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SOME APPROACHES TO HANDLING HYDROGEN SULPHIDE IN COAL SEAMS

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ABSTRACT

The study addresses Hydrogen Sulphide (H₂S) in coal seams. The objectives of the project were to undertake a comprehensive series of interrelated studies to gain a full understanding of this complex mine production problem. The goal was to understand how, where and why high concentration zones of H₂S occur, how does gas release from the coal mass occur, can concentrations be diluted or neutralised through improved ventilation, water, chemical or microbiological infusion, chemical solution sprays and can mining approaches be modified to contain the problem. A multidisciplinary approach has been used for related investigations.

Systems and the output streams available for H₂S detection and monitoring have been examined. The large variations in H₂S concentration measurements from different face sources and the physical differences in the longwall face, ventilation plan, and operating procedures make the interpretation of gas concentration data difficult. Respiratory filters represent a cost-effective and short-term safe way to protect miners from potentially lethal environment. A selection of cartridge and Racal airstream helmet filters has been described and some tests into filter life and efficiency undertaken.

The mine ventilation system can be modified to allow safe production through H₂S affected zones. Designs for maximising safe production through affected mine panel or development headings have been tested. Mining options to reduce H₂S emissions have also been examined. A major program of in-seam chemical neutralisation infusion trials was undertaken. The basic aim of the chemical infusion process is to prestrip a significant proportion of H₂S to allow coal mining to proceed in a safe working environment at an economic production rate. Some approaches to analysis of results and evaluating the efficiency of the approach have been given.

KEYWORDS

Hydrogen sulphide, Longwall, Infusion, Respirator filters, Ventilation network simulation

INTRODUCTION

The presence of H₂S in coal seams causes a significant number of operational and safety problems during mining that may result in low production and development rates, poor efficiency and high ventilation costs. High concentration occurrences during mining of development headings and longwall panels have raised a number of potential problems. These were seen to warrant a significant research effort to gain an understanding of a problem that has industry wide implications and to put in place a system of safe mining that ensures minimum production down time and loss.

The occurrence of H₂S in coal seam gases is rare around the world and it has been detected in coal seams in North East Asia, France, the US and Australia. In Australia significant occurrences have been found in a number of mines in Queensland (Ryan, *et al.*, 1998; Harvey, *et al.*, 1998). H₂S is an extremely toxic gas and can cause death. Stringent limits apply to ensure safe practices when mining in the presence of the gas in most coal mining countries using modern mining practices.

A project was undertaken in a number of sections with an objective of gaining a full understanding of this complex problem (Gillies, *et al.*, 2000). The goal was to understand:

- How, where and why high concentration zones of H₂S occur,
- How does gas release from the coal mass occur,
- Can concentrations be diluted or neutralised through improved ventilation, water, chemical or microbiological solution sprays or infusion and
- Can mining approaches be modified to contain the problem efficiently?

A multi-disciplined approach has been used for related investigations on a number of fronts to establish the cause of and alternative solutions to the problem. The project was undertaken with funding from the Australian Coal Association Research Program (ACARP) and the Queensland Oaky Creek and German Creek Southern collieries (Figure 1). This paper gives an overview of some aspects of the research undertaken.

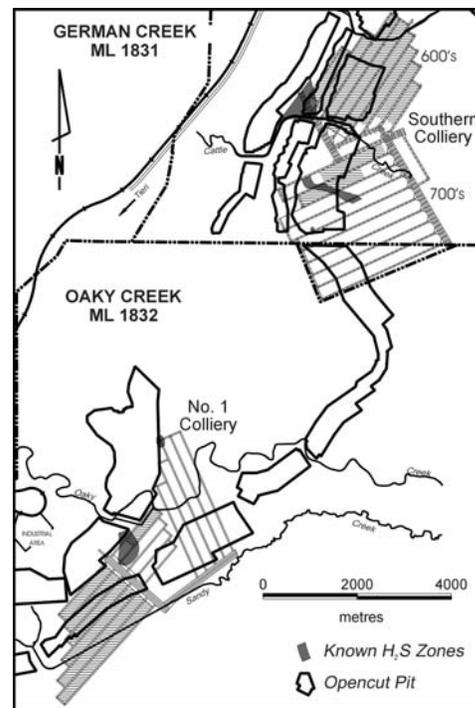
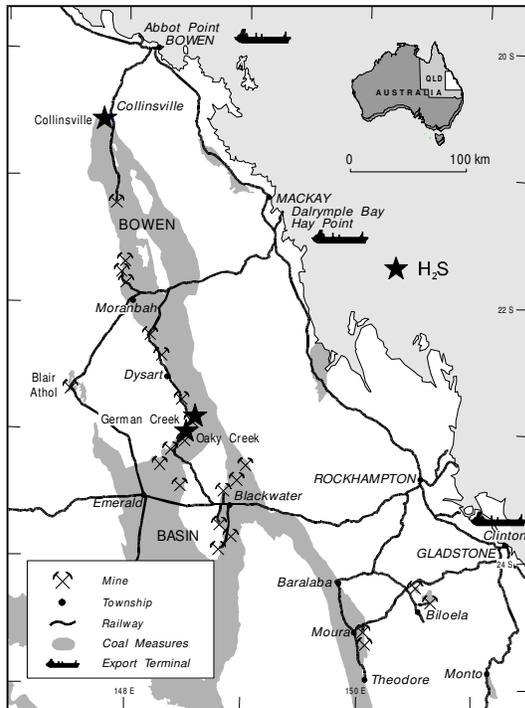


Figure 1. Locality maps of some Australian coal mines with H₂S seam gas (After Ryan, et al., 1998)

GENERAL INFORMATION ABOUT H₂S

Properties of H₂S

H₂S, also known as sulphuretted hydrogen or rotten egg gas, has no colour but a powerful and unpleasant odour. It is liquid at high pressure and low temperature. It has a specific gravity of 1.19 and burns in air with a bright blue flame producing sulphur dioxide and water vapour. The human nose can detect concentrations as low as 0.02 ppm, however increasing exposure desensitises the olfactory organ and concentration levels above 50 ppm can no longer be smelt. H₂S forms flammable mixtures in air in the range of 4.5-45 percent. It is highly reactive and corrosive to all organic and metallic compounds.

Physiological Effects of H₂S

H₂S is an extremely toxic gas and can cause death at exposures above 500 ppm. It irritates the lungs and respiratory tract and has a narcotic effect on the central nervous system (Strang and Mackenzie-Wood, 1990). The reaction of H₂S with fluids in the nose and lungs forms sulphuric acid. The toxicity of H₂S is due to the H₂S molecule itself rather than to Hydrosulphide or sulphur ions (Elvers, et al., 1989). The effect of H₂S on a person's health can be extreme, depending on the concentration to which they are exposed. The duration of exposure, while still important, is of secondary interest as indicated in Figure 2.

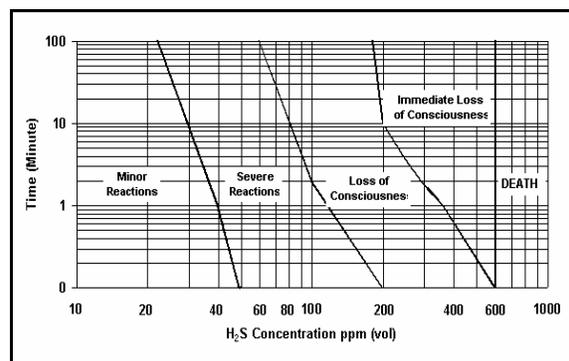


Figure 2. Physiological effects of H₂S (After Shell Safety Committee, 1996)

Threshold Limits of H₂S

The Australian Standard for exposure to H₂S is 10 ppm (TWA-8 hrs) or 15 ppm (STEL-15 min.). The US Department of Labor, Occupational Safety and Health Administration's acceptable ceiling concentration is 20 ppm for 10 minutes once only if no other measurable exposure occurs. The acceptable maximum peak concentration above the acceptable ceiling concentration for an 8-hour shift is 50 ppm.

OCCURRENCE OF H₂S

The occurrence of fossil H₂S gas in coal measure strata has been noted in France, Canada, China, Russia and Australia (Ko Ko and Ward, 1996). In a study by Smith and Phillips (1990) on the sulphur isotope ratio ³⁴S/³²S, the source of coal seam H₂S was proposed as a biological reduction of sulphate supplied from a marine transgression which was generated in a low iron environment and was not converted to pyrite. This allowed large quantities of H₂S to react with organic matter and to be trapped within the coal seam during the maturation. Moelle (1987) (cited Phillips, *et al.*, 1990) suggests that the occurrence of H₂S in Europe was associated with sapropelic muds containing the remains of the Carboniferous plants. Recent research into the sources of H₂S in Australia coal mines has given more weight to an organic rather than an inorganic source (Gillies, *et al.*, 2000).

The H₂S–organic sulphur link is supported by positive correlation between bitumen/pyro-bitumen and H₂S, between carbon and sulphur and between sulphur isotope data of coexisting H₂S and organic sulphur. The organo-sulphur compounds dominate the sulphur gases generated by coal pyrolysis although substantial quantities of SO₂ are present. K-Ar dating indicates that the coals containing the high H₂S zones were subjected to a complex thermal history that included at least three separate thermal/hydrothermal and intrusive events.

PREDICTION OF IN-SITU COAL H₂S GAS LIBERATION

Sampling

The prediction of in-situ coal H₂S gas liberation levels which will be released in the mining sequence during cutting, breakage and transport can be achieved by testing exploration cores or rib coal samples exposed during development. Obtaining representative samples from coal containing H₂S is complex. H₂S is a difficult gas to contain as it is highly reactive and is able to permeate through most container walls. Each sample collected for testing must be sealed on site. For longer-term storage of samples Teflon containers or a plastic pipe capped at both ends can be used.

A number of different sampling and testing methods were utilised pre-mining to predict the levels of H₂S concentration in the gassy zones including rib sampling, vertical drilling and in-seam horizontal drilling core sampling methods (Gillies, *et al.*, 2000).

Determining H₂S Content of Coal

There was no established technique for determining H₂S content of coal when the contaminant was first encountered within Queensland's Bowen Basin. An early form of drum tumbler system was developed to determine the H₂S

content of coal (Phillips, *et al.*, 1990). A modified design with the ability to constantly sample gas during coal breakage was developed by O&B Scientific (Figure 3) in 1996.

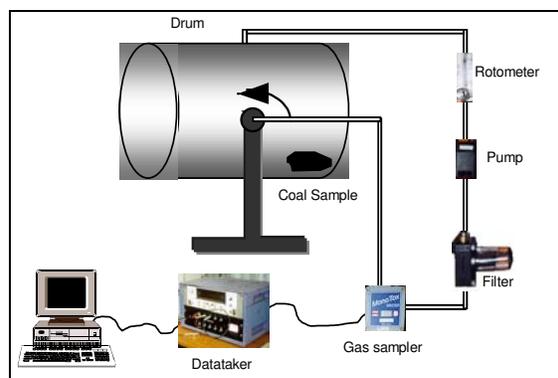


Figure 3. Drum tumbler system and portable gas analyser

The system consisted of a rotating high-density polyethylene 255-litre drum. The drum tumbled a sample at 20 rpm for approximately 180 seconds to produce coal breakage representative of the size of coal on the armoured face conveyor. The sample was sized after testing. The test was used to determine the volume of H₂S released into the atmosphere from a given sample under controlled conditions (Gillies and Kizil, 1997). This testing method was reliable but was labour intensive.

Coal samples collection from the mine face and transporting to the surface for testing for H₂S is a labour intensive and time consuming process. To simplify the process and save time, an instrument called the Portable Gas Analyser (PGA) was designed in the University of Queensland Department of Mining, Minerals and Materials Engineering (Figure 3).

The PGA is a portable coal sample crusher that is intrinsically safe and can be taken directly to the mining face for in-situ coal seam sample testing for gases. The construction of stainless steel was chosen to avoid corrosion and to allow use in gassy underground coal mine areas.

Prediction of H₂S Release

A comprehensive examination of approaches to prediction of in-situ coal H₂S gas liberation potential has been undertaken. The important gas content level sought is that released in the mining sequence during cutting, breakage and transport (Figure 4). An understanding of H₂S sources is mainly obtained by monitoring the velocity and movement pattern of the ventilation air on longwall faces. Generally, the higher the air velocity the more H₂S will be carried away from the source. Over the past years several H₂S source surveys have been carried out in German Creek Southern Colliery as part of a study aimed at understanding the mechanisms of H₂S generation on mechanised longwall faces.

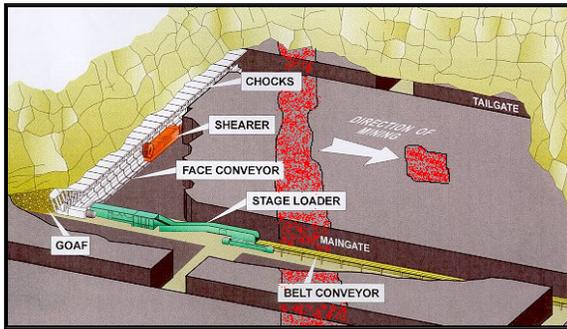


Figure 4. Sources of H₂S in longwall mining

The liberation of large quantities of H₂S along the face was found to be primarily from the shearing and breaking of the coal. Other important sources of H₂S were identified as:

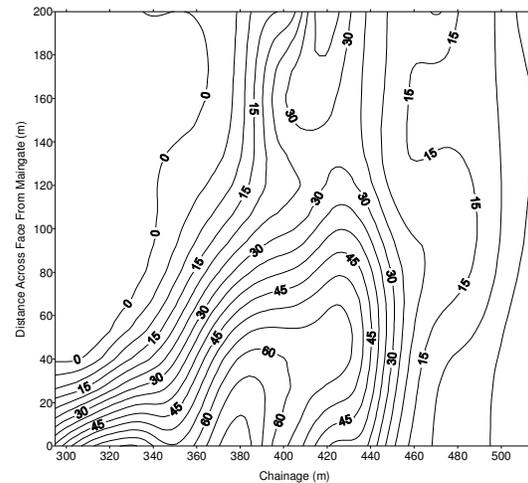
- H₂S contaminating the intake airway,
- Coal transport via the Armoured Face Conveyor (AFC),
- Coal transport via the Breaker Stage Loader (BSL),
- The breaking of coal through the crusher,
- AFC & BSL side discharge unit (corner at MG) and
- Coal transport via the longwall panel belt.

The multiple sources of H₂S make the analysis difficult due to the behaviour of the H₂S and the distribution and ventilation dilution in the longwall section. However, the shearer was the major primary H₂S source. Other sources, in particular the support movement and coal transport on the AFC also contributed a significant proportion of the total of the H₂S generated on the longwall face.

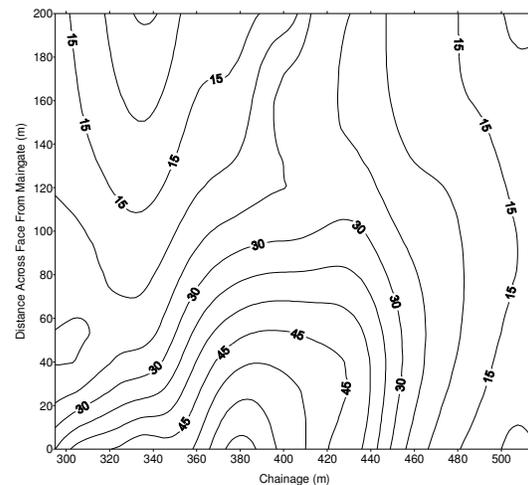
Modelling of H₂S Gas Distribution

Modelling H₂S concentrations with geostatistical approaches was found to be complex due to uncertainties associated with the nature of the technique and errors in sampling and testing (Gillies, *et al.*, 1999). Use of

geostatistical analysis has been very beneficial in terms of improving understanding of models of “indicated” H₂S seam concentration levels from the given data. Kriging was determined to be the most appropriate approach in the modelling of the H₂S data sets. This study has demonstrated that care is needed in applying a geostatistical approach to obtain a valid model (Figure 5).



Kriging



Inverse Distance to a Power

Figure 5. The effect of different geostatistical methods on modelling H₂S distribution within the coal seam

Detection and Monitoring of H₂S

H₂S detection and monitoring can be achieved in a number of ways. To protect against overexposure to H₂S continuous monitoring instruments are installed on face and in outbye areas. These instruments are based on the diffusion characteristics of toxic gases and usually incorporate an electrochemical detector that delivers an audible and/or visual display signal. These sensors are used to continuously monitor H₂S gas concentration levels in face areas and outbye ventilation

circuits. Portable sensors, set to alarm at 10ppm and to record TWA and STEL levels, are carried by mine officials and were provided to operators when mining in H₂S zones.

Both case study mines in the project, Oaky Creek and German Creek Southern collieries had permanent mine telemetry systems that were adapted to record H₂S concentration levels in the airflow within longwall panels and along mine returns. Both mines also recorded mine airflow with main fan pressure sensing gauges. Regular monitoring was used to identify areas and operations likely to exceed threshold limits. Direct reading/recording personal monitor instruments also had an important place in the study and in the mining operations through H₂S zones.

SAFE PRODUCTION THROUGH H₂S AFFECTED ZONES

Personal Protective Equipment

Filters represent a cost-effective and short-term safe way for miners to work in a potentially lethal environment. A series of laboratory tests were undertaken under conditions simulating mine H₂S laden atmospheres to establish safe operating limits for some filter types available. An initial set of tests was undertaken to determine the efficiency of cartridge type filters. The cartridges were tested at H₂S concentration of 148 ppm for duration of 12.7 hours and found to maintain 100 percent efficiency throughout. It was demonstrated that cartridges far exceeded their manufacturer's life.

A second set of tests was carried out to test Racal Health and Safety EP3 type filters used on a Racal

powered turbo unit attached to an airstream helmet. An atmosphere of 100 percent humidity and concentration of 50 ppm of H₂S were used. The findings from this experiment were that the Racal EP3 combination type filter could be used in parallel with other filters on the Racal turbo unit for a conservatively estimated total of nine 8 hour shifts. It is recommended that they be available as standard equipment to all longwall crews where H₂S is present as a hazard.

At both mines the personal protective equipment used consisted of full face masks fitted with a particle filter Class P3 and a Gas filter Class B2E2 which offers the highest level of protection for an apparatus of this type. A full-face mask fitted with this protection is rated for use in 100 times the TLV level or 5000ppm, which ever is the lowest.

Ventilation

The mine ventilation system can be modified to allow safe production through H₂S affected zones. Designs for maximising safe production through affected mine panel or development headings were tested. These involved increasing face ventilation rates, use of panel belt homotropical or panel and main belts homotropical ventilation, full homotropical panel ventilation, the gaining of exemption on maximum H₂S concentration levels permitted and use of forms of remote mining. Ventilation network simulation models of whole mines with H₂S variations were developed, fan capacity examined and alternatives costed. Employee positioning was another key aspect during remote or partially remote mining sequences. Figure 6 show the full homotropical ventilation system, which can be used to maximise the quantity of airflow on the longwall face as well as improving the air quality at the same time.

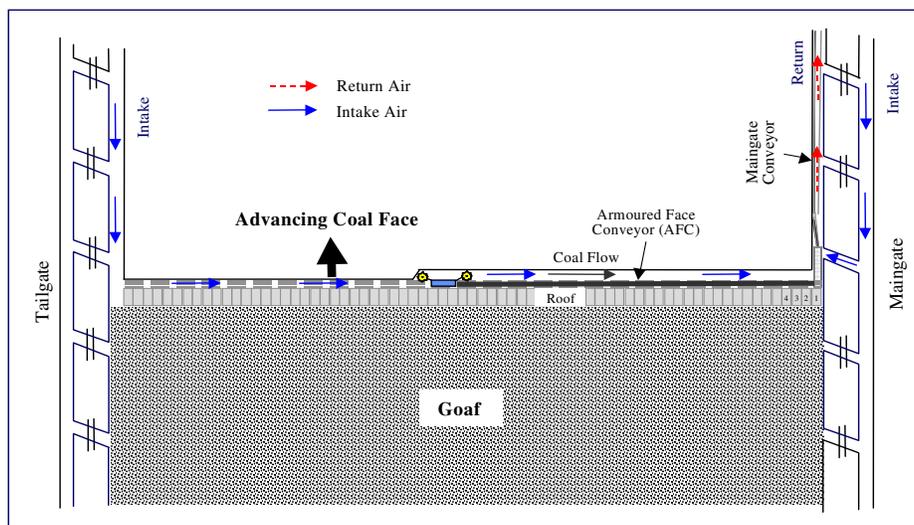


Figure 6. Full homotropical ventilation system for longwall mining

Mining Options

Rate of H₂S emission is generally a function of mined particle size; the finer the coal cut the higher the H₂S released. A reduction in H₂S emissions during mining can be achieved by cutting coal at a slower rate and by reducing the amount of fines produced. At German Creek Southern Colliery operators quickly learned that they could control the emission level on their personal H₂S monitors by varying the cutting rate. This combined with feed back on the H₂S released on previous shift contributed to the production rates achieved in the H₂S zone.

Other methods might include use of various pick lacings, use of water jet assist cutting and the use of ploughs with or without water jet assist. Furthermore, training of operators should occur with implementation of appropriate safety guidelines, provision of protective equipment and breathing apparatus and continuous monitoring of H₂S by electronic devices. Placement of all face personnel on the intake side of the shearer while cutting coal, increasing distance between the shearer operator and the shearer H₂S liberation point and reduction in the number of persons on the face to the absolute minimum are other operational options. Many of the approaches used to minimise exposure of face personnel to respirable dust have application here.

Spray Chemical Neutralisation of the Gas

The approach of adding chemicals through the mine face water spray system to neutralise H₂S gas released from breaking coal can use large quantities of chemicals and produce a corrosive environment hazardous to employees health. Corrosion can cause a great deal of

damage to the longwall panel machinery and equipment and in particular to chock legs and electronic instrumentation. An examination was made of different available chemicals to reduce the corrosive effects of any solutions. The toxicity of chemicals used within the mining process is another important aspect here.

To reduce the level of H₂S gas entering the ventilation system, trials were performed where chemical spray neutralisers were placed at key H₂S source points. Tests were performed at the corner of AFC where coal was being transferred to the BSL conveyor. This point was believed to be one of the major sources of H₂S liberation. The chemicals used were Sodium Carbonate and Sodium Bicarbonate. The transfer point between AFC and BSL was sprayed with these chemical solutions for one shear and the H₂S liberation levels were recorded. Although there was only limited testing, the indication was that the spray chemical neutralisation of the atmospheric H₂S gas had a positive effect.

A venturi Scrubbing unit using buffer solution was tried on the crushing unit to reduce dust and gases entering the face ventilation. When the H₂S monitor on the face read a H₂S gas level of more than 10 ppm the sprays in BSL and scrubber switched from water to buffer solution. This saturation process eliminated up to 70 percent of the H₂S gas emissions at the BSL. An illustration of the system is shown in Figure 7.

In Seam Chemical Neutralisation

A major program of in-seam chemical neutralisation infusion trials was undertaken at German Creek Southern Colliery. The basic aim of the chemical

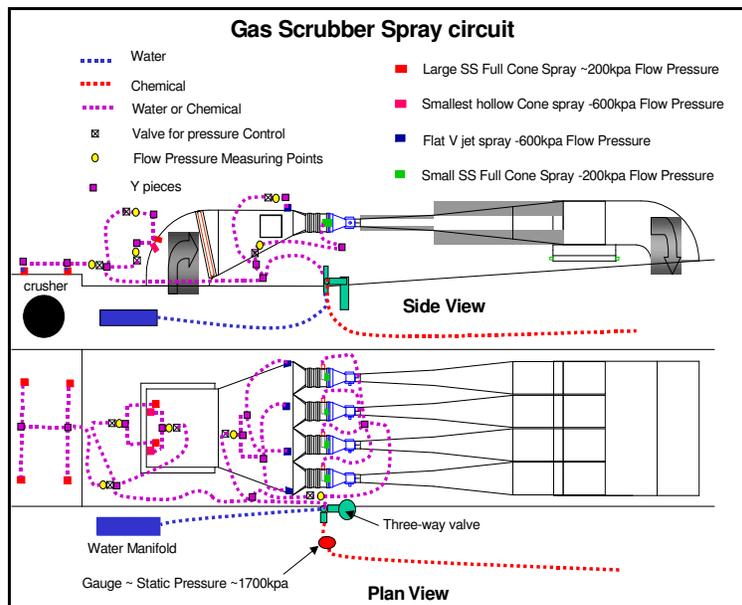


Figure 7. H₂S scrubber spray circuit

infusion process was to pre-strip a significant proportion of H₂S to allow coal mining at a production rate that ensures a safe working environment at all times while ensuring that adequate production levels are maintained to safeguard the mine lifespan. The area to be infused in each of these panels varied significantly resulting in different approaches to spacing of boreholes and other design aspects.

Extensive data was collected on infusion fluid flow rate, H₂S pick up, effect on face atmospheric quality and the mining schedule during these trials. The chemical buffer chosen for this operation was sodium sesquicarbonate, which is essentially sodium bicarbonate and sodium carbonate with two water molecules. This form was chosen because it is readily soluble in water whereas sodium carbonate is difficult to dissolve.

After the zone of H₂S was identified, the appropriate infusion design was determined. Horizontal boreholes were drilled into the zone (as an example six bore holes rib to rib, 40 m apart), required chemicals obtained, surface (mixing plant, storage tanks and boreholes) and underground facilities (manifold, pump, tank, packers) established and monitoring equipment (pressure gauges, underground and surface flowmeters) set up as shown in Figure 8.

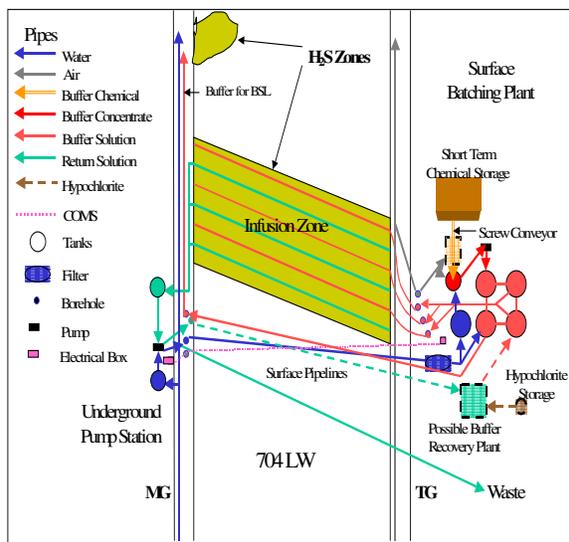


Figure 8. Longwall infusion infrastructure

The infusion process was carried out as follows:

- Infusion fluid was prepared on the surface by mixing of Sesquicarbonate and water.
- The mixture flowed to the underground manifold to be distributed into the odd number boreholes under static head pressure.
- The fluid filled the boreholes under pressure.

- As each borehole end was blocked by a high-pressure packer the fluid was forced to flow through the coal seam (cleats, matrix and pores).
- The fluid migrated towards the even number boreholes. As the fluid flowed through the seam H₂S from the coal passed into solution.
- The H₂S laden fluid flowed from the even boreholes into an underground tank for pumping to the surface.
- On the surface neutralisation occurred and sulphides present in the fluid broke down quickly.

The chemical infusion process significantly reduced the H₂S emissions within the panel, decreased risks to employees and improved the productivity of the longwall retreat operation. The infusion process was analysed for ability to reduce H₂S gas emissions whilst maintaining the required longwall production rates.

Microbiological Oxidation of H₂S

A study was undertaken to obtain preliminary evidence for microbiological oxidation of H₂S and its removal from coal. The major matters for investigation were the resistances of the organism to toxic levels of H₂S, the ability of the organism to remove H₂S from voids in the coal, and to sustain growth and metabolic activity in the coal environment. The study found that it was possible to grow the cultures of *T. denitrificans* on sulphide as the sole source of energy but the bacteria grew more slowly on sulphide than on the less toxic thiosulphate.

The culture of *T. denitrificans* tolerated sulphide concentrations up to 1500 µm (48 ppm S²⁺) but could only be passaged up to five times at 800 µm (26 ppm S²⁺) before losing viability. The presence of thiosulphate allowed a few more passages before also dying out. It was not possible to obtain a stable sulphide-tolerant mutant of *T. denitrificans* during the time available.

Preliminary evidence has been obtained to show that *T. denitrificans* is able to utilise H₂S evolved from a coal core. However, the level of H₂S only reached 0.69 ppm in the surrounding solution due to the low levels in the coal core used. This level of H₂S was removed from solution in two days. It was demonstrated that in a coal sample of low porosity with high levels of H₂S, the removal of the H₂S might be limited by the ability of the H₂S to be released into solution. It is likely that pressure would be required to assist with the solubilisation of the H₂S in the surrounding water medium. There is sufficient evidence to suggest that the microbiological removal of H₂S from coal could be achieved with *T. denitrificans* provided the H₂S can be extracted from the coal and provided the H₂S concentration does not exceed toxic levels that can be handled by the microbiological agent.

Permeability Study

A programme of laboratory permeability studies was undertaken to gain data necessary for the design of the infusion tests undertaken at German Creek Southern Colliery. Extensive physical testing was undertaken principally using permeability facilities developed at the University of Queensland for testing HQ sized core. This data was needed to allow development of a system of infusion boreholes with the ability to drain and flood the seam with chemicals to convert H₂S to an inert substance before release to atmosphere. Permeability tests were also undertaken on core from Oaky Creek Colliery in an attempt to understand the apparent significant differences in desorption characteristics of coals between the two mines lying on adjacent leases.

The German Creek Southern Colliery core sample exhibited greater permeability parallel to the cleats than perpendicular to the cleats. This was in contrast to the Oaky Creek core sample for which the permeability in the direction perpendicular to the cleats was of the order of 50 times greater than parallel to the cleats. The increased permeability perpendicular to the cleat direction is contrary to the expected trend. A possible explanation is the presence of faults within the sample not visually discernible from the sample ends and running perpendicular to the cleat direction providing a relatively low resistance flow path compared with the cleats.

CONCLUSIONS

A comprehensive study has been undertaken on a major impediment to mining in a number of areas in Queensland, Australia. It has been approached using a multi-disciplined team. Some aspects have been of a fundamental nature and laboratory based while others have involved implementation of applied engineering technology on-site at the mining operations supporting the project.

The study was the first of its kind. Prediction of future occurrences of H₂S zones can occur with greater reliability. A major benefit has been that mines facing extraction in H₂S coal seam zones have greater confidence due to the findings of studies and trials undertaken. Safety risk assessments can be undertaken from a base of objective data.

There is a greater ability to quantify the cost of not mining through or sterilising H₂S affected coal compared to the cost of proactively altering (and possibly slowing down) the mining system and incorporating aspects such as changed ventilation, chemical sprays and seam neutralisation. Respiratory filters represent a cost-effective and short-term safe way for miners to work in a potentially lethal environment.

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