

METALS AND OTHER COMPONENTS OF COAL MINE DRAINAGE AS RELATED TO AQUATIC LIFE STANDARDS¹

by

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Abstract. The objective of this study was to characterize the occurrences of various metals and other contaminants in 128 different water samples from untreated coal mine drainage (CMD) as related to aquatic life water quality criteria. The water quality analyses were of untreated drainage from active, reclaimed, and abandoned surface and underground mines, as well as coal waste materials. About 75% of the study sample set had pH values less than 4.5, and the remaining samples had pH values ranging from 4.5 to 6.9. The following metals were included in the chemical analyses: ferrous and ferric iron, aluminum, manganese, arsenic, beryllium, cadmium, cobalt, chromium, copper, antimony, and zinc. As would be expected by pH-controlled solubility relationships, higher metal concentrations were generally associated with lower pH values. Water hardness values were somewhat independent of pH over the range of the study sample set, but were generally very hard. This is significant since hardness usually raises the aquatic toxicity threshold for most metals (e.g., cadmium, chromium, copper, lead, manganese, nickel, and zinc). No clear correlations were found between the occurrence of manganese, which has been used as a CMD treatment surrogate, and other more toxic metals. Potentially toxic concentrations of some of these metals were found at manganese concentrations less than 2 mg/L, which is the normal effluent standard for CMD discharges. Traditional active and abandoned mine land reclamation practices have focused on discharge water quality parameters that conform to usual National Pollution Discharge Elimination System (NPDES) standards. This particularly applies to the use of manganese levels as a surrogate for threshold concentrations of toxic and heavy metals in discharge waters. Given the lack of good correlation in the occurrence of manganese with these metals, the occurrences of these metals in CMD, and their concentrations relative to aquatic life criteria reclamation practices can be more protective of aquatic life if individual metal concentrations are more thoroughly considered.

Additional Key Words: acid mine drainage, heavy metals

Introduction

This study investigated the various components that constitute untreated coal mine drainage (CMD) and, in particular, the occurrences of metals in CMD in 128 different discharges. This study addresses the occurrence and abundance of metals in "at source" drainages from active, reclaimed, and abandoned surface and underground mines as well as coal waste materials. Coal mine drainage, while often acidic (often termed acid mine drainage (AMD)), may be alkaline. The primary cationic components usually include ferrous iron, ferric iron, aluminum, calcium, sodium, potassium, magnesium, and manganese. The primary anionic components usually include the sulfate and bicarbonate ions. A variety of complexes of these

ions may exist depending on water quality component concentrations and solution ionic strength (Hem 1989). Only pH, total iron, total manganese, total suspended solids, and settleable solids are generally regulated (U.S. Code of Federal Regulations 1991a). Total manganese is included in this perspective because it is deemed a treatment surrogate for a number of other ions whose solubilities are less than manganese under conventional treatment conditions (Weidman 1982, Kleinmann and Watzlaf 1988). This report, while not completely representative of the very broad multidimensional spectrum of the chemistry of coal mine drainage, illustrates the wide range of metals and other contaminant concentrations that occur.

The analyses used for this study include samples collected specifically to develop this study as well as from other studies on the prediction, control, and treatment of CMD where a selected list of trace and heavy metals was analyzed in addition to the conventional CMD suite of analytes. Many of the studies of the Pittsburgh Research Center have been concentrated in the states of Pennsylvania, West

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Virginia, and Ohio, as have many of the analyses. Samples from Tennessee, Maryland, Montana, Kentucky, Colorado, Oklahoma, and Missouri are also included. Particular efforts were made to obtain samples from other coal mining districts, either by directed sampling or through the scientific or regulatory agency literature. In general, the concentrations are technically "total" as many samples were not filtered. Most of these "total" samples closely approximate "dissolved" samples, as results from filtered and unfiltered analyses have shown little differences when samples are taken carefully to avoid turbidity.

Background

A number of studies have reported the occurrence of metals in CMD from coal mined areas (Gang and Langmuir 1974, Martin 1974, Massey and Barnhisel 1972, Blevins and Ziegler 1992). In addition to CMD studies, there have been numerous studies on the occurrences of metals in coal combustion products (Wewerka et al. 1976, Watcher and Blackwood 1978, and Williams et al. 1981). Other mining and reclamation studies have incidentally presented detailed water quality analyses (Baker-Wibberlet & Associates 1977, Nichols 1983). In general, zinc, nickel, and copper are the most commonly encountered metals after the primary cationic components Fe, Mn, Ca, Mg, and Al. One of the more definitive studies done to date on the occurrence of metals in CMD is the USEPA comprehensive analysis that led to the development of point source discharge standards for CMD (Weidman 1982). Twenty-five acid drainages and 44 alkaline drainages were analyzed. As is to be expected, the more acidic drainages had higher concentrations of metals than alkaline drainages.

Water Quality Standards

To put the water quality of mine drainages into perspective, the environmental constraints of the receiving water and its uses need to be considered. Drinking water standards are relatively well defined and are commonly used to compare the water quality impacts of contamination by various sources. From an environmental quality perspective, the prospective or potential uses of receiving surface and ground waters often have significantly different and more stringent water quality criteria and/or standards associated with them. Aquatic habitat water quality criteria and/or standards are less well defined and uniform than drinking water standards and are often functions of water hardness and durations of impact. These standards vary between States as well as aquatic lifeforms considered. Table 1 presents an summary of US (U.S. Code of Federal Regulations 1991 c, U.S.

Code of Federal Regulations 1991 d (primary and secondary), Canadian (Canadian Council of Ministers of the Environment 1987), and European (Carney 1991) drinking water standards for inorganic components of the CMD analyte list.

Table 2 presents aquatic life criteria for the CMD analytes addressed by the USEPA's National Ambient Water Quality Criteria and used in Canada (Canadian Council of Ministers of the Environment 1987). There also exists other criteria used by different states (State Water Res. Control Board 1992, Canadian Council of Ministers of the Environment 1987). The criteria and guidelines are quite variable and, for certain metals (e.g., Cd, Cr, Cu, Ni, and Pb), are based on water hardness and duration of exposure, such as 24-hour, 96-hour, and 30-day exposures. To provide a context for the potential impacts that unmitigated CMD can have on aquatic life in receiving waters as well as to provide some measure of "water treatment distance," Table 2 is presented and represents a generalized summary of two selected sets of criteria and guidelines from the literature (Flora et al. 1984 and Canadian Council of Ministers of the Environment 1987). When a guideline or criteria is a function of hardness, some maximum value is often stated. Although this is not always the case (Flora et al. 1984 and State Water Res. Control Board 1992). It is not clear what constitutes a maximum concentration. For specific problems, the reader is advised to consult with an appropriate regulatory agency.

The water quality of effluents from mines and mineral processing operations are included in the National Pollution Discharge Elimination System (NPDES) regulations for point source discharges. These standards are specified for the coal industry in 40 CFR part 434 (U.S. Code of Federal Regulations 1991 e). Various standards are applicable to coal mining operations, both active and under reclamation, as well as coal preparation facilities. In general, the standards for metals and pH are:

	<u>1-day Max.</u>	<u>30-day Avg.</u>
pH, s.u.	6.0-9.0	6.0-9.0
Iron, mg/L	6.0, 7.0	3.0, 3.5
Manganese, mg/L	4.0	2.0

It is important to remember that manganese levels are used as a treatment surrogate for other metals that may occur in the discharge waters. The theory is that conditions supporting removal of manganese (precipitation at high pH) ensure that other metals will be removed as well. The different iron standards are a function of the age of the operations. Other water quality parameters mandated by the coal

Table 1. Drinking water quality standards for United States, Canada, and Europe (pH in standard units, other ion concentrations as mg/L).

	<u>United States*</u>	<u>Canada</u>	<u>European</u>
pH	6.5-8.5	6.5-8.5	6.5-8.5, 9.5 max.
Iron	0.3	0.3	0.2
Magnesium			50
Aluminum	0.05-0.20		0.20
Manganese	0.05	0.05	0.05
Sulphate	250	500	250
Chloride	250	250	
Potassium			12
Silver	0.1	0.05	
Arsenic	0.05*	0.05	0.05
Barium	2.0*	1.0	
Beryllium	0.004*		
Cadmium	0.005*	0.005	0.005
Chromium	0.1*	0.05	0.05
Copper	1.0	1.0	
Nickel	0.1*		0.05
Lead	0.05*	0.05	0.05
Mercury	0.002*	0.001	0.001
Antimony	0.006*		0.010
Selenium	0.05*	0.01	0.01
Thallium	0.002*		
Zinc	5.0	5.0	

* Primary US drinking water maximum contaminant levels (MCL); others are secondary MCLs.

Table 2. Summary of example freshwater aquatic life protection criteria or guidelines of CMD analytes (pH in standard units, other ion concentrations as mg/L, conductivity in umho/cm).

ANALYTE	NAWQC	CANADIAN WATER QUALITY GUIDELINE
pH	6.5-9.0	6.5-9.0
Iron	1.0	0.3
Magnesium	-	-
Aluminum	0.087	0.005 pH<6.5 0.1 pH>6.5
Sodium	-	-
Chloride	230	-
Potassium	-	-
Silver	0.00012	0.00010
Arsenic (As ³⁺)	0.190	0.05
Barium	-	-
Beryllium	0.0053*	-
Cadmium	0.0011*	0.0002 H=0-60 0.0008 H=60-120 0.0013 H=120-180 0.0018 H>180
Chromium	Cr ⁶⁺ : 0.011 Cr ³⁺ : 0.210*	0.002-0.02
Copper	0.012*	0.002 H=0-60 0.002 H=60-120 0.003 H=120-180 0.004 H>180
Nickel	0.160*	0.025 H=0-60 0.065 H=60-120 0.110 H=120-180 0.150 H>180
Lead	0.0032*	0.001 H=0-60 0.002 H=60-120 0.004 H=120-180 0.007 H>180
Mercury	0.000012	0.0001
Selenium	0.005	0.001
Zinc	0.110*	0.03
Conductivity	2000-4000	-

* Hardness-dependent. Value based on 100 mg CaCO₃/L hardness.

standards are total suspended solids and settleable solids.

For the noncoal mineral industries, parts 436 and 440 of 40 CFR may be applicable with effluent water quality standards being a function of the commodity involved (U.S. Code of Federal Regulations 1991f and U.S. Code of Federal Regulations 1991g). Table 3 presents NPDES standards for all those mineral industries combined into a single table for the purpose of comparing concentrations of certain metals in CMD with metals standards from other mining and mineral preparation operations. The multiple standards arise because different commodities may have different standards for the same metals. These NPDES standards are met by active operations through water treatment prior to discharge.

Methods

Sample Collection

Of the 128 samples used in this study, 102 were collected and analyzed by the former US Bureau of Mines (USBM) Pittsburgh Research Center (PRC). The remaining samples were collected by various State agencies, the USEPA, or the USGS and were also considered very high quality. The samples collected by the USBM were not filtered unless they contained observable particulates or had a field pH greater than about 5. Comparison between filtered and unfiltered samples which did not contain observable particulates showed negligible differences based upon the experiences of the authors. Samples were filtered through 0.2 or 0.45 micron filters. Hydrochloric acid was used for acidification to permit speciation of ferric and ferrous iron.

Analytical Methods

The following analytical methods are for the samples collected and analyzed by the USBM. The other samples were analyzed using USGS methods. Field and laboratory pH were measured by an electrode using a two-point calibration method. Conductivity was also measured using electrodes. Field alkalinity was measured using the Orion Field Alkalinity Test Kit, which compared extremely well with standard alkalinity titrations ($r^2=0.99$) (Watzlaf and Hedin 1993). Laboratory alkalinity and acidity titrations were performed using standard methods (American Public Health Association 1992). An additional measurement was taken on net alkaline samples using a modified alkalinity titration. The modification involved adding hydrogen peroxide and heating prior to the alkalinity

titration (as recommended for standard acidity titrations for samples containing hydrolyzable metal ions and reduced forms of polyvalent cations). Ferrous iron was measured using a potassium dichromate titration (Fales and Kinny, 1940). Bromide and chloride was analyzed using liquid chromatography. All other parameters were analyzed using inductively coupled argon plasma spectroscopy. The USEPA quality control guidelines of one duplicate, one standard recovery, and one spike recovery for every 10 analyses was employed (USEPA, 1979). Detection limits are given in Table 4. The range in detection limits is due to dilution of contaminated samples by up to 10:1, as well as matrix effects.

The analyses that form the foundation of this report were selected on the basis of the extra trace element analyses that were performed. The basic criteria for selecting water quality samples for consideration in this study included sampling performed at direct sources (such as in-mine, mine pool monitoring wells, and surface discharge points) and cation-anion balance to within 10%.

Result and Discussion

The Components of CMD

Table 5 summarizes the water quality analyses used in this study. The second column represents the number of times the parameter was analyzed for and found to be above detection limits. The mean represents the mean of the non-zero values. The following discussion is based on the data set of this report as presented in Tables 2 and 5. It assumes that all concentrations represent the dissolved species.

Figure 1 presents, as a Ficklin Plot, the sum of zinc, copper, cobalt, cadmium, nickel, and lead concentrations as a function of pH. This graph is analogous to that developed and used by the USGS (Ficklin et al. 1992) to characterize drainages that result from various metal mining districts in Colorado. The data from the CMD data set display the same general trend as the metal mine drainages, but slightly depressed in concentration. The implication is that CMD can have similar metals concentrations as some metal mine drainages. This means that AML reclamation strategies that seek to mitigate adverse environmental impacts to aquatic life need to specifically consider the various individual toxic metals that may be present in the CMD to be remediated, not just the "traditional" CMD components of acidity-generating metals iron, aluminum, and manganese as well as pH.

Table 3. Combined noncoal mineral industry NPDES standards summarized and combined from 40 CFR parts 436 and 440 (pH in standard units, other ion concentrations as mg/L).

	<u>1-day Maximum</u>	<u>30-day Average</u>
pH	6.0-9.0	6.0-9.0
Iron	1.0, 2.0	0.5, 1.0
Aluminum	2.0	1.0
Arsenic	1.0	0.5
Cadmium	0.10	0.05
Copper	0.30	0.15
Nickel	0.2	0.1
Lead	0.6	0.3
Mercury	0.002	0.001
Zinc	1.0, 1.50	0.5, 0.75

Table 4. Detection limits for analyses performed at PRC.

<u>Analyte</u>	<u>Detection Limit (mg/L)</u>
Alkalinity (CaCO ₃)	10
Acidity (CaCO ₃)	10
Ferrous Iron	0.3-3.0
Ferric Iron	0.01-0.1
Iron, total	0.01-0.10
Calcium	0.02-0.2
Magnesium	0.02-0.2
Aluminum	0.02-0.2
Sodium	0.05-0.5
Manganese	0.003-0.03
Sulphate	10
Chloride	0.05-0.5
Potassium	0.05-0.5
Bromide	0.05-0.5
Arsenic	0.04-0.4
Barium	0.005-0.05
Beryllium	0.001-0.01
Cadmium	0.003-0.03
Cobalt	0.003-0.03
Chromium	0.005-0.05
Copper	0.005-0.05
Nickel	0.005-0.05
Lead	0.04-0.4
Mercury	0.0002-0.002
Antimony	0.04-0.4
Selenium	0.1-0.01
Thallium	0.04-0.4
Vanadium	0.04-0.4
Zinc	0.003-0.03

Table 5. Water quality analyses from the 128 discharges. "Times reported" indicates the number of times the parameter was analyzed for and does not indicate that it was present above detectable levels.

<u>Parameter</u>	<u>Times Reported</u>	<u>Mean</u>	<u>Median</u>	<u>Minimum</u>	<u>Maximum</u>
Flow (L/min.)	49	333	67.0	5.50	3690
pH	128	2.84	3.24	1.2	7.8
Alkalinity, field	8	52	28	5	153
Alkalinity, lab	125	18.2	0.00	0.0	275
Acidity	128	1,500	410	-270	55,300
Conductivity	60	2,970	2,125	360	27,000
Sulphate	128	2,360	1320	71.1	52,700
Aluminum	123	88.0	27.3	0.0	930
Antimony	94	0.004	0	0.000	0.150
Arsenic	115	0.189	0	0	16.1
Barium	108	0.01	0	0	0.200
Beryllium	114	0.021	0	0	0.270
Cadmium	119	0.014	0	0	0.820
Calcium	128	183	170	6.90	483
Chloride	43	61.3	7.90	0	849
Chromium	128	0.077	0	0	7.18
Cobalt	110	0.794	0.265	0	6.0
Copper	128	0.139	0	0	2.49
Iron, Ferric	123	142	6.4	0	4,106
Iron, Ferrous	120	291	69.7	0	15,700
Iron, Total	128	410	96.5	0	19,800
Lead	117	0.023	0	0	1.84
Magnesium	128	112	92.7	2.75	638
Manganese	128	21.9	7.45	0	164
Nickel	123	1.19	0.56	0	10
Potassium	116	4.61	3.25	0.04	47.3
Selenium	109	0.000	0.000	0.000	0.003
Silver	22	0.0005	0	0	0.010
Sodium	128	34.9	8.90	0.330	437
Vanadium	19	0.121	0.053	0	0.660
Zinc	126	4.27	0.920	0.010	146

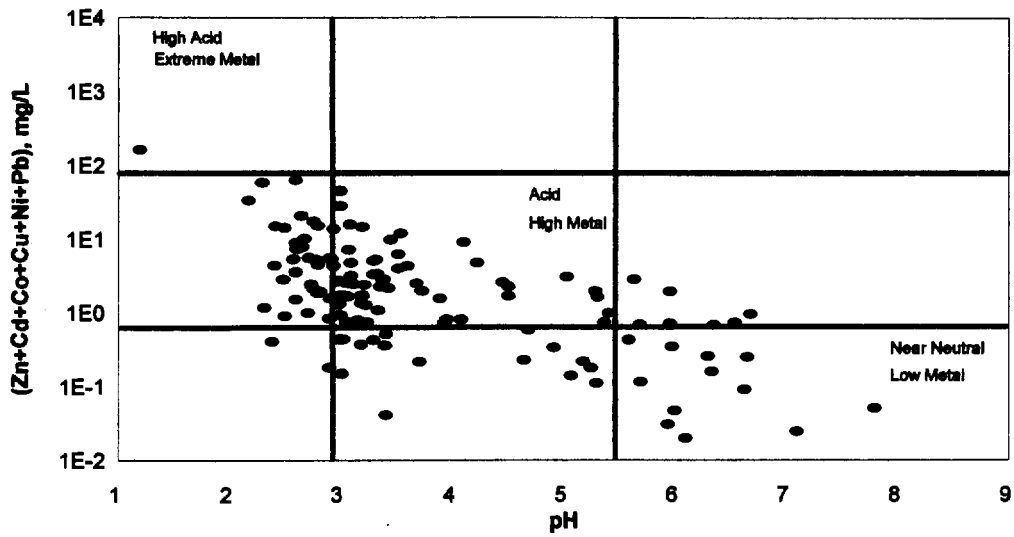


Figure 1. Ficklin plot of CMD data.

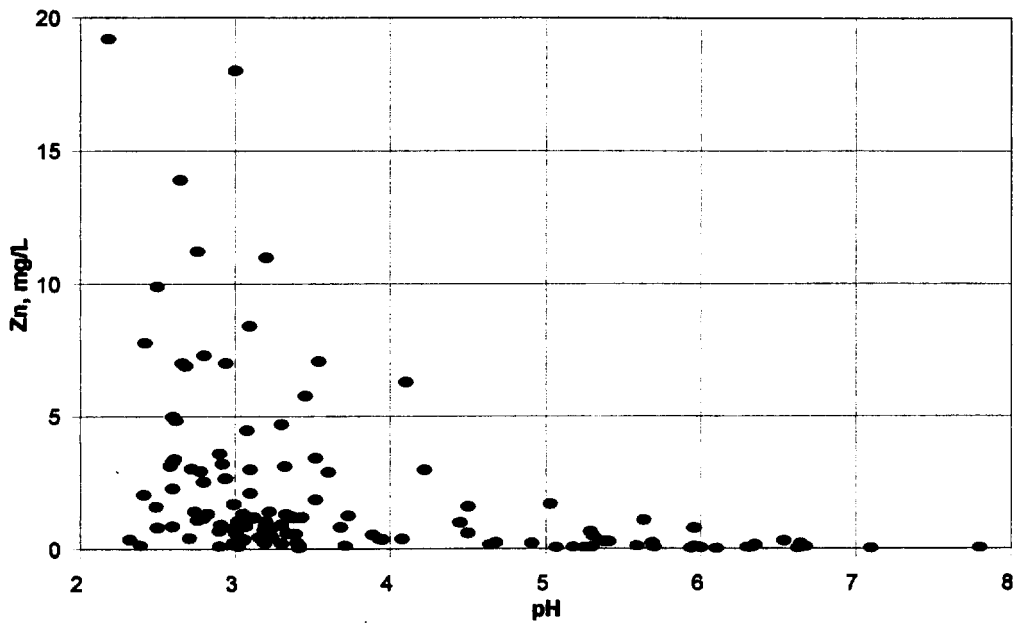


Figure 2. Total zinc concentration vs. pH.

Zinc is generally the most dominant metal in the sum of base metals used in a Ficklin plot for CMD. Its aquatic life criteria is hardness dependent and is just under 1 mg/L. Figure 2 shows that zinc can occur in toxic concentrations up to about a pH value of 6 in the study data set.

The occurrence of aluminum as a function of pH is shown in Figure 3. The concentrations found in this report's data set range up to about 1.3 g/L. Figure 3 presents a subset of this data with values up to about 900 mg/L down to pH values of about 3. Above a pH value of about 3, concentrations drop off markedly up to a pH value of about 4.5, where they are less than 1 mg/L. This implies that CMD below a pH value of 4.5 are likely to contain concentrations of aluminum that are above aquatic life criteria.

The data indicate that copper can occur at concentrations that are above aquatic life criteria at pH values below about 4 (Figure 4). While aquatic life criteria for copper are hardness dependent, the majority of samples with pH values below about 4 were above 0.1 mg/L, significantly greater than the criteria even for hard waters. The implication of this data is that copper must be considered for mitigation.

Figure 5 shows the occurrence of nickel as a function of pH. It shows a maximum concentration of 10 and a decrease to the 1 mg/l value at pH values up to about 7. Aquatic life criteria are variable, but are about 0.1 mg/L depending on water hardness. Nickel presents a similar toxicity problem as copper.

Cadmium was rarely found in CMD (Figure 6) in concentrations above detectable levels. However, cadmium is extremely toxic and some of the aquatic life criteria are below the detectable limits of the analyses. Therefore, cadmium can be a potentially toxic element in CMD, but more sensitive analyses are needed to determine this.

Figure 7 shows ferrous and ferric iron concentrations versus pH. Ferric iron is much less soluble than ferrous iron as pH rises above about 3. Iron does not have an established aquatic life criteria, but does form a significant precipitate that not only "blankets" benthic environments, but can also sorb, and subsequently desorb, significant toxic metals (Ficklin et al. 1992).

Manganese is present in variable concentrations in CMD and shows a general decrease

as a function of increasing pH. Unlike most other CMD metals concentrations, which significantly decrease to relatively low levels within the typical CMD pH range (3-7), manganese shows wide variation in concentration over this range. This is because its solubility is not significantly limited within this pH range. It can occur at concentrations above NPDES effluent levels up to pH values of at least 7 as shown in Figure 8. Figure 9 is an example of a bivariate plot of the sum of the concentrations of a sum of base metals (as in the Ficklin plot) versus manganese. This graph does not illustrate a particularly strong correlation between the "occurrence" of base metals and manganese concentrations. While manganese has no significant aquatic life criteria established, it is used as a "treatment" surrogate for a number of toxic metals. The theory behind this surrogacy is that the achieving of sufficient oxidizing conditions and elevated pH levels to precipitate manganese will also precipitate those toxic metals. Unfortunately, those treatment conditions may not be needed to be achieved to meet aquatic life criteria for toxic metals, assuming they are present in CMD. This resultant over-treatment to remove manganese may not only represent an unnecessary treatment expense, but an environmental problem if the effluents are not pH-adjusted down to the normal 6.5-9.0 range. The context of reclamation treatment may not warrant the removal of manganese itself, allowing the reclamation efforts and resources to focus on the actual toxic metals.

While many of the toxic metal concentrations were a function of pH, figure 10 shows that hardness did not correlate well with pH. Therefore, at low pH, where the toxic metal concentrations are highest, hardness concentrations may not always be high enough to protect aquatic life.

Summary and Conclusions

A study based on water quality analyses of 128 coal mine drainages has shown that toxic metals occur in these drainages. Their occurrences in CMD display a striking similarity to some metal mine drainages from Colorado. These metals can occur in concentrations that are significantly above aquatic life criteria as well as NPDES effluent standards. The study shows that the CMD water quality "spectrum" is quite wide. Despite this variation, most metals as well as the metal-dependant acidity value, show decreasing concentrations as a function of pH increase. Other water quality parameters such as specific conductance

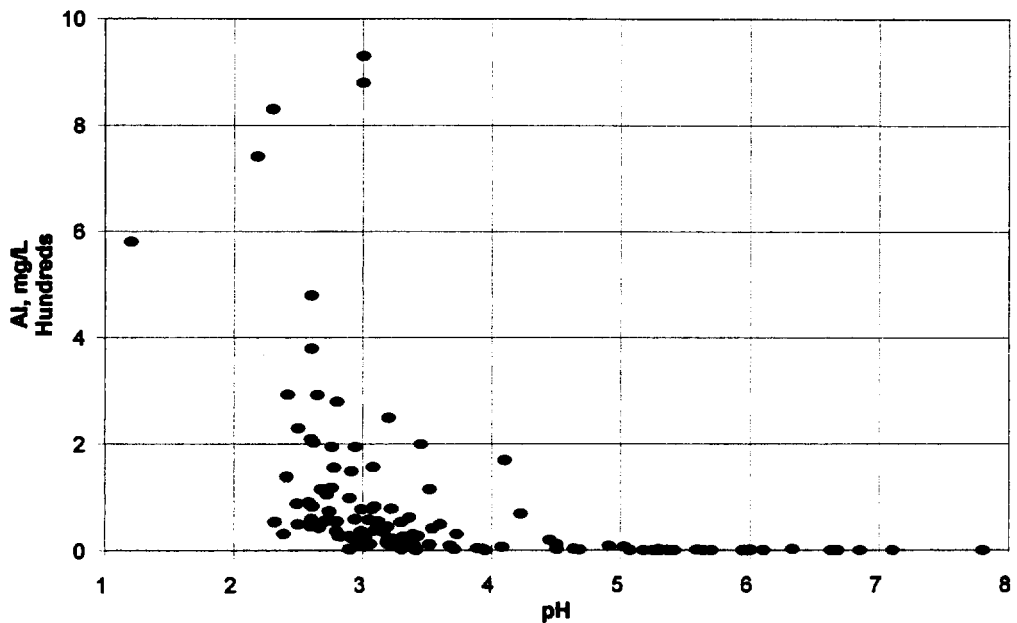


Figure 3. Total aluminum concentration vs. pH.

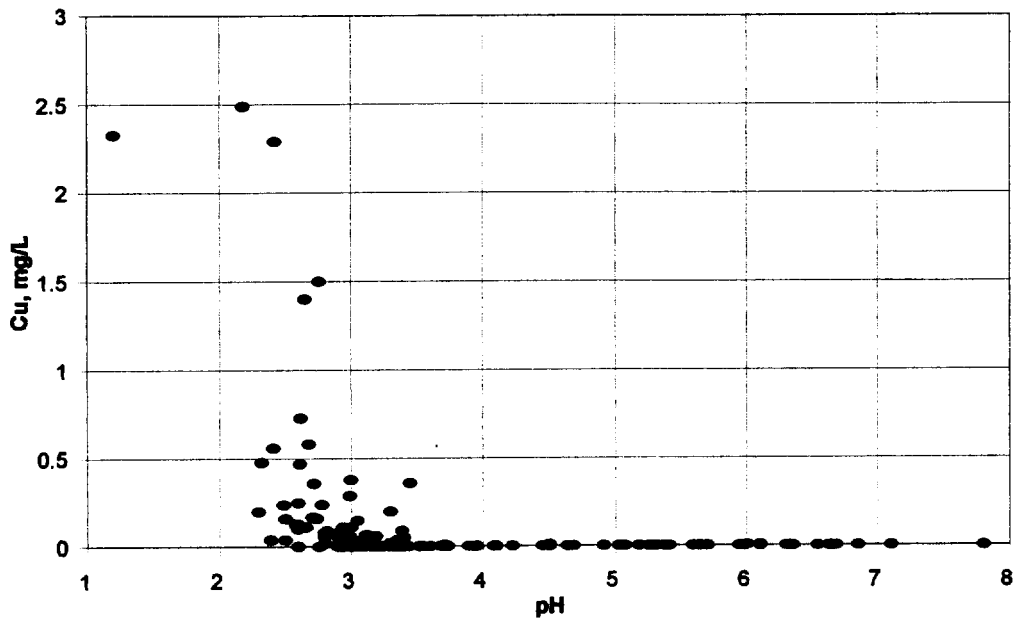


Figure 4. Total copper concentration vs. pH.

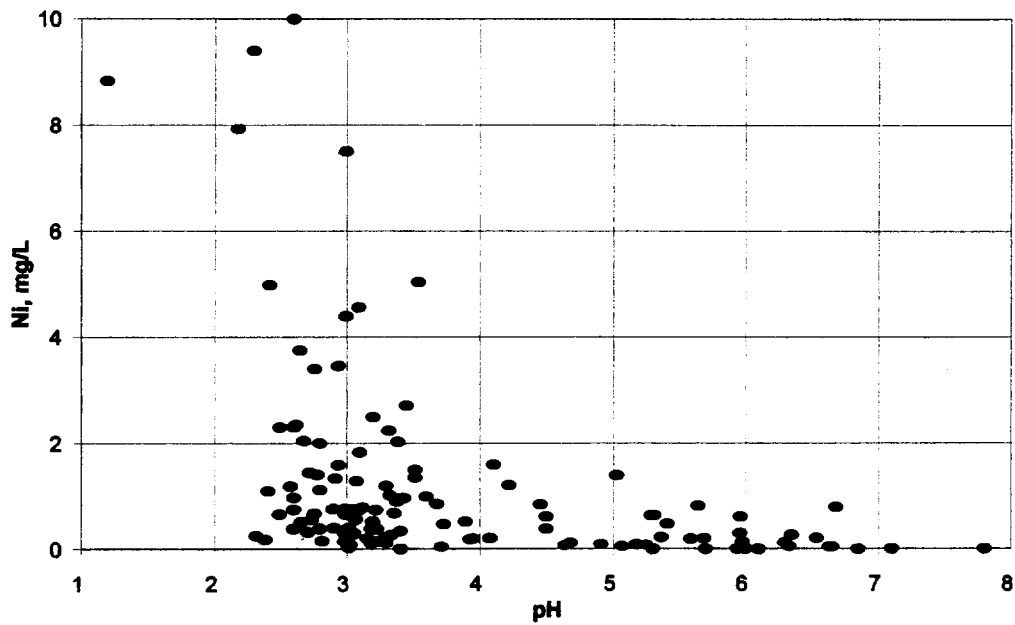


Figure 5. Total nickel concentration vs. pH.

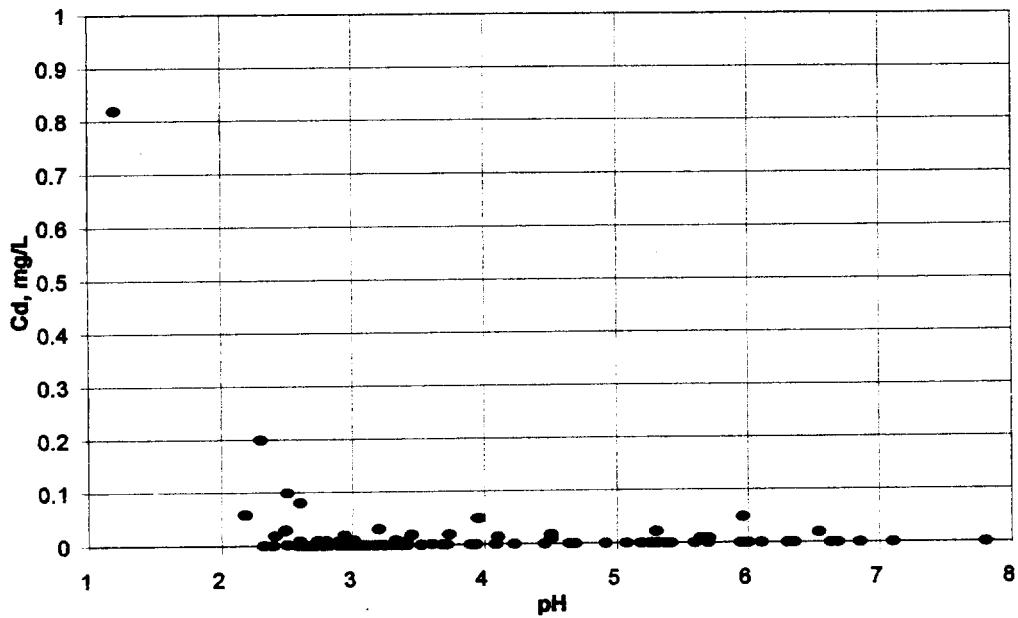


Figure 6. Total cadmium concentration vs. pH.

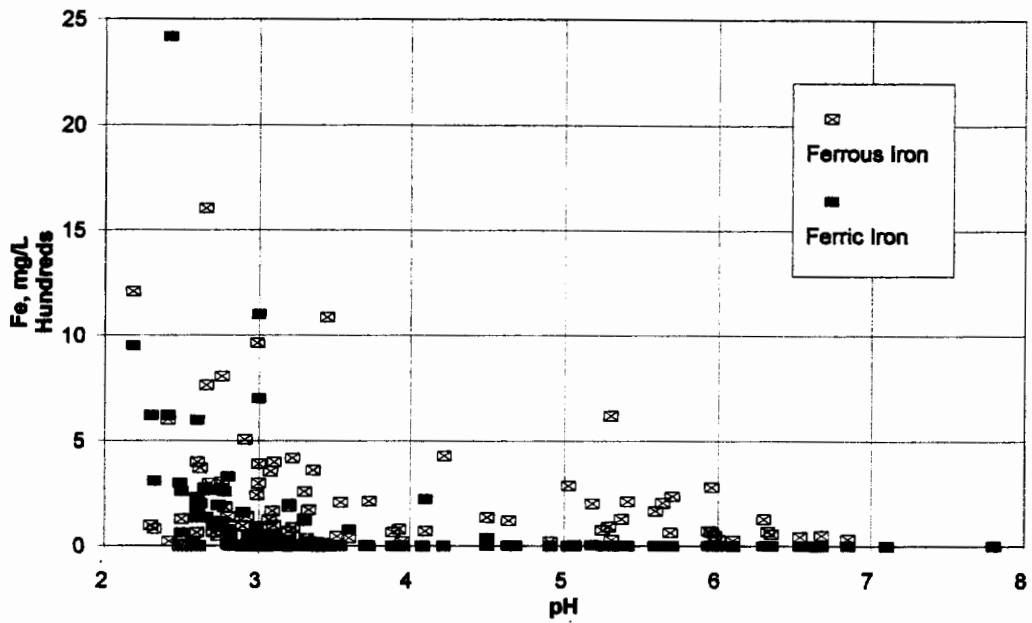


Figure 7. Iron species vs. pH.

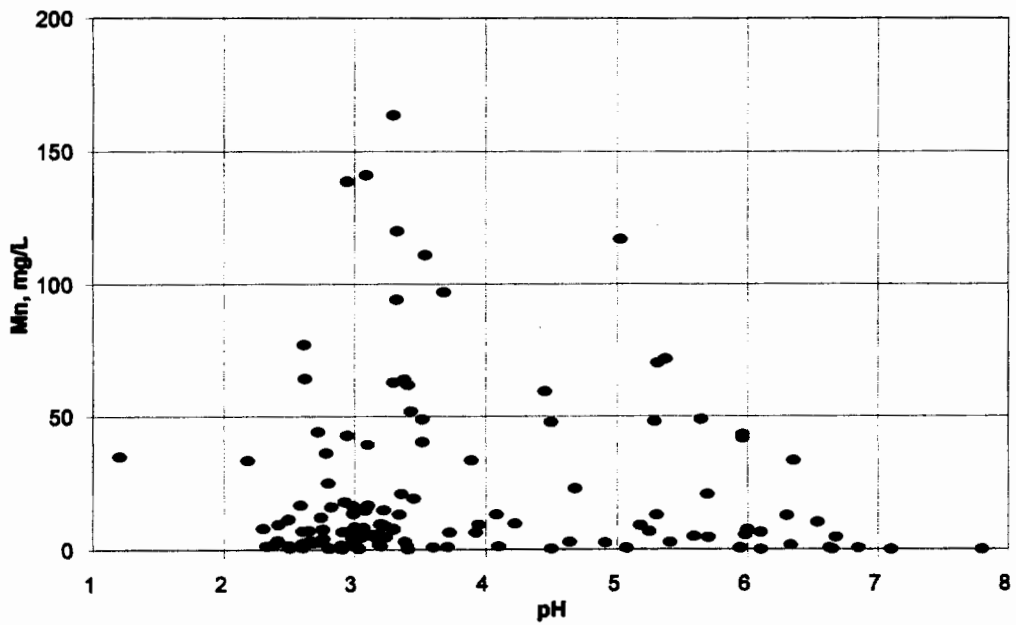


Figure 8. Total manganese concentration vs. pH.

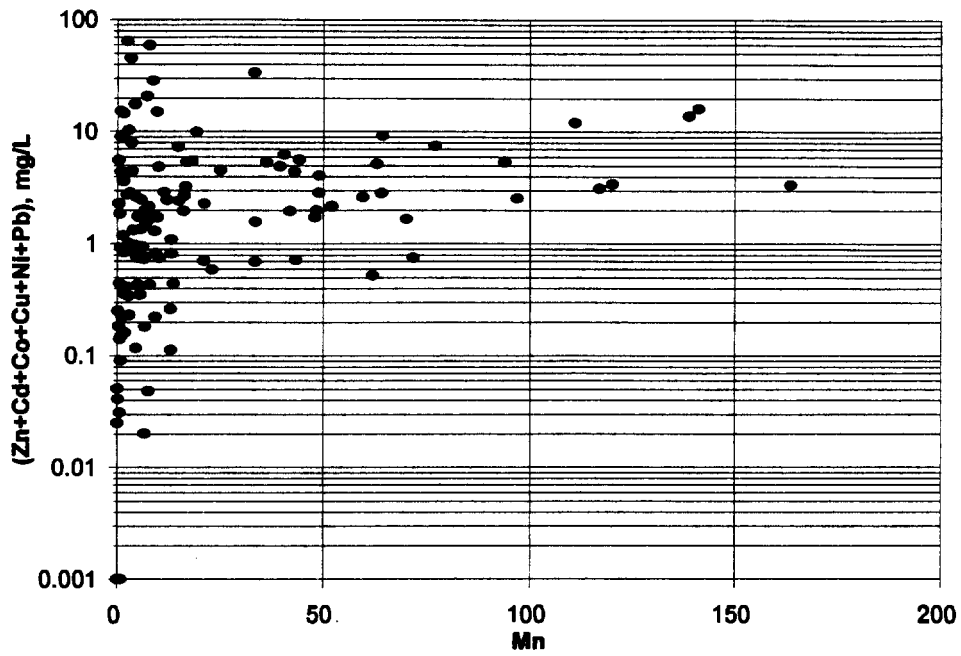


Figure 9. Sum of base metals vs. total manganese concentrations.

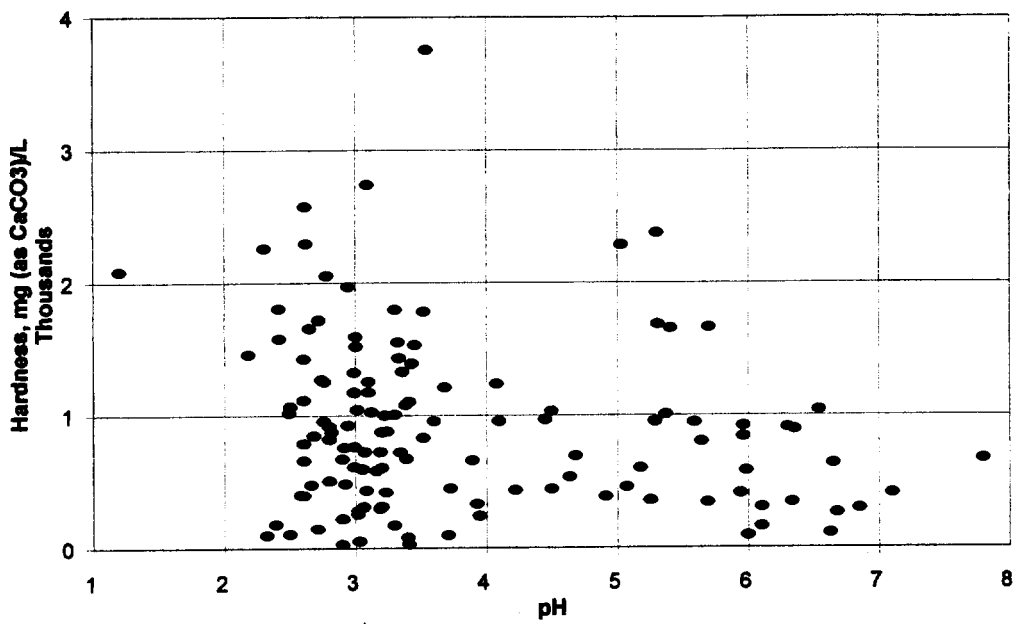


Figure 10. Hardness vs. pH.

and hardness do not show such a relationship.

Despite the generally high hardness values for CMD, toxic metals can often exceed hardness-dependent aquatic life criteria. The high hardness values found in CMD may also inhibit the neutralizing effectiveness of limestone in some limestone-based passive treatment systems, such as anoxic limestone drains and in-stream dosers.

The data indicate that mine drainage treatment challenges to AML reclamation efforts should include a full characterization of the water quality of contaminated mine drainages. Analyses should move beyond the "traditional" CMD contaminants to consider toxic metals and hardness in developing the chemistry behind the reclamation plan for a site. This means that AML reclamation strategies that seek to mitigate adverse environmental impacts to aquatic life need to specifically consider the various individual toxic metals that may be present in the CMD to be remediated, not just the "traditional" CMD components of acidity-generating metals iron, aluminum, and manganese as well as pH.

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