IN-SITU DETERMINATION OF SULPHUR IN COAL SEAMS AND OVERBURDEN ROCK BY PGNAA

M. Borsaru[a*], M. Berry[a], M. Biggs[b] and A. Rojc[a]
[a]CSIRO Exploration and Mining, P.O. Box 883, Kenmore, Qld 4069, Australia
[b]Capricorn Coal Management Pty. Ltd., Private Mail Bag, Middlemount, Qld 4746, Australia

Abstract

The PGNAA technique was tested successfully for the determination of sulphur in coal seams and overburden rock. The logging tool employs a 3 µg ^{252}Cf neutron source and a 50 mm dia x 100 mm BGO detector.

Keywords: PGNAA; In-situ analysis; Sulphur; Coal; Nuclear logging

1. Introduction

Nuclear logging is well established in the coal mining industry. In many countries, all of the exploration holes drilled by the coal mines are logged. The most common geophysical techniques employed for logging are: sonic, resistivity, neutron-neutron, gamma-gamma and natural gamma. The gamma-gamma technique, commonly used by the logging companies, is non spectrometric. It measures the density of the matrix surrounding the borehole and is therefore, capable of delineating the coal seams due to the difference in density between coal and the interseam sediments. This technique can also be calibrated to measure the ash content of the coal seams, based on the correlation ash/density that exists for many coals. However, this indirect method for ash determination is not accurate for coals where the ash/density correlation does not hold. The logging tool is normally fitted with three NaI(Tl) detectors: two of the detectors record the backscattered gamma radiation and one detector is used to record the natural gamma radiation present in the borehole. As is the case with gamma-gamma logging, most of the logging companies only record the total natural gamma. Spectrometric natural gamma is not commonly used in the coal mining industry. Total natural gamma logging is useful for delineating the coal seams on the basis that coal releases less natural gamma rays than the interseam sediments. Spectrometric natural gamma logging would provide more information and probably will replace total natural logging in the future. In the natural gamma-ray spectral log, the potassium, uranium and thorium components of the gamma radiation are determined and the K, U, Th, and their ratios are useful for borehole lithology determinations and correlations.

* Corresponding author. Tel: +61-7-3327-4627; fax: +61-7-3327-4455
E-mail address: mihai.borsaru@csiro.au

Prompt gamma neutron activation analysis (PGNAA) is another technique developed for coal logging [1-4]. It has been demonstrated that this technique can be used for the determination of density, ash, Fe, Si, Al, and to delineate the coal seams. The technique is also able to determine in situ the deformation temperature of coals for which a correlation exists between the deformation temperature and the percentage of Al, Si and Fe present in coal [4].

The purpose of the present work was to test the suitability of PGNAA for the determination of sulphur in both coal seams and overburden.

Sulphur creates problems in many areas of coal quality and marketability and when contained in host rock causing Acid Mine Drainage (AMD). Sources of acid drainage in the coal mining industry are overburden stockpiles, rejects, tailings and coal washery wastes. In coal marketing, sulphur limits are commonly specified in sales contracts and unacceptably high concentration of sulphur can attract heavy penalties or even cargo rejection, especially from countries with stringent environmental laws. The ability to accurately assess sulphur and its distribution in overburden rocks will also enhance planning to optimize rehabilitation management of spoil and AMD. A technique to measure sulphur in-situ in both coal seams and overburden rocks is likely to find applications also in environmental studies.

2 Methodology

2.1 Principle of sulphur determination

The in-situ determination of sulphur is based on prompt gamma neutron activation analysis (PGNAA). This technique employs a neutron source as the primary source of radiation. The fast neutrons released by the source undergo many interactions in the slowing down process. During this process some neutrons will disappear through different neutron reactions and some will reach thermal energy (< 0.1 eV). Thermal neutrons will continue to diffuse through the medium without further loss of energy until their life is terminated by other processes, such as, radiative capture.

Due to its high hydrogen content, coal is an excellent matrix for the PGNAA technique. The average number of scatterings calculated for a few elements present in coal to slow down a 14 MeV neutron produced by a neutron generator to thermal energy are: H(19), C(112), O(154), Al(290), Si(297), Fe(539). This shows the unique position of hydrogen in slowing down neutrons. Hydrogen's importance in the slowing down process is further enhanced when taking into account the scattering cross-section. Most of the common nuclei abundant in rocks have scattering cross-sections of several barns. The proton's scattering cross-section in the energy range ~10^5 eV and 0.5 eV is about 20 barns. The neutrons released by the neutron source are therefore thermalised by colliding with the hydrogen nuclei and consequently induce capture reactions with the nuclei present in coal. The major gamma-rays produced by the main constituents of the mineral matter in coal, Al, Si, Fe, Ca, Ti, S have energies above 3 MeV which makes PGNAA less sensitive to other neutron reactions or natural gamma radiation that produce gamma-rays of lower energy. Also, the deeply penetrating neutrons and high energy gamma-rays allows PGNAA to sample a large volume of coal or rock. This makes the technique less sensitive to the rugosity of the borehole than the gamma-gamma technique and provides for better sampling statistics, especially in heterogeneous deposits.

The most intensive gamma-rays released by sulphur have energies of 0.84, 2.38 and 5.4 MeV. The 5.4 MeV gamma-ray is most suitable for the determination of sulphur in coal. This gamma-ray is well separated from the major gama-rays released by the other major elements present in coal. The determination of sulphur in this work is based on recording the variation of count-rate in this energy peak. The 0.84 and 2.38 MeV gama-rays are also predominant. However, the very strong 2.2 MeV peak produced by hydrogen in coal may interfere with both 0.84 and 2.38 MeV peaks through its Compton tale or due to the inadequate resolution of the scintillation detector.

2.2 Choice of the neutron source and gamma-ray detector

The neutron sources most commonly used in borehole logging or industrial applications are ^{252}Cf, Am-Be and the neutron generator. The neutron generator has the advantage that it can be turned off when it is outside the borehole. However, the neutron flux is not reliably steady and the life time of the generator tube is limited. Taking into account its high cost, one can say that at the present time the neutron generator is not a cost-effective choice for this application. The mean energy of the fission neutron spectrum of ^{252}Cf is appreciably lower than that of Am-Be and therefore ^{252}Cf is better suited for neutron-capture applications. Also, ^{252}Cf is more environmentally acceptable for routine borehole applications because of its shorter half-life (2.64 y). For these reasons, it was used for this work. However, one disadvantage with using the ^{252}Cf neutron source is that the source must be replaced every 4-5 years due to its fairly rapid decay.

There are four types of spectrometric gamma-ray detectors commonly used: the high resolution solid state Ge detector and the scintillation detectors NaI(Tl), CsI(Na) and $Bi_4Ge_3O_{12}$ (known as BGO). The high-resolution Ge detector is needed where full elemental analysis is required. However, one disadvantage is its low efficiency for high-energy gamma rays. The BGO detector is best suited for neutron capture measurements due to its greater stopping power than either NaI(Tl) or CsI(Na) and the fact that it is less sensitive to activation and capture than the other scintillation detectors. The logging tool built for the present work employed a BGO scintillation detector. The constraint on the BGO detector was that it had to fit into a logging tool of diameter less than 72 mm. This implies that the diameter of the scintillation detector should not exceed 50 mm. A 100 mm x 50 mm dia BGO detector was chosen for the 72 mm diameter logging tool.

2.3 Description of the PGNAA logging tool

The logging tool has a diameter of 72 mm and was manufactured from a Carbon Fiber/Kevlar composite. The logging tool employed a ^{252}Cf source of strength 3 μg and a 100 mm x 50 mm dia BGO detector. As ^{252}Cf releases both gamma-rays and neutrons, the BGO detector and the neutron source were separated by 80 mm of lead to stop the gamma radiation emerging from the neutron source to reach the scintillation detector. The lead shielding also scatters the neutrons released by the ^{252}Cf neutron source. The lead shielding has a conical shape and was placed in a high density polyethylene block. A 15 mm spacer made of high density polyethylene was also placed between the neutron source and the scintillation detector. The polyethylene contributes to the thermalisation of neutrons and produces a 2.2 MeV hydrogen peak in the capture spectrum, which is used to stabilize the gain especially when the logging tool is not in the coal seam and the hydrogen gamma-ray peak is not so pronounced. The BGO scintillation detector was covered with an aluminium cup coated with a 16-mg/cm^2 layer of ^{10}B (mixed with epoxy resin) to shield the detector assembly from thermal neutrons and therefore reduce the number of capture gamma-rays produced from the photomultiplier and detector assembly. Such gamma rays would interfere with the capture gamma-rays produced by the ash constituents in coal. The gain of the electronic equipment was automatically stabilized by using the 2.22 MeV capture gamma-ray peak of hydrogen. This peak is positioned at channel 111 in the energy spectrum, so that the energy dispersion is ~20 keV per channel. Gain stabilization is especially important with the BGO detector because of its extreme sensitivity to temperature variations.

The logging system is a single wire system using a common conductor for communications as well as powering the tool. Pulses produced by the gamma-ray detector are processed by a microprocessor incorporated in the probe and transmitted to the uphole computer. The system is using a high speed A2D (analog to digital) converter with the data being processed into 480 channels. The full logging system consists of the tool, winch, a laptop computer and the 18.5 x 18.5 x 6.5 cm 'SWISS' box. The SWISS box provides the power supply and the interface between the tool and the laptop computer. The logging system is portable and so does not necessarily require a dedicated logging truck.

3 Laboratory tests

Three bulk coal samples of 270-litres volume each with different sulphur concentrations were prepared for the laboratory tests of the logging tool. The coal in two of the samples was mixed with pure sulphur so that the sulphur concentration in the samples was 1.6 and 3.2% S respectively. The third sample was made from coal collected from the clean coal stockpile after the washery; no sulphur was added. The coal samples were placed in 270-litre tapered plastic drums, 850 mm height and 700 mm and 530 mm top and bottom diameter respectively, with a tube in the middle. The tube was made from ABS, a material that does not contain chlorine, Cl. Chlorine has a large absorption cross-section for neutrons and would interfere with the measurements. The external and internal diameters of the tube were 90 mm and 78 mm, respectively. This 4π geometry resembles borehole geometry. The laboratory tests were carried out to view the tool's response to sulphur and also to compare the 100 mm x 50 mm dia BGO detector used in the current tool with other BGO detectors of different sizes used in two other tools of 100 mm external diameter. It is important to test the response to sulphur of larger diameter BGO detectors. If the response to sulphur of larger diameter detectors that can be accommodated in larger diameter tools (e.g. 100 mm), is significantly better, larger diameter tools should be used in quality control holes drilled of larger diameter. The sizes of the other two BGO detectors were: 75 mm x 75mm dia and 75 mm x 62.5 mm dia. The source-detector-shielding configurations of the three tools available for the laboratory tests were slightly different. However, the slight difference in configurations should not influence significantly the tools response to sulphur and useful information can be obtained. Figures 1a and 1b show the neutron-gamma spectra recorded in the coal samples with the 72 mm tool using the 100 mm x 50 mm dia BGO detector. Figure 1a shows the energy range 0 – 3000 keV of the spectrum. There are two prominent peaks in the spectrum: the superposition of the 480 keV peak (produced by the ^{10}B coated aluminium cup) with the 511 keV gamma-ray peak and the 2.23 MeV hydrogen peak. Figure 1b shows the energy range 3000 – 9000 keV of the spectrum. The 5.42 MeV sulphur peak and the 4.9 and 3.54 MeV silicon peaks are well defined. The strong peak at 4.9 MeV is a superposition of two peaks: 4.9 MeV gamma-ray released by Si following the neutron-capture reaction and the first escape peak from the sulphur 5.42 MeV peak.

Figure 2 shows the neutron-gamma spectra given by the three logging tools in the coal model with 3.2% sulphur content. The figure shows that the 100 mm x 50 mm dia BGO detector compares favorable with the other two detectors and it was chosen in the current application. The figure also proves that this 72 mm diameter tool can be as effective as the larger diameter tools for logging holes of larger diameter.

4. **Discussion of the work**

The capability of the 72 mm PGNAA logging tool to determine sulphur in coal seams and overburden was evaluated at three coal mines in Queensland: Capcoal German Creek Mine, Curragh Mine and a third mine from the Bowen Basin.

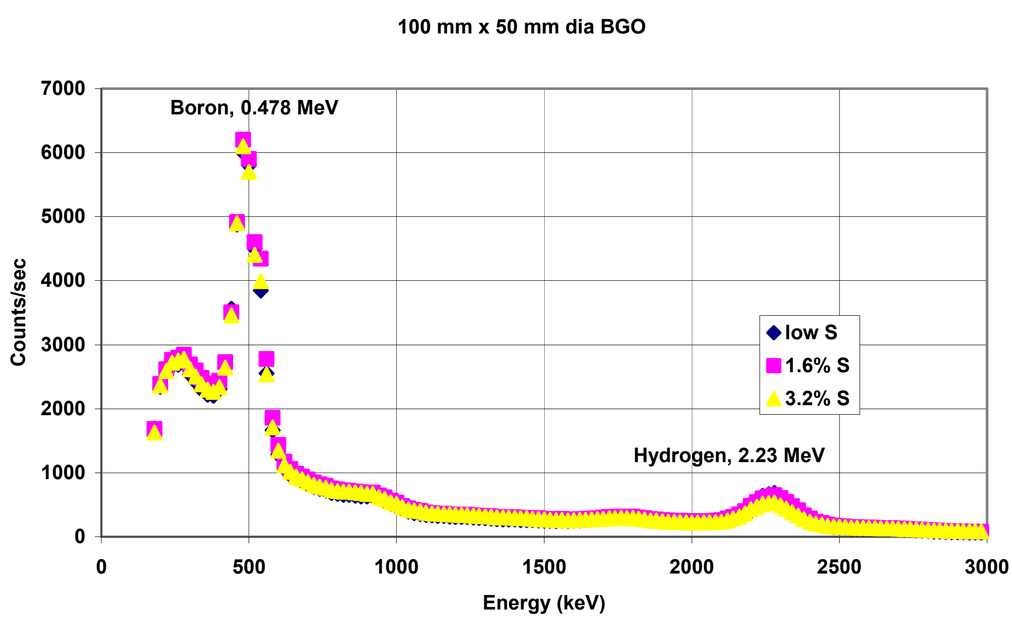

Figure 1a: Neutron-gamma spectra collected in bulk coal samples with the 100 mm x 50 mm dia BGO detector. Energy range 0 – 3000 keV

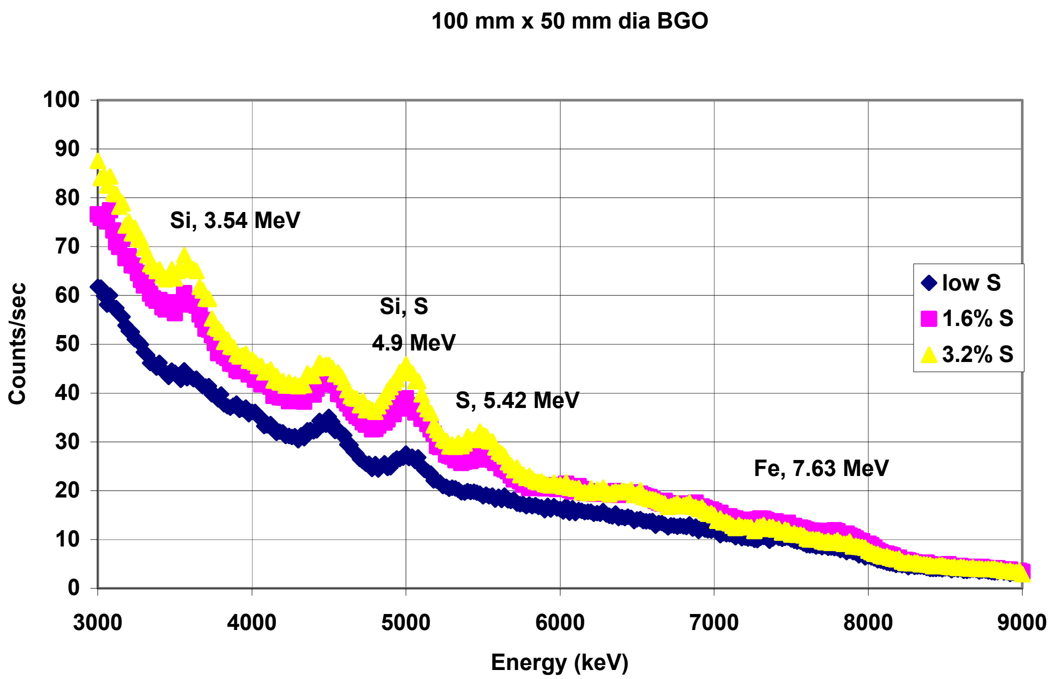

Figure 1b: Neutron-gamma spectra collected in bulk coal samples with the 100 mm x 50 mm dia BGO detector. Energy range 3000 – 9000 keV

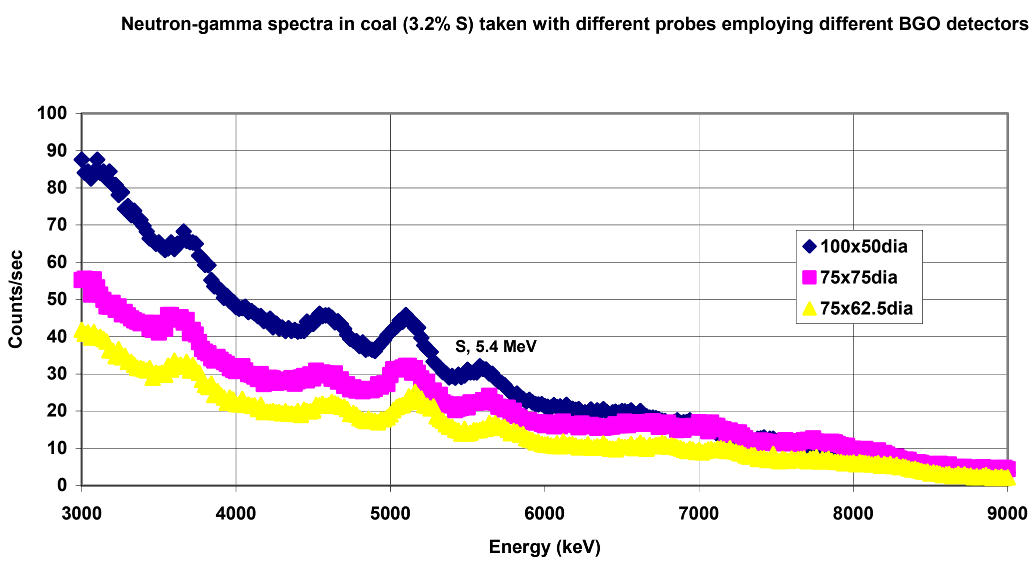

Figure 2: Neutron-gamma spectra collected with the three tools in the sample with 3.2% sulphur content.

Three cored holes and one open hole were logged at Capcoal Mine. Two of the cored holes, 366c and 367c, were drilled to a depth of 380 m. The other cored hole, DDR1316, was only 60 m deep. A special open hole, 60 m deep, was drilled in the overburden and sampled for total sulphur at 1.0 m or 0.5 m intervals. This hole was specially drilled to test the suitability of the tool for the determination of sulphur in overburden.

Two cored holes, 306c and 367c were logged at Curragh Mine. The core was sampled at 1 m intervals and the assays for total sulphur and ash were made available.

Four cored holes were logged at the third mine from Bowen Basin. The complete ash analysis and total sulphur of the samples taken from one of the coal seams were made available. Unfortunately, the sulphur in the coal seam was very low (<0.3%) and did not show any variation.

4.1 Data analysis and interpretation

Multiple regression analysis was used to calibrate and test the accuracy of nuclear logging for the prediction of sulphur. The method entailed setting windows in the gamma-ray spectrum and fitting a linear regression model of the form:

Percent S $= a_o + a_1X_1 + \ldots + a_nX_n$,

where a_0, a_1, …,a_n are constants and $X_1,\ldots, X_n$ are count rate variables for ratios of selected windows chosen in the gamma-ray energy spectrum. The windows were chosen to correspond to the Sulphur, Hydrogen or Boron peaks, the whole gamma-ray spectrum or other regions in the gamma-ray spectrum that could interfere with the count rates recorded in the sulphur peak. Ratios are chosen as variables for two reasons: i. as normalization of the neutron flux required because the neutron flux produced by the ^{252}Cf source is distorted by the presence of hydrogen and other elements present in coal or overburden and ii. to avoid corrections for the decay of the ^{252}Cf neutron source with a half-life of 2.64 years.

4.2 Results from field tests

The determination of sulphur in coal.

Table 2 shows the results from field tests for the sulphur determination given by the regression analysis. Different combinations of the logging data were used in the regression analysis. Due to the low sulphur content and small variation in sulphur at the Curragh and the Bowen Basin Mines, the data from these mines, ~350 km apart, were combined for the analysis. Although it is preferable to analyse the data from different mines separately and have different calibrations for different mines, the cored holes at the Curragh and Surat Basin Mines were drilled in similar type of coal and were analysed together. *At* Capcoal Mine all the boreholes *(*with the exception of DDR1316) were drilled into and intersected various seams within the Fairhill and German Creek Formations. DDR1316 was located at the Little Parrot Creek deposit, 10 km east of German Creek and intersected seams within the Rangal Coal Measures and Burngrove Formation. The logging data for DDR1316 were treated separately.

In one analysis, the cored holes 366c and 367c and the section of coal intersected in the open hole were analysed together having identical diameters.

Table 2: Results from field tests at three coal mines

Mine and type of holes	Number of strata	Sulphur range %	RMS deviation (wt%)	Correlation coefficient	Standard deviation of population (wt%)
CAPCOAL Cored Hole DDR1316	21	0 – 0.7	0.09	87	0.18
CURRAGH Cored Holes 306c, 340c MINE BOWEN BASIN Cored Holes	10	0.1-0.8	0.1	90	0.2
CAPCOAL Cored Holes 366c, 367c Open Hole: coal section	11	0.5-3.9	0.4	96	1.3
CAPCOAL Open Hole: Overburden	12	0–11.7	0.44	99	3.3
CAPCOAL Open Hole: Overburden	11	0 - 2	0.33	88	0.62

The variation in the sulphur content of coal is small both in the coal logged at the Curragh Mine and the coal mine from the Bowen Basin. The sulphur content is generally below 0.3% S. The data collected from the two mines were analysed together. A number of coal strata with sulphur content below 0.3% S were randomly excluded from the analysis so that the regression equation is not biased towards the region of low sulphur.

The determination of sulphur in overburden.

The open hole drilled at Capcoal has been used to assess the capability of the PGNAA tool for the determination of sulphur in overburden. Table 2 shows the results of the regression analysis for 12 strata of overburden with the sulphur concentration varying from 0 to 11.7% S. Another regression analysis was carried out on the same data set but with the exclusion of the 11.7% S point. This was done due to the fact that there is a sizeable gap between the 11.7% S point and the next lower S concentration point 2% S. The results for the 11 strata varying in S from 0 to 2% S are also given in table 2.

A comparison of predicted sulphur content and sulphur content determined by laboratory analysis in coal is shown in figure 3.

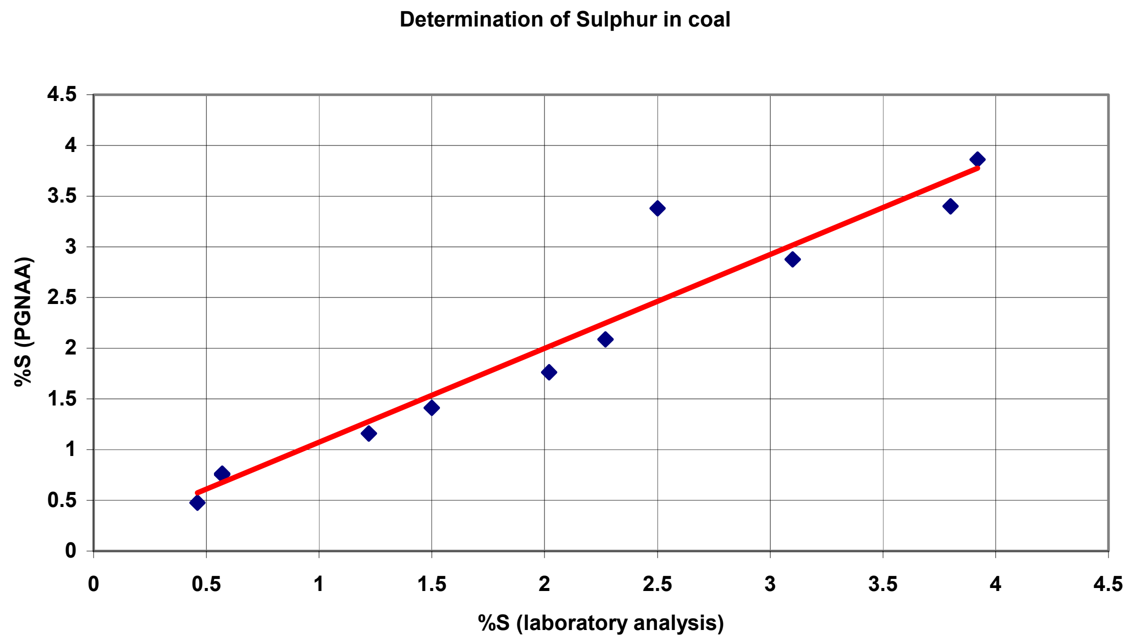

Figure 6. %S (in coal) – laboratory analysis vs. PGNAA prediction at CAPCOAL for cored holes 366c and 367c and the coal seam intersected by the open hole.

5. Summary and Conclusions

The present work proves that the PGNAA technique can be employed for the in-situ determination of sulphur in coal and overburden. The logging tool manufactured for this work has an external diameter of 72 mm. The tool is suitable for logging HQ holes (96 mm diameter) or larger diameter holes. The logging speed is 1 – 1.5 m/min. This is slower than the logging speed used by the commercial logging companies. However, when the tool is used for the determination of sulphur in coal seams, the logging speed outside the coal seams can be much higher (3 – 4 m/min) so that the extra time for logging 20 m of coal is ~15 minutes.

The PGNAA technique provides the most comprehensive set of petrophysical and elemental quality data for the coal seams and overburden of any currently available. The technique is capable to determine the ash, Fe, Si, Al, Ca, S and the density of coal seams (Borsaru et al., 2001). The slagging index of coal can also be determined for some types of coals for which a correlation exists between the deformation temperature and percentage of Al, Si and Fe present in coal.

The present PGNAA technique developed for coal logging could have applications for in-situ determination of salinity by measuring the chlorine concentration in boreholes.

The strength of the neutron source was 3 μg. This is not considered a high activity radioactive source and does not cause extra problems than the routine logging currently carried out by logging contractors.

In order to get the best predictions of the coal parameters mentioned above, the tool must be calibrated in cored holes drilled in the same deposit. The density and elemental composition of the ash must be determined in the laboratory and the results used for the calibration. Once the tool is calibrated, the cost of logging with the PGNAA tool is only slightly higher than the conventional logging. This is due mostly to the lower logging speed and the extra money in the initial capital cost of the tool and neutron source.

It should be stressed again that the gamma-gamma technique currently used for borehole logging for coal can only determine the density while the PGNAA technique described in this work and an earlier publication [4] can determine the density as well as other coal parameters. The PGNAA tool could find applications in environmental work for acid mine drainage due to the fact that it can measure sulphur and Fe.

Acknowledgements

The authors wish to thank Capricorn Coal Management Pty. Ltd. And Curragh Queensland Mining Limited for their support. The authors also wish to thank Simon Brady (Curragh Queensland Mining Pty. Ltd.) and John Merritt (Capricorn Coal Management Pty. Ltd.) for their help and support during this work. This work was supported under Australian Coal Association Research Program (ACARP).

References

[1] J. Charbucinski, S.F. Youl, P.L. Eisler, M. Borsaru, Geophysics, 51 (1986) 1110.

[2] M. Borsaru, J. Charbucinski, P. Eisler, C. Ceravolo, Nucl. Geophys. 2 (1988) 201.

[3] M.Borsaru, M.S. Biggs, W.J.F. Nichols, Nucl. Geophys. 7 (1993) 539.

[4] M. Borsaru, M. Biggs, W. Nichols, F. Bos, Appl. Rad. Isot. 54 (2001) 335.

Figure Captions

Fig 1a Neutron-gamma spectra collected in bulk coal samples with the 100 mm x 50 mm dia BGO detector. Energy range 0 – 3000 keV

Fig 1b Neutron-gamma spectra collected in bulk coal samples with the 100 mm x 50 mm dia BGO detector. Energy range 3000 – 9000 keV

Fig 2 Neutron-gamma spectra collected with the three tools in the sample with 3.2% sulphur content.

Fig 3 . %S (in coal) – laboratory analysis vs. PGNAA prediction at CAPCOAL for cored holes 366c and 367c and the coal seam intersected by the open hole.