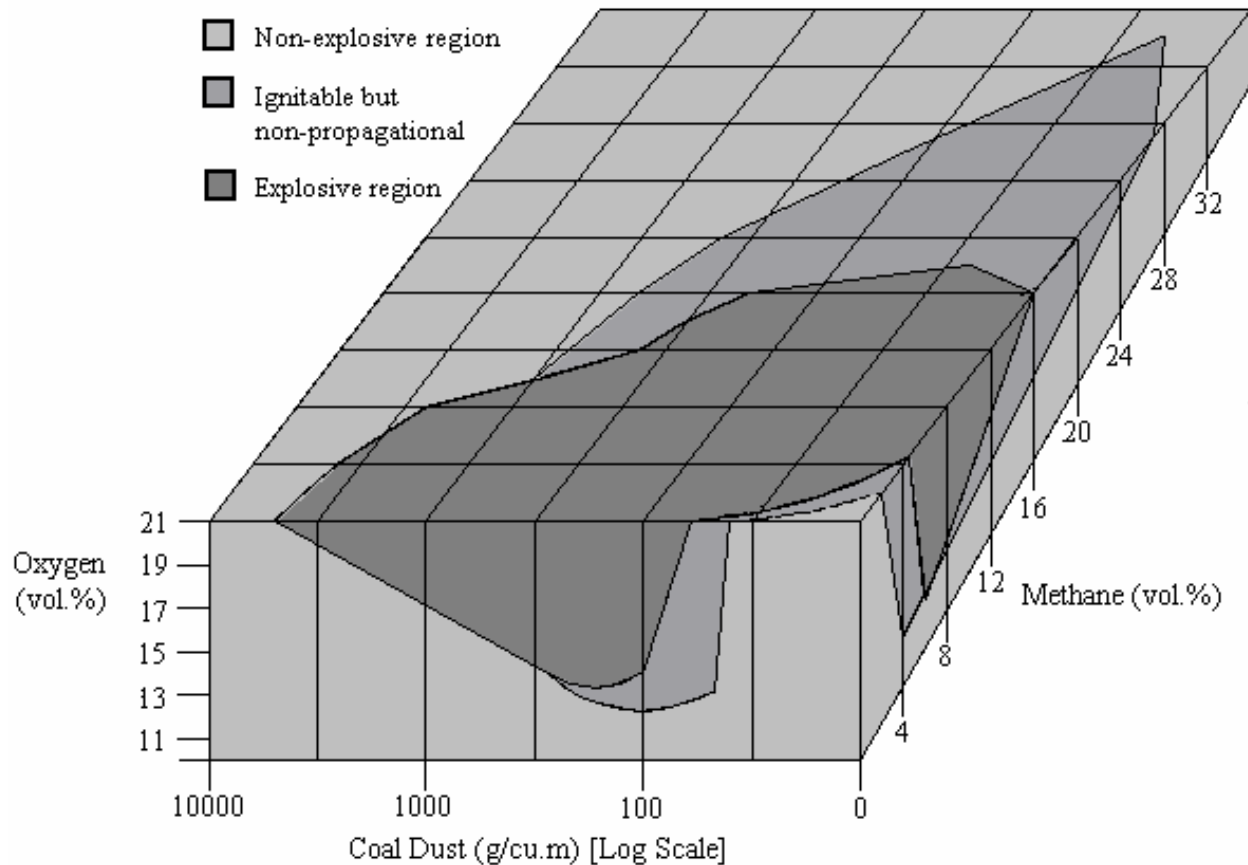


Figure 5 Absolute flammability limit surface for the coal sample

THE INFLUENCE OF NO_x ON EXPLOSIBILITY OF COAL DUST/METHANE GAS HYBRID MIXTURES

A comprehensive experimental series was undertaken to determine the lean limits of flammability for dust, gas and hybrid mixtures in the presence of NO_x gas. The tests were conducted at methane concentrations from 1.0 to 18.0 per cent by volume with addition of 2000 ppm of NO_x. This test concentration level of NO_x was selected as representative of the upper statutory limit allowable under some Australian mine regulations. Results indicated that the NO_x gas can reduce the lean limit concentration for methane under ISO standards with an ignitable mixture of gas being formed from as little as 1.5 per cent methane by volume. Data has been plotted in figure 6 under ISO standards and figure 7 under ASTM standards. These curves clearly show the reduction in the lean limit values in the presence of the 2000 ppm NO_x. The effect of the radical on the ISO standard is substantial. The effect on the ASTM standard curve is also significant with the methane lean limit reduced to 3.5 per cent by volume and the dust lean limit to 40 g/m³.

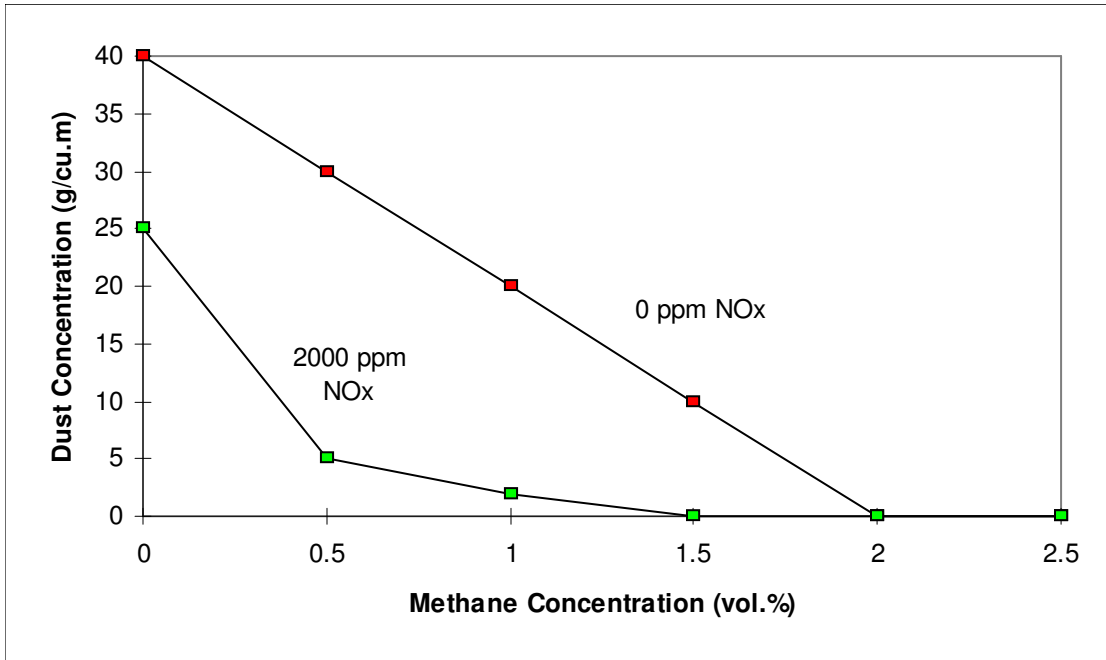


Figure 6 Influence of NO_x on lean limits of hybrid mixtures under ISO standards.

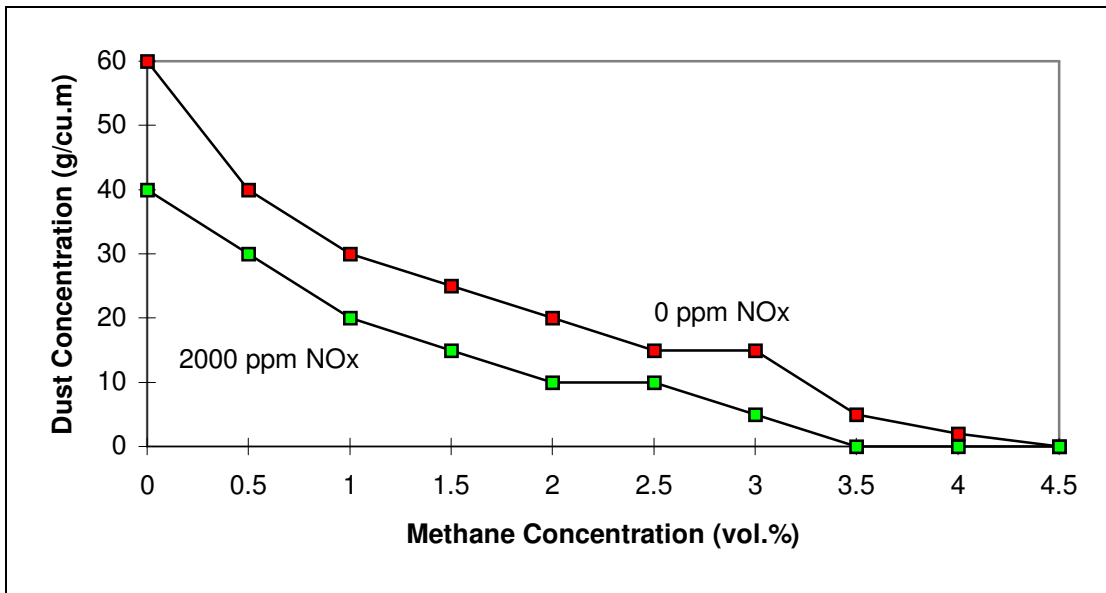


Figure 7 Influence of NO_x on lean limits of hybrid mixtures under ASTM standards.

Figures 6 and 7 curves have characteristic shapes dividing the region into three distinctive sections. Under both standards the maximum decrease in the lean limit values occurred at less than 1.5 per cent by volume methane.

The experimental series also investigated the influence of the radical initiator upon coal dust at lowered oxygen concentrations. This testing could not be expanded to include the testing of methane gas at lower oxygen concentrations due to the difficulties in adding the methane and NO_x to the 20 litre test chamber in accurate quantities. When the NO_x/air mixtures were formed, the resulting oxygen/nitrogen ratio was no longer 21:78. The results from limited oxygen concentration testing on dust at a single concentration of NO_x of 2000 ppm are shown in table 5.

Table 5 Limiting oxygen concentration (LOC) for dust in air under the influence of NO_x free radicals.

NO _x Concentration	0 ppm		2000 ppm	
	ISO Coal Dust (g/m ³)	ASTM Coal Dust (g/m ³)	ISO Coal Dust (g/m ³)	ASTM Coal Dust (g/m ³)
21.0	40	60	25	40
15.0	50	60	30	50
10.0	60	120	40	80
9.0		LOC		LOC
8.5	70		50	
7.0	LOC		70	
6.0			LOC	

At standard atmospheric oxygen concentrations the presence of the radical acts by reducing the influence of the rate determining reactions which form part of the methane gas flame system. However at lower oxygen concentrations, the presence of NO_x acts to remove the dependence of the reaction on the oxidation process and replaces it with a nitration process. This effect is only limited owing to the small quantity of NO_x present in the tests with the result that LOC values did not extend below 10 per cent by volume.

HYBRID MIXTURES IN ADMIXTURE WITH OXIDES OF NITROGEN

Testing was conducted upon concentrations of hybrid mixtures of methane gas and coal dust. A laboratory produced gas mixture of NO, NO₂ and air at a concentration of approximately 2000 ppm of NO_x was added to these mixtures. The results indicated that the presence of NO_x has a significant effect on the explosibility of coal dust/methane/air hybrid mixtures. Figure 8 graphically sets down lean concentration findings under ASTM definition standards.

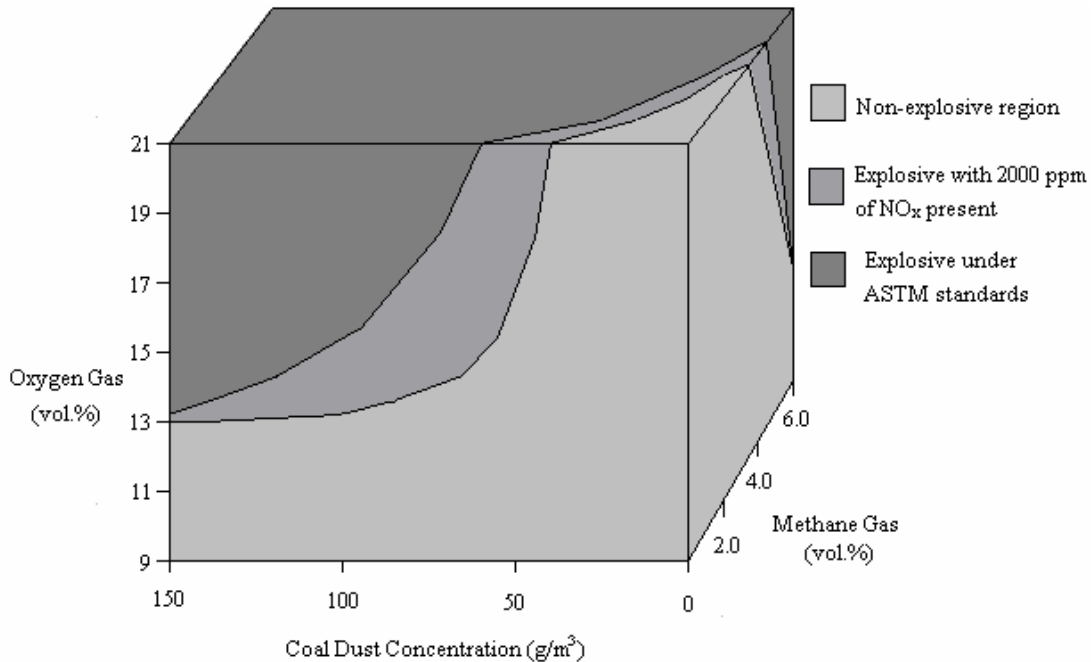


Figure 8 Effect of presence of free radicals upon coal dust/methane/air hybrid explosibility under ASTM definition standards

This three dimensional block represents the explosive envelope for the hybrid mixtures at varying oxygen concentrations. The lightest shaded region illustrates atmospheric concentrations under normal temperature and pressure conditions at which an underground coal mine may operate without the potential of ignitions occurring. If, however, 2000 ppm of NO_x gas is present in the atmosphere, the dark potentially explosive region is expanded to include the marginal grey region to account for reductions in the lean limit values for dust/gas hybrid mixtures. The situation using the ISO standards interpretation is illustrated in figure 9.

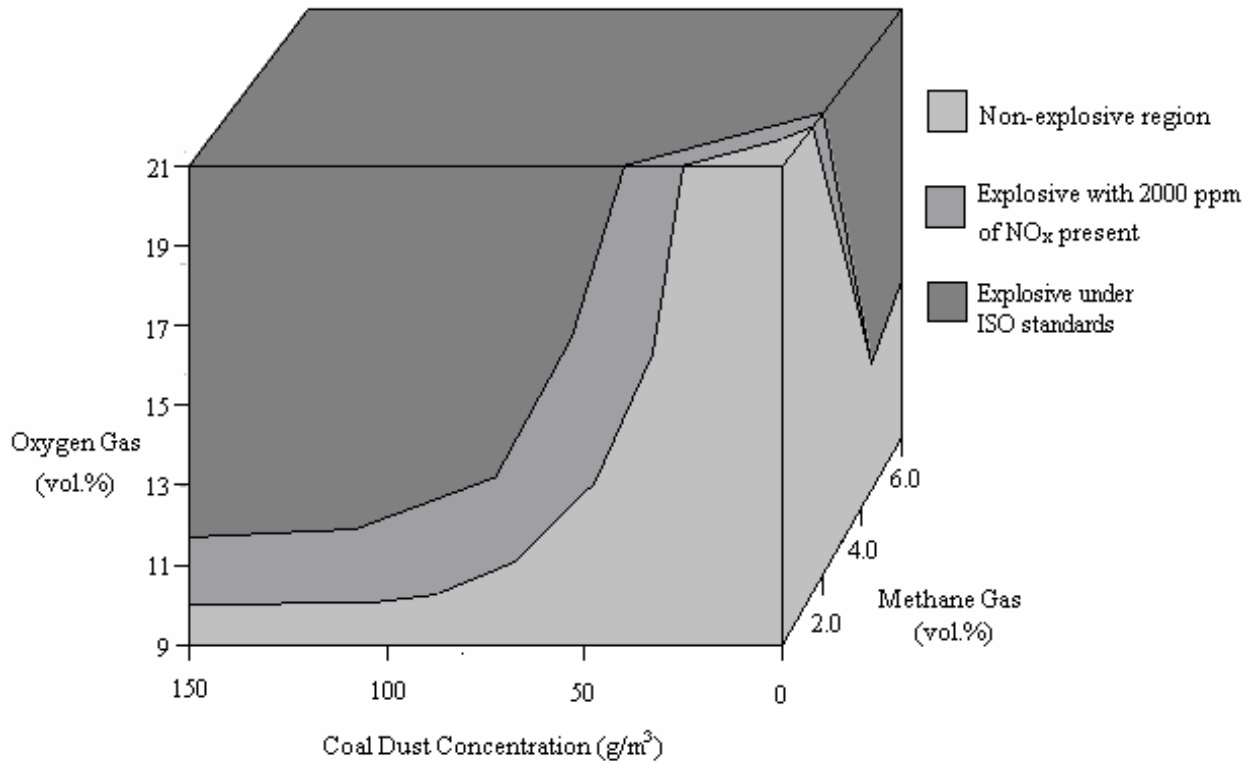


Figure 9 Effect of presence of free radicals upon hybrid atmosphere explosibility under ISO standards.

It can be seen that the oxides of nitrogen gas have a significant effect upon minimum oxygen concentration levels required for a potentially explosive mixture. This is due to the fact that the oxidation of the fuel has been replaced to some degree by the nitration of the methane gas. This allows the methane to produce the methyl free radical readily at low oxygen concentrations. However the reaction system requires some oxygen due to the low concentrations of nitrates and so a limiting oxygen concentration is observed. The effect of nitrates upon coal dust in the absence of methane is largely due to the volatile gases produced by the initial heating of the coal grains. The nitrate radical will attack these volatiles thereby reducing the lean limit concentration for dust.

The influence of nitrous fumes acting as free radicals to increase the rate of reaction for combustible gases has been examined and the effect shown to be significant. Of particular significance is the effect of the radical upon lean limit concentrations necessary for an ignition leading to a propagating explosion to occur. However the probability of nitrous fumes from diesel exhausts building to sufficient quantities to constitute a hazard is low due to the high quantities of mine ventilating air that are found under modern mining method.

Coal mine regulations have been formulated based on generally understood combustion behaviour of gases tested in isolation or commonly occurring mixtures such as coal dust/methane atmospheres. It would appear

that empirically based studies are required to confirm the behaviour of complex gas mixtures that may be found underground with increasing use of mechanisation and introduction of various "artificial" manmade materials.

The possibility exists that the action of the radicals can be used to increase the safety of underground operations. A methane flame will only propagate as long as enough radicals are produced by the chain branching reactions to maintain production of the methyl free radical. If an impurity in the form of a radical scavenger were to be introduced to the system, the scavenger could act to inert the radicals being produced by the branching reactions and therefore remove the ability of the methane to form the methyl radical. In such a situation, although the methane concentration may be within the explosive region, the flame would not propagate thereby causing flame extinction. It is therefore concluded that the action of appropriate radicals could be used as a method of atmospheric extinction within sealed panels.

CONCLUSIONS

A coal sample from Queensland's Bowen Basin has been studied for explosibility behaviour under laboratory conditions using a 20 litre capacity testing chamber. The lean and rich limit concentrations for the dust sample in air were determined utilising ISO and ASTM standards. Further, the trends in the limit concentrations were examined while reducing the oxygen concentrations until the point of limiting oxygen concentration had been established. For the explosion testing of methane in oxygen, the results mirrored those of Coward (1929) with respect to the triangular shape of the flammability limit surface. The test apparatus indicated a lean limit of explosibility for methane of 4.5 per cent by volume. However methane gas will produce a high rate of pressure rise at 2.0 percent by volume under the influence of high ignition energy. This low concentration can therefore be considered to be flammable. The limiting oxygen concentration for the methane explosion test was determined to be 12.2 per cent by volume, a finding that agrees with published work (Bartknecht, 1989, Mintz, 1993).

Lean limit concentrations for the hybrid mixture of coal and methane generally followed Le Chatelier's law. However the ISO standard results exhibit a phenomenon in which the lean limit of the hybrid is less than the sum of its components. This occurs due to the fact that not all of the coal mass is involved in the explosion when the lean limit for the coal is determined. The addition of methane enables more of the coal mass to ignite and thereby reduces the lean limit for the hybrid mixture.

The two dimensional flammability limit surfaces developed were used to construct a three dimensional flammability limit surface. This surface describes the explosion limits of the coal dust/methane/oxygen system and is most significantly influenced by the explosibility characteristics of coal dust with the limiting oxygen concentration for the system paralleling that of the coal. Methane presents a stronger influence over the explosion limits when low volatile content coals are considered.

An examination has been made of the action of free radical initiators and in particular the influence of the NO_x radical on the lean limits of explosibility of mine atmospheres carrying coal dust/ methane gas mixtures. Two and three dimensional geometry has been used to illustrate the effects. It is concluded that the presence of radical species can significantly change explosibility characteristics of methane gas, airborne coal dust and hybrid mixtures and substantially reduce flammability limits of the atmospheric mixtures.

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REFERENCES

- ASTM E1226-88, 1994. Pressure and Rate of Pressure Rise for Combustible Dusts. *Annual Book of ASTM Standards*, Section 14: General Methods and Instrumentation, Volume 14.02, American Society for Testing and Materials, Philadelphia, PA.
- ASTM E1515-93, 1994. Minimum Explosible Concentration of Combustible Dusts. *Annual Book of ASTM Standards*, Section 14: General Methods and Instrumentation, Volume 14.02, American Society for Testing and Materials, Philadelphia, PA.
- Bartknecht W., 1989. Dust Explosions - Course, Prevention, Protection, Springer-Verlag, 270p
- Coward H.F., 1929. Explosibility of Atmospheres Behind Stoppings, *Transactions of the Institution of Mining Engineers*, vol. 77: 94-108.
- Coward, H.F., 1934. Ignition Temperatures of Gases. "Concentric Tube" Experiments of (the late) Harold Baily Dixon. *Chemical Society Journal*, 304: 1382-1406
- Deguingand B., and Galant S., 1981. Upper Flammability Limits of Coal Dust-Air Mixtures. *The Eighteenth Symposium (International) on Combustion*, The Combustion Institute, Waterloo: 705-715.
- Fairhall D.J., 1993. A Review of Factors Affecting the Ignition Temperature and Flammability Limits of Combustible Mine Gases, with Research into the Effects of Oxides of Nitrogen on the Ignition Temperature of Methane. Unpublished Bachelor of Engineering Thesis, The University of Queensland.
- Foniok R., 1985. Hybrid Dispersive Mixtures and Inertized Mixtures of Coal Dust - Explosiveness and Ignitability, *Luft*, vol. 45 no. 4: 151-154.
- Gillies A.D.S., and Jensen B., 1994. Coal Dust Explosibility and the Coward Triangle, *AusIMM Proceedings*, vol 299 no. 2: 3-8.
- Woll9815.doc

- Hertzberg M., Cashdollar K.L., Lazzara C.P., and Smith A.C., 1982. Inhibition and Extinction of Coal Dust and Methane Explosions. *U.S. Bureau of Mines Report of Investigations*, 8708, Pittsburgh, Pa.
- ISO 6184/1, 1995. Explosion Protection Systems - Part 1: Determination of Explosion Indices of Combustible Dusts in Air, International Organisation of Standardisation.
- ISO 6184/2, 1995. Explosion Protection Systems - Part 2: Determination of Explosion Indices of Combustible Gases in Air, International Organisation of Standardisation.
- ISO 6184/3, 1995. Explosion Protection Systems - Part 3: Determination of Explosion Indices of Fuel/Air Mixtures other than Dust/Air and Gas/Air Mixtures, International Organisation of Standardisation.
- Jackson S, Gillies A D S and Golledge P, 1997. Investigation into the limits of explosibility of hybrid mixtures of coal dust and methane gas, *Institution of Mining and Metallurgy Transactions*, London vol 106 ppA69 - A76.
- Krzystolik P., and Sliz J., 1988. Effectiveness of Ignition Sources of Dust-Air Mixtures. *Proceedings of the 22nd International Conference of Safety in Mines Research Institutes* (ed. D. Guoquan), Ministry of Coal Industry, Beijing: 501-509.
- Landman G.v.R., and Phillips H.R., 1993. Explosibility of Methane/Dust Mixtures at the Coal Face. *Proceedings of the 25th International Conference of Safety in Mines Research Institutes*, Pretoria: 49-59.
- Lebecki K., 1991. Gas Dynamics of Coal Dust Explosions-Theory and Experiment. *Proceedings of the 24th International Conference of Safety in Mines Research Institutes*, Moscow: 357-367.
- Leffler, J.E., 1993. An Introduction to Free Radicals. John Wiley, New York.
- Le Roux, W.L., 1990. Le Roux's Notes on Mine Environmental Control - 4th ed.. The Mine Ventilation Society of South Africa, Johannesburg, 190 pp.
- McPherson M.J. 1993. Subsurface Ventilation and Environmental Engineering, Chapman & Hall London.
- Ministry of Fuel and Power, UK.1941. Twentieth Annual Report of the Safety in Mines Research Board.
- Ministry of Fuel and Power, UK 1942. Twenty-First Annual Report of the Safety in Mines Research Board.
- Ministry of Fuel and Power, UK 1943. Twenty-Second Annual Report of the Safety in Mines Research Board.
- Ministry of Fuel and Power, UK 1944. Twenty-Third Annual Report of the Safety in Mines Research Board.
- Mintz K.J., 1993. Upper Explosive Limit of Dusts: Experimental Evidence for its Existence Under Certain Circumstances. *Combustion and Flame* 94, The Combustion Institute: 125-130.
- Nonhebel, D.C., and Walton, J.C., 1974. Free-radical Chemistry, Structure and Mechanism. Cambridge University Press, Cambridge.
- Peters, N., 1991. Reducing Mechanisms. Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane-Air Flames, (Ed. M.D. Smooke), Lecture Notes in Physics Series No. 384, Springer Verlag, Berlin.
- Reeh D., 1980. The Influence of Small Concentrations of Methane on the Explosion Characteristics of Coal Dust. *International Conference on Coal Mine Safety Research*, Washington D.C.
- Siwek R, 1982. Explosion Characteristics and Influencing Factors. *International Symposium on Control and Prevention of Dust Explosions*, Basel, Switzerland: 149-164.
- Torrent J.G., and Arevalo J.J., 1993. Increase in Coal Explosibility due to Methane Adsorption. *Proceedings of the 25th International Conference of Safety in Mines Research Institutes*, Pretoria, South Africa: 1-19.
- Sosnovsky, G., 1964. Free Radical Reactions in Preparative Organic Chemistry. The Macmillan Company, New York.
- Wolanski P., 1992. Dust Explosion Research in Poland. *Powder Technology*, 71: 197-206, Elsevier Sequoia.

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