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Long-term changes in quality of discharge water from abandoned underground coal mines in Uniontown Syncline, Fayette County, PA, USA

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Abstract

Changes in water quality over 25 years have been documented for discharges from an extensive network of abandoned underground coal mines in the Uniontown Syncline, Fayette County, PA, USA. A baseline study of 136 mine discharges in the syncline was conducted in 1974–1975. In 1998–2000, follow-up water flow and quality monitoring was conducted at 21 selected discharges for 2 years to assess the degree of mine water-quality improvement since 1974–1975. The data from the two periods of time were compared, with consideration of differences in measurement methods. The degree and rate of water-quality improvement was found to be highly dependent on the amount and duration of flooding in the mine voids. Water quality of discharges from the substantially flooded mine voids improved significantly, going from acidic water with high sulfate and iron concentrations in 1974–1975 to alkaline water with substantially lower sulfate and iron concentrations in 1998–2000. In contrast, the water quality in the unflooded mines showed less improvement over the 25 years between studies. The water discharging from the unflooded mines in 1974–1975 was acidic with high sulfate concentrations and in 1998–2000 was still acidic but showed somewhat lower sulfate and iron concentrations, reflecting depletion of readily available pyrite. The data obtained provide insight into the potential and rate of natural amelioration of mine water quality in different abandoned underground coal mine systems.

Keywords: Natural attenuation; Coal; Mine; Drainage; Pyrite; Flood

1. Introduction

Abandoned mine drainage (AMD) is and has long been the most serious water-quality and watershed-degradation problem in the Appalachian region of the United States. and other mining regions [1,2]. AMD is generated when oxygenated water flows into mining cavities with exposed coal and confining rocks high in pyrite ($FeS_2(s)$), resulting in dissolution of the pyrite and the associated generation of acidic water with relatively high concentrations of iron and other metals. In several areas of the Appalachian coal fields and in coal mining regions of the UK, it has been observed that mine water acidity and iron load are most severe in the first years after a discharge begins, but can improve steadily and substantially with time [3–6]. The nature and extent of natural amelioration varies significantly among abandoned coal mines, however.

In this work, the evolution of mine water quality over 25 years was studied for a subset of discharges in the Uniontown Syncline, Fayette County, PA. The study area was chosen because the abandoned mine network comprises both mines that have flooded naturally as well as free-draining mines that have not flooded (unflooded mines). Differences in the nature and extent

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of water-quality improvements were expected to exist between mines of these types, based on the long-recognized but minimally documented (e.g., [7,6]) benefits of flooding. In addition, an extensive data set was available for discharges in this area for the mid-1970s. The water quality and flow characteristics of 136 discharges in the Uniontown Syncline were studied in 1974–1975 under Operation Scarlift [8], a program aimed at evaluating the feasibility of AMD remediation in various areas of the Commonwealth of Pennsylvania.

A new monitoring program was established at 21 representative sites from the 1974–1975 study in the Uniontown Syncline, and these sites were monitored monthly between September 1998 and September 2000. Flow and water-quality measurements parallel to those obtained in 1974–1975 were performed, including pH, alkalinity, acidity, total iron, and sulfate. These and additional water-quality measurements were made for the selected sites in 1998–2000.

The purpose of this study was to document the extent of water-quality changes in the Uniontown Syncline AMD discharges, and to investigate geochemical and hydraulic factors responsible for the changes. Results of the 1998–2000 AMD water-quality monitoring in the Uniontown Syncline were compared with the 1974–1975 water-quality data from the same discharges. The Uniontown Syncline mine discharges have evolved in water quality naturally, as no measures were taken to influence long-term water quality upon abandonment.

2. Background

The short- and long-term water-quality evolution of mine drainage depends on the infiltration water quality and minerals exposed in the abandoned coal mines. The mineral primarily responsible for the iron and acid load in AMD is pyrite, FeS_2 [9]. The chemical reactions governing the oxidative dissolution of pyrite are as follows:

$$FeS_2(s) + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

$$FeS_2(s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (2)$$

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O \quad (3)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^+. \quad (4)$$

Pyrite can be oxidized by oxygen and ferric iron in solution, as seen in Eqs. (1) and (2). The resulting ferrous iron may be further oxidized to ferric iron (Eq. (3)), which precipitates as amorphous hydrous ferric oxide, $Fe(OH)_3(s)$ (Eq. (4)). Hydrous ferric oxide is the yellow/orange precipitate that is widely associated with AMD, and that coats stream banks and sediments causing aesthetic degradation as well as damage to aquatic and benthic life [4,6].

The above reactions indicate that oxygen has an important role in the production of AMD. The availability of oxygen in solution can control the amount of pyrite that is oxidized, and thus the production of AMD, especially at pH values approaching the neutral range [10]. It has been shown that controlling oxygen in water/coal systems limits the amount of AMD produced [11]. In mined-out areas where mine discharge water quality has been observed to improve, an important common factor has been the absence of atmospheric oxygen in the system [12,7,13,6].

The availability of oxygen for AMD production is related to the extent of flooding in the mine voids, and mine flooding is governed by the geometry of the mines [7,6,14]. A flooded mine will have a supply of oxygen for pyrite oxidation limited to that dissolved in the water (solubility in water at 15°C is approximately 10.2 mg/l). The presence of air, as occurs in an unflooded mine, provides an abundant source of oxygen. For example, a cubic meter of air at 15°C with $P_{O_2} = 0.21$ atm contains 285 g O_2, but a cubic meter of water at the same temperature and 1 atm total pressure can hold a maximum of only 10.2 g O_2.

Changes in mine water quality over time have been observed in discharges from coal mines in the USA, the UK, and elsewhere. The water quality of the initial discharge upon flooding of abandoned mines is highly acidic [15,4,6]. The ‘‘first-flush’’ phenomenon results from the highly oxygenated environment that exists around the pyrite as the mine floods. Since oxygen is abundantly available due to the presence of air before and as a mine floods, a large amount of pyrite can be oxidized resulting in acidic water with high concentrations of sulfate and iron. Also contributing to the acid input in the initial flooding of mine voids is the dissolution of ferrous/ferric hydroxy-sulfate evaporite minerals (salts) formed on the walls of the mine voids during active mining as a result of pyrite oxidation [16,5]. The first-flush acidity has been termed ‘‘vestigal acidity’’ by Younger [4].

After the first flush, improvements in mine water discharge quality have been observed in mines that flood to a significant extent, especially in the vicinity of the discharge [13,6,5]. Flooding of mines serves to limit the oxygen supply, and thus to control the dissolution of pyrite. It also removes readily soluble ferrous/ferric hydroxy-sulfate salts accumulated on the walls of the mine voids [5]. The extent and effectiveness of flooding in bringing about improvements will be site specific; the size and geometry of the system determine how effectively it is flooded.

The evolution of water quality in unflooded mines is different than in flooded mines (e.g., [13]). Since the mines do not flood, the initial discharge water quality can be maintained as there is no significant reduction in oxygen availability with time. Pyrite dissolution will likely continue to occur and acidity levels will remain high in these non-flooded environments. However, continued pyrite dissolution means that there is greater potential for depletion of readily available pyrite.

3. Methods

3.1. Study area

The area of study for this research project was the Uniontown Syncline located in Fayette County, PA (Fig. 1). A major geologic feature of the Uniontown Syncline is the 2.4 m (8 ft) thick Pittsburgh Coal seam which stretches from southwest of Uniontown, beneath Uniontown, toward Connellsville. It is the thickest and most extensively mined of several coal seams in the Uniontown Syncline and throughout Western Pennsylvania. Within the Uniontown Syncline, numerous mine drainage discharges originate from the mined-out Pittsburgh Coal seam. These discharges flow into two major streams, or their tributaries: the Youghiogheny River in the north part of the Syncline, and Redstone Creek in the south part (Fig. 1).

The Pittsburgh Coal seam in the Uniontown Syncline is essentially mined out [17]. Some of the first mining in Western Pennsylvania began here, in the 1870s [18,19] and by the early 1970s the deep mining in this area ceased [8,19]. Some coal remains in place in certain portions of the basin, though there is only a small percentage of solid coal in place that could be mined. Coal in place is mostly in the form of barriers between mines. Some blocks in place were heavily but not completely mined. The existing mine void network and coal in place has been mapped using mine maps from the Syncline [20].

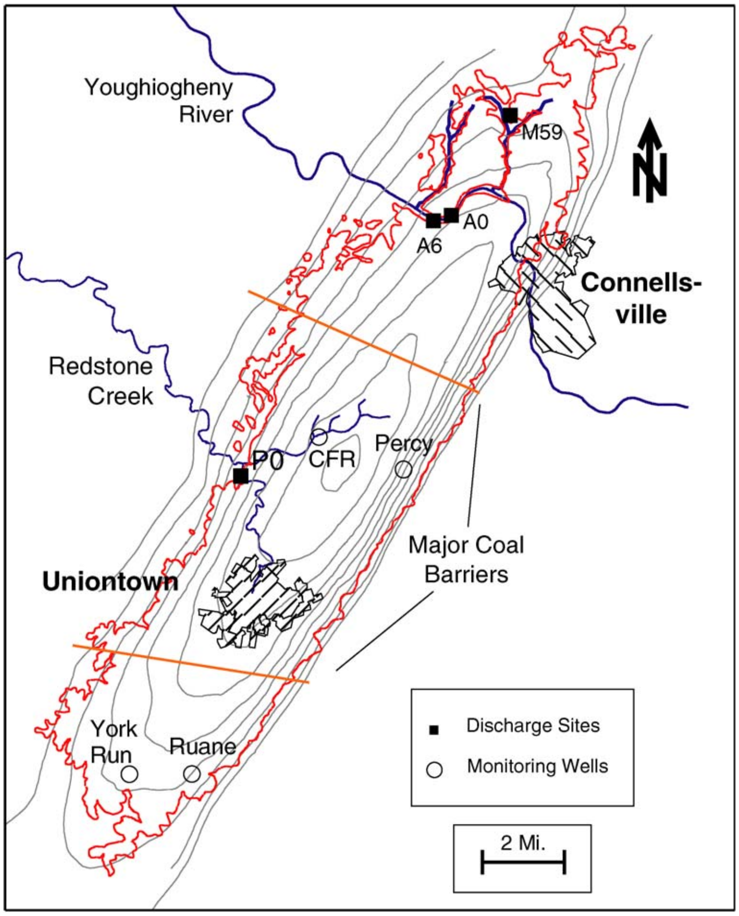

Fig. 1. Map of Uniontown Syncline showing elevation contours of Pittsburgh Coal Seam [ranging from 152 m (500 ft) above mean sea level at the center contour to 396 m (1300 ft) above mean sea level at the outer edge of the syncline, in 30.5 m (100 ft) increments], selected AMD discharge locations, mine pool monitoring well locations, and locations of major in-place coal barriers south of the Youghiogheny River.

There are several reasons why the Uniontown Syncline was selected as a good study area for an evaluation of long-term natural improvements in the water quality of mine drainage discharges. First, comprehensive monitoring data are available from the Scarlift Study for 1974–1975. Secondly, the Uniontown Syncline has discharges from both flooded and unflooded mines, which were expected to exhibit distinct patterns in long-term water quality. Finally, many of the mine drainage discharges are still in existence and can be monitored, which allows for evaluation of long-term changes in water quality.

There are two basic configurations of coal mines that significantly influence the extent of flooding in and hence the flow and chemistry of water discharging from abandoned mine voids. These configurations are distinguished by the location of the discharge, which is typically at the coal outcrop, where the coal seam meets the ground surface. Unflooded mines discharge at a coal outcrop at the lowest elevation in the mine (Fig. 2). Flooded mines discharge at the lowest elevation at which the mine or mine entry shaft meets the surface, which may be far above the lowest elevation of the mine (Fig. 2).

Most of the mines north of the Youghiogheny River are designated as unflooded due to the geometry of the mines. These mines were developed updip, meaning that the mines were excavated starting at an outcrop at the lowest elevation of the mine. While in operation, the advantage of these mines was the fact that water did not pool and hinder mining activities, but rather traveled down slope and out of the mine. The flows from these mines exhibit seasonal variations with highest flows in the late winter and spring and lowest flows in the summer and fall. At times, some of the discharges are dry. Because the flows respond dynamically to relatively short-term changes in hydrologic conditions, it can be inferred that significant storage does not occur and the mines are for the most part unflooded.

The unflooded mines north of the Youghiogheny River typically have less than 60 m (200 ft) of overburden and drainage areas less than 2.4 km^2 (500 acres). The mines dip upward from the discharge at approximately 1% grade. These mines were all abandoned before 1930, and the mines are assumed to have been discharging before and since that time.

The mines south of the Youghiogheny River are a series of abandoned, largely interconnected mines that were developed either updip from shafts in the middle of the coal basin, or downdip from the coal outcrop. These mines are configured such that the coal outcrops are far above the lowest elevation in the mine, and therefore the mines flood before discharging at the surface (Fig. 2). Discharges from these mines began in 1960 and in following years of the decade [8].

The flooded mines south of the Youghiogheny River have up to 180 m (600 ft) of overburden and discharge in two primary locations where the outcrop is cut by streams, the Youghiogheny River and Redstone Creek. Static water levels in various wells located in this interconnected mine pool system indicate the existence of at least three hydraulically distinct mine pools, separated by coal barriers as indicated in Fig. 1.

Monitoring data from three mine pools south of the Youghiogheny River (the southern, central and northern pools (Fig. 1)) indicate that water levels are relatively constant in the three pools, thus supporting the flooded assessment. The mine pool data are presented in Appendix A of Dzombak et al. [20]. The 1974–1975 and 1998–2000 mine discharge flow data, discussed later, also support the mine flooding assessments.

3.2. Monitoring sites

Twenty-one sites were chosen for the 1998–2000 monitoring program, encompassing discharges that originated from flooded, unflooded and partially flooded mines. Sites for the sampling program were chosen based on consistency and/or proximity with Scarlift sites, mine pool origin, and accessibility for flow monitoring and sampling. Maps, past site descriptions, and measured flow rates were used to evaluate the similarity of sites.

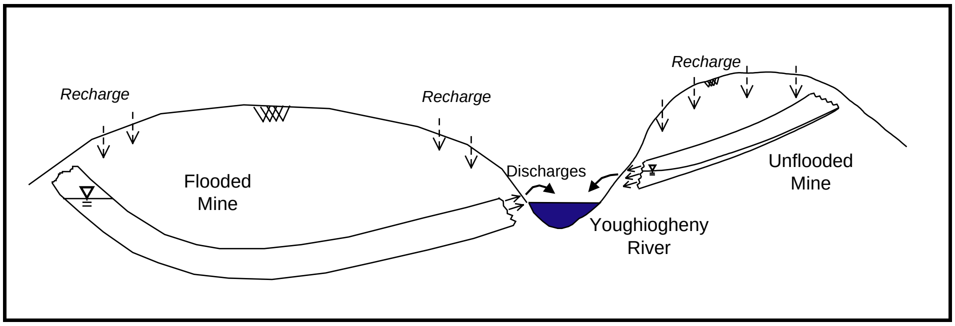

Fig. 2. Schematic showing discharges from flooded and unflooded mines adjacent to the Youghiogheny River.

The network established for the 1998–2000 monitoring in the Uniontown Syncline basin involved eight different locations with 19 individual discharge sites plus two in-stream sites on small tributaries, downstream of multiple seep inputs. Seven of the discharges were from unflooded mines north of the Youghiogheny River. Three of the discharges appeared to originate from partially flooded mines, as indicated by flow and chemical characteristics. Nine of the discharges were from the deep, flooded mine complex on the south side of the Youghiogheny River. Two measurements were from in-stream monitoring sites. Appendix B in Dzombak et al. [20] provides a complete description of site locations and site location maps for the 1998–2000 monitoring program.

Partially flooded mines have a significant amount of unflooded area as well as some flooded portions. Water from the unflooded portions of these mines receive recharge flows into the flooded portion of the mine, from which discharge occurs. Flow characteristics of a discharge from a partially flooded mine complex resemble that of a flooded mine, but chemical characteristics indicate the influence of water from an unflooded zone.

3.3. Study methodology

The 1998–2000 monthly monitoring program included field measurements of pH, temperature, dissolved oxygen, conductivity, ferrous iron and flow. Water samples were collected in the field and analyzed at both the Carnegie Mellon Hauck Environmental Engineering Laboratories and the Pennsylvania Department of Environmental Protection (PADEP) Central Laboratory in Harrisburg. Carnegie Mellon analyses included alkalinity, acidity (pH 8.3 endpoint; also referred to as CO_2 acidity and phenolphthalein acidity), chloride, sulfate, and dissolved iron. The PADEP laboratory analyzed for alkalinity, total suspended solids, iron, aluminum, magnesium, manganese, calcium, and sodium. Appendix C of Dzombak et al. [20] presents the quality-assurance and quality-control procedures implemented.

Flow measurement methods varied from site to site. At 14 of the monitoring sites, permanent weirs were installed for monitoring flow. For the remaining sites, flow was measured via bucket and stopwatch, portable flume, or flow meter. The velocity–area method [21] was employed with a Marsh–McBirney Model 2000 flow meter at sites where weirs could not be constructed and no other method was convenient.

Field measurements for pH, dissolved oxygen, and conductivity were made with Corning Checkmate M90 field meters. Each meter was calibrated in the field with appropriate standard solutions prior to measurement, at least twice per day. Temperature was recorded from the probe built into the pH meter. Ferrous iron was measured in the field using a Hach colorimeter for total iron using a modification of the phenanthroline method of *Standard Methods* 315B [22]. The acidity and alkalinity were measured at Carnegie Mellon using NPDES-approved titration methods for acid mine drainage [23,24]. Chloride and sulfate were measured at Carnegie Mellon via ion chromatography [25]. Dissolved iron was measured on field-filtered (0.45 μm membrane filters), acid-preserved samples in the lab via flame atomic adsorption spectrometry [26]. Total iron, sodium, calcium, magnesium, manganese, and aluminum were measured on acid-preserved samples by PADEP with inductivity-coupled plasma (ICP) emission spectroscopy using EPA-approved methods [27]. The PADEP analyzed alkalinity using *Standard Methods* 2320B [22], total suspended solids using EPA Method 160.2 [28], and sulfate using EPA Method 375.4 [29].

3.4. Scarlift study methodology

Field measurement and laboratory techniques for the 1974–1975 Scarlift Study in the Uniontown Syncline [8] were not well documented. Discharge flow rates were measured in the field with weirs or timed buckets and are considered reliable. Field pH measurements were made concurrent with water sampling. Total iron, ferrous iron, sulfate, pH, alkalinity and acidity were measured at a commercial laboratory. Communications with the laboratory indicated that alkalinity and acidity would have been measured using titration methods similar to the current EPA methods [23,24], sulfate would have been analyzed using a turbidimetric method similar to EPA Method 375.4 [29] and total iron by flame atomic adsorption spectrometry, as in EPA Method 236.1 [26]. Mine drainage samples in 1977 were filtered in the lab and ferrous iron was measured via the phenanthrolene colorimetric method identical to *Standard Methods* 315B [22].

3.5. Comparison of 1998–2000 study and Scarlift Study methodologies

Reliable, consistent methods were employed in both studies for field pH, alkalinity, acidity, and flow, and the results for these measurements are directly comparable. Although sulfate and total iron were measured via different methods, comparable results are expected as discussed in Dzombak et al. [20]. The ferrous iron measurements made during Scarlift were considered to be of questionable accuracy, as they were performed in the laboratory and it is not known if adequate preservation (to low pH with hydrochloric acid) was employed.

4. Results

4.1. Data from 1998–2000

Monthly sampling and flow measurements were performed at 21 sites in the Uniontown Syncline from 1998 to 2000. The complete data for each site can be found in Appendices D and E of Dzombak et al. [20].

Because discharges from sites with similar degrees of flooding and from similar geographical locations exhibited similar water quality, four representative sites with various degrees of flooding are selected for focus here. The sites chosen are A0, P0, A6, and M59 (Fig. 1). Discharges A0 and P0 are from flooded mines south of the Youghiogheny River. Discharge P0 is located south and upgradient of A0 and A6, near Redstone Creek. A6 is a discharge from a partially flooded mine south of the Youghiogheny River and M59 is a discharge from an unflooded mine north of the Youghiogheny River. The years in which these discharges were initiated, and the average discharge flows in 1974–1975 and 1998–2000 are provided in Table 1. For these four sites the typical acid mine drainage parameters, pH, alkalinity, total iron, and sulfate, are examined in detail below.

The field pH data for each of the representative discharge sites for both years of sampling in 1998–2000 are presented in Fig. 3. As Fig. 3a shows, the pH was circumneutral in the discharges from the flooded and partially flooded mines, A0, P0, and A6. The pH was acidic in M59, the discharge from the unflooded mine. The pH values for all of the discharges were fairly consistent over the 2-year sampling period.

The alkalinity data for the sampling sites A0, P0, A6, and M59 in 1998–2000 are presented in Fig. 4a. As seen in Fig. 4a, the alkalinity was the highest at discharge site A0, in the range of 300–350 mg/l as $CaCO_3$. The other discharge from a flooded mine, P0, exhibited high alkalinity values in the 200–250 mg/l as $CaCO_3$ range. A6, the discharge from a partially flooded mine, was also alkaline. Discharge from M59, the unflooded mine, was acidic.

Fig. 5a contains the total iron data for sampling sites A0, P0, A6, and M59 in 1998–2000. Total iron was higher at site P0 than at the other sites. Sites A0 and A6 had similar iron concentrations and site M59, an old discharge, had very little iron. The sites with similar iron concentrations, A0 and A6, are located near one another and drain mine voids that have been flooded (or partially flooded) for a longer period than P0.

The sulfate data for each of the discharges in 1998–2000 are provided in Fig. 6a. As Fig. 6a shows, the sulfate concentrations were high in all of the discharges. The sulfate concentrations were consistently higher in the flooded mine discharges than in the partially flooded or unflooded mine discharges. The discharges from the flooded mines, A0 and P0, exhibited sulfate concentra-

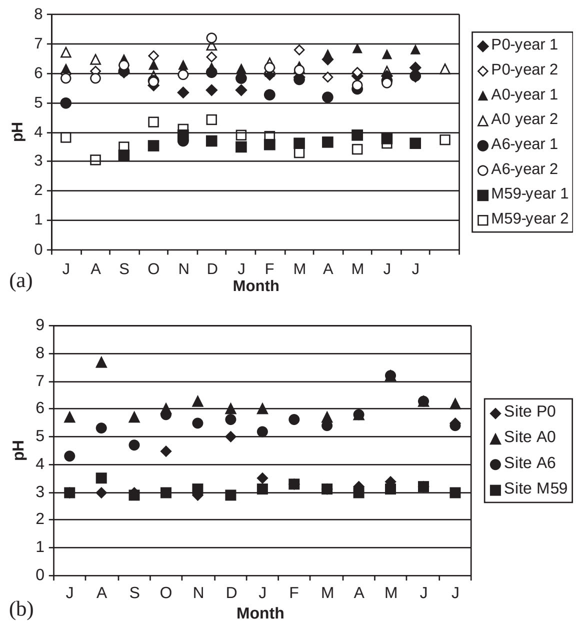

Fig. 3. Field pH data from monitoring sites A0, P0, A6, and M59 in the Uniontown Syncline for (a) 1998–2000 and (b) the Scarlift Study in 1974–1975.

Table 1
Characteristics of four selected abandoned coal mine discharges in the Uniontown Syncline, Fayette County, PA, USA

Site[a]	Flooded state	Discharge start date	Discharge flow (l/s), 1974–1975[b]	Discharge Flow (l/s), 1998–2000[c]
A0	Flooded	ca. 1960[d]	200 (±35)	144 (±33)
A6	Partially flooded	ca. 1960[d]	34.4 (±7.7)	10.7 (±6.5)
P0	Flooded	ca. 1965[d]	282 (±85)	248 (±77)
M59	Unflooded	ca. 1911[e]	4.9 (±3.2)	9.4 (±9.7)

[a] Locations shown in Fig. 1.
[b] Arithmetic average (±standard deviation) shown; data from Ackenheil and Associates [8].
[c] Arithmetic average (±standard deviation) shown; data from Dzombak et al. [20].
[d] From Ackenheil and Associates [8].
[e] Personal communication, A. Graziani, USS Mineral Resources, Uniontown, PA.

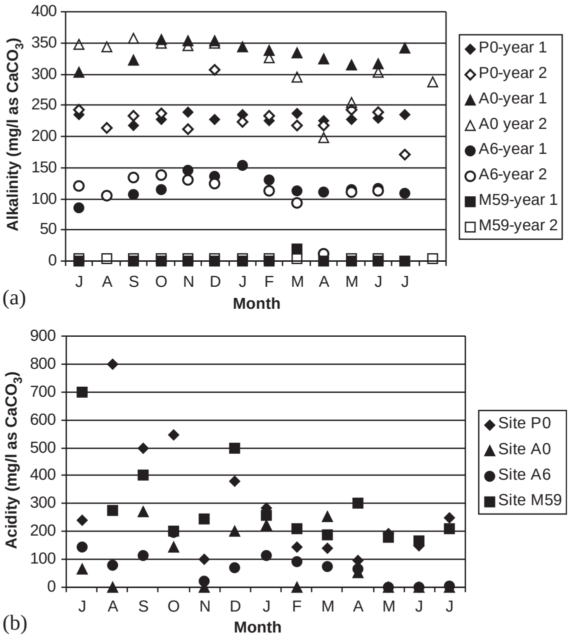

Fig. 4. (a) Alkalinity data from monitoring sites A0, P0, A6, and M59 in the Uniontown Syncline for 1998–2000. (b) Acidity data from monitoring sites A0, P0, A6, and M59 in the Uniontown Syncline from the Scarlift Study in 1974–1975.

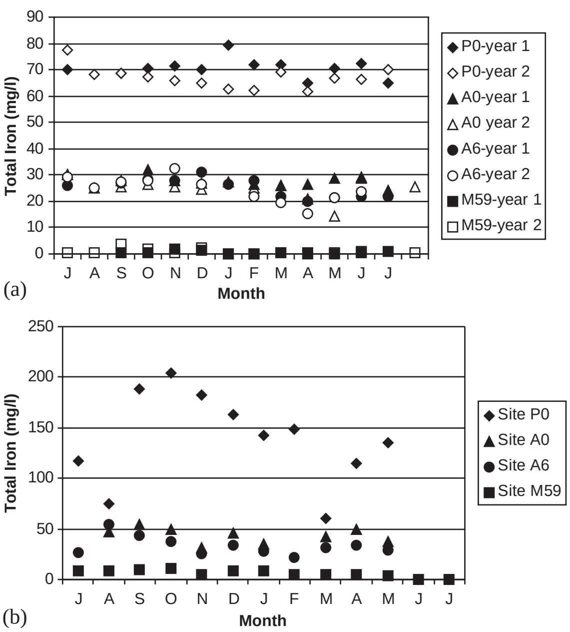

Fig. 5. Total iron data from monitoring sites A0, P0, A6, and M59 in the Uniontown Syncline for (a) 1998–2000 and (b) the Scarlift Study in 1974–1975.

tions in the 800–1000 mg/l range. Discharges from the partially flooded and unflooded mines, A6 and M59, had sulfate concentrations in the 500–800 mg/l range.

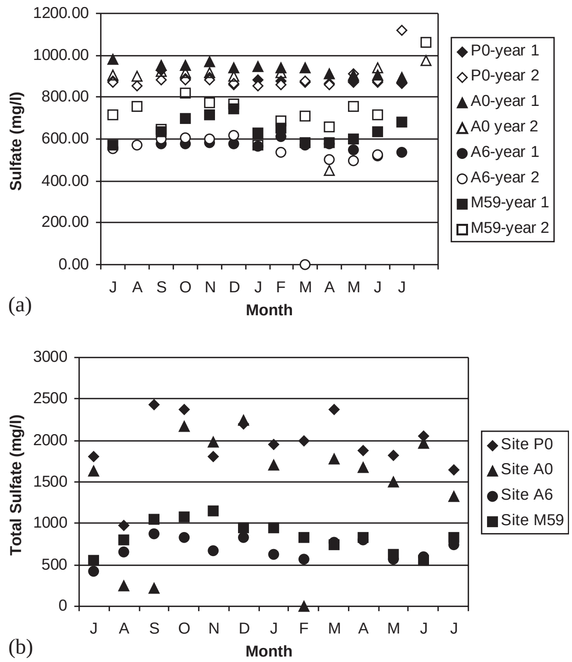

Fig. 6. Sulfate data from monitoring sites A0, P0, A6, and M59 in the Uniontown Syncline for (a) 1998–2000 and (b) the Scarlift Study in 1974–1975.

As seen in Figs. 3a and 4a and Table 2, the flooded and partially flooded sites have reached alkaline conditions with near-neutral pH. The unflooded sites, represented by M59 with an average (arithmetic) pH of 3.8, were acidic. The ferrous, total dissolved, and total iron measurements were all higher at flooded site P0, than at the other three sites. The only site with a notable amount of aluminum in the discharge was M59, the unflooded site. Magnesium, calcium, and sodium concentrations were all higher in the flooded mines than in the partially flooded or unflooded mines.

The dissolved oxygen was significantly higher in the unflooded mine water compared to the discharges from the partially flooded or flooded mines. The flooded mines exhibited average dissolved oxygen concentrations of less than 1.0 mg/l, while M59 was consistently near saturation with respect to dissolved oxygen (Table 2).

For all of the sites monitored there was little variation of chemical quality with flow. This may be seen in Figs. 7 and 8 where magnesium, calcium, sodium, aluminum, total iron, and dissolved iron are shown versus flow for sites P0 and M59. At site P0, the concentration was fairly constant for all of the constituents over a flow range of 100–400 l/s (Fig. 7). The flow at site M59 varied from 0 to 35 l/s and concentrations were again constant in all of the constituents except calcium where some scatter occurred (Fig. 8).

Table 2
Water-quality data[a] for AMD sites A0, P0, A6, and M59 in the Uniontown Syncline for the 1998–2000 sampling period

Parameter	Site A0	Site P0	Site A6	Site M59
Field pH	6.2 (±1.0)	6.0 (±0.4)	5.7 (±0.6)	3.8 (±0.8)
Acidity (mg/l as $CaCO_3$)	0.0 (±0.0)	7.5 (±19)	7.4 (±15)	54.6 (±22)
Alkalinity (mg/l as $CaCO_3$)	323 (±37)	230 (±22)	114 (±27)	5.2 (±12)
Ferrous iron (mg/l)	26.5 (±12)	60.5 (±30)	27.5 (±15)	0.3 (±0.2)
Dissolved iron (mg/l)	20.6 (±3.1)	53.2 (±6.3)	18.0 (±5.6)	0.1 (±0.2)
Total iron (mg/l)	26.3 (±3.4)	68.7 (±4.3)	24.2 (±5.1)	0.7 (±0.9)
Sulfate (mg/l)	927 (±27)	886 (±52)	565 (±33)	694 (±100)
Chloride (mg/l)	20.1 (±1.5)	19.5 (±2.1)	11.6 (±2.3)	8.1 (±1.6)
Aluminum (mg/l)	ND[b]	ND	ND	6.8 (±1.5)
Manganese (mg/l)	0.8 (±0.1)	2.6 (±0.2)	1.6 (±0.2)	1.1 (±0.2)
Magnesium (mg/l)	73.7 (±11)	81.1 (±8.0)	55.5 (±5.6)	49.7 (±6.8)
Calcium (mg/l)	242 (±32)	204 (±13)	172 (±15)	176 (±21)
Sodium (mg/l)	165 (±23)	97.5 (±4.3)	19.1 (±2.0)	4.9 (±1.2)
TSS (mg/l)	23.3 (±17)	25.7 (±16)	45.6 (±120)	17.9 (±26.4)
Unfiltered conductivity (mS)	2.1 (±0.1)	1.9 (±0.2)	1.2 (±0.1)	1.1 (±0.3)
Water temp. (°C)	14.5 (±2.0)	14.7 (±3.2)	13.2 (±3.1)	15.1 (±6.1)
Dissolved oxygen (mg/l)	0.7 (±1.3)	0.10 (±0.1)	2.6 (±1.2)	7.3 (±2.3)

[a] Arithmetic average (± standard deviation) shown; data from Dzombak et al. [20].
[b] ND means non-detectable.

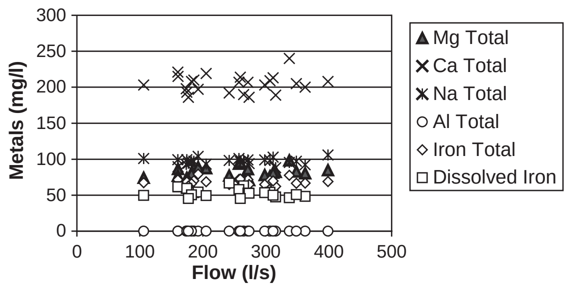

Fig. 7. Magnesium, calcium, sodium, aluminum, total iron, and dissolved iron versus flow for site P0, 1998–2000.

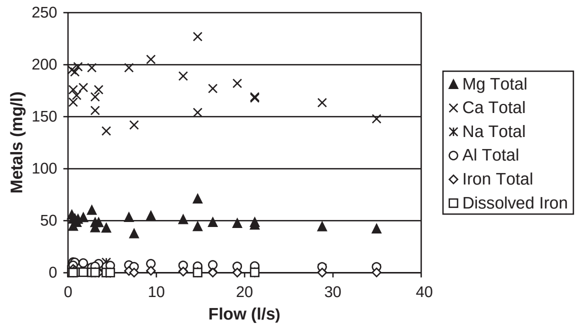

Fig. 8. Magnesium, calcium, sodium, aluminum, total iron, and dissolved iron versus flow for site M59, 1998–2000.

Fig. 7 also shows that the flows from the flooded mine site P0 varied over a narrower range (factor of four) compared to the flows from the unflooded mine site M59 in Fig. 8 (factor of 35+). Also, discharge flows from sites A0 and P0 and from other flooded mines in this study exhibited no seasonal dependence. This was not the case for site M59 or for any of the other unflooded mines in this study, which exhibited high flows in response to increased rainfall [20]. The discharge flow data thus support the mine flooding assessments presented earlier.

The cation to anion ratio was calculated for all of the sites and the results can be found in Appendix D of Dzombak et al. [20]. The cation–anion balance was within 5% for 15 of the sites, including the four representative sites examined here, and the other sites were within 20% except for one site, which was dry for many sampling periods, that was within 26%. The cation–anion balance was fairly accurate considering that ion analyses were not exhaustive, e.g., no potassium measurements were made.

4.2. Scarlift data

The water-quality data that are comparable between the 1998–2000 study and the 1974–1975 Scarlift Study are pH, acidity, alkalinity, total iron, and sulfate. Graphs containing the 1998–2000 and 1974–1975 data for each site are presented in Appendix E of Dzombak et al. [20]. Here, the Scarlift data corresponding to the representative discharges A0, P0, A6, and M59 from the 1998–2000 study are examined.

Fig. 3b presents the pH data from the Scarlift Study for sites A0, P0, A6, and M59. In 1974–1975, the pH was

Table 3
Comparable water-quality data[a] at AMD sites P0, A0, A6, and M59 in the Uniontown Syncline from the 1974–1975 Scarlift[b] Study and the 1998–2000 Carnegie Mellon[c] study

Parameter	Site P0		Site A0		Site A6		SiteM59	
	1974–1975	1998–2000	1974–1975	1998–2000	1974–1975	1998–2000	1974–1975	1998–2000
Field pH	3.6 (±0.8)	6.0 (±0.4)	6.2 (±0.6)	6.2 (±1.0)	5.5 (± 0.7)	5.7 (±0.6)	3.1 (±0.2)	3.8 (±0.8)
Alkalinity (mg/l as $CaCO_3$)	6.8 (±18)	230 (±22)	195 (±71)	323 (±6.8)	35.8 (± 19)	114 (±27)	0.0 (±0.0)	5.2 (±12)
Acidity (mg/l as $CaCO_3$)	294 (±210)	7.5 (±19)	101 (±110)	0.0 (±0.0)	74.8 (± 59)	7.4 (±15)	294 (±150)	54.6 (±22)
Total iron (mg/l)	139 (±45)	68.7 (±4.3)	43.6 (±7.6)	26.3 (±3.4)	32.9 (± 9.2)	24.2 (±5.1)	7.1 (±2.4)	0.7(±0.9)
Sulfate (mg/l)	1950 (±380)	886 (±52)	1540 (±660)	927 (±27)	690 (± 130)	565 (±33.4)	841 (±192)	694 (±103)

[a] Arithmetic average (± standard deviation) shown.
[b] Data from Ackenheil and Associates [8].
[c] Data from Dzombak et al. [20].

circumneutral at discharges A0 and A6. The pH for sites P0, a flooded mine, and M59, an unflooded mine, was acidic, in the range of pH 3.1–3.6.

The acidity data for sites A0, P0, A6, and M59 from the Scarlift Study are presented in Fig. 4b. P0 had the highest acidity measurements during the Scarlift Study. Site M59 also had high acidity readings in the 200–300 mg/l as $CaCO_3$ range. Sites A0 and A6 exhibited varying acidity, in the 0–300 mg/l as $CaCO_3$ range.

Fig. 5b gives the total iron data for sites P0, A0, A6, and M59 from the Scarlift Study. As seen in Fig. 5b, site P0 had the highest concentration of total iron in the discharge, with concentrations ranging from 100 to 200 mg/l. Sites A0 and A6 had similar total iron concentrations but lower concentrations than P0 which began discharging at least 5 years after A0 and A6 (Table 1). Unflooded mine discharge M59, a very old discharge, contained very little iron.

The sulfate data for the representative discharges in 1974–1975 are presented in Fig. 6b. All of the discharges had high sulfate concentrations. The discharges from the flooded mines, A0 and P0, had very high sulfate concentrations in the 1500–2500 mg/l range. The discharges from the partially flooded and unflooded mines also had high sulfate concentrations, in the 500–1000 mg/l range. Higher sulfate concentrations generally would be expected for unflooded mine discharges relative to flooded mine discharges, but the unflooded mine discharges in this study were very old compared to those from the flooded mines in the study area.

5. Discussion

The changes in water quality at sites P0, A0, A6, and M59 from the 1974–1975 Scarlift Study to the 1998–2000 study provide insight into the long-term water quality evolution in abandoned underground coal mines. Table 3 gives arithmetic average values and standard deviations for pH, alkalinity, acidity, total iron, and total sulfate for the four representative discharge sites and the two monitoring periods.

As seen in Table 3, the most significant change in water quality occurred at site P0. The average pH at site P0 in 1974–1975 was 3.6 and 25 years later the pH had risen to 6.0. The alkalinity also increased significantly at site P0 going from 6.8 mg/l as $CaCO_3$ in 1974–1975 to 230 mg/l as $CaCO_3$ in 1998–2000. In correspondence with the increase in pH and alkalinity, the acidity decreased significantly over the 25-year period from 294 to 9.4 mg/l as $CaCO_3$. The total iron and sulfate also decreased significantly over the same time period. Table 3 shows that the average dissolved oxygen concentration in 1998–2000 at site P0 was 0.2 mg/l. The decrease in sulfate and iron concentrations and increase in pH and alkalinity as well as the lack of dissolved oxygen indicate that pyrite dissolution decreased significantly in the flooded mine feeding the P0 discharge. With no dissolved oxygen present in the mine water, the dissolution of pyrite is significantly inhibited [9]. In addition, the solubilization and removal of ferrous/ferric hydroxy-sulfate salts (acid-generating salts) from the mine voids with the initial flushing likely contributed to the decrease in iron and sulfate concentrations with time [5].

The other discharge originating from a flooded mine, A0, did not have as drastic a change in water quality over the 25-year period as P0. During the Scarlift Study, site A0 already had circumneutral pH and a significant amount of alkalinity. The acidity decreased from 101 mg/l as $CaCO_3$ in 1974–1975 to 0.0 mg/l as $CaCO_3$ in 1998–2000. The total iron decreased from 43.6 to 26.3 mg/l and the sulfate concentration decreased from 1540 to 927 mg/l. The decrease in sulfate and iron concentrations again indicate that the dissolution of pyrite decreased over time in the flooded mines.

The differences in water quality discharging from A0 and P0, the two flooded mine discharges, are due in part to the fact that the discharges were initiated at different times. Younger [4] and Wood et al. [6] compiled quality data for numerous discharges from multiple flooded mines in the UK and showed that total iron and sulfate consistently decrease with time since mine abandonment, with the amount of decrease dependent on the time elapsed. The mine from which the discharge A0 originates ceased operations in 1938 while the mine where the discharge P0 originates did not cease operations until 1961. A0 began discharging around 1960 [8] indicating that the mine voids immediately adjacent were flooded at this point. A0 was therefore emanating from a mine section flooded approximately 14 years before the 1974–1975 study. From water elevation readings in a nearby mine shaft, the mine voids contributing to P0 were estimated to be completely flooded around 1965 [8]. Therefore, the P0 discharge derived from a mine section only flooded for about 9 years before the 1974–1975 study. Since the amount of dissolved oxygen in an abandoned mine pool is related to the length of time a mine has been flooded and the dissolution of pyrite is inhibited in the absence of oxygen, it is clear that the duration of flooding in a mine section will greatly affect the discharge water quality.

The discharge from the partially flooded mine, A6, had some water-quality improvement over the 25-year period. The alkalinity increased from 35.8 to 114 mg/l as $CaCO_3$ and the acidity correspondingly decreased from 74.8 to 7.4 mg/l as $CaCO_3$. There was also a decrease in the average total iron and sulfate concentrations, but not to as great an extent as in the flooded mines, indicating that pyrite dissolution decreased over time in the partially flooded mine but not as significantly as in the flooded mines.

The discharge from the unflooded mine, M59, exhibited only a small degree of water-quality improvement with respect to pH over the 25-year period. The average pH increased slightly, from 3.1 to 3.8. However, the acidity significantly decreased from 294 to 54.6 mg/l as $CaCO_3$. Also, the M59 discharge exhibited decreases in total iron (from 7.1 to 0.7 mg/l) and sulfate (from 841 to 694 mg/l) over the 25 years between studies. These decreases occurred despite the persistent acidity and low pH, and apparent availability of atmospheric oxygen. The low concentration of total iron in the M59 discharge reflects the age of the discharge, which was about 90 years at the time of the 1998–2000 sampling. Younger [4] and Wood et al. [6] also observed, over time periods of this magnitude, decreases in total iron concentrations to <10 mg/l for discharges from mines encompassing a range of flooded conditions. The long-term decreases in iron and sulfate may be due to a decrease in available surface area of pyrite for oxidation, i.e., to depletion of readily available pyrite; and also, for iron, to other sink reactions (adsorption, precipitation) that can redeposit mobilized iron in the mine voids [6].

6. Conclusions

Long-term changes in the quality of abandoned underground coal mine discharges were studied for the Uniontown Syncline, Fayette County, PA, USA. More than 130 discharges have been documented in the Uniontown Syncline, where deep mining was completely ceased by the early 1970s after about 100 years of operations. These discharges originate from an extensive network of flooded deep mines, as well as from a number of more isolated, unflooded, free-draining mines. Water quality and flow data for the abandoned mine discharges in the Uniontown Syncline were obtained in 1974–1975 to assess the magnitude of the AMD problem in the basin. A follow-up monitoring program was performed from 1998 to 2000 to assess water-quality improvements in the Uniontown Syncline over 25 years.

The data reported here present clear evidence for natural improvement of the quality of drainage for abandoned mine discharges. The type and magnitude of water-quality changes that occurred over time appear mainly dependent on the degree of flooding within the mine voids contributing to the discharges, and the time elapsed since mine abandonment. In flooded mines of the Uniontown Syncline, acidic discharges have become alkaline in less than 25 years. The A0 discharge was alkaline in 1974–1975, 14 years after it was flooded, and increased in alkalinity from that time until 1998–2000. The P0 discharge, from mine voids farther upgradient in the Syncline, was acidic in 1974–1975 but had positive alkalinity in 1998–2000. The discharges from the flooded mines improved in water quality in the form of reduced iron and sulfate concentrations between 1974–1975 and 1998–2000.

In the discharges from unflooded mines, M59 and others north of the Youghiogheny River, improvements in water quality have also occurred over 25 years, but to a smaller extent than observed for the flooded mines. There is a persistence of low pH and acidity, likely due to the abundance of oxygen available for the oxidation of pyrite in this low cover, unflooded environment. Concentrations of iron and sulfate in the unflooded mines were lower than might have been expected, due to the age of the discharges and the apparent depletion of readily available pyrite.

Overall, the mine discharge data from the two time periods 25 years apart indicate that flooding significantly mitigates acid production compared to mines with significant amounts of open mine voids. The AMD quality data from the flooded and unflooded mines indicate that flooding is a necessary condition for the transition from acidic to alkaline conditions and the associated upward pH shift. However, all mine discharges studied, including those from unflooded and partially flooded mines, showed some degree of improvement in quality over the 25 years. While rates of pyrite dissolution are much higher under unflooded or partially flooded conditions, there will be a decrease in available pyrite surface area with time, leading to decrease in total mass of pyrite dissolution products released with time. In the flooded mine voids, the first-flush water is highly acidic from high rates of pyrite dissolution as the voids fill, as well as from the dissolution of acid generating salts on the walls of the mine voids. With subsequent flushing of the mine voids under flooded conditions, pyrite dissolution is mitigated by the limitation in available oxygen and reduction in available pyrite surface area, and the dissolved acid generating salts are flushed out.

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