COMET™ – A New Ventilation Air Methane (VAM) Abatement Technology

Reducing greenhouse gas potential from the mining industry

By Peter Hinde
Johnson Matthey Technology Centre, Blounts Court, Sonning Common, RG4 9NH, UK

Ian Mitchell* and Martin Riddell

*Email: ian.mitchell@matthey.com

Ventilation air methane (VAM) found in coal mines is a huge and global problem because it acts as a greenhouse gas (GHG) contributing to climate change. Methods for removing this methane and reducing its impact have to date been limited due to a lack of legislative drivers and a technological focus on reducing the emissions of higher hydrocarbons. Now a new technology, known as COMET™, has been developed at Johnson Matthey in collaboration with Anglo Coal for abating this methane emission source. This article describes the development of the catalytic system and its engineering aspects to the point where the technology is ready for commercial launch.

What is VAM?

To understand VAM one has to understand the effect methane has as a GHG. A GHG is a gas in or released to the atmosphere that absorbs and emits radiation within the thermal infrared range. This process is the fundamental cause of the greenhouse effect which is identified as a contributory factor to global warming (1). Methane is a potent GHG and has been shown to have a global warming potential (GWP) of at least 21 times higher than carbon dioxide (1).

Methane is often found around and within coal. In open cast mining the methane is lost to the atmosphere as the coal is removed from the ground. With deep shaft mining the methane is contained within the mine system. This methane is classified according to its concentration, location and method of extraction. Figure 1 shows the different types of methane associated with coal mines along with the source, methane concentrations, relative flow rates and GHG impact. In 2012 VAM accounted for 61% of all methane emissions from coal mines in the US with 91.2 billion cubic feet (BCF) of emissions, whilst coal bed methane only accounted for 5% (7.0 BCF) of emissions (2).

Looking at each type of methane associated with coal mining in turn:

- **Coal bed methane**
  - Gas drained from coal seam pre-mining or unmineable coal seam
  - CH₄ concentration: 60–94% CH₄
  - Flow rate: Few m³ sec⁻¹
  - Easiest to capture or use
  - Highest GHG impact

- **Coal mine methane**
  - Gas drained from worked areas of mine
  - CH₄ concentration: 30–95% CH₄
  - Flow rate: Few m³ sec⁻¹

- **Ventilation air methane**
  - Extracted from mine to allow safe working
  - CH₄ concentration: 0.1–0.8% CH₄ in air
  - Flow rate: 100s m³ sec⁻¹

Fig. 1. The different types of methane emissions associated with coal mines
Coal Bed Methane is present in very small quantities (<10% of methane associated with coal mining) and is typically used as a fuel as the methane concentration is sufficiently high that it can be used, after appropriate treatment, in natural gas pipelines. Coal Mine Methane has sufficient methane that it can be combusted, therefore depending on location and nearby requirements for heat, it is either combusted to provide heat for nearby users or flared to reduce environmental impact. Due to the varying and reduced concentration of coal mine methane, especially when compared to coal bed methane, it is not suitable for use as a pipeline gas. Ventilation Air Methane is present in huge quantities (>60% of methane associated with coal mining) and has insufficient methane to support combustion without supplementation with additional fuel and is seen as difficult and uneconomic to combust.

One should also consider the safety aspects associated with methane. Methane has an explosive range between 5 and 15% by volume in air (3). Coal bed methane and coal mine methane have concentrations of methane above the upper explosive limit although through further dilution, from air ingress, explosive compositions can be formed as the methane concentration is lowered. The concentration of VAM is below the explosive limit and therefore is less of a risk.

When looking at the GHG potential of methane there are varying measures to compare to that of CO₂. The chemistry shows that oxidising methane to CO₂ produces 2.7 tonnes of CO₂ for every tonne of methane. The US Environmental Protection Agency (EPA) states that methane is more than twenty-one times more potent than CO₂ as a GHG (2). Therefore by oxidising methane the benefit in greenhouse reduction is at least 17.3 tonnes of CO₂ equivalent compared to letting methane escape to the environment.

Drivers for Abatement

There is a clear environmental benefit to abating methane as it will reduce the amount of GHG emitted to the atmosphere. This has been recently underlined at the United Nations Conference of Parties (COP21) in Paris held in December 2015 (4), as for the first time ever, there is now a single global agreement in place to tackle climate change as summarised by the authors in the key points below:

- global temperature rises should be capped at 2.0°C with ambitions to achieve 1.5°C
- within a century there should be net zero CO₂ emissions (i.e. human sources = natural sinks)
- every five years there will be a stocktake of each country’s contribution to cutting emissions
- the richer countries will provide at least £67 billion per year of ‘climate finance’ to help poorer countries adapt to climate change and switch to renewable energy.

Prior to the global Paris agreement, some progressive thinking mining companies (5, 6) had already embraced environmental control technologies in principle. Fiscal incentives and other benefits will help motivate others to adopt the technologies required to reduce these emissions. At time of writing there are two legislative schemes in place that have clear guidelines for abatement of methane as a GHG; the European Union Emissions Trading Scheme (EU ETS) (7) and California’s Cap-and-Trade Program (8). Due to current pricing and the inclusion of a price floor the Californian scheme is of most interest to companies wanting to abate methane emissions with an economic return.

There are other schemes either in place, rescinded or under consideration in other parts of the world that could harness and benefit from methane abatement, although this may not be currently viable either economically or legislatively. The impact of last December’s Paris conference is yet to be fully understood although one can say with reasonable certainty that control of GHG emissions is important and that GHG abatement technologies, such as COMET™, are a method of achieving this aim.

The EPA estimated that the worldwide mine methane emissions for 2010 contributed more than 584 million tonnes of CO₂ equivalent to the atmosphere each year which is around 8% of total man-made methane emissions (9).

The EPA also estimated that 236 million tonnes of CO₂ equivalent was released to atmosphere from coal mine VAM during the calendar year 2000 (10). Global coal production and consumption since 2000 has increased considerably from 4.72 billion tonnes per annum to 8.16 billion tonnes per annum (11). This increased coal production has increased VAM emissions to an estimated 410 million tonnes of CO₂ equivalent, split globally as shown in Figure 2.

This article will focus on efforts to abate emissions of VAM since this is currently the most difficult to address and the most damaging source of methane emissions from deep coal mines.
Current Technologies for Methane Abatement

The simplest way to reduce methane emissions is to oxidise the methane to produce CO$_2$ and water (Equation (i)):

$$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad (i)$$

This can be done by flame combustion, such as flaring or as a fuel, for higher concentrations of methane, but for the lower concentrations present in VAM streams, it is oxidised thermally at high temperatures (1000ºC) or at lower temperature (<600ºC) catalytically.

Due to the relative lack of toxicity of methane and hence lack of historical legislative requirement for methane control, most commercially available hydrocarbon oxidation catalysts have been developed to oxidise longer chain hydrocarbons in volatile organic compounds (VOC) abatement, for example propene and automotive emission applications have little ability to oxidise methane effectively at low temperature.

Regenerative thermal oxidiser (RTO) technology (Figure 3) was developed to reduce VOC emissions from ventilation streams. VOC are chemicals which typically have a significantly larger global warming potential with hundreds or thousands of times that of CO$_2$ (12). Typically VOC abatement is carried out on exhaust streams from chemical production sites with flowrates considerably lower than that encountered on a coal mine ventilation stream. The technology has subsequently been adapted to deal with methane abatement.

Only a handful of VAM abatement installations exist worldwide as the application of the technology is novel. The problem is that these systems operate at temperatures in the region of 1000ºC and cannot
effectively convert the methane at an economic cost. The high temperature of operation has also been a barrier to adoption on safety grounds, as it is above the auto-ignition temperature of methane (617ºC) (13) which could increase the likelihood of explosion in the mine or mine ventilation system.

Recuperative catalytic oxidation (RCO) systems have also been developed (14). However for VAM and general methane abatement these offerings still operate above the auto-ignition temperature of methane and therefore safety concerns limit their usefulness in this application.

Recently, Johnson Matthey chemical engineers and scientists and Anglo Coal mining engineers, have developed COMET™: a new, lower temperature abatement solution for VAM from active or abandoned coal mines which overcomes many of these challenges.

Catalytic Materials for Methane Oxidation

Many academic groups have studied catalytic materials for methane oxidation over the last 50 years; of the metal oxides studied, tin oxide (15) and chromium(III) oxide (16) are considered among the most active. Of the aluminium oxide (Al₂O₃) supported metals studied, the following ranking under their chosen conditions, in order of decreasing activity per gram of metal, has been given in the literature (16): platinum, palladium, chromium, manganese, copper, cerium, cobalt, iron, nickel and silver. It is not just the metal that has an influence on the catalytic activity with high surface area support materials such as Al₂O₃ also playing an important role, contributing to the performance of the catalyst through interaction with the supported metal particles for example by maintaining a high dispersion of the metal particles.

One of the products of the methane oxidation reaction, water, strongly inhibits the reaction (17). It has been suggested that the inhibition is due to the formation of water which covers the active sites for CH₄ oxidation (18). The presence of 4–5% water in the ventilation air exhaust (from 80–100% humidity at 25–30ºC) further inhibits the reaction, over and above the effect of water as a product of the reaction and this effect is only reduced at elevated temperatures (>500ºC).

Sulfur is widely known to be a poison for oxidation catalysts and may be present as low levels of hydrogen sulfide (H₂S) within the mine. It is also possible for a gaseous region to be exposed during mining operations that can lead to a rapid increase in the amount of H₂S present in the ventilation air exhaust.

Pt is widely considered to be a sulfur tolerant metal that is active for hydrocarbon oxidation reactions, while Pd is often selected for methane oxidation duties due to its higher activity and lower cost. For these reasons, a bimetallic catalyst based on Pt and Pd was selected for development. Pd catalysts can be readily poisoned by exposure to high levels of sulfur and while this can be improved by adding Pt, even with Pt present sulfur can still be a significant poison to a bimetallic PtPd catalyst.

COMET™ Catalyst Development

Criteria for a viable commercial process technology for the abatement of VAM are a catalyst that can:
- achieve high conversion of methane throughout its lifetime at temperatures below 600ºC
- enable lower grade materials of construction to be used
- be manufactured at sufficiently low catalyst cost for economic viability
- withstand the arduous and variable feed conditions experienced in a mine environment
- be suitably robust for coating onto a low pressure drop support.

To tackle this challenge Johnson Matthey utilised its research and development facilities and its experience in the development of platinum group metals (pgm) catalysts to carry out an extensive experimental programme to develop the selected catalyst formulation and physical form. This work programme was undertaken using purpose built experimental testing rigs (see Figures 4 and 5) to study pgm catalysts.

Following initial formulation development work using powdered catalysts in a screening rig (Figure 4), catalysts in a range of physical forms were tested with experiments being extended to other variables including long term poison resistance, coating technique and particulate loading.

Further experimental work on the most promising catalysts in their final form suitable for commercial application was then carried out using innovative purpose built equipment (Figure 5) under actual feed conditions. An understanding of likely contaminants in the feed gas was obtained from development partner Anglo Coal. Table I shows conditions that were tested.
The following characteristics of the catalyst formulation were investigated and optimised for the conditions present in a typical coal mine:

- ratio of active materials, Pt:Pd (Figure 6)
- active metal loading
- metal-metal physical state
- support material.

For each of the above variables the effect of changing the reaction conditions was also studied. These changes included:

- methane concentration, see Figure 7
- water concentration
- sulfur concentration
- temperature (of pre-treatment and operation) see Figure 8
- space velocity – ratio of catalyst volume to gas flow
- start-up and shutdown regimes.

Multiple studies (21) have reported different methane oxidation kinetics (between first and half order). It is important to derive a representative model appropriate to our system for control purposes. During these studies an understanding of the reaction kinetics was gained which proved to be of a higher complexity than first expected. This is due to the complex nature of the catalyst and the methane oxidation mechanism taking place via a Mars-van Krevelen redox reaction (22) that included the active metals. This complexity was further compounded by the impact of the support material and oxygen supply mechanism on the dynamic performance of the catalyst. Multiple approaches to understand the behaviour of the catalyst were employed including, for example, the use of isotopic labelled gas to determine
Fig. 5. The long term aged rig used to simulate realistic gas composition and flow rates for extended time periods (thousands of hours) over coated components made to production standard.
the temperatures at which oxygen transport became apparent by different mechanisms.

It was also important to consider the catalyst presentation. As well as the catalyst formulation, the way the catalyst is presented to the incoming gas, for example in terms of size, shape, substrate material and coating thickness can have a significant impact on the performance of the system. These variables can affect the pressure drop, heat and mass transfer and attrition resistance of the system and need to be selected in parallel to the design of the reactor to ensure optimum performance. The method of catalyst presentation used in this instance is a development of a standard Johnson Matthey technique mixing novel support variants and coating techniques with established industrial processes.

Johnson Matthey has successfully demonstrated the lifetime of the catalyst by testing the catalyst over a period of two years in an experimental pilot rig (Figure 9). Extensive experimental testing was also carried out to develop a kinetic model sufficiently robust to accurately predict the performance of the technology when applied to mines with varying VAM composition and conditions. Technical success has been achieved by developing a long lived catalyst that can maintain approaching 100% methane conversion, at low temperatures.

COMET™ Engineering Development Process

The development objectives were to engineer a complete solution for the catalytic oxidation of VAM whilst providing distinct advantages over existing RTO and RCO abatement technologies. Once the
catalyst was selected, the remaining challenges were engineering based. Desired characteristics of the COMET™ system included:

- operating at low temperatures
- keeping the process simple with a simple control scheme to match
- enabling easy relocation of the unit, low maintenance requirements and operational flexibility
- maintaining a high level of safety with a fail-safe design
- minimising operating and capital expenditure.

The process safety of the COMET™ technology was considered paramount in the engineering development phase due to the working coal mine environment. Anglo Coal’s participation in the project has enabled Johnson Matthey to gain an understanding of the associated safety requirements. Johnson Matthey process engineers worked to address the concerns of the potential for sudden methane releases by using quantitative methods to carry out a hazard and risk analysis. This was carried out in accordance with the well established functional safety standards of International Electrotechnical Commission (IEC) 61508 (23) and IEC 61511 (24), as used in the petrochemical industry. The use of these safety standards is recommended in guidelines issued by the US Mine Safety and Health Administration (MSHA) (25).

Operating at temperatures significantly below the auto-ignition temperature of methane will provide an invaluable benefit as the level of safety is increased by removing a permanent source of ignition. In a once-through process such as COMET™, it is the performance of the catalyst which determines the operating temperature range. As the catalyst had been already developed with this in mind, the unit was then designed around the catalyst.

The low temperature operation, when compared to an RTO system, allows the system to be constructed from lower grade materials reducing capital expenditure (CAPEX) investment, as well as avoiding operation above the auto-ignition temperature of methane as already described.

The developed unit has been designed using pre-existing equipment items, all of which are well proven and commonly used in similar petrochemical applications. There are few moving parts, all in low temperature service, increasing operational reliability and reducing the level of maintenance required. The control scheme has been developed to give optimal control whilst enabling the unit to be almost completely automated, limiting the required attention by operators. These aspects were incorporated within the design as by doing so capital investment, operating costs, operator resources required and level of technology risk were all reduced.

Normal mining operations require the ventilation shafts which expel the VAM to the atmosphere to change location (26), as the focus of mining activities move with time. The location of underground coal mines are quite often at remote, difficult to access sites which could make the transport of large process equipment items expensive. The COMET™ unit addresses these potential issues having been developed to comprise of modules which are ‘bolted together’ on site. All selected equipment items are scalable for high flows of VAM, eliminating the need for several smaller process trains and reducing the footprint required.

The COMET™ technology provides a method for removing methane from feed gas by passing the feed gas through a heat exchanger to raise the temperature of the gas to the desired inlet temperature; passing the resulting heated stream to the oxidation reactor containing the oxidation catalyst, where the methane is adiabatically oxidised; removing a gas stream including the products of the oxidation reaction from the reactor at an outlet temperature and passing the oxidised gas stream through the heat exchanger against the feed gas to allow the heat to be recovered, wherein the inlet temperature is controlled by means of a bypass around the heat exchanger in which the amount of bypass is controlled by measuring the outlet temperature.

The engineering design has yielded a comprehensive safe, controlled system that meets the requirements of the coal mining industry at a cost that could prove attractive under current conditions. The COMET™ technology is very different from the currently available solution to VAM abatement (Figure 10) and its economic advantages are summarised below.

Economic Benefits

Utilising a once through catalytic system has some features which are advantageous when applied to VAM abatement. The design can utilise economy of scale from using a single stream system. It is suitable for use on a wide range of flowrates and a high methane conversion can be maintained at all times whilst operating with a high thermal efficiency. The system performance envelope allows the technology to be adapted to varying VAM concentrations.
Running below the auto-ignition temperature of methane gives a safe and robust VAM abatement solution.

The viability of the technology is largely dependent upon carbon credit prices (28) therefore it has been vital to reduce the capital and operating expenditures. The operating expenditure of the technology has been successfully reduced by developing the catalyst and the process together. This has resulted in a system with minimal pressure drop to minimise power consumption. At sufficient VAM concentrations the Johnson Matthey technology will be power neutral or even able to export power to the grid.

Given sufficient methane concentration there is an option to generate power and export power. With lower concentrations there may not be sufficient energy to export electrical power although there may be an option for power neutral operation.

Conclusions

The COMET™ VAM abatement technology provides a novel solution to the problem of VAM and is ready for deployment.

By using novel approaches to a problem that was identified by Anglo Coal, Johnson Matthey has successfully developed a catalyst and process which provides a safe, easy to operate, scalable, GHG reducing and economically viable technology for the abatement of large quantities of VAM which, if not treated, would be released into the atmosphere as a potent GHG. Both the catalyst and the process have undergone significant development to ensure all the required objectives to make this technology commercially attractive on a global scale have been met. This has resulted in a technology which excels in all the key areas when compared to existing technologies.

Johnson Matthey is currently further developing the COMET™ VAM abatement technology to broaden the range of methane containing vent streams to which the catalyst and process can be applied. This will maximise both the commercial and environmental benefits of the technology.

COMET™ is a registered trademark of the Johnson Matthey group of companies.

Acknowledgements

The authors would like to acknowledge the contributions made by all colleagues across the Johnson Matthey organisation who were involved in the COMET™ project.
References


The Authors

Peter Hinde is a Senior Scientist at Johnson Matthey Plc. Peter obtained his PhD in the field of Photocatalysis from the University of Bradford, UK, and has been working at the Johnson Matthey Technology Centre supporting multiple global business units for more than 10 years. His research and development experience includes catalysts for vehicular exhaust emission control, methane abatement, reforming, photocatalysis and he currently leads the plasma catalysis research group.

Ian Mitchell is a Chartered Chemical Engineer currently working as a Business Manager at Johnson Matthey Plc, where he has responsibility for the COMET™, Amines and Purified Terephthalic Acid businesses. Ian started his working life as a Chemical Engineer with Johnson Matthey Davy Technologies in 1997 after graduating from the University of Newcastle Upon Tyne, UK. He has progressed through the posts of Process Engineer and Senior Process Engineer into his current role.

Martin Riddell is a Process Engineer at Johnson Matthey Plc, where he is the lead process engineer for the COMET™ technology. Martin graduated from the University of Sheffield, UK, in 2011 before starting his current role at Johnson Matthey.