1998

Report on hydrogen sulphide experience at Southern Colliery

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**Publication Details**

ABSTRACT

Hydrogen sulphide (H$_2$S) as a seam gas has occurred in several locations in the German Creek seam at Southern Colliery. This paper overviews the techniques developed to quantify the H$_2$S content of the seam, overviews research into controlling and reducing H$_2$S emissions from the seam, and details the procedures used to mine through the H$_2$S zone in 702 longwall panel. Learning points from research and mining experience are reviewed for application in the next longwall block.

INTRODUCTION

Southern Colliery is operated by Capricorn Coal Management Pty. Ltd. and is situated inland from the coastal cities of Mackay and Rockhampton Qld (See Fig. 1).
The colliery is an underground longwall operation, mining the German creek seam, the lower most major economic seam of the Bowen Basin's Permian German Creek formation.

Hydrogen Sulphide (H₂S) gas was first detected in the open cut workings adjacent to the proposed entries for Southern Colliery in October 1987.

Subsequent development of the mine (1988) encountered H₂S for the first 800m of mains and during the development and extraction of the first longwall block (601) (Smith, Phillips and Byrnes, 1990) (See Fig. 2). Significant H₂S was not found again until the development of the gate roads for the 701 longwall block in January 1995 (Ko Ko and Ward, 1996). The H₂S zone was not mined in 701 longwall panel as poor roof and weak floor conditions required the longwall face to be relocated outbye of the H₂S zone. In June 1996, H₂S was encountered again during development of the 702 panel maingate. Development, drilling and testing has delineated a continuous H₂S zone through at least four longwall panels (701 to 704) (See Fig. 3).

Other significant occurrences of H₂S have been found in the Bowen Basin, at Oaky Creek Mine 15 km west of Southern Colliery and at Collinsville 300 km to the north. Minor occurrences have been found at Newlands, Crinum, Gregory and Gordonstone mines (See Figs. 1 and 2).

This paper reports on the experiences of mining through the H₂S in the 700's district of the mine.
A surface drilling program of eight holes coring the German Creek seam commenced in February 1995. The coal was analysed using drum tumble and silver nitrate tests to quantify the H₂S content of coal. In June 1995, during the development of 701 main gate B heading, H₂S was encountered between 18 and 23 cut-throughs. Rib samples of coal were taken and tested. The results of these samples showed minor quantities of H₂S, despite deputy’s reports indicating high levels.

In August 1995, it was decided to conduct further drilling programs from the surface and from underground to define the extent of the H₂S zone and to facilitate a trial chemical infusion of the zone.

Underground drilling program for 701 longwall

The drilling program started in September 1995 drilling horizontal holes using a ProRam from 701 tailgate at 22 cut-through. These holes were not successful; one hole reached its target, the other holes terminated in the roof or floor close to the collar. In October 1995 a Diamac 260 rig was used to drill five 170m holes in a fan pattern from 701 tailgate at 22 cut-through. Core samples were analysed for H₂S content. The drilling program and associated tests gave an indication of the levels of H₂S present and the extent of the zone (see Fig. 3).

It was discovered that the Drum tumbler, silver nitrate tests and delays between sampling and testing were providing varying and questionable results.
INITIAL RESEARCH INTO QUANTIFYING AND REMOVING OF H₂S FROM COAL

Infusion by hydraulic fracture method

In October 1995, five vertical holes were drilled from the surface, into the 701 longwall panel. Staff from CSIRO Petroleum conducted permeability and stress measurement tests. This was followed by a trial infusion, injecting zinc chloride (ZnCl₂) with a fluorescein dye tracer using the hydrofrac method. This proved unsuccessful as post infusion drilling showed no evident reduction in H₂S levels, or any trace of the 35 000 litres of the dye solution (Ko Ko and Ward, 1996). Had the area been mined then a better assessment of the success of hydrofrac could have been made.

Spray technology

After the failure of the infusion trials, efforts turned to developing a chemical spray to absorb H₂S from the atmosphere. Laboratory tests were conducted using a range of chemicals in US in the oil industry for the removal of H₂S from drilling mud. Efforts were made to source a chemical used in China (Peng et al, 1992) without success. However literature research revealed the importance of pH levels in neutralising H₂S.

The pH has to be high enough to ionise the H₂S thus enabling it to be removed by oxidation. Fig. 4 shows the equilibrium of the aqueous system, H₂S, HS⁻ and S⁻ with relative concentrations versus pH (Garrett et al, 1979).

Following initial discussions with Shell, CSIRO, ICI and mine personnel a test rig was set up by the CSIRO. The aim was to simulate a H₂S contaminated mine roadway, and to test the effects of different chemicals, varying pH, varying flow rates, and varying spray droplet size on H₂S contaminated air in the test rig (See Fig. 5). Three series of duct tests were undertaken producing some positive results, the best giving a 91% reduction in H₂S levels (see Fig. 6). The initial test used sodium hydroxide to control pH and sodium hypochlorite to oxidise H₂S. This test proved effective, however the pH of the solution at 12.4 was unacceptable for the mining environment. Varying spray droplet size between 50 and 150 micron produced little difference in the effective removal of H₂S. Later tests replaced sodium hydroxide with a buffer solution to keep the pH below 10 and these produced acceptable results. However tests without hypochlorite, using buffer only, reduced the effectiveness of H₂S removal by more than 50%.

![Fig. 4 - pH effect on equilibrium of sulphur species in aqueous solution (Garrett et al, 1979)](image-url)
The tests proved that levels of H$_2$S in the atmosphere could be controlled with economic quantities of chemical sprays, however the best results were achieved at pH levels above those acceptable in the mining environment. The most successful chemical, sodium hypochlorite, was potentially more corrosive on face equipment than the H$_2$S itself.

Fig. 5 - Set up for H$_2$S spray tests

Fig. 6 - Typical spray test result
Drum tumbler

A Drum tumbler system with the ability to constantly sample gas during coal breakage was designed and manufactured by O&B Scientific (see Fig. 7).

The system rotated a 255 litre drum constructed from High Density Polyethylene (HDPE), end for end about a central stainless steel shaft. The drum tumbled the sample at 20 RPM for 60 revs. The period of rotation produced coal breakage representative of the size of coal on the armoured face conveyor (AFC). The test enabled the prediction of the volume of H_2S released into the atmosphere from a given sample.

DEVELOPMENT OF 702 MAINGATE

H_2S was encountered during development at 16 cut-through 702 maingate in June 1996. A monitoring program was set up to compare the predicted and actual amount of H_2S released. The predicted H_2S released was determined from face and rib samples gathered during mining operations and tested using the drum tumbler. The actual release was determined by logging coal production, measuring ventilation quantities at regular intervals, and monitoring the H_2S levels in the return at 15-seconds intervals. Reasonable correlation was found between the results of predicted and actual H_2S released (Harvey, 1996). A similar monitoring program was set up when 703 maingate intersected the H_2S zone in June 1997.

ACARP PROJECT

A research project, “Maximising Coal Production in the Presence of H_2S Seam Gas” jointly funded by ACARP, Oaky Creek and Southern Collieries, was set up to investigate:
• Occurrence of H₂S;
• Prediction of H₂S release;
• Storage Mechanisms;
• Mine ventilation system and control measurements;
• Mining options;
• Permeability; and
• In seam chemical neutralisation.

The project is being staffed by a research team from the University of Queensland, Departments of Mining, Minerals and Materials Engineering, Earth Sciences and Chemistry.

The project was started with mine funding to enable monitoring of Oaky Creek Longwall 8 as it mined through a H₂S zone in October/November 1996. Samples were taken from the ribs, at 10m intervals in both headings of the H₂S zone and from the face during production. These samples were tested for H₂S content using the modified drum tumbler. Sub samples were sent to University of Queensland for further analysis. The data from H₂S sensors on face, ventilation and production for each shift was recorded and analysed to determine the actual H₂S release in litres per tonne.

At Southern Colliery, in April/May 1997 a surface and underground drilling program was conducted to determine the extent of the 702 H₂S zone and to investigate the 703 zone. Analysis of the drum tumble results from this program and from previous rib sample data was correlated with actual H₂S release from continuous miner development at Southern Colliery and from Oaky Creek Longwall 8. The results of this analysis were used to produce a contour model of the predicted H₂S release in 702 and 703 longwall panels (See Fig. 3).

UNDERGROUND INFUSION FROM HORIZONTAL HOLES

In July 1997 it was decided to conduct a trial infusion with a buffer solution of sodium carbonate and sodium bicarbonate in an attempt to reduce the H₂S emission from 702 longwall. Another attempt at infusion was made because:

• Infusion provided a pro-active approach to reducing H₂S emissions;
• mining the infused area would enable effective evaluation of its success; and
• research into chemicals to absorb H₂S enabled appropriate infusion chemicals to be selected.

Nine holes were drilled using a ProRam, from “C” heading in 702 maingate, between 16 and 17 cut-throughs. The holes were approximately, 6 m apart, 90 m in length and at an angle of 45 degrees to the main cleat direction (See Fig. 3). The holes via a shut off valve were fed into two separate manifolds, connecting alternate holes back to a pump and 8000 litres storage tank. Initially underground water supply was connected to the system and pressure and flow rates recorded to establish the permeability of the seam. Over a period of 14 days approximately 50 000 Litres of buffer solution was pumped into the seam, at a maximum pressure of 1800 kPa, using different valve configurations and various pump and flow-back sequences to ensure the maximum saturation of the seam in the time provided. During the flow-back process the return fluid was sampled and H₂S content. Preliminary analysis of results indicates that approximately 18 000 L of H₂S was taken into solution during infusion, which represents approximately 20% of the measured H₂S release from the infused zone.
MANAGEMENT PLAN

A management plan was developed at Southern Colliery with the primary aim of preserving the health and safety of those working in areas affected by H₂S. In order to achieve this, the plan was designed to:

- Prevent any persons from being exposed to concentrations of H₂S above 10 ppm in the general body of air;
- prevent the maximum concentration of H₂S anywhere in the mine from exceeding 200 ppm;
- protect mining equipment from H₂S corrosion; and
- maintain adequate production.

The ACARP research team worked closely with mine operators during the extraction of the 702 H₂S zone. Their purpose was to monitor emissions and worker exposure levels each shift and prepare data for feedback to operators each day.

VENTILATION

Ventilation in the panel was conventional antitropical on the face and homotropical in the maingate conveyor road. Compressed air venturi fans were placed in an exhausting vent duct system from the BSL to outbye of the pantechnicon. The system was designed to duct H₂S-laden air generated in the BSL to outbye of the pantechnicon into the homotropical conveyor road (Fig. 9).

MINING PROCEDURE

The rate of cutting coal was used to control the release of H₂S. When H₂S levels approached 10 ppm the shearer haulage was stopped to reduce H₂S emissions.

Some of the procedures that were put in place to limit access to the face and reduce risk and exposure to H₂S were:

- All people on the face were to be located on the intake side of the shearer, when the shearer was cutting,
- all people inbye of the last accessible cut-through on the intake roadway were required to carry a face mask at all times,
- face masks were worn by all persons on the face line when the armoured face conveyor was conveying coal and/or the shearer was cutting coal, and
- personal H₂S monitors were carried by the deputy, the chock operator and the shearer operator.

Several alarms, both visual and audible were situated in the face area to warn when H₂S was approaching pre-determined levels. These alarms were set at the following levels:

- The H₂S monitor on the maingate drive was set to give a visible alarm at 10 ppm;
- the power to shearer was cut off if the tailgate H₂S monitor recorded a level of 200 ppm; and
- coal cutting was stopped if the monitor in the homotropical conveyor road reached 100 ppm.
Face samples

During the mining of the H₂S zone in 702 longwall panel, a total of 153 coal samples were taken from the face for testing. The data from these samples was used to produce a contour map of the H₂S zone (See Fig. 8). Samples taken approximately 20 cm from the intersection of infusion holes and face showed a 75% reduction in H₂S content compared with samples taken over a metre away from holes.

Fixed detection systems

Electro-chemical H₂S sensors (AMR) were used to continuously monitor H₂S gas concentration levels within the longwall ventilation circuit. Sensors were placed at either end of the longwall face (See Fig. 9), outbye in the longwall homotopal conveyor return, in the tailgate return and at two locations along the main trunk conveyor system.

CORROSION

Corrosion of materials due to H₂S in moist atmospheres is well known. Damage that occurs to steel is minimal compared to damage caused to copper and some copper alloys. The most noticeable damage experienced at Southern Colliery was to the coating (92% copper and 8% tin) on chock legs. Field and laboratory tests undertaken by consultants (ETRS, 1997) on behalf of CapCoal have shown that the coating is attacked by H₂S, leaving an outer coating of copper sulphide, underlain by layers of tin oxide and tin. This coating, when mixed with coal dust, forms a rough crust on Chock Legs. Damage to chock leg seals can be attributed to this crust. To reduce the corrosion potential, the chock legs on 702 longwall were coated with raw solsenic oil and wrapped in plastic. This method worked well provided the wrapping remained intact.

To check the corrosion risk to electrical components, copper strips were placed in electrical boxes on the face area and along outbye conveyor roadways. Each strip was weighed and numbered prior to installation. After mining through the H₂S zone these copper strips were checked. Those placed in flameproof boxes in the face area were unaffected. However minor corrosion was found on strips in the outbye belt starters.

Fig. 8 - H₂S contour based on face samples correlated to measured H₂S release per shear
PERSONAL PROTECTIVE EQUIPMENT

The specifications of personal protective and monitoring equipment issued and used during mining in \( H_2S \) zone is given in Table 1. Face masks and filter units were accepted by operators and proved to be a viable protective device for the situation.

Personal monitors gave repeatable results and proved reliable if charged correctly.

LEARNING POINTS AND COMMENTS

Exploration and testing

The detection of \( H_2S \) zones during exploration drilling has proven difficult due to the size and shape of zones. The ACARP research program includes a study of indicators in coal that may improve detection.

Drum tumbling of core or rib samples can give a good estimate of the \( H_2S \) released during mining. A reliable estimate requires the results to be correlated with actual release from mining in a \( H_2S \) zone in that seam and the samples must be tested on the same day that they are collected. The ACARP project is investigating the bonding between \( H_2S \) and coal and release mechanisms of \( H_2S \) from coal.

Control of emissions

Initial attempts at infusion and using hydrofracing were unsuccessful due to use of an unsuitable chemical and the inability to determine the extent of infused zone in coal. Subsequent infusion tests using parallel holes in seam and a buffer solution did reduce \( H_2S \) emissions. The extent of this reduction is still being evaluated and a more extensive infusion program for next panel is being considered.
Atmospheric control of H₂S levels by sprays has been shown the potential to greatly reduce H₂S levels, however the chemicals used are too corrosive for the face environment. A test using buffer solution to wet coal as it entered the Beam Stage Loader (BSL) gave encouraging results and this concept is being evaluated for control of H₂S release on (AFC) and maingate for the next panel.

Mining experience

The workforce accepted the operating procedures, protective equipment and monitoring equipment. This was in no small part due to the previous experience of mining H₂S affected coal in the mine, the training given to the workforce and the daily feedback of exposure levels and face emissions. This feedback enabled longwall operators to gain confidence in their ability to control H₂S emissions. Overall productivity in the zone was reduced by about 20%.

Sources of H₂S during mining

Data on H₂S sources has not been fully evaluated but initial indications are shown in table 2.

<table>
<thead>
<tr>
<th>Source</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shearer</td>
<td>50% to 70%</td>
</tr>
<tr>
<td>AFC (depends on location of H₂S zone)</td>
<td>5% to 10%</td>
</tr>
<tr>
<td>Maingate corner</td>
<td>10% to 15%</td>
</tr>
<tr>
<td>Desorbed from face</td>
<td>5% to 10%</td>
</tr>
<tr>
<td>BSL and longwall conveyor</td>
<td>10% to 20%</td>
</tr>
</tbody>
</table>

The most difficult gas source to control is the AFC. Three options available for emission control in the next longwall panel are:

- To infuse the face with buffer solution;
- to wet coal on the face and AFC with buffer solution; or
- to install a curtain along the face to segregate air.

A fourth option of reversing the ventilation is not currently approved under Queensland legislation. Minor amounts of H₂S were recorded in outbye conveyor roadways but these were less than expected. A duct and hood arrangement was installed at the longwall conveyor transfer as a precaution.

Ventilation

The use of homotropal ventilation of longwall conveyor and an exhausting fan duct system on BSL proved successful. The use of an electric fan and smaller duct system to replace the venturi fans is being investigated for the next panel.

ACKNOWLEDGEMENTS

The authors acknowledge the contribution made to the control and study of H₂S at Southern Colliery by staff from CapCoal, Oaky Creek, Shell Coal, CSIRO and The University of Queensland and associated researchers. The opinions expressed in the paper are those of the authors and not necessarily those of these organisations.
### WARNING DEVICE (ENVIRONMENTAL MONITORING UNIT)

Zellweger (neotronics) - Analitics minigas - 4 sensor gas unit, measuring:

- O₂ - high and low
- CH₄ - % by volume
- CO – ppm
- H₂S – ppm

### RESPIRATORY PROTECTION / EYE PROTECTION


- Clear polycarbonate visor which offers full eye and face protection;
- Less than one ppm leakage when fitted correctly; and
- Full training given including negative pressure testing and individual practical use of mask and filters.

### FILTERS

The two filters used are:

1. Sundstrom 210/310 - Particle filter Class P3 - high standard filter
   - Dust, viruses, bacteria, asbestos, smoke, aerosols;
   - Conforms to - AS 1716 – 1991; and
   - Licence No – 0766

2. Combined with Sundstrom - Gas filter B2E2 High standard filter
   - Class 2 filter when used with a full face mask and the 210/310 particulate filter;
   - Offers highest level of protection for apparatus of this type;
   - Conforms to - AS 1716 – 1991;
   - Licence No. – 0766; and
   - Filter exceeds Australian licensing requirements for H₂S.

Full face mask with this protection is approved for use up to 100 times TLV level or 5000 ppm which ever is lowest.