

# A Source of Manganese Pollution in Appalachian Coal Shales

By P.A. DRYBURGH<sup>1</sup>, P.J. NORTON<sup>2</sup> and W.B. SCOTT<sup>3</sup>

<sup>1</sup>Head of Technical Services, Power Inc., Pennsylvania, USA

<sup>2</sup>Principal, Peter J Norton Associates, Richmond, Yorks, UK

<sup>3</sup>Senior Lecturer, Sunderland Polytechnic, Tyne and Wear, UK

## ABSTRACT

In the USA and in particular in Pennsylvania the pollution laws are probably the strictest in the world. They are also unique in the fact that there is a very severe limitation of 4 mg/l on the Manganese content of mine effluent water. In order to chemically treat the effluent the pH of the water must be raised to 10 in order to precipitate the Mn. The cost of this treatment is very high resulting in many coal mining companies going bankrupt because of it.

The authors believe that on future mine sites there could be considerable environmental and cost benefits if the water could be prevented from becoming polluted with the Mn in the first place. A research programme in conjunction with Power Incorporated on their planned surface mines was therefore started.

By taking samples and using the latest X-Ray Analysis techniques a major source of Mn has been found associated with siderite nodules in the strata immediately beneath some of the coal seams. Manganese contents as high as 3.5% have been found in "basic" or "alkaline" siderite nodules. These are very susceptible to attack by acidic water percolating downwards particularly from the overlying seams which have a high sulphur content.

By isolating this Mn bearing strata during the operational and restoration phases in the mining process it is hoped that this pollution problem will be solved in a more economic and effective way than in the past.

## INTRODUCTION

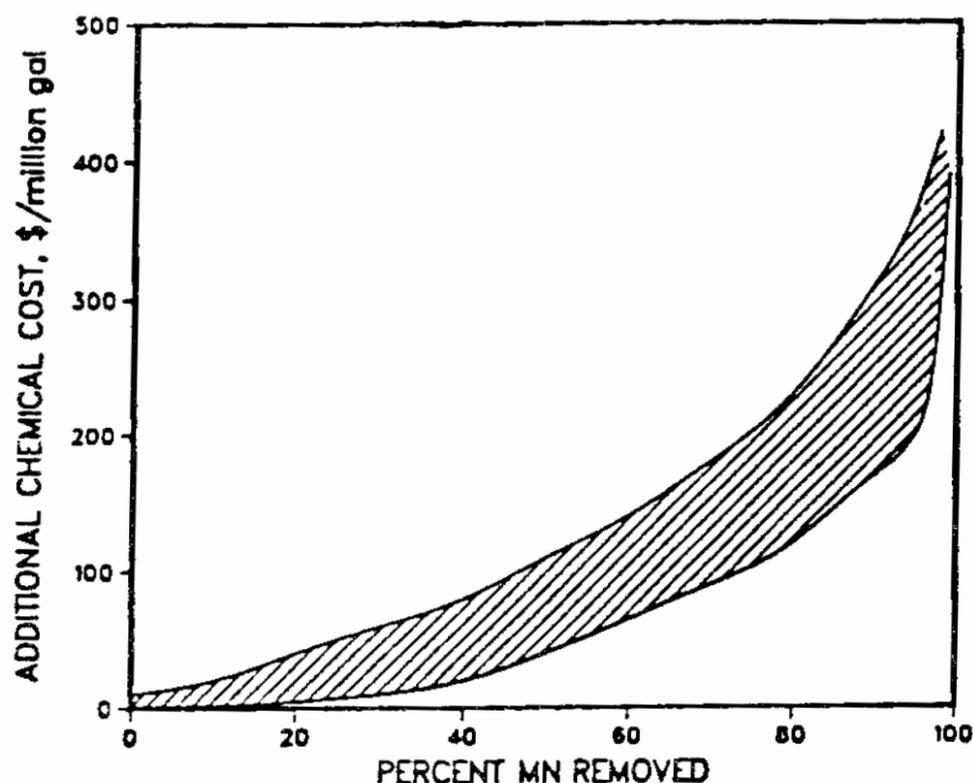
Power Incorporated, a US subsidiary of Crouch Mining wish to expand their North American mining operations which includes several potential new surface coal mines in Clearfield and Centre Counties, Pennsylvania. The coals in this area are high in sulphur and the mining is subject to severe environmental legislation regarding pollution of downstream watercourses<sup>(1)</sup>.

The State Department of Environmental Resources (DER) regulates the pollution to the following limits:

|                        |          |
|------------------------|----------|
| Iron (Fe)              | : 7 mg/l |
| Manganese (Mn)         | : 4 "    |
| Total Suspended Solids | : 70/ "  |
| pH                     | : 6 to 9 |

## 40 Dryburgh, Norton & Scott - Source of Manganese in Coal Shales

Where mine effluent is high in Manganese the last proviso is a particular problem as mine operators have found that they must raise the pH to over 10 in order to remove the Mn and hence not only break the law but also incur considerable costs:



**FIGURE 1:** Cost of manganese removal (after Kleinmann & Watzlaf<sup>2</sup>)

Many operators have filed for bankruptcy as a result of these problems and operators wishing to expand their mining find that they cannot meet the strict permitting requirements regarding Mn pollution for their future mine sites.

Some of the Manganese discharges from abandoned previous mining activity on the proposed mine sites can rise as high as 243 mg/l and are listed and monitored by DER Inspectors. In order to obtain approval for these new sites it is necessary to convince the DER that abatement of the pollution will be achieved not only during the operational phase but also the restoration phase and for the foreseeable future.

Surprisingly, very little research has been carried out in North America into the Mn problem and as recently as 1990 one American author can be quoted as stating "because the source of Mn in coal bearing strata is poorly understood, predicting the occurrence of Mn in mine drainages is difficult"<sup>(3)</sup>.

It was therefore decided to initiate a research programme at one of the future mines where Mn was a considerable problem in order to find out in the first place, the source of the Mn, secondly, the mechanism whereby it is transferred into the groundwater and lastly to find the most cost effective remedy for the problem.

### BACKGROUND HYDROGEOLOGY

#### Geology

The strata to be excavated at the proposed mine is within the Allegheny Group of the Pennsylvanian Period and extends from the Lower Kittanning (B Coals) up to the Lower Freeport (D Coals). The sequence is composed of 75% fine grained sandstones with the

4<sup>th</sup> International Mineral Water Association Congress, Ljubljana (Slovenia)-Pörschach (Austria), September 1991

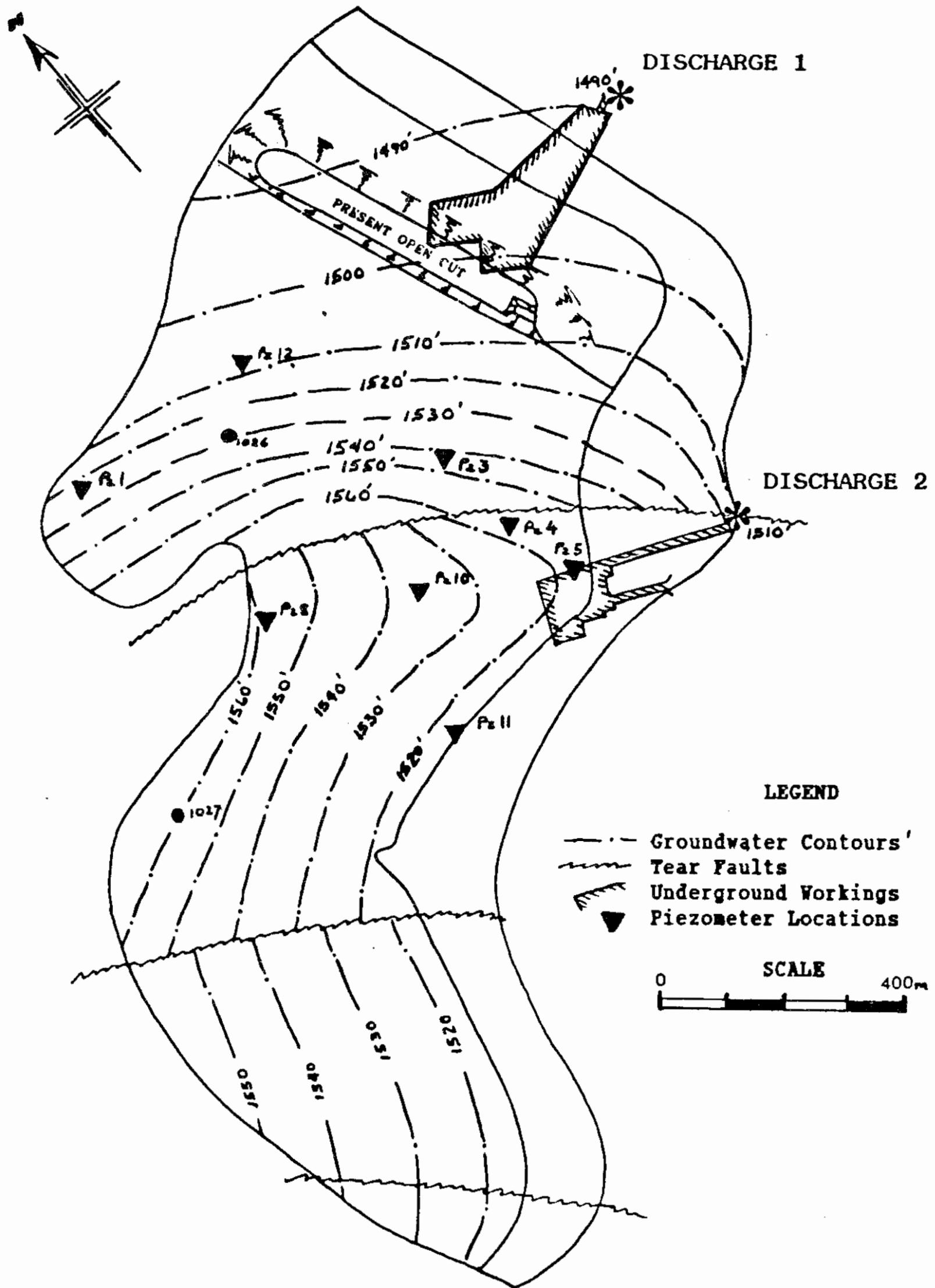


Figure 2: Hydrogeological plan of proposed mine

## 42 Dryburgh, Norton & Scott - Source of Manganese in Coal Shales

remainder silty mudstones, seatearths and coals. Many of the mudstones between the B and C Coals have interbedded thin bands and nodules of Siderite ( $\text{FeCO}_3$ ).

The strata on site dips gently north westwards and is dissected by tear faults with a north west-south east trend. The faults have small vertical throws but the fault planes themselves often act as acquicludes.

### Hydrogeology

The groundwater flow in the rock is seasonal and perched in distinct units above the seatearths occurring below the B, C and D Coals. The main water table is above the B Coal and has been monitored with piezometers. (See Figure 2). The presence of abandoned underground and surface mine workings interrupts what would be the normal flow of the groundwater to the west and it collects in the voids before flowing out at the discharge points.

The discharge points have been monitored and two in particular are regarded as grossly polluting acid mine discharges which are high in iron and manganese although the flows are minimal:

|                    | FLOW<br>1/s | pH  | Fe<br>mg/l | Mn<br>mg/l | Al<br>mg/l | Specific<br>Conductance<br>(micromhos) |
|--------------------|-------------|-----|------------|------------|------------|--|
| <b>DISCHARGE 1</b> |             |     |            |            |            |  |
| Average            | 0.5         | 3.8 | 92         | 94         | 74         | 4780                                   |
| Maximum            | 1.9         | 2.8 | 380        | 243        | 95         | 7100                                   |
| Minimum            | DRY         | 5.2 | 0.5        | 3          | 57         | 370                                    |
| <b>DISCHARGE 2</b> |             |     |            |            |            |  |
| Average            | 0.5         | 3.8 | 1.9        | 20         | 20         | 1214                                   |
| Maximum            | 4.5         | 2.6 | 20         | 114        | 36         | 3600                                   |
| Minimum            | DRY         | 4.1 | 0.1        | 0.9        | 10         | 163                                    |

**Table 1: ANALYSIS RESULTS AT THE MAIN AMD DISCHARGES**

As can be seen there is a large variation in the acidity and chemical content of the discharges but the average results all show that the pollution limits are being exceeded.

### FIELD STUDY

It has been known for over 100 years that Fe tracks with Mn in a chemical fashion and especially where Siderite nodules in marine deposits are concerned<sup>(4)</sup>. The fact that Mn oxides are reduced by the activity of similar bacteria to those involved in Fe reduction has also been well documented. In acidic lakes Mn and Fe will replace Ca as the dominant cation contributors to alkali production.

Because of the location of the discharges at the mine site it was reasonable to assume that the source of the Mn must lie within the strata associated with the B Coals. There is also

**Dryburgh, Norton & Scott - Source of Manganese in Coal Shales**

a high incidence of Siderite in this part of the sequence, especially in the mudstones between the B and C Coals.

Field studies of outcrops of these strata (See Figure 3) were therefore undertaken and the ironstone bands and nodules identified, sampled and analyzed at Sunderland Polytechnic Geology Department in the UK.

Some of the nodules were very large, up to 0.7 metres in diameter and there were also very frequent and continuous thin layers of Siderite in the vicinity of the B Coal.

**LABORATORY ANALYSIS**

The analysis was carried out using a "Link AN 10/25S" Type X-Ray Analyzer attachment to a Hitachi 2300 Scanning Electron Microscope. The results below are an average based on several measurements taken at random over the surface of a freshly fractured specimen of the Siderite nodule. The results for the major elements are given below:

| SAMPLE ELEMENT (%) | 1     | 2     | 3     | 4     | 5     | 6     |
|--------------------|-------|-------|-------|-------|-------|-------|
| Mg                 | 0.02  | 0.65  | 0.47  | 0.39  | 0.59  | 0.20  |
| Al                 | 5.93  | 4.91  | 5.16  | 9.20  | 2.39  | 10.40 |
| Si                 | 20.79 | 15.82 | 15.17 | 21.36 | 10.69 | 21.90 |
| K                  | 2.67  | 2.09  | 2.31  | 0.72  | 1.48  | 4.00  |
| Ca                 | 1.78  | 1.42  | 2.44  | 1.66  | 4.05  | 1.10  |
| Mn                 | 0.76  | 1.31  | 1.55  | 0.92  | 3.49  | 0.10  |
| Fe                 | 26.13 | 34.40 | 34.57 | 21.82 | 40.70 | 17.10 |
| Ti                 | -     | -     | 0.34  | -     | 0.06  | 0.50  |
| S                  | -     | -     | 0.54  | 0.13  | -     | 0.10  |
| P                  | -     | -     | -     | -     | 0.08  | -     |

Table 2: X-RAY ANALYSIS RESULTS

**CONCLUSION**

The results show quite conclusively that there is a high incidence of Mn in the Siderite layers and nodules at the proposed mine site. This varies from almost nil in the sandstones (Sample No. 6) to between 0.76% (7,600 mg/l) and 3.49% (34,900 mg/l) in the Siderite.

This last figure is of considerable significance, especially as Sample no. 5 (See Table 2) was taken from close to the worst discharge No. 1. The sample, because of its high Mn content could be better described as a compound of Rhodocrosite (MnCO<sub>3</sub>) and Siderite (FeCO<sub>3</sub>). It is also of note because of its high Fe and Ca content and its low Al and Si content. In this respect it is much more "basic" or alkaline than the rest and therefore much more susceptible to acid attack.

# 44 Dryburgh, Norton & Scott - Source of Manganese in Coal Shales

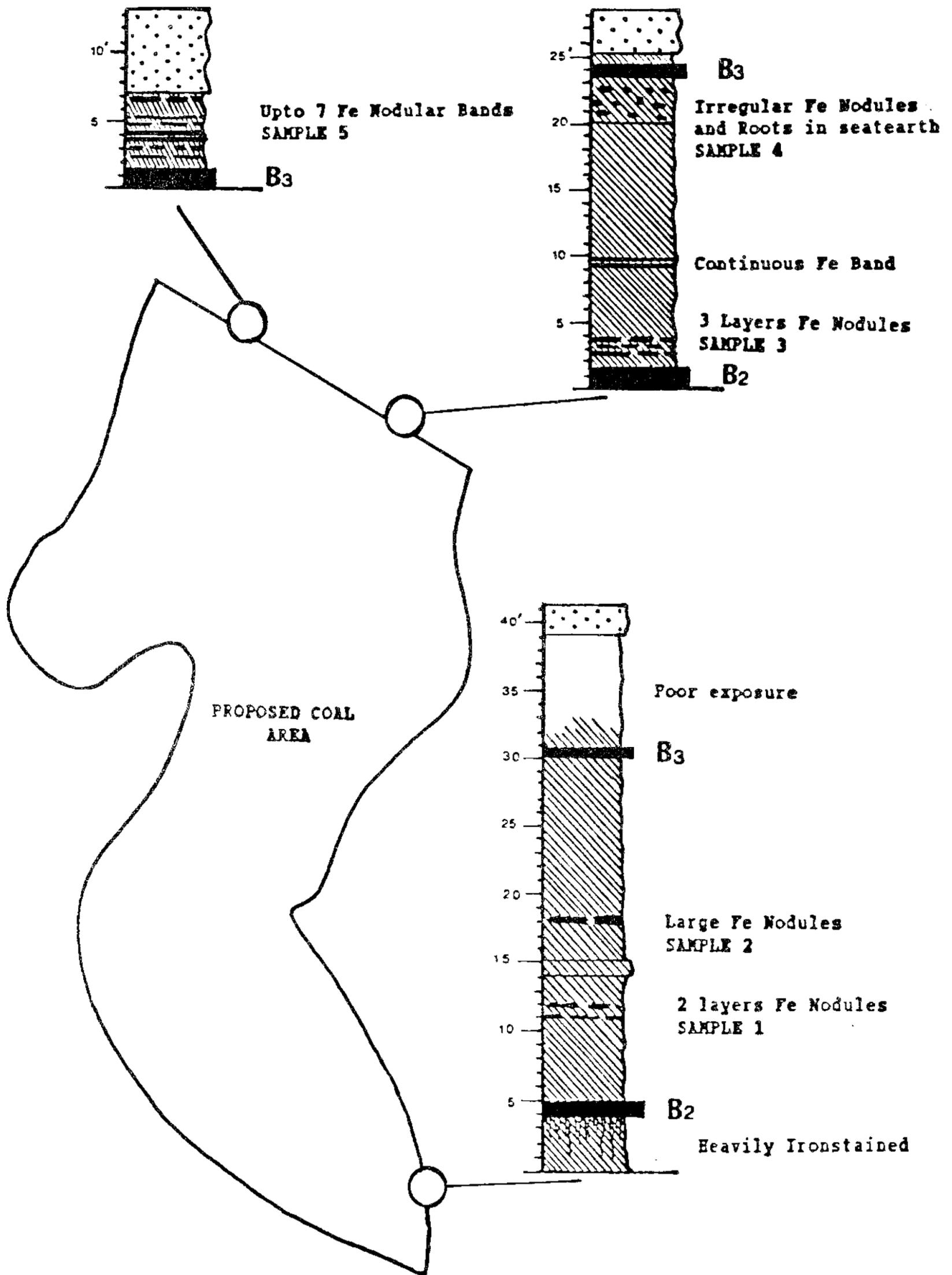


Figure 3: Siderite sample lokations

## Dryburgh, Norton & Scott - Source of Manganese in Coal Shales

However, the rest of the samples also contain relatively high amounts of Mn and there is no doubt that they are the primary source of Mn in the polluted groundwaters in this part of the Appalachian Coalfields.

The mechanism for the Mn pollution would now seem to be clear. Most importantly the nodules are surrounded by coals and shales which are high in Sulphur and produce acidic groundwater. This water percolates through the strata containing the MnCO<sub>3</sub> in the siderite and especially in oxidising environments where the strata has been exposed the acid water reacts vigorously with the MnCO<sub>3</sub> to release the metal into solution.

In order to reduce the pollution it is obviously better to prevent the water becoming polluted in the first place<sup>(1,5)</sup> and the most effective answer would be during backfilling of the excavation to remove the Mn bearing strata and place it above any future water table level. In this way the Mn is removed from the harmful effects of any acidic groundwater that may arise in the backfill and any pollution is restricted to Fe and acidity which can be dealt with by simpler and cheaper methods of treatment such as engineered wetlands.

The use of clay seals at the top of the backfill will prevent the ingress of surface water and precipitation and the use of similar seals along the exposed fault planes as they are exposed in the excavation will do much to prevent the horizontal flow of groundwater into potentially polluting areas of the backfill.

A rapid growth of vegetation and compaction of the backfill immediately underneath the topsoil layer will also assist in preventing water gaining access to the restored void.

### ACKNOWLEDGEMENTS

The authors would like to thank the Directors and Staff of Power Incorporated in the USA and their parent company Crouch Mining in the UK for their assistance in the production of this paper.

### REFERENCES

1. Norton P.J. The impact of Environmental Legislation on the International Mining Industry. Proceedings of Conference on European Trade and Technology. UK. (1990).
2. Kleinmann R.L.P. and Watzlaf G.R. Should the Effluent Limits for Manganese be Modified? Proceedings of Conference on Mine Drainage and Surface Mine Reclamation. Pittsburgh, USA (1988).
3. Morrison J., Atkinson S. and Scheetz B. Delineation of Potential Manganese Sources in the Coal Overburdens of Western Pennsylvania. Proceedings of Conference on Mining and Reclamation. Charleston, USA (1990).
4. Vernadsky W. Histoire Geochemique du Manganese. La Geochemie, Paris (1924).
5. Norton P.J. (Editor). Lisboa 90 International Symposium on Acid Minewater in Pyritic Environments. Lisbon, Portugal (1990).