

DELINEATION OF POTENTIAL MANGANESE SOURCES IN THE COAL
OVERBURDENS OF WESTERN PENNSYLVANIA¹

by

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Abstract. Manganese is a common and regulated metal in acidic mine effluents. Because the precipitation and removal of manganese from mine effluents is complex and expensive, it is advantageous to ascertain the distribution of manganese in the stratigraphic section prior to mining. By identifying certain stratigraphic horizons that have high amounts of manganese, it may be possible to implement special handling plans to minimize or prevent mine drainages from having elevated manganese contents. Because the source of manganese in mine drainages is poorly documented, the overburden from a mine site having drainages characterized by elevated manganese concentrations (70 to 80 ppm Mn) was examined in detail. Bulk manganese analyses determined the majority of the manganese to be present in a 13.5 foot thick sequence of black to dark gray shales which also contained highly variable amounts of sulfur. CO₂ coulometry, and x-ray diffraction determined this stratigraphic interval to be enriched in siderite (FeCO₃). Increases in the manganese were accompanied by increases in the siderite content. Manganese substitution in the siderite structure appears to be the source of manganese in this mine site.

Additional key words: Siderite, CO₂ coulometry, solid solution, microprobe analyses and bulk Mn determinations.

Introduction

Because the source of the Mn in coal-bearing strata is poorly understood, predicting the occurrence of Mn in mine drainages is difficult. To gain a better understanding of why certain mine drainages have elevated concentrations of manganese, the overburden from a mine site having an acidic high-Mn drainage was examined using a variety of techniques.

The primary objective of the overburden analysis is to characterize the overburden from this particular mine site using a variety of techniques that will provide more information than the typical acid-base accounting data. Although the source of Mn in coal-bearing strata is poorly documented, the following sources are potential candidates: 1) pyrolusite (MnO₂), and/or 2) Mn in solid solution associated with the various carbonate phases (e.g. siderite and/or calcite).

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One particular area of interest is the characterization of the various carbonate phases present. The characterization of carbonates involves: 1) determining both the nonreactive carbonate (e.g. siderite) and the reactive carbonate (e.g. calcite and/or dolomite) phases and 2) determining if the presence of Mn is related to the occurrence of carbonates. The occurrence of Mn in solid solution in carbonates is well documented in the literature (Hurlbut

and Klein 1977; Pearson 1979; Teodorovich 1961; Mozley 1989; and Pye 1984).

Materials and Methods

The majority of overburden in this surface mine is characterized by low sulfur ($S_T < 0.35$ wt. %) and low NP (NP < 20) in which fine to medium grained sandstones are the dominant lithology. The conventional acid/base accounting data (total sulfur, NP, and fizz rating) were obtained from Geochemical Testing of Somerset, PA. CO₂ coulometry, bulk Mn determinations, x-ray diffraction, and the simulated weathering experiments were performed at The Pennsylvania State University.

Total Sulfur

Total sulfur analyses were performed using a Leco SC-32 sulfur analyzer. Vanadium pentoxide was used as an accelerator. This high temperature combustion technique is described in Noll, Bergstresser, and Woodcock (1988). Total sulfur can then be converted to maximum potential acidity by multiplying total sulfur by 31.25.

Neutralization Potential

Neutralization potential, as the name implies, is used to determine the neutralization ability of a given sample. This entails determining the amount of calcite, and/or dolomite and expressing these contents as tons of CaCO₃ equivalent/1000 tons of overburden. The determination of neutralization potential is described in Noll, Bergstresser, and Woodcock (1988).

In theory, siderite does not report in the NP determination and is believed not to have the neutralization ability of calcite or dolomite. As a consequence, siderite may be very abundant in a given overburden, yet will go undetected in the NP determination. As a result of this, CO₂ coulometry was used to determine the carbonate content.

CO₂ Coulometry

CO₂ coulometry is a highly accurate analytical technique that is routinely used in the determination of both inorganic and carbonate carbon. Because the various carbonate phases react at different rates, the CO₂ coulometer was used to measure the rate of CO₂ evolution when the sample is introduced to an acid. Because siderite reacts much slower than the other carbonate phases (e.g. calcite and/or dolomite), CO₂ coulometry was used to quantify the occurrence of siderite. The methodology employed here is described in detail by Morrison et al. (1990). In theory, this is a very similar approach to Evangelou, Roberts, and Szekeres (1985).

Bulk Manganese Analyses

Bulk manganese analyses were performed on selected samples to determine the distribution of manganese throughout the stratigraphic sequence. Overburden samples were digested in a HF - H₂SO₄ solution, until only a minimal residue remained. The solution was boiled to drive off the volatile silica. The residue from the HF - H₂SO₄ leach was then introduced to a HNO₃ leach, to ensure complete digestion. Manganese, if present in any form, (e.g. pyrolusite and/or Mn in solid-solution) would leach out under these various acid leaches. The combined leachates from these digestions were analyzed for manganese using a Spectrametrics Spectra Span III atomic emission spectrometer. The excitation source was a DC plasma sustained in argon gas. Liquid aliquots were serially diluted to the linear range of 1 to 5 ppm. All unknowns were analyzed by first running a series of reference solutions and then the unknowns. This procedure was then repeated in reverse order to account for instrumental drift. The duplicate values were averaged and these averages reported. When operated in this manner, the experimental detection limits were estimated to be 0.01 ppm (10 ppb).

Simulated Weathering Experiments

Simulated weathering experiments are a useful technique to compare overburden samples under controlled laboratory conditions. Their usefulness in predicting the field occurrence of acidic mine drainage is more problematic. Overburden samples were prepared by stage crushing to -1/4 inch. The samples were placed in one quart HDPE plastic storage containers (Figure 1). Deionized water was added to the plastic leaching vessels and allowed to react in an enclosed chamber in which humidified air was circulated. Leachates were collected on a weekly basis (hourly and weekly leachates combined) and characterized with respect to pH, acidity, sulfate, total iron, manganese, and aluminum.

X-Ray Diffraction

Overburden samples were examined for their crystalline phase composition using conventional x-ray powder diffraction methods. All data were collected with copper K-alpha radiation on a fully automated Scintag PAD V diffractometer equipped with a cryogenic detector. All specimens were ground to -325 mesh and mounted on a zero background substrate cut from a single crystal of quartz which was oriented just off the c-axis. The range of data collection was from 15 to 55 degrees 2-theta at 1 degree/minute and a step size of 0.02 degrees. Phase identifications were made by comparison to the JCPDS-ICDD reference patterns. The lower detection limit is estimated to be approximately 1%.

Results and Discussion

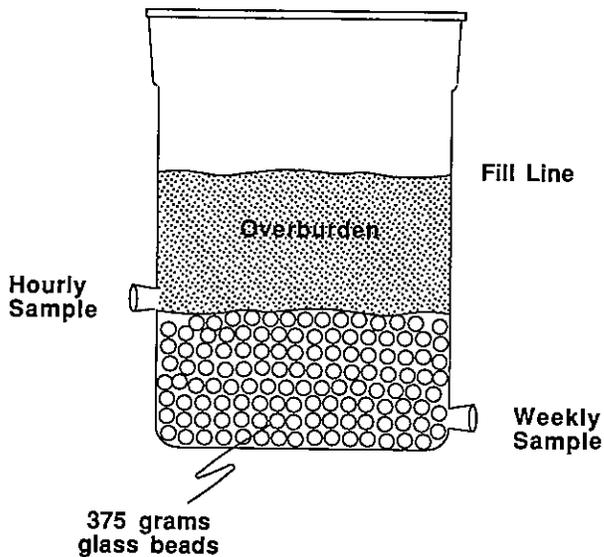


Figure 1: Simulated Weathering Vessles.

ETEC Microprobe

Overburden specimens were processed to -20 mesh and then pelletized. The -20 mesh particles were mixed with a Hexacol epolite resin and hardener, pressed into one inch diameter stainless steel molds at 10,000 psi for two minutes. After the two minute press, the resin was allowed to cure overnight. These pellets were polished with 400 and 600 grit paper for three minutes each. The next phase of polishing involved using 0.3 micron aluminum slurry on a Texmet cloth for two minutes, followed by the final polish using a 0.5 micron aluminum slurry on a silk polishing cloth. The samples were washed in an ultrasonic bath between all polishing steps. The polished pellets were wiped dry and analyzed within 18 to 24 hours.

An ETEC Auto Microprobe was employed to analyze the chemical composition of siderite by a combination of energy dispersive and wavelength dispersive techniques. Siderite grains were selected from the overburden fragments based upon the chemical composition determined by using semi-quantitative EDX. The criterion used to establish a grain of siderite versus clays was the presence of significant amounts of silica (> 1.00 wt %). In this case, these grains were not counted due to clay contamination. Grains which contained only traces of silica (< 1.00 wt %) were analyzed for Mg, Al, Ca, Mn, and Fe. This latter category of grains was analyzed individually by wavelength dispersive techniques using LIF, PET, and TAP crystal monochromators. All analyses were run at 15Kv acceleration potential with a sample current of 0.02 microamps.

Figure 2 summarizes the stratigraphic and overburden data from one of the core holes on the mine site. Total sulfur contents were generally less than 0.35% except in samples 170, 171, 185, and 189. NP's were typically less than two except for samples 170 to 175 and 183 to 185. The majority of the total sulfur and NP occurred within a 13.5 foot thick sequence of black to dark gray shale/siltstones. The NP from this horizon would typically be considered negligible as a neutralizer by Pa DER (Brady and Hornberger 1989) because of the assigned fizz rating and the low NP's. These NP's would be interpreted as being the result of siderite and therefore discounted because of siderite's inability to neutralize acidic drainages (Williams et al. 1982).

Because NP determinations do not accurately quantify all of the carbonates present (excludes the majority of siderite) carbonate carbon measurements were performed on selected samples. The majority of the carbonate present was associated with samples 170 - 175. CO₂ coulometry data, as interpreted and discussed by Morrison et al. (1990) indicated that the dominant carbonate phase present in these overburdens was siderite. This interpretation was also verified using x-ray diffraction.

Figure 3 shows a portion of the x-ray diffractograph for sample 173. The portion of the diffractograph presented here represented the 2 theta interval where the main carbonate peaks would occur if present (27 to 33 degrees 2 theta). The stick figures below the x-ray diffractograph are the JCPDS-ICDD reference patterns for siderite, calcite, and ankerite respectively.

Bulk manganese determinations revealed that the majority of manganese present in the overburden also occurred in this 13.5 foot thick shale sequence. Of particular importance to note here was that increasing carbonate carbon (siderite) contents were accompanied by both increasing amounts of NP and Mn. The increase in NP's with increasing siderite contents exemplifies the shortcomings of the conventional NP determination. As the amount of siderite increased, the accuracy of the NP determination became questionable because of the increased Fe in solution Morrison et al. (1990). The parallel increase in both siderite and Mn strongly suggested that the Mn is associated with the siderite probably occurring in solid solution.

Rosenberg (1960, 1963, 1967) described the subsolidus relationships in the system CaCO₃-MgCO₃-FeCO₃-MnCO₃. His data and more recent studies reported by Essene (1983) demonstrated that complete solid solution exists in the MgCO₃-FeCO₃-MnCO₃ system. Figure 4 gives an example of the subsolidus relationships in the MgCO₃-FeCO₃-MnCO₃

Log Interval	Thickness	Scale	Graphic Log	Lithologic Description	OB Analys No.	% Total Sulfur	NP	Fizz Rating	CC	Mn	
0-3	36"			Light gray, medium grain sandstone	153	0.01	0.54	none		95	
3-6	36"				154	0.00	0.26	none		15	
6-9	36"	10			155	0.00	0.41	none			
9-12	36"				156	0.00	0.51	none		15	
12-15	36"				157	0.00	0.28	none	0.01	15	
15-18	36"				Light gray, medium to fine grained sandstone	158	0.00	0.33	none		
18-21	36"	20		159		0.00	0.48	none			
21-24	36"			160		0.00	0.66	none			
24-27	36"			161		0.00	1.02	none			
27-30	36"				Light gray, medium grained sandstone with increasing amounts of organic debris with depth	162	0.00	0.51	none		20
30-33	36"	30		163		0.00	0.43	none			
33-36	36"			164		0.00	0.64	none	0.00	15	
36-39	36"			165		0.02	0.74	none			
39-42	36"	40		166		0.01	0.56	none			
42-45	36"			167		0.03	0.46	none			
45-47'1	25"			168		0.01	0.54	none			
47'1-49'2	25"	50	169	0.15		0.26	none				
49'2-52'2	36"			Dark gray shale with increasing siltstone laminate with depth	170	4.42	2.81	none	0.04	220	
52'2-55'2	36"				171	0.66	10.20	none	0.69	1650	
55'2-58'2	36"	60			172	0.20	16.43	none	1.23	2700	
58'2-61'2	36"				173	0.26	18.29	none	1.30	3100	
61'2-62'10	17"				174	0.32	10.25	none	0.80	2050	
62'10-65'10	36"			Light gray medium-grain sandstone, black shale partings	175	0.25	4.03	none	0.36	550	
65'10-68'10	36"	70			176	0.24	1.91	none		290	
68'10-71'10	36"			Light to whitish gray, medium-grain sandstone with some pyritic nodules, decreasing organic debris with depth	177	0.09	-1.32	none			
71'10-74'10	36"				178	0.02	0.20	none	0.00	30	
74'10-77'10	36"				179	0.02	0.41	none			
77'10-80'10	36"	80			180	0.00	0.00	none			
80'10-83'10	36"				181	0.03	0.38	none	0.00	30	
83-86'10	36"				182	0.07	0.64	none		30	
86'10-89'10	36"		183	0.01	3.01	none					
89'10-92'5	31"	90	184	0.13	13.47	slight	0.25	270			
92'5-94'5	24"			Dark gray laminated siltstones	185	0.51	2.58	none			
94'5-96'5	24"				186	0.27	-2.21	none		240	
96'5-99'5	36"			Olive to dark gray poorly indurated shale/underclay with plant fragments	187	0.01	-0.22	none	0.01	130	
99'5-101'11	30"	100			188	0.35	0.87	none		105	
101'11-104'11	36"			Coal	189	1.50	1.38	none			
104'11-106'5	18"			Dark gray underclay	190	0.06	1.61	none		115	
106'5-107'10	17"			Black carbonaceous/boney shale	191	0.23	1.35	none			
107'-110'4	30"	110		Dark gray siltstone with small vitrinite bands	192	0.00	0.48	none	0.00	75	
110'4-112'10	30"				193	0.02	0.66	none		65	
112'10-115'5	31"				194	0.08	1.05	none	0.01	90	

Figure 2: Overburden Characterization Data.

system showing extensive solid solution between siderite and magnesite and a limited solid solution with Fe in calcite. The pure Fe-analog of dolomite, ankerite, was seen from this data not to exist, but exhibited a partial solid solution between dolomite and ankerite. Limited solid solution was reported (Reeder and Dollase, 1989) in the binary compounds in this system with increased amounts increasing with temperatures. A large three phase area was present in this diagram in which calcite solid solution/ankerite solid solution and siderite-magnesite solid

solution coexist. The diagram was representative of the phase relationship at 400°C. All of these studies were reported on experimental or natural samples that were formed at elevated temperatures or pressures above 350°C and 400MPa.

In contrast, literature citations of sedimentary carbonates were restricted mainly to calcite and dolomite with only very limited data reported on siderite (Mozely 1989; Pearson 1979). Mozley (1989) reported on the differentiation between marine and fresh water diagenetic

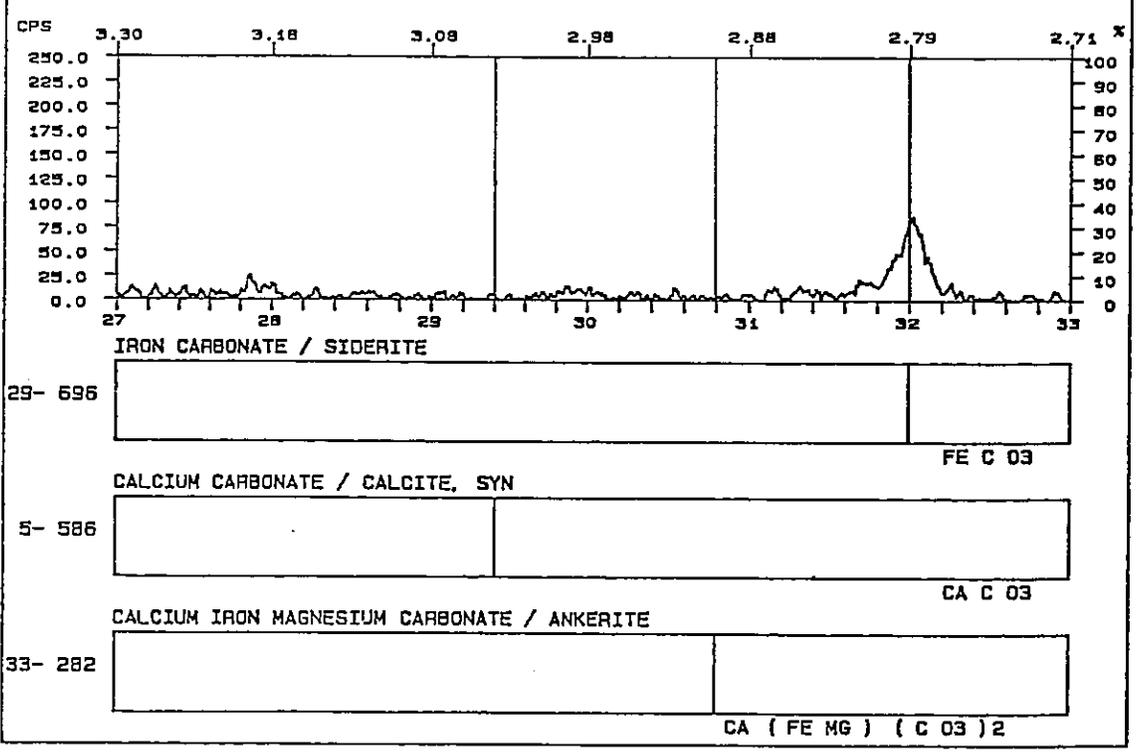


Figure 3: X-ray Diffractograph of Overburden Sample #173.

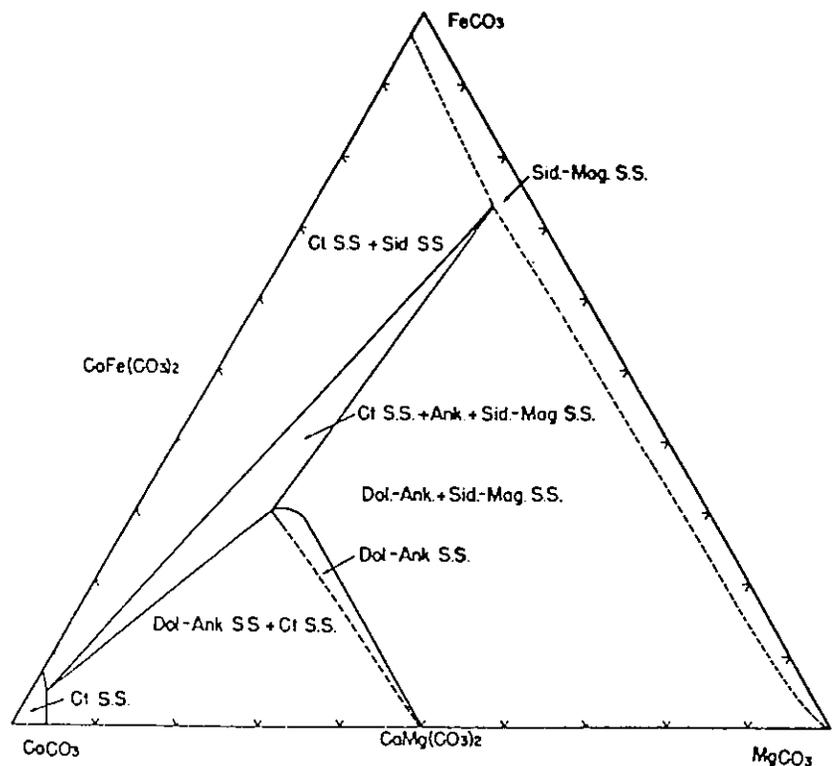


Figure 4: Subsolidus Relationships in the $MgCO_3$ - $FeCO_3$ - $CaCO_3$ System (after Rosenberg, 1960).

siderites, based upon the crystal chemical substitution of Ca, Mg and Mn for Fe in siderites. The observed degree of substitution in Mozley (1989) was larger at lower temperatures than reported by other authors, perhaps reflecting the differences in depositional environments. This sparsity of information was attributed by Dresel (1989) to the inability to identify fine-grained siderite in the field. As a consequence, very little is known with regards to the degree of solid solutions that form in siderite under these depositional conditions. The subsolidus phase relations of this system at lower temperatures (as in sedimentary siderite) will change from those presented in Figure 4.

Further data to support the observation that Mn is contained in siderite as a crystal chemical substituent was obtained from a siderite concretion (not from this mine site), (Morrison et al. 1990) for which 40 grains of siderite were analyzed for Fe, Mn, Mg and Ca. These data, Table 1, show an average Mn-substitution of 3500 ppm which is equated to a molar substitution of: $(Fe_{.86}Mg_{.02}Ca_{.1}Mn_{.01})CO_3$. Table 2 further supports the presence of a nearly constant, within experimental error, concentration of Mn in this 13.5 foot sequence of black shales. With the exception of the first three foot interval in this section (an interval with high pyrite concentrations) the concentration of Mn in the siderite (carbonate carbon) was relatively constant, showing perhaps a slight trend to higher concentrations with depth.

Table 1: Microprobe Analysis of Siderite (Wt.%)

	Fe	Mn	Ca	Mg
Avg.	39.05	0.35	3.52	0.38
std. dev.	1.42	0.26	0.93	0.10
number	41	41	41	41

Simulated weathering experiments were conducted on selected overburden samples within this 13.5 foot sequence of shales. Figure 5 summarizes the simulated weathering data for samples 170, 171, and 175. Sample 171 produced the highest weekly average of Mn among these three samples and also possessed both the highest amount of Mn and siderite in these samples. Mn concentrations in the mine backfill were approximately an order of magnitude greater (ranged from 78 to 84 ppm Mn) than the sample 171 simulated weathering Mn levels.

Table 2: Ratio of Mn to Carbonate Carbon

Sample #	Carbonate Carbon (wt %)	Mn (ppm)	Mn/C. Carbon Ratio
170	0.04	220	5.5×10^{-1}
171	0.69	1650	2.2×10^{-1}
172	1.23	2700	2.4×10^{-1}
173	1.30	3100	2.6×10^{-1}
174	0.80	2050	2.6×10^{-1}

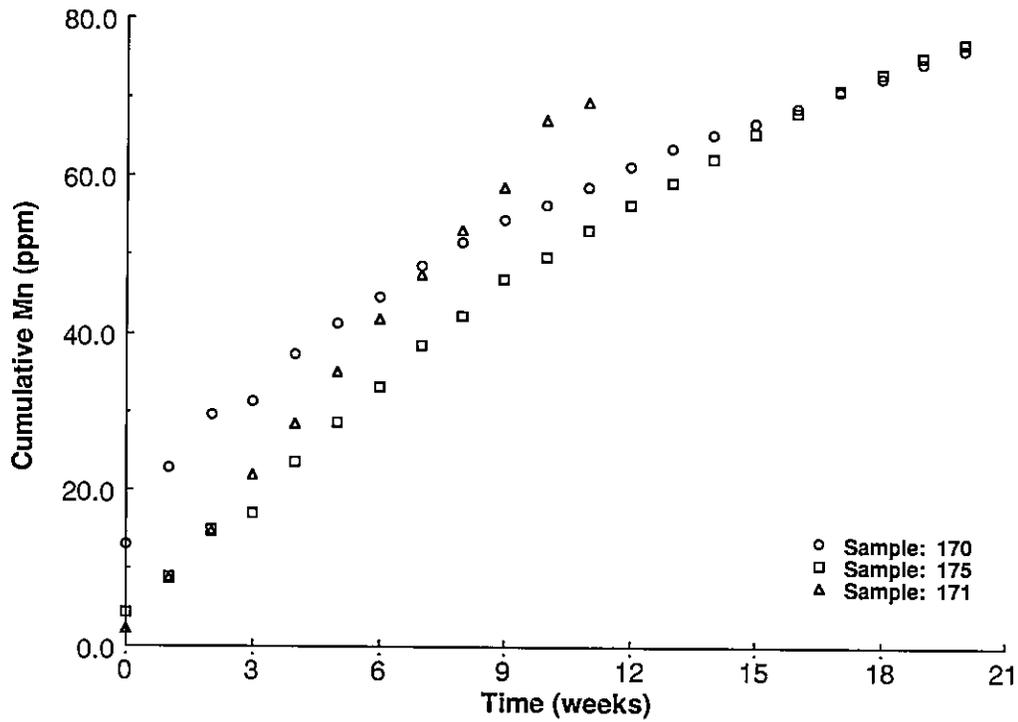
Conclusions

It is clear that increasing amounts of manganese in this particular mine site, are accompanied with increasing amounts of both carbonate carbon and NP. CO_2 coulometry and x-ray diffraction data indicates that this carbonate is solely in the form of siderite. Therefore, at this particular site, the source of the manganese appears to be a Mn-bearing siderite. Of particular importance is that the siderite in this stratigraphic horizon occurs in intimate contact with some of the highest sulfur contents encountered. This accelerates the dissolution of siderite and therefore the release of Mn. Simulated weathering experiments produced leachates with Mn levels approximately an order of magnitude less than those values found in the mine backfill.

The occurrence of Mn in carbonates is well documented. Although the Mn in this particular mine site appears to be in the siderite, ongoing research at The Pennsylvania State University is establishing a Mn database in order to gain a better understanding of the distribution of Mn-bearing phases in coal-bearing strata. Such a database will hopefully lead to determining what level of Mn in the overburden has the potential to produce a mine drainage with elevated levels of Mn.

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Sample	Acid / Base Account Data			Carbonate Carbon	Bulk Mn (ppm)	Simulated Weathering	
	Total Sulfur (wt %)	Neutralization Potential	Flizz Rating			Range Mn (ppm)	Weekly Avg. Mn (ppm)
170	4.42	2.81	none	0.04	220	1.7-12.9	3.4
171	0.66	10.20	none	0.69	1650	2.2-7.1	5.8
175	0.25	4.03	none	0.36	550	1.8-6.0	3.5

Figure 5: Characterization of Manganese Levels in Simulated Weathering Experiments.

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