GEOCHEMICAL CHARACTERIZATION OF MINE DRAINAGE SOURCES IN THE CHALK CREEK DISTRICT, COLORADO[1]

Mary E. Lanphear, Ronald W. Klusman, Ronald R.H. Cohen[2]

Abstract: High concentrations of zinc, manganese, cadmium, and other metals have been measured in waters throughout the Chalk Creek district since 1985, when contaminated spring runoff resulted in a substantial loss of trout fingerlings within Chalk Creek and the Chalk Creek hatchery. Chalk Creek is located in Central Colorado within a region of several abandoned mining districts. Initially, the treatment of mine drainage discharged from the Golf Tunnel adit was considered to be the primary remediation action required at the site. The hypothesized bedrock fractures within the floor of the Golf Tunnel as well as contaminated water at several monitoring wells indicate that ground-water flow paths are present within the system and serve to transport metals. These findings hold significant implications for remediation, which may need to be expanded into the treatment of contaminated ground water and tailings seepage. In this study, geochemical modeling was used to attempt to locate subsurface flow paths and characterize the weathering processes generating contamination. It was found that the availability of site chemistry, mineralogy, and hydrology assisted in confirming predictions from the modeling of geochemical processes. Therefore, geochemical modeling data will ultimately assist in appropriate remediation decisions.

Additional Key Words: Zinc, Manganese, Geochemical Modeling.

Introduction

Site Location and Geology

The Chalk Creek mining district is located in the Sawatch Mountains of Colorado at an elevation of approximately 3048 m (10,000 ft.) to 3658 m (12,000 ft.). In 1985, heavy metal contamination to Chalk Creek was attributed to the abandoned mining activities of the Mary Murphy and Iron Chest Mines (Science Applications International Corporation, 1993). The Golf Tunnel adit is located approximately 53 m (175 ft.) upslope from Chalk Creek and serves as the main drainage mechanism for upper mine levels of the Mary Murphy and Iron Chest Mines (see Figure 1). The water discharged from the adit is high in zinc and manganese, but the pH is near-neutral (SAIC, 1993). Discharge from the Golf Tunnel is currently estimated to be from 3.8 L/s to 4.4 L/s (60 gal/min to 70 gal/min) (SAIC, 1993).

Roughly 75% of the ore obtained from the district was from the Mary Murphy mine. The ore consisted of gold, lead, zinc, silver and some copper. Most of the ore was mined from pyritic veins in the Mount Princeton quartz monzonite, which is the dominant intrusive body of the region. The pyritic quartz veins primarily are made up of galena, sphalerite, and some chalcopyrite. Local occurrences of calcite, rhodonite, rhodochrosite, barite, and fluorite have also been observed (Dings and Robinson, 1957).

The remediation of the Chalk Creek site falls under the jurisdiction of the United States Environmental Protection Agency (USEPA) through Section 319 of the Clean Water Act, which deals with nonpoint pollution sources. Chalk Creek was specifically selected for the nonpoint source program, due to its flow into the

[2]Mary E. Lanphear is a Masters degree candidate, Division of Environmental Science and Engineering, Ronald W. Klusman is a Professor, Department of Chemistry and Geochemistry, and Ronald R.H. Cohen is an Associate Professor, Division of Environmental Science and Engineering, Colorado School of Mines, Golden, CO, 80401.

Arkansas River drainage basin. In 1993, the Colorado School of Mines (CSM) was brought into the project. The CSM role was to conduct a geochemical investigation of the processes controlling the observed site chemistry, which would serve to contribute to the current knowledge and understanding of the generation and remediation of mine drainage.

Initial Site Remediation

The Region VIII Groundwater Branch of the USEPA has been sampling ground and surface waters in the Chalk Creek region since 1990. The EPA conducts seasonal sampling of a number of surface waters, seeps, and ground-water monitoring wells which have been installed throughout the area. The locations of relevant sampling areas can be seen in Figure 1.
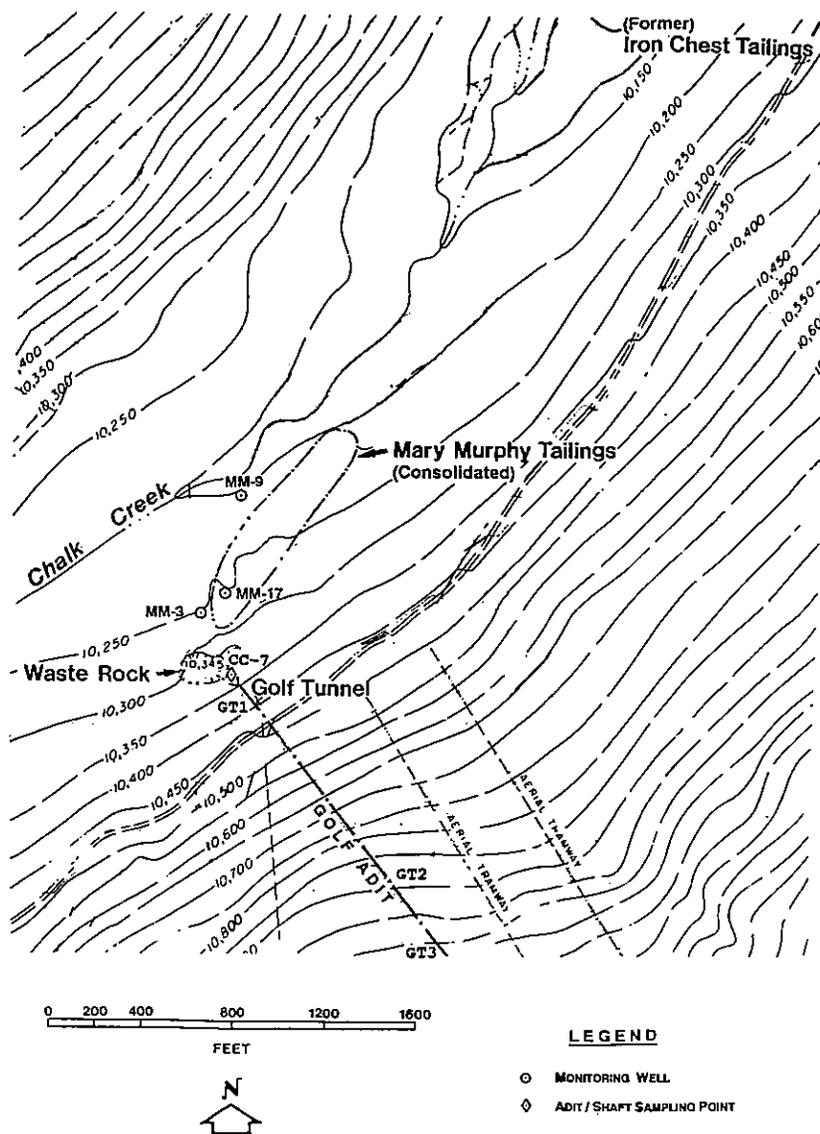

Figure 1: Site Location Including Ground-Water Monitoring Wells and Surface Sampling Points.

Prior to the fall of 1991, one of the major causes of contamination appeared to be the surface erosion and weathering of mine tailings (SAIC, 1993). Therefore, initial remediation at the site consisted of consolidation and stabilization of the waste rock and tails, with diversion of the Golf Tunnel drainage around the new consolidated tailings pile. The diversion of the Golf Tunnel drainage was first into a lined settling pond,

then through an area of reconstructed and natural wetlands, before dispersed entry into Chalk Creek.

Before the onset of the consolidation activities, the Golf Tunnel had been plugged with earth fill. The adit environment was most likely micro-aerobic or even anaerobic. Part of the consolidation project consisted of opening the Golf Tunnel, which created an aerobic environment. In June 1994 the wind was strong within the tunnel, blowing out of the adit. The reverse flow is suspected to take place in the winter (Orville Kiehn, personal communication). This suggests open connections with upper levels of the Mary Murphy mine and with the surface high on Chrysolite Mountain.

Inverse Geochemical Modeling

The first step in retrospective modeling was the use of NETPATH (Plummer et al., 1991), a program that uses an initial and final water composition to predict the mineral precipitation and dissolution along a given flow path. NETPATH does not include some metals normally found in trace concentrations, such as zinc, into its data base. Zinc is a major contributor to the water contamination at Chalk Creek. Therefore, the use of NETPATH was not as productive as anticipated. However, NETPATH still can serve as a preliminary indication of the chemical processes along a flow path, guiding the modeler's decisions concerning dissolution and precipitation of minerals. Without the use of the NETPATH results as a guide, the construction of more complex geochemical models would be inherently more difficult.

The subsequent modeling incorporating trace elements and particular flow paths within the Chalk Creek system was performed using the computer program MINTEQAK (Klusman et al., 1993), which is an altered version of MINTEQA2 (Allison et al., 1990) that is designed specifically for mine drainage scenarios. Like NETPATH, MINTEQAK predicts the processes taking place between two locations on a specific flow path using geochemical modeling. MINTEQAK is used to follow NETPATH modeling because all trace metals measured at the site can be incorporated into the model.

Methods

Golf Tunnel Precipitates

The walls and floor of the Golf Tunnel adit are coated with orange, black, and white sludges up to the level of the former high water mark. In August 1994 three sludge cores were obtained from the adit floor and sectioned based on color. Sludge samples were also obtained from the walls of the adit. The samples were analyzed by x-ray diffraction to determine sludge composition.

Golf Tunnel Aqueous Composition

Prior to the Colorado School of Mines (CSM) involvement in the project, a detailed characterization of the aqueous composition within the Golf Tunnel had not been performed. During June 1994 a series of three aqueous samples from within the Golf Tunnel were obtained by the CSM team. The chosen sampling locations represented conditions within the raise room (GT3), at the portal (GT1), and an incoming seep emanating from the roof and side walls (GT2), between the two previously mentioned sampling points. The approximate locations of the Golf Tunnel sampling points are shown in Figure 1.

Geochemical Modeling Requirements

In order to better understand the possible chemical fate and transport processes taking place at the site, the use of geochemical modeling was implemented. Inverse geochemical modeling is most appropriate for this system and available data. The purpose of inverse modeling is to define net mass transfer within a system. Requirements for this modeling include: 1) known water chemistry along a given flow path 2) mineralogy of

a volume of rock interacting with the aqueous phase and 3) hydrology (Plummer, 1994). The water chemistry at the Chalk Creek site has been well documented since 1990 (SAIC, 1993). The mineralogy of the area is known to a limited extent based on field observations and an investigation conducted by the United States Geological Survey (Dings and Robinson, 1957). The working hydrologic conceptual model is one of fracture flow in crystalline work and has been partially verified by tracer tests.

The previous mineralogy studies performed for the Chalk Creek region were based only on mineral identification as opposed to a quantitative analysis of mineral compositions. The primary unknowns in the mineralogy were the actual compositions of the plagioclase and hornblende, which contribute to the major ion composition of the waters. To better understand the site mineralogy, compositions of the host rock were analyzed using electron microprobe analysis. The results of the analysis showed the plagioclase composition to be $(Ca_{0.36},Na_{0.64})Al_{1.36}Si_{2.64}O_8$ and hornblende composition to be $Ca_2(Mg_{3.04},Fe_{0.96})Al_2(Si_8O_{22})(OH)_2$. These compositions were entered into the geochemical data base, so that the modeling would reflect the compositions of the easily weathered minerals in the quartz monzonite.

The geochemical process method alone can help reject certain hypotheses about flow paths. The method can offer support for the feasibility of some flow paths, but cannot demonstrate conclusively that those flow paths exist. Hydrologic tracer studies can be useful in confirming the predictions from the geochemical process modeling. Preliminary tracer studies were performed in August 1994 by the Bureau of Mines to develop an understanding of the possible hydrologic connections between the MM3, MM17, and MM9 ground-water monitoring wells (Nadia Miller, USBM; personal communication). The tracer used was NaCl. The tracer was injected into well MM3, and conductivity changes were monitored at the MM9 and MM17 bedrock wells (locations are given in Table 1). A similar tracer study was performed in October 1994 using NaBr. This tracer was also injected into well MM3 and conductivity changes were monitored at MM17 and MM9.

Formulation of NETPATH Modeling Problem

The NETPATH model formulation uses a composite rainfall water chemistry based on data obtained from Wolf Creek Pass, CO, as the initial water falling onto the surface of Chrysolite Mountain (National Atmospheric Deposition Program, 1994). Wolf Creek Pass is roughly 160 km from the study area in the direction of prevailing winds and at a similar altitude, so data obtained from this location should be representative of the conditions at Chalk Creek. Data from the GT3 sampling point, or raise room, represents the final water composition. The specific minerals allowed to dissolve and/or precipitate are given in Tables 2 and 3 of the results and discussion section.

Formulation of MINTEQAK Modeling Problem

The formulation of the Golf Tunnel models before and after re-opening the adit used the composite rainfall composition as the initial water feeding the system, and the CC-7 sampling point as the final water composition. CC-7 is located at the Golf Tunnel portal. Two separate models were run using these initial and final points with data obtained in 1991 and 1993. Both sets of data modeled were collected in June for means of comparison of model output.

The Golf Tunnel was also modeled between the GT3 and GT1 sampling points mentioned above as a control experiment because their flow path connection is easily observable. GT3 was used as the initial water composition and GT1 represented the final composition. The bedrock wells of MM17 and MM9 were likewise modeled with each, respectively, representing initial and final waters.

All of the models run with MINTEQAK, allowed kaolinite, ferrihydrite, smithsonite, rhodochrosite, manganite, $Al(OH)_3$, chalcedony and calcite to precipitate if supersaturation should occur. Element concentrations, pH, and pE were entered into the input file, while the partial pressure of carbon dioxide was excluded. The exclusion of CO_2 prevents atmospheric interaction of aqueous carbon dioxide with the system.

It is not expected that atmospheric CO_2 would come in contact with the water as it passes through bedrock. Additionally, trial models constructed and run with CO_2 included in the input file predicted inaccurate aqueous compositions.

Results and Discussion

Modeling of Golf Tunnel Aqueous Composition Before and After Opening

The Golf Tunnel drainage flow path was modeled using the data of June 1991 and then June 1993 to determine how conditions at the site changed as a result of the Golf Tunnel opening. The modeling indicates that in June 1991, there seemed to be very little precipitation of secondary minerals within the tunnel. The amount of precipitation increased once the drainage was external to the Golf Tunnel adit. The opening and subsequent oxygenation of the Golf Tunnel led to a drastic increase in the mineral precipitation within the tunnel. A consequence was that precipitation decreased in external areas downslope of the adit. Therefore, the major result of the tunnel opening, shown by the geochemical modeling, was a shift in the location of the majority of mineral precipitation from downslope of the Golf Tunnel before opening, to within the Golf Tunnel itself after the opening.

Inspection and sample analysis of sludges obtained within the Golf Tunnel in August 1994 confirms the current degree of precipitation within the adit. Analysis by x-ray diffraction was performed on each of the colored sludges obtained from the adit walls and floor. The XRD analysis indicated that the white material on the adit walls and floor was primarily kaolinite. The orange and black material were ferrihydrite and possibly manganite, respectively. The sludges obtained from the adit floor additionally contained gypsum, quartz, calcite, and chlorite.

Cause of near-neutral pH

X-ray diffraction (XRD) analyses provided insights into the cause of the circum-neutral pH. Past sampling has shown that the pH of waters obtained from the Mount Chrysolite area, upslope from the area of investigation, are in the range of pH 3.5 (SAIC, 1993). Therefore, some neutralization processes must be taking place in the subsurface to result in the pH readings of 6.5-8.0 measured in the Golf Tunnel and surrounding ground-water monitoring wells.

Calcite and rhodochrosite, present in the area of the mine complex, are suspected to be the source of the neutralization. Only a small amount of these minerals, roughly 1% calcite, is necessary to neutralize acid mine drainage (Mast and Drever, 1990) originating on Chrysolite Mountain if the flow paths opened by mining contain these minerals. The XRD studies, as well as field tests, confirm the presence of calcite in the Golf Tunnel. Therefore, the predominant neutralization mechanism consists of the flow of acidic mine drainage through carbonate-containing materials, thus reaching the Golf Tunnel with a near-neutral pH.

Characterization of the Golf Tunnel Drainage

Analysis of the aqueous samples obtained within the Golf Tunnel gave the dissolved concentrations and field parameters shown in Table 1. The sampling locations represented the raise room (GT3), incoming seep (GT2), and Golf Tunnel portal (GT1).

Table 1: June 1994 Water Quality within the Golf Tunnel Adit.

Parameter	GT3	GT2	GT1
Eh (mV)	855	875	885
pH	6.05	7.00	6.37
Zn (mg/L)	157	0.50	68.1
Mn (mg/L)	131	0.05	56.8
Cd (mg/L)	0.86	<0.005	0.39
Cu (mg/L)	1.16	<0.01	0.26
Al (mg/L)	5.00	<0.10	0.30
Fe (mg/L)	<0.10	<0.10	0.10
SO$_4$ (mg/L)	1262	60.5	541
Cl (mg/L)	20.0	<0.50	<0.50
Na (mg/L)	5.00	2.20	3.40
Mg (mg/L)	38.4	1.50	18.4
Ca (mg/L)	214	34.5	125
Alkalinity (mg/L)	10.0	51.0	33.0

The June 1994 water quality data shows that the highest concentrations of contaminants are located at GT3, upstream of a major incoming seep, which is at GT2. The GT2 fracture source water contains very low concentrations of the ions listed in Table 1. A comparison of the GT3 versus GT1 compositions shows that the water quality at the Golf Tunnel portal is considerably better than that of the raise room. These data indicate that either metal precipitation is taking place between the GT3 and GT1 sampling points, and/or dilution from the seep at GT2 is reducing metal concentrations.

The apparent dilution capacity of the seep holds significant implications for remediation. A bioreactor or other passive system treating the Golf Tunnel discharge at the portal would result in the treatment of a larger volume of water than necessary - the combined flows of the contaminated drainage and the clean seep water. Treatment upstream of the seep would only treat the contaminated water. A method of tapping the water coming from the seep, thereby bypassing treatment, would be beneficial by reducing the size of the treatment unit.

Weathering Processes Contributing to Golf Tunnel Drainage

The following NETPATH output tables (Table 2 & 3) show two possible models of the weathering processes taking place between the surface and the stopes drained by the Golf Tunnel after the adit was unplugged. The pluses and minuses in the second column of each table refer to minerals that are dissolving and/or precipitating, respectively. The third column lists minerals that were either forced to be included into the model calculations, or were optional species (unforced). The last column gives the calculated amount of each mineral that must precipitate or dissolve in order to maintain mass and charge balance.

Table 2: NETPATH Model #1 of Predicted Initial Weathering Processes

Mineral	Dissolved / Precipitated	Forced / Unforced	Amount (mg/L)
rhodochrosite	dissolved (+)	forced	2.39
plagioclase	dissolved (+)	forced	0.36
pyrite	dissolved (+)	forced	6.58
goethite	precipitated (-)	forced	-7.07
CO_2 (g)	dissolved/precipitated (+/-)	unforced	-6.03*
SiO_2	dissolved/precipitated (+/-)	unforced	-3.04
calcite	dissolved (+)	unforced	4.16
kaolinite	precipitated (-)	unforced	-0.68
hornblende	dissolved (+)	unforced	1.04

*Expelled to the atmosphere

Table 3: NETPATH Model #2 of Predicted Initial Weathering Processes

Mineral	Dissolved / Precipitated	Forced / Unforced	Amount (mg/L)
rhodochrosite	dissolved (+)	forced	2.39
plagioclase	dissolved (+)	forced	0.36
pyrite	dissolved (+)	forced	6.58
goethite	precipitated (-)	forced	-7.07
gibbsite	precipitated (-)	unforced	-1.35
CO_2 (g)	dissolved/precipitated (+/-)	unforced	-6.03*
SiO_2	dissolved/precipitated (+/-)	unforced	-4.40
calcite	dissolved (+)	unforced	4.16
hornblende	dissolved (+)	unforced	1.04

*Expelled to the atmosphere

Modeling of Flow Paths Using MINTEQAK

The following models performed with MINTEQAK, are based on data obtained in June 1994. The first model discussed represents a known hydrologic flow path, while the second model is for a suspected connection. The suspected connection is the result of the downgradient position of the two sampling locations to each other. These two varying situations will serve to illustrate the type of information that can be obtained through the use of geochemical modeling.

The modeling of the known hydrologic flowpath was performed using two sampling points within the Golf Tunnel (GT3 and GT1). The aqueous compositions, and Eh and pH values at GT3 and GT1 were given in Table 1. Tables 4 and 5 show the hypothesized precipitation processes occurring between the GT3 and GT1 sampling locations and measured and predicted chemical compositions.

Table 4: Precipitation Processes Occurring Between GT3 and GT1 Sampling Points as Predicted by MINTEQAK.

Mineral Species	Amount of Precipitated solid (mg/L)	Saturation Index
kaolinite	13	0.0
ferrihydrite	0.1	0.0
smithsonite	0.0	-3.1
rhodochrosite	0.0	-1.8
manganite	1.6×10^{-6}	0.0
$Al(OH)_3$ (am)	0.0	-13
chalcedony	0.0	-16
calcite	0.0	-3.9

Table 5: Actual and Predicted Chemical Compositions of GT3 and GT1 Waters as Modeled by MINTEQAK.

Parameter	GT3 Aqueous Composition (mg/L)	GT1 Predicted Aqueous Composition (mg/L)	GT1 Actual Composition (mg/L)
CO_3^{-2}	0.16	0.54	0.54
Ca^{+2}	214	125	125
Cd^{+2}	0.86	0.40	0.39
Zn^{+2}	157	68.4	68.1
Fe^{+2}	0.06	0.11	0.10
Mn^{+2}	131	56.0	56.8
SO_4^{-2}	1262	543	541

Initial examination of the model output appears to present some inconsistencies. For example, the calcium, zinc, manganese, and sulfate concentrations decrease between GT3 and GT1 while little to no solid zinc, manganese, and sulfate containing phases form. Given the presence of the incoming seep at GT2 between GT3 and GT1, it is apparent that dilution is occurring. The dilution effect is illustrated in Figure 2.
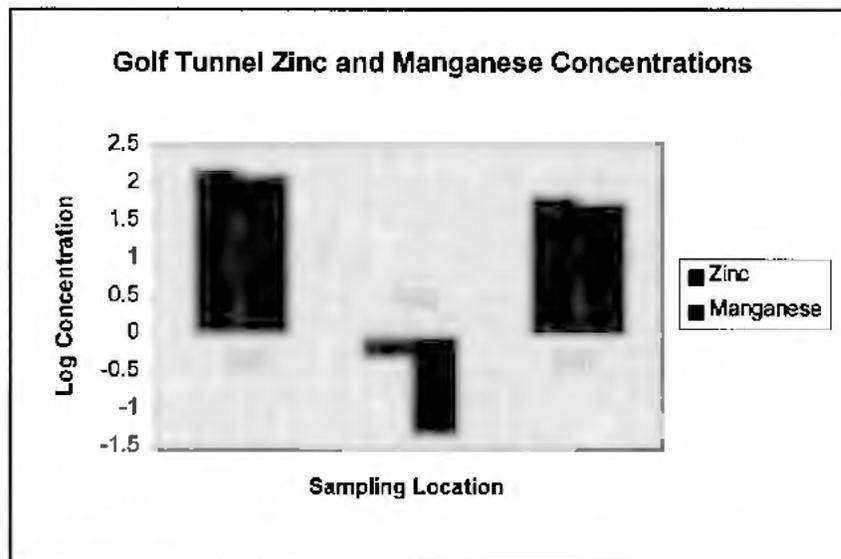
Figure 2: Effect of GT2 dilution on Golf Tunnel Water Composition.

The other problem is that the concentration of iron in the system is increasing, yet solid $Fe(OH)_3$ is predicted to be removed. Given the minor difference in iron concentrations between GT3 and GT1, it was presumed that this discrepancy falls within analytical and sampling error, and can thus be discounted.

The model constructed between locations along the suspected flowpath used the MM17 and MM9 ground-water wells as respective initial and final water compositions. The water at MM17 has a pH of 7.92 and an Eh of 166 mV, while the water at MM9 has a pH of 5.93 and Eh of 282 mV. Therefore, the presumption of these points being connected require a source of acidity to the system, and to a lesser extent, some means of oxidation. Tables 6 and 7 give the precipitation and aqueous chemical changes between the two points using data obtained in June 1994.

Table 6: Precipitation Processes Occurring Between MM17 and MM9 Sampling Points as Predicted by MINTEQAK.

Mineral Species	Amount of Precipitated Solid (mg/L)	Saturation Index
kaolinite	5.0×10^{-1}	0.0
ferrihydrite	0.0	-4.1
smithsonite	0.0	-3.7
rhodochrosite	0.0	-5.6
manganite	1.6×10^{-6}	0.0
$Al(OH)_3$ (am)	0.0	-3.3
chalcedony	0.0	-0.5
calcite	0.0	-4.6

Table 7: Actual and Predicted Chemical Compositions of MM17 and MM9 Waters as Modeled by MINTEQAK.

Parameter	MM17 Aqueous Composition (mg/L)	MM9 Predicted Aqueous Composition (mg/L)	MM9 Actual Composition (mg/L)
CO_3^{-2}	1.42	0.27	0.27
Ca^{+2}	103	226	226
Cd^{+2}	0.00	0.27	0.27
Zn^{+2}	0.03	115	115
Fe^{+2}	0.01	0.01	0.01
Mn^{+2}	0.32	0.07	0.07
SO_4^{-2}	183	155	155

Analysis of this model shows that from MM17 to MM9, calcium and zinc concentrations increase by a significant amount. Looking at the mineral species, the increase in zinc is not possible unless a new zinc phase dissolves. Likewise, calcium increases while both carbonate and sulfate are decreasing, indicating that the formation of a calcium carbonate or calcium sulfate phase is also not reasonable.

The only conclusion that subsequently can be drawn from the modeling alone is that the MM17 and MM9 wells are not hydrologically connected, or if they are connected there must be a new source of high Zn and Ca water to MM9 allowing for the observed changes in compositions. The preliminary tracer studies performed at the site confirmed that a connection between MM9 and MM17 does not exist, since the tracer injected into MM3 appeared at MM9, but not at MM17 which is located between the two previously mentioned wells. (Nadia Miller, USBM; personal communication).

Effectiveness of Modeling

A final note in examining the MINTEQAK model output needs to be made regarding the predicted versus actual compositions of the given endpoints. In both cases, there is very little if any difference in the actual compositions compared to those predicted from the model. It can then be concluded that the minerals used in the weathering and precipitation processes were valid and serve to be the most important phases in the evolution of the actual water composition at a given location.

Summary and Conclusions

The geochemical modeling presented in this research illustrates how the use of two individual modeling techniques can be used to construct an overall picture of the important geochemical processes taking place at a site contaminated by mine drainage. The differences seen in the NETPATH and MINTEQAK models reflects the compositions of the individual data bases used by each program. With the availability of hydrologic data, the modeling can effectively be used to assist in planning remediation activities by providing indications as to the source and locations of flow paths carrying contaminated water. The use of geochemical modeling at a site suspected to represent a variety of subsurface flow paths can lead to the implementation of cost effective treatment techniques for contaminated water, for example by locating uncontaminated flow paths which need little remediation. Geochemical modeling can also aid in the understanding of processes controlling the

contaminant generation and natural attenuation.

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