Ventilation Air Methane (VAM) Destruction the new challenge to the underground coalmining industry

Dr. Mike Clarke*, CPEng, FIEAust, FAusIMM, RPEQ
CEO M.E.T.T.S. Pty. Ltd.

&

Dr. Duncan Seddon#, FRACI, MSPE
CEO, Duncan Seddon & Associates Pty. Ltd.

Abstract

With the advent of ‘Carbon Taxes’ the carbon footprint of coal has become an economic as well as an environmental issue and the emission of methane in mine out-bye air as ventilation air methane (VAM) is a pending liability. As well as being economic and environmental concerns, VAM and VAM management have safety, social licence and operational factors that must also be addressed. The need to mitigate (oxidise) methane to produce carbon dioxide and water vapour (VAM destruction) and thus lower the Greenhouse footprint is coming to be seen as a necessary mining activity. However, there are several key issues to be addressed with present technology using high temperature (1000°C) thermal oxidisers. Emerging technology may involve a catalytic approach. This technology aims to lower the oxidation temperature and produce a more efficient combustion process. Several systems (based on both precious metals and transition metals) have been shown to operate below 400°C. An ultimate solution would be oxidation at ambient temperature, which is clearly demonstrated by the enzyme methane mono-oxygenase (MMO) which oxidises methane to methanol. However, the rate of oxidation at ambient temperature is too low and the structure of the bio-reactors required would be very large. The challenge is to marry the natural oxidation with modern catalytic approaches and achieve high rates of methane oxidation, in compact equipment, well below the methane auto-ignition temperature.

Introduction

Underground collieries need to address the fact that ventilation air methane (VAM) is an emission that is likely to result in ‘carbon taxes’ or other impositions. The current preferred method for VAM mitigation is the conversion by oxidation of the VAM with it global warming potential (GWP) of 21 to carbon dioxide with a GWP 1, thus considerably reducing the tax to be paid.

VAM derived from the coal bearing strata is normally kept below 1% (preferably <0·6%) in the mine ventilation air through effective ventilation. With the combustible limits of methane in air being 5 – 15%¹ the concentration of VAM is kept well below the combustible limits for normal combustion to occur. When methane is burnt in air it is converted into carbon dioxide and water vapour with the release of considerable energy. The general reaction for complete combustion is:

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 \quad \text{Enthalpy} = -802 \text{ kJ/mole} \]

The first challenge is to develop systems for oxidising (burning) methane in very low concentrations. The secondary challenge is to develop an oxidation system that can manage a very impure gas stream that contains dust, moisture (with dissolved salts) and gases other than air and methane. The VAM

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* Mike Clarke has been the research engineer on Vale’s VAM mitigation project
# Duncan Seddon has consulted in the area of VAM destruction technologies
‘cocktail’ not only varies from mine to mine but also from time to time, with flow rates that also vary with the ventilation fluctuations.

One solution is to utilise the mine air as the oxidant in a combustion process where the VAM is a supplementary fuel with gas (for instance mine drainage gas) or solid fuel (e.g. coal) being the primary fuel. In this case the energy content of the VAM is utilised, but a considerable investment in infrastructure must be made. Another solution is to oxidise VAM without energy recovery. This second option needs less infrastructure, but wastes the fossil energy. With either option there are common challenges.

**VAM Destruction Technologies**

Mine ventilation air (MVA) can be used as a source of oxygen in power generation. The matching of the MVA flow with a power station’s oxygen requirements can be challenging, and for a large mine with a large MVA flow requiring a very large generation plant. Suitable power generation technologies for utilising MVA are fluidised bed combustion, pulverised fuel combustion and with significant gas cleaning, gas turbine technologies.

Another approach to VAM destruction is to supplement VAM with gas (goaf gas or coal seam methane) and combust it in especially designed lean-burn gas turbines. The methane composition in the lean burn mixture would be 2 – 3%. These systems would suit mines with goaf gas management issues.

VAM destruction without energy recovery in flameless thermal oxidisers, where VAM is oxidised by coming into contact with hot thermal media surfaces, is being developed by a number of companies. These units are generally reverse flow systems, where heating and oxidation in one chamber is matched with heat removal from a second chamber and *visa-versa*. The ideal VAM destruction would operate in the following manner, Figure 1.

![Figure 1: Layout for VAM oxidation](image.png)
Characterising Mine Ventilation Air (MVA)

MVA is mine out-bye air with a small percentage of methane (VAM), during normal mining operations. It will contain marginally increased concentrations of carbon plus small percentages of nitrogen oxides, sulphur oxides and hydrogen sulphide. If the mine has heating operations, then carbon monoxide, hydrocarbons and hydrogen will be present. The gas content will be marginally acidic due to the presence of the minor gas constituents.

Of major concern for VAM destruction units will be the presence of dust, moisture and saline droplets. The dust will consist of combustible coal, stone dust (calcium and magnesium carbonate) used for dust explosion suppression, rock dust and possibly some saline evaporites. MVA flows vary on a diurnal basis through variations in fan output, mine ventilation changes including air regulator adjustments, and changes in atmospheric conditions.

The Hazards of Mitigating VAM

Connecting a colliery ventilation system to a source of possible ignition has long been banned. VAM destruction units, such as flameless thermal oxidisers and VAM fed power stations all have the potential of being ignition points, under the following scenario:

1. There is an interruption to a colliery’s ventilation system, and simultaneously,
2. There is a release of goaf gas containing a high concentration of methane (say > 60% CH₄),
3. On the restoration of ventilation, an explosive mixture of VAM in MVA exits in the evasée, and
4. There is a blow-back from the VAM oxidiser unit into the mine.

Therefore, blow-back protection will be required on VAM oxidation installations.

Managing the dust plus moisture in the MVA is a major technical challenge and a very significant technical risk. Dust has the potential to be the killer to all VAM destruction processes because:

1. Dust when mixed with moisture can clog systems and reduce the flow of MVA,
2. Dust, if it contains a significant fraction of coal, can combust leading to hot-spots,
3. Dust plus moisture can become a corrosion hazard for ducting and monitoring instruments,
4. Dust is an abrasion hazard on ducts, monitoring instruments,
5. Dust containing stone dust combined with saline salts has the potential to be a fluxing agent causing sintering of dust particles and the thermal media in the unit.

Monitoring, validation and certification of VAM destruction is required for the creation of tradable carbon financial instruments. Poor monitoring, validation and certification could lead to financial losses, the loss of trust in the financial instruments, and the opening of opportunities for criminal activities. The creation of financial instruments based on VAM destruction in some developing economies could have serious safety and criminal implications.

A specific challenge is the certification of emissions reductions in a dynamic system, where VAM concentrations can vary such that the thermal inertia of flameless oxidation systems can be insufficient to guarantee methane destruction.

Two ‘housekeeping’ considerations re VAM destruction are:
1. The space required for the VAM destruction hardware may not be available at many colliery sites, and
2. Back-pressure from the VAM destruction units will reduce the efficiency of mine ventilation system.

Overcoming the Hazards and Challenges

Figure 1 is a simple schematic of a VAM destruction system. What is needed however is an understanding of VAM mitigation in terms of mining, ducting and destruction. In Figure 2, these are shown as three distinct zones, but zones with distinct relationships and sequential functions, with the Hazard Reduction Connection Zone being the key to resolving challenges.

![Figure 2: Sections of the VAM abatement system](image)

The Mine Zone terminating at the end of the evasé, is a zone where monitoring of gas flow, composition and physical properties is undertaken. If monitoring equipment is placed at shaft bottom, there will be additional time for changes in gas flow and composition to be registered and acted upon before VAM enters the destruction unit. The Hazard Reduction Connection Zone is where blow-back and dust hazards can be addressed and mitigated. The VAM Destruction Zone is the business end of the sequence. Monitoring gas flow, composition and physical properties (pressure, temperature) at the evasé (or before) and after the ID fan on the VAM destruction unit can be used for measuring process efficiency and producing quantifying the VAM destruction.

In the Mine Zone the physical conditions can be expected to be harsh, with high MVA velocities, moisture, particulates and some acid gases. The automated monitoring systems would need to be rugged to manage such conditions and would also need to be duplicated. As a back-up, manual monitoring by mine deputies or ventilation officers would also be required.

The Hazard Reduction Connection Zone (HRCZ) offers the opportunity for VAM venting in emergencies and non-operational periods for the VAM destruction units. It could be designed to collect
dust and be a dilution zone for sharp spikes in methane concentrations. The HRCZ should have both passive and reactive safety systems, with the reactive being connected to the Mine Zone monitoring systems. The VAM Destruction Zone should likewise have monitoring systems that will cause VAM venting if overpressures and/or high temperatures are detected.

The question remains however, ‘does the system offer enough passive and redundant safety features to satisfy colliery statutory officials of the overall safety of the entire VAM destruction system?’

**Emerging Technology – Catalytic Converters**

One method which would assist in overcoming the flash-back hazard would be to reduce the operating temperature of the VAM destruction unit. The objective would be to reduce the operating temperature to well below the auto-ilgnition temperature of methane (about 540°C) preferably by several hundred degrees Celsius. Conventional flameless oxidisers operate at 1000°C so that should the VAM content transition into the flammability range (5 to 15 vol.%) an explosion would be inevitable.

Emerging technology may involve a catalytic approach. This technology aims to both lower the oxidation temperature and produce a more efficient combustion process. Several systems (based on both precious metals and transition metals) have been shown to operate below 400°C.

One technology developed by National Resources Canada and known as CANMET and marketed as CH4MIN will soon be demonstrated in China at the Duerping Middle Station VAM project in Shanxi province. The demonstration will be concurrent with a conventional thermal oxidizer so that both systems can be compared on the same basis. However, reports indicate the reaction temperature required is over 400°C.

The use of platinum group metals (PGM) supported on ceramic or metal monoliths have been developed for the destruction of residual hydrocarbons in auto-engines, both gasoline and diesel. Because to-date methane has not been a regulated pollutant from engines, work has concentrated on the destruction of higher hydrocarbons along with carbon monoxide and nitrogen oxides.

However, with the increase in use of compressed natural gas as automotive fuel and the regulation of greenhouse emissions from vehicles, the catalytic destruction of methane is of keen interest to the automotive industry and auto-catalyst companies and academic research. Although auto-catalyst reaction temperatures are high, the research and development issues concerning methane destruction in auto-catalysts is similar to VAM issues in that the process gas is at low pressure and the residual methane is diluted by a very large excess of excess air and there is potential for significant technology cross-over.

As examples of this field, Williamson and Silver describe Pt/Pd auto-catalysts which convert 90% of the methane 500°C with some formulations giving good conversion at 450°C. Carlsson et alia has shown that light-off temperature (start of combustion) for methane can be below 300°C and complete combustion achieved at 400°C on ceria supported platinum catalysts.

Interestingly, PGM catalysts are not the only catalysts that can oxidise methane at low temperatures. For example workers at the Boreskov Institute of Catalysis (Bukhiyarova et alia) have shown that strontium ferrites promoted by manganese show light-off temperatures of about 300°C.
An ultimate solution would be oxidation at ambient temperature, which is clearly demonstrated by the enzyme methane mono-oxygenase (MMO) which oxidises methane to methanol. These enzymes are widely distributed in nature and are found in areas of high methane concentration such as water springs (Bath), coal mine water or rice paddies. The mode of action and the nature of the active site for methane oxidation (as in many other biological systems) is still in doubt but probably involves an multicentre iron REDOX complex activating oxygen which attacks a methane molecule held in a pocket within the protein complex.

Several proposals have been made for the use of bio-reactors for the oxidation of VAM. In an early NERDDC Project Sly et alia illustrated that coal mine water could be a source of methanotrophic bacteria which operated in a bench unit for 8 months converting 70% of methane (<1 vol.%) with a residence time of 15 minutes. More recently Yu et alia have developed a bioreactor aimed at converting higher concentration of methane (goaf gas); the bacteria was harvested from a rice paddy.

However, the rate of oxidation at ambient temperature is too low and the structure of the bio-reactors required would be very large. The challenge is to marry the natural oxidation with modern catalytic approaches and achieve high rates of methane oxidation, in compact equipment, well below the methane auto-ignition temperature. There are several approaches to this problem.

An active area of research is the low temperature partial oxidation of methane to methanol or formates. These are generally conducted at elevated pressure, so although of no direct benefit to the VAM problem, the work may generate clues to the design of a novel catalytic system. For example Molinari et alia describe the liquid phase partial oxidation of methane to methanol using hydrogen peroxide and iron catalysts at 25°C and moderate pressure (0.4MPa).

**Critique of the Catalyst Approach: An Opinion**

The salient features of the catalytic conversion of methane is shown in Figure 3. This analysis is based on assuming first order kinetics for determining the rate constant (k) with different values for the Arrhenius constant (A) and the activation energy (Ea) in the rate equation:

\[ k = A \cdot e^{-Ea/RT} \]
The figure illustrates the conversion of methane over two typical catalysts. Examination of the figure in the region shows that both catalysts have similar light-off temperatures at near 300°C. One catalyst shows a rapid increase in the conversion whilst the second is much slower and requires a significantly higher temperature to attain 90% conversion.

At point in Figure 3 the theoretical conversion tends towards 100%. However, examination of published data indicates the approach to 100% conversion is more sluggish, more like that shown in the second curve. This is probably due to the kinetics NOT being first order which is assumed in many publications.

In his seminal book on reaction kinetics, showed that the homogeneous gas phase oxidation of methane is second order in methane, that is the rate is proportional to the methane concentration squared. At low methane concentrations the rate of oxidation rapidly falls. This leads to the proposition that it may be very difficult to totally extinguish methane, in other words it may be difficult to eliminate more than about 90% of the methane present in VAM.

In the literature there is a paucity of information on the actual achieved (i.e. measured) conversion of commercial thermal and catalytic oxidisers; carbon credits produced under the CDM often use the manufacturers stated efficiency factor. The failure to properly measure the output of the oxidisers (which are assumed to be over 95% efficient) could compromise carbon trading credits that arise from their use.

Finally we should ask why is it necessary to use a 400°C sledgehammer to oxidise methane when biological systems oxidise methane at ambient temperature. Maybe the approach is wrong and would be improved by attempting to activate oxygen (as the biological system) rather than attempt to make the inert methane molecule react.

**Other Systems**

Oxidation is not the only approach to mitigating VAM. Other approaches include absorbents and membrane separation systems and novel vortex separators which aim to separate out the methane as a
pure or enriched stream. However, none of these appear to be the magic bullet and all face serious
development hurdles at least as great as those for the catalytic approach. But that is another story.

Conclusion

VAM destruction involves new science and new engineering practice, combined with uncertain
economics and politics. It has major elements of hazard reduction and risk management in its
application. On the positive side, successful application could reduce the carbon footprint of the up-
stream end of underground coal mining.

As to the cost/benefit analysis of VAM mitigation, political, social and economic developments will
partially determine the outcome. At this time it would be wise to monitor the major demonstrations of
VAM destruction plant in Australia and overseas, watch the political and social developments with
respect to coal mining, and be aware of the economics of carbon.

One prospective method of overcoming some of the problems in VAM mitigation is the use of catalytic
oxidisers. These would be required to oxidise methane well below the auto-ignition temperature of
methane. This target is as yet someway off, but biological processes which convert methane at ambient
temperatures may give clues on how to design a viable catalytic system.

There are several possible approaches but one key objective should be the accurate determination of
reaction kinetics and to be able to verify the claimed extinction efficiencies for commercial operations.

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1. The AGL Natural Gas Technical Data Book, January 1995
2. M Clarke, Hybrid ventilation air methane (VAM) and coal waste fired power generation. AusIMM Bulletin, June 2010, PP 61 - 64
8. The subject of methane mono-oxygenase (MMO) as biocatalysts and the operation of cytochrome P450 oxidation cycle is a very large field of research. General overviews are available on Wikipedia with more detailed discussion in reviews such as R.J.P. Williams “A comparison of types of catalyst: The quality of metallo-enzymes”, J. Inorg. Biochem., 102, 1 (2008).
12. Data extracted from various publications by Duncan Seddon & Associates Pty. Ltd.
14. See for example: http://cdm.unfccc.int/Projects/Validation/DB/BXIACRJ2JE9ABIOTY7HV1ZH08DJH8V/view.html