

# Manganese Contaminated Discharges: Treatment and Prevention

by

Randall Maggard  
Monte Hieb  
Robert Marsh  
Phil Evans

Abstract Pen Coal Corporation has developed an intensive program involving several water treatment strategies on past surface mining operations and designed and fully implemented a Toxic Materials Handling Plan (TMHP) to prevent water quality problems on active surface operations. The development of the treatment strategies involved the assessment of existing treatments and a detailed raw water quality study including treatability studies. The most prevalent contaminant was manganese. The most practical and cost effective systems were evaluated and installed. The prevention of water quality problems on active operations involved a detailed hydrogeological and geochemical investigation of the affected overburden and coal. This investigation resulted in the development of a (TMHP) that has yielded significant reductions in manganese in the mine water regime.

Key Words: Treatability, Calcium Oxide, Sludge Disposal, Hydrologic Flow Paths, Cumulative Manganese, Neutralization, Leachability, Dilution



1 Paper presented at the 1997 Annual Meeting of the West Virginia Acid Mine Drainage Task Force, Morgantown, WV, April 15,16, 1997.

2 Randall Maggard, Environmental Specialist, Pen Coal Corporation, Dunlow, W, Monte Hieb, Manager of Engineering, Pen Coal Corporation, Dunlow, W, Robert Marsh, Permit Supervisor, Pen Coal Corporation, Dunlow, WV, Phil Evans, REIC Laboratory, Beaver., WV.

3 Publication in this proceedings does not prevent authors from publishing their manuscripts, whole or in part, in other publication outlets.



## Introduction

Pen Coal Corporation has an extensive mining operation located near Dunlow, in southern Wayne County, West Virginia. The operation consists of two active underground mines in the Coalburg Seam, one active underground mine in the 5-Block Seam, an active surface mine in the Coalburg Seam, an active surface mine in the 5-Block Seam, a preparation plant, a refuse fill and an impoundment. These operations are located in the watersheds of the East Fork and

## West Fork of Twelvepole Creek-




Mining operations began at the Honey Branch Surface Mine in September 1987, this operation consisted of the contour mining of the Coalburg Seam. During the summer of 1988, Pen Coal began mining operations at the Frank Branch Surface Mine which involved contour mining and point removal of the 5-Block Seam in the watershed of the East Fork of Twelvepole Creek, which is the major tributary of East Lynn Lake, a U.S. Army Corps of Engineers project.

The mining operations involving the 5 Block Seam have continued to expand to also involve the drainage areas of Kiah Creek, also a tributary of the East Fork of Twelvepole Creek-

Some minor water quality problems were detected during 1990, but were easily treated and corrected. As mining has progressed the elevation of the 5-Block Seam has continued to drop closer to drainage. This created some operational problems due to the lack of spoil storage areas. This also caused an increase in the quantity of surface water which encountered the mining area. During 1993 the water quality problem associated with the surface mining of the 5-Block Seam became more pronounced and has required a more intensive effort to control and abate. Pen Coal began an extensive "Water Quality Improvement Plan" in February 1994 to determine the most cost effective methods for treatment of the existing problems and methods to prevent or minimize future problems.

### Statement of Purpose

The purpose of this paper is to share the experience of Pen Coal Corporation with the coal mining industry. The writers would like to specifically address the following points of significance:

-  The most difficult contaminant to remove in AMD treatment is manganese. This dictates the type of treatments utilized on an operation where manganese concentrations exceed allowable regulatory limits.
-  The development of a TMHP (Toxic Materials Handling Plan) to prevent the formation of acid or alkaline discharges which are contaminated with manganese, require a thorough understanding of the sources of the manganese and the post mining hydrologic regime.
-  The success of water treatment and an on-going TMHP requires the cooperation and understanding of the scope of the problems by a wide range of individuals. This group consists of the company's upper management, supervisors, operators, and also involves the members of the regulatory agencies involved in the situation.

### Water Treatment

The first phase of the "Water Quality Improvement Plan" was to utilize respected environmental consultants, to evaluate and recommend improvements in water treatment at our existing facilities. As a result of these evaluations it was determined that the most problematic contaminated waters were located on our Queens Fork surface mine. The discharges from this reclaimed operation flow into Kiah Creek which is a tributary of the East Fork of Twelvepole Creek.

## Queens Fork

### Typical Raw Water Quality

pH	Iron	Manganese	Aluminum	Flow
2.9-6.0	10-80	14-450	1-100	5-850 gpm

<u>pH</u>	<u>Iron</u>	<u>Manganese</u>	<u>Aluminum</u>	<u>Flow</u>
2.9-6.0	10-80	14-450	1-100	5-850 gpm

A brief review of the above data illustrates that these discharges will require a good dose of alkalinity to counter the low pH's and high metals. The most difficult contaminant to remove based on bench scale treatability studies and actual field experiences was the manganese.

The most cost effective methods for the removal of manganese appeared to be elevation of the pH to the 10.0 range. Three chemicals were evaluated to determine their effectiveness: 20% sodium hydroxide, anhydrous ammonia, and calcium oxide. A typical analysis for one Queens Fork outlet is presented below:

Chemical	Treat. pH	Final pH	Final Mn	Sludge	\$/gal
NaOH	10.20	9.46	1.20	0.50"	\$,000238
NH <sub>3</sub>	10.15	9.36	1.30	0.20"	\$,000203
CaO	10.40	9.33	0.60	0.25"	\$,000119

A brief review of the data will show that the lowest final pH and chemical consumption cost was provided by utilizing calcium oxide. The calcium oxide cost was only half as much as sodium hydroxide or anhydrous ammonia. The sludge volume generated by calcium oxide was only half as much as sodium hydroxide and about the same as anhydrous ammonia.

The main cost considerations when evaluating a treatment strategy are listed below:

1. Equipment cost
2. Chemical cost
3. Sludge disposal cost
4. Labor

A more detailed water quality inventory was conducted on the entire operation which indicated water quality problems of varying degrees existed at approximately twenty five sites associated with the surface mining of the 5 Block Seam. The degrees of contamination ranged from a manganese concentration of 3 to 5 mg/l to sites with severe acidity and metals problems. The treatment plan developed for each site was based on manganese removal since it appeared to be the primary contaminant at all the sites.

After careful review by Pen Coal Corporation and the participating regulatory agencies a plan was developed which is listed below:

1. Calcium oxide would be utilized as the treatment chemical of choice.
2. Aqua-Fix units would be purchased to dispense the calcium oxide.
3. A mobile dredge and pumping system would be purchased to aid in sludge disposal.

4. The sodium hydroxide treatment systems already in place on Queens Fork would remain as backup systems.
5. Additional ponds would be constructed where possible to increase retention time.
6. A staff of one supervisor and four hourly positions would be created to monitor and operate the systems.
7. An intensive effort would be made to improve access to all the sites to insure more effective treatment and monitoring of the sites.

By the end of 1994 approximately five miles of access roads were constructed, ten additional ponds were built, twenty-three aqua-fix units were purchased and installed, a dredging and pumping system was acquired, and three on-bench cells were constructed for sludge disposal.

### Water Treatment Concerns

The primary problems associated with the use of calcium oxide are solubility. A staged treatment system was developed, where possible, at some sites. Treatment occurs at three different locations. See figure 1:

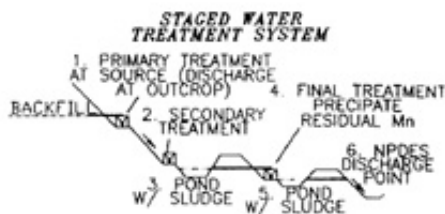


Figure 1

1. Initial dose of calcium oxide consumes acidity, and precipitates some iron, aluminum, and manganese.
2. Second dose of calcium oxide elevates pH > 10, and precipitates remaining iron, aluminum, and some manganese.
3. Sludge deposited in pond consists mainly of calcium, magnesium, iron, aluminum, some manganese, and pH drops to a range of 8 to 9 at pond discharge.
4. Third dose of calcium oxide elevates pH in excess of 10 to precipitate remaining manganese.
5. Sludge deposited in pond consists mainly of calcium, magnesium, iron, manganese, and aluminum.
6. The pH drops to a range of 9 to 10, for discharge into receiving stream, calcium content approximately 100 mg/l higher than raw inflow, manganese is typically less than 2 mg/l.

### Pond Cleaning and Sludge Disposal

The precipitated metals are metal hydroxides which produce a gelatinous mixture with only a 5 to 10% solids content. This material is most effectively removed by pumping and dewatering. See figure below:

### POND CLEANING & SLUDGE DISPOSAL SYSTEM

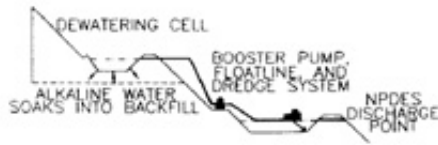


Figure 2

The content of the dried sludge was interesting -See figure below comparing raw water quality.

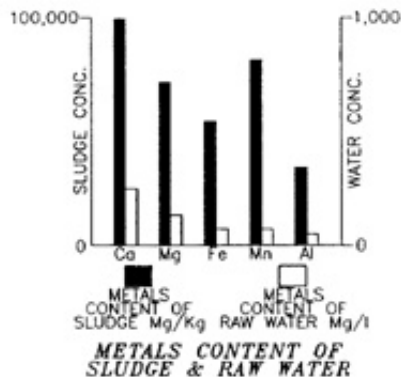


Figure 3

### Water Treatment Costs Reduction

During the first six months of utilizing calcium oxide and Aqua-Fix units successfully to treat our discharges, we noticed several areas where improvements could be made to increase efficiency and reduce costs. The major problem incurred was delivery of the calcium oxide to the treatment units. We were currently utilizing calcium oxide delivered in 50 lb. bags on pallets. This system was time consuming and created a disposal problem with bags and pallets. We were currently using approximately two tons per day of calcium oxide which involved the handling of 80 bags per day or 2400 bags per month.

Pen Coal decided to determine the feasibility of going to a mobile bulk system. Since daily consumption was spread out over a dozen different sites, the installation of a large bin at each site would be very costly. We decided on the installation of a 55 ton bulk bin (approximately one month consumption) and a delivery truck of 2-1/2 ton capacity (approximately one days consumption). The delivery truck consisted of a bulk delivery bin similar to a small ANFO system used on surface mines. This bin was mounted on a four-wheel drive truck for easy access to our units.

The cost bulk calcium oxide was approximately 60% cheaper than the bagged material. This system was completed in February 1996 and has resulted in considerable savings in chemical costs.

### Prevention

The second phase of the "Water Quality improvement Plan" was to identify the stratigraphical sources of the acidity and metals, and to develop and implement a prevention plan on our present and future operations.

A much more intensive overburden drilling program was initiated with a more detailed geochemical analysis of the overburden. Areas in the stratigraphic column were identified as being potential sources of the acidity, but it was somewhat unclear the source of the manganese. The typical AMD situation results in low pH water with the associated elevated iron levels, but the manganese content seems to be more variable and the most persistent contaminant.

Pen Coal has determined that in certain areas the manganese contaminant is similar in character to sulfate concentration. The manganese is **an indicator** of acidic conditions somewhere in the hydrologic flow path. Like sulfate, the manganese tends to be cumulative, with the only reduction in concentration due more to dilution rather than actual precipitation.



Figure 4—Cumulative Impact of Manganese Dissolution

A procedure was developed in conjunction with Pen Coal and REIC Laboratories to determine the availability and the concentration of manganese in the coals and overburden material. The results of this analysis indicated that there were certain sensitive units which could easily liberate excessive concentrations of manganese.

A series of extractions were performed to first determine the total manganese content of the sample. Then two more extractions were performed to determine the leachability of the manganese. One extraction utilized 20 milliliters of pH 3 sulfuric acid solution and the other extraction utilized a 1 molar ammonium acetate/0.2% hydroquinone solution. Refer to the appendix for the detailed procedure and analysis.

The results of the analysis were very interesting. Total manganese values ranged from 3.25 mg/kg to 4,350 mg/kg while the pH 3 sulfuric acid extraction yielded values from 0.00(ND) to 16.4 mg/kg and the 1 molar ammonium acetate/0.2% hydroquinone extraction yielded values from 0.00(ND) to 340 mg/kg. There were some samples that yielded high values for both extractions and what was particularly interesting was that these samples had relatively low total manganese values. For example, sample No. 47 had a total manganese value of 77.6 mg/kg with a pH 3 sulfuric acid extractable manganese of 11.8 mg/kg and a 1 molar

ammonium acetate/0.2% hydroquinone extraction manganese of 13.5 mg/kg. Sample No. 70 had a total manganese of 510 mg/kg pH 3 sulfuric acid extractable manganese of only 1.02 mg/kg and a 1 molar ammonium acetate/0.2% hydroquinone extractable manganese of only 6.41 mg/kg.

By utilizing data such as this, along with the acid base accounting data, a materials handling plan was developed with the prevention of manganese solubilization being a main concern.

### Development of a Toxic/Alkaline Materials Handling Plan

Based on the results of the detailed analysis of the 5-Block overburden sequence, a plan was developed to minimize hydrologic contact with acid producing/manganese leaching material, and to maximize hydrologic contact with alkaline high pH material.

As a result of the previously discussed overburden analysis, effort was made to place the alkaline overburden adjacent to highwalls, on pit floors and as blankets under hollow fills to induce alkalinity into the hydrologic flow paths. The acidic material and other material prone to easily leachable manganese would be placed high above the pit floor and away from hydrologic flow paths. The most acidic of this material would be placed in specially designated areas known as encapsulation cells. These encapsulation cells would then be covered with approximately eight feet of alkaline shales and siltstones to reduce permeability and then topsoiled and revegetated.



Figure 5

The water that does come in contact with the overburden that has a large amount of easily leachable manganese should be minimized. The small contaminated amount of water that does occur in the vicinity of the encapsulation cells should be adequately diluted with other alkaline water as it finally reaches the major hydrologic flow parts.

### Conclusions

The effective treatment of manganese contaminated discharges requires a thorough understanding of all the variables such as site accessibility, flow rates, and degree of contamination. The success of the treatment also requires a commitment by the mining company to supply the needed manpower and equipment to perform the work effectively.

The development and implementation of a materials handling plan to prevent manganese contaminated discharges requires the ability to locate the sources of the contamination and to be able to hydrologically isolate this material during active mining and reclamation.

The success of both the treatment and prevention of manganese contaminated discharges requires a great degree of cooperation between the mining company and associated regulatory agencies.

## Acknowledgments

The authors wish to acknowledge the contributions and hard work made in preparation of this paper by Kenneth Lawson, Richard Childers, Kris Aldridge, Michael Sublett, Greg Pugh, and Gary Chambers of Pen Coal Corporation. Sharon Baker with Standard Laboratories, Inc. is to be recognized for her assistance in editing and final manuscript preparation.

## References

Caruccio, F. T. and G. Geidel 1996, "Acid Mine Drainage: The Laboratory and Field Settings", Workshop 6-13th Annual Meeting of the American Society for Surface Mining and Reclamation, Knoxville, TN, 58p.

Faulkner, B. and J. Skousen. 1991, "Field Experiences in Acid Prevention", Proceedings-12th Annual West Virginia Surface Mine Drainage Task Force Symposium.

Faulkner, B. and Skousen, J. 1991, "Field Trials in Acid Treatment" 12th Annual West Virginia Surface Mine Drainage Task Force Symposium.

Galya, T. 1994, Personal Communication West Virginia Division Environmental Protection, Logan, WV.

Hilton, T. 1994, "Pen Coal Corporation Water Treatability Assessments".

Kleinmann, R. L. P.G. R- Watzlaf, and T. Ackman, 1985, Treatment of mine water to remove manganese. Proc. 1985 Symp. On Surface Mining, Hydrology, Sedimentology, and Reclamation, Dec. 9-13, 1985 ed., by D. Graves, Univ. of KY, Lexington, KY, pp. 211-217.

Kleinmann, R. L. P., G. R- Watzlaf, and T. E. Ackman, 1988, Should the effluent limits for manganese be modified? Proceedings for 1988 Mine Drainage Surface Mine Reclamation conference, American Society for Surface and U. S. Department of Interior (Bureau of Mines and OSMRE), Pittsburgh, PA

Lovett, R. 1991, "Chemistry of Manganese in Acid", Proceedings-12th Annual West Virginia Surface Mine Drainage Task Force Symposium.

Morrison, J. L. and B. E. Scheetz 1994, "Overburden Characterization: An Examination of the Neutralization Potential Determination and Identifying Potential Sources of Manganese", PEDAFR-486-043, The Materials Research Laboratory, Pennsylvania State University

Naumann, H. E. and V. P. Wiram 1996, "Improving Ground Water Quality in the Backfill with Alkaline Additions", Proceedings-13th Annual Meeting of the American Society for Surface Mining and Reclamation, Knoxville, TN.

Nicholas, G. D. and E. G. Force, 1979, Chemical treatment of mine drainage for removal of



manganese to permissible limits. In Proc. Symp. On Surface Mining, Hydrology, Sedimentology, and Reclamation, ed. by D. Graves, Univ. of KY, Lexington, KY, pp. 181-187.

Page, A- L. Miller, R- H. and R- O. Keeny 1982, Methods of Soil Analysis Part 2, Chemical & Microbial Properties, American society of Agronomy, Inc., Soil Science Society of America, Inc., Madison, Wisconsin U.S.A.

Sengupta, M. 1993, Environmental Impacts on Mining: Monitoring, Restoration, and Control, Lewis Publishers, Boca Raton, Florida, 494 pp.

Sobek, A. A., Schuller, W. A., Freeman, J.R-, and Smith, R-M. 1978, Field and Laboratory Methods.

U. S. EPA, Nov 1986, Test Methods for Evaluating Solid Waste, Physical /Chemical Methods SW-846 3d edition and SW-846 3d edition Final updates, Office of Solid Waste and Emergency Response, Washington, D. C. 20460

Watzlaf, G. R- 1985. Comparative tests to remove manganese from acid mine drainage. In Control of acid mine drainage, BuMines IC 9027, pp. 41-47.

Wiram, V. P. 1992, "Siderite Masldng A Factor to Consider in Overburden Acid-Base Balancing", Proceedings - 13th Annual West Virginia Surface Mine Drainage Task Force Symposium.

## APPENDIX A

### Principle

The presence of manganese in AMD is of concern to both generators and regulatory agencies. We were hoping to gain insight into the process that leaches manganese into drainage water, and perhaps reduce the amount of manganese loading that takes place by special handling units that were visually obvious, and proven in the laboratory to leach high levels of manganese.

Overburden in the backfill consists predominately of sandstone and shale. It is one assumption that the shales contain manganese as manganese carbonates, whereas the manganese in sandstone is present as manganese oxides. To differentiate between the sources of manganese, overburden samples were extracted by dilute oxidation and by dilute reduction. Oxidation was accomplished by leaching samples in dilute sulfuric acid in an attempt to free manganese present as manganese carbonate. Reduction was attempted by using a 0.2% hydroquinone solution to reduce manganese oxides.

Total manganese was determined and compared to the result of the two leaching procedures to establish the percentage of manganese leached- The results of the leachings were then compared to the core description in an attempt to determine if units that leached high level of manganese could be identified in a highwall by visual cues.

Total Manganese by EPA SW-846 for manganese - see methodology shown below.

I. Method 3050 - Acid Digestion of Sediments, Sludges and Soils for Total Metals Analysis

## II. Scope and Purpose

Method 3050 is an acid digestion procedure used to prepare sediments, sludges, soils, and many other solid samples for total metals analysis by flame or graphite furnace atomic absorption spectroscopy (FAA and GFAA, respectively) or by inductively coupled argon plasma emission spectroscopy (ICP).

## III. Method Summary

A representative 2.0 g sample is digested in nitric acid ( $\text{HNO}_3$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). The digestate is then refluxed with either  $\text{HNO}_3$  or  $\text{HCl}$ , depending on which instrumentation will be used for the analysis.  $\text{HCl}$  is used as the final reflux acid where FAA or ICP analysis is to be used.  $\text{HNO}_3$  is employed as the final dilution acid when GFAA analysis is required. Filtration is often required after final volume adjustment to remove remaining insoluble material.

## IV. Apparatus and Materials

- A. Whatman #41 filter paper, filter funnels, and filtration rack
- B. Heavy-walled, 250 ml beakers
- C. Laboratory Balance, with readout to 0.01 g
- D. Hot plates, with variable temperature controls
- E. Disposable plastic pipettes, graduated
- F. Ribbed watch glasses
- G. Electronic timer
- H. 125 ml polyethylene bottles
- I. 1 ml Eppendorf pipette, with tips

Note: All glassware must be thoroughly detergent washed and rinsed with ASTM Type 11 mineralized water. Acid washing may be necessary, depending on analysis results for reagent blanks.

## V. Reagents

- A. Type II demineralized water
- B. Concentrated nitric acid, reagent grade
- C. Concentrated hydrochloric acid, reagent grade
- D. Hydrogen peroxide (301/o), high purity
- E. Appropriate analyte spiking solutions

## VI. Procedure

- A. Mix sample thoroughly to achieve homogeneity. Weigh out 2.0 g (to nearest 0.01 g) of sample and transfer to a heavy-walled beaker,
- B. Add 10 ml 1: 1  $\text{HNO}_3$  (5 ml Type 11 water and 5 ml concentrated  $\text{HNO}_3$  mix, and cover with a watch glass. Heat sample to 95 degrees C (setting of 3.5) and reflux for 10 to 15 minutes without boiling. Cool sample and add 5 ML of concentrated  $\text{HNO}_3$  cover and reflux for 30 minutes. Add another 5 ML of concentrated  $\text{HNO}_3$ , and evaporate to around 5 ML (without boiling or drying

the sample). Some samples may require additional  $\text{HNO}_3$  for complete digestion. Cool the sample.

- C. Add 2 ML of Type 11 water and 3 ML 30%  $\text{H}_2\text{O}_2$ . Cover the beaker and return to the hot plate. Care must be taken to prevent losses of sample and analyte during the peroxide reaction. Heat until the reaction subsides and then Cool.
- D. Continue adding  $\text{H}_2\text{O}_2$  in 1 ML aliquots with warming until the peroxide reaction is minimal or until the sample's appearance remains unchanged. Do not add more than a total of 10 ML of 30%  $\text{H}_2\text{O}_2$ .
- E. If the sample is being prepared for analysis via...
  - 1. FAA or ICP, then add 5 ML concentrated  $\text{HCl}$  and 10 ML Type II water, cover, and return beaker to the hot plate. Reflux for 15 more minutes. Cool and dilute to final volume (usually 5 ML) in a 125 ML polyethylene bottle.
  - 2. GFAA, cover the beaker and continue heating the digestate until the volume has been reduced to approximately 5 ML. Cool and dilute to final volume (usually 50 ML) in a 125 ML polyethylene bottle.
- F. Filtration is generally necessary to remove remaining insoluble material. Filtration should be carried out after final volume adjustment to minimize analyte losses. Filtering of the sample prior to volume adjustment can lead to reduced analyte recovery due to entrapment by the filter.
- G. Calculate the dilution factor for the sample using the following formula:

$$\text{Dilution Factor (DF)} = \frac{\text{wt of total sample after volume adjustment}}{\text{wt of initial sample}}$$

For a 2.0 g sample and a final volume of 50 ml (50 g), the dilution factor will be 25: 1. Label the sample container with job #, sample #, dilution factor, and digestion method (3050). If the sample was digested for FAA or ICP analysis, label the bottle as "3050-flame". For GFAA analysis, label as "3050-fur". Analytes to be quantified should also be included in the labeling.

Note: Quite often, sample sizes other than 2.0 g and final volumes other than 50 ml (50 g) will be necessary. Possible reasons for these deviations include...

- 1. Very small amounts of sample (less than 2.0 g)
- 2. The need for lower quantifying/detection levels-Thus the need for a lower dilution factor. Lower dilution factors can be achieved by using a sample weight higher than 2.0 g and/or using a lower final volume.
- 3. The need to minimize matrix complexity, interference, etc. This is generally accomplished by increasing the dilution factor, i.e. Using a larger final volume or a

smaller initial sample size.

## VII. Quality Control

- A. Reagent Blanks: For each batch of samples, a reagent blank is prepared. The reagent blank consists of a 50 ml aliquot of Type 11 demineralized water carried through the entire digestion procedure, i.e., treated just as a sample. Labeling for blanks should include the word "Blank," the digestion method (3050), flame or furnace (fur) analysis, and the job #'s to which the blank applies.
- B. Duplicates: Duplicate samples are processed on a 10% basis. Samples with uncommon or questionable matrices are given priority for duplication. Jobs with three or more samples are also given priority for duplication. Duplicates are denoted by an "x" after the sample
- C. Spikes:
  - 1. A matrix digestion spike and a distilled water digestion spike are to be prepared for each batch of samples digested. Spiking is accomplished by adding one or more 1 ml aliquots of appropriate spiking solutions to a duplicate of the sample to be spiked. The spike must contain all of the analytes that are to be measured for that sample. A 5 ml aliquot of Type II water is also to be spiked (just as the matrix spike) and processed just like a sample.
  - 2. Samples with uncommon or questionable matrices are to be given priority for spiking. Jobs with three or more samples are also given priority for spiking.
  - 3. Several different multielement spiking solutions have to be made up and maintained to cover the wide range of analyte combinations that are possible. Two different concentrations of each spiking solution have to be made up and maintained. Which concentration (high or low level) of spiking solution to be used is dependent on which instrument is to be used for the analysis. The low level spiking solutions will be used for GFAA work and the high level solutions for FAA and ICP work
  - 4. Clearly mark all spiked samples as to how they were spiked. Spiked samples are denoted by an "S" after the sample #.

## VIII. Corrective Action

Corrective action, usually in the form of redigestion, will be necessary if any of the quality control (reagent blanks, duplicates, spikes) fails during the analysis.

## X. References

1. SW-846, Test Methods for Evaluation Solid Waste, Volume I A, Revision 0,

September 1986

2. EPA, Methods for Chemical Analysis of Water and Wastes, Revised March 1983.

Easily Reducible Manganese - determined by using method 18-3.5 from Methods of Soil Analysis part 2, 2nd edition (Sherman et al., 1942; Adams, 1965)

For the study the sample weight was changed from 10 grams to 5 grams, but the 10: 1 ratio of milliliters of leaching solution to gram of sample was maintained. -We also modified the method by using a stir bar and stir plate set at 4(on a scale of 1-10) instead of a mechanical shaker. We stirred the solution for 30 minutes.

#### I. Method

Add 50 milliliters of ammonium acetate-hydroquinone solution buffered to a pH of 7 to 5 grams of solute. Stir on stir plate at a speed of 4 out of 10 for 30 minutes. Filter through a Whatman #41 cellulose filter and run on ICP or AA.

#### II. Reagents

1. Type II distilled water
2. Neutral ammonium acetate (1 N), containing 0.2% hydroquinone

#### III. Apparatus

1. Beakers
2. Stir plate & stir bar
3. Funnels
4. Whatman #41 filter paper

#### Manganese solubility in varying pH solutions

Manganese was determined by adding 10 grams of <2 millimeters material to 50 milliliters of digestion solution ( pH from 8 to 2) and stirring at medium speed for 30 minutes. To achieve pH 8 calcium oxide was carefully added to distilled water while being monitored by a pH meter. For pH 7 through 2 sulfuric acid was carefully added until the desired pH was reached. This is a very exacting procedure because the distilled water lacks buffering. After stirring for 30 minutes the solution is filtered through a 0.45 micron filter, acidified, and 0. 5 milliliters of concentrated nitric acid (15 M) and run on the AA or ICP.

#### I. Reagents

1. Distilled water
2. Sulfuric acid
3. Calcium Oxide

#### II. Apparatus

# REIC LABORATORY

## Acid-Base Account ~

Company: PEN COAL CORPORATION

Site: CORE 95-21

Date: October 17, 1995

REIC Job #: 0895-36981 and 0895-37716

Site: CORE 95-21

Date: October 17, 1995

REIC Job #: 0895-36981 and 0995-37716

Calcium Carbonate Equivalent In Tons/1000Tons of Material

mg/kg

SAMPLE NUMBER	SAMPLE INTERVAL	THICKNESS	ROCK TYPE	% SULFUR ** Pyritic	POTENTIAL ACIDITY	NEUTRALIZATION POTENTIAL	NET NEUTRALIZERS		PASTE PH	TOTAL MANGANESE	ACID LEACHABLE MN*	EASILY REDUCIBLE MN **
							DEFICIENCY	EXCESS				
1	0.00-6.00	6.00	EM	0.02*	0.63	-4.29	4.92		4.2	73.7	0.75	8.35
2	6.00-12.00	6.00	SS	0.02	0.63	1.77		1.15	5.7	720	8.74	340
3	12.00-16.95	4.95	SS	0.19	5.94	9.85		3.91	7.2	642	3.65	6.56
4	16.95-22.00	5.05	SS	0.21	6.56	13.01		6.45	7.5	424	3.53	10.7
5	22.00-27.05	5.05	SS	0.04	1.25	18.95		17.70	8.2	538	3.22	22.4
6	27.05-31.40	4.35	SS	0.03	0.94	13.52		12.58	8.5	375	1.84	14.5
7	31.40-35.70	4.30	SS	0.11	3.44	227.50		224.06	8.5	1100	0.42	31.1
8	35.70-36.10	0.40	SS	0.27	8.44	210.00		201.56	8.1	4350	0.54	36.3
9	36.10-37.00	0.90	SS/MS	0.09*	2.81	1.27	1.54		7.7	43.2	0.36	3.22
10	37.00-37.55	0.55	COAL	3.38*	105.63	-23.48	129.11		3.3	16.4	1.89	2.87
11	37.55-37.90	0.35	SH	0.75*	23.44	-12.62	36.06		4.7	37.7	3.52	6.96
12	37.90-40.40	2.50	SH	0.13*	4.06	1.01	3.05		7.7	28.4	ND	1.52
13	40.40-42.65	2.25	SH/EM	0.13	4.06	5.31		1.25	7.9	50.8	ND	1.34
14	42.65-44.85	2.20	SH	0.09	2.81	4.30		1.49	8.4	192	0.38	0.99
15	44.85-48.85	4.00	SH	0.12	3.75	9.73		5.98	8.6	527	ND	2.33
16	48.85-51.35	2.50	SH	0.10	3.13	7.08		3.95	8.6	286	0.30	1.47
17	51.35-56.10	4.75	SS	0.04	1.25	10.74		9.49	8.4	516	2.29	4.53
18	56.10-58.70	2.60	SS	0.07*	2.19	2.28		0.09	7.8	221	1.78	2.51
19	58.70-62.00	3.30	SS	0.04*	1.25	-1.00	2.25		7.0	94.0	3.43	3.04
20	62.00-63.15	1.15	SS	0.38*	11.88	-6.31	18.19		6.0	162	10.5	12.3

-As Reference in EPA manual: EPA-600/2-78-054; Field and Laboratory Methods Applicable to Overburden and Minesoils.

Research, Environmental and Industrial Consultants INC.

P.O. Box 286 Beaver, WV 25813 Phone: 1-800-999-0105 / (304) 255-2500 / FAX: (304) 255-2572

\* - pH 3 Sulfuric Acid Manganese Extraction

\*\* - 1M Ammonium Acetate/0.2% Hydroquinone Manganese Extractant

1. Beakers
2. Stir plate and stir bars
3. pH meter

# REIC LABORATORY

## Acid-Base Account ~

Company: PEN COAL COMPANY

Site: CORE 95-21

Date: October 17, 1995

REIC Job #: 0995-36981 and 0995-37716

Calcium Carbonate Equivalent in Tons/1000Tons of Material

mg/kg

SAMPLE NUMBER	SAMPLE INTERVAL	THICKNESS	ROCK TYPE	% SULFUR ** PYRIC	POTENTIAL ACIDITY	NEUTRALIZATION POTENTIAL	NET NEUTRALIZERS		PASTE pH	TOTAL MANGANESE	ACID LEACHABLE MN*	EASILY REDUCIBLE MN**
							DEFICIENCY	EXCESS				
21	63.15-68.40	5.25	SS	0.04*	1.25	0.26	0.99		8.2	81.9	1.66	1.20
22	68.40-69.30	0.90	SS	0.17*	5.31	7.45		2.14	7.1	1330	15.3	18.5
23	69.30-72.80	3.50	SS	0.09	2.81	7.08		4.26	8.4	306	4.84	5.26
24	72.80-74.30	1.50	SS	0.03*	0.94	0.26	0.68		8.2	190	16.4	49.0
25	74.30-74.40	0.10	SH	0.30*	9.38	-0.12	9.50		7.5	133	0.94	14.1
-	74.40-76.80	2.40	LOSS	-	-	-	-	-	-	-	-	-
26	76.80-78.00	1.20	SH/EM	0.04*	1.25	1.52		0.27	7.6	27.8	0.34	4.37
27	78.00-80.80	2.80	SH	0.09*	2.81	4.17		1.36	8.0	318	0.34	2.49
28	80.80-83.30	2.50	SS	0.04	1.25	4.42		3.17	8.1	210	0.58	1.53
29	83.30-86.80	3.50	SH	0.01*	0.31	0.51		0.20	8.3	4.30	ND	0.96
30	86.80-88.20	1.40	SH	0.08	2.50	3.92		1.42	8.7	193	ND	1.41
31	88.20-89.25	1.05	SS	0.03	0.94	12.26		11.32	8.2	1610	1.02	3.02
32	89.25-92.00	2.75	SS	0.04	1.25	315.00		313.75	8.8	352	ND	5.33
33	92.00-95.20	3.20	SS	0.03*	0.94	0.01	0.93		8.3	38.2	0.63	1.14
34	95.20-98.20	3.00	SS	0.10	3.13	10.23		7.11	8.3	1590	1.28	3.17
35	98.20-99.40	1.20	SH	0.03*	0.94	0.51	0.43		8.4	36.4	ND	ND
36	99.40-101.00	1.60	SH	0.29	9.06	11.87		2.81	8.5	20.8	ND	ND
37	101.00-103.65	2.65	SH	0.02*	0.63	1.65		1.02	8.3	35.2	ND	ND
38	103.65-109.55	6.00	SS	0.02*	0.63	0.38	0.25		7.8	38.6	0.40	ND
39	109.55-112.00	2.35	SS	0.02*	0.63	1.14		0.51	7.8	90.4	0.72	0.66

~As Reference in EPA manual: EPA-600/2-78-054; Field and Laboratory Methods Applicable to Overburden and Minesoils.

Research, Environmental and Industrial Consultants INC.

P.O. Box 286 Beaver, WV 25813 Phone: 1-800-899-0105 / (304) 255-2500 / FAX: (304) 255-2572

\* - pH 3 Sulfuric Acid Manganese Extraction

\*\* - 1M Ammonium Acetate/0.2% Hydroquinone Manganese Extractant

# REIC LABORATORY

## Acid-Base Account ~

Company: PEN COAL CORPORATION

Site: CORE 95-21

Date: October 17, 1995

REIC Job #: 0895-36981 and 0895-37716

Calcium Carbonate Equivalent in Tons/1000Tons of Material

mg/kg

SAMPLE NUMBER	SAMPLE INTERVAL	THICKNESS	ROCK TYPE	% SULFUR ** Pyritic	POTENTIAL ACIDITY	NEUTRALIZATION POTENTIAL	NET NEUTRALIZERS		PASTE pH	TOTAL MANGANESE	ACID LEACHABLE MN*	EASILY REDUCIBLE MN*
							DEFICIENCY	EXCESS				
40	112.00-115.50	3.50	SS	0.03	0.94	58.75		57.81	8.5	926	0.50	20.4
41	115.50-120.00	4.50	SS	0.02*	0.63	1.27		0.64	7.8	54.5	0.77	0.73
42	120.00-125.05	5.05	SS	0.03	0.94	3.29		2.35	7.9	89.0	1.02	0.91
43	125.05-130.00	4.95	SS	0.01*	0.31	-0.63	0.94		7.8	38.0	1.22	0.62
44	130.00-135.00	5.00	SS	0.02*	0.63	-0.50	1.13		8.1	40.2	1.48	0.53
45	135.00-140.00	5.00	SS	0.04*	1.25	0.38	0.87		7.6	109	1.32	0.83
46	140.00-144.40	4.40	SS	0.03*	0.94	0.64	0.30		7.5	143	1.67	1.08
47	144.40-145.60	1.20	SS	0.26*	8.13	-6.31	14.44		5.0	77.6	11.8	13.5
48	145.60-151.25	5.65	SS	0.07	2.19	3.67		1.48	7.3	364	2.82	3.26
49	151.25-154.90	3.65	SS	0.13	4.06	9.85		6.79	7.8	744	3.24	4.69
50	154.90-158.30	3.40	SS	0.08	2.50	4.30		1.80	7.9	201	2.61	2.70
51	158.30-158.90	0.60	SS	0.13*	4.06	1.77	2.29		7.4	1270	3.42	4.84
52	158.90-159.25	0.35	SS	0.52*	16.25	10.87	5.38		7.3	5290	8.71	11.6
53	159.25-161.00	1.75	MS	0.02*	0.63	1.39		0.76	8.3	253	ND	ND
54	161.00-162.40	1.40	MS	0.08	2.50	10.74		8.24	8.4	28.0	ND	ND
55	162.40-164.30	1.90	SS	0.05*	1.56	3.92		2.36	8.3	1330	0.45	1.30
56	164.30-164.80	0.50	MS	0.06*	1.88	-0.25	2.13		8.1	141	ND	ND
57	164.80-167.00	2.20	SH	0.08	2.50	10.11		7.61	8.3	1300	0.38	2.99
58	167.00-167.20	0.20	SH	0.15*	4.69	0.01	4.68		7.7	111	ND	ND
59	167.20-171.30	4.10	SH	0.10	3.13	7.08		3.95	8.3	745	0.32	2.50

~As Reference in EPA manual: EPA-600/2-78-054; Field and Laboratory Methods Applicable to Overburden and Minesoils.

Research, Environmental and Industrial Consultants INC.

P.O. Box 286 Beaver, WV 25813 Phone: 1-800-999-0105 / (304) 255-2500 / FAX: (304) 255-2572

\* - pH 3 Sulfuric Acid Manganese Extraction

\*\* - 1M Ammonium Acetate/0.2% Hydroquinone Manganese Extractant



# REIC LABORATORY

## Acid-Base Account ~

Company: PEN COAL CORPORATION

Site: CORE 95-21

Date: October 17, 1995

REIC Job #: 0895-36981 and 0995-37716

Calcium Carbonate Equivalent in Tons/1000Tons of Material										mg/kg		
SAMPLE NUMBER	SAMPLE INTERVAL	THICKNESS	ROCK TYPE	% SULFUR ** Pyrite	POTENTIAL ACIDITY	NEUTRALIZATION POTENTIAL	NET NEUTRALIZERS		PASTE PH	TOTAL MANGANESE	ACID LEACHABLE MN*	EASILY REDUCIBLE MN**
							DEFICIENCY	EXCESS				
60	171.30-171.55	0.25	SH/C	0.57*	17.81	-1.64	19.45		7.0	13.4	0.32	4.14
61	171.55-172.70	1.15	SH	0.05*	1.56	0.84	0.92		7.9	76.1	ND	ND
62	172.70-172.90	0.20	COAL	0.70*	21.88	8.46	13.52		6.8	36.2	1.64	6.26
63	172.90-173.10	0.20	SH	0.04*	1.25	2.66		1.41	8.1	11.7	ND	4.23
64	173.10-174.50	1.40	MS	0.01*	0.31	1.01		0.70	8.3	3.25	ND	ND
65	174.50-175.60	1.10	SH	0.01*	0.31	0.38		0.07	8.4	3.40	ND	ND
66	175.60-175.75	0.15	SH	0.03*	0.94	0.64	0.30		7.9	3.50	ND	ND
-	175.75-178.00	2.25	COAL	-	-	-	-	-	-	-	-	-
67	178.00-178.70	0.70	SH	0.09	2.81	3.92		1.11	8.3	156	ND	ND
68	178.70-180.45	1.75	SH	0.09	2.81	6.07		3.25	8.2	168	ND	ND
69	180.45-185.55	5.10	SS	0.04	1.25	13.01		11.76	8.3	431	1.04	6.37
70	185.55-190.15	4.60	SS	0.06	1.88	14.65		12.78	8.3	510	1.02	6.41
71	190.15-191.80	1.65	SH	0.13	4.06	9.22		5.16	8.2	875	0.62	4.69
72	191.80-193.30	1.50	SS	0.13	4.06	8.59		4.53	7.4	539	3.30	6.03
73	193.30-194.35	1.05	SH	0.09	2.81	6.95		4.14	8.1	457	0.55	3.71
74	194.35-194.50	0.15	SH	0.06	1.88	6.57		4.69	8.2	407	0.32	3.11
-	194.50-204.45	9.95	COAL	-	-	-	-	-	-	-	-	-
75	204.45-204.55	0.10	SH	0.48*	15.00	-5.80	20.80		6.8	57.8	0.42	1.59
76	204.55-208.05	3.50	SH	0.04*	1.25	1.90		0.65	8.1	131	ND	1.36
77	208.05-213.05	5.00	SS	0.06	1.88	4.55		2.68	8.1	81.7	1.28	2.76

~As Reference in EPA manual: EPA-600/2-78-054; Field and Laboratory Methods Applicable to Overburden and Minesoils.

Research, Environmental and Industrial Consultants INC.

P.O. Box 286 Beaver, WV 25813 Phone: 1-800-999-0105 / (304) 255-2500 / FAX: (304) 255-2572

\* - pH 3 Sulfuric Acid Manganese Extraction

\*\* - 1M Ammonium Acetate/0.2% Hydroquinone Manganese Extractant

Acid-Base Account ~

REIC Job #: 0895-36981 and 0995-37716

84/85

-As Reference in EPA manual: EPA-600/2-78-054: Field and Laboratory Methods Applicable to Overburden and Minesolls.

.. - 1M Ammonium Acetate/0.2% Hydroquinone Manganese Extractant

---

Phil Evans

**CORE #: 95-21**

Pen Coal Sample #	pH	Aluminum	Iron	Manganese
#2 pH 2.0	2.29	36.05	48.0	47.95
#2 pH 3.0	3.80	0.50	2.80	5.10
#2 pH 4.0	5.34	ND	ND	0.35
#2 pH 5.0	5.54	ND	ND	ND
#2 pH 6.0	5.70	ND	ND	0.30
#2 pH 7.0	5.82	0.80	ND	ND
#2 pH 8.0	5.78	1.10	ND	ND
#10 pH 2.0	2.09	85.0	6150.0	2.45
#10 pH 3.0	2.58	86.0	6800.0	2.35
#10 pH 4.0	2.69	74.0	6150.0	2.00
#10 pH 5.0	2.72	70.0	5400.0	2.10
#10 pH 6.0	2.68	83.0	6450.0	2.35
#10 pH 7.0	2.67	91.0	6400.0	2.70
#10 pH 8.0	2.68	86.0	860.0	2.45
#20 pH 2.0	2.14	33.80	855.0	20.15
#20 pH 3.0	3.16	17.60	142.5	17.30
#20 pH 4.0	3.70	13.15	96.5	16.25
#20 pH 5.0	3.79	13.05	109.0	16.10
#20 pH 6.0	3.92	11.90	109.0	16.60
#20 pH 7.0	3.83	12.15	104.0	16.85
#20 pH 8.0	3.82	11.65	117.0	14.35
#24 pH 2.0	2.17	20.45	113.5	35.95
#24 pH 3.0	3.98	ND	14.20	8.45
#24 pH 4.0	6.50	ND	ND	0.25
#24 pH 5.0	6.63	ND	ND	0.35
#24 pH 6.0	6.72	ND	ND	0.35
#24 pH 7.0	6.82	ND	ND	ND
#24 pH 8.0	6.90	ND	ND	ND

ND - None Detected at MQL  
 MQL - Minimum Quantifying Level

CORE #: 95-21

Pen Coal Sample #	pH	Aluminum	Iron	Manganese
#44 pH 2.0	2.13	12.40	234.0	2.00
#44 pH 3.0	4.45	ND	73.5	0.90
#44 pH 4.0	6.34	ND	ND	ND
#44 pH 5.0	6.60	ND	ND	ND
#44 pH 6.0	6.83	ND	0.90	4.55
#44 pH 7.0	6.84	0.55	ND	ND
#44 pH 8.0	6.96	17.30	4.05	ND
#47 pH 2.0	2.14	36.1	545.0	16.65
#47 pH 3.0	3.02	31.4	413.50	15.90
#47 pH 4.0	3.37	28.95	361.50	15.95
#47 pH 5.0	3.44	27.20	349.0	16.0
#47 pH 6.0	3.31	28.95	316.5	15.60
#47 pH 7.0	3.40	28.60	347.5	16.70
#47 pH 8.0	3.30	28.50	332.5	16.55
#70 pH 2.0	2.73	21.60	454.5	13.35
#70 pH 3.0	6.61	ND	ND	0.80
#70 pH 4.0	7.82	ND	ND	ND
#70 pH 5.0	8.05	ND	ND	ND
#70 pH 6.0	8.10	ND	ND	ND
#70 pH 7.0	8.04	ND	ND	ND
#70 pH 8.0	8.25	ND	ND	ND

ND - None Detected at MQL  
 MQL - Minimum Quantifying Level

DATE: 3/3/97

APPROVED: Phil Evans  
 Phil Evans

**CORE #: 95-21**

Pen Coal Sample #	pH	Aluminum	Iron	Manganese
#44 pH 2.0	2.13	12.40	234.0	2.00
#44 pH 3.0	4.45	ND	73.5	0.90
#44 pH 4.0	6.34	ND	ND	ND
#44 pH 5.0	6.60	ND	ND	ND
#44 pH 6.0	6.83	ND	0.90	4.55
#44 pH 7.0	6.84	0.55	ND	ND
#44 pH 8.0	6.96	17.30	4.05	ND
#47 pH 2.0	2.14	36.1	545.0	16.65
#47 pH 3.0	3.02	31.4	413.50	15.90
#47 pH 4.0	3.37	28.95	361.50	15.95
#47 pH 5.0	3.44	27.20	349.0	16.0
#47 pH 6.0	3.31	28.95	316.5	15.60
#47 pH 7.0	3.40	28.60	347.5	16.70
#47 pH 8.0	3.30	28.50	332.5	16.55
#70 pH 2.0	2.73	21.60	454.5	13.35
#70 pH 3.0	6.61	ND	ND	0.80
#70 pH 4.0	7.82	ND	ND	ND
#70 pH 5.0	8.05	ND	ND	ND
#70 pH 6.0	8.10	ND	ND	ND
#70 pH 7.0	8.04	ND	ND	ND
#70 pH 8.0	8.25	ND	ND	ND

ND - None Detected at MQL  
 MQL - Minimum Quantifying Level

DATE: 3/3/97

APPROVED: Phil Evans  
 Phil Evans

Acid-Base Account ~

Site: CORE 94-7

REIC Job #: 0494-25126 and 0696-43146

[illegible]

-As Reference in EPA manual: EPA-600/2-78-054; Field and Laboratory Methods Applicable to Overburden and Minesoils.

Research, Environmental and Industrial Consultants INC.

P.O. Box 286 Beaver, WV 25813 Phone: 1-800-999-0105 / (304) 255-2500 / FAX: (304) 255-2572

• - pH 3 Sulfuric Acid Manganese Extraction

-- - 1M Ammonium Acetate/0.2% Hydroquinone Manganese Extractant

APPROVED

---

Phil Evans