Is mine water a source of hazardous gas?

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Keywords: Mine gas; blackdamp; firedamp

ABSTRACT
Most coal and coal bearing strata contain significant quantities of gases. These gases are either potentially explosive in critical concentrations when mixed with air, others are toxic. Gases found in a mine are almost certainly a mixture of atmospheric air, inert gases, water vapour and one or more of the following: oxygen, carbon monoxide, methane, hydrogen sulphide, hydrogen and nitrous oxides. Gases such as “firedamp” and “blackdamp” may accumulate in poorly ventilated workings; these pose no threat provided they stay in the mine; however, gases can migrate through voids and strata and be emitted. All underground workings are affected by atmospheric pressure variations; mines can “breathe” over periods of rapid barometric pressure falls. Gas in confined underground atmospheres can come from three possible sources: desorption from exposed coal strata; exsolution from mine waters; and fossil gas trapped in pockets within the strata. Desorption from rock and exsolution from mine water are being quantified experimentally within coal measure strata at Caphouse Colliery in Yorkshire. This paper will present the findings to date and will conclude that mine water is a source of hazardous gas in mine atmospheres.

INTRODUCTION
Mine gases are as hazardous to the underground environment as they are to the surface environment. Between 1851 and 1980 there were 186 major explosions in British Coal mines resulting in almost 10000 fatalities, most of these prior to nationalisation in 1947, as a direct result of a build up of firedamp with an ignition source (Turton, 1980). This methane is predominately believed to have desorbed from the coal strata within the mine and from the release of fossil gas pockets within the strata. The problems of low oxygen gas (stythe) in mines have been known for many years culminating in the Bill of 1842 stating that “an adequate amount of artificial ventilation shall be consistently produced in all coal mines, collieries and iron mines to render harmless, noxious gases, to an extent that all accessible places of the pits, levels and workings of every such colliery and mine shall, under ordinary circumstances, be in a fit state to work therein.” This gas is particularly noticeable in times when there has been a rapid barometric pressure fall resulting in the expansion of the gas and the emission of the fringe of the noxious gas concentration.

Although during mining gas is controlled through the colliery ventilation system and exhausted appropriately, it is in areas of poorly ventilated and/or abandoned mine workings which have given rise to a number of case histories within the coalfield area of the North East of England.

Background to Project
Apart from the conurbations of southern England and parts of the Merseyside, the main centres of population in the UK are located over coalfields. This proximity of the population and the Coal Measures is a direct legacy of the industrial revolution of the 18th century and the first part of the 19th century (Knill, 1975) when coal was extracted in the agricultural areas around industrial towns. With this in mind there are a potentially large number of people who may be affected by this legacy of the mining heritage.

Mine gas problems
Any noxious or explosive gas present in the abandoned mine workings pose little or no threat whilst they remain underground however mine gases may migrate through voids and strata and emit at the surface some distance away from the original source. Throughout the last 25 years there have been a number of case histories regarding mine gas emissions into properties, in some cases causing fatalities.

Firedamp
One of the most notable case histories occurred in the North Derbyshire village of Arkwright when on the 9th November 1988 more than 40 families were evacuated by the council after methane was found to be seeping into houses. The council and villagers believed the gas to be coming through subsidence cracks in the houses as a result of the rising mine water table levels forcing the mine gas out. In 1995 the whole village was demolished and relocated nearby. British Coal had admitted the village was at risk from methane emissions from the former Arkwright Colliery (closed early 1988) but did not admit liability.
Blackdamp (stythe)
There are a number of case histories over the last 25 years of stythe gas entering properties in Northumberland, one of which resulted in the fatality of a 61 year old man entering business premises in February 1995. It is still the only recorded death directly attributed to mine gas entering into a domestic or industrial property. As a result of these and other case histories, this project was proposed to investigate the links between the origins and pathways of mine gas in poorly ventilated and/or abandoned workings.

Barometric pressure influences
All underground workings are affected by atmospheric pressure. Gases such as firedamp and blackdamp may accumulate in old workings that are not adequately ventilated. When the barometric pressure falls rapidly, these gases expand and the fringe may be emitted at the surface. Conversely when the barometric pressure rises, fresh air is drawn into the workings and will assist in the oxidation process and further noxious gas formation.

Water level
Following the cessation of deep underground mining in the North East region the groundwater table is slowly recovering after some 200 years of industrial activity in the region. As this groundwater level rises, the current gas migration pathways may change and the underground void spaces decrease thus increasing the pressure of the underground gases. This may lead to a series of ever changing emission locations within the region, some with potentially life threatening outcomes if this legacy is not controlled.

ORIGIN OF MINE GASES
Mine gases may be of geological, biological or chemical origin. These gases will exhibit characteristics diagnostic of their age and origin (Creedy, 1989) following burial, compression and heating of organic material (thermogenic methane) but in some instances these characteristics may be modified by biological or chemical agents introduced as a result of mining. Thermal degradation becomes the principal methane generating mechanism in mature sediments, such as coal seams. The volumes of methane found in the coal seams of Northumberland and Durham vary from trace to 20 m$^3$/t (Creedy, 1988). The difference arises from variations in the composition of vegetation undergoing coalification, variation in the geological conditions under which coalification took place and the proportion of methane lost subsequently over geological time through various processes. Carbon Dioxide will predominately originate as a result of either geological (ancient) or chemical (recent / modern) processes in a mine. Under the influence of normal geothermal temperature, the formation of coal from organic matter releases carbon dioxide and methane in varying volumes (Hooker and Bannon, 1993). Chemical reactions with carbonates, oxidation of carbonaceous material and high temperature oxidation of mining materials will all liberate carbon dioxide into the atmosphere. It is probable that much of the gas generated through coalification is dispersed through the surrounding strata and that some is removed in solution as the moisture content of the consolidating rock is progressively reduced. In coal measures, methane is usually adsorbed on coal or held mechanically within the naturally occurring fractures of the rock. It may also be trapped in gas pockets, dissolved in groundwaters within other coal measure strata or even in commercial gas reservoirs.

Gas release into the mine environment
There are a number of ways in which gases may be generated in a mine; however, there are only three main processes which will release significant quantities of gas into the mine environment. These are:

- Release of fossil pockets of gas stored in the strata
- Exsolution from groundwaters in the mine
- Desorption from the strata

Fossil gas
Through mining history, miners have always been wary of the hazard of explosions at the face of the coal strata. These are often due to rapid expansion (due to the release of pressure) of a pocket of trapped gas which is then ignited and explodes. During the coalification process, considerably more gas was produced then could be accommodated in the coal substances. The gas not retained by the coal was dispersed into the strata around the coal seams; a portion became trapped in rock pres and fracture spaces within the “reservoir structures”. There is evidence from surface exploration drilling and coalfield records for the occurrence of methane in porous or well jointed rocks such as limestone and sandstone (Hooker and Bannon, 1993). In addition, higher than expected methane flows which occur in some operational collieries have been attributed to contributions of methane from sandstone reservoirs. Methane can also be adsorbed on carbonaceous surfaces as a solid hydrate (Creedy, 1991).

Desorption of gases
Methane
The process of adsorption is particularly important as it explains why methane is found highly concentrated on coals and other carbonaceous materials. Fine pores within carbon atoms provide a vast surface onto which specific gas molecules may be tightly packed, so close in fact that the density of the gas can be similar to that of a liquid. The quantity of methane adsorbed depends on the composition, rank and moisture content of the coal substance and the temperature and partial pressure of the gas.
In addition, the production of methane gas in coal bearing strata by coal desorption depends partly on particle size, for example a 1mm particle will achieve 90% degassing in 1 month and a 1 cm particle in 15 years (Staff et al. 1991). Thus, coal remaining in abandoned workings will continue to emit methane by desorption over a considerable period of time.

**Carbon Dioxide**
Carbon dioxide forms in a variety of diverse environments. It may be adsorbed onto the surfaces of rocks, liberated from chemical reactions of acid waters on carbonates and sulphides in strata, be the product of anaerobic bacterial activity and be exhaled from animal and plant respiration into the atmosphere. High carbon dioxide concentrations have been recorded in unsaturated zones above coal and lignite deposits and up to 8% CO$_2$ was reported over mine waste dumps undergoing pyritic oxidation (Harris & Richie, 1985). Even though the sorptive capacity of coal for carbon dioxide is three times that for methane, CO$_2$ tends not to be trapped at depth by coal forming material since it occurs prior to methane generation and escapes during the thermogenic processes of coalification.

**Exsolution of Methane and Carbon Dioxide from groundwater**
Groundwater can be an important transport and storage medium for gases in solution. The migration of gases in groundwater depends on viscosity. Dissolved gases may be carried by the groundwater; when the pressure is reduced and the solubility limit of the gas exceeded will they bubble out of solution and form a separate gaseous phase.
Methane has a very low solubility at atmospheric pressure but at elevated pressures significant volumes can be held in solution in groundwater. It is also influenced by temperature and the concentration of other gases or minerals present within the water. In general it is accepted that the abundance of methane increases with depth in groundwater systems, probably due to a combination of factors including degredation of indigenous traces of organics in the rock phase, influx of methane from other sources and slower groundwater movements at depth (Appleton et al. 1995).
Carbon dioxide dissolved in groundwaters may have mixed origins including dissolution from the atmosphere and soil at times of recharge, production in both shallow and deep crustal rocks from biological processes and rarely migration from the mantle of areas of tectonic activity. Carbon dioxide is only one component of a complex set of gas-liquid equilibria which govern the carbonate system in groundwaters: therefore the actual partial pressure of CO$_2$ is dependant on pH and its equilibria with the other carbonate minerals.

**AIM OF PROJECT**
The aim of the project is to determine if mine water is a source of hazardous gas in abandoned working.

**Study Site**
An initial underground study site has been identified and secured at Caphouse Colliery in Wakefield, West Yorkshire. At this site, six water sampling locations incorporating the full depth of worked seams were identified. Driven piezometers and wattrra tubing have been installed in two of these locations down the secondary access drift of Caphouse Colliery, one into the upper worked seam (Flockton thick) and the second into the lowest worked seam (Wheatley lime). In addition four samples are taken down the shaft at the intercept of the main coal strata seams into the shaft, namely, Flockton thick, Flockton thin, Old Hards and Green Lane seams.
Headspace analysis was carried out on all samples to investigate the amount of CO$_2$ present within the samples. In addition a surface site has been procured to investigate desorption of gas directly from carboniferous strata and recently compacted backfill. At the time of writing this paper the fieldwork phase is awaiting commencement.

**PRELIMINARY RESULTS**
Gas monitoring

![Figure 1: The relationship between atmospheric pressure and mine gases at Caphouse Colliery](image)

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Figure 1 shows that there is a relationship between atmospheric pressure and increased hazardous gas emissions of both methane and carbon dioxide within the underground environment. It is not possible at this stage to conclude to exact source of this gas.

**Water monitoring**

Table 1 shows the average water quality data taken from the two main sample locations. As is seen in this table there is an apparent discrepancy between the alkalinity and the pH value, as a pH of less than 4.5 would not be expected to show any alkalinity measurement as all of the carbonate in the system is as free CO2 (carbonic acid derivative).

<table>
<thead>
<tr>
<th></th>
<th>FLOCKTON THICK</th>
<th>WHEATLEY LIME</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALKALINITY (MG/L)</td>
<td>440</td>
<td>350</td>
</tr>
<tr>
<td>PH</td>
<td>4.15</td>
<td>4.36</td>
</tr>
<tr>
<td>TOTAL DISSOLVED SOLIDS</td>
<td>1220</td>
<td>1550</td>
</tr>
<tr>
<td>CONDUCTIVITY (µS)</td>
<td>1650</td>
<td>2090</td>
</tr>
<tr>
<td>TEMPERATURE (ºC)</td>
<td>11.5</td>
<td>15.5</td>
</tr>
</tbody>
</table>

Table 1: An average summary of water quality field measurements for the Flockton thick and the Wheatley Lime sample locations

Figure 2 shows the increased levels of CO2 equilibrated into the headspace of the sample vial found in the Flockton waters. Although these waters are elevated in carbon dioxide there is no obvious relationship between amount of CO2 present and atmospheric pressure. It is not possible to conclude that the atmospheric pressure has a significant influence on the degassing of the CO2 from the waters from these results at present.

**CONCLUSIONS AND FURTHER WORK**

As can be seen from the preliminary results the waters sampled are very much elevated with respect to carbon dioxide and they readily equilibrate in the headspace analysis sampling vessels. Methane was analysed for in the initial sample runs but it does not readily equilibrate with waters and as such the detection limit of the GCMS machine was out with of any methane content of the waters.

There is a discrepancy between the in field alkalinity measurements and the pH, further work is required to investigate this.

In conclusion, the preliminary results indicate that with elevated levels of dissolved CO2, mine water could be a source of hazardous gas within the mine environment.
REFERENCES


