Geochemical and Hydrologic Assessment of Drainage from Cherry Valley Coal Mine, Ohio

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ABSTRACT

Drainage from abandoned underground coal mines negatively impacts many miles of stream habitat throughout the Appalachian region. The drainage is commonly called acid mine drainage (AMD) due to its low pH; however, not all mine drainage is acidic. The quantity and quality of the water discharged from a coal mine depend upon numerous variables, such as the design of the mine, chemical composition of the coal and surrounding rocks, and local climate. Coal extracted from the now-abandoned Cherry Valley Coal Mine near Leetonia, Ohio, was reached by a slope entry such that the mine is not entirely up-dip, and a significant area is flooded. Recharge water that enters the unsaturated area of the mine mobilizes soluble iron-sulfate salts as it flows down-dip and adds pyrite oxidation products to the mine pool. The bedrock overburden is covered by calcareous glacial till that imparts alkalinity to the shallow groundwater, buffers the acidity, and keeps the pH inside the mine circumneutral. Maintaining a circumneutral pH reduces pyrite oxidation by decreasing the solubility of ferric iron, the primary oxidizing agent of pyrite at low pH, which reduces the positive feedback mechanism that drives pH down and concentration of oxidation products up. Shallow groundwater is brought to the mine via subsidence fractures, which facilitate a rapid increase in discharge from the mine (and dilution of oxidation products) in response to surface runoff events. The loadings of all dissolved ions, except iron, are controlled by the changes in discharge rather than the changes in concentration.

INTRODUCTION

Eastern Ohio is part of the Appalachian Plateau, which extends from northeastern Pennsylvania to Alabama. The Appalachian Plateau is rich in coal deposits, and like Pennsylvania and West Virginia, they were extensively mined in eastern Ohio for more than a hundred years. Many of these mines were operated and abandoned long before passage of the Clean Water Act of 1972 and the Surface Mining Control and Reclamation Act (SMCRA) of 1977, which regulates the environmental effects of coal mining.

During active operations, the underground mines were drained by gravity, or accumulating water was pumped out. After abandonment, the water continues draining via gravity or fills the mine void once the pumping stops. Water then begins discharging at the surface, typically through the old mine entry (e.g., Winters and Capo, 2004). The water that discharges from these abandoned mines is commonly acidic, with high concentrations of dissolved metals and sulfate that are produced from the oxidation of pyrite or leached from other minerals by the acidic water (Singer and Stumm, 1970; Stumm and Morgan, 1981). Mine drainage is referred to as acid mine drainage (AMD). There are over 2,000 km of stream in Ohio that have been impacted by AMD (Ohio Department of Natural Resources, 2013).

The amount of water discharged from old underground mines and its chemical composition are highly

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variable due to a number of different factors related to the local geology and the design of the underground mine. It is also important to understand the temporal and spatial variations in the local hydrology and land cover. The thickness and composition of the overburden play key roles in determining the amount and chemical composition of the recharge water the mine receives. Coal-bearing rock and overlying material composed of limestone or other calcareous rocks have the potential to produce sufficient alkalinity to buffer the acidity produced by oxidation reactions in mines (Capo et al., 2001). Overburden composed primarily of more competent strata (e.g., sandstone and limestone) will undergo brittle deformation and therefore is more prone to fracturing. However, less competent strata (e.g., shale) will undergo ductile deformation and is less prone to fracturing (Whittaker and Reddish, 1989). Therefore, overburden composed primarily of competent strata is more likely to have fractures that can capture surface runoff and allow it to enter the mine. According to case studies of room-and-pillar and longwall mines, the fractured zone produced when the roof of the mine collapses can extend anywhere from 24 to 54 times the thickness of the coal extracted (Singh and Kendorski, 1981).

The design of an underground mine determines whether a mine will flood after it is abandoned. Up-dip mines, where the entry is the lowest point of the mine, have water removed via gravity drainage, while down-dip mines must have their water pumped out. Lambert et al. (2004) characterized 21 mines that had different degrees of flooding in southwestern Pennsylvania in 1974–1975 and again in 1998–2000. Flooded mines had higher average discharge flow rates (>8,000 m³/d) and tended to be alkaline, while un-flooded mines tended to have lower average discharge flow rates (<900 m³/d) and were acidic. After abandoned mines flood, the mine water eventually reaches alkaline conditions with a near-neutral pH. Even partially flooded mines reach a similar condition of near-neutral pH over time. As the duration during which a mine is flooded increases, the dissolved oxygen in the water will decrease and reduce its capacity to complete oxidation reactions in the mine, even though iron may still be available. However, because up-dip mines constantly drain and oxygen can circulate, the water being discharged remains acidic with a low pH.

Changes in seasonal climate and associated weather events play a large role not only in determining the amount of water being discharged from the mine but its chemistry as well. Increased recharge in the fall through the spring can result in flooding of previously dry areas of the mine, and any pyrite oxidation products (e.g., hydrated iron sulfate salts) will be flushed out (Cravotta, 1994). This seasonal effect on the dissolved ion concentrations was called the "spring flush" by Lopez and Stoertz (2001). The degree to which the discharge from a mine increases in response to seasonal recharge is dependent on the depth of the mine, the amount of subsidence fractures, and the amount of runoff available to be captured by the fractures (Lopez and Stoertz, 2001).

The objective of this study was to characterize the discharge from the abandoned Cherry Valley Mine in eastern Ohio and determine the factors that control the quantity and chemical composition of its drainage water. This paper expands upon the studies mentioned previously by investigating the influence of subsidence fractures in the overburden, seasonality, and the presence of calcareous rocks in the overburden that may lead to development of acid mine drainage or more benign net alkaline mine drainage (NAMD).

SITE HISTORY AND DESCRIPTION

The Cherry Valley Mine is located in the glaciated region of eastern Ohio beneath a hill, at the top of which lies the Village of Leetonia (Figure 1). The coal that was mined at Leetonia had low sulfur (low pyrite) content (0.82 weight percent) and therefore was suitable for coking (Orton, 1884). Mining operations started at Leetonia as early as 1865 (Village of Leetonia, 2010). At the mine entry, 205 coke ovens were built in which the coal burned at high temperature to produce coke to fire local blast furnaces that produced iron from local ore deposits (Village of Leetonia, 2010). According to an underground mine map, by the time it closed, the mine entries extended under an area of 2.3 km². The mine, coke ovens, and iron works were all abandoned by the time of the Great Depression, and drainage from the old mine entry has been noted by local people since at least 1950 (Village of Leetonia, 2010). The drainage flows through the coke oven area and down into Cherry Valley Run in the valley below, from which it then flows into the Middle Fork of Little Beaver Creek and on to the Ohio River (Figure 1).

The coal seam mined at the Cherry Valley Mine was the Middle Kittanning (No. 6) seam, which is part of the Middle Pennsylvanian Allegheny Formation (Orton, 1884). The annual Ohio mine inspector’s reports and Ohio Geological Survey reports provide a detailed look into the Cherry Valley Mine when it was in operation (Roy, 1876; Newberry, 1870; and Orton, 1884). The coal seam at the Cherry Valley Mine was reached by means of a sloped entry that was excavated into the hillside. Accordingly, the lower
portions of the mine where the slope entry intercepts the coal seam would likely be flooded, while the up-dip areas would be un-flooded but have water flowing over the mine floor by gravity drainage.

The rooms of coal that were excavated were only the thickness of the coal seam itself (~71 cm). During mining operations, pillars of coal were left every 3 m between the rooms. Once mining was finished, the pillars themselves were removed, a process called “retreat mining,” designed to maximize the amount of coal extracted. The removal of the pillars would also increase the susceptibility of the mine roof to collapse and produce subsidence fractures.

The main slope entry was 3.3 m wide and 1.5 m thick; it reached the coal seam after 30 m. The coal was then mined as the entry traveled west and upward farther into the hill at an angle according to the dip of the seam (<1 degree). The main entry shaft ran west

Figure 1. (A) Regional view of the watershed. (B) Map of the Little Beaver Creek watershed with the three major tributaries shown: West Fork (W), Middle Fork (M), and North Fork (N) of Little Beaver Creek. (C) Areal extent of the Cherry Valley Mine (cross-section A-A’ shown in Figure 4).
for approximately 1.1 km under the hill, with other entries jutting off farther into the hill to the northwest and the southwest (Figure 2). There is also a drain that was dug to the southwest from the main entry. The main entry and the drain intersect before reaching the mine entry at the surface. These two conduits are the most probable sources of the water discharging at the surface; therefore, in 2010, the Ohio Department of Natural Resources (ODNR) drilled a monitoring well into each conduit just before their confluence (Tammy Richards, personal communication, 2011). ODNR drilled two wells at location CV-1, one into the mine drain and another shallower well into the glacial till. A monitoring well was also drilled into the main entry of the mine at location CV-4 (Figure 2).

On the hillside above the mine, a gully developed between the drain and main entry; it channels stormwater runoff from the village down the hillside towards the discharge point (Figure 2). In 1950, a section of Main Street at the end of the gully (and just above the mine discharge point) collapsed, but it was repaired, and the street continues to pass above the discharge area. The gully channels runoff water into a pipe where the street collapsed (Village of Leetonia, 2010). The pipe does not have an outlet on the opposite side of the street. A dye test by Village of Leetonia officials confirmed that the water that enters the pipe under Main Street reappears at the mine’s discharge point after approximately 2 days (Gary Phillips, personal communication, 2011). Based on these observations, we suspect that the fill in the collapsed area beneath Main Street creates a conduit for bringing surface runoff from the gully via the pipe into the mine.

The overburden of the mine has a maximum thickness of 37 m at the top of the hill, but it thins to just 16 m on the hillside near the mine entry. The overburden is composed primarily of sandstone, shale, and glacial till (Figure 3). Above the Middle Kittanning coal, there is the Washingtonville Shale, a layer of iron-rich, marine shale, and beneath the coal,
there is a clay layer (fireclay). Caving of the iron-rich shale roof of the mine could expose pyrite to oxygen, in addition to the pyrite from the mined coal seam. Above the shale is the Lower Freeport Sandstone. Therefore, if the shale roof of the mine collapsed, it is likely that the fractures could propagate through the more competent sandstone. A layer of calcareous glacial till is present on top of the sandstone bedrock (White, 1982). Figure 4 displays a cross section of the hillside.

**METHODS**

Data collection began on May 11, 2011, and continued approximately every 2 weeks until May 20, 2012. The water sampling and in situ measurement methods and equipment employed were similar to those used by the ODNR and Ohio Environmental Protection Agency as outlined below.

**Hydrologic Characterization**

The flow rate of the discharge was measured using a Marsh McBirney Flow-mate 2000 Flow Meter during each visit to the site. The flow rate was measured from a pipe that was installed in the flow path of the mine discharge. A hydrograph of the discharge was produced during the study period. A method developed for analyzing karst spring hydrographs (Padilla et al., 1994) was used to separate the discharge into its quick-flow and base-flow components during the 2011 recession period following Lopez and Stoertz (2001). This method was chosen because karst springs and abandoned underground mines have a similar mechanism for recharge (Pigati and Lopez, 1999). This method only utilizes the recession portion of the hydrograph and is valid when the discharge exhibits an exponential decay from the peak discharge to base-flow. By identifying the beginning of base-flow conditions and extrapolating back to the beginning of the recession, it is possible to calculate the volume of quick-flow and base-flow draining from the mine at the beginning of the recession (Lopez and Stoertz, 2001).

Daily precipitation and maximum surface temperature values were taken from local weather stations that list their data in the National Oceanic and Atmospheric Administration’s (NOAA) National Climatic Data Center (NCDC, http://www.ncdc.noaa.gov/). The station providing precipitation values was Salem 1.0 NNE, located 8.3 km to the northwest. The station providing temperature values was Millport 2 NW, located 15.3 km to the southwest. The potential evapotranspiration (PET) was calculated by the Thornthwaite method using the average daily temperature provided by the weather stations (Thornthwaite, 1948).

**Chemical Characterization**

Physical and chemical parameters, including pH, water temperature, dissolved oxygen, specific conductivity, and redox potential, were measured in situ using a YSI Professional Plus Multi-parameter Probe. The in situ measurements and water samples were taken directly at the discharge point. Water samples were filtered into acid-cleaned bottles in the field using 0.45 μm HTTP filter paper. Cations (Al, Fe, Mn, Na, Ca, Mg, K) were analyzed with an inductively coupled plasma–optical emissions spectrometer (ICP-OES). Anions (Cl, SO$_4$) were analyzed using ion chromatography (IC). The relative difference between duplicate samples analyzed by the IC was <0.5 percent. The samples that were run on the ICP-OES were acidified using trace metal grade nitric acid to preserve the dissolved metal ions. The relative difference between duplicate samples analyzed by the ICP-OES was always <0.5 percent, and the percent error between quality control standards throughout the analytical run was <3 percent. A 1 L plastic cubic container was filled with unfiltered sample for acidity and alkalinity measurements done in the laboratory immediately upon arrival from the field using a Hach digital titrator. The relative difference between duplicate samples measured by the digital titrator was <5 percent.
Local Climate during 2011 and 2012

The potential evapotranspiration (PET) (in cm) was subtracted from the total monthly precipitation (in cm) to determine when infiltration and runoff were favored (Figure 5). In Leetonia during 2011, the monthly PET was only greater than the total monthly precipitation during the summer months of June, July, and August. In 2012, the PET was greater than or equal to precipitation during the spring months of April and May (project ended in May). During spring 2012 (March, April, and May), the area only received 17.7 cm of precipitation, compared to 44.7 cm of precipitation during the same time period in 2011.

Hydrograph Analysis

Measurements of the discharge from the mine started in May 2011, just before the hydrograph...
recession began. The maximum discharge of 2,468 m$^3$/d occurred on May 28, 2011, and then decreased exponentially to a minimum value of 342 m$^3$/d on September 17, 2011. The hydrograph separation for the 2011 recession period (see Methods) determined that the discharge is predominantly base-flow (80 percent), but there is a significant quick-flow component (20 percent) that likely originates from fractures and subsidence features similar to those observed where Main Street collapsed above the discharge point. The quick-flow discharge at the beginning of the recession period of 2011 was 1,931 m$^3$/d.

After September 17, 2011, the discharge began to increase as the total monthly precipitation exceeded the monthly PET, and recharge occurred. During the recharge period, the discharge increased slowly and then began to respond rapidly to large precipitation events. There were four quick-flow events identified during the 2011/2012 recharge period (Figure 5). Quick-flow event 1 was recorded on December 3, 2011, when the discharge more than doubled from 480 to 1,035 m$^3$/d within 2 weeks. That event was preceded by a large amount of rainfall totaling 9.5 cm between November 15 and December 3. Quick-flow event 2 was measured on January 7, 2012, when the discharge increased from 756 m$^3$/d on December 21, 2011, to 945 m$^3$/d. This quick-flow event was in response to another series of large rainfall events totaling 6.6 cm between December 21 and January 7.

Quick-flow event 3 was measured on February 5, 2012, when the discharge increased from 955 m$^3$/d on January 20, 2012, to 1,506 m$^3$/d, the highest discharge measured during the 2011/2012 recharge period. During January 2012, there was a total of 45.2 cm of snowfall, which accumulated in early to mid-January when the temperature was below freezing and then melted in late January when the temperature rose. On January 27, a 3 cm rainfall event along with snowmelt produced a large runoff event; however, by February 19, the discharge had decreased back to 905 m$^3$/d due to the low precipitation/runoff during the month of February.

Quick-flow event 4 was measured on March 20, 2012, when the discharge increased from 968 m$^3$/d on March 3, 2012, to 1,283 m$^3$/d. The event was preceded by several significant rainfall events totaling 7.0 cm between March 1 and March 20.

### Mine Pool Elevation

The mine pool elevation was determined based on water-level measurements taken from wells drilled into the mine’s main entry at location CV-4 and the mine’s drain at location CV-1 on August 17, 2010 (Table 1). The water-level elevation in the drain was 320.3 m above sea level (masl), while the water level in the main entry was 318.5 masl when the discharge was estimated to be 2,400 m$^3$/d (without any flow-measuring equipment). On November 18, 2011, when

### Table 1. Chemistry of the discharge and well samples taken on August 17, 2010, by the Ohio Department of Natural Resources and a sample taken from the Leetonia High School well on November 18, 2011.

<table>
<thead>
<tr>
<th>Location</th>
<th>Discharge Point</th>
<th>CV-4 Main Entry</th>
<th>CV-1 Drain</th>
<th>CV-1 Till</th>
<th>Leetonia High School</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface elevation (masl)</td>
<td>318.0</td>
<td>324.3</td>
<td>324.3</td>
<td>324.3</td>
<td>356.0</td>
</tr>
<tr>
<td>Well depth (m)</td>
<td>N/A</td>
<td>18.0</td>
<td>19.5</td>
<td>5.2</td>
<td>74.7</td>
</tr>
<tr>
<td>Casing depth (m)</td>
<td>N/A</td>
<td>14.9</td>
<td>N/D</td>
<td>N/D</td>
<td>38.7</td>
</tr>
<tr>
<td>Mine floor elevation (masl)</td>
<td>N/A</td>
<td>307.5</td>
<td>306.6</td>
<td>N/A</td>
<td>317.9</td>
</tr>
<tr>
<td>Static water level (m)</td>
<td>N/A</td>
<td>5.8</td>
<td>4.0</td>
<td>N/D</td>
<td>51.8*</td>
</tr>
<tr>
<td>Water-level elevation (masl)</td>
<td>N/A</td>
<td>318.5</td>
<td>320.3</td>
<td>N/D</td>
<td>304.2</td>
</tr>
<tr>
<td>pH (SU)</td>
<td>6.51</td>
<td>6.59</td>
<td>7.17</td>
<td>6.98</td>
<td>7.56</td>
</tr>
<tr>
<td>Specific conductivity (μS/cm)</td>
<td>562</td>
<td>503</td>
<td>658</td>
<td>491</td>
<td>496</td>
</tr>
<tr>
<td>Total acidity (mg/L as CaCO$_3$)</td>
<td>39</td>
<td>25</td>
<td>16.8</td>
<td>15.2</td>
<td>34</td>
</tr>
<tr>
<td>Total alkalinity (mg/L as CaCO$_3$)</td>
<td>157</td>
<td>115</td>
<td>265</td>
<td>208</td>
<td>366</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>218</td>
<td>165</td>
<td>185</td>
<td>74</td>
<td>104</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>33</td>
<td>55</td>
<td>39</td>
<td>56</td>
<td>5.8</td>
</tr>
<tr>
<td>Calcium (mg/L)</td>
<td>98</td>
<td>84</td>
<td>112</td>
<td>78</td>
<td>19</td>
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<tr>
<td>Magnesium (mg/L)</td>
<td>28</td>
<td>18</td>
<td>29</td>
<td>12</td>
<td>5.8</td>
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<tr>
<td>Sodium (mg/L)</td>
<td>18.8</td>
<td>31</td>
<td>36</td>
<td>42</td>
<td>154</td>
</tr>
<tr>
<td>Potassium (mg/L)</td>
<td>3.3</td>
<td>4.1</td>
<td>17</td>
<td>5.3</td>
<td>2.1</td>
</tr>
<tr>
<td>Iron (mg/L)</td>
<td>2.7</td>
<td>0.21</td>
<td>3.9</td>
<td>0.41</td>
<td>2.1</td>
</tr>
<tr>
<td>Manganese (mg/L)</td>
<td>3.0</td>
<td>2.1</td>
<td>1.8</td>
<td>0.94</td>
<td>0.7</td>
</tr>
<tr>
<td>Aluminum (mg/L)</td>
<td>0.05</td>
<td>0.08</td>
<td>0.17</td>
<td>0.25</td>
<td>0.1</td>
</tr>
</tbody>
</table>

N/A = not applicable, N/D = not determined.

*Measured when well was installed on June 21, 2003.
the discharge was 480 m$^3$/d, the water-level elevation of the main entry was 317.1 masl.

**Chloride Analysis**

Chloride concentrations were measured at the main entry of the mine from the well at location CV-4, the mine drain from the deep well at location CV-1, the groundwater within the glacial till from the shallow well at location CV-1, and at the mine discharge point prior to our study on August 17, 2010, by ODNR (Table 1). The chloride concentrations in the mine’s main entry and drain were 55 mg/L and 39 mg/L, respectively, compared to 33 mg/L at the discharge. The chloride concentration of the shallow groundwater taken from the glacial till was 56 mg/L. The chloride concentration of the deeper groundwater taken from the well located at the Leetonia High School on top of the hill, which was cased below the mine (to a depth of 38.7 m with a total well depth of 74.7 m), was only 5.8 mg/L during November 2011. The highly elevated chloride concentration of the shallow groundwater compared to all the other samples measured could be explained by the local application of road deicing salt. The chloride concentrations from the main entry, drain, and discharge samples all fall between those of the deep and shallow sources; therefore, a simple mixing analysis was used to determine the relative contribution of each source (Pinder and Jones, 1969). According to the mixing analysis (assuming chloride acts as a conservative tracer), the contribution of shallow groundwater was 46 percent at the discharge, 97 percent at the main entry, and 64 percent at the drain in August 2010. Seasonally, the chloride concentration of the discharge water (Figure 6) is higher during the recharge period (i.e., fall through spring) compared to the base-flow condition of the summer and can be observed to increase in response to quick-flow events. The Spearman correlation coefficient (SCC) of the chloride concentration and discharge was 0.83, indicating a strong positive correspondence between the two variables (Table 2). Chloride concentration is the only ion concentration to strongly correlate with discharge. The concentrations of all the other ions except aluminum are independent or have an inverse correlation with discharge.

**In Situ Water Properties**

The temperature of the discharge was nearly constant, with a range of 11.3–12.3°C, with only two values out of 26 being higher than 12°C. The dissolved oxygen concentration was always below 1.0 mg/L (range of 0.15 to 0.89 mg/L), with no discernible seasonal effect, and it was only weakly correlated with any other variable (Table 2). The pH of the discharge was circumneutral throughout the study period, with a range of 6.20 to 6.68. Like dissolved oxygen, pH showed no seasonal effects and was only weakly correlated with any of the other variables (Table 2). On August 17, 2010, the pH of the main entry at CV-4, mine drain at CV-1, and glacial till at CV-1 were all circumneutral. The main entry was 6.51, the mine drain was 7.17, and the glacial till was 6.98. Table 3 presents the range and average of the geochemical data collected from 26 samples at the discharge point between May 11, 2011, and May 20, 2012.

The redox potential (measured in mV) shows a relationship with discharge (Figure 7A). In general, as discharge decreases, the redox potential becomes less oxidizing (less positive), and as the discharge increases, the redox potential becomes more oxidizing (more positive). The SCC of the redox potential and discharge was 0.72, indicating a positive correspondence between the two variables. There was a period of time between July 23 and October 29 when the discharge exhibited little variation but the redox potential increased from 23.7 mV to 91.0 mV and then decreased back to 38.4 mV. In 2012, the beginning of a similar trend appears to occur, with the redox potential decreasing during the recession and then rebounding. Specific conductivity (measured in $\mu$S/cm) also shows a strong response to changes in discharge (Figure 7B). The SCC of specific conductivity and discharge was $-0.69$, indicating an inverse relationship between the two variables. The specific conductivity is highest during the summer months, when recharge is diminished or eliminated, and lowest during the late fall to early spring, when recharge is highest.

The measured values of pH and Eh for several selected samples throughout the sampling period (chosen to highlight the range of seasonal changes observed) are shown in Figure 8 relative to the
The theoretical stability fields for the pyrite, ferrihydrite, and siderite minerals. The Eh-pH diagram was generated using the Act2 program from the Geochemist’s Workbench software suite. The activities for all species used to construct the Eh-pH diagram were calculated based on their average concentrations measured at the mine’s discharge point throughout the study period (Table 3). All mine discharge samples throughout the study period and the sample from the mine’s main entry at CV-4 plotted within the aqueous Fe$^{2+}$ stability field. The more alkaline groundwater from the Leetonia High School well plotted within the siderite mineral stability field. No Eh measurement was obtained from the CV-1 mine drain sample taken by the ODNR; however, based on its pH (7.17), it would likely plot somewhere between the discharge samples and the high school well.

### Alkalinity and Acidity

At the discharge, changes in acidity and alkalinity (reported in units of mg/L as CaCO$_3$) appear to be correlated and of similar magnitude (i.e., when one increased or decreased, so did the other) (Figure 9). However, the SCC between alkalinity and acidity was 0.02, indicating the two variables are independent. Divergence between the two variables during the 2011/2012 recharge period (i.e., when alkalinity was high and acidity was low) largely explains the near-zero SCC.

Alkalinity was also independent of discharge (SCC = 0.02), while acidity had an inverse relationship with discharge (SCC = −0.73). Alkalinity ranged from 105 to 152 mg/L, with the highest values generally occurring during the 2011/2012 recharge period. However, alkalinity had its lowest value (approximately equal to acidity) during the end of the 2010/2011 recharge period.
2011 recharge period, when the discharge was at its highest level during the study. Acidity ranged from 104 to 135 mg/L, with the highest values generally occurring during the base-flow period and low values occurring during the recharge period. Acidity only exceeded alkalinity toward the end of the quick-flow recession in summer 2011 as the discharge decreased from 1,234 m$^3$/d on June 11 to 569 m$^3$/d on July 9. During the 2012 recession, acidity did not rise above alkalinity for a short time as it did in 2011.

On August 17, 2010, the samples from the mine drain had higher alkalinity than the mine discharge (265 mg/L compared to 157 mg/L), while the samples from the main entry had lower alkalinity (115 mg/L). The alkalinity of the shallow groundwater from the glacial till was 208 mg/L. The deep well cased below the mine had water with high alkalinity (300 mg/L) and sodium (154 mg/L), but low calcium (19 mg/L).

Sulfate and Metals

The sulfate concentration of the discharge varies throughout the year (Figure 10A), ranging from 231 to 292 mg/L, with an average of 260 mg/L. The SCC of the sulfate concentration and discharge was −0.63, indicating an inverse relationship between the two variables. The sulfate concentration increased during the months of May, June, and July in 2011 and March, April, and May in 2012. During 2011, in the month following the beginning of the recession on May 28, the sulfate concentration increased by 24 mg/L, from 261 mg/L to 285 mg/L. During 2012, in the month following the beginning of the recession on March 20, the sulfate concentration increased by only 12 mg/L, from 237 mg/L to 249 mg/L. On August 17, 2010, the sulfate concentration was 165 mg/L in the main entry and 185 mg/L in the mine drain. Both had a lower sulfate concentration than the discharge (218 mg/L) on the same day. The daily chemical loadings were calculated in kilograms per day by multiplying the concentration by the discharge. The sulfate loading showed a perfect correlation with the discharge (SCC = 1.00) (Figure 10B). The loading of all other dissolved ions had the same perfect or strong positive correlation with discharge, except the iron loading, which had an inverse relationship (SCC = −0.46).

Iron, manganese, and aluminum are three trace metals that are commonly elevated above their normal natural background concentration at coal mine drainage sites. Iron ranged from 0.16 to 6.9 mg/L during this study (Figure 10C). Manganese showed lower variation, ranging from 3.3 to 4.5 mg/L (Figure 10C). The aluminum concentration was always low (<0.15 mg/L). The iron loading does not show the same trend as the discharge throughout the study period, as do all the other dissolved ions measured for this study (Figure 10D). The SCC values of the iron and manganese concentrations and discharge were −0.88 and −0.50, respectively, indicating an inverse relationship. During the summer, as the discharge decreased during the recession, the iron concentration increased to over 40 times its concentration during the end of the recharge period (0.16 to 6.9 mg/L). On August 17, 2010, the iron concentration in the main entry was 0.2 mg/L, which was much lower than the discharge (2.7 mg/L), while the mine drain had a higher iron concentration at 3.9 mg/L.

DISCUSSION

The result of the hydrograph separation from the Cherry Valley Mine during the sampling period was compared to the results from two completed studies of coal mine discharges in southeastern Ohio that used the same method of calculating quick-flow, the Majestic Mine and the Carbondale Mine (Lopez and Stoertz, 2001). It was calculated that at the beginning...
of the 2011 recession, 20 percent of the water draining from the Cherry Valley Mine was quick-flow. At the Majestic Mine, which had documented subsidence features that captured runoff, the quick-flow component represented 52 percent of the water discharging from the mine during the spring. At the Carbondale Mine, which had no documented subsidence features, the quick-flow component represented only 3 percent of the water discharging from the mine. The Cherry Valley Mine, with 20 percent quick-flow, falls between those two documented cases.

At the Majestic Mine during 1996, spring precipitation totals for March, April, and May were 14.0 cm, 10.0 cm, and 20.0 cm, respectively (44 cm total) (Lopez and Stoertz, 2001). The Cherry Valley Mine received an almost identical 44.7 cm during the same time period during 2011. Despite the similar precipitation amounts, the Majestic Mine had a peak flow of 6,050 m$^3$/d on June 12 (Lopez and Stoertz, 2001), compared to a peak of 2,468 m$^3$/d on May 28 from the Cherry Valley Mine. The quick-flow discharge from the Majestic Mine at the beginning of the recession was 4,403 m$^3$/d (Lopez and Stoertz, 2001), while the quick-flow discharge from the Cherry Valley Mine was less than half of that.

Since the precipitation amounts were similar for the Majestic Mine and the Cherry Valley Mine during the years under study, the reason for the difference in quick-flow could be the different sizes of the mines. The Cherry Valley Mine covers an area of 2.3 km$^2$, compared to the 1.3 km$^2$ area of the Majestic Mine; however, the Majestic Mine is directly connected to other nearby mines, giving it a total potential contributing area of 4.9 km$^2$ (Lopez and Stoertz, 2001). To compare the quick-flow discharges of two mines with different contributing areas, the discharge flows were converted to yields equal to the discharge flow divided by the drainage area (e.g., Goode et al., 2011). The Cherry Valley Mine had a yield of 840 m$^3$/d/km$^2$ compared to a yield of 899 m$^3$/d/km$^2$ from the Majestic Mine. The similarity between the yields suggests that the Majestic Mine has a higher discharge than the Cherry Valley Mine, given similar
precipitation amounts because the Majestic Mine receives recharge from a larger contributing area (including that from connected mines) than the Cherry Valley Mine.

The recharge water can enter the mine through rapid flow within fractures or slow seepage through the overburden. The recharge water then enters the mine pool (i.e., the saturated area of the mine) or unsaturated area of the mine, and the path it takes determines the effect of the chemistry of the discharge (Cravotta, 1994). When the recharge water enters the mine pool directly without coming into contact with the unsaturated area of the mine, the water is discharged after only a short time (on the order of 2 days based on the dye test at the pipe under Main Street for the Cherry Valley Mine). The short residence time and minimal contact with soluble iron-sulfate salts result in dilution of the dissolved oxidation products in the discharge water. This direct recharge would likely enter the slope entry section of the mine below the gully through subsidence fractures, and then it would travel quickly to the discharge point.

This direct recharge pathway to the mine pool appears to be partially responsible for producing the four quick-flow events during fall 2011 through spring 2012 (Figure 5). The sudden increase in the chloride concentration (elevated in the shallow groundwater), with a corresponding decrease in sulfate (a pyrite oxidation product), is consistent with mixing (or dilution) of mine pool water with shallow groundwater. This effect is confirmed by comparing the SCC of sulfate and chloride with discharge. Chloride positively correlates with discharge (SCC = 0.83), while sulfate has a strong inverse relationship with discharge (SCC = −0.63). In contrast, when recharge water enters the unsaturated area of the mine, whether by subsidence fractures or slow seepage through the overburden, it then flows down-dip to the mine pool. As it does, it will mobilize any soluble iron-sulfate salts that have formed in the presence of oxygen, and therefore, unlike the "direct"
recharge, it will add oxidation products to the mine pool and discharge.

The mine pool elevations taken on August 17, 2010, should represent a low point of the mine pool's elevation for the year (Table 1). However, there were several rainfall events between August 12 and August 15 in 2010 totaling 4.5 cm, including a large 2 cm rainfall event on the 15th. On August 17, the ODNR estimated the discharge (without any flow-measuring equipment) at 2,400 m$^3$/d. This is unusually high for the recession period; for example, during August 2011, the highest discharge was 401 m$^3$/d. Also, the chloride concentration of the mine discharge was elevated on August 17, 2010, at 33 mg/L. This is higher than any concentration measured during the 2011/2012 study period, which is evidence of a large influx of surface runoff into the mine in 2010. Based on these observations, it is likely that the mine pool elevation on August 17 was temporarily raised by a large quick-flow event and is likely to be representative of the upper extent of the mine pool.

The mine pool elevation in the main entry on November 18, 2011, is likely to be more representative of the lower extent of the mine pool in the main entry and was 1.4 m lower than the mine pool during the August 17, 2010, quick-flow event. Based on the mine pool elevations, the majority of the mine is flooded, with only the western up-dip fringes left unsaturated. According to dip of the coal seam, a fluctuation of 1.4 m in the mine pool elevation would result in the flooding or draining of at least 80 lateral meters of the main entry. This intermittently flooded part of the mine would be the beach area where oxygen is available for pyrite oxidation and where water can mobilize the oxidation products that form. The reason for the difference between the mine pool elevations of the mine's main entry and drain (~1 m) measured in 2010 could be due to the different drainage areas of the two conduits or the different size of the conduits themselves.

The chloride concentrations at the discharge and wells on August 17, 2010, during the apparent quick-flow event appear to reflect changes in the relative contribution of shallow and deeper groundwater to the discharge. Both the mine’s main entry and drain have higher chloride concentrations than the discharge; therefore, mixing between the water from those two conduits does not explain the decrease in the chloride concentration at the discharge. An additional source of groundwater that is largely unaffected by road deicing salt must contribute to the discharge. The unknown source could be groundwater with a lower chloride concentration from a deeper origin, similar to the groundwater from the Leetonia High School well (Table 1).

The similarity between the chloride concentrations of the till water at CV-1 and the main entry at CV-4 suggests that the water in the main entry originated in the shallow subsurface till layer and was brought to the mine via subsidence fractures. Once the water enters the unsaturated portion of the main entry, the dissolution of iron-sulfate salts lowers the alkalinity (208 to 115 mg/L) and raises the sulfate concentration (74 to 165 mg/L); however, the chloride concentration remains the same. As expected, alkalinity and sulfate in the discharge have a strong inverse correlation (SCC = −0.64). The mine drain and main entry both receive substantial recharge from the shallow subsurface, and both are net alkaline with a circumneutral pH. Therefore, the alkalinity imparted to the recharge water is sufficient to buffer the acidity produced by oxidation reactions within the mine. Although the samples from August 17, 2010, discussed here represent a quick-flow event with an unusually large influx of surface water to the mine, the sample taken from the main entry on November 18, 2011, under more normal precipitation conditions, showed the same concentration of chloride (55 mg/L). Therefore, the addition of surface water recharge into the main entry is the typical condition of the mine and is not just a response to large precipitation/runoff events at the surface.

The deeper groundwater taken from the Leetonia High School well is highly alkaline (300 mg/L), with high sodium (154 mg/L), low calcium (19 mg/L), and low chloride (5.8 mg/L) concentrations. These conditions are indicative of a cation exchange process whereby calcium ions are exchanged for sodium ions, which can lead to additional dissolution of calcareous rocks and increased alkalinity (Capo et al., 2001). However, neither the drain nor the discharge showed any influence from a source with such a high sodium concentration. If a deeper source of groundwater with the same chemistry as the Leetonia High School well contributes ~36 percent of the water in the drain (based on the chloride simple mixing analysis outlined previously), then the sodium concentration should be approximately twice as high as it was in the drain. However, sodium and alkalinity are not considered to be conservative like chloride and could be removed from the system through cation exchange and neutralization, respectively.

The discharge has a higher sulfate concentration than the mine’s drain and main entry, suggesting that oxidation reactions and the dissolution of iron-sulfate salts are still occurring within the slope entry before the water reaches the discharge point. In the unsaturated area of the mine, pyrite is exposed to oxygen, and iron-sulfate salts are produced by pyrite oxidation. During the recharge period, as the unsaturated area of the mine fills, the stored
oxidation products are mobilized, enter the mine pool, and then flow to the discharge point. Lopez and Stoertz (2001) observed that the sulfate concentration of the mine discharge was highest when these stored oxidation products were flushed from the mine (i.e., during the “spring flush”).

During the recharge period at the Cherry Valley Mine, the sulfate concentration decreases due to dilution by an increase in recharge. However, the sulfate loading increases as the discharge increases (SCC = 1.00). The decrease in the sulfate concentration is minor compared to the increase in discharge, showing that additional sulfate is mobilized by the flow of recharge water through the up-dip section of the mine. Even during the large quick-flow event occurring in the recession period of 2010 on August 17, the sulfate concentration only dropped to 218 mg/L. Therefore, a flushing effect is occurring at the Cherry Valley Mine during the recharge period.

The increasing sulfate concentration of the discharge during the recession period in 2011 and 2012 could be the result of reduced dilution by a reduction in recharge and/or partially attributable to the draining of the intermittently flooded areas of the mine. As the unsaturated area of the mine increases, more pyrite is exposed to oxygen, resulting in the production of more soluble iron-sulfate salts. The recharge water in the unsaturated section of the mine dissolves these salts as it flows to the mine pool. The sulfate concentration in the discharge increases steadily as the flow decreases during the recession period.

Once the mine drained to its lowest point in 2011, the sulfate concentration stopped increasing because the unsaturated area of the mine was no longer expanding. In early August 2011, the sulfate concentration reached a maximum and began slowly decreasing even before recharge began and dilution could occur. This observation supports the conclusion that there is an increase in the production of oxidation products as the unsaturated area expands, and this effect diminishes once the mine pool elevation has stabilized.

The redox potential responds to changes in the amount of recharge entering the mine as well as the unsaturated area of the mine. During the recharge period, the amount of oxygenated water from the surface entering the mine increases, thereby increasing the redox potential. During the recession period, the recharge diminishes, resulting in less oxidizing discharge water (i.e., redox potential decreases) as the proportion of base-flow groundwater increases. This is the general trend throughout the study; however, by early August 2011, the discharge stabilized after the beach area of the mine had drained, and the redox potential began to increase. The increase in redox potential could be explained by the size of the unsaturated area of the mine at this time. When the mine pool is near its lowest level of the year, it maximizes the amount of air that can be introduced to the mine workings, resulting in an increase in the redox potential. When the discharge increases as recharge begins in mid-September 2011, the redox potential initially begins to decrease as the mine pool rises. After mid-November 2011, as the amount of recharge increases, the redox potential begins increasing following the previously described general trend.

The amount of precipitation was much greater during the spring of 2011 (44.7 cm) compared to 2012 (17.7 cm), resulting in a much higher discharge before the recession began during 2011 compared to 2012. During the first month of the recession in 2011, the sulfate concentration started out higher and increased by twice as much as the same period of time in 2012 (Figure 10A). The lower sulfate concentrations and smaller increase in sulfate concentrations following the recession in 2012 suggest that the amount of precipitation largely influences the amount of sulfate added to the mine pool from the dissolution of soluble salts in the unsaturated area of the mine. Even though there is a large unsaturated area where soluble pyrite oxidation products are produced, there is limited recharge to bring them to the mine pool during the recession.

Manganese concentrations show less variation than iron (Figure 10C), because, once dissolved, manganese will not oxidize and precipitate until the pH is greater than 8.5 (Klusman and Machemer, 1991). The aluminum concentration was always low because of its low solubility at a circumneutral pH (Nordstrom and Ball, 1986). Due to the circumneutral pH (>6), dissolved iron is expected to be in the ferrous (Fe^{2+}) form because ferric iron (Fe^{3+}) is insoluble above pH 4 (Stumm and Morgan, 1981; Figure 8). The consistently low concentration of iron throughout the year could be due to the circumneutral pH and net alkaline condition of the mine water.

With a pH >6, the solubility of ferric iron is limited in the mine water (Figure 8), and any ferric iron that forms should undergo hydrolysis and precipitate out as amorphous ferrihydrite (Fe[OH]_3). However, due to the kinetic barrier to the formation of iron mineral phases, some ferric iron may remain in solution (Cravotta, 2008). In a solution with high alkalinity, the dissolved ferrous iron may also precipitate out as siderite (FeCO_3) (Cravotta, 2008). Therefore, sulfate could be flushed out of the mine while iron is retained as siderite and/or amorphous ferrihydrite. Siderite and amorphous ferrihydrite are supersaturated within the mine drain, where a saturation index of 0.62 and
The iron loading does not show the same correlation with discharge throughout the study period as the other dissolved ions. During the 2011 recession, the iron concentration increased to over 40 times its concentration during the end of the recharge period. Therefore, unlike all the other ions measured, the large magnitude of change in iron concentration did not control the iron loading throughout the year. The large magnitude of the change in iron concentration is likely a result of the precipitation of iron mineral phases within the mine, which lock up the iron and cause the very low concentrations. When some of this iron is released, it causes the iron concentration to increase by a larger magnitude than the other ions. At the mines in southeastern Ohio, where iron concentrations are higher and the magnitude of change in concentration is lower, the iron loading is controlled by discharge like all the other measured ions (Lopez and Stoertz, 2001). The peak loading of iron during the quick-flow event 1 on December 3, 2011 (Figure 10D), was likely the result of a sudden displacement of the older mine pool water (with higher iron concentration) by new recharge water.

CONCLUSIONS

The abandoned Cherry Valley Mine in eastern Ohio is directly connected to the surface and shallow subsurface via subsidence fractures. The fractures facilitate the addition of recharge water to the mine. The path the recharge water takes to reach the mine pool determines how it influences the chemistry of the mine discharge. Recharge water that enters the mine pool directly will produce a dilution effect with regard to pyrite oxidation products. Recharge water that enters the up-dip, unsaturated area of the mine and then flows down to the mine pool will mobilize the soluble iron-sulfate salts produced during pyrite oxidation to the mine pool.

Flooding of the unsaturated area of the mine during the recharge period did not cause the concentration of pyrite oxidation products to increase, as was seen in previous studies (Lopez and Stoertz, 2001). The input of alkalinity from the recharge waters and dilution of the mine pool water influenced the concentrations of oxidation products in the discharge from the mine more than the “flushing effect” observed in the study by Lopez and Stoertz (2001). However, the sulfate loading increased as the discharge increased, showing that additional pyrite oxidation products were added to the mine pool by recharge through the unsaturated area of the mine (even though the concentrations in the discharge decreased). An increase in the sulfate concentration was observed after recharge ended and the beach area of the mine began to drain. The increase in concentration was due to the expansion of the unsaturated area of the mine where more pyrite oxidation could occur. The amount of sulfate added to the mine pool from the unsaturated area is dependent upon the amount of recharge (i.e., precipitation) a mine receives. Therefore, the timing and magnitude of the seasonal flushing effect are dependent on the hydrology of the specific mine under investigation.

The presence of subsidence fractures allows significant quantities of groundwater from the glacial till with high alkalinity and chloride to be quickly transmitted into the mine. The circumneutral pH and generally net alkaline conditions of the drainage from Cherry Valley Mine can be attributed to the dissolution of calcareous rocks from the glacial till in the shallow subsurface and the addition of alkaline groundwater from the deep subsurface. Based on the simple mixing analysis, the water in the mine’s main entry originated from shallow groundwater in contact with the glacial till. The main entry is circumneutral and net alkaline; therefore, the alkalinity generated by water moving through the till is sufficient to buffer the acidity produced within the mine’s main entry. This prevents significantly more pyrite oxidation than would occur if the pH decreased below 4. The conditions of circumneutral pH and elevated alkalinity within the mine result in precipitation of dissolved iron out of solution as amorphous ferrihydrite or siderite, therefore limiting the concentration of iron at the mine discharge and decoupling it from sulfate and most other dissolved ion concentrations. The large variations in iron concentration in the discharge through the year control the iron loading in the discharge rather than the magnitude of the discharge, which controls the loading of all other ions in solution.

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